6-5-2017 12:00 AM

A Chlorine-Free Protocol for Processing Silicon, Germanium, and Tin

Michael J. Krause
The University of Western Ontario

Supervisor
Dr. Kim M. Baines
The University of Western Ontario

Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

Recommended Citation
Krause, Michael J., "A Chlorine-Free Protocol for Processing Silicon, Germanium, and Tin" (2017). *Electronic Thesis and Dissertation Repository*. 4581.
https://ir.lib.uwo.ca/etd/4581

Abstract

Replacing molecular chlorine and hydrochloric acid with less energy- and risk-intensive reagents would dramatically improve the environmental impact of metal manufacturing at a time when demand for metals is rapidly increasing. Germanium and tin are classified as “critical” elements based on growing demand for these elements in technological applications, lack of suitable substitutes, and, for germanium, high dispersion in the environment making extraction of the element process-intensive. This thesis describes a recyclable quinone / catechol redox platform that provides an innovative replacement for elemental chlorine and hydrochloric acid in the conversion of germanium metal or tin metal to element tetrachloride substitutes. The approach described in this thesis replaces the oxidizing capacity of chlorine with molecular oxygen, and replaces germanium tetrachloride and tin tetrachloride with air- and moisture-stable germanium or tin catecholate complexes that are kinetically competent for conversion to high-purity organogermanes and organostannanes. Also described in this thesis are the conversions of tetraethyl orthosilicate and germanium dioxide to air- and moisture-stable silicon and germanium catecholate complexes, thus replacing silicon tetrachloride and germanium tetrachloride as Group 14 precursors to organosilanes and organogermanes. The germanium catecholate complex developed in this thesis generates a pure stream of germane when reacted with hydride sources.

Keywords

Catechol, quinone, pyridine, 4-dimethylaminopyridine, triethylamine, silicon, germanium, tin, oxidation, reduction, oxygen, hydrochloric acid, chlorine, redox, green chemistry, industrial processes, refining.

Acknowledgements

I would like to thank my supervisor, Prof. Kim Baines, for allowing me to continue my graduate studies with her, for her time and guidance, and for many interesting discussions about chemistry. I would also like to thank the Baines group, for the good times both inside and outside the lab.

Many thanks are in order to Prof. J.P. Lumb, Prof. Tomislav Friščić, and Martin Glavinović for the exciting collaboration and discussions about new opportunities in the chemistry of germanium.

I am very thankful and grateful for all of the data, helpful discussions about analysis, and humor from Mat Willans (NMR) and Doug Hairsine (MS).

I am indebted to Yves Rambour for generously sharing his knowledge, his patience as a teacher, and for "seeing my defaults" so I can improve my technique. I have never seen such skill with glass before, and it really does appear that Yves can control the glass with his mind.

I would like to thank my family and friends for their kind support during this challenging journey, especially my brothers Matt and Dan, my parents Frank and Maureen, Geraldina's parents Adolfo and Maria, our crazy neighbors, and our beloved cat Simon.

Most importantly, I would like to thank the love of my life, Geraldina, for her sense of humor, encouragement, support, love, and many awesome meals during my time at UWO. She means the world to me, and without her I could not have accomplished this.

Table of Contents

List of Tables

List of Figures

List of Schemes

List of Abbreviations

Å = Angstrom

All = allyl

Bn = benzyl

br = broad

bs = broad singlet

Bu = butyl

^{s}Bu = *sec*-butyl

^{t}Bu = *tertiary*-butyl

calcd = calculated

d = doublet (NMR); day (time)

DAD = diazadiene

DCM = dichloromethane

bipy = bipyridine

DMAP = 4-dimethylaminopyridine

DME = dimethoxyethane

DMSO = dimethylsulfoxide

3,5-dtbc = 3,5-di-*tert*-butylcatechol

3,5-dtbq = 3,5-di-*tert*-butyl-*ortho*-quinone

EI = electron impact

eq = equivalent

ESI = electrospray ionization

Et = ethyl

FT = fourier transform

GC-MS = gas chromatography mass spectrometry

gCOSY = gradient correlation spectroscopy

gHMBC = gradient heteronuclear multiple bond correlation

gHSQC = gradient homonuclear spin quantum coherence

h = hour

Hex = hexyl

HMPA = hexamethylphosphoramide

Hz = hertz

J = coupling constant

m = multiplet

Me = methyl

Mes = mesityl = 2,4,6-trimethylphenyl

MHz = megahertz

min = minute

MS = mass spectrometry

m/z = mass-to-charge units

NEt_3 = triethylamine

NMI = N-methylimidazole

NMR = nuclear magnetic resonance

Ph = phenyl

phen = phenanthroline

PPh_3 = triphenylphosphine

ppm = parts per million

^{i}Pr = *iso*-propyl

PVC = polyvinyl chloride

py = pyridine

q = quartet

RT = room temperature

s = singlet

t = triplet

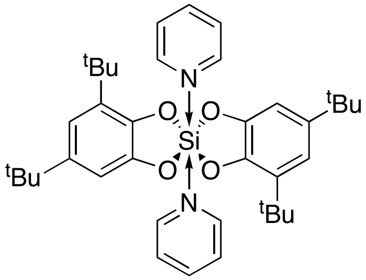
THF = tetrahydrofuran

TMEDA = tetramethylethylenediamine

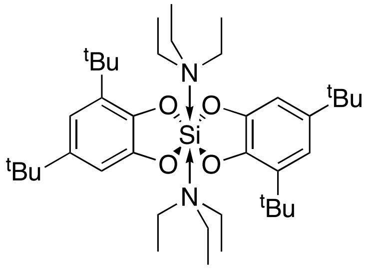
TMS = trimethylsilyl

Tol = $p\text{-}CH_3C_6H_4$

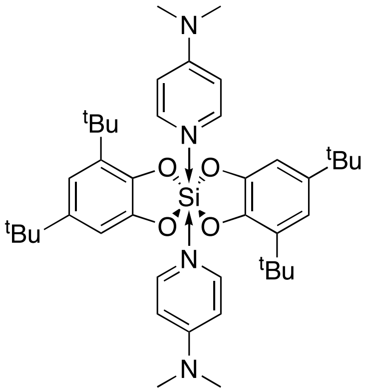
Compounds



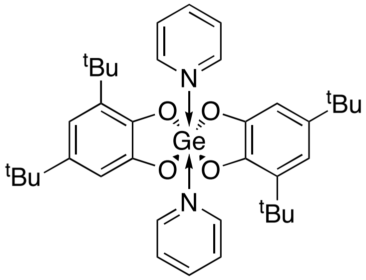
Si(3,5-dtbc)$_2$(py)$_2$



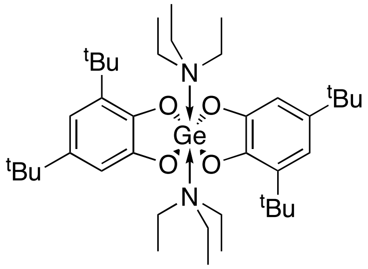
Si(3,5-dtbc)$_2$(NEt$_3$)$_2$



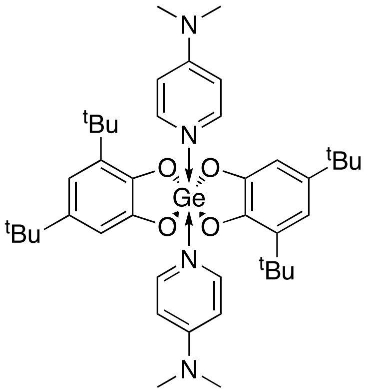
Si(3,5-dtbc)$_2$(DMAP)$_2$



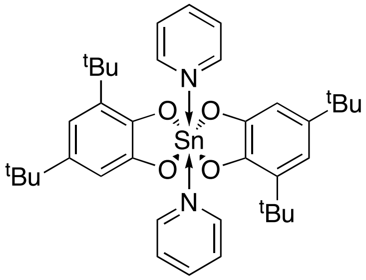
Ge(3,5-dtbc)$_2$(py)$_2$



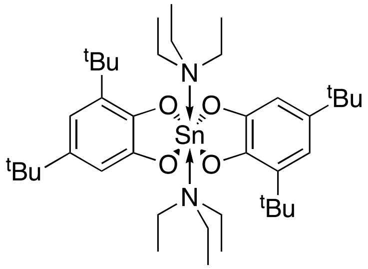
Ge(3,5-dtbc)$_2$(NEt$_3$)$_2$



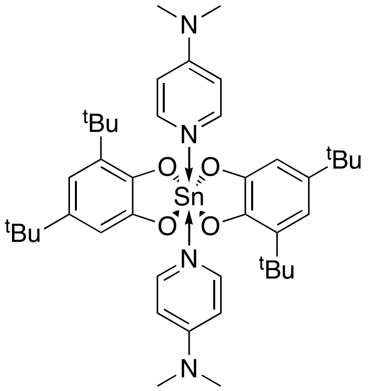
Ge(3,5-dtbc)$_2$(DMAP)$_2$



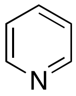
Sn(3,5-dtbc)$_2$(py)$_2$



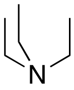
Sn(3,5-dtbc)$_2$(NEt$_3$)$_2$



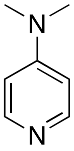
Sn(3,5-dtbc)$_2$(DMAP)$_2$



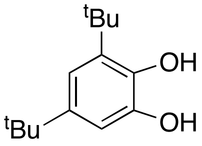
py



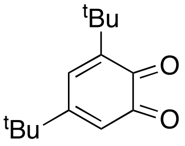
NEt$_3$



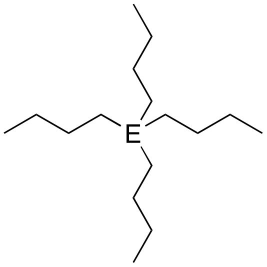
DMAP



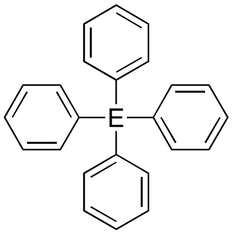
3,5-dtbc



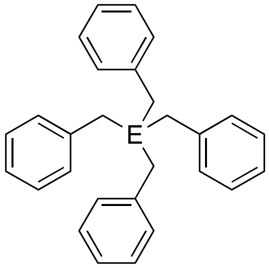
3,5-dtbq



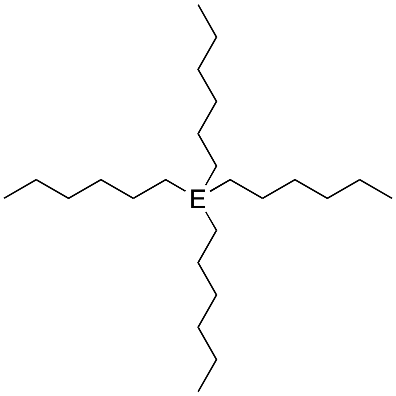
EBu$_4$ (E = Si, Ge, Sn)



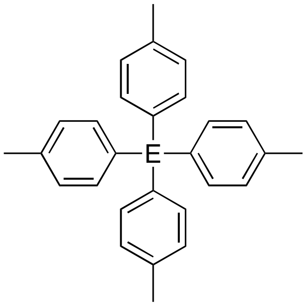
EPh$_4$ (E = Si, Ge, Sn)



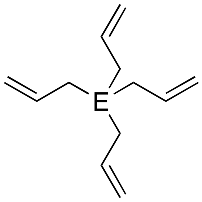
EBn$_4$ (E = Si, Ge, Sn)



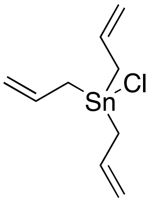
EHex$_4$ (E = Ge, Sn)



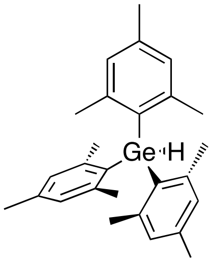
ETol$_4$ (E = Ge, Sn)



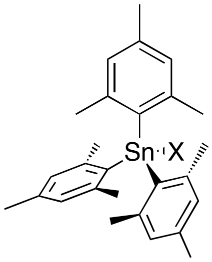
EAll$_4$ (E = Ge, Sn)



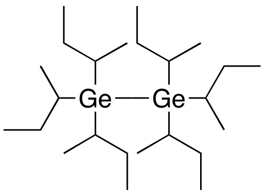
All$_3$SnCl



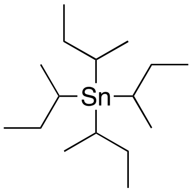
Mes$_3$GeH



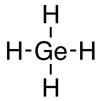
Mes$_3$SnX (X = Cl, Br)



^{s}Bu$_3$GeGe^{s}Bu$_3$

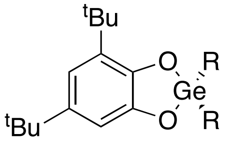


Sn^{s}Bu$_4$

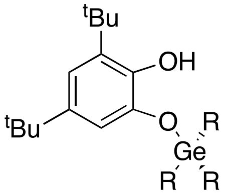


$H\text{-}GeH_2\text{-}H$

GeH$_4$



R$_2$Ge(3,5-dtbc-κ^2) (R = Bu, Ph)



R$_3$Ge(3,5-dtbc-κ^1) (R = Bu, Ph)

Co-Authorship Statement

The synthetic work and writing of chapters 3, 4, and 5 was performed by Michael Krause. Chapter 2 is based on a manuscript, published in *Science Advances*, co-authored by Martin Glavinović, Michael Krause, Linju Yang, John McLeod, Lijia Liu, Kim Baines, Tomislav Friščić, and J.-P. Lumb (*Sci. Adv.*, **2017**, *3*, e1700149). Michael Krause was responsible for writing the first draft of the manuscript and for contributing to the editing of the manuscript. The optimization of the reaction of Grignard reagents with $Ge(3,5\text{-dtbc})_2(py)_2$, the synthesis of $Ge(3,5\text{-dtbc})_2(py)_2$ from $GeCl_4$ and from GeO_2, as well as the synthesis of GeH_4 from $Ge(3,5\text{-dtbc})_2(py)_2$ were performed by Michael Krause. The mechanochemical syntheses of $Ge(3,5\text{-dtbc})_2(py)_2$, $Ge(3,5\text{-dtbc})_2(NMI)_2$, and $Ge(3,5\text{-dtbc})_2(TMEDA)$, as well as the extraction of germanium from germanium / zinc mixtures by mechanochemistry were performed by Martin Glavinović of McGill University. XAS analysis of $Ge(3,5\text{-dtbc})_2(py)_2$ was performed by Linju Yang, John A. McLeod, and Lijia Liu of Soochow University. The acquisition of GC-MS data, as well as the EI analysis of GeH_4, were performed by Doug Hairsine (Manager, Mass Spectrometry Facility, UWO).

Chapter 1: Introduction

1.1 The Importance of Silicon, Germanium, and Tin

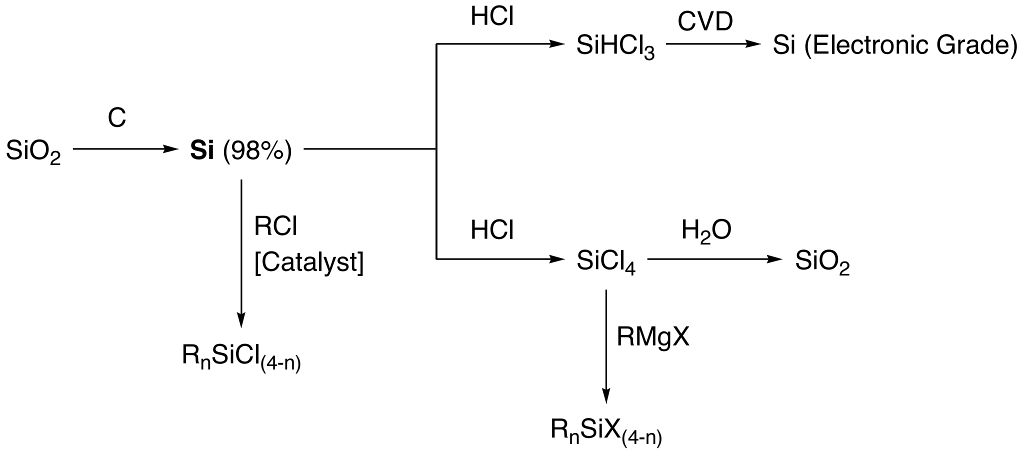
Silicon, germanium, and tin are key elements in many important modern technological applications and some examples of the most important applications are described here.[1, 2] More than 95% of modern electronic devices are based on highly purified silicon.[1] While silicon is useful in elemental form, it is also useful as an alloy. For example, silicon carbide is a hard material used as an abrasive in cutting tools.[2] Ferrosilicon (FeSi) alloys are used in the steel industry as reductants.[2] SiO_2, in the form of quartz, is used as a piezoelectric material.[3] SiO_2 is also the major component of pyrex (borosilicate) and quartz glasses.[2] Silicone polymers, derived from $R_nSiX_{(4-n)}$ compounds, are very useful materials with many applications ranging from insulation for electrical equipment to biomaterials.[1-4]

Germanium is an important component of electronic devices and is used in transistors, photoresists, and semiconductors because it has good mobility characteristics for charge carriers.[1] Germanium is a critical component of "strained silicon" ($Si_{1-x}Ge_x$), a material with superior electrical properties compared to silicon.[5, 6] Germanium is also used in fiber optics because it has a high refractive index which confines the optical signal to the core of the fiber optic cable.[1] Germanium,[3] germanium monoxide,[1] and germanium dioxide[7] find applications in IR windows, prisms, and lenses. Germanium dioxide is used as a catalyst in the production of polyesters, such as polyethylene terephthalate,[7] and synthetic textile fibers because of its low toxicity and especially when the product must be a colourless fiber or plastic such as photographic film.[1] Some germanium complexes have shown good catalytic activity in the polymerization of *rac*-lactide (a cyclic ester), which forms the biodegradable polymer, polylactide.[8] Germanium compounds are being investigated as catalysts for the fluorination of hydrocarbons, to generate hydrofluorocarbons (HFCs) to replace chlorofluorocarbons (CFCs).[7]

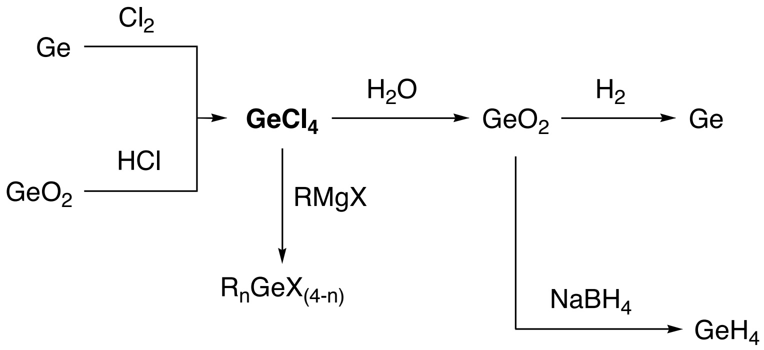
The major use of metallic tin is in alloys such as solder, bronze, babbit (heavy duty bearing metal for locomotive and rail car bearings), and pewter (a decorative and easily workable alloy for ornaments, trays, etc.).[3] SnO_2 is used as an opacifier in glazes and ceramics, and, because of its low solubility in glass, it is used as the base of some pigments.[3] Organotin compounds, mainly of the type R_2SnX_2 (X = OR, SR), find several industrial uses, mainly as industrial biocides (antifouling paints for ships, slime inhibitors in industrial water systems, wood and textile preservatives, disinfectants, insecticides, fungicides) and as poly(vinyl chloride) (PVC) stabilizers.[1, 2]

1.2 Industrial Production of Silicon, Germanium, and Tin

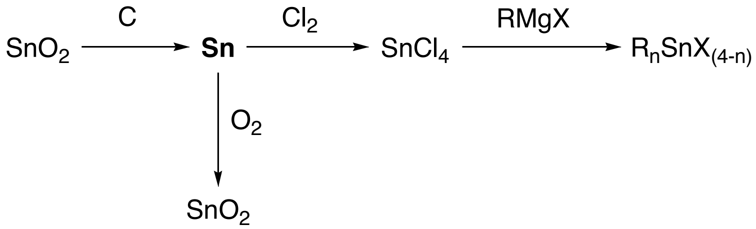
Examination of the methods for the extraction, refinement, and diversification of silicon, germanium, and tin reveals that for each element, there is one central compound from which all downstream products are derived. Metallurgical grade silicon is the central compound from which all other silicon compounds are derived (Scheme 1.1). For germanium, the central compound is $GeCl_4$ (Scheme 1.2), and for tin, it is tin metal (Scheme 1.3). As with the production of many metals, chlorine and hydrochloric acid are important chemicals in silicon, germanium and tin production (Scheme 1.1, Scheme 1.2, Scheme 1.3). It is highly desirable to replace chlorine and hydrochloric acid in these processes because of the toxicity, corrosiveness, and potential for environmental disasters involving these reagents and this is the overarching goal of the research described in this thesis.



Scheme 1.1: Overview of silicon refining.



Scheme 1.2: Overview of germanium refining.



Scheme 1.3: Overview of tin refining.

1.3 Major Challenges Facing Society

The world's population is increasing, and becoming more affluent, with certain technologies that used to be considered luxuries now becoming standard, and so the demand for technological devices is also increasing. Accordingly, there is an increasing demand for metals. To protect the environment during a time of increased metal production, scientists must be stewards of the environment and incorporate sustainable practices into new and existing industrial processes.[9] Hydrochloric acid and chlorine are toxic and highly corrosive chemicals that are used on a large scale, particularly in the production of metals including silicon, germanium and tin. The large scale handling and disposal of these chemicals can lead to environmental disasters and the loss of life.[10] Not only are current industrial refining processes of silicon, germanium, and tin not environmentally friendly, many elements, including germanium and tin, have limited sources that are being depleted. To preserve our resources, more efficient extraction processes and better recycling strategies are needed.[11] Mine waste is an equally important environmental issue, and improved scrap metal recycling could reduce the demand placed on mines.[10] A major societal challenge is to reduce the reliance on HCl and Cl_2 in the processing of metals. The focus of this thesis is on the production, refining, and recycling of silicon, germanium, and tin. The goal is to develop an alternative strategy for the processing of these Group 14 elements which does not compromise the production of downstream chemicals such as organosilanes, organogermanes, and organostannanes. Any new strategies developed should adhere to the established 12 principles of green chemistry (POGC).[11]

1. "**Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less hazardous chemical synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
4. **Designing safer chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer solvents and auxiliaries.** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for energy efficiency.** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and

should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of renewable feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce derivatives.** Unnecessary derivatization (use of blocking groups, protection / deprotection, temporary modification of physical / chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time analysis for pollution prevention.** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently safer chemistry for accident prevention.** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires."[11]

By following these principles, the environmental impact of an industrial process can be reduced.

1.4 Goals of this Thesis

The overall goal of this thesis is to reduce the amount of HCl and Cl_2 used in silicon, germanium, and tin mining, processing, and recycling. Some specific areas to address include the development of a replacement for $SiCl_4$ / $GeCl_4$ / $SnCl_4$, the development of a high-yield, reliable synthesis of $R_nEX_{(4-n)}$ for E = Si, Ge, and Sn which utilizes the replacements of $SiCl_4$ / $GeCl_4$ / $SnCl_4$, the development of alternative syntheses of GeH_4 / GeO_2, the development of an alternative process for the recycling (functionalization) of Ge / Sn metals which does not involve use of HCl / Cl_2, and the development of an alternative extraction process for GeO_2 from Ge concentrates. Given that the industrial production of silicon, germanium, and tin is central to this thesis, the currently used processes are presented in detail.

1.5 Silicon

1.5.1 Industrial Production of the Primary Products in the Silicon Industry

The carbothermal reduction of silicon dioxide is the most important and widely used method to generate metallurgical-grade silicon, with a purity of approximately 98% (Scheme 1.1).[1] The reaction proceeds according to equation 1:[1]

$$\mathrm{SiO_2 + 2\ C \rightarrow Si + 2\ CO} \tag{1}$$

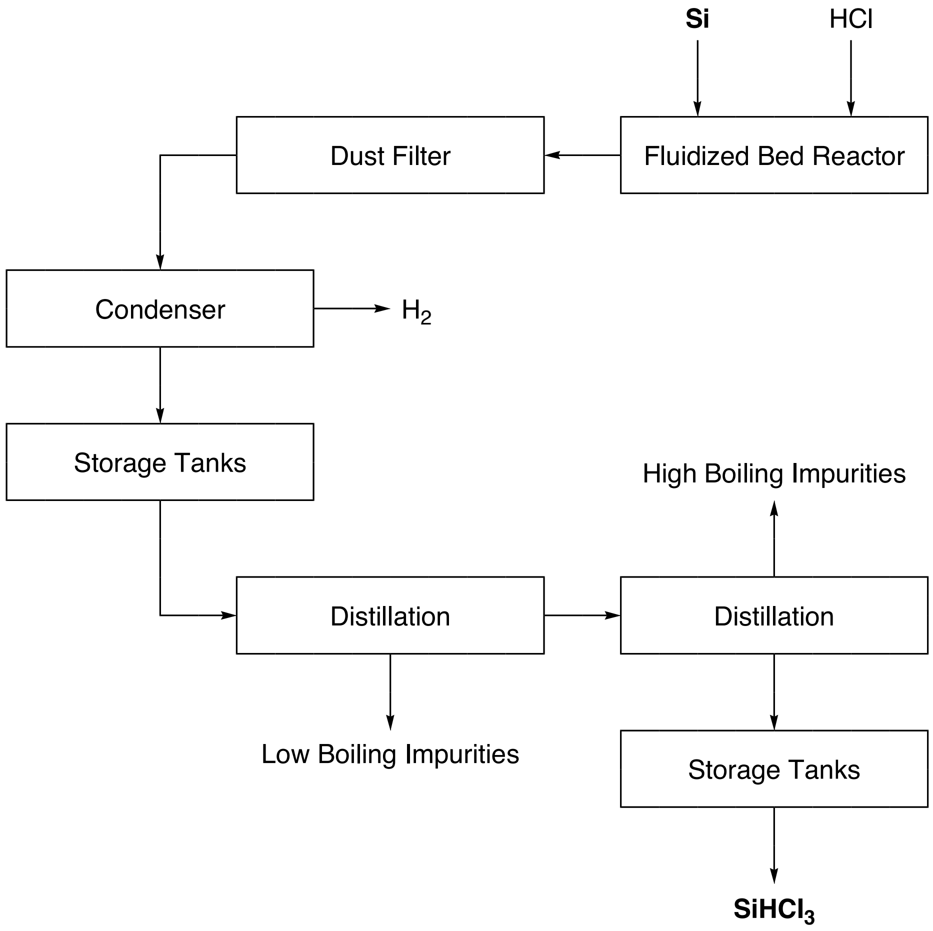
using quartzite or sand as the source of SiO_2, and coke, charcoal, or wood chips as the source of carbon in an electric-arc furnace with graphite electrodes.[1] The following side reactions also take place (equations 2 and 3):

$$\mathrm{SiO_2 + C \rightarrow SiO + CO} \tag{2}$$

$$\mathrm{SiO_2 + 3\ C \rightarrow SiC + 2\ CO} \tag{3}$$

and can be minimized by keeping the temperature of the electric-arc furnace above 2000 °K, and by using an excess of quartzite or sand.[1, 3]

Purified silicon is manufactured from $SiHCl_3$. The industrial production of $SiHCl_3$ is accomplished by the reaction of metallurgical-grade silicon with hydrochloric acid at 650 °C in high-pressure, corrosion resistant equipment: fluidized bed reactors that feed HCl gas into finely milled powder of metallurgical-grade silicon (Scheme 1.4).[1] To purify $SiHCl_3$, several fractional distillations, some in the presence of complexing agents, to remove traces of boron and phosphorus compounds as involatile distillation residues, are utilized (Scheme 1.4). The removal of boron and phosphorus is an important step considering that these are the two most important elements for altering the electrical properties of silicon.[1] The reaction that produces $SiHCl_3$ also produces $SiCl_4$, which is purified by fractional distillation.[1] $SiCl_4$ is hydrolyzed and processed to yield high-purity SiO_2.[1]



Scheme 1.4: Industrial production of $SiHCl_3$ from metallurgical-grade silicon and hydrochloric acid.[1]

Silicon, purified to the ppm level (99.999999% pure or better), is manufactured by chemical vapor deposition (CVD) of $SiHCl_3$, whose production by distillation is energy-intensive (Scheme 1.4).[1] Despite how pure the silicon produced by this method is, it is not pure enough for electronic applications. The two methods used to generate extremely pure silicon, at the part per billion level (99.999999999% pure, or better),[1] suitable for electronic applications, are zone refining and crystal pulling. In zone refining, a rod of silicon metal is melted in a continuous moving band. As the silicon recrystallizes, impurities are less likely to be incorporated into the silicon lattice. By moving the melt band over the rod several times, great improvements in purity can be achieved.[1] Crystal pulling, known as the "Czochralski Crystal Growth Process" relies on a seed crystal of ultra pure silicon. The silicon to be purified is melted in a graphite crucible and a seed crystal is dipped in and slowly pulled and turned, causing crystallization of silicon on the seed crystal, and the growth of large silicon rods with very low levels of impurities.[1]

1.5.2 Synthesis of Specialty Organosilanes

The direct process is the most important industrial synthesis of organic silicon compounds of the type $R_nSiX_{(4-n)}$ and is performed by heating silicon metal powder and alkyl halides, sometimes with HX, in a fluidized bed reactor with a copper catalyst.[2, 3] Dichlorodimethylsilane [Me_2SiCl_2], used extensively in the production of silicones, is an example of an important compound of this type that is manufactured industrially using the direct process (equation 4).[2]

$$Si + 2\ MeCl \rightarrow Me_2SiCl_2 \qquad (4)$$

A complex mixture of products, including $SiCl_4$, is obtained from the direct process.[12] The advantages are that a large distribution of useful compounds is produced, and the starting materials of the reaction are inexpensive. The disadvantages of the direct process are that the separation of the complex mixture is necessary, and the copper catalyst can sometimes react with the alkyl halide producing volatile organocopper compounds.[12]

The reaction of $H_{(4-n)}SiX_n$ (especially $SiCl_4$) with Grignard reagents is the traditional route to organosilanes according to equation 5.[2, 12]

$$H_{(4-n)}SiX_n + n\ RMgX \rightarrow R_nSiH_{(4-n)} \qquad (5)$$

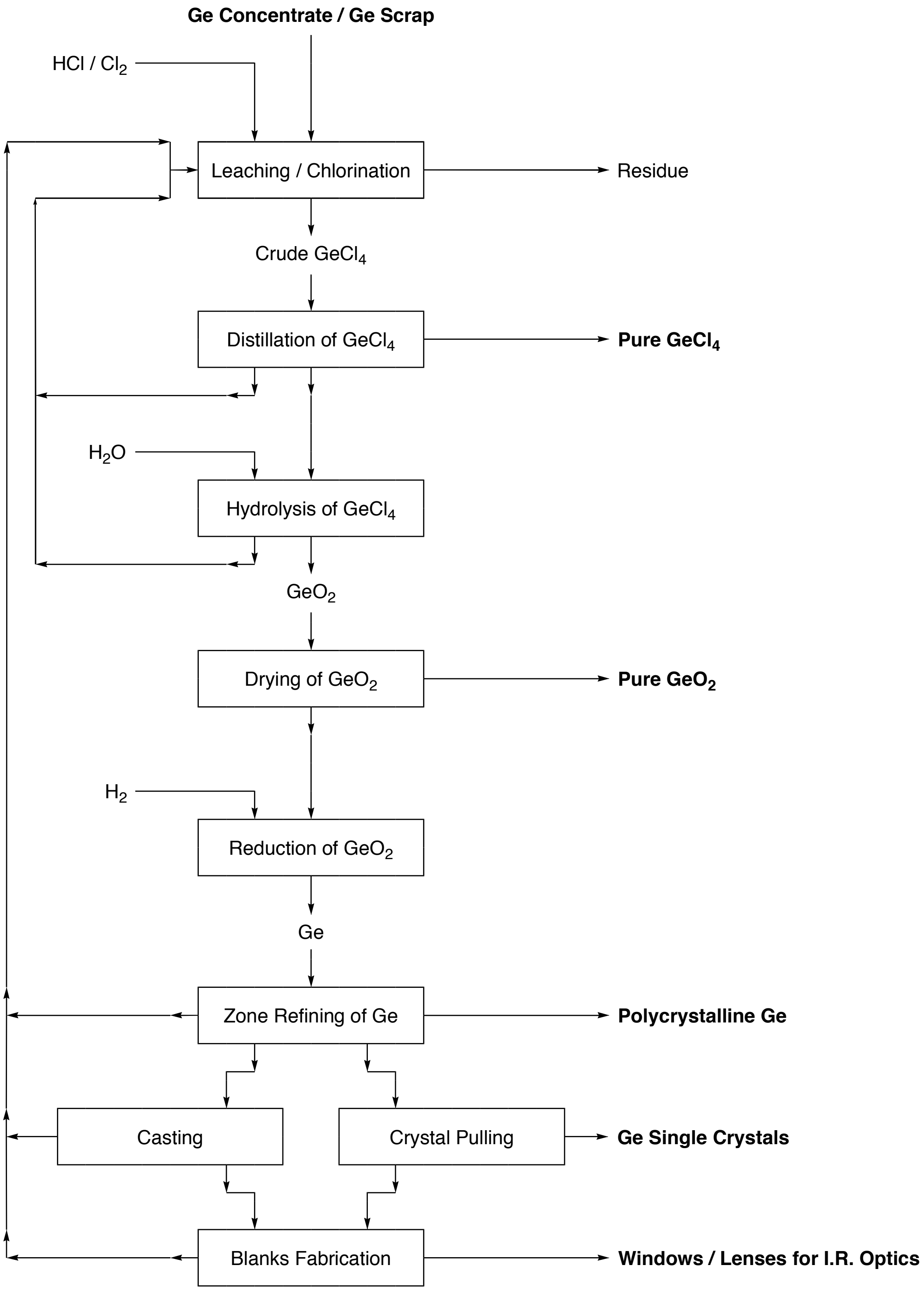
When $SiCl_4$ is reacted with four or more equivalents of a Grignard reagent, R_4Si is the main or only product formed; however, when $SiCl_4$ is reacted with less than four equivalents of a Grignard reagent, a mixture of products normally results: R_4Si, R_3SiCl, R_2SiCl_2, and $RSiCl_3$.[12] The progressive substitution of alkyl groups for chlorides becomes more difficult as the number of alkyl groups bonded to silicon increases because of both steric and electronic reasons. The steric bulk of the alkyl groups is greater than that of chlorine, inhibiting further substitution, and, as the level of substitution increases, the Lewis acidity of the silicon atom decreases.[12] There is not a large amount of literature on the synthesis of tetraorganosilanes where all the organic groups are identical, and some highlights are mentioned here. Gilman and Ingham synthesized tetrahexadecylsilane, a tetraorganosilane with long alkyl chains, as well as three other long-chain silanes of the type Ph_2SiR_2, where R = octadecyl, hendecyl, and

10-hendecenyl.[13] Fishwick *et al.* obtained good yields of $Si(CH_2CH{=}CH_2)_4$ starting from excess $H_2C{=}CHCH_2MgCl$ and $SiCl_4$.[14]

1.6 Germanium

1.6.1 Industrial Production of Germanium

The industrial production of germanium metal consumes a large quantity of HCl / Cl_2 and is outlined in Scheme 1.5.[1] Historically, germanium was recovered from coal-ash from electric power plants. Currently, the main source of raw material for germanium production is the zinc industry, and from germanium metal scrap.[1] Sphalerite is the main mineral source of zinc and there are high quality sources at thousands of locations around the world. Sphalerite contains primarily zinc, iron, and sulfur.[1] There are a few ways that germanium concentrates can be obtained during the processing of sphalerite. In a thermic process, germanium monoxide can be sublimed from the zinc byproducts at 1200 °C, leached from the fumes, and precipitated using tannic acid.[1] Another method for obtaining germanium concentrates from zinc processing byproducts is by solvent extraction using alkaline solutions to first extract the germanium rich materials which are then precipitated under acidic conditions.[1] At the Utah Apex mine, gallium concentrates, which also contain germanium, are leached with sulfuric acid and SO_2 to remove iron and copper.[1] The addition of H_2S to the resulting residue, followed by solvent extraction to remove gallium, yields a germanium concentrate which is about 3% by weight.[1]



Scheme 1.5: Industrial production of germanium metal, germanium tetrachloride, and germanium dioxide.[1]

Oxidation increases the weight percent of that small fraction (GeO_2), and the concentrate is then sent to the chlorination step (Scheme 1.5).[1] It is also possible to obtain germanium from a zinc / germanium mixture by separation of the zinc as a volatile material, however, this method is energy intensive (distillation of zinc metal, b.p. 907 °C) and has ecological problems, and so, it is becoming obsolete.[1]

Germanium concentrates, containing GeO_2, and germanium scrap are processed in the same way.[1] The leaching and chlorination step is run under an atmosphere of chlorine in 6 M hydrochloric acid.[1] These harsh conditions are required to remove impurities as precipitates, and to convert the germanium to $GeCl_4$, and to prevent hydrolysis of the $GeCl_4$ produced (Scheme 1.5).[1] The primary reactions taking place are shown in equations 6 and 7:[1]

$$GeO_2 + 4\ HCl \rightarrow GeCl_4 + 2\ H_2O \tag{6}$$

$$Ge + 2\ Cl_2 \rightarrow GeCl_4 \tag{7}$$

and the main advantage of this method is the volatility of $GeCl_4$ which can then be separated and purified by distillation.

Germanium dioxide is produced by hydrolyzing purified germanium tetrachloride with purified water according to equation 8 (Scheme 1.5):[1]

$$GeCl_4 + 2\ H_2O \rightarrow GeO_2 + 4\ HCl \tag{8}$$

which is then further purified by thorough washing and drying of the product.

Germanium metal is produced by the hydrogen reduction of germanium dioxide at 650 °C in electrically heated tubular furnaces (Scheme 1.5). The temperature must not be allowed to go above 700 °C or germanium monoxide will be produced, leading to losses of valuable germanium. Other reduction processes were employed, however, they have lost importance because the purity of germanium metal produced was lower than that from the hydrogen reduction method. Some of these obsolete methods include reduction with carbon, flux electrolysis, and the reaction of germanium tetrachloride with zinc metal.

Purification of germanium metal is accomplished by zone-refining (Scheme 1.5). Several zone-refining runs must be conducted because the partition coefficients of impurities in the germanium prevent high levels of purity from being acheived in a single run. The portions of germanium that contain the most impurities are mechanically cut away and recycled back into the early stages of the refinement process (Scheme 1.5). Many of the steps in the germanium manufacturing process recycle impure germanium back to the previous step to minimize the amount of waste produced. For most applications, further processing of germanium metal is required to improve the purity. In casting, a seed crystal of germanium is introduced to a crucible of molten germanium and slow, controlled crystal growth is initiated. This results in large single crystals of germanium metal of high purity. Another method for purifying germanium metal is known as “crystal pulling” (similar to that for silicon), resulting in single crystals of germanium that measure up to 30 cm in diameter. From the single crystals, precision parts are made by grinding and cutting with ultrapure diamond cutting tools. Germanium metal is very brittle and does not cast well, so parts must be made by cutting and tooling.

1.6.2 Synthesis of Organogermanes

GeH$_4$ is a volatile, highly flammable and toxic gas at room temperature, whose considerable risks are offset by its high value as a reagent for chemical vapor deposition of germanium.[15] Due to stringent requirements of purity, the preparation and purification of GeH$_4$ have been extensively studied.[16, 17] Most commonly practiced are chemical reductions of GeCl$_4$, GeO$_2$, or Na$_2$GeO$_3$ with metal hydrides in either organic solvents or aqueous solutions below pH 7.

The primary method used to synthesize organogermanes is the reaction of Grignard reagents with germanium tetrachloride or germanium tetrabromide, according to equation 9.[4]

$$\mathrm{RMgX} + \mathrm{GeX_4} \rightarrow \mathrm{R_nGeX_{(4\text{-}n)}} \qquad (9)$$

Although the Grignard reaction for the production of organosilanes and stannanes works well, in the case of germanium, the reactions often lead to incomplete substitution (n < 4 for R$_n$GeX$_{(4\text{-}n)}$), and also give rise to oligo- and polygermanes, including cyclic derivatives.[18-25] If free magnesium is present in the reaction mixture, digermanes R_3GeGeR_3 are produced from the reaction of R_3GeMgX with $XGeR_3$.[18] The following examples are representative of typical results. When R = vinyl, not only was the tetra-substituted germane $Ge(CH{=}CH_2)_4$ obtained, but so was the digermane $Ge_2(CH{=}CH_2)_6$ and the trigermane $Ge_3(CH{=}CH_2)_8$.[20] For the reaction of germanium tetrabromide with excess phenylmagnesium bromide, a range of products is obtained: $GePh_4$, $BrGePh_3$, Br_2GePh_2, and Br_3GePh.[22] Under some conditions, the range of products from the reaction of germanium tetrabromide with phenylmagnesium bromide can include polygermanes $Ph(GePh_2)_nPh$, where n = 1, 2, 3, or even 4.[24]

The direct synthesis of organogermanes can be accomplished using methyl chloride and germanium powder at high temperatures to yield Me_2GeCl_2 as the main product, with small amounts of $MeGeCl_3$ and Me_3GeCl also being produced.[26] Reaction of p-ClC_6H_4Ph with germanium using a copper catalyst and high temperatures yields a mixture of $(p\text{-}PhC_6H_4)_2GeCl_2$ and $(p\text{-}PhC_6H_4)GeCl_3$.[27] Under similar conditions, the high temperature, copper-catalyzed reaction of germanium with $X(CH_2)_nX$ (X = Cl, Br; n = 1 – 5) gave mainly linear products such as $X(CH_2)_nGeX_3$ and $X_3Ge(CH_2)_nGeX_3$, with no ring compounds being formed.[28] By varying the reaction conditions, it is also possible to obtain $(X(CH_2)_n)_2GeBr_2$ from germanium and $X(CH_2)_nBr$.[4] By variation of the copper catalyst, it is possible to influence the product distribution.

For example, in the reaction of germanium with PhCl, all four chlorophenylgermanes ($Ph_nGeCl_{(4-n)}$) are formed, in a total yield of 76%, however, if CuCl is used, $PhGeCl_3$ (65%) and Ph_2GeCl_2 (35%) are the two major products.[4] Although the direct synthesis of organogermanes generally leads to a much wider product distribution compared to the Grignard synthesis, the direct synthesis is very simple to perform. While reaction temperature and type of reactants and solvent will affect the product distribution, reaction time is the variable that most greatly influences the product distribution.[4]

1.7 Tin

1.7.1 Industrial Production of Tin

Tin concentrates are obtained by crushing and grinding ores containing cassiterite, SnO_2, the most abundant tin mineral, into more manageable particle sizes.[1] Screen jigs or shaking tables of various designs are used to separate the cassiterite from other ore components on the basis of the density of the materials.[1] Alternatively, the cassiterite-containing ore is ground to a very fine particle size and a flotation method is used to separate the components. There are various stages of flotation (removing impurities from the surface layer) and desludging (removing impurities as precipitates) of the cassiterite before an acceptable concentration is achieved.[1]

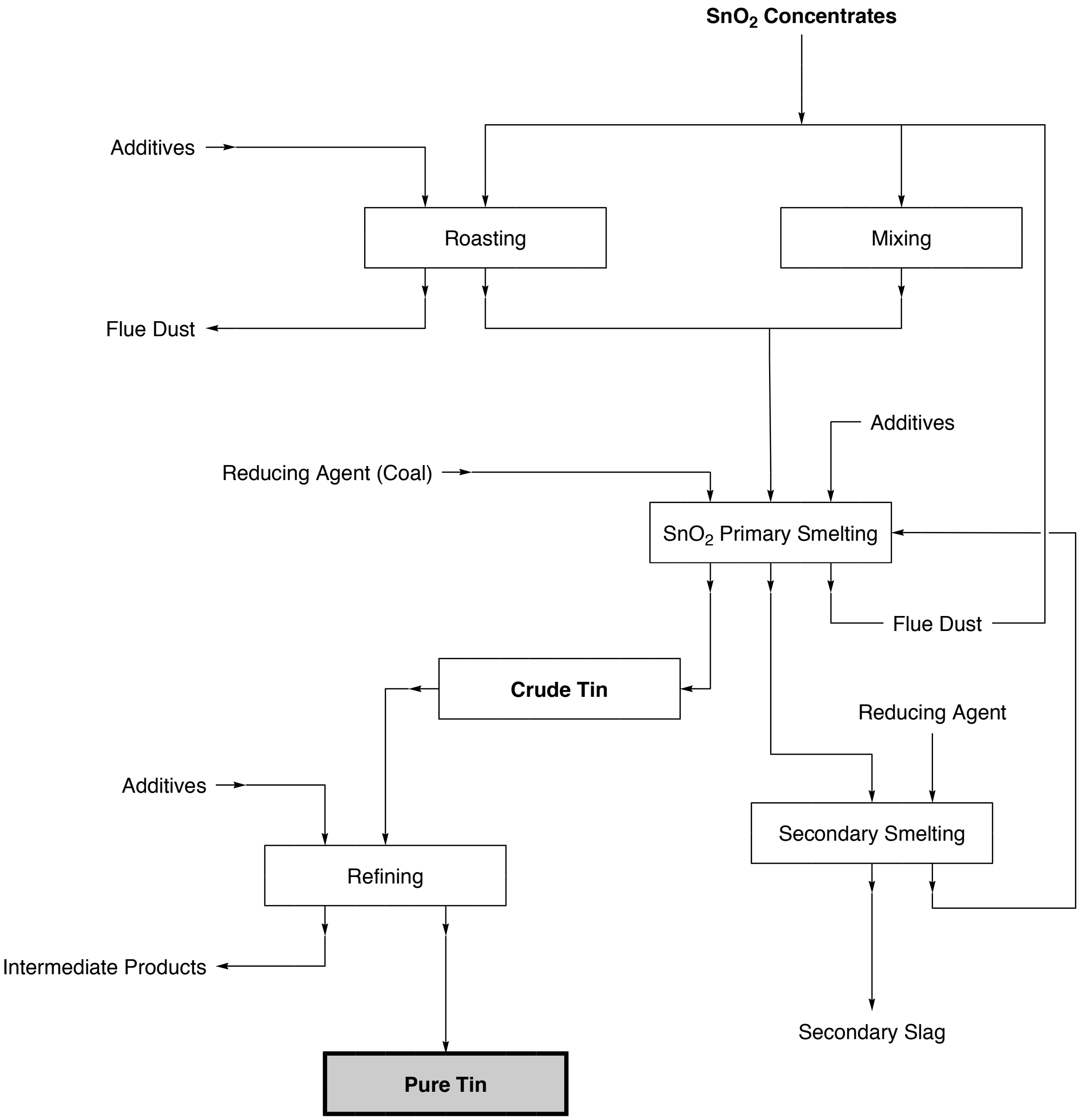


Figure 1.1: Industrial production of tin metal.[1]

In primary smelting, cassiterite (SnO_2) is reduced to tin metal using coal as a carbon source in a large furnace (Figure 1.1).[1] Oxygen must be added to the process because the active reductant is carbon monoxide according to equation 10.[1]

$$SnO_2 + 2\,CO \rightarrow Sn + 2\,CO_2 \qquad (10)$$

The carbon monoxide is generated according to equation 11:[1]

$$C + CO_2 \rightarrow 2\ CO \tag{11}$$

and the initial CO_2 comes from the reaction of oxygen with coal (equation 12).[1]

$$C + O_2 \rightarrow CO_2 \tag{12}$$

In primary smelting, the furnace must be operated between 1000 °C and 1100 °C.[1] Below 1000 °C, elements including copper, lead, and antimony are reduced which then alloy with the tin lowering the purity.[1] At temperatures above 1100 °C, iron is reduced along with tin and the purity of the product tin is much lower.[1] The maximum yield of tin (≈ 80%) at the highest possible purity (Fe ≈ 1%) is obtained when the temperature of the furnace is kept in the appropriate range.[1]

In secondary smelting (Figure 1.1), the slag from primary smelting is reduced using more forcing conditions, and this leads to a secondary slag that can be discarded because it is mainly iron.[1] The end result of secondary smelting is that most of the iron is removed from the tin waste of the primary smelting process.[1]

Tin refining is done by the stepwise removal of unwanted elements.[1] Iron is removed by heating the crude tin to 250 °C, at which temperature iron-tin alloys (FeSn and $FeSn_2$) are not very soluble in tin and are removed as precipitates.[1] Copper is removed next. Elemental sulfur (5 kg / tonne) is added to the molten tin to precipitate copper as its sulfide.[1] Arsenic is then removed by alloying it with aluminum to form AlAs precipitates.[1] Excess aluminum remaining in the tin can be removed by adding sodium hydroxide or sodium.[1]

Electrorefining is sometimes used to purify tin but it is a costly process so it is only done if the tin contains noble metals to offset the purification costs.[1]

Tin metal is then chlorinated, by the reaction of tin metal with Cl_2, producing $SnCl_4$, or oxidized, by the reaction of sprayed molten tin with a hot stream of air, producing SnO_2 (Scheme 1.3).[1]

1.7.2 Synthesis of Organostannanes

As with silicon and germanium, the primary method used to synthesize organostannanes is the reaction of Grignard reagents with tin tetrachloride or tin tetrabromide, according to equation 13.[1]

$$RMgX + SnX_4 \rightarrow R_nSnX_{(4-n)} \qquad (13)$$

Unless the alkyl groups are bulky, the reaction of Grignard reagents with $SnCl_4$ usually gives fully alkylated products SnR_4.[4] Tetra-substituted organostannanes are used to generate the required chlorostannanes[1] by Kocheshkov redistribution reactions (equations 14-16):

$$3\ SnR_4 + SnCl_4 \rightarrow 4\ R_3SnCl \quad (14)$$

$$SnR_4 + SnCl_4 \rightarrow 2\ R_2SnCl_2 \quad (15)$$

$$SnR_4 + 3\ SnCl_4 \rightarrow 4\ RSnCl_3 \quad (16)$$

The generation of R_3SnCl and R_2SnCl_2 works reliably for many alkyl groups, but only works well in a few cases for $RSnCl_3$.[1, 29] Good yields of monoroganosubstituted chlorostannanes are obtained only for R = Et, vinyl, and Ph.[29]

The direct synthesis of $R_nSnX_{(4-n)}$ is possible from tin metal and organic halides at elevated temperatures in the presence of a catalyst, usually a tetraalkylammonium halide.[1]

The objectives of this project are to 1) synthesize complexes of Silicon, Germanium, and Tin that are suitable substitutes for the corresponding metal chlorides, without the use of HCl or Cl_2, to improve worker safety by replacing metal chlorides and thus reducing chlorine consumption, 2) to use these complexes to synthesize tetraorganosilanes, tetraorganogermanes (including GeH_4), and tetraorganostannanes, and 3) to use these complexes to synthesize functionalized compounds of the three elements studied.

1.8 References

1. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, F. Ullmann: *Ullmann's Encyclopedia of Industrial Chemistry,* VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany; Deerfield Beach, Fla, **1985**.

2. R. E. Kirk, D. F. Othmer, J. I. Kroschwitz, M. Howe-Grant: *Encyclopedia of Chemical Technology,* Wiley, New York, **1991**.

3. N. N. Greenwood, A. Earnshaw: *Chemistry of the Elements,* Butterworth-Heinemann, Boston, Mass., **1997**.

4. D. M. P. Mingos, R. H. Crabtree: *Comprehensive Organometallic Chemistry III,* Elsevier, Amsterdam; London, **2007**.

5. M. Chu, Y. Sun, U. Aghoram, S. E. Thompson: *Annu. Rev. Mater. Res.,* **2009**, *39*, 203-229.

6. S. S. Chung: *ECS Trans.,* **2011**, *41*, 27-41.
7. J. D. J. W.C. Butterman: *U.S.G.S. Mineral Commodity Profiles,* **2005**.

8. C. M. Thomas: *Chem. Soc. Rev.,* **2010**, *39*, 165-173.

9. C. Licht, L. T. Peiró, G. Villalba: *J. Ind. Ecol.,* **2015**, *19*, 890-903.

10. K. Hudson-Edwards: *Science,* **2016**, *352*, 288-290.

11. P. Anastas, N. Eghbali: *Chem. Soc. Rev.,* **2010**, *39*, 301-312.

12. C. Eaborn: *Organosilicon Compounds,* Butterworths Scientific Publications, London, **1960**.

13. H. Gilman, R. K. Ingham: *J. Am. Chem. Soc.,* **1955**, *77*, 1680-1681.

14. M. Fishwick, M. G. H. Wallbridge: *J. Organometal. Chem.,* **1970**, *25*, 69-79.

15. R. Venkatasubramanian, R. T. Pickett, M. L. Timmons: *J. Appl. Phys.,* **1989**, *66*, 5662-5664.

16. R. Russotti: Method of Synthesis of Gaseous Germane: US4668502, **1987**.

17. H. P. Withers, P. B. Henderson: Production and Purification of Germane: US20050191854, **2005**.

18. F. Glockling, K. A. Hooton: *J. Chem. Soc.,* **1962**, 3509-3512.

19. F. Glockling: *Q. Rev. Chem. Soc.,* **1966**, *20*, 45-65.

20. F. Glockling, M. A. Lyle, S. R. Stobart: *J. Chem. Soc., Dalton Trans.,* **1974**, 2537-2542.

21. C. A. Kraus, L. S. Foster: *J. Am. Chem. Soc.,* **1927**, *49*, 457-467.

22. G. T. Morgan, H. D. K. Drew: *J. Chem. Soc., Trans.,* **1925**, *127*, 1760-1768.

23. D. Quane, R. S. Bottei: *Chem. Rev.,* **1963**, *63*, 403-442.

24. S. Roller, D. Simon, M. Draeger: *J. Organomet. Chem.,* **1986**, *301*, 27-40.

25. R. Schwarz, M. Schmeisser: *Ber. Dtsch. Chem. Ges. B,* **1936**, *69B*, 579-585.

26. M. E. Lee, K. L. Bobbitt, D. Lei, P. P. Gaspar: *Synth. React. Inorg. Met. Org. Chem.,* **1990**, *20*, 77-81.
27. E. A. Chernyshev, V. L. Rogachevskii, T. L. Krasnova, N. M. Babaeva: *Zh. Obshch. Khim.,* **1978**, *48*, 636-639.

28. V. F. Mironov, T. K. Gar, A. A. Buyakov: *Zh. Obshch. Khim.,* **1973**, *43*, 798-801.

29. S. H. L. Thoonen, B. Deelman, G. Van Koten: *J. Organomet. Chem.,* **2004**, *689*, 2145-2157.

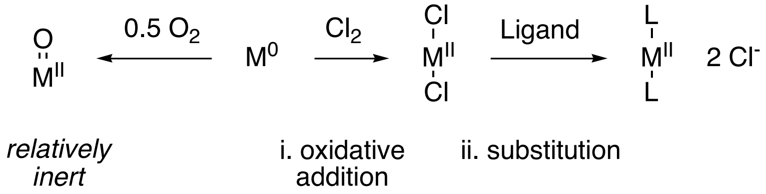
Chapter 2: A Chlorine-Free Protocol for Processing Germanium

2.1 Co-Authorship

The synthetic work and writing of chapters 3, 4, and 5 was performed by Michael Krause. Chapter 2 is based on a manuscript, published in *Science Advances*, co-authored by Martin Glavinović, Michael Krause, Linju Yang, John McLeod, Lijia Liu, Kim Baines, Tomislav Friščić, and J.-P. Lumb (*Sci. Adv.*, **2017**, *3*, e1700149). Michael Krause was responsible for writing the first draft of the manuscript and for contributing to the editing of the manuscript. The optimization of the reaction of Grignard reagents with $Ge(3,5\text{-dtbc})_2(py)_2$, the synthesis of $Ge(3,5\text{-dtbc})_2(py)_2$ from $GeCl_4$ and from GeO_2, as well as the synthesis of GeH_4 from $Ge(3,5\text{-dtbc})_2(py)_2$ were performed by Michael Krause. The mechanochemical syntheses of $Ge(3,5\text{-dtbc})_2(py)_2$, $Ge(3,5\text{-dtbc})_2(NMI)_2$, and $Ge(3,5\text{-dtbc})_2(TMEDA)$, as well as the extraction of germanium from germanium / zinc mixtures by mechanochemistry were performed by Martin Glavinović of McGill University. XAS analysis of $Ge(3,5\text{-dtbc})_2(py)_2$ was performed by Linju Yang, John A. McLeod, and Lijia Liu of Soochow University. The acquisition of GC-MS data, as well as the EI analysis of GeH_4, were performed by Doug Hairsine (Manager, Mass Spectrometry Facility, UWO).

2.2 Introduction

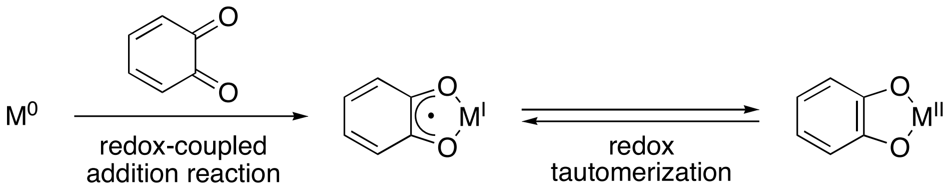
The quality of modern life is increasingly dependant upon the unique properties of metal – containing materials.[1] This has prompted significant efforts to improve the efficiency of metal extraction and refinement, as well as metal – recycling from post – consumer products.[2] In mineral deposits and early stages of refinement, metals are typically present in the form of relatively inert oxides, whose processing is challenged by high lattice energies, high melting points, and low solubility.[3] This requires their conversion into more labile derivatives for both purification and functionalization. Chief amongst these derivatives are metal chlorides, whose ubiquity in metal – manufacturing belies an energy and risk intensive life cycle (Scheme 2.1). Metal chlorides are prepared by either dehydration of the oxide with hydrochloric acid (HCl), or reduction of the oxide to the metal accompanied by re-oxidation with molecular chlorine (Cl_2).[3]



Scheme 2.1: Oxidation of low-valent metals for the preparation of organometallics.

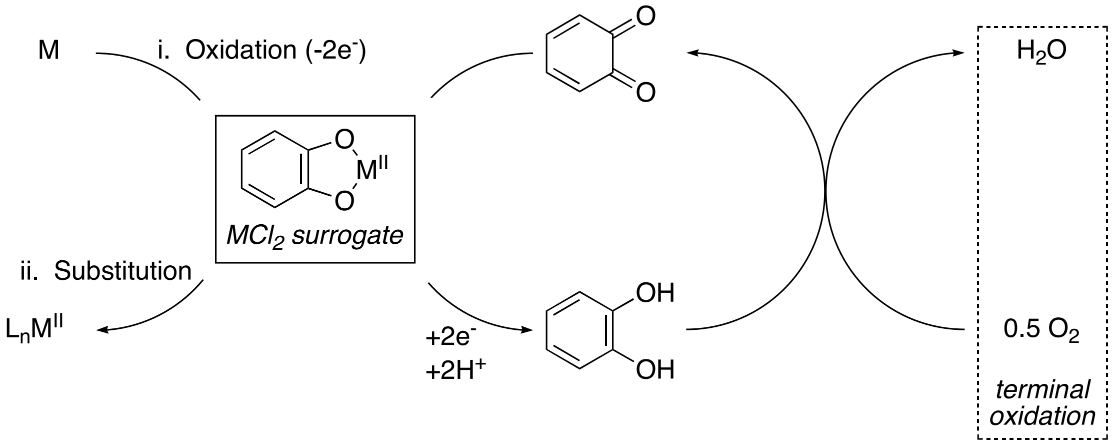
To appreciate the scale and impact of these processes, it is helpful to consider that the global synthesis of inorganic chemicals consumes $\approx 9 \times 10^6$ metric tons of Cl_2 per year, representing an energy demand exceeding 2×10^{10} kWh, estimated by assuming the maximum efficiencies of the chlor-alkali process.[4] The industrial synthesis of HCl is linked to Cl_2 by either reduction with hydrogen (H_2) or dehydrohalogenation of chlorinated organic compounds. Once produced, stringent regulations must be in place to transport and utilize Cl_2 and HCl, including corrosion resistant facilities, and precautions to rigorously maintain worker exposure below 1 ppm and 5 ppm for Cl_2 and HCl, respectively. Many of these precautions must be maintained to manipulate downstream metal chlorides, which are generally moisture sensitive and corrosive. The combination of these features create clear motivations to replace Cl_2, and its associated products with more environmentally sensitive alternatives.[5, 6]

In their capacity as versatile intermediates for inorganic synthesis, metal chlorides provide invaluable flexibility, for which air and moisture – tolerant replacements, that do not employ Cl_2 or HCl in their production, are scarce.[7] Metal chlorides are equally important in extraction and refinement processes, requiring a suitable replacement strategy to address issues of synthetic utility as well as separation science. In considering these challenges, we were drawn to metal complexes of catechols, which can be prepared from either a low – valent metal by two – electron oxidation with an *ortho*-quinone, or substitution from a higher valent metal with a catechol (Scheme 2.2).[8]



Scheme 2.2: Redox-coupled organometallic synthesis (A).

While metal catecholates, and their related semi-quinone redox tautomers, have been extensively studied as redox non – innocent ligands,[9-12] their use as pseudo halides for inorganic synthesis has received considerably less attention.[13, 14] Ligand exchange of these complexes with a nucleophile could provide an organometallic complex retaining an oxidized metal centre along with a displaced catechol (Scheme 2.3).



Scheme 2.3: Redox-coupled organometallic synthesis (B).

Assuming high – efficiencies in the recovery of catechol, an attractive feature of this system could be its re-oxidation to the *ortho*-quinone with air. This would close a redox cycle that ultimately links the oxidation of metals to the terminal reduction of molecular oxygen (O_2), in a manner that draws inspiration from Backvall's bio – inspired electron transfer mediators for aerobic oxidations of organic substrates.[15] This would replace the oxidizing capacity of Cl_2 with O_2, which could have a transformative effect on inorganic synthesis. Oxygen is a readily available, naturally occurring oxidant, whose complete reduction to water (H_2O) provides a clean source of chemical energy that has been extensively investigated for improving the efficiency of organic synthesis.[16, 17] Current uses of O_2 in metal manufacturing are mostly limited to the synthesis of metal oxides, which suffer from the poor synthetic and processing utility discussed above. By segregating aerobic oxidation from the re-oxidation of an organic co-factor, our system would draw from this naturally occurring and clean source of energy to drive inorganic synthesis, while avoiding the formation of inert metal oxides.

To demonstrate the utility of this system, we report here a low – energy synthesis of organogermanes (GeR_4), including germane (GeH_4), from either germanium metal (Ge^0) or germanium dioxide (GeO_2) (Figure 2.1).

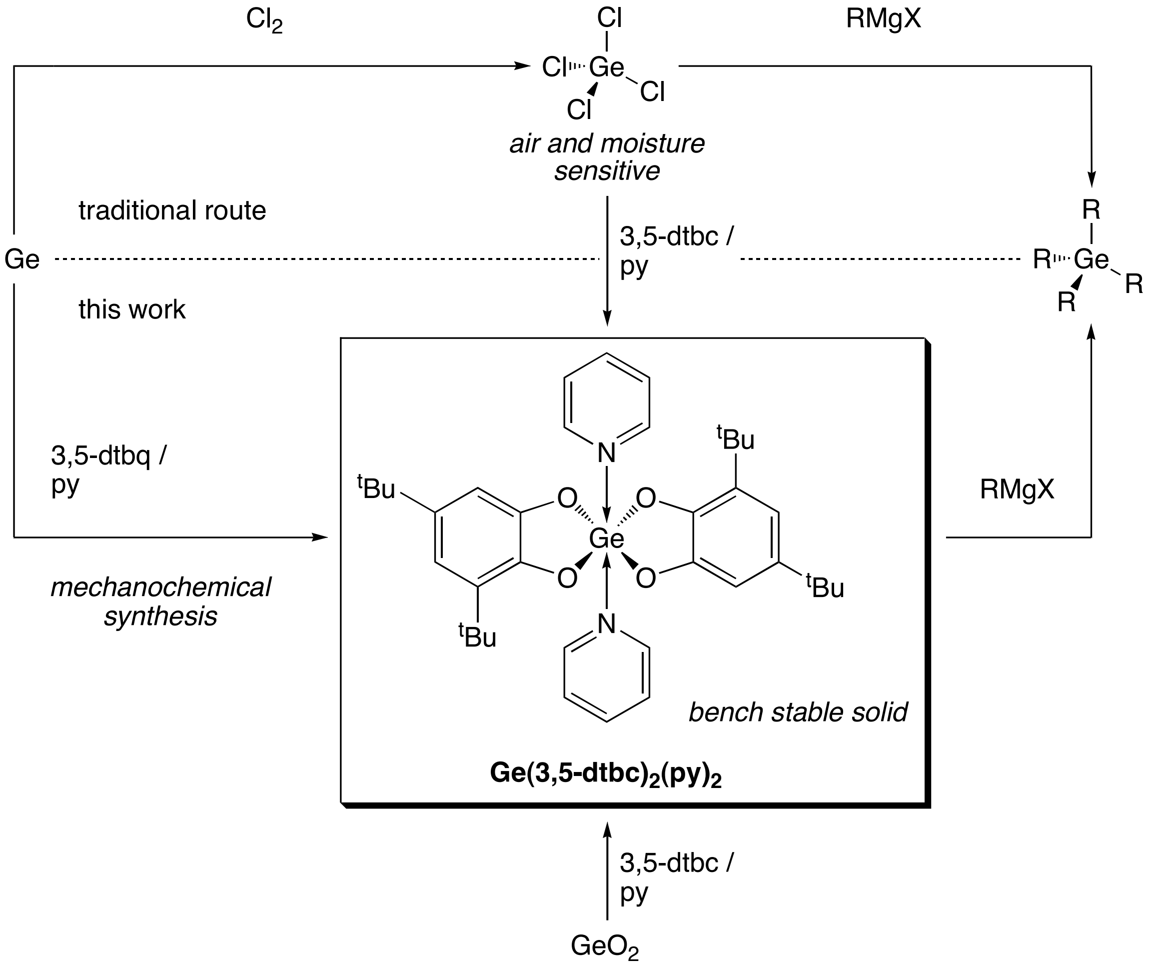


Figure 2.1: Synthesis of tetraorganogermane precursor Ge(3,5-dtbc)$_2$(py)$_2$ from Ge^0, 3,5-di-*tert*-butyl-1,2-quinone (3,5-dtbq) and pyridine, or either $GeCl_4$ or GeO_2 combined with 3,5-di-*tert*-butylcatechol (3,5-dtbc) and pyridine.

GeH_4 is widely used for the vapor deposition of germanium in electronic and optical device fabrication.[18, 19] Germanium is a non-renewable resource that is classified by Licht *et al.* as a “critical” element due to low concentration in mineral ores, low producer diversity, lack of substitutes, and growing demand, which Is estimated to increase by > 2,000% by the year 2050.[20] This has lead to new recovery efforts from post-consumer products, which accounted for about 30% of the 118 tons of germanium used industrially in 2011.[20] While Ge^0 does not occur naturally, it is widely distributed in commercial products, and is thus an important input into the industrial life – cycle through post – consumer recycling, where it is first converted to germanium tetrachloride ($GeCl_4$) by oxidation with Cl_2.[4] Germanium is more commonly derived as a co-product of zinc refinement, which requires a multi – step extraction from zinc oxide (ZnO) that involves leaching distillation residues containing GeO_2 with HCl to produce $GeCl_4$.[4, 20, 21] As with many metal halides, $GeCl_4$ is a moisture – sensitive, corrosive liquid that hydrolyses to HCl and GeO_2 in the presence of water. It is a poor reagent for substitution reactions,[13] as evidenced by the low yields and low purity of GeH_4 streams that are produced by its reaction with metal hydrides,[19] and the formation of incomplete substitution products and oligogermanes in its reaction with Grignard reagents.[22, 23] Nevertheless, $GeCl_4$ is a critical intermediate in the contemporary germanium life – cycle, from which all downstream products are currently derived. Recognizing its central role, but energy and risk intensive use, we targeted a replacement of $GeCl_4$ that would exhibit bench-top stability and improved performance for the synthesis of germanes.

2.3 Discussion

Building upon early investigations of Tuck[24] and the recent development of 3,5-dtbq as a mild and selective metal oxidant for solid-state chemistry,[8] the mechanochemical[25] oxidation of germanium powder (1 equivalent) by ball milling with 3,5-dtbq (2 eq) in the presence of pyridine (2 eq) as an auxiliary complexing ligand was evaluated. The use of liquid-assisted grinding (LAG) conditions was paramount,[26] as efforts to grind the reactants in neat form returned unreacted starting materials, as determined by powder X-ray diffraction (PXRD). By contrast, the addition of 60 μL of a 1 : 1 mixture of toluene and water for a total reactant mass of 200 mg provided $Ge(3,5\text{-}dtbc)_2(py)_2$ in 88% isolated yield following milling at 30 Hz for 3 h at room temperature and recrystallization from toluene. This efficiency was maintained on gram scale, to provide $Ge(3,5\text{-}dtbc)_2(py)_2$ in 83% isolated yield. $Ge(3,5\text{-}dtbc)_2(py)_2$ is a bench-top stable, beige solid, whose structure was unambiguously identified by NMR spectroscopy, single crystal X-ray crystallography (Figure 2.2), and X-ray absorption spectroscopy (XAS) (Figure 2.3).

The octahedral complex has the two pyridine ligands in *trans*-disposition (Figure 2.2) with a Ge-N(1) bond length of 2.098(1) Å, which Is comparable to the Ge-N distances in a series of pyridyl Ge^{IV} halide complexes (2.01-2.11 Å).[27-30] Not surprisingly, the pyridine nitrogen-germanium bond distances are elongated compared to standard Ge-N acyclic bond distances (1.85-1.86 Å).[31]

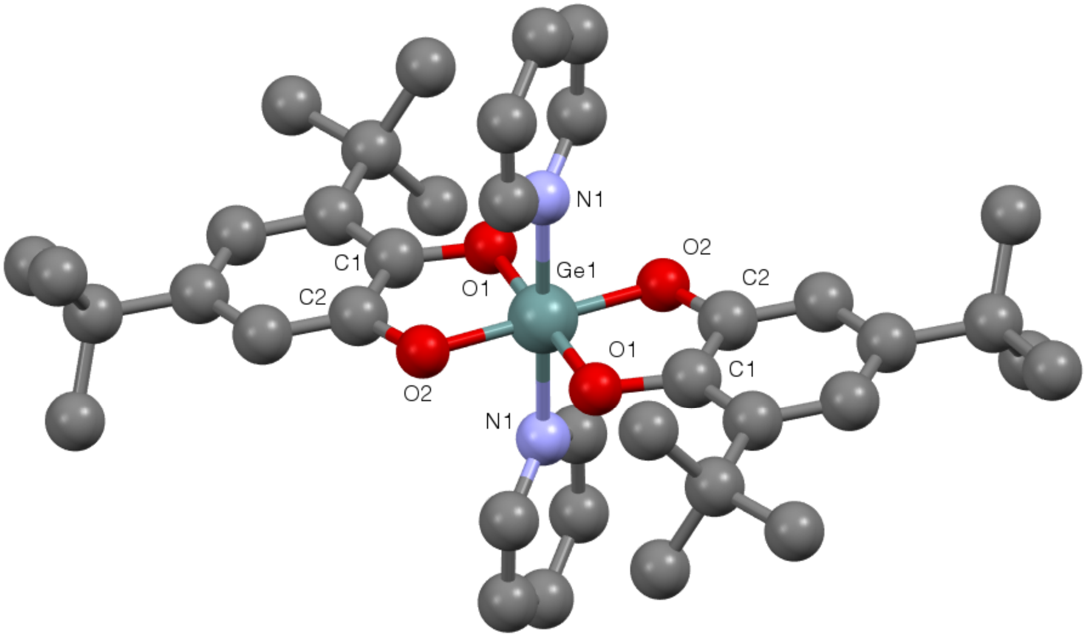


Figure 2.2: Thermal ellipsoid plot (50% probability) of Ge(3,5-dtbc)$_2$(py)$_2$•$C_6H_5CH_3$. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and bond angles (°): Ge1-O1 1.847(1), Ge1-O2 1.849(1), Ge1-N1 2.098(1), C1-O1 1.366(2), C2-O2 1.365(2), C1-C2 1.412(2); O1-Ge1-O2 89.41(5), O1-C1-C2 115.4(1), O2-C2-C1 116.2(1).

The catecholato ligands are arranged in a plane about the germanium (O-Ge-O bond angles of 89.41(5)° and 90.59(5)°) (Figure 2.2). The Ge-O bond distances of 1.847(1) Å and 1.849(1) Å fall clearly within the range reported for related bis(catecholato)Ge^{IV} complexes with alcohol or ether – based donor ligands.[31-33] The C-O bond distances of 1.366(2) Å and 1.365(2) Å are typical for catecholate ligands,[9] suggesting a 2-electron reduction of each *ortho*-quinone unit, and a net oxidation of Ge^0 to Ge^{IV}. This assignment was further established by XAS (Figure 2.3): the absorption peak maxima of Ge(3,5-dtbc)$_2$(py)$_2$ falls between that of GeO_2 and $Ge(HPO_4)_2$ confirming that the germanium atom has an oxidation state of +4.

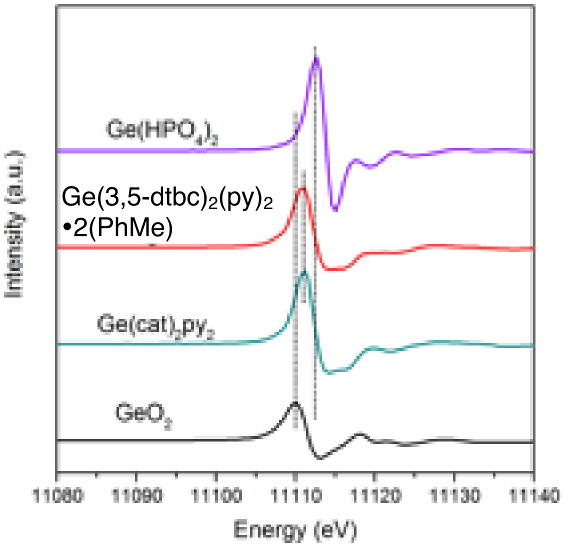
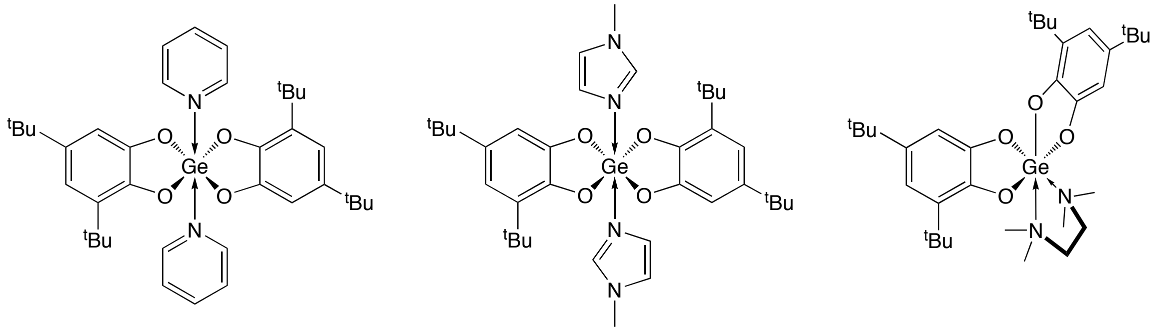


Figure 2.3: First derivatives of the Ge K-edge XAS of Ge(3,5-dtbc)$_2$(py)$_2$•2(PhMe) and Ge(3,5-dtbc)$_2$(py)$_2$ using Ge(HPO$_4$)$_2$ and GeO$_2$ as reference materials.

The mechanochemical protocol for the synthesis of Ge(3,5-dtbc)$_2$(L)$_2$ provides flexibility in the choice of the amine ligand, which in turn provides a means of controlling the relative stereochemistry of the catecholate complex. For example, replacing py with N-methyl-imidazole (NMI) affords an isostructural octahedral complex with *trans* – disposed nitrogen ligands, whereas a *cis* – relationship between the nitrogen atoms can be enforced by employing a chelating diamine, so that tetramethylethylenediamine (TMEDA) provides an octahedral complex under otherwise identical conditions (Figure 2.4).



Ge(3,5-dtbc)$_2$(py)$_2$ **Ge(3,5-dtbc)$_2$(NMI)$_2$** **Ge(3,5-dtbc)$_2$(TMEDA)**

Figure 2.4: Structures of Ge(3,5-dtbc)$_2$(py)$_2$, Ge(3,5-dtbc)$_2$(NMI)$_2$, and Ge(3,5-dtbc)$_2$(TMEDA).

Our optimized LAG conditions can be extended to the dehydration of GeO_2 by simply replacing 3,5-dtbq with 3,5-dtbc (2 eq), under otherwise identical conditions. This provides Ge(3,5-dtbc)$_2$(py)$_2$ in 84% isolated yield on gram scale. Activation of metal oxides at room temperature in a chloride – free process that generates H_2O as the sole stoichiometric byproduct is noteworthy,[34] and allows us to approach the challenge of oxide separation under mild conditions. From natural deposits, germanium is separated from ZnO by leaching with HCl to provide mixtures of $GeCl_4$ and $ZnCl_2$ that are separated by distillation (b.p. $GeCl_4$ = 86.5 °C; b.p. $ZnCl_2$ = 732 °C).[4, 20, 21] By employing our mechanochemical approach, we are able to selectively functionalize GeO_2 in both 1 : 1 and 1 : 5 mixtures with ZnO (by weight), by simply milling with 3,5-dtbc under our standard conditions. This selectively activates GeO_2 as the complex Ge(3,5-dtbc)$_2$(py)$_2$, which is readily separated from ZnO by washing with methylene chloride.[34] Ge(3,5-dtbc)$_2$(py)$_2$ is then isolated in yields of 64% and 66%, respectively, following recrystallization from cyclohexane. This provides a proof – of –

principle demonstration of a low – energy and chloride – free approach for the separation of germanium from zinc in the mineral oxide form.

Initial reactions of Ge(3,5-dtbc)$_2$(py)$_2$ with BuMgCl using THF as solvent and a 20:1 ratio of Grignard reagent to complex produced $GeBu_4$ in excellent yields and purities, indicating that Ge(3,5-dtbc)$_2$(py)$_2$ may serve as a replacement for $GeCl_4$. To have enough material for the optimization of the reaction conditions, multi-gram quantities of Ge(3,5-dtbc)$_2$(py)$_2$ were required. However, the mechanochemical synthesis of Ge(3,5-dtbc)$_2$(py)$_2$ can only be run on a 500 mg scale due to the physical size of the milling jars, so, a larger-scale synthesis of Ge(3,5-dtbc)$_2$(py)$_2$ had to be developed. The reaction of $GeCl_4$ with 2 eq of 3,5-dtbc in pyridine lead to Ge(3,5-dtbc)$_2$(py)$_2$ in good yields (80%) and quantities (Scheme 2.5). To avoid the use of $GeCl_4$, the direct reaction of GeO_2 with 2 eq of 3,5-dtbc in pyridine was investigated, and several grams of Ge(3,5-dtbc)$_2$(py)$_2$ were synthesized according to this method (Scheme 2.6). The only byproduct from the synthesis of Ge(3,5-dtbc)$_2$(py)$_2$ from GeO_2, 3,5-dtbc, and pyridine is H_2O. Corriu *et al.* have also reported the synthesis of hypercoordinate complexes from germanium dioxide, but their method relies on anionic conditions and a more labor-intensive purification strategy, while our system uses neutral conditions and requires fewer purification steps.[14]

The optimization of the reaction of Ge(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents was performed using BuMgCl because: 1) quenching of the excess Grignard reagent yields butane gas, which is volatile and is easily removed, and

2) $GeBu_4$ is a liquid that is easily separated and isolated from 3,5-di-*tert*-butylcatechol and the impurities of the reaction using a thin layer chromatography purification strategy. The first variable optimized was the reaction time. A 24 hour time period was determined to be the ideal time period for the reaction since at shorter reaction times lower yields of $GeBu_4$ were obtained (Table 2.1: entries 1-3). To test the effect of solvent on yield, the reaction of BuMgCl with $Ge(3,5\text{-dtbc})_2(py)_2$ was examined using mixtures of diethyl ether, dibutyl ether, or 1,4-dioxane with THF (Table 2.1: entries 1, 4-6). Ethers were selected because they are standard solvents for Grignard reagents. Higher boiling ethers were selected to see if better yields could be achieved in shorter time periods. Mixtures of 1,4-dioxane / THF, dibutyl ether / THF and pure THF gave similar yields of $GeBu_4$, however, the yield of $GeBu_4$ was lower when diethyl ether / THF is used, likely because of the low boiling point of diethyl ether, and therefore a lower rate of reaction. Given that no improvement in yields was observed using mixed solvent systems, THF was selected as the standard solvent. The effect of the number of eq of the Grignard reagent was also investigated. When the number of eq of BuMgCl was lowered from 20 to 5, the yield of $GeBu_4$ dropped from 52% to 37% (Table 2.1: entries 1 and 7), and thus, a ratio of 20 eq of Grignard reagent to one equivalent of $Ge(3,5\text{-dtbc})_2(py)_2$ was retained as the standard mole ratio. Similarly, the concentration of the Grignard reagent was investigated. When the concentration of BuMgCl was increased from 0.75 M to 2.0 M, the yield of $GeBu_4$ dropped from 52% to 31% (Table 2.1: entries 1 and 8). To investigate the action

of lithium, chloride, and bromide ions on the yield of $GeBu_4$, LiCl or LiBr was added to the reaction mixtures (Table 2.1: entries 1, 9, and 10). The addition of 4 eq of LiCl to the reaction mixture increases the yield of $GeBu_4$ to 68% from 52%, however, the addition of 4 eq of LiBr decreased the yield of $GeBu_4$ to 5%. As Lewis acids, the lithium cations can be expected to facilitate the removal of the 3,5-dtbc ligands from $Ge(3,5\text{-dtbc})_2(py)_2$, however, the bromide anions have a clear detrimental effect on the outcome of the reaction, and thus, the use of additives was not pursued.

Table 2.1: Optimization of reaction conditions for the reaction of $Ge(3,5\text{-dtbc})_2(py)_2$ with Grignard reagents.

Entry	**RM** [1]	**Complex : RM**	**Solvent** (amount)	**Time** (hrs)	**Temp** (°C)	**Workup** [2]	**Yield** [3]	**Catechol Recovery** [4]
1	BuMgCl 2.0 M THF	1 : 20	THF (10 mL)	0.5	65	A	52%	94%
2	BuMgCl 2.0 M THF	1 : 20	THF (10 mL)	5	65	A	65%	98%
3	BuMgCl 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	91%	92%
4	BuMgCl 2.0 M THF	1 : 20	THF (3.75 mL) + Et_2O (6.25 mL)	0.5	65	A	28%	80% [5]
5	BuMgCl 2.0 M THF	1 : 20	THF (3.75 mL) + 1,4-Dioxane (6.25 mL)	0.5	65	A	42%	81%
6	BuMgCl 2.0 M THF	1 : 20	THF (3.75 mL) + Bu_2O (6.25 mL)	0.5	65	A	48%	87%
7	BuMgCl 2.0 M THF	1 : 5	THF (10 mL)	0.5	65	A	37%	70%
8	BuMgCl 2.0 M THF	1 : 20	THF (3.75 mL)	0.5	65	A	31%	20%
9	BuMgCl 2.0 M THF [6]	1 : 20	THF (10 mL)	0.5	65	A	68%	81%
10	BuMgCl 2.0 M THF [7]	1 : 20	THF (10 mL)	0.5	65	A	5%	62%

1. Commercial sources of RM, used as received unless indicated otherwise.
2. See reaction descriptions for details of the workup.
3. Isolated yield.
4. GC yield.
5. Recovery: 25% 3,5-di-*tert*-butylcatechol, 75% 3,5-di-*tert*-butyl-1,2-quinone.
6. 4 eq LiCl added.

7. 4 eq LiBr added.

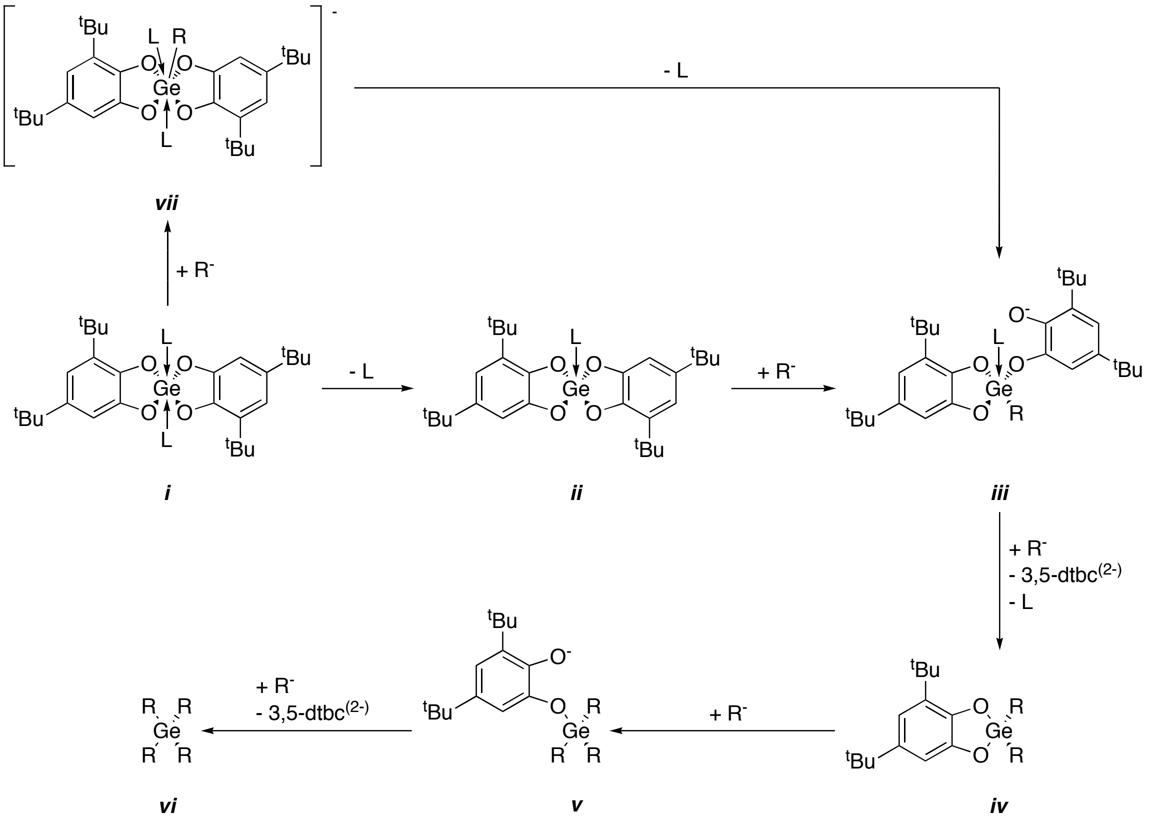
Under our optimized conditions, a variety of alkyl and aryl Grignard reagents (20 eq) in THF were added to a suspension of Ge(3,5-dtbc)$_2$(py)$_2$ in THF to evaluate the scope of the reaction. The resulting heterogeneous mixtures were then warmed to 65 °C for 24 h before aqueous work-up and chromatographic separation to provide the organogermanes with isolated yields generally above 80% (Table 2.2). Substitution with BnMgCl presents an exception (Table 2.2, entry 3), where we attribute the decreased yield of 60% to competitive formation of bibenzyl. Substitution with $H_2C{=}CHCH_2MgCl$ proceeds in near quantitative yield (Table 2.2, entry 5), and provides a favorable point of comparison to the related substitution using $GeCl_4$, which proceeds in only 45% yield.[35] The reaction of Ge(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents for R = Mes and R = ^{s}Bu do not proceed as cleanly as the less sterically bulky R groups, with mixtures of products being formed. For R = Mes (Table 2.2, entry 6), the large steric bulk prevents more than 3 ligands from being attached to germanium. For R = ^{s}Bu (Table 2.2, entry 7), formation of digermanes takes place. In each of these cases, the unusually high selectivity and isolated yield of the organogermanes is accompanied by good to excellent recoveries of 3,5-dtbc. This allows us to indirectly link the 4 electron oxidation of Ge^0 to the reduction of O_2, by using well – established methodologies for the catalytic aerobic oxidation of 3,5-dtbc to 3,5-dtbq.[36]

Table 2.2: Synthesis of organogermanes GeR_4 from the reaction of Ge(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents.

Entry	RM [1]	Complex : RM	Solvent (amount)	Time (hrs)	Temp (°C)	Workup [2]	Yield [3]	Product	Catechol Recovery [4]
1	BuMgCl 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	91%	$GeBu_4$	92%
2	PhMgCl 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	83%	$GePh_4$	83%
3	BnMgCl 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	60%	$GeBn_4$: Bn_2 10 : 1 by moles > 95% by mass	74% [5]
4	HexMgCl 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	97%	$GeHex_4$	67%
5	AllMgCl 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	97%	$GeAll_4$	80%
6	MesMgBr 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	14%	$GeMes_3H$: crude mixture contains $Mes_2Ge(OH)_2$: $Mes_2Ge_2H_4$: $Mes_2Ge(dtbc)_1$ in a 5:1:5 ratio	84%
7	^{s}BuMgCl 1.2 M THF	1 : 20	THF (10 mL)	24	65	B	22%	Stereo-isomers of $^{s}Bu_3Ge\text{-}Ge^{s}Bu_3$: crude mixture contains $^{s}Bu_2GeH_2$: $(H_3C\text{-}HC{=}(H_3C)C\text{-})_2Ge^{s}Bu_2$: $^{s}Bu_3Ge_2H_3$: $^{s}Bu_3Ge\text{-}Ge^{s}Bu_3$ in a 1:1:2:2 ratio	83%
8	TolMgBr 2.0 M THF	1 : 20	THF (10 mL)	24	65	A	85%	$GeTol_4$	91%

1. Commercial sources of RM, used as received unless indicated otherwise.
2. See reaction descriptions for details of the workups.
3. Isolated yield.
4. GC yield.
5. 4 : 1 mole ratio of 3,5-di-tert-butylcatechol : $GeBn_4$.

We attribute the unusually high selectivity for the substitution reaction of Ge(3,5-dtbc)$_2$(py)$_2$ to a unique mechanism (Scheme 2.4), in which steric strain is relieved as substitution progresses.[14] This is distinct from substitution reactions of $GeCl_4$, where exchange of a chloride ligand with a carbon nucleophile creates a more sterically encumbered complex, so that substitution becomes increasingly difficult as the reaction progresses. In contrast, partially replacing the catecholate ligands of Ge(3,5-dtbc)$_2$(py)$_2$ should create a more accessible germanium centre, so that substitution with a second equivalent of the Grignard reagent is faster than the first. Subsequent substitutions with additional eq of Grignard reagent should then become increasingly facile, as the sterically encumbered catecholate ligands are progressively displaced.



Scheme 2.4: Proposed mechanism of formation of $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ (***iv***), $R_3Ge(3,5\text{-dtbc-}\kappa^1)$ (***v***), and GeR_4 (***vi***) from $Ge(3,5\text{-dtbc})_2(L)_2$ and Grignard reagents.

Recognizing the unique performance of $Ge(3,5\text{-dtbc})_2(py)_2$ in the complete and selective 4-fold substitution reaction with Grignard reagents, we evaluated its performance as a precursor to GeH_4, using lithium aluminum hydride ($LiAlH_4$) as a hydride donor. GeH_4 is a volatile, highly flammable and toxic gas at room temperature, whose considerable risks are offset by its high value as a reagent for vapor deposition.[18] Due to stringent requirements of purity, the preparation and purification of GeH_4 have been extensively studied.[19, 37] Existing methodologies starting from germanium include electrochemical oxidation, plasma – based bombardment with high energy protons, or sintering with alkaline earth metals to provide germanides (e.g. Mg_2Ge) followed by protonation. More commonly practiced are chemical reductions of $GeCl_4$, GeO_2, or Na_2GeO_3 with metal hydrides in either organic solvents or aqueous solutions below pH 7. Drawbacks to these methodologies include any one or more of the following: use of highly purified Ge, $GeCl_4$, or GeO_2; high energy demands; and the co-production of unwanted byproducts, including digermane (Ge_2H_6).[19, 37] To address the challenge of preparing a high – quality GeH_4 stream, we evaluated the substitution of $Ge(3,5\text{-dtbc})_2(py)_2$ with $LiAlH_4$ at room temperature, using dibutyl ether as solvent and argon as an inert carrier gas. Substitution reactions were carried out in a modified J. Young tube reactor (Figure 2.5), directly connected to a mass spectrometer with a detection limit of ≈ 20 femtograms.

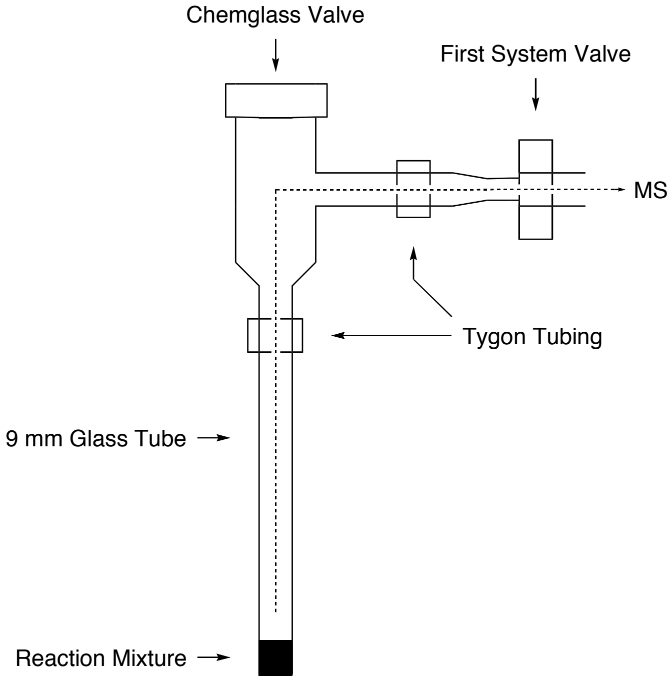


Figure 2.5: Reaction apparatus for the generation of GeH_4 gas from Ge(3,5-dtbc)$_2$(py)$_2$ and $LiAlH_4$ in Bu_2O.

Upon agitation of a heterogeneous mixture of Ge(3,5-dtbc)$_2$(py)$_2$ and $LiAlH_4$, moderate gas evolution was observed for ≈ 20 min. The resulting headspace was then directly sampled by EI-MS, to reveal only the formation of GeH_4 as a gaseous mixture with argon, with no other volatile compounds being detected over the course of the experiment (Figure 2.6, Figure 2.7). The obtained results compare favorably to the library EI-MS of GeH_4 (Figure 2.8) and to the previously published EI-MS data of GeH_4.[38]

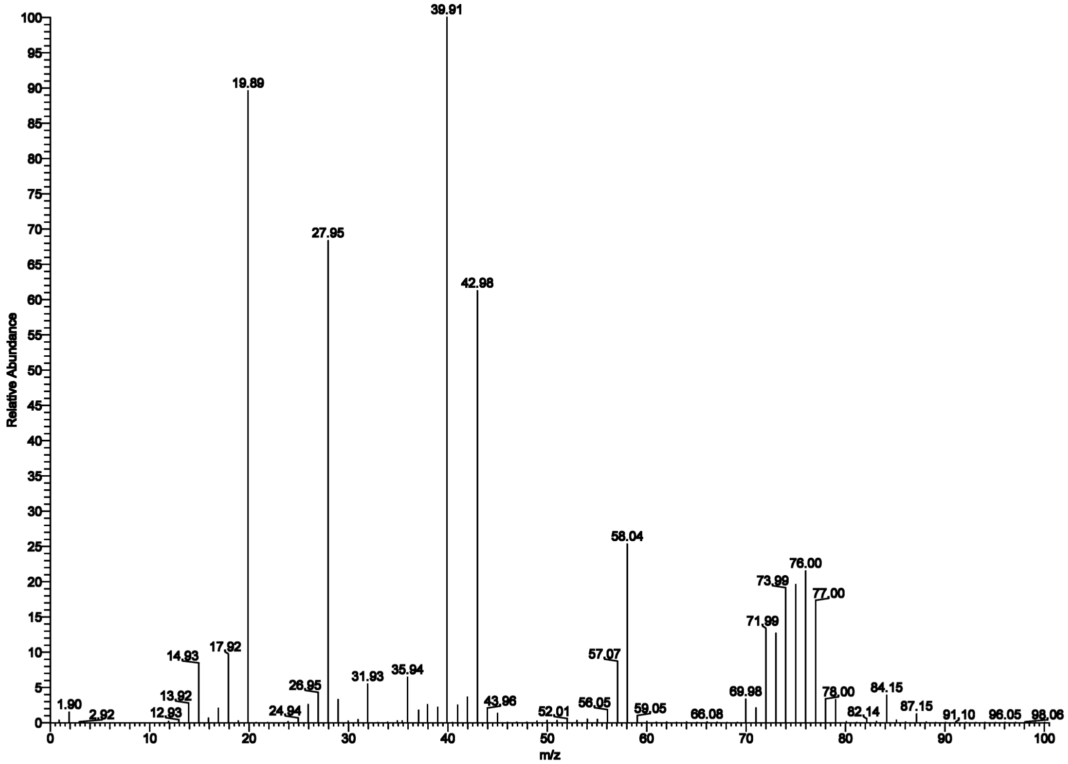


Figure 2.6: EI mass spectrum of GeH_4 generated from $Ge(3,5\text{-dtbc})_2(py)_2$ and $LiAlH_4$, background included.

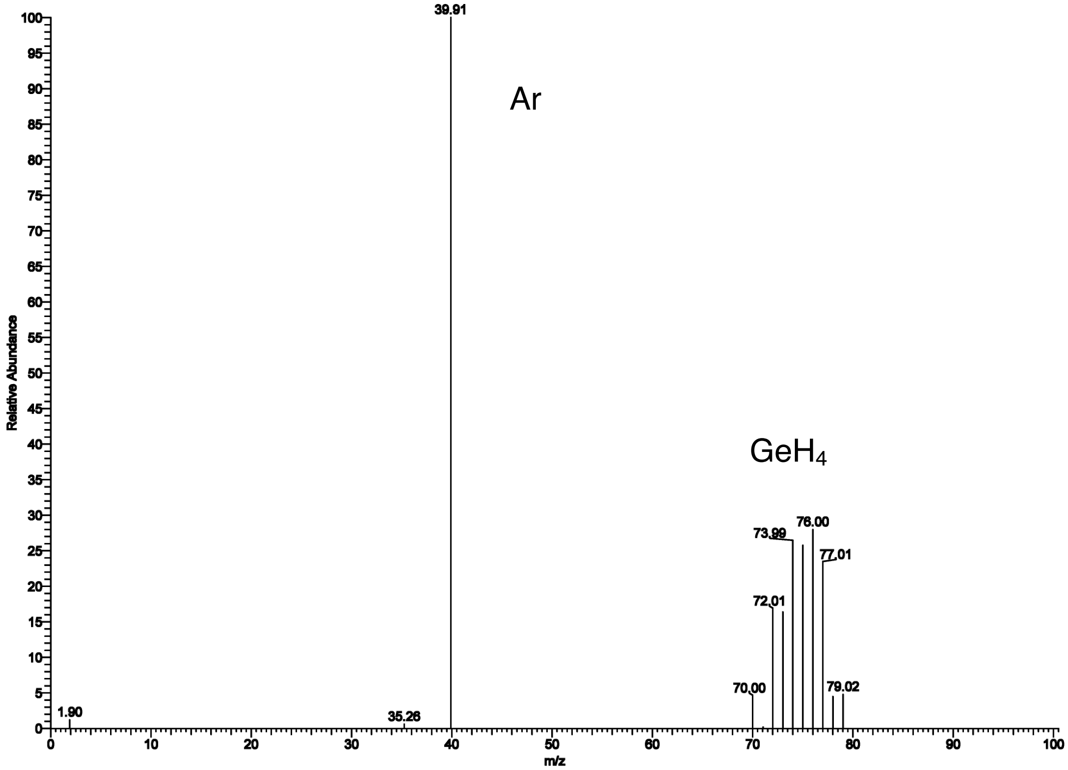


Figure 2.7: EI mass spectrum of GeH_4 generated from $Ge(3,5\text{-dtbc})_2(py)_2$ and $LiAlH_4$, background subtracted.

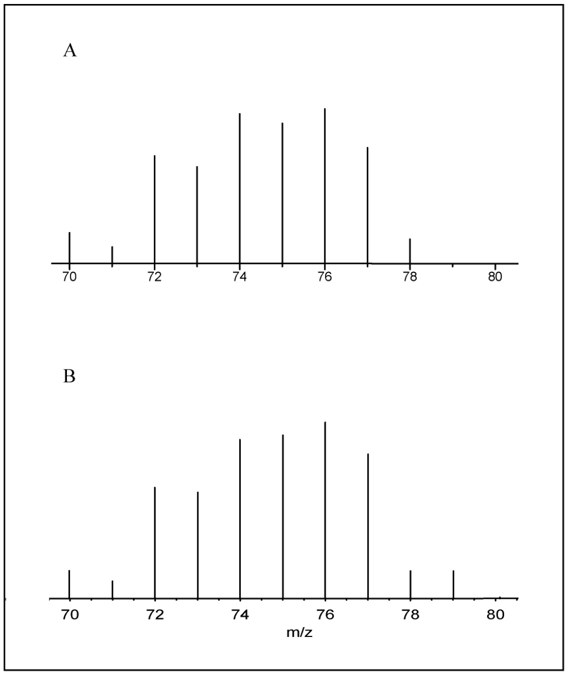


Figure 2.8: Isotopic distribution of the signal assigned to germane A) library spectrum and B) experimentally obtained spectrum.

Analysis of the resulting liquid phase by ^{1}H NMR spectroscopy was equally clean, showing only unreacted $LiAlH_4$, and no sign of oligomeric germanes. Comparably pure germane streams from GeO_2 or $GeCl_4$ require post – synthesis purification, suggesting that Ge(3,5-dtbc)$_2$(py)$_2$ as the starting material may provide a number of competitive advantages.

2.4 Conclusions

The quinone / catechol redox platform described herein adheres well to some of the Principles of Green Chemistry (POGC), offers a potential method of conserving valuable germanium reserves, and improves upon the current industrial processes for the production of organogermanes.

The research described herein especially applies the POGC points 1: prevention, 3: less hazardous chemical synthesis, 4: designing safer chemicals, and 12: inherently safer chemistry for accident prevention.[39] No HCl and Cl_2 were used in the transformation of Ge or GeO_2 into a $GeCl_4$ substitute (POGC point 1). Chemicals safer than HCl and Cl_2 were used in the research described herein: 3,5-dtbc, 3,5-dtbq, organic ligands (POGC point 3). The complex $Ge(3,5\text{-dtbc})_2(py)_2$ is not only bench stable, but is safer to use than $GeCl_4$, but toxicity studies must be conducted to confirm this (POGC point 4). Overall safer processes were used in the research conducted herein (POGC point 12) by replacing metal chlorides with complexes $Ge(3,5\text{-dtbc})_2(L)_2$, effectively replacing Cl_2 with O_2 through the use of 3,5-dtbc and 3,5-dtbq.

Viable sources of germanium are limited, so to meet the increasing demand for germanium in manufacturing and technology there are two options: 1. to conserve the current resources, or 2. to develop more effective recycling strategies. For germanium, no alternative materials currently exist.[1] The recycling of germanium, particularly the elemental form, is an attractive option to preserve this valuable element that is essential to maintain the current standard of living. Our systems have the potential to recycle germanium from scrap into functional and useful forms, the complexes $Ge(3,5\text{-dtbc})_2(L)_2$.

The current industrial process for germanium refining relies on HCl and Cl_2 to transform germanium concentrate (mainly GeO_2) or germanium scrap (mainly Ge metal) into crude $GeCl_4$,[40] which is then distilled to produce pure $GeCl_4$.[40]

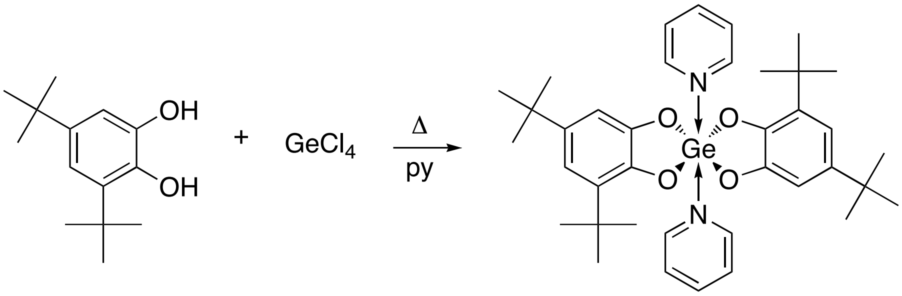
$GeCl_4$ is then used in the synthesis of organogermanes.[41] The primary method used to synthesize organogermanes is the reaction of Grignard reagents with germanium tetrachloride or germanium tetrabromide.[41] The quinone / catechol redox platform described here has the potential to eliminate the use of HCl and Cl_2 in the transformation of germanium concentrate or germanium scrap into value-added materials, using the complex Ge(3,5-dtbc)$_2$(py)$_2$ as a bench-stable intermediate. In most cases the only products obtained from the reactions of Ge(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents are tetraorganogermanes GeR_4, a major advantage over $GeCl_4$. No germanium-containing side products were detected such as incomplete substitution products, oligo- or polygermanes, or cyclic polygermanes. Further research needs to be conducted to investigate the possibility of hydrolyzing Ge(3,5-dtbc)$_2$(py)$_2$ to produce pure GeO_2, an important technological material.[40]

The quinone / catechol redox platform described here provides a valuable strategy for addressing issues of sustainability in metal – organic synthesis. While calls to reduce, and in some cases ban, the use of Cl_2 and HCl have been made, few technological advances to address these important challenges have been made. The current system provides a unique methodology for replacing the oxidative capacity of Cl_2 and HCl with O_2, while preserving the functional utility of metal chlorides in both separations and downstream synthetic transformations. Given the ubiquity of metal chlorides in metal – organic manufacturing, and the precedent for oxidizing a range of transition metals with *ortho*-quinones, a number of opportunities beyond germanium for applying this system are anticipated, including silicon and tin.

2.5 Experimental

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques or a glove box unless specified otherwise. Solvents were dried using a solvent purification system: a PureSolv MD 7 from Innovative Technology. All remaining chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Varian Mercury 400 MHz, Inova 400 MHz, or an Inova 600 MHz NMR spectrometer using $CDCl_3$ as the solvent. ^1H NMR spectra were referenced to residual $CHCl_3$ (7.27 ppm); $^{13}C\{^1H\}$ spectra were referenced to the central transition of $CDCl_3$ (77.00 ppm). All ^1H and ^{13}C NMR signals were assigned using gCOSY and/or ^{13}C-^1H gHSQC NMR spectroscopy. GC- mass spectra were obtained on a GCMS-QP2010S instrument with a GC-2010 gas chromatograph at an ionizing voltage of 70 eV and a DB-5MS 30 m × 0.25 μm column from J & W Scientific utilizing the following temperature program: 3 min at 65 °C; 17 min constant heating rate of 15 °C / min; 5 min at 320 °C. Mass spectral data are reported in mass-to-charge units, *m/z*, with ion identity and peak intensities (%) in parentheses. Melting point data are uncorrected.

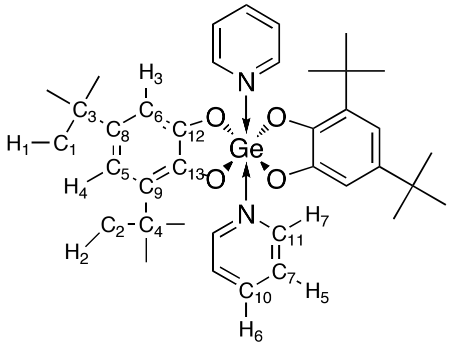
2.5.1 Ge(3,5-dtbc)$_2$(py)$_2$ from GeCl$_4$



2 eq 1 eq **Ge(3,5-dtbc)$_2$(py)$_2$**

Scheme 2.5: Synthesis of Ge(3,5-dtbc)$_2$(py)$_2$ from GeCl$_4$, 3,5-dtbc, and pyridine.

This procedure is a modification of the procedure reported by Yoder *et al.*.[42] In a 100 mL flask equipped with a magnetic stirring bar and reflux condenser, GeCl$_4$ (0.065 mL, 0.562 mmol) was added quickly to a mixture of 3,5-di-*tert*-butylcatechol (0.250 g, 1.125 mmol) dissolved in pyridine (5.23 mL, 64.7 mmol). The mixture was allowed to reflux with efficient stirring for 120 h and then toluene (20 mL) was added. The mixture was refluxed for an additional 10 min. The insoluble material was removed by filtration. The filtrate was washed with deionized water (2 × 3 mL). The toluene was removed by distillation until the solution was saturated. The product was allowed to crystallize, was isolated by filtration, and left under vacuum at 100 °C for 24 h to yield Ge(3,5-dtbc)$_2$(py)$_2$ as a white powder, 0.310 g, 80 %.

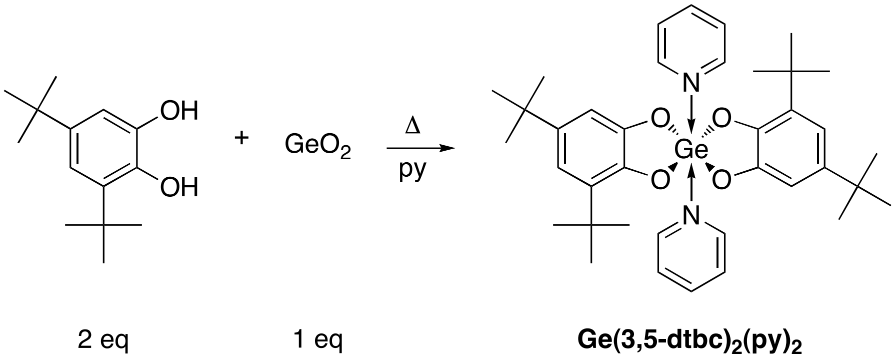


Ge(3,5-dtbc)$_2$(py)$_2$

Figure 2.9: Ge(3,5-dtbc)$_2$(py)$_2$

M.p. = 280 °C (decomposes); **^{1}H NMR** (600 MHz, CDCl$_3$): 8.96 (4H, bs, H$_7$), 7.78 (2H, bt, H$_6$), 7.38 (4H, bt, H$_5$), 6.79 (2H, bs, H$_{4/3}$), 6.51 (2H, bs, H$_{3/4}$), 1.41 (18H, s, H$_{2/1}$), 1.19 (18H, s, H$_{1/2}$); **^{13}C NMR** (600 MHz, CDCl$_3$): 215.8 (C$_{13/12}$), 213.6 (C$_{12/13}$), 147.4 (C$_{11}$), 140.1 (C$_{10}$), 139.5 (C$_{9/8}$), 133.2 (C$_{8/9}$), 125.0 (C$_7$), 112.8 (C$_{6/5}$), 109.1 (C$_{5/6}$), 34.9 (C$_{4/3}$), 34.6 (C$_{3/4}$), 32.9 (C$_{2/1}$), 31.6 (C$_{1/2}$); **Elemental Analysis** calcd for $C_{38}H_{50}N_2O_4Ge$: C, 67.97; H, 7.51; N, 4.17; found: C, 68.18; H, 7.74; N, 4.26; **High-Resolution ESI-TOF MS** for $[C_{38}H_{50}N_2O_4{}^{70}Ge + H^+]^+$: (*m/z*) calcd 669.30913, found: 669.30595; **FT-IR**: 2948, 2902, 2865, 1611, 1570, 1478, 1452, 1417, 1385, 1360, 1329, 1285, 1262, 1234, 1213, 1106, 1068, 1044, 1025, 984, 915, 854, 828, 809, 755, 717, 691, 670, 657, 641, 613, 551, 524, 504, 460, 399 cm^{-1}.

2.5.2 Ge(3,5-dtbc)$_2$(py)$_2$ from GeO$_2$



Scheme 2.6: Synthesis of Ge(3,5-dtbc)$_2$(py)$_2$ from GeO$_2$, 3,5-dtbc, and pyridine.

In a 100 mL flask equipped with a magnetic stirring bar and reflux condenser, pyridine (28.8 mL, 356 mmol) was added to a mixture of 3,5-di-*tert*-butylcatechol (1.38 g, 6.19 mmol) and GeO$_2$ (0.324 g, 3.09 mmol). The suspension was allowed to reflux with efficient stirring for 72 h, then the pyridine was removed by rotovap, and then toluene (25 mL) was added. The mixture was refluxed for an additional 10 min to give a clear solution. After crystallization, Ge(3,5-dtbc)$_2$(py)$_2$ was isolated as a light yellow powder (1.548 g; 75%). If toluene is present in the product it can be removed by trituration with 50 mL chloroform for 24 h. Residual chloroform is easily removed by heating the triturated product under dynamic vacuum at 100 °C for 24 h.

2.5.3 Preparation of Tetraorganogermanes

Procedure A (used to isolate GeBu$_4$, GePh$_4$, GeBn$_4$, GeHex$_4$, GeAll$_4$, Mes$_3$GeH, GeTol$_4$): All equipment was flame-dried prior to use and kept under an argon atmosphere. In a 100 mL flask equipped with magnetic stirring and a reflux condenser, RMgCl (~ 8 mmol) was added to a suspension of Ge(3,5-dtbc)$_2$(py)$_2$ (250 mg, 0.372 mmol) dissolved in 6.25 mL of the same solvent as the organometallic reagent (THF). The mixture was allowed to reflux for 24 h. After cooling to room temperature, 15 mL of hexanes were added to the crude reaction mixture followed by 5 mL water and the reaction mixture was allowed to stir for 5 minutes. The organic layer was washed with 5 mL water, then concentrated using a rotary evaporator. The crude reaction mixture was purified using preparative thin layer chromatography on a 2 mm × 20 cm × 20 cm silica gel plate using hexanes as eluent. In general, there are two compounds evident, one band containing GeR_4 and one band containing recovered catechol. The solid phase was extracted by allowing it to stir overnight in 40 mL of chloroform, decanting, and then washing with 40 mL of chloroform. The extraction was repeated one more time. For smaller scale reactions, chromatography on a 0.2 mm TLC plate followed by stirring the isolated fractions with 30 mL of chloroform overnight followed by washing with 30 mL of chloroform is sufficient. Both $GePh_4$ and $GeBn_4$ were isolated using column chromatography over silica gel rather than TLC.

Procedure B (used to isolate $^{s}Bu_3GeGe^{s}Bu_3$) followed a different purification protocol. The crude reaction mixture was analyzed by GC-MS and contained $^{s}Bu_2GeH_2$, 3,5-di-*tert*-butylcatechol, $(H_3C\text{-}CH{=}(H_3C)C\text{-})_2Ge^{s}Bu_2$, $^{s}Bu_3Ge_2H_3$, and $^{s}Bu_3GeGe^{s}Bu_3$, in a 1:2:1:2:2 ratio. The crude reaction mixture was separated using a Kugelrohr distillation apparatus to give three fractions:

3,5-di-*tert*-butylcatechol (bp ≈ 150 °C / 0.25 mm Hg), $^{s}Bu_3GeGe^{s}Bu_3$ (bp ≈ 175 °C / 0.25 mm Hg), and a mixture of $^{s}Bu_2Ge(H)(OH)$ / 3,5-di-*tert*-butyl-1,2-quinone / $^{s}Bu_2Ge(3,5\text{-dtbc})_1$ / $^{s}BuMe_2GeGeMe_2{}^{s}Bu$ / $^{s}Bu_3GeGe^{s}Bu_3$ / polymeric compounds (residue), as determined by GC-MS. Attempts to separate the crude reaction mixture using TLC did not give any pure compounds.

Procedure C (used to generate and analyze GeH_4): A suspension of $LiAlH_4$ (12 mg, 0.33 mmol) in dibutyl ether (1.0 mL) was added to $Ge(3,5\text{-dtbc})_2(py)_2$ (44 mg, 0.065 mmol) under argon using the reaction apparatus depicted in Figure 2.5. Once the valve was firmly closed, the reaction tube was vortexed a few times to thoroughly agitate the mixture. The solution bubbled moderately. After agitating the mixture for 20 minutes, the headspace gas was directly injected into the EI-MS for analysis.

$GeBu_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 1.39-1.23 (16H, m), 0.97-0.82 (12H, m), 0.77-0.62 (8H, m); **^{13}C NMR** (600 MHz, $CDCl_3$): 27.51, 26.65, 13.79, 12.47; **GC-MS**: 99% pure: *m/z* 245 (Bu_3Ge^+, 35%), 189 (Bu_2Ge^+H, 96%), 133 ($BuGe^+H_2$, 100%), 103 ($EtGe^+$, 30%), 89 ($MeGe^+$, 45%), 75 (HGe^+, 15%), 57 (Bu^+, 85%), 41 ($H_3C\text{-}CH{=}CH^+$, 32%).

$GePh_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 7.61-7.51 (8H, m), 7.47-7.36 (12H, m); **^{13}C NMR** (600 MHz, $CDCl_3$): 136.07, 135.37, 129.08, 128.25; **GC-MS**: 99% pure: *m/z* 304 (Ph_3Ge^+, 100%), 227 (Ph_2Ge^+, 80%), 150 ($PhGe^+$, 33%), 77 (Ph^+, 10%).

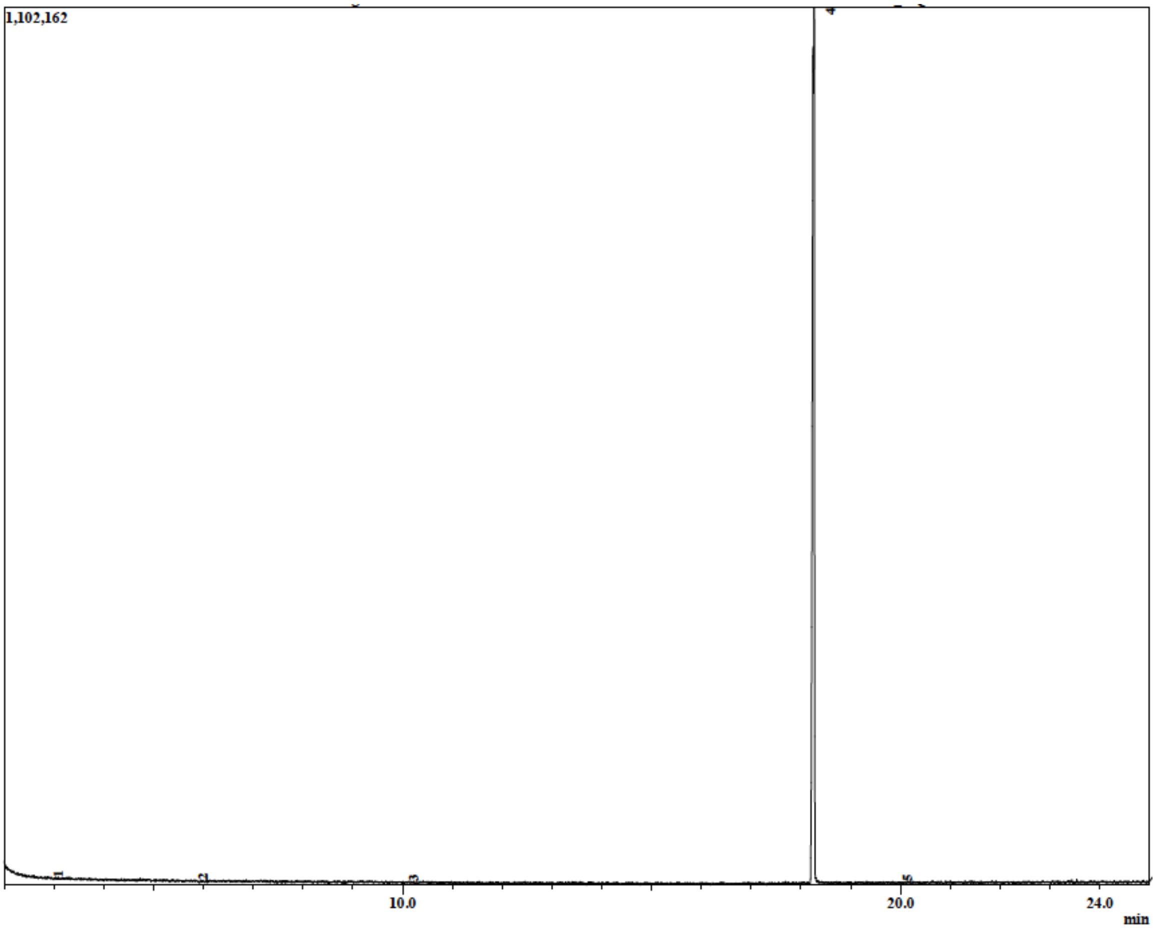


Figure 2.10: GC of isolated $GeBu_4$.

$GeBn_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 7.26-7.19 (8H, m), 7.14-7.08 (4H, m), 6.90-6.84 (8H, m), 2.19 (8H, s); **^{13}C NMR** (600 MHz, $CDCl_3$): 139.61, 128.42, 128.29, 124.28, 21.50; **GC-MS**: 99% pure: *m/z* 346 (Bn_3Ge^+, 75%), 164 ($BnGe^+$, 54%), 91 (Bn^+, 100%).

$GeHex_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 1.37-1.25 (32H, m), 0.93-0.88 (12H, m), 0.73-0.66 (8H, m); **^{13}C NMR** (600 MHz, $CDCl_3$): 33.41, 31.60, 25.24, 22.68, 14.15, 12.82; **GC-MS**: 96% pure: *m/z* 329 (Hex_3Ge^+, 21%), 245 (Hex_2Ge^+, 100%), 161 ($HexGe^+$, 86%), 131 (15%), 117 (13%), 103 (33%), 89 (17%), 83 (81%), 55 (44%), 41 (37%).

$Ge(All)_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 5.91-5.75 (1H, m, $CH_2\text{-}C\underline{\mathbf{H}}{=}CH_2$), 4.96-4.80 (2H, m, $CH_2\text{-}CH{=}C\underline{\mathbf{H_2}}$), 1.78 (2H, d, ^3J = 8.6 Hz, $C\underline{\mathbf{H_2}}\text{-}CH{=}CH_2$);[35] **^{13}C NMR** (600 MHz, $CDCl_3$): 135.05, 113.16, 19.04; **GC-MS**: 98% pure: *m/z* 197 ($Allyl_3Ge^+$, 22%), 153 ($Allyl_2Ge^+$, 17%), 127 (14%), 115 ($Allyl_1Ge^+$, 100%), 89 (43%), 39 (22%).

Mes_3GeH: **^{1}H NMR** (600 MHz, $CDCl_3$): 6.82 (6H, s, *m*-$C\underline{\mathbf{H}}$), 5.87 (1H, s, $Ge\underline{\mathbf{H}}$), 2.28 (9H, s, *p*-$C\underline{\mathbf{H_3}}$), 2.17 (18H, s, *o*-$C\underline{\mathbf{H_3}}$); **^{13}C NMR** (600 MHz, $CDCl_3$): 143.60, 138.15, 134.82, 128.72, 23.57, 21.04; **GC-MS**: 98% pure: *m/z* 431 (Mes_3Ge^+, 4%), 312 (Mes_2Ge^+, 60%), 297 (14%), 192 (Mes_1Ge^+, 100%), 119 (Mes^+, 27%), 105 (42%), 91 (18%), 77 (10%).

$^sBu_3GeGe^sBu_3$: **^{1}H NMR** (600 MHz, $CDCl_3$): 1.79-1.69 (1H, m, $H_3C\text{-}CH(Ge)\text{-}C(\underline{\mathbf{H}})(H)\text{-}CH_3$), 1.36-1.21 (2H, m, $H_3C\text{-}C\underline{\mathbf{H}}(Ge)\text{-}C(H)(\underline{\mathbf{H}})\text{-}CH_3$), 1.17-1.13 (3H, m, $\underline{\mathbf{H_3}}C\text{-}CH(Ge)\text{-}C(H)(H)\text{-}CH_3$), 0.98-0.93 (3H, m, $H_3C\text{-}CH(Ge)\text{-}C(H)(H)\text{-}C\underline{\mathbf{H_3}}$); **^{13}C NMR** (600 MHz, $CDCl_3$): 27.68-27.43 (several isomers of $^sBu_3GeGe^sBu_3$, $H_3C\text{-}CH(Ge)\text{-}\underline{\mathbf{C}}H_2\text{-}CH_3$), 24.15-23.90 (several isomers of $^sBu_3GeGe^sBu_3$, $H_3C\text{-}\underline{\mathbf{C}}H(Ge)\text{-}CH_2\text{-}CH_3$), 16.62-16.39 (several isomers of $^sBu_3GeGe^sBu_3$, $H_3\underline{\mathbf{C}}\text{-}CH(Ge)\text{-}CH_2\text{-}CH_3$), 13.91-13.77 (several isomers of $^sBu_3GeGe^sBu_3$, $H_3C\text{-}CH(Ge)\text{-}CH_2\text{-}\underline{\mathbf{C}}H_3$); **GC-MS**: 99% pure: *m/z* 431 ($^sBu_5Ge_2^+$, 10%), 375 ($^sBu_4Ge_2^+$, 20%), 319 ($^sBu_3Ge_2^+$, 50%), 263 ($^sBu_2Ge_2^+$, 70%), 245 ($^sBu_3Ge_1^+$, 14%), 207 ($^sBu_1Ge_2^+$, 45%), 189 ($^sBu_2Ge_1^+$, 100%), 147 (30%), 133 ($^sBu_1Ge_1^+$, 97%), 105 (33%), 89 (54%), 57 ($^sBu^+$, 75%), 41 (62%).

GeTol$_4$: ^{1}**H NMR** (600 MHz, CDCl$_3$): 7.44 (8H, d, ^3J = 7.7 Hz, Ph-**H**), 7.21 (8H, d, ^3J = 7.7 Hz, Ph-**H**), 2.38 (12H, s, CH$_3$); ^{13}**C NMR** (600 MHz, CDCl$_3$): 138.69, 135.31, 132.99, 128.98, 21.45; **GC-MS**: 99% pure: *m/z* 438 (GeTol$_4^+$, 1%), 347 (GeTol$_3^+$, 90%), 256 (GeTol$_2^+$, 100%), 181 (GeTol$_1$Me$_1^+$, 47%), 165 (GeTol$_1^+$, 41%), 139 (10%), 91 (PhCH$_2^+$, 52%), 65 (15%), 39 (5%).

2.6 References

1. T. E. Graedel, E. M. Harper, N. T. Nassar, B. K. Reck: *Proc. Natl. Acad. Sci. U.S.A.,* **2015**, *112*, 6295-6300.
2. E. D. Doidge, I. Carson, P. A. Tasker, R. J. Ellis, C. A. Morrison, J. B. Love: *Angew. Chem. Int. Ed.,* **2016**, *55*, 12436-12439.
3. J. J. Moore, E. A. Boyce: *Chemical Metallurgy,* Butterworths, London; Toronto, **1990**.
4. G. B. Kauffman: *"Chlorine"* in *Ullmann's Encyclopedia of Industrial Chemistry,* Wiley-VCH Verlag GmbH & Co. KGaA, **2000**, 532-622.
5. R. Ayres: *J. Ind. Ecol.,* **1997**, *1*, 81-94.
6. C. C. Cummins: *Daedalus,* **2014**, *143*, 9-20.
7. M. N. Temnikov, A. S. Zhiltsov, V. M. Kotov, I. V. Krylova, M. P. Egorov, A. M. Muzafarov: *Silicon,* **2015**, *7*, 69-78.
8. M. Glavinović, F. Qi, A. D. Katsenis, T. Friščić, J. Lumb: *Chem. Sci.,* **2016**, *7*, 707-712.
9. C. G. Pierpont, R. M. Buchanan: *Coord. Chem. Rev.,* **1981**, *38*, 45-87.
10. L. Sun, M. G. Campbell, M. Dinca: *Angew. Chem. Int. Ed.,* **2016**, *55*, 3566-3579.
11. Z. Huang, J. Lumb: *Angew. Chem. Int. Ed.,* **2016**, *55*, 11543-11547.
12. L. E. Darago, M. L. Aubrey, C. J. Yu, M. I. Gonzalez, J. R. Long: *J. Am. Chem. Soc.,* **2015**, *137*, 15703-15711.

13. G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Organometallics,* **1991**, *10*, 1510-1515.

14. C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young: *Chem. Rev.,* **1993**, *93*, 1371-1448.

15. J. Piera, J. Backvall: *Angew. Chem. Int. Ed.,* **2008**, *47*, 3506-3523.

16. T. Punniyamurthy, S. Velusamy, J. Iqbal: *Chem. Rev.,* **2005**, *105*, 2329-2363.

17. E. Wendlandt, A. M. Suess, S. S. Stahl: *Angew. Chem. Int. Ed.,* **2011**, *50*, 11062-11087.

18. R. Venkatasubramanian, R. T. Pickett, M. L. Timmons: *J. Appl. Phys.,* **1989**, *66*, 5662-5664.

19. R. Russotti: Method of Synthesis of Gaseous Germane: US4668502, **1987**.

20. C. Licht, L. T. Peiró, G. Villalba: *J. Ind. Ecol.,* **2015**, *19*, 890-903.

21. G. Gunn, British Geological Survey, American Geophysical Union: *Critical Metals Handbook,* Wiley, Chichester, West Sussex, **2014**.

22. D. Quane, R. S. Bottei: *Chem. Rev.,* **1963**, *63*, 403-442.

23. M. L. Amadoruge, C. S. Weinert: *Chem. Rev.,* **2008**, *108*, 4253-4294.

24. A. El-Hadad, B. R. McGarvey, B. Merzougui, R. G. W. Sung, A. K. Trikha, D. G. Tuck: *J. Chem. Soc., Dalton Trans.,* **2001**, 1046-1052.

25. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell: *Chem. Soc. Rev.,* **2012**, *41*, 413-447.

26. T. Friščić, W. Jones: *Cryst. Growth Des.,* **2009**, *9*, 1621-1637.

27. D. T. Tran, P. Y. Zavalij, S. R. J. Oliver: *Acta Crystallogr., Sect. E,* **2002**, *58*, m742-m743.

28. K. Hensen, A. Faber, M. Bolte: *Acta Crystallogr., Sect. C,* **1999**, *C55*, 1774-1775.

29. M. Bolte, K. Hensen, A. Faber: *Acta Crystallogr., Sect. C,* **2000**, *C56*, E499-E500.

30. M. Bolte, K. Hensen, A. Faber: *Acta Crystallogr., Sect. C,* **2000**, *C56*, E497-E498.

31. K. M. Baines, W. G. Stibbs: *Coord. Chem. Rev.,* **1995**, *145*, 157-200.

32. V. Lado, A. V. Piskunov, I. V. Zhdanovich, G. K. Fukin, E. V. Baranov: *Russ. J. Coord. Chem.,* **2008**, *34*, 251-255.

33. H. Chiang, S. Hwang, C. Ueng: *Acta Crystallogr., Sect. C,* **1996**, *C52*, 31-33.

34. F. Qi, R. S. Stein, T. Friščić: *Green Chem.,* **2014**, *16*, 121-132.

35. M. Fishwick, M. G. H. Wallbridge: *J. Organometal. Chem.,* **1970**, *25*, 69-79.

36. S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski: *Chem. Rev.,* **2013**, *113*, 6234-6458.

37. H. P. Withers, P. B. Henderson: Production and Purification of Germane: US20050191854, **2005**.

38. E. Yoshimura, H. Watanabe, S. Yamazaki, S. Toda: *Anal. Lett.,* **1997**, *30*, 135-146.

39. P. Anastas, N. Eghbali: *Chem. Soc. Rev.,* **2010**, *39*, 301-312.

40. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, F. Ullmann: *Ullmann's Encyclopedia of Industrial Chemistry,* VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany; Deerfield Beach, Fla, **1985**.

41. D. M. P. Mingos, R. H. Crabtree: *Comprehensive Organometallic Chemistry III,* Elsevier, Amsterdam; London, **2007**.

42. C. M. S. Yoder, J. J. Zuckerman: *Inorg. Chem.,* **1967**, *6*, 163-164.

Chapter 3: Synthesis and Reactivity of $Sn(3,5\text{-dtbc})_2(py)_2$

Tetraorganostannanes, SnR_4, are important precursors for the synthesis of diorganodichlorostannanes, R_2SnCl_2, which are used extensively in a variety of industrial applications, such as biocides and PVC stabilizers.[1] The synthesis of tetraorganostannanes SnR_4 can be traced back to the mineral cassiterite. The process of converting cassiterite to SnR_4 involves numerous production steps that are hazardous to both humans and the environment.[2, 3] Cassiterite is reduced to tin metal (Sn^0) which is then oxidized to $SnCl_4$ using Cl_2. The use of Cl_2 not only presents problems to the well being of humans and the environment,[2, 3] but also requires expensive corrosion-resistant equipment to generate and handle in its production and downstream reactions. These problems apply to the synthesis of tetraorganostannanes from $SnCl_4$. The work in this chapter focuses on the development of a more environmentally-friendly synthesis of SnR_4 which does not involve the use of Cl_2. The synthesis of the hypercoordinate complex $Sn(3,5\text{-dtbc})_2(py)_2$ was targeted, with the expectation that the chemistry of the tin derivative would parallel that of the germanium analog described in chapter 2.

3.1 Hypercoordinate Tin Complexes

Hypercoordinate tin complexes, both pentacoordinate and hexacoordinate, are well-known.[4] While there are some exceptions, the ligands in hypercoordinate complexes of tin follow three general trends. Firstly, the electronegativity of the donor atoms of the ligands is typically greater than the electronegativity of the central tin atom. Secondly, the ligands with the lowest donor ability occupy the axial positions and are *trans* to one another, not *cis*. Thirdly, the tin-ligand bond lengths of hypercoordinate complexes are longer than the same bond lengths in tetracoordinate tin derivatives.

3.2 Traditional Synthesis of $R_nSnX_{(4-n)}$

The primary method used to synthesize organostannanes is the reaction of Grignard reagents with tin tetrachloride or tin tetrabromide.[5] Unless there are steric constraints, the reaction of Grignard reagents with $SnCl_4$ usually gives fully alkylated products SnR_4.[6] The tetrasubstituted stannanes are used to generate the desired functional chlorostannanes by Kocheshkov redistribution reactions with $SnCl_4$ (equations 1, 2, 3).[5]

$$3\ SnR_4 + SnCl_4 \rightarrow 4\ R_3SnCl \qquad (1)$$

$$SnR_4 + SnCl_4 \rightarrow 2\ R_2SnCl_2 \qquad (2)$$

$$SnR_4 + 3\ SnCl_4 \rightarrow 4\ RSnCl_3 \qquad (3)$$

The generation of R_3SnCl and R_2SnCl_2 works well for many alkyl groups, however, the reaction only works well in a few cases for $RSnCl_3$.[5, 7] For $RSnCl_3$, good yields are obtained only when R = Et, Vinyl, and Ph.[7, 8]

3.3 Direct Synthesis of Organotin Compounds

Diorganotin dihalides are important intermediates in the preparation of diorganotin-based industrial reagents, and a direct synthesis of these compounds is the simplest method to obtain them and avoids the synthesis of tetraorganostannanes.[1] A direct synthesis of $R_nSnX_{(4-n)}$ is possible from tin metal and organic halides at elevated temperatures in the presence of a catalyst, usually a tetraalkylammonium halide.[5, 9]

The most commonly used diorganotin dihalide intermediates for industrial applications are R_2SnX_2 where R / X = Me / Cl and Bu / I. Dimethyltin dichloride can be produced from molten tin and methyl chloride at 235 °C with copper metal as a catalyst.[1] Similarly, dibutyltin diiodide can be prepared from butyl iodide and tin metal.[1] A rare case where a triorganotin halide can be prepared directly from tin metal is the reaction with benzyl chloride according to equation 4.[1, 10]

$$3\ PhCH_2Cl + 2\ Sn \rightarrow (PhCH_2)_3SnCl + SnCl_2 \qquad (4)$$

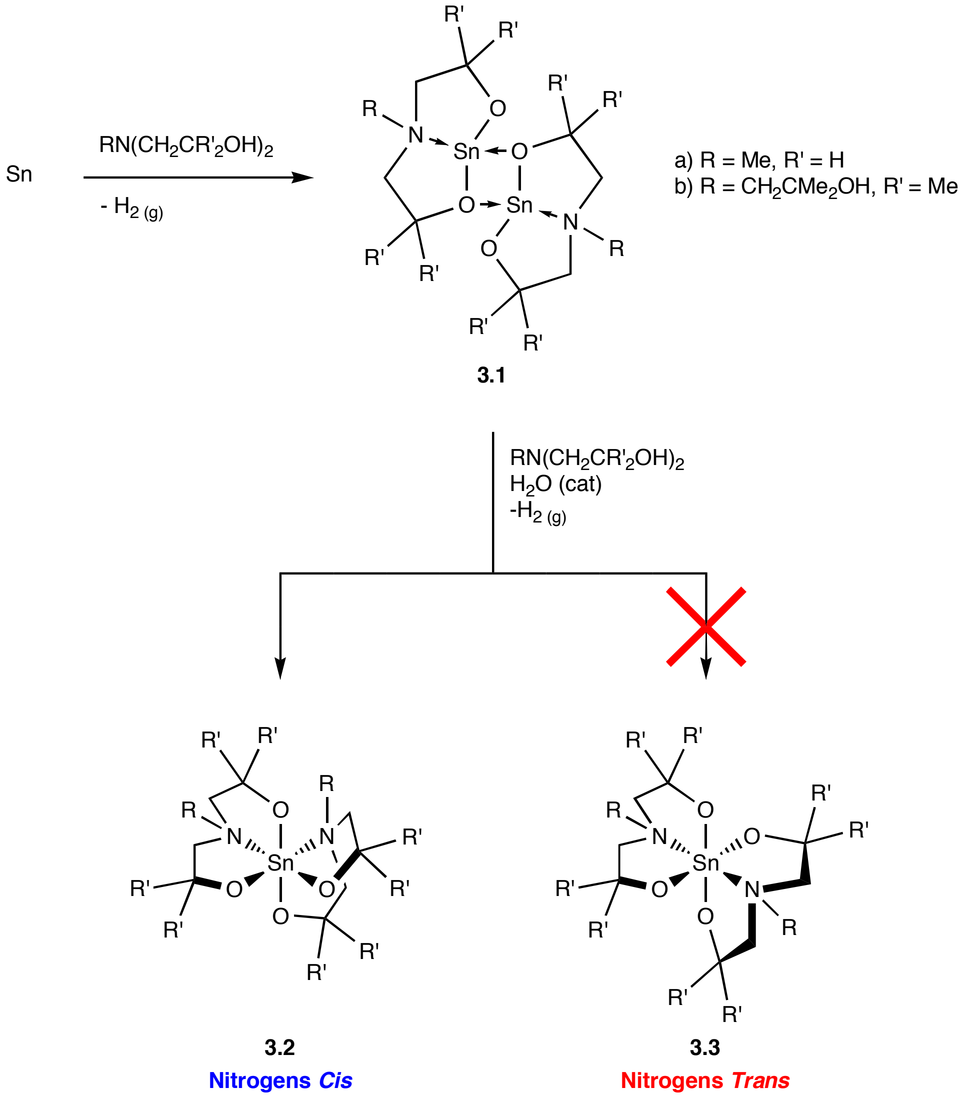
The reaction must be conducted under aqueous conditions;[1, 10] if the reaction is run in toluene, the major product is $(PhCH_2)_2SnCl_2$.[11]

Some of the many other compounds that have not yet become industrially relevant, but will undergo a direct reaction with tin metal, and show good functional group tolerance, include haloalkanes, e.g. $Cl_2Sn((CH_2)_7CH_3)_2$ from $Cl(CH_2)_7CH_3$,[12] haloethers, e.g. $I_2Sn((CH_2)_3OPh)_2$ from $I(CH_2)_3OPh$,[13] halobutyramides, e.g. $X_2Sn(CH_2CHMeCONR_2)_2$ from $XCH_2CHMeCONR_2$,[14-16] amide esters, e.g. $X_2Sn(CHRCHRCONHCH_2CO_2Et)_2$ from $XCHRCHRCONHCH_2CO_2Et$,[17] esters, e.g. $X_2Sn(CH_2CH_2CO_2R)_2$ from $XCH_2CH_2CO_2R$,[18, 19] ketones, e.g. $X_2Sn(CH_2CH_2COR)_2$ from XCH_2CH_2COR,[18] halonitriles, e.g. $I_2Sn(CH_2CH_2CN)_2$ from ICH_2CH_2CN,[20] and allyl halides, e.g. $Br_2Sn(CH_2CH{=}CH_2)_2$ from $BrCH_2CH{=}CH_2$.[21] The focus of this chapter is the synthesis of SnR_4; the synthesis of difunctional tin compounds will be targeted in chapter 5.

3.4 Oxidation of Tin with Alcohols or *ortho*-Quinones

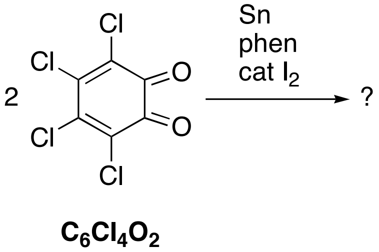
There have only been a few pioneering studies on the oxidation of metallic tin with organic-based oxidizing agents. Jurkschat has shown that alcohols oxidize tin and evolve hydrogen gas, to give hypercoordinate tin-diethanolamine complexes,[22] while Tuck has reported the oxidation of tin using a quinone to form tin-catecholate complexes.[23]

Alcohols, such as butanol, have been utilized to oxidize tin to form the corresponding tin^{II} alkoxides, $Sn(OR)_2$. The reaction takes place upon heating a mixture of the alcohol and tin at the boiling point of the alcohol for several days. Using this methodology, the synthesis of several tin-diethanolamine complexes was achieved.[22] Oxidation of tin metal first to the divalent state using diethanolamines leads to the evolution of hydrogen gas and the formation of a dimeric complex **3.1** in which the tin is tetracoordinate (Scheme 3.1).[22] Further oxidation with another equivalent of diethanolamine leads to the hypercoordinate complex of tin, **3.2**, with tin in the oxidation state of IV and having a coordination number of 6 (Scheme 3.1).[22] Notably, the nitrogen atoms are *cis* to one another in complex **3.2**. Complex **3.3**, with the nitrogen atoms *trans*, was not isolated, which differs from the general trends, referred to previously and shown by the majority of hypercoordinate tin complexes.[4]



Scheme 3.1: Oxidation of tin metal with diethanolamines to yield hypercoordinate tin complexes.

Tin powder can be oxidized to Sn($C_6Cl_4O_2$), with $C_6Cl_4O_2$ in refluxing toluene (Scheme 3.2).[23] Further oxidation with another equivalent of $C_6Cl_4O_2$ in the presence of phenanthroline (phen) and a catalytic amount of iodine presumably, but not certainly, leads to Sn($C_6Cl_4O_2$)$_2$(phen) (Scheme 3.2), which was characterized only by elemental analysis and IR spectroscopy.



Scheme 3.2: Reaction of tin metal, $C_6Cl_4O_2$, and phen with a catalytic amount of iodine.

On the basis of the successful synthesis of Ge(3,5-dtbc)$_2$(py)$_2$, we have explored the synthesis of the analogous tin complex. The goal is to achieve the synthesis of the complex Sn(3,5-dtbc)$_2$(py)$_2$ without the use of Cl_2. Three different strategies were explored. The direct synthesis of Sn(3,5-dtbc)$_2$(py)$_2$ from SnO_2, 3,5-dtbc, and pyridine would be optimal as, in principle, the reduction of SnO_2 to Sn metal could be avoided. A second strategy to obtain Sn(3,5-dtbc)$_2$(py)$_2$ involves the oxidation of tin metal with 3,5-dtbq, inspired by the work of Tuck.[23] Inspired by the work of Jurkschat, a third strategy to obtain Sn(3,5-dtbc)$_2$(py)$_2$, involving the oxidation of tin metal with 3,5-dtbc was explored.[22] Complexes similar in structure to Sn(3,5-dtbc)$_2$(py)$_2$ have previously been described and their syntheses are now presented.

3.5 Synthesis of Complexes Structurally Related to $Sn(3,5\text{-dtbc})_2(py)_2$

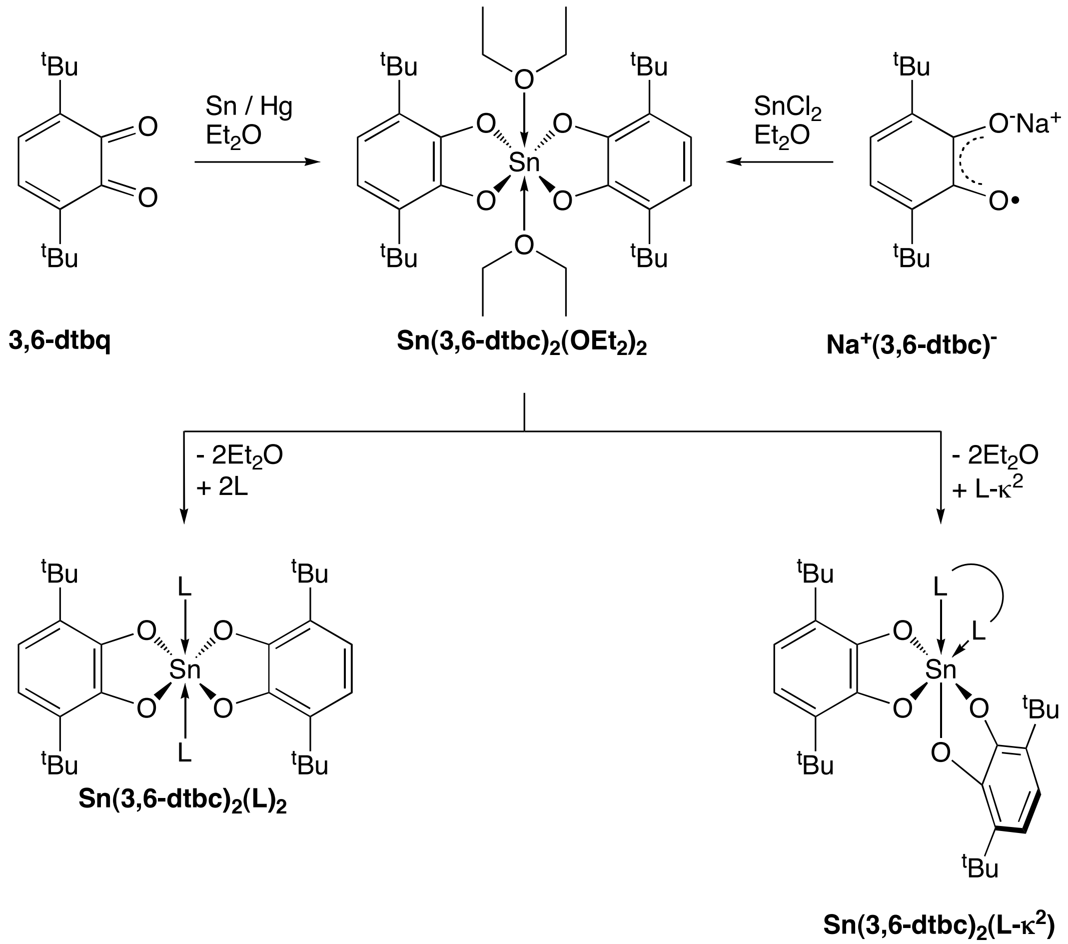
The hypercoordinate complex $Sn(o\text{-}C_6H_4O_2)_2(py)_2$ can be synthesized according to equation 5.

$$SnCl_4 + 2\ o\text{-}C_6H_4(OH)_2 + 2\ py \rightarrow Sn(o\text{-}C_6H_4O_2)_2(py)_2 \qquad (5)$$

The reaction is conducted using carbon tetrachloride as solvent.[24] Carbon tetrachloride is a restricted chemical because of environmental and health concerns. Acute toxicity (oral, dermal, inhalation), respiratory sensitization, germ cell mutagenicity, and reproductive toxicity are the known dangers. CCl_4 has an LD_{50} of 2.4 g / kg.[25]

The synthesis of $Sn(3,6\text{-dtbc})_2(py)_2$ has been accomplished by heating a mixture of tin amalgam (tin metal dissolved in liquid mercury) and 3,6-dtbq in excess pyridine as solvent (Scheme 3.3).[26] While $Sn(3,6\text{-dtbc})_2(py)_2$ was obtained in good yield (>70%), the serious drawback to this reaction procedure is the use of liquid mercury which is harmful to the aquatic environment and especially harmful to people (LD_{50} of 100 mg / kg). Acute toxicity (oral, dermal, inhalation), respiratory sensitization, germ cell mutagenicity, reproductive toxicity, and a wide spectrum of physical symptoms, are the known dangers.[25] Using the same methodology, the complex, $Sn(3,6\text{-dtbc})_2(OEt_2)_2$, was obtained (Scheme 3.3). The ether complex can also be obtained by the reaction of $SnCl_2$ with two eq of the monosodium radical cation of 3,6-dtbq in excess diethyl ether (Scheme

3.3).[26] Unfortunately, this method relies on hydrochloric acid to generate the tin dichloride.[27] The complex $Sn(3,6\text{-dtbc})_2(OEt_2)_2$ reacts with 2 eq of donor molecules to yield complexes $Sn(3,6\text{-dtbc})_2(L)_2$, and this technique was used to synthesize $Sn(3,6\text{-dtbc})_2(^t\text{BuN=CHCH=N}^t\text{Bu})$ (Scheme 3.3).[26]



Scheme 3.3: Synthesis of $Sn(3,6\text{-dtbc})_2(OEt_2)_2$ from tin amalgam, 3,6-dtbq, and diethyl ether or from tin dichloride, $Na^+(3,6\text{-dtbc})^-$, and diethyl ether, and ligand exchange reactions of the complex. L = py, DAD, PPh_3, phen, bipy, DME, THF.

3.6 Results and Discussion

3.6.1 Attempted Synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$ from SnO_2

Using the same conditions employed for the synthesis of $Ge(3,5\text{-dtbc})_2(py)_2$ from GeO_2, 1 equivalent of SnO_2 with 2 eq of 3,5-dtbc were refluxed in excess pyridine for an extended period of time. Surprisingly, no reaction was observed. Tin dioxide was also reacted with the sodium catecholates under identical reaction conditions; however, once again, no reaction was observed. Even using $SnCl_4$ as the tin reagent under the same conditions used to synthesize $Ge(3,5\text{-dtbc})_2(py)_2$, did not produce the desired complex; only $SnCl_4(py)_2$ was isolated. With the unsuccessful synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$ from either $SnCl_4$ or SnO_2, the synthesis of the tin complex from tin metal and either 3,5-dtbc or 3,5-dtbq was explored.

3.6.2 Synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$ from Sn

Numerous reactions for the synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$ from tin metal, 3,5-dtbc or 3,5-dtbq, and pyridine were explored and the results are summarized in Table 3.1.

Table 3.1: Optimization of the synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$.

Entry *	Reagents	Product
1	1) 1 eq Sn, 8 eq 3,5-dtbc, *p*-xylene, reflux 3 d 2) 115 eq py, reflux 2 d * 250 mg scale	No Reaction
2	1) 1 eq Sn, 8 eq 3,5-dtbc, *p*-xylene,	Poly-3,5-dtbc

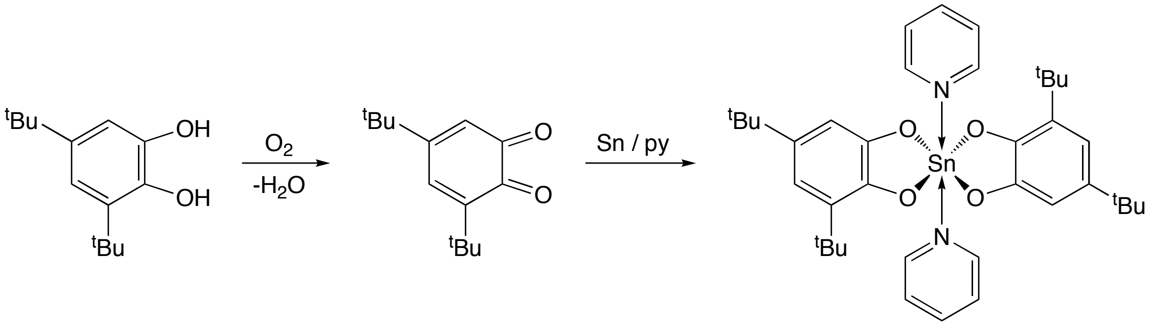
	cat H_2SO_4, reflux 3 d 2) 115 eq py, reflux 2 d * 250 mg scale	
3	1) 1 eq Sn, 8 eq 3,5-dtbc, reflux 3 d 2) 115 eq py, reflux 2 d * 250 mg scale	$Sn(3,5\text{-dtbc})_2(py)_2$ (40%)
4	1) 1 eq Sn, 4 eq 3,5-dtbc, reflux 3 d 2) 115 eq py, reflux 2 d * 250 mg scale	$Sn(3,5\text{-dtbc})_2(py)_2$ (40%)
5	1) 1 eq Sn, 4 eq 3,5-dtbc, reflux 5 d 2) 115 eq py, reflux 2 d * 2.5 g scale	$Sn(3,5\text{-dtbc})_2(py)_2$ (5%)
6	1) 1 eq Sn, 2 eq 3,5-dtbc, 60 eq py, bubble O_2, reflux 2 d * 1.0 g scale	$Sn(3,5\text{-dtbc})_2(py)_2$ (10 experiments: average = 45%)
7	1) 1 eq Sn, 2 eq 3,5-dtbq, 60 eq py * 250 mg scale	$Sn(3,5\text{-dtbc})_2(py)_2$ (3 experiments: average = 74%)

* The scale 250 mg refers to theoretical yield of product, and solvent volumes were 10 mL.

As a starting point for the reactions, elements of Tuck's (oxidation of tin with quinones) and Jurkschat's (oxidation of tin with alcohols) work were incorporated. Tin metal and 8 eq of 3,5-dtbc were refluxed in a high-boiling solvent for 3 days. Next, excess pyridine was added and the mixture was refluxed for an additional 2 days; however, no reaction was observed (Table 3.1, Entry 1). The experiment was performed again under identical conditions, with a catalytic amount of H_2SO_4; however, the product formed appeared to be a polymer (Table 3.1, Entry 2). The effect of concentration was investigated, and 1 equivalent of tin metal was combined and heated with 8 eq of 3,5-dtbc for 3 days.

The temperature was kept identical to previous reactions. After 3 days of heating, excess pyridine was added and the mixture was refluxed for 2 days to give Sn(3,5-dtbc)$_2$(py)$_2$ in 40% yield (Table 3.1, Entry 3). With the successful synthesis of Sn(3,5-dtbc)$_2$(py)$_2$, the influence of reducing the amount of 3,5-dtbc was explored since it is an expensive reagent. Upon reducing the number of eq of 3,5-dtbc to 4 from 8, Sn(3,5-dtbc)$_2$(py)$_2$ was obtained in the same yield (Table 3.1, Entry 4). Although the synthesis of Sn(3,5-dtbc)$_2$(py)$_2$ worked well on a 250 mg scale, upon scaling the reaction to 2.5 g, only a 5% yield of the complex was obtained (Table 3.1, Entry 5). An observation that was made about the successful reactions to produce Sn(3,5-dtbc)$_2$(py)$_2$ (Table 3.1, Entries 3 and 4) was the tin metal clumps into a small shiny ball while in the unsuccessful reactions (Table 3.1, Entry 5) the tin metal remains as a flowing grey powder. The tin clump has a much smaller surface area than the flowing tin powder, and this could dramatically influence the rate of reaction. Building on the successful reaction Table 3.1, Entry 4, four changes were simultaneously made: the amount of 3,5-dtbc was reduced to the stoichiometrically required 2 eq, the reaction was carried out in one step, the reaction time was reduced to 2 days, and oxygen was bubbled through the reaction mixture to oxidize 3,5-dtbc to 3,5-dtbq in situ (Table 3.1, Entry 6). An average yield of 45% of Sn(3,5-dtbc)$_2$(py)$_2$ was obtained when the reaction was run on a 1 g scale (Table 3.1, Entry 6). The oxygen in the reaction mixture presumably oxidizes the 3,5-dtbc to 3,5-dtbq (Scheme 3.4), and thus, 3,5-dtbq was used instead of 3,5-dtbc (Table 3.1, Entry

7). The yield of the complex did increase; however, the reaction was only successful on a 250 mg scale, (Table 3.1, Entry 7) and 3,5-dtbq is 5 times more expensive than 3,5-dtbc. As a result, the synthesis of complex Sn(3,5-dtbc)$_2$(py)$_2$ was carried out using the conditions detailed in Table 3.1, Entry 6.



3,5-dtbc **3,5-dtbq** **Sn(3,5-dtbc)$_2$(py)$_2$**

Scheme 3.4: Synthesis of Sn(3,5-dtbc)$_2$(py)$_2$ from 3,5-dtbc and pyridine.

On occasion, the formation of a small amount of a second isomer of Sn(3,5-dtbc)$_2$(py)$_2$ is observed. The approximate molar ratio of the two isomers is 6.5 : 1 (Figure 3.1). It is hypothesized that the minor isomer has ^{t}Bu groups cis to one another (Figure 3.2) and that it forms through an establishment of equilibrium during gentle heating of the complex under dynamic vacuum to remove the last traces of pyridine.

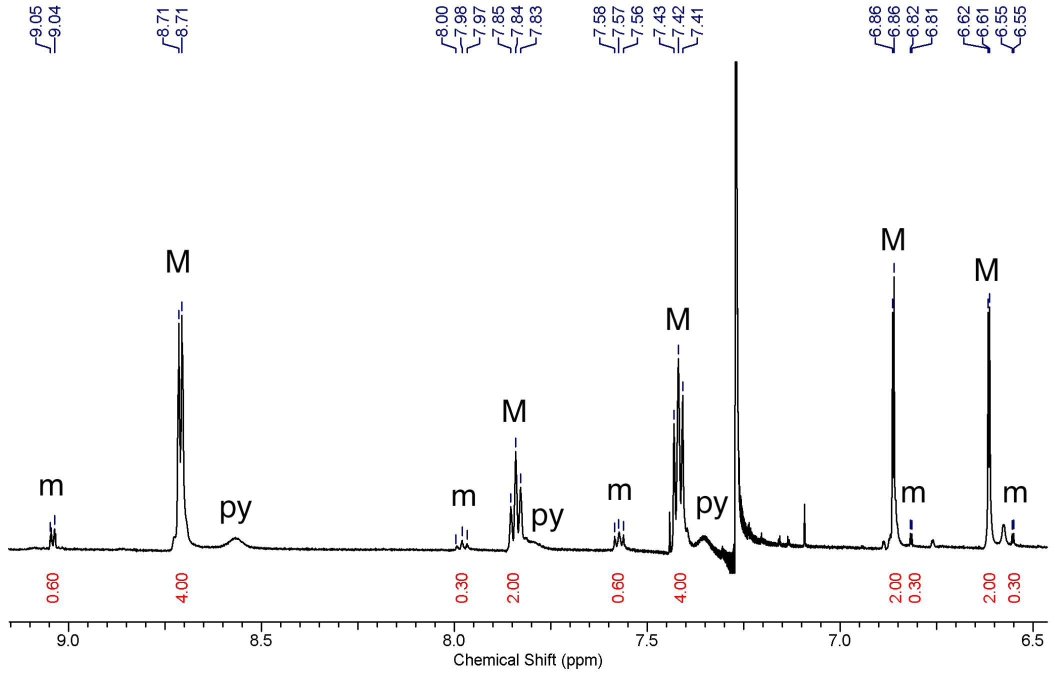
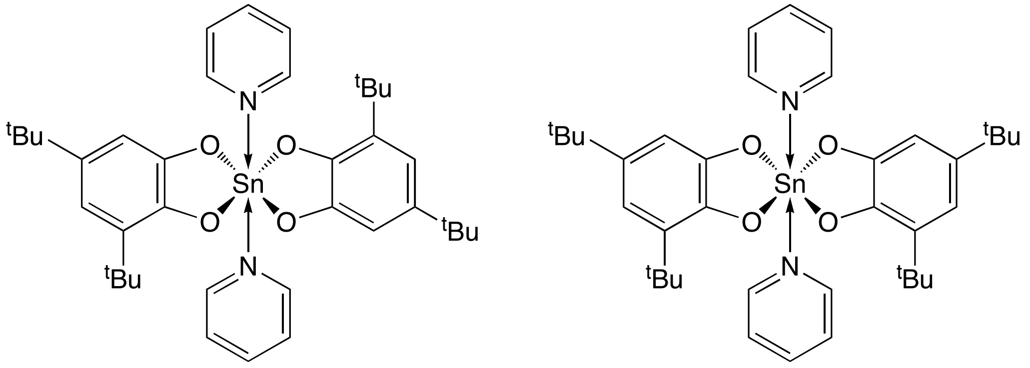


Figure 3.1: ^{1}H NMR spectrum (600 MHz) of Sn(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$ from 9.15 – 6.50 ppm, showing the two isomers of the complex in an approximate 6.5 : 1 molar ratio. The major isomer is indicated with an M, the minor isomer with an m, and pyridine with py.



Sn(3,5-dtbc)$_2$(py)$_2$
Major Isomer

Sn(3,5-dtbc)$_2$(py)$_2$
Minor Isomer

Figure 3.2: Major and minor isomers of Sn(3,5-dtbc)$_2$(py)$_2$.

To summarize, the most effective method discovered for the synthesis of Sn(3,5-dtbc)$_2$(py)$_2$ was from tin metal, 3,5-dtbc, and pyridine (Table 3.1, Entry 6). This method works on a 1 g scale, which means the average yield of complex is about 450 mg per batch, a quantity that is sufficient for exploring its reactivity. The issue of scalability needs further investigation.

The structure of the major isomer of Sn(3,5-dtbc)$_2$(py)$_2$ was confirmed by X-ray crystallography (Figure 3.3). The pyridine ligands and *tert*-butyl groups are *trans* to one another. Important structural metrics of Sn(3,5-dtbc)$_2$(py)$_2$ include the length of the tin-nitrogen (2.2507(10) Å) and tin-oxygen (2.0061(9) Å) bonds. The Sn-N and Sn-O bond distances are longer than the corresponding bond distances in Ge(3,5-dtbc)$_2$(py)$_2$ (Ge-N = 2.098(1) Å, Ge-O = 1.847(1) Å, respectively). Complex **3.2**, Scheme 3.1, also has four Sn-O and two Sn-N bonds.[22] The average Sn-N bond distances in **3.2** are 2.333(6) Å, and the average Sn-O bond distances in **3.2** are 2.0035(4) Å, similar to those in Sn(3,5-dtbc)$_2$(py)$_2$.[22] Sn(3,6-dtbc)$_2$(THF)$_2$ and Sn(3,6-dtbc)$_2$(OEt$_2$)$_2$ have been characterized by X-ray crystallography.[26] Both complexes have similar tin-catechol bond distances (average of Sn-O bonds = 1.9928(4) Å) and tin-ether bond distances (average of Sn-O bonds = 2.2347(6) Å).

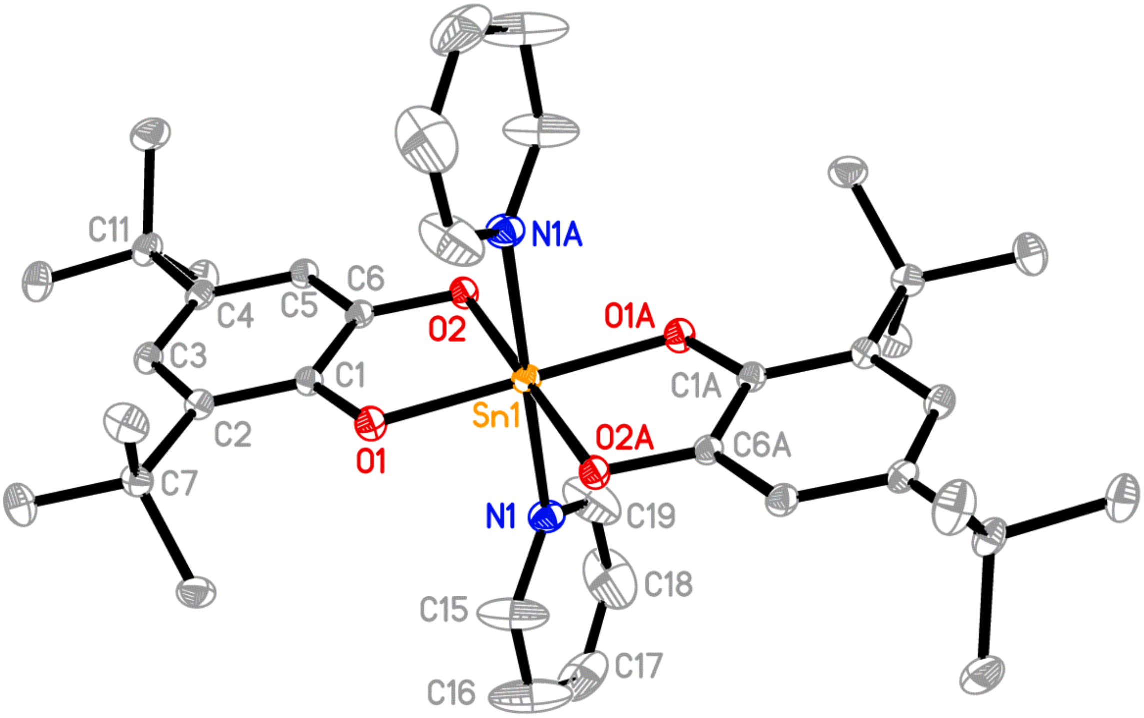


Figure 3.3: Thermal ellipsoid plot (50% probability surface) of Sn(3,5-dtbc)$_2$(py)$_2$•2(CHCl$_3$). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1-N1 2.2507(10), Sn1-O1 2.0061(9), Sn1-O2 2.0215(9); O1-Sn1-O2 84.90(3), O1-Sn1-O2A 95.10(3), O1-Sn1-N1 90.96(4), O1A-Sn1-N1 89.04(4), O2-Sn1-N1 90.13(4), O2A-Sn1-N1 89.87(4), N1-Sn1-N1A 180.0, O1-Sn1-O1A 180.0, O2-Sn1-O2A 180.0.

The tin-catechol bond distances in the THF and ether complexes are comparable to those in Sn(3,5-dtbc)$_2$(py)$_2$. The bond angles around the central tin atom of all three complexes, Sn(3,6-dtbc)$_2$(THF)$_2$, Sn(3,6-dtbc)$_2$(OEt$_2$)$_2$, and Sn(3,5-dtbc)$_2$(py)$_2$, are in the range of 85°-95°. The complex Sn(3,6-dtbc)$_2$(^{t}BuN=CHCH=N^{t}Bu) was also characterized by X-ray crystallography,[26] and has *cis* nitrogen ligands by virtue of the geometric constraints of the diazadiene ligand. The tin-catechol bond distances (average of Sn-O bonds = 2.0207 Å) and tin-nitrogen bond distances (average of Sn-N bonds = 2.312 Å) are also comparable to those of Sn(3,5-dtbc)$_2$(py)$_2$, as are the bond angles around the central tin atom (~85°-95°).

3.6.3 Reaction of Sn(3,5-dtbc)$_2$(py)$_2$ with Grignard Reagents

The synthesis of tetraorganostannanes from the reaction of Sn(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents was investigated. The conditions used were the same as the optimized conditions for the reaction of Grignard reagents with Ge(3,5-dtbc)$_2$(py)$_2$ (Chapter 2). The Grignard reagents investigated included both alkyl and aryl as well as allyl and benzylmagnesium halides. The bulkiness of the reagent was also varied from butyl to *sec*-butyl and phenyl to mesityl. The results of the reaction of Sn(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents are summarized in Table 3.2. The yields of the tetraorganostannanes are isolated yields, whereas 3,5-dtbc recoveries were determined by GC. In general, the yields of SnR$_4$ from the reaction of Sn(3,5-dtbc)$_2$(py)$_2$ with Grignard reagents are very good (Table 3.2), and the recovery of 3,5-dtbc was, in general, good. Two protocols were developed for the isolation of the tetraorganostannanes: a chromatographic based procedure (Workup A) as well as a selective dissolution procedure (Workup B). Some key points about the synthesis of each tetraorganostannane are mentioned, organized by the organic sustituent.

Table 3.2: Synthesis of SnR_4 from $Sn(3,5\text{-dtbc})_2(py)_2$ and Grignard reagents.

Entry	RM [1]	Complex : RM	Solvent (amount)	Time (hrs)	Temp (°C)	Workup [2]	Yield [3]	Product	3,5-dtbc Recovery [3]
1	BuMgCl 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	A	100%	$SnBu_4$	88%
2	PhMgCl 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	B	70%	$SnPh_4$	71%
3	BnMgCl 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	A	89%	$SnBn_4$	94%
4	HexMgCl 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	A	96%	$SnHex_4$	61%
5	AllMgCl * 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	A	100%	$Sn(All)_4$ (67%) [4] $Sn(All)_3Cl$ (33%) [4]	64%
6	MesMgBr * 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	A	80%	$SnMes_3Br$ (12%) [4] $SnMes_3Cl$ (68%) [4]	69%
7	^{s}BuMgCl 1.2 M THF	1 : 20	THF (3.8 mL)	24	65	A	93%	$Sn^{s}Bu_4$ (82%) [4] $Sn^{s}Bu_3Cl$ (11%) [4]	60%
8	TolMgBr * 2.0 M THF	1 : 20	THF (3.8 mL)	24	65	B	68%	$SnTol_4$	100%

1. Commercial sources of RM, used as received unless indicated otherwise (*).
2. See reaction descriptions for details of the workups.
3. Average of two runs.
4. Isolated as mixtures with other listed compounds.

In general, the tetraorganostannanes were identified on the basis of a comparison of the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectral data to those in the literature. For some of the compounds, no NMR data has been reported.

$SnBu_4$[28] (Table 3.2, Entry 1): $SnBu_4$ is traditionally synthesized from $SnCl_4$. For example, upon refluxing a mixture of BuMgCl and $SnCl_4$ for 3 h, a 95% yield of $SnBu_4$ was obtained with small amounts of Bu_3SnCl and Bu_2SnCl_2.[29] The synthesis of $SnBu_4$ from $Sn(3,5\text{-dtbc})_2(py)_2$ is superior because only $SnBu_4$ is obtained in excellent yield and high purity.

$SnPh_4$[30, 31] **and $SnTol_4$**[32, 33] (Table 3.2, Entries 2 and 8): The reaction of PhMgCl with $SnCl_4$ to produce $SnPh_4$ was patented in 1951, and little if any efforts have been made since then to make the process greener.[29] The yields of

$SnPh_4$ and $SnTol_4$ were the lowest of the series, and this is attributed to the workup used for these two compounds. It was not possible to separate SnR_4 for R = Ph and Tol from the crude reaction mixtures by chromatography (Workup A), and thus, $SnPh_4$ and $SnTol_4$ were isolated using trituration with a small amount of pentane (Workup B). Pentane was selected out of a range of solvents because it has good solubility for 3,5-dtbc and only moderate solubility for $SnPh_4$ and $SnTol_4$. Nonetheless, a significant portion of the tetraarylstannane was lost during this separation procedure. In comparison, a continuous flow procedure has yielded $SnPh_4$ from PhMgCl and $SnCl_4$ in 97% yield using a mixture of THF and toluene as the solvent system.[34] While this method has excellent yield and selectivity, it relies on $SnCl_4$ and requires special equipment to generate the product. The method developed in this study, starting from tin metal, uses no Cl_2 and can be conducted in standard laboratory equipment.

$SnBn_4$ (Table 3.2, Entry 3): $SnBn_4$ can be synthesized from $SnCl_4$ and excess BnMgCl in 75% yield,[35] which is not as high as the yield of $SnBn_4$ derived from $Sn(3,5\text{-dtbc})_2(py)_2$. Some dibenzyl ($C_6H_5CH_2CH_2C_6H_5$) was formed during the reaction of $Sn(3,5\text{-dtbc})_2(py)_2$ with BnMgCl and was isolated as a separate fraction on the TLC plate. The dibenzyl formation may be related to the Schlenk equilibrium.[27] The reported ^1H NMR data for $SnBn_4$ differs by more than experimental error in comparison to the data obtained by us and completely misses a signal.[36] Nonetheless, we are confident in the identification of the product because the product was also characterized by ^{13}C NMR spectroscopy and mass spectrometry.

$SnHex_4$ (Table 3.2, Entry 4): $SnHex_4$ has been prepared from HexMgBr with $SnCl_4$.[37] The yield was not reported but the purity was good after fractional distillation as determined by elemental analysis.[37] Two byproducts were identified by GC-MS in the reaction of HexMgCl with Sn(3,5-dtbc)$_2$(py)$_2$: dodecane (3%), and Hex_3SnOct (3%). The dodecane was inseparable from $SnHex_4$ by chromatography. The formation of Hex_3SnOct was somewhat surprising. The most reasonable explanation for the formation of Hex_3SnOct was the presence of OctMgCl as a contaminant in the HexMgCl. Indeed, when HexMgCl was quenched with water, GC-MS analysis of the product showed the presence of both hexane and octane.

$SnAll_4$[38] **and $ClSnAll_3$** (Table 3.2, Entry 5): A 53% yield of tetraallyl tin was obtained from the reaction of allylmagnesium chloride with tin tetrachloride. An undisclosed quantity of $ClSnAll_3$ was also produced in the same reaction.[39] Our reaction provides tetraallyl tin in 67% yield along with $ClSnAll_3$ (33%).

$ClSnMes_3$ & $BrSnMes_3$ (Table 3.2, Entry 6): Only the formation of $ClSnMes_3$ and $BrSnMes_3$, in a 1:3 ratio, as identified by GC-MS, was observed in the reaction of Sn(3,5-dtbc)$_2$(py)$_2$ with MesMgBr; no $SnMes_4$ was formed. It is surprising that we obtain $ClSnMes_3$ as a product in this reaction given that no source of chloride was purposefully introduced. It is hypothesized that the

$CDCl_3$, used as the NMR solvent to examine the crude product mixture, contains some HCl, and an exchange reaction takes place (equation 6).

$$BrSnMes_3 + Cl^- \rightarrow ClSnMes_3 + Br^- \quad (6)$$

Surprisingly, $SnMes_4$ was not formed but a similar compound[6] was synthesized using conditions similar to our own (equation 7); however, using $SnCl_4$ as the starting material.

$$4\ (2,6\text{-}C_6H_3Me_2)MgBr + SnCl_4 \rightarrow Sn(2,6\text{-}C_6H_3Me_2)_4 \quad (7)$$

$Sn(2,6\text{-}C_6H_3Me_2)_4$ is expected to be almost as sterically congested. Perhaps, using longer reaction times and more forcing conditions, $Sn(3,5\text{-dtbc})_2(py)_2$ could lead to $SnMes_4$ using an excess of MesMgBr.

Sn^sBu_4 (Table 3.2, Entry 7): Several isomers of Sn^sBu_4 are evident after analyzing the ^1H NMR, $^{13}C\{^1H\}$ NMR, and GC-MS data of the product derived from $Sn(3,5\text{-dtbc})_2(py)_2$ and ^sBuMgCl. Unlike the analogous reaction with germanium, the formation of Sn^sBu_4 from $Sn(3,5\text{-dtbc})_2(py)_2$ is possible, because the tin-carbon bond is longer than the germanium-carbon bond, and thus, there is less steric crowding of the ^sBu groups around tin. There is one major byproduct evident in the GC of the product mixture, which was identified as $ClSn^sBu_3$ by GC-MS. Although it appears that there are only two compounds present in the

^{1}H NMR spectrum of the product mixture (Figure 3.4), the signals are actually from several isomers of Sn^{s}Bu$_4$ and ClSn^{s}Bu$_3$. The doublet at 1.21 ppm and the triplet at 1.02 ppm in the ^{1}H NMR spectrum of the products derived from the addition of ^{s}BuMgCl to Sn(3,5-dtbc)$_2$(py)$_2$ are assigned to ClSn^{s}Bu$_3$ (Figure 3.4), since they are in a 1 : 9 ratio with the signals assigned to Sn^{s}Bu$_4$. The ratio of the two compounds closely matches that obtained by GC. The formation of ClSn^{s}Bu$_3$ is believed to result from the relief of steric pressure in ^{s}Bu$_3$Sn(3,5-dtbc-η^1) by substitution of the 3,5-dtbc ligand by chloride.

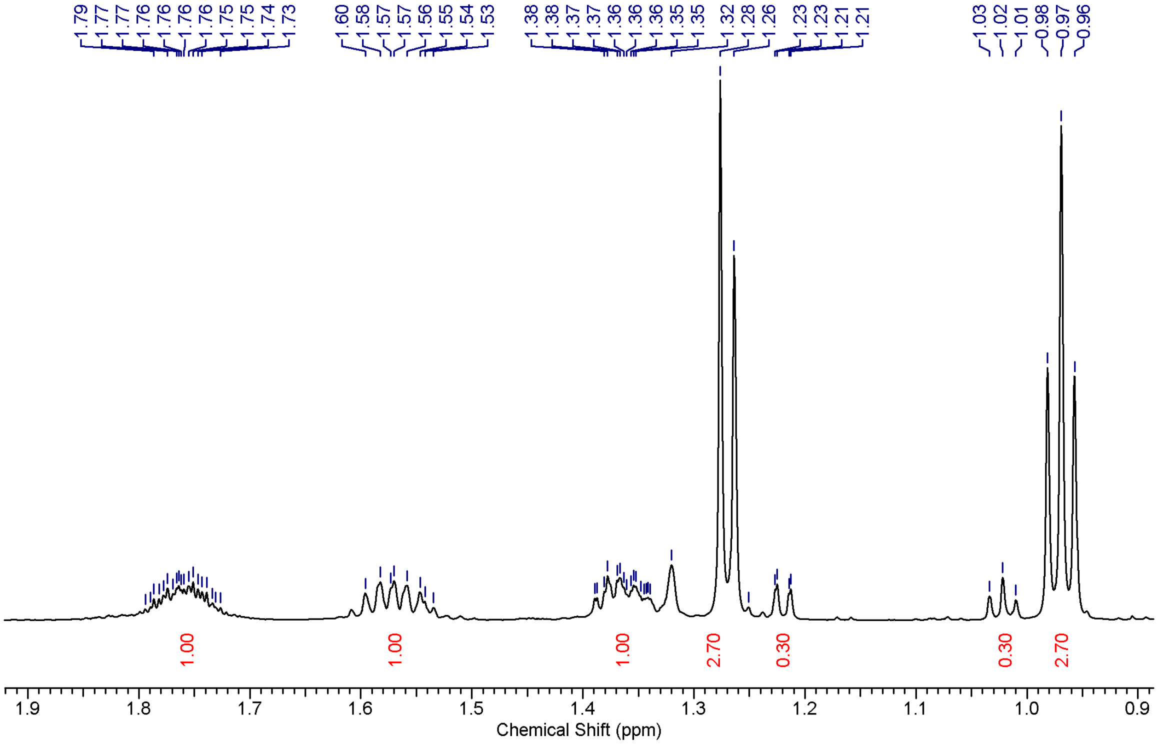


Figure 3.4: ^{1}H NMR spectrum (600 MHz) of the isomers of Sn^{s}Bu$_4$ and ClSn^{s}Bu$_3$ in CDCl$_3$ from 1.90 – 0.90 ppm.

At first glance, it appears there is only one major compound present in the ^{13}C{^{1}H} NMR spectrum (Figure 3.5) of the reaction mixture, because of the four prominent signals. Expansion of the spectrum reveals there are many more signals (Figure 3.6). Further expansion of the signal at ~29 ppm reveals the presence of at least five isomers of Sn^{s}Bu$_4$ (Figure 3.7).

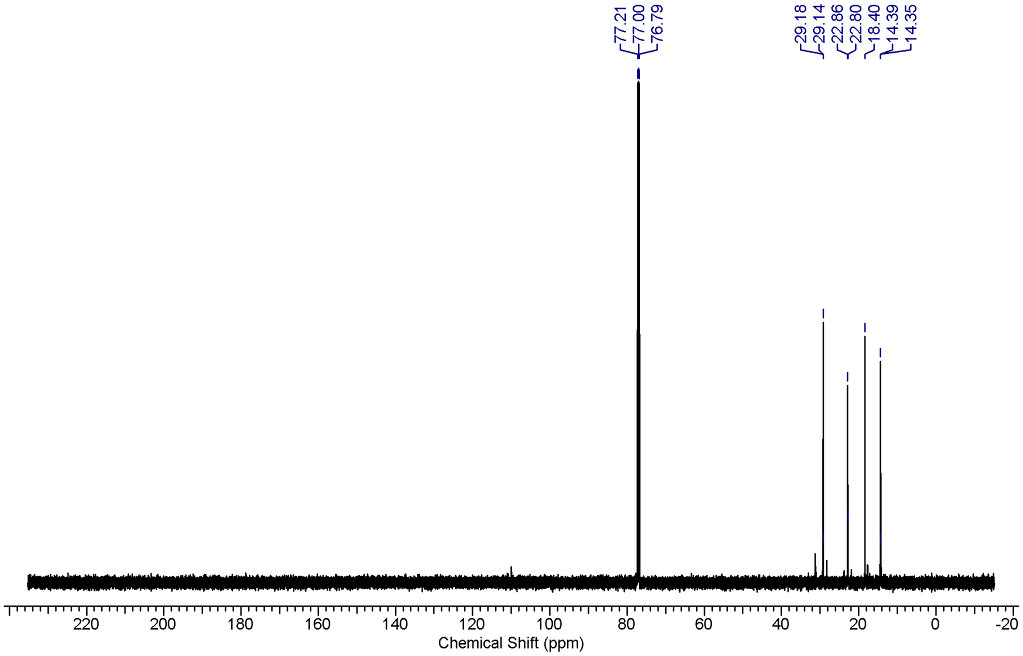


Figure 3.5: $^{13}C\{^1H\}$ NMR spectrum (150 MHz) of the isomers of Sn^{s}Bu$_4$ and ClSn^{s}Bu$_3$ in CDCl$_3$ from 220.00 – -20.00 ppm.

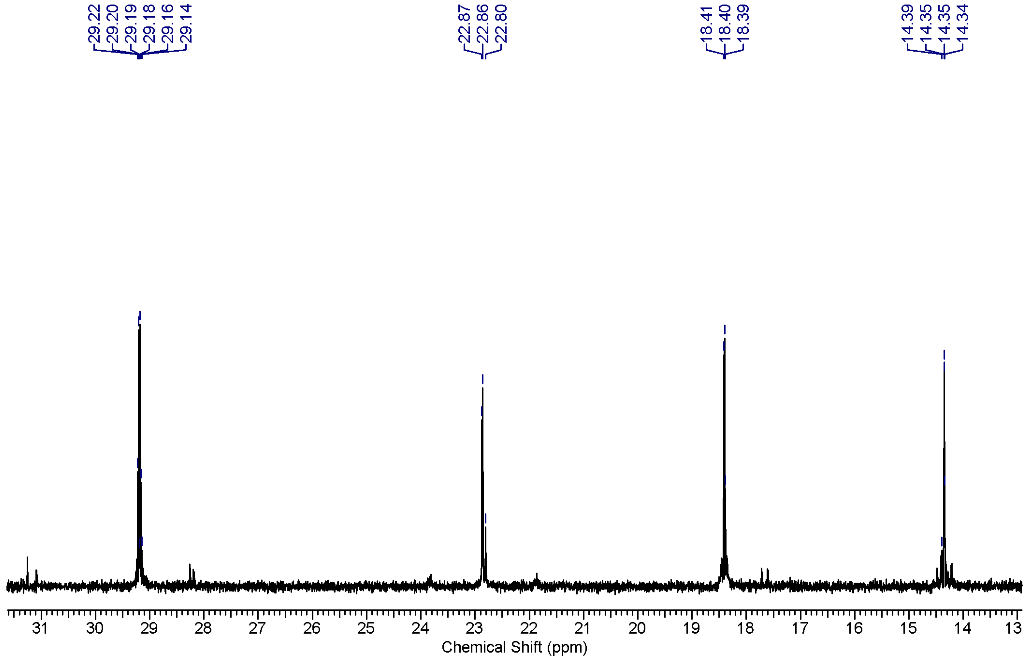


Figure 3.6: $^{13}C\{^1H\}$ NMR spectrum (150 MHz) of the isomers of Sn^{s}Bu$_4$ and ClSn^{s}Bu$_3$ in CDCl$_3$ from 31.50 – 13.00 ppm.

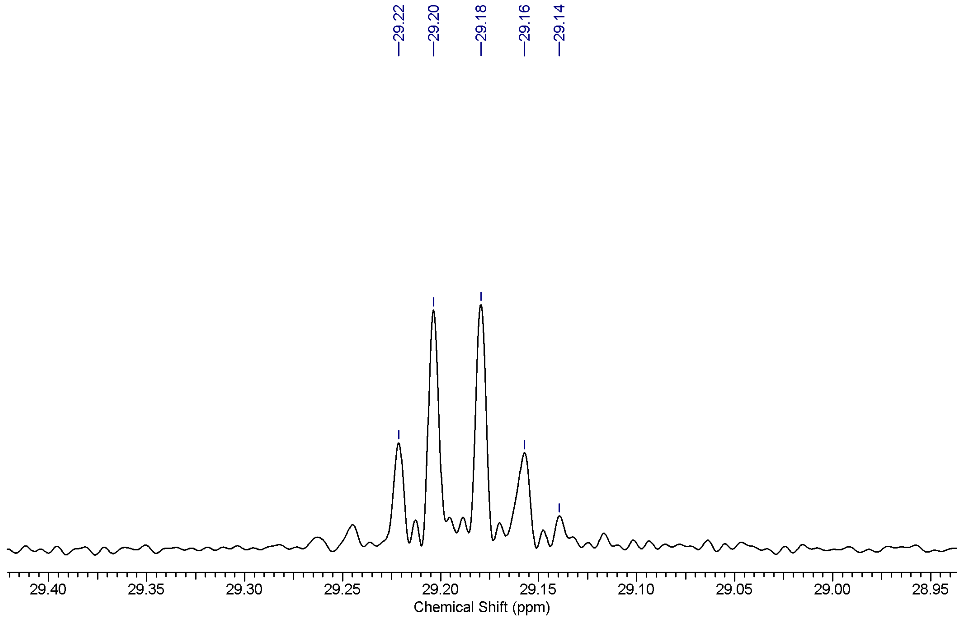


Figure 3.7: $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of the isomers of $Sn^{s}Bu_4$ and $ClSn^{s}Bu_3$ in $CDCl_3$ from 29.40 – 28.95 ppm.

The $^{119}Sn\{^{1}H\}$ NMR spectrum of the reaction mixture also reveals that at least five isomers of $Sn^{s}Bu_4$ are present (Figure 3.8), which matches the data evident in the $^{13}C\{^{1}H\}$ NMR spectrum.

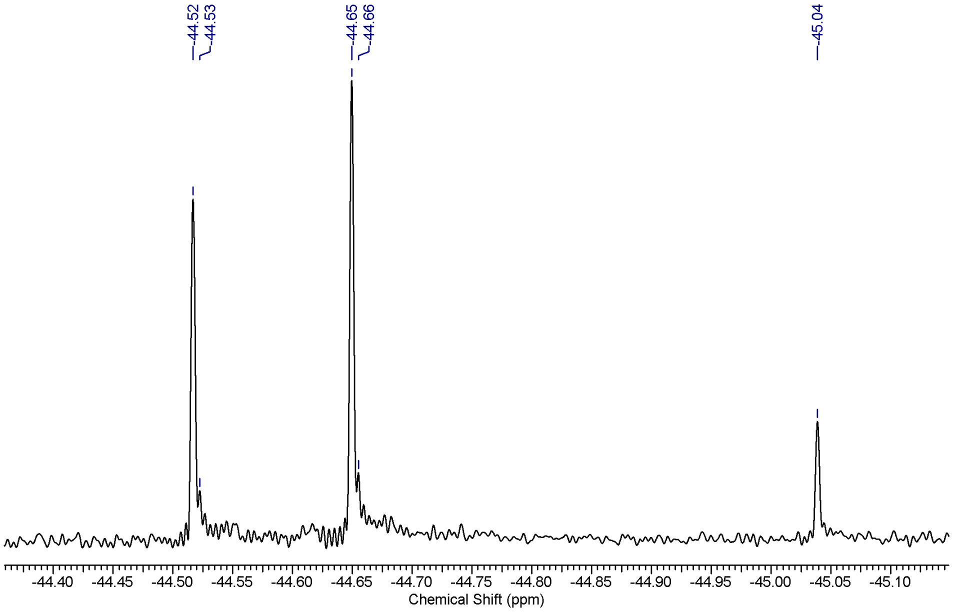


Figure 3.8: $^{119}Sn\{^{1}H\}$ NMR spectrum (223 MHz) of the isomers of $Sn^{s}Bu_4$ and $ClSn^{s}Bu_3$ in $CDCl_3$ from -44.40 – -45.10 ppm.

3.7 Conclusions

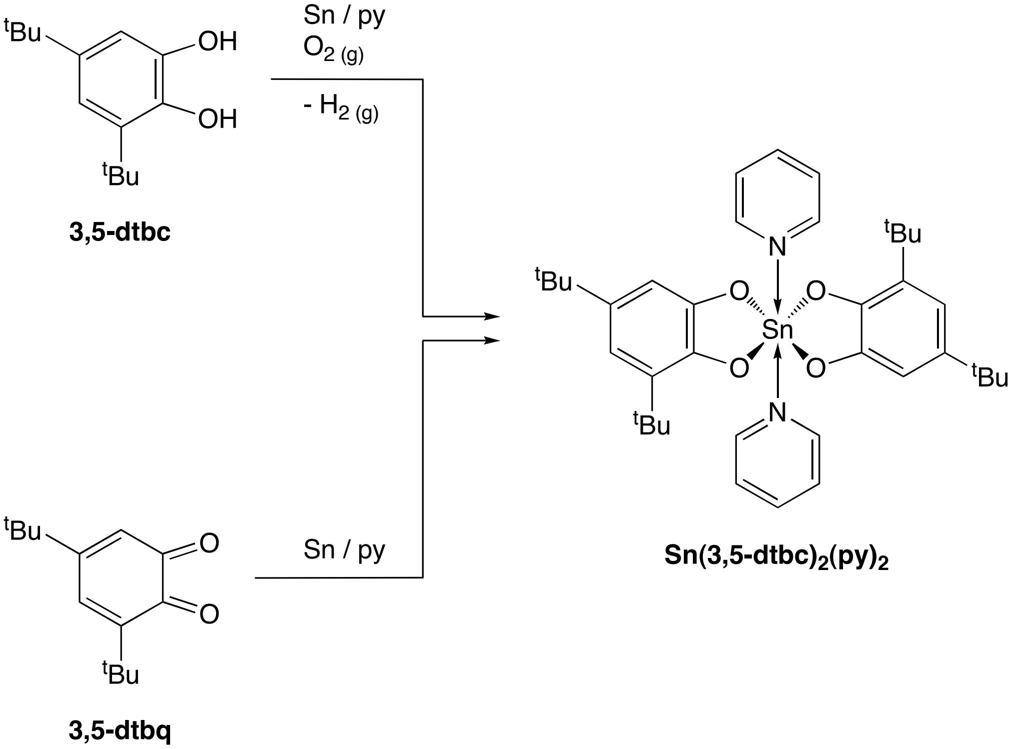
In conclusion, a new hypercoordinate tin complex $Sn(3,5\text{-dtbc})_2(py)_2$ has been synthesized in good yield. The complex $Sn(3,5\text{-dtbc})_2(py)_2$ has proven to be reliable in the synthesis of a broad range of tetraorganostannanes SnR_4, just as $Ge(3,5\text{-dtbc})_2(py)_2$ was shown to be reliable in the synthesis of a broad range of tetraorganogermanes GeR_4. This creates a link between tin metal and tetraorganostannanes without relying on the corrosive and chlorine-intensive synthesis of $SnCl_4$, and thus, many of the principles of green chemistry have been applied.[3] However, while chlorine has been eliminated from the synthesis of the Sn^{IV} starting material, there is still chlorine involved in the synthesis of Grignard reagents. Alkyl (aryl) chlorides are used to synthesize the Grignard reagents, and are derived from the reaction of hydrocarbons with chlorine. Therefore, the new route to tetraorganostannanes is reduced in the amount of chlorine used. Furthermore, the synthesis of functional stannanes, $R_nSnX_{(4-n)}$, are often derived from the Kocheshkov redistribution reaction, which requires the use of $SnCl_4$. Preliminary studies on using $Sn(3,5\text{-dtbc})_2(py)_2$ as the Sn^{iv} reactant, in place of $SnCl_4$, in the Kocheshkov redistribution reaction are underway, with the goal being to replace all the halogen-containing compounds of this system with more environmentally-friendly compounds. An alternative synthesis of R_2SnX_2, used in the synthesis of downstream tin chemicals, is still needed and this is the focus of chapter 5.

3.8 Experimental Procedures

3.8.1 General Experimental Procedures

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques unless specified otherwise. Solvents were dried using a solvent purification system: a PureSolv MD 7 from Innovative Technology. All remaining chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Varian Mercury 400 MHz, Inova 400 MHz, or an Inova 600 MHz NMR spectrometer using $CDCl_3$ as the solvent. ^1H NMR spectra were referenced internally to residual $CHCl_3$ (7.27 ppm); $^{13}C\{^1H\}$ spectra were referenced to the central transition of $CDCl_3$ (77.00 ppm). All ^1H and ^{13}C NMR signals were assigned using gCOSY and/or ^{13}C-^1H gHSQC NMR spectroscopy. GC-MS mass spectra were obtained on a GCMS-QP2010S instrument with a GC-2010 gas chromatograph at an ionizing voltage of 70 eV and a DB-5MS 30 m × 0.25 μm column from J & W Scientific utilizing the following temperature program: 3 min at 65 °C; 17 min constant heating rate of 15 °C / min; 5 min at 320 °C. Mass spectral data are reported in mass-to-charge units, *m/z*, with ion identity and peak intensities (%) in parentheses. Single crystal X-ray diffraction data were collected on a Bruker APEX II diffractometer with MoKα [λ=0.71073 Å] source and CCD detector at 110 K.

3.8.2 Synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$ from Sn



Scheme 3.5: Synthesis of $Sn(3,5\text{-dtbc})_2(py)_2$ from tin metal, pyridine, and either 3,5-dtbc with O_2 or 3,5-dtbq.

Powdered tin metal (165 mg, 1.39 mmol), 3,5-dtbc (620 mg, 2.79 mmol), and pyridine (7.0 mL, 87 mmol) were combined in a 20 mm diameter Schlenk tube equipped with a magnetic stirring bar and reflux condenser. The grey heterogeneous mixture was refluxed (115 °C) for 2 days while oxygen gas was bubbled through at a moderate rate using a stainless steel needle, until the mixture becomes homogeneous and transparent orange / brown. Precipitation with 20 mL pentane followed by centrifugation to remove the solvent mixture, followed by washing with 20 mL pentane affords $Sn(3,5\text{-dtbc})_2(py)_2$ in an average yield of 45% (10 experiments).

An alternative method to synthesize Sn(3,5-dtbc)$_2$(py)$_2$ is from 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-dtbq). Powdered tin metal (41 mg, 0.35 mmol), 3,5-dtbq (154 mg, 0.70 mmol), and pyridine (4.2 mL, 52 mmol) were combined in a 20 mm diameter Schlenk test tube equipped with a magnetic stirring bar and a reflux condenser. The mixture was refluxed for 2 days during which time the mixture changes from heterogenous and grey to homogeneous and clear orange / brown. Precipitation with 5 mL pentane followed by centrifugation to remove the solvent mixture, followed by washing with 10 mL pentane affords Sn(3,5-dtbc)$_2$(py)$_2$ in an average yield of 74% (3 experiments). On a 1000 mg scale, no product was obtained (0% yield).

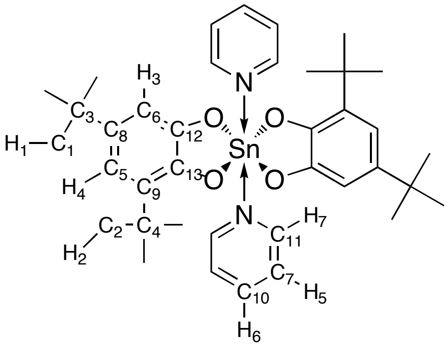


Figure 3.9: Sn(3,5-dtbc)$_2$(py)$_2$.

M.p. = 315 – 317 °C (decomposes): **^{1}H NMR** (600 MHz, CDCl$_3$): 8.71 (4H, m, H_7), 7.84 (2H, m, H_6), 7.42 (4H, m, H_5), 6.86 (2H, d, ^4J = 2.3 Hz, $H_{4\,/\,3}$), 6.62 (2H, d, ^4J = 2.3 Hz, $H_{3\,/\,4}$), 1.46 (18H, s, $H_{2\,/\,1}$), 1.23 (18H, s, $H_{1\,/\,2}$); **Elemental Analysis** calcd for $C_{38}H_{50}N_2O_4Sn$: C, 63.61; H, 7.02; N, 3.90; found: C, 63.27; H, 7.04; N, 3.80

3.8.3 Reaction of $Sn(3,5\text{-dtbc})_2(py)_2$ with Grignard Reagents

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques unless specified otherwise. All equipment was flame dried prior to use and kept under an argon atmosphere. In a 100 mL flask equipped with magnetic stirring and a reflux condenser, RMgCl (~ 3 mmol) was added to a suspension of $Sn(3,5\text{-dtbc})_2(py)_2$ (100 mg, 0.139 mmol) dissolved in 2.4 mL of the same solvent as the organometallic reagent (THF). The total volume of solvent was 3.8 mL and the concentration of RMgCl was 0.75 M. The mixture was allowed to reflux for 24 h. After cooling to room temperature, 1 mL of deionized water was added to the crude reaction mixture which was stirred for 5 minutes. The two layers were separated. The organic layer was then concentrated using a rotary evaporator. Procedure A (used to isolate $SnBu_4$, $SnBn_4$, $SnHex_4$, $ClSnAll_3$, $SnAll_4$, $ClSn^{s}Bu_3$, $Sn^{s}Bu_4$, $ClSnMes_3$, and $BrSnMes_3$): The crude reaction mixture was purified using preparative thin layer chromatography on a 0.2 mm × 20 cm × 20 cm silica gel plate using hexanes as eluent. In general, there were two bands evident, one containing SnR_4 and one containing 3,5-dtbc. Each band was scraped from the plate and extracted by allowing it to stir for 30 minutes in 30 mL of chloroform. The solids were separated using filtration and the solvent removed using a rotary evaporator.

Procedure B (used to isolate $SnPh_4$ and $SnTol_4$): The residue was washed 2 × 10 mL pentane and then dried.

$SnBu_4$: **^{1}H NMR** (600 MHz, $CDCl_3$):[28] 1.53-1.45 (8H, m), 1.34-1.26 (8H, m), 0.94-0.86 (12H, m), 0.86-0.76 (8H, m); **^{13}C NMR** (150 MHz, $CDCl_3$):[28] 29.27, 27.41, 13.72, 8.75; **^{119}Sn{^{1}H} NMR** (223 MHz, $CDCl_3$):[40] -11.6 (J_{Sn-H} = 49.3 Hz); **GC-MS** 97% pure; (*m/z*): 291 (Bu_3SnH^+, 50%), 235 ($Bu_2SnH_2^+$, 75%), 179 ($BuSnH_3^+$, 100%), 121 (SnH_2^+, 70%), 57 (Bu^+, 10%), 41 (30%).

$SnPh_4$: **^{1}H NMR** (400 MHz, $CDCl_3$):[30] 7.70-7.54 (8H, m), 7.45-7.36 (12H, m); **^{13}C NMR** (100 MHz, $CDCl_3$):[31] 137.89, 137.22, 129.12, 128.62; **^{119}Sn{^{1}H} NMR** (223 MHz, $CDCl_3$):[41] -129.5 (J_{Sn-H} = 14.0 Hz); **GC-MS** 95% pure; (*m/z*): 351 (Ph_3SnH^+, 90%), 274 (Ph_2SnH^+, 25%), 197 ($PhSnH^+$, 50%), 152 (10%), 120 (SnH^+, 100%), 77 ($C_6H_5^+$, 15%), 51 (28%).

$SnBn_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 7.20-7.15 (8H, m), 7.05-7.00 (4H, m), 6.78-6.73 (8H, m), 2.24 (8H, s); **^{13}C NMR** (150 MHz, $CDCl_3$): 141.46, 128.54, 127.41, 123.60, 18.82; **^{119}Sn{^{1}H} NMR** (223 MHz, $CDCl_3$): -36.0 (J_{Sn-H} = 61.5 Hz); **GC-MS** 99% pure; (*m/z*): 393 (Bn_3SnH^+, 40%), 211 ($BnSnH^+$, 100%), 120 (SnH^+, 18%), 91 ($C_7H_7^+$, 98%), 65 (20%).

$SnHex_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 1.53-1.45 (8H, m), 1.35-1.23 (24H, m), 0.93-0.87 (12H, m), 0.84-0.78 (8H, m); **^{13}C NMR** (150 MHz, $CDCl_3$): 34.15, 31.52, 26.97, 22.67, 14.15, 9.10; **^{119}Sn{^{1}H} NMR** (223 MHz, $CDCl_3$): -12.2 (J_{Sn-H} = 50.0 Hz); **GC-MS** 94% pure; (*m/z*): 375 (Hex_3SnH^+, 40%), 291 ($Hex_2SnH_2^+$, 57%), 207 ($HexSnH_3^+$, 100%), 149 (10%), 121 (SnH_2^+, 43%), 83 (40%), 56 (15%), 43 (63%).

SnAll$_4$: **^{1}H NMR** (600 MHz, CDCl$_3$):[38] 5.94 (4H, tdd, ^3J = 8.7, 10.2, 17.0 Hz, $^3J_{Sn\text{-}H}$ = 18.8 Hz), 4.88 (4H, tdd, J = 0.1, 1.3, 17.0 Hz, $^4J_{Sn\text{-}H}$ = 41.5 Hz), 4.75 (4H, tdd, J = 0.7, 1.3, 10.2 Hz, $^4J_{Sn\text{-}H}$ = 21.5 Hz), 1.92 (8H, ddd, J = 0.1, 0.7, 8.7 Hz, $^2J_{Sn\text{-}H}$ = 61.9 Hz); **^{13}C NMR** (150 MHz, CDCl$_3$): 136.56, 111.07, 16.13; **^{119}Sn{^{1}H} NMR** (223 MHz, CDCl$_3$):[38] -46.7 ($J_{Sn\text{-}H}$ = 61.9, 41.5, 21.5 Hz); **GC-MS** 96% pure; (m/z): 243 (($H_2C{=}CHCH_2)_3SnH^+$, 23%), 202 (($H_2C{=}CHCH_2)_2SnH^+$, 7%), 161 (($H_2C{=}CHCH_2)SnH^+$, 100%), 135 (13%), 121 (SnH_2^+, 20%), 41 (($H_2C{=}CHCH_2)^+$, 15%).

ClSnAll$_3$: **^{1}H NMR** (600 MHz, CDCl$_3$):[38] 5.97 (3H, tdd, ^3J = 8.6, 10.2, 17.0 Hz, $^3J_{Sn\text{-}H}$ = 18.8 Hz), 5.04 (3H, dtd, J = 0.1, 0.7, 17.0 Hz, $^4J_{Sn\text{-}H}$ = 2.1 Hz), 4.95 (3H, dtd, J = 0.7, 0.7, 10.2 Hz), 2.32 (6H, ddd, J = 0.1, 0.7, 8.6 Hz, $^2J_{Sn\text{-}H}$ = 70.0 Hz); **^{13}C NMR** (150 MHz, CDCl$_3$): 133.25, 114.50, 22.80; **^{119}Sn{^{1}H} NMR** (223 MHz, CDCl$_3$):[38] -154.5 (from HMBC); **GC-MS** 96% pure; (m/z): 237 (($H_2C{=}CHCH_2)_2SnHCl^+$, 20%), 196 (($H_2C{=}CHCH_2)SnHCl^+$, 10%), 155 ($SnHCl^+$, 100%), 120 (SnH^+, 15%), 41 (($H_2C{=}CHCH_2)^+$, 48%).

ClSnMes$_3$: **^{1}H NMR** (600 MHz, CDCl$_3$): 6.90 (6H, s), 2.39 (18H, s, $^4J_{Sn\text{-}H}$ = 6.7 Hz), 2.29 (9H, s); **^{13}C NMR** (150 MHz, CDCl$_3$): 144.14, 141.40, 137.88, 129.01, 25.25, 21.05; **^{119}Sn{^{1}H} NMR** (223 MHz, CDCl$_3$): -84.7; **GC-MS** 63% pure; (m/z): 511 (Mes_3SnCl^+, 1%), 391 (10%), 357 (Mes_2Sn^+, 4%), 237 (100%), 222 (15%), 207 (13%), 195 (10%), 131 (17%), 119 (Mes^+, 30%), 91 ($C_7H_7^+$, 27%), 77 ($C_6H_5^+$, 12%), 41 (15%).

BrSnMes$_3$: **^{1}H NMR** (600 MHz, CDCl$_3$): 6.91 (8H, s), 2.41 (24H, s, $^{4}J_{\text{Sn-H}}$ = 6.7 Hz), 2.25 (12H, s); **^{13}C NMR** (150 MHz, CDCl$_3$): 141.10, 139.54, 136.26, 129.04, 25.64, 21.03; **^{119}Sn{^{1}H} NMR** (223 MHz, CDCl$_3$): -120.6; **GC-MS** 24% pure; (*m/z*): 557 (Mes$_3$SnBr$^+$, 1%), 437 (Mes$_2$SnBr$^+$, 10%), 357 (Mes$_2$Sn$^+$, 4%), 237 (100%), 222 (10%), 207 (9%), 195 (8%), 131 (13%), 119 (Mes$^+$, 30%), 91 (C$_7$H$_7$$^+$, 23%), 77 (C$_6H_5$$^+$, 10%), 41 (13%).

Sn^{s}Bu$_4$ (several isomers evident): **^{1}H NMR** (600 MHz, CDCl$_3$): 1.85-1.70 (4H, m), 1.64-1.48 (4H, m), 1.42-1.32 (4H, m), 1.29-1.25 (12H, m), 0.99-0.95 (12H, m); **^{13}C NMR** (150 MHz, CDCl$_3$):[42] 29.30-29.00 (m), 22.95-22.70 (m), 18.50-18.20 (m), 14.55-14.15 (m); **^{119}Sn{^{1}H} NMR** (223 MHz, CDCl$_3$): -44.5, -44.7, -45.0; **GC-MS** 91% pure; (*m/z*): 291 (^{s}Bu$_3$SnH$^+$, 30%), 235 (^{s}Bu$_2$SnH$_2$$^+$, 50%), 179 (^{s}BuSnH$_3$$^+$, 100%), 121 (SnH$_2$$^+$, 60%), 57 (Bu$^+$, 33%), 41 (60%).

SnTol$_4$: **^{1}H NMR** (600 MHz, CDCl$_3$):[33] 7.51 (8H, qd, J = 5.0, 8.0 Hz, $^{3}J_{\text{Sn-H}}$ = 46.6 Hz), 7.22 (8H, qd, J = 1.5, 8.0 Hz, $^{4}J_{\text{Sn-H}}$ = 12.7 Hz), 2.38 (12H, dd, J = 1.5, 5.0 Hz, $^{6}J_{\text{Sn-H}}$ = 0 Hz); **^{13}C NMR** (150 MHz, CDCl$_3$):[32] 138.76, 137.14, 134.43, 129.37, 21.49; **^{119}Sn{^{1}H} NMR** (223 MHz, CDCl$_3$):[32] -123.6 ($J_{\text{Sn-H}}$ = 46.6, 12.7 Hz); **GC-MS** 98% pure; (*m/z*): 393 (Tol$_3$SnH$^+$, 100%), 302 (Tol$_2$SnH$^+$, 55%), 211 (TolSnH$^+$, 40%), 181 (33%), 165 (22%), 120 (SnH$^+$, 86%), 91 (C$_7$H$_7$$^+$, 87%), 65 (18%).

3.8.4 X-Ray Structure Determination of $Sn(3,5\text{-dtbc})_2(py)_2$

Data Collection and Processing: Clear yellow crystals were grown from chloroform. The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9814 reflections with $5.78° < 2\theta < 84.08°$. The data collection strategy was a number of ω and φ scans which collected data up to 98.36° (2θ). The frame integration was performed using SAINT.[43] The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[44] Structure Solution and Refinement: The structure was solved by using a dual space methodology using the SHELXT program.[45] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on F^2. The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELXTL suite of crystallographic software.[46] Graphic plots were produced using the XP program.[47] Additional information and other relevant literature references can be found in the reference section of the following website (http://xray.chem.uwo.ca).

Table 3.3: Summary of crystal data for Sn(3,5-dtbc)$_2$(py)$_2$•2(CHCl$_3$).

Compound Formula	$C_{40}H_{52}Cl_6N_2O_4Sn$
Formula Weight (*g/mol*)	956.22
Crystal Dimensions (*mm*)	0.326 _ 0.132 _ 0.104
Crystal Color and Habit	colourless prism
Crystal System	monoclinic
Space Group	P 2_1/n
Temperature, K	110
a, Å	10.537(3)
b, Å	9.4734(10)
c, Å	21.863(6)
α,°	90
β,°	91.191(13)
γ,°	90
V, Å^3	2182.0(8)
Number of reflections to determine final unit cell	9814
Min and Max 2θ for cell determination, °	5.78, 84.08
Z	2
F(000)	980
r (*g/cm*)	1.455
l, Å, (MoKα)	0.71073
m, (*cm*$^{-1}$)	0.994
Diffractometer Type	Bruker Kappa Axis Apex2
Scan Type(s)	phi and omega scans
Max 2θ for data collection, °	98.36
Measured fraction of data	0.997
Number of reflections measured	149128
Unique reflections measured	21761
R_{merge}	0.0563
Number of reflections included in refinement	21761
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	$w=1/[\mathrm{sigma}^2(F_o^2)+(0.0506P)^2+1.1576P]$ where $P=(F_o^2+2F_c^2)/3$
Number of parameters in least-squares	247
R_1	0.0435
ωR_2	0.1036
R_1 (all data)	0.0753
ωR_2 (all data)	0.1169

GOF	1.017
Maximum shift/error	0.001
Min & Max peak heights on final DF Map (e^-/Å)	-2.106, 1.405

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$

$\omega R_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]$

$GOF = [\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns. - No. of params.})]$

Table 3.4: Bond distances of Sn(3,5-dtbc)$_2$(py)$_2$•2(CHCl$_3$).

	2.0061(9)	C10-H10C	0.9800
Sn1-O1	2.0061(9)	C11-C14	1.5317(17)
Sn1-O2^1	2.0215(9)	C11-C13	1.5403(18)
Sn1-O2	2.0215(9)	C11-C12	1.5409(18)
Sn1-N1^1	2.2507(10)	C12-H12A	0.9800
Sn1-N1	2.2507(10)	C12-H12B	0.9800
O1-C1	1.3649(12)	C12-H12C	0.9800
O2-C6	1.3652(13)	C13-H13A	0.9800
C1-C2	1.4028(14)	C13-H13B	0.9800
C1-C6	1.4232(14)	C13-H13C	0.9800
C2-C3	1.4081(14)	C14-H14A	0.9800
C2-C7	1.5361(14)	C14-H14B	0.9800
C3-C4	1.3961(15)	C14-H14C	0.9800
C3-H3	0.9500	N1-C19	1.3210(19)
C4-C5	1.3991(15)	N1-C15	1.335(2)
C4-C11	1.5335(14)	C15-C16	1.383(3)
C5-C6	1.3855(14)	C15-H15	0.9500
C5-H5	0.9500	C16-C17	1.380(4)
C7-C10	1.5341(17)	C16-H16	0.9500
C7-C8	1.5359(16)	C17-C18	1.375(4)
C7-C9	1.5400(16)	C17-H17	0.9500
C8-H8A	0.9800	C18-C19	1.386(3)
C8-H8B	0.9800	C18-H18	0.9500
C8-H8C	0.9800	C19-H19	0.9500
C9-H9A	0.9800	C1S-Cl2S	1.754(3)
C9-H9B	0.9800	C1S-Cl3S	1.755(2)
C9-H9C	0.9800	C1S-Cl1S	1.758(2)
C10-H10A	0.9800	C1S-H1S	1.0000
C10-H10B	0.9800		

1. 1-x,1-y,1-z

Table 3.5: Bond angles of Sn(3,5-dtbc)$_2$(py)$_2$•2(CHCl$_3$).

^{1}-Sn1-O1	180.0	C7-C10-H10B	109.5
O1^1-Sn1-O2^1	84.90(3)	H10A-C10-H10B	109.5
O1-Sn1-O2^1	95.10(3)	C7-C10-H10C	109.5
O1^1-Sn1-O2	95.10(3)	H10A-C10-H10C	109.5
O1-Sn1-O2	84.90(3)	H10B-C10-H10C	109.5
O2^1-Sn1-O2	180.0	C14-C11-C4	112.81(10)
O1^1-Sn1-N1^1	90.97(4)	C14-C11-C13	108.53(10)
O1-Sn1-N1^1	89.04(4)	C4-C11-C13	108.62(10)
O2^1-Sn1-N1^1	90.13(4)	C14-C11-C12	108.09(10)
O2-Sn1-N1^1	89.87(4)	C4-C11-C12	109.73(9)
O1^1-Sn1-N1	89.04(4)	C13-C11-C12	109.00(11)
O1-Sn1-N1	90.96(4)	C11-C12-H12A	109.5
O2^1-Sn1-N1	89.87(4)	C11-C12-H12B	109.5
O2-Sn1-N1	90.13(4)	H12A-C12-H12B	109.5
N1^1-Sn1-N1	180.0	C11-C12-H12C	109.5
C1-O1-Sn1	109.59(6)	H12A-C12-H12C	109.5
C6-O2-Sn1	108.48(6)	H12B-C12-H12C	109.5
O1-C1-C2	122.23(9)	C11-C13-H13A	109.5
O1-C1-C6	117.74(8)	C11-C13-H13B	109.5
C2-C1-C6	120.03(9)	H13A-C13-H13B	109.5
C1-C2-C3	117.59(9)	C11-C13-H13C	109.5
C1-C2-C7	120.61(9)	H13A-C13-H13C	109.5
C3-C2-C7	121.80(9)	H13B-C13-H13C	109.5
C4-C3-C2	123.09(9)	C11-C14-H14A	109.5
C4-C3-H3	118.5	C11-C14-H14B	109.5
C2-C3-H3	118.5	H14A-C14-H14B	109.5
C3-C4-C5	118.14(9)	C11-C14-H14C	109.5
C3-C4-C11	122.86(9)	H14A-C14-H14C	109.5
C5-C4-C11	118.99(9)	H14B-C14-H14C	109.5
C6-C5-C4	120.80(9)	C19-N1-C15	119.01(14)
C6-C5-H5	119.6	C19-N1-Sn1	120.85(10)
C4-C5-H5	119.6	C15-N1-Sn1	120.12(10)
O2-C6-C5	120.74(9)	N1-C15-C16	121.5(2)
O2-C6-C1	118.91(8)	N1-C15-H15	119.2
C5-C6-C1	120.35(9)	C16-C15-H15	119.2
C10-C7-C8	106.92(10)	C17-C16-C15	119.7(2)
C10-C7-C2	111.97(9)	C17-C16-H16	120.2
C8-C7-C2	111.39(9)	C15-C16-H16	120.2
C10-C7-C9	108.17(10)	C18-C17-C16	118.06(16)
C8-C7-C9	108.97(10)	C18-C17-H17	121.0
C2-C7-C9	109.31(9)	C16-C17-H17	121.0

C7-C8-H8A	109.5	C17-C18-C19	119.14(19)
C7-C8-H8B	109.5	C17-C18-H18	120.4
H8A-C8-H8B	109.5	C19-C18-H18	120.4
C7-C8-H8C	109.5	N1-C19-C18	122.43(18)
H8A-C8-H8C	109.5	N1-C19-H19	118.8
H8B-C8-H8C	109.5	C18-C19-H19	118.8
C7-C9-H9A	109.5	Cl2S-C1S-Cl3S	108.79(13)
C7-C9-H9B	109.5	Cl2S-C1S-Cl1S	109.83(12)
H9A-C9-H9B	109.5	Cl3S-C1S-Cl1S	109.70(13)
C7-C9-H9C	109.5	Cl2S-C1S-H1S	109.5
H9A-C9-H9C	109.5	Cl3S-C1S-H1S	109.5
H9B-C9-H9C	109.5	Cl1S-C1S-H1S	109.5
C7-C10-H10A	109.5		

1. 1-x,1-y,1-z

3.9 References

1. R. E. Kirk, D. F. Othmer, J. I. Kroschwitz, M. Howe-Grant: *Encyclopedia of Chemical Technology*, Wiley, New York, **1991**.

2. K. Hudson-Edwards: *Science,* **2016**, *352*, 288-290.

3. P. Anastas, N. Eghbali: *Chem. Soc. Rev.,* **2010**, *39*, 301-312.

4. A. Khan, D. Foucher: *Coord. Chem. Rev.,* **2016**, *312*, 41-66.

5. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, F. Ullmann: *Ullmann's Encyclopedia of Industrial Chemistry,* VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany; Deerfield Beach, Fla, **1985**.

6. D. M. P. Mingos, R. H. Crabtree: *Comprehensive Organometallic Chemistry III*, Elsevier, Amsterdam; London, **2007**.

7. S. H. L. Thoonen, B. Deelman, G. Van Koten: *J. Organomet. Chem.,* **2004**, *689*, 2145-2157.

8. W. Caseri: *J. Organomet. Chem.,* **2014**, *751*, 20-24.

9. K. Sisido, S. Kozima, T. Tuzi: *J. Organomet. Chem.,* **1967**, *9*, 109-115.

10. K. Shishido, Y. Takeda, J. Kinugawa: *J. Am. Chem. Soc.,* **1961**, *83*, 538-541.

11. K. Sisido, S. Kozima, T. Hanada: *J. Organomet. Chem.,* **1967**, *9*, 99-107.

12. R. Malguzzi, M. Sandri, M. Rosenthal: Process for Direct Synthesis of Organotin Compounds: CN1052676, **1991**.

13. T. Hayashi, S. Kikkawa, S. Matsuda: *Kogyo Kagaku Zasshi,* **1968**, *71*, 710-715.

14. T. Hayashi, S. Kikkawa, S. Matsuda: *Kogyo Kagaku Zasshi,* **1967**, *70*, 1389-1393.

15. T. Hayashi, S. Kikkawa, S. Matsuda, J. Uchimura: *Technol. Rep. Osaka Univ.,* **1968**, *18*, 233-245.

16. T. Hayashi, J. Uchimura, S. Matsuda, S. Kikkawa: *Kogyo Kagaku Zasshi,* **1967**, *70*, 714-718.

17. T. Hayashi, S. Kikkawa, S. Matsuda, K. Fujita: *Kogyo Kagaku Zasshi,* **1967**, *70*, 2298-2301.

18. S. Matsuda: *Asahi Garasu Kogyo Gijutsu Shorei-kai Kenkyu Hokoku,* **1966**, *12*, 329-338.

19. M. Nomura, S. Kashiwagi, S. Kikkawa, S. Matsuda: *Kogyo Kagaku Zasshi,* **1968**, *71*, 1021-1024.

20. S. Matsuda, S. Kikkawa, T. Hayashi: *Kogyo Kagaku Zasshi,* **1966**, *69*, 256-259.

21. K. Shishido, Y. Takeda: *J. Org. Chem.,* **1961**, *26*, 2301-2304.

22. T. Zoeller, L. Iovkova-Berends, C. Dietz, T. Berends, K. Jurkschat: *Chem. Eur. J.,* **2011**, *17*, 2361-2364.

23. T. A. Annan, D. G. Tuck: *Can. J. Chem.,* **1989**, *67*, 1807-1814.

24. K. S. Siddiqi, S. A. A. Nami: *J. Serb. Chem. Soc.,* **2005**, *70*, 1389-1393.

25. Sigma Aldrich: www.sigmaaldrich.com: last accessed April 15th, 2017.

26. A. V. Piskunov, A. V. Lado, G. K. Fukin, E. V. Baranov, L. G. Abakumova, V. K. Cherkasov, G. A. Abakumov: *Heteroat. Chem.,* **2006**, *17*, 481-490.

27. N. N. Greenwood, A. Earnshaw: *Chemistry of the Elements,* Butterworth-Heinemann, Boston, Mass., **1997**.

28. I. L. Marr, D. Rosales, J. L. Wardell: *J. Organomet. Chem.,* **1988**, *349*, 65-74.

29. H. E. Ramsden: Alkyl- or Aryltin Compounds: GB701714, **1953**.

30. G. Eng, C. R. Dillard: *Inorg. Chim. Acta,* **1978**, *31*, 227-231.

31. J. Holecek, M. Nadvornik, K. Handlir, A. Lycka: *J. Organomet. Chem.,* **1983**, *241*, 177-184.

32. I. Wharf: *Inorg. Chim. Acta,* **1989**, *159*, 41-48.

33. G. Barbieri, F. Taddei: *J. Chem. Soc., Perkin Trans. 2,* **1972**, 1323-1326.

34. P. A. Storozhenko, A. A. Grachev, A. O. Klochkov, V. I. Shiryaev: *Russ. J. Appl. Chem.,* **2013**, *86*, 387-393.

35. B. S. Seo, I. K. Lee: *Taehan Hwahakhoe Chi,* **1979**, *23*, 392-395.

36. P. Legzdins, D. T. Martin: *Organometallics,* **1983**, *2*, 1785-1791.

37. W. J. Jones, D. P. Evans, T. Gulwell, D. C. Griffiths: *J. Chem. Soc.,* **1935**, 39-47.

38. Y. Naruta, Y. Nishigaichi, K. Maruyama: *Tetrahedron,* **1989**, *45*, 1067-1078.

39. M. Fishwick, M. G. H. Wallbridge: *J. Organometal. Chem.,* **1970**, *25*, 69-79.

40. W. F. Howard Jr., R. W. Crecely, W. H. Nelson: *Inorg. Chem.,* **1985**, *24*, 2204-2208.

41. A. Zickgraf, M. Beuter, U. Kolb, M. Dräger, R. Tozer, D. Dakternieks, K. Jurkschat: *Inorg. Chim. Acta,* **1998**, *275-276*, 203-214.

42. T. N. Mitchell, G. Walter: *J. Organomet. Chem.,* **1976**, *121*, 177-184.

43. Bruker-AXS, SAINT version 2013.8, **2013**, Bruker-AXS, Madison, WI 53711, USA.

44. Bruker-AXS, SADABS version 2012.1, **2012**, Bruker-AXS, Madison, WI 53711, USA.

45. Sheldrick, G. M.: *Acta Cryst.*, **2015**, *A71*, 3-8.

46. Sheldrick, G. M.: *Acta Cryst.*, **2015**, *C71*, 3-8.

47. Bruker-AXS, XP version 2013.1, **2013**, Bruker-AXS, Madison, WI 53711, USA.

Chapter 4: Synthesis and Reactivity of $Si(3,5\text{-dtbc})_2(py)_2$

The organic functionalization of SiO_2 is a challenge that has received much attention,[1] and currently this is accomplished with chlorine-based reagents: metallurgical-grade silicon is reacted with HCl to produce $SiHCl_3$ and $SiCl_4$. It would be beneficial to the environment and human safety to reduce or remove the HCl and Cl_2 from the silicon refining process, from the first stage of processing SiO_2, through to the last stage of synthesizing functionalized silanes. The key to accomplishing this goal is finding a functional intermediate that can replace $SiCl_4$, the compound most central to industrial processes involving silicon. This chapter describes a chlorine-reduced synthetic pathway, from silicon dioxide to tetraorganosilanes.

4.1 Synthesis of Specialty Organosilanes

The synthesis of specialty organosilanes relies extensively on chlorosilanes, and therefore, on HCl and Cl_2 since chlorosilanes are produced from the reaction of metallurgical-grade silicon with HCl. The reaction of $H_{(4-n)}SiX_n$ with Grignard reagents is the standard route to organosilanes according to equation 1.[2, 3]

$$H_{(4-n)}SiX_n + n\ RMgX \rightarrow R_nSiH_{(4-n)} \quad (1)$$

When $SiCl_4$ is reacted with four or more eq of a Grignard reagent, R_4Si is the main or only product formed; however, when $SiCl_4$ is reacted with less than four eq of a Grignard reagent, a mixture of products normally results including: R_4Si, R_3SiCl, R_2SiCl_2, and $RSiCl_3$.[3] The progressive substitution of alkyl groups for chlorides becomes more difficult as the number of alkyl groups bonded to silicon increases for both steric and electronic reasons. The steric bulk of the alkyl groups is greater than that of chlorine, inhibiting further substitution, and, as the level of substitution increases, the Lewis acidity of the silicon atom decreases.[3]

4.2 Direct Synthesis of $R_nSiX_{(4-n)}$

Silanes $R_nSiX_{(4-n)}$ are also synthesized by the direct synthesis,[2, 4] which yields silicon compounds of the type $R_nSiX_{(4-n)}$ by heating silicon and alkyl halides in a fluidized bed reactor with a catalyst, typically copper.[2, 4] Dimethyldichlorosilane [Me_2SiCl_2], used extensively in the production of silicones, is an example of an important compound that is manufactured industrially using this process (equation 2).[2]

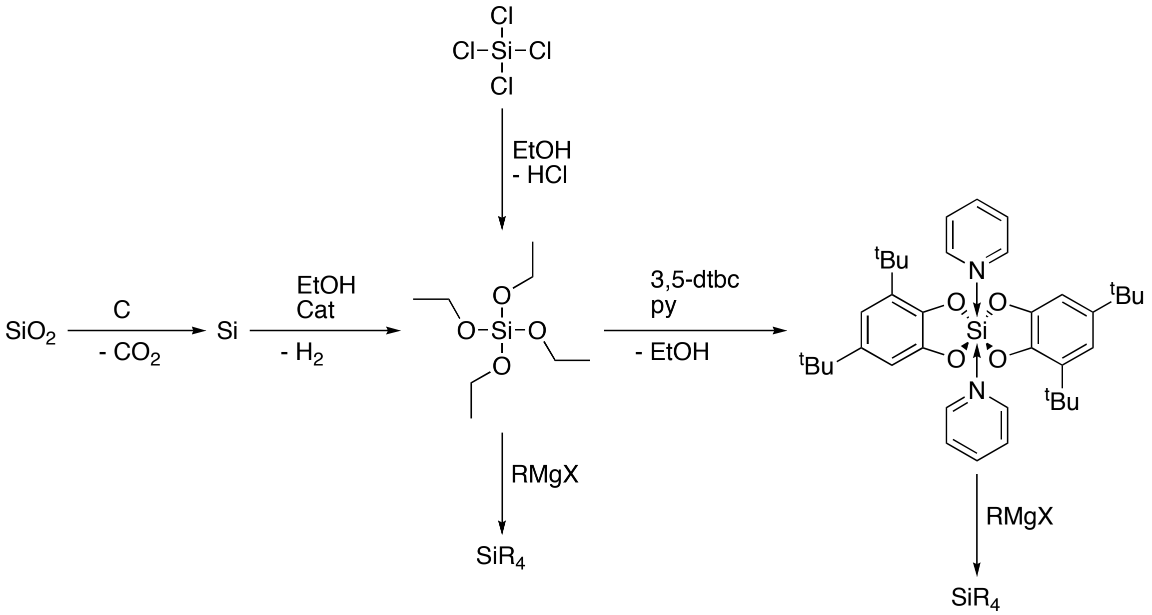
$$Si + 2\ MeCl \rightarrow Me_2SiCl_2 + \text{many other products} \qquad (2)$$

For the reaction of silicon powder and methyl chloride with copper as a catalyst a complex mixture of useful compounds (>15, including $SiCl_4$) is obtained.[3] The main reasons chlorosilanes are used in the production of silicones is that they are inexpensive, and the byproduct of the curing process (HCl) is volatile and will dissipate out of the polymer.[2-4] Me_2SiCl_2 is approximately half the cost of $Me_2Si(OEt)_2$.[5] Alkoxysilanes are also used as components of silicones because they form harmless byproducts in the curing process and they have a longer shelf life than the corresponding chlorosilanes.[4]

4.3 Direct Synthesis of $Si(OEt)_4$

The conversion of SiO_2 or Si to organosilanes, SiR_4, without the use of chlorine-based reagents is a challenge that has received much attention, and may require several approaches (Scheme 4.1). Tetraethyl orthosilicate, $Si(OEt)_4$, a potential replacement for $SiCl_4$, is manufactured in environmentally benign ways. The synthesis of $Si(OEt)_4$ by the direct method was initially investigated by Rochow *et al.* and, since then, some improvements have been made to the yield and selectivity of the process by other groups or companies.

In 1949, Rochow patented the production of $Si(OMe)_4$ by the direct reaction of methanol with a mixture of silicon and copper.[6] This was the first example of a direct reaction of silicon with an alcohol. In 1970, Rochow reported general conditions for the direct reaction of a variety of alcohols, including ethanol, with silicon;[7] the procedure was patented in 1972.[8]



Scheme 4.1: Synthesis of Si(3,5-dtbc)$_2$(py)$_2$ from SiO_2 in three steps, with tetraethyl orthosilicate (Si(OEt)$_4$) as an intermediate.

The industrial grade catalyst for the reaction is prepared by heating a 9:1 powdered mixture of industrial grade silicon and copper to 1000-1100 °C for 2 h under hydrogen gas in a quartz tube.[7] After cooling, the catalyst is used directly. The direct synthesis is performed by heating a rapidly stirred mixture of the catalyst in silicone oil, and slowly injecting ethanol under the surface of the suspension. After isolation, the products are separated by distillation, yielding a 3:1 mixture of $(EtO)_3SiH$ and Si(OEt)$_4$ for a total yield of 15%. Secondary and tertiary alcohols, ethers, and amines did not react in a direct reaction with silicon powder under similar conditions. Rochow *et al.* proposed that the reactivity of the primary alcohols in the direct synthesis is related to their acidity, and that several compounds studied were not sufficiently acidic to react.

Herdle *et al.* further investigated the nature of the silicon / copper alloy.[9] Both metals must be in intimate contact which can be achieved by melting them together at high temperatures, cooling, and then grinding the resulting solid into a powder. The surface of the particles must be cleansed of oxides, and this can be accomplished by exposing the powder to HCl gas. The use of HCl gas, along with running the reaction with dimethylamine (1%), allows the conversion of silicon / copper alloy to $Si(OEt)_4$ in better yields (40%). The following improvements to the direct process do not rely on the use of HCl.

Magee *et al.* found the yield of $Si(OEt)_4$ was almost quantitative from the reaction of silicon powder with ethanol at 200 °C, using $KO(CH_2)_2O(CH_2)_4O(CH_2)_2OK$, rather than copper, as a catalyst.[10] The corresponding sodium salt, $NaO(CH_2)_2O(CH_2)_4O(CH_2)_2ONa$, also gave excellent yields and high selectivities.[11-13]

One of the greatest challenges in the direct reaction of silicon with ethanol is to control the ratio of $(EtO)_3SiH$ and $Si(OEt)_4$ formed.[7, 8] Mendicino *et al.* found that a high yield of $Si(OEt)_4$ can be obtained using any commercial grade silicon powder, catalyzed by copper or cupric oxide, in a heavy hydrocarbon oil as solvent, at about 200 °C.[14] Shimizu *et al.* found that by using $CuCl_2$ as a cocatalyst with EtONa, it was possible to reduce the pressure of the system to room pressure for the direct reaction of silicon powder with ethanol, while other researchers had to rely on high-pressure systems, a major disadvantage.[15] The yield of $Si(OEt)_4$ was 47%. Some solvents are counterproductive in the direct process, for example, when alkylated naphthalene is used as solvent, the yield of

$Si(OEt)_4$ drops to about 10% while the yield of $(EtO)_3SiH$ increases to about 30%.[16]

The goal of this chapter is to synthesize a functional intermediate for the synthesis of organosilanes which avoids chlorine-based reagents. Ideally, this intermediate would be synthesized in a direct process from SiO_2 or Si, but, if this is not possible (yet), then given that tetraethyl orthosilicate, $Si(OEt)_4$, is synthesized directly from silicon and ethanol, it is a good alternative as a starting material. The synthesis of the complex $Si(3,5\text{-dtbc})_2(py)_2$ from $Si(OEt)_4$ will be investigated and its reactions with Grignard reagents evaluated as a possible method to obtain organosilanes.

4.4 Results and Discussion

4.4.1 Attempted Synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ from SiO_2

Initial attempts to synthesize $Si(3,5\text{-dtbc})_2(py)_2$ were carried out using SiO_2 and 3,5-dtbc in a 1:2 ratio, with excess pyridine, following the conditions used for the synthesis of $Ge(3,5\text{-dtbc})_2(py)_2$ from GeO_2. SiO_2 and 3,5-dtbc were refluxed in excess pyridine; however, no reaction was observed (Table 4.1, entry 1). To enhance the nucleophilicity of the 3,5-dtbc, 5 eq of NaOH were added (Table 4.1, entry 2); again, no reaction took place. Refluxing SiO_2 and 3,5-dtbc in pyridine with 2 eq of either LiCl or NaCl (Table 4.1, entries 3 and 4 respectively), gave unknown insoluble solids. Corriu *et al.* synthesized $[Si(o\text{-}C_6H_4O_2)_3^{2-}{\bullet}2K^+]$ from SiO_2 and $o\text{-}C_6H_4(OK)_2$ in methanol.[17, 18] Thus, potassium was added to a mixture of SiO_2, 3,5-dtbc, and pyridine in either 1-hexanol or ethanol, which was then refluxed (Table 4.1, entries 5 and 6 respectively). The reaction with ethanol produced no products while the one with 1-hexanol produced an unknown insoluble material. Finally, a mixture of SiO_2, 3,5-dtbc, and pyridine were milled for 10 h with no reaction taking place (Table 4.1, entry 7).

It is somewhat surprising that using almost identical conditions (Table 4.1, entry 6), that no reaction took place between SiO_2 and the catechol considering that Corriu *et al.* were able to synthesize $[Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2K^+]$ in good yield. Even performing the reaction at elevated temperatures was unsuccessful (Table 4.1, entry 5). The lack of reactivity of SiO_2 under these conditions is not presently understood.

Table 4.1: Attempted synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ from SiO_2.

Entry *	**Conditions**	**Result**
1	1 eq SiO_2 + 2 eq 3,5-dtbc + 150 eq py; reflux 3 d.	No reaction.
2	1 eq SiO_2 + 2 eq 3,5-dtbc + 150 eq py + 5 eq NaOH; reflux 3 d.	No reaction.
3	1 eq SiO_2 + 2 eq 3,5-dtbc + 150 eq py + 2 eq LiCl; reflux 1 d	Unidentified insoluble solid.
4	1 eq SiO_2 + 2 eq 3,5-dtbc + 150 eq py + 2 eq NaCl; reflux 1 d	Unidentified insoluble solid.
5	1 eq SiO_2 + 2 eq 3,5-dtbc + 125 eq py + 250 eq 1-hexanol + 2 eq K; reflux 1 d	Unidentified insoluble beige solid.
6	1 eq SiO_2 + 2 eq 3,5-dtbc + 125 eq py + 250 eq EtOH + 2 eq K; reflux 1 d	No reaction.
7	1 eq SiO_2 + 2 eq 3,5-dtbc + 150 eq py; mixer mill; 300 RPM for 10 h.	No reaction.

* The scale of the reactions was 250 mg (theoretical yield of product) except for entry 7 where the scale was 5 g. The silica gel used had a pore size of 150 Å and a particle size of 200-425 mesh.

4.4.2 Attempted Synthesis of Si(3,5-dtbc)$_2$(py)$_2$ from Si and $SiCl_4$

With the unsuccessful attempts to synthesize the complex Si(3,5-dtbc)$_2$(py)$_2$ from SiO_2, the use of silicon metal as the starting material for Si(3,5-dtbc)$_2$(py)$_2$ was investigated. Attempts to synthesize Si(3,5-dtbc)$_2$(py)$_2$ from silicon powder by oxidation with 3,5-dtbc (similar to Jurkschat's oxidation of tin with alcohols)[19] or 3,5-dtbq (similar to Tuck's oxidation of tin with quinones)[20] (Table 4.2, entries 1 and 2) did not work. Silicon is probably too inert under the conditions used, because of the protective surface layer, and because silicon has a higher ionization potential compared to germanium and tin.[4] Perhaps using mechanochemistry, reactive surfaces of silicon might be generated, facilitating the reaction with substrates.

With the unsuccessful synthesis of Si(3,5-dtbc)$_2$(py)$_2$ from SiO_2 or Si, utilizing $SiCl_4$ as a starting material for Si(3,5-dtbc)$_2$(py)$_2$ became the focus, in an effort to obtain Si(3,5-dtbc)$_2$(py)$_2$, and obtain characterization data. In doing so, it would be easier to identify Si(3,5-dtbc)$_2$(py)$_2$ in reaction mixtures. Since the reaction of $GeCl_4$ with 3,5-dtbc and pyridine produced Ge(3,5-dtbc)$_2$(py)$_2$ in excellent yields, an attempt was made to synthesize Si(3,5-dtbc)$_2$(py)$_2$ under identical conditions using $SiCl_4$ (Table 4.2, entry 3), however, only $SiCl_4py_2$ was isolated from the reaction mixture in quantitative yield. In an attempt to avoid the formation of $SiCl_4py_2$, $SiCl_4$ was first allowed to react with 3,5-dtbc, and then pyridine (Table 4.2, entry 4); no reaction took place between $SiCl_4$ and 3,5-dtbc, and thus, when the pyridine was added, $SiCl_4py_2$ was again formed. The conversion of 3,5-dtbc into a dianion will increase its reactivity towards $SiCl_4$ (Table 4.2, entry 5), however, after refluxing the lithium salt of 3,5-dtbc with $SiCl_4$, followed by the addition of pyridine, a blue insoluble solid precipitated, which could not be characterized. In a different approach (Table 4.2, entry 6), $SiCl_4py_2$ was first synthesized, then refluxed with 3,5-dtbc; no reaction took place.

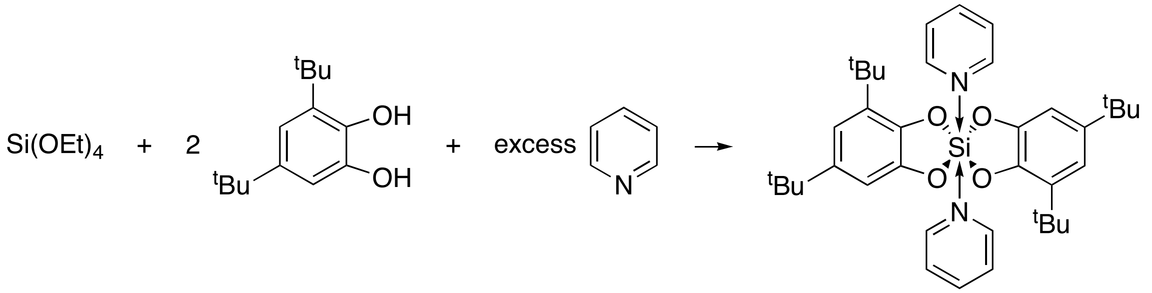
Table 4.2: Attempted synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ from Si or $SiCl_4$.

Entry *	**Conditions**	**Result**
1	1 eq Si + 2 eq 3,5-dtbc + 150 eq py; reflux 3 d.	No reaction.
2	1 eq Si + 2 eq 3,5-dtbq + 150 eq py; reflux 3 d.	No reaction.
3	1 eq $SiCl_4$ + 2 eq 3,5-dtbc + 150 eq py; reflux 1 h.	$SiCl_4(py)_2$.
4	1 eq $SiCl_4$ + 2 eq 3,5-dtbc; reflux 1 h; then 150 eq py; reflux 2 d.	$SiCl_4(py)_2$.
5	2 eq 3,5-dtbc + 4 eq BuLi; mix 15 min; then 1 eq $SiCl_4$; reflux 15 min; then 150 eq py; mix 15 min	Unidentified blue solid.
6	1 eq $SiCl_4$ + 150 eq py to make 1 eq $SiCl_4(py)_2$; then 1 eq $SiCl_4(py)_2$ + 2 eq 3,5-dtbc; reflux 1 h	$SiCl_4(py)_2$.

* The scale of the reactions was 250 mg (theoretical yield of product).

4.4.3 Synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ from $Si(OEt)_4$

Rao *et al.* synthesized [$Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2R_3NH^+$] complexes using $Si(OEt)_4$ as starting material under mild conditions and in good yields.[21, 22] Tetraethyl orthosilicate, $Si(OEt)_4$, is an easily handled clear liquid that is moisture sensitive, however, less so than $SiCl_4$. Inspired by the research of Rao, the reaction of $Si(OEt)_4$ with 3,5-dtbc in excess pyridine was studied, with excellent results: $Si(3,5\text{-dtbc})_2(py)_2$ was synthesized in good yields (62%) and purities (> 95% by ^1H NMR spectroscopy) (Scheme 4.2).



Scheme 4.2: Synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ from $Si(OEt)_4$, 3,5-dtbc, and py.

According to Scheme 4.1, tetraethylorthosilicate ($Si(OEt)_4$) can be synthesized by the esterification of $SiCl_4$ with ethanol[1] or by the direct reaction of ethanol with silicon metal.[8, 12, 14] Given that $Si(OEt)_4$ can be synthesized directly from Si, without the use of HCl or Cl_2, then the complex $Si(3,5\text{-dtbc})_2(py)_2$, a product of $Si(OEt)_4$, is formally synthesized without the use of HCl or Cl_2, and thus, the synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ adheres to the Principles of Green Chemistry (POGC) and our goal is achieved.

The synthesis of $Si(3,5\text{-dtbc})_2(py)_2$ conducted in this study, and the industrial synthesis of $Si(OEt)_4$ described above, applies the POGC, especially

POGC points 1 (prevention), 3 (less hazardous chemical synthesis), 4 (designing safer chemicals), and 12 (inherently safer chemistry for accident prevention) in comparison to the synthesis of $SiCl_4$ which is heavily reliant on chlorine-based chemicals.[23] No HCl / Cl_2 was used, in both the synthesis of $Si(OEt)_4$ and $Si(3,5\text{-dtbc})_2(py)_2$, leading to increased safety for the environment and for people. Less hazardous chemical synthesis was conducted and chemicals much safer than HCl and Cl_2 were used: Si, EtOH, Cu, $Si(OEt)_4$, 3,5-dtbc, py, $Si(3,5\text{-dtbc})_2(py)_2$. A safer chemical was designed: the complex $Si(3,5\text{-dtbc})_2(py)_2$. Inherently safer chemistry for accident prevention was used and the overall processes were less hazardous by replacing $SiCl_4$ with $Si(OEt)_4$, leading to the complex $Si(3,5\text{-dtbc})_2(py)_2$.

4.4.4 Reaction of $Si(3,5\text{-dtbc})_2(py)_2$ with Grignard Reagents: R = Bu, Ph, Bn

The reactivity of $Si(3,5\text{-dtbc})_2(py)_2$ with excess Grignard reagents was studied to investigate whether $Si(3,5\text{-dtbc})_2(py)_2$ works as well as the analogous germanium and tin complexes for the generation of tetraorganosilanes, and to explore the possibility of an alternate route to tetraorganosilanes. In general, the yields of SiR_4 from the reaction of $Si(3,5\text{-dtbc})_2(py)_2$ with Grignard reagents are good (Table 4.3), and the purities are above 98% (GC). An exception is the yield of $SiBu_4$ (b.p. = 230 °C), and this may be because the compound is more volatile than $SiPh_4$ or $SiBn_4$, and a significant quantity may have been removed during the workup procedure. While the yields were lower, the purities of the tetraorganosilanes produced were comparable to those of the tetraorganogermanes and tetraorganostannanes generated using the same method. For RMgCl where R = Bu, Ph, and Bn, the only products detected were SiR_4, and this selectivity is a major advantage for the synthesis of SiR_4.

In comparing the use of $Si(3,5\text{-dtbc})_2(py)_2$ with that of $Si(OEt)_4$ for the synthesis of tetraorganosilanes, $Si(3,5\text{-dtbc})_2(py)_2$ adds a step in the procedure. Surprisingly, there are no reported studies about the synthesis of tetraorganosilanes from $Si(OEt)_4$, and thus, a comparison of the two methods cannot be made.

Table 4.3: Yields for the reaction of $Si(3,5\text{-dtbc})_2(py)_2$ with Grignard reagents.

Entry	**RM** [1]	**Complex : RM**	**Solvent** (amount)	**Time** (hrs)	**Temp** (°C)	**Workup** [2]	**Yield** [3]	**Product**	**Catechol Recovery** [4]
1	BuMgCl 2.0 M THF	1 : 20	THF (4 mL)	24	65	A	18%	$SiBu_4$	25%
2	PhMgCl 2.0 M THF	1 : 20	THF (4 mL)	24	65	A	75%	$SiPh_4$	67%
3	BnMgCl 2.0 M THF	1 : 20	THF (4 mL)	24	65	A	75%	$SiBn_4$	17%

1. Commercial sources of RM, used as received unless indicated otherwise.
2. See experimental section for details of the workup.
3. Isolated yield (average of two runs).
4. Yield (average of two runs) determined by GC.

4.4.5 Mechanisms of Substitution of Hypercoordinate Silicon Compounds

For $Si(OEt)_4$, and for SiX_4 in general, it has been found that the rates of sequential substitution follow the order $k_1 > k_2 > k_3 > k_4$ (Scheme 4.3) due to a decrease in the electrophilicity of silicon with the loss of electronegative X groups, and because the steric bulk around silicon increases due to substitution by alkyl groups that are bulkier than the halide ligand.[24] The sequential substitution reactions of the complex Si(3,5-dtbc)$_2$(py)$_2$ are proposed to decrease, that is $k_4 > k_3 > k_2 > k_1$ (Scheme 4.3). The steric bulk around silicon in Si(3,5-dtbc)$_2$(py)$_2$ decreases as alkyl groups from Grignard reagents sequentially replace the sterically bulky ligands of the complex, leading to a more accessible target for nucleophiles. Corriu was the first to develop the above hypothesis, on the basis of the reactivity of [Si(o-$C_6H_4O_2$)$_3^{2-}$•2K$^+$] with Grignard reagents, and found that the complex [Si(o-$C_6H_4O_2$)$_3^{2-}$•2K$^+$] is a good electrophile, and readily reacts with numerous Grignard reagents.[18, 25]

$$\mathrm{RMgCl} + \mathrm{SiX_4} \xrightarrow{k_1} \mathrm{RSiX_3}$$

$$\mathrm{RMgCl} + \mathrm{RSiX_3} \xrightarrow{k_2} \mathrm{R_2SiX_2}$$

$$\mathrm{RMgCl} + \mathrm{R_2SiX_2} \xrightarrow{k_3} \mathrm{R_3SiX}$$

$$\mathrm{RMgCl} + \mathrm{R_3SiX} \xrightarrow{k_4} \mathrm{R_4Si}$$

$SiCl_4$, $SiBr_4$, Si(OMe)$_4$, Si(OEt)$_4$:
$k_1 > k_2 > k_3 > k_4$

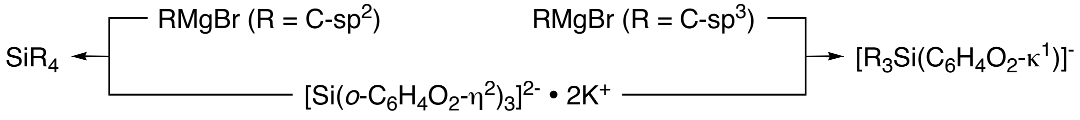
Si(3,5-dtbc)$_2$(py)$_2$:
$k_4 > k_3 > k_2 > k_1$

Scheme 4.3: Sequential rates of substitution of X groups on silanes by Grignard reagents.

Corriu observed only the formation of tri- (R_3Si(o-$C_6H_5O_2$-η^1)) or tetrasubstituted products, when 4 or fewer eq of Grignard reagent were reacted with [Si(o-$C_6H_4O_2$)$_3^{2-}$•2K$^+$].[17, 18, 25] When 4 eq of Grignard reagent (aryl, allyl, vinyl, alkynyl) were reacted with [Si(o-$C_6H_4O_2$)$_3^{2-}$•2K$^+$], the major product is usually SiR_4, except for R = alkyl, where the major product was R_3Si(o-$C_6H_5O_2$-

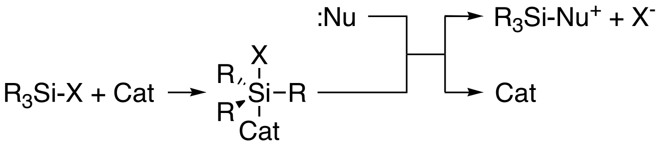
η^1) (Scheme 4.4).[18] Bis-alkyl Grignard reagents appeared to be anomalous: spiro compounds (R_4Si with two R groups tethered together) were formed as the major products when bis-Grignard reagents $ClMg(CH_2)_nMgCl$ were reacted with $[Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2K^+]$.[17] However, the facile formation of the tetraalkylated silane in these cases may be attritubed to the chelate effect, that is, the rate of the reactions are enhanced due to the formation of a ring. In fact, Corriu *et al.* found that SiR_4 or $R_3Si(o\text{-}C_6H_5O_2\text{-}\eta^1)$ were formed (depending on the R group) despite the conditions or number of eq of Grignard reagent used, which strongly supports their hypothesis that reaction rate constants become larger as the degree of substitution increases (Scheme 4.3).[25]

The selective formation of SiR_4 or $R_3Si(o\text{-}C_6H_5O_2\text{-}\eta^1)$ was explained in terms of the relative electrophilicity of the silicon atom when R = alkyl compared to when R = aryl, allyl, vinyl, or alkynyl. When R = alkyl (C is sp^3 hybridized), the electrophilicity of the silicon in $R_3Si(o\text{-}C_6H_5O_2\text{-}\eta^1)$ is likely too low to react with the last equivalent of Grignard reagent (Scheme 4.4). On the other hand, when R = Ph (C is sp^2 hybridized), the silicon atom in the intermediate $R_3Si(o\text{-}C_6H_5O_2\text{-}\eta^1)$ is electrophilic enough to react with the last equivalent of Grignard reagent.[18]



Scheme 4.4: Nucleophilic attack by Grignard reagents RMgBr on the hexacoordinate complex $[Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2K^+]$, resulting in tri- or tetrasubstituted products depending on the R group.[18]

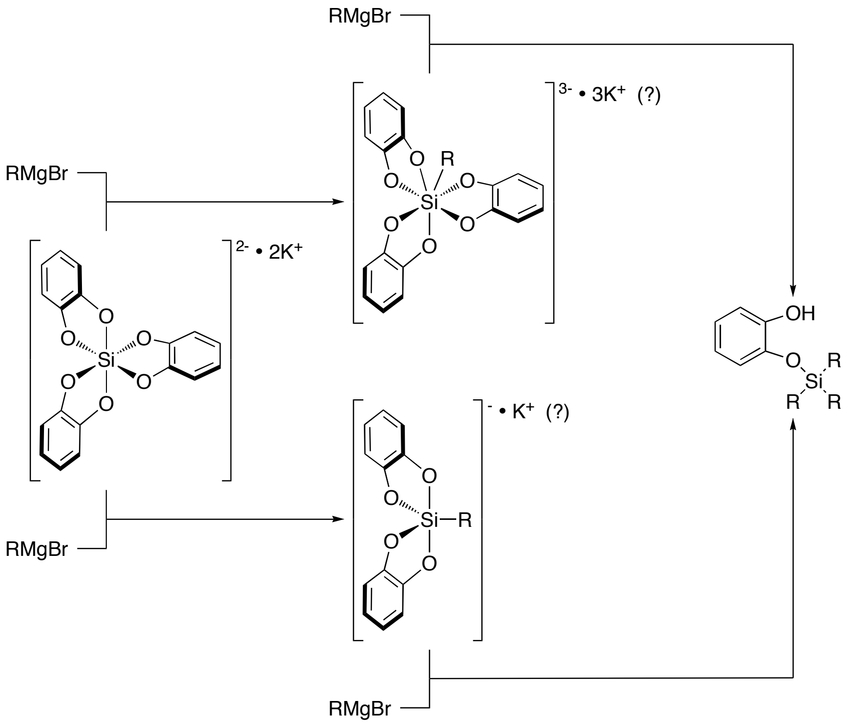
Corriu[26] and others[27] hypothesized that the reaction of triorganohalosilanes, R_3SiX, with Grignard reagents proceeds through a pentacoordinated intermediate to a tetracoordinated product (Scheme 4.5).



Cat = F^-, RCO_2^-, HMPA, DMSO

Scheme 4.5: Nucleophilic attack on a molecule with a tetracoordinated silicon atom, through a pentacoordinate silicon intermediate.[26]

Through a comparative kinetic study, Corriu demonstrated that the reaction of $[Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2K^+]$ with Grignard reagents does not proceed through a pentacoordinate intermediate to form tri- or tetraorganosilanes as shown in Scheme 4.6.[25] A heptacoordinate intermediate has been proposed by Corriu to explain the reactivity of $[Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2K^+]$ towards Grignard reagents, but no direct evidence for such an intermediate has been obtained.



Scheme 4.6: Nucleophilic attack by Grignard reagents on the hexacoordinate complex [$Si(o\text{-}C_6H_4O_2)_3^{2-}$•$2K^+$], through an unknown intermediate, resulting in a tetracoordinate product.[25]

4.5 Conclusions

The complex $Si(3,5\text{-dtbc})_2(py)_2$ favors the formation of SiR_4 when reacted with Grignard reagents, and is advantageous for the synthesis of SiR_4, compared to the reaction of SiX_4 with Grignard reagents, due to lower reliance on chlorine-based reagents and because of the selectivity of the substitution reactions. $Si(3,5\text{-dtbc})_2(py)_2$ is simple to synthesize, the yield and purity of the complex is good, and the complex is not air- or moisture-sensitive. Most important of all, $Si(3,5\text{-dtbc})_2(py)_2$ links SiO_2 to silanes SiR_4 without the use of HCl or Cl_2 (unlike $SiCl_4$), and with further research, its chemistry may lead to functional silanes $R_2Si(3,5\text{-dtbc-}\eta^2)$ and $R_3Si(3,5\text{-dtbc-}\eta^1)$ where the R groups can be identical or mixed. The synthesis of difunctional compounds R_2EX_2 (E = Si, Ge, Sn) will be investigated in the next chapter.

4.6 Experimental Procedures

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques unless specified otherwise. Solvents were dried using a solvent purification system: a PureSolv MD 7 from Innovative Technology. Chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Varian Mercury 400 MHz, Inova 400 MHz, or an Inova 600 MHz NMR spectrometer using $CDCl_3$ as the solvent. ^1H NMR spectra were referenced internally to residual $CHCl_3$ (7.27 ppm); $^{13}C\{^1H\}$ spectra were referenced to the central transition of $CDCl_3$ (77.00 ppm). Gas chromatography – mass spectrometry (GC-MS) spectra were obtained on a GCMS-QP2010S instrument with a GC-2010 gas chromatograph at an ionizing voltage of 70 eV (EI), with a quadrupole mass filter, and a DB-5MS 30 m x 0.25 μm column from J & W Scientific utilizing the following temperature program: 3 min at 65 ^oC; 17 min constant heating rate of 15 ^oC / min; 5 min at 320 ^oC. Mass spectral data are reported in mass-to-charge units, m/z, with ion identity and peak intensities (%) in parentheses. Melting point data are uncorrected.

4.6.1 Synthesis of $Si(3,5\text{-}dtbc)_2(py)_2$ from $Si(OEt)_4$

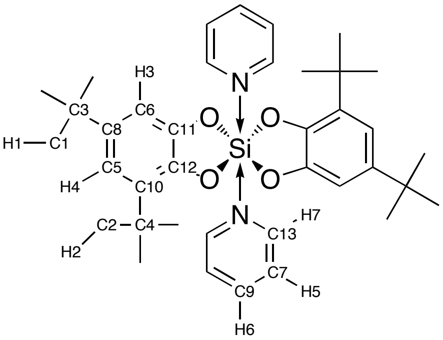


Figure 4.1: $Si(3,5\text{-}dtbc)_2(py)_2$

In a 250 mL flask equipped with a reflux condenser and a magnetic stir bar, tetraethyl orthosilicate ($Si(OEt)_4$) (1.78 mL, 7.98 mmol) was added to a mixture of 3,5-dtbc (3.55 g, 16.0 mmol) in pyridine (48.4 mL, 598 mmol). The homogeneous mixture was refluxed for 48 h, after which time some beige solid precipitated (Scheme 4.2). Pentane (50 mL) was added to the reaction mixture; solid precipitated. The solid was separated by centrifugation and the solvent removed by decanting. The solid was washed with 50 mL pentane two times, then left under dynamic vacuum for 24 h at 75 °C, yielding $Si(3,5\text{-}dtbc)_2(py)_2$ as an off-white powder. Yield: 62% (average of 6 runs); mp = 233 – 234 °C (decomposes); the stereochemistry of the complex (with ^{t}Bu groups *trans* to one another; Figure 4.1) was assumed by comparison to the known stereochemistry of the analogous germanium and tin compounds; **^{1}H NMR** (600 MHz, $CDCl_3$): 8.64 (4H, bd, H7), 7.79 (2H, bt, H6), 7.39 (4H, bt, H5), 6.89 (2H, d, ^4J = 2.2 Hz, H4/3), 6.78 (2H, d, ^4J = 2.2 Hz, H3/4), 1.43 (18H, s, H2/1), 1.27 (18H, s, H1/2); **^{13}C NMR** (150 MHz, $CDCl_3$): 149.16 (C13), 142.51 (C12/11), 142.02 (C11/12), 140.88 (C10/8), 136.67 (C9), 135.56 (C8/10), 124.02 (C7), 115.81 (C6/5), 110.36 (C5/6), 34.83 (C4/3), 34.32 (C3/4), 31.58 (C2/1), 29.64 (C1/2); **ESI-MS**: 1054.4 (40%), 975.4 (100%), 661.3 (45%), 540.5 (20%), 512.5 (25%), 346.1 (20%), 300.2 (22%), 243.1 (30%).

4.6.2 Reaction of Si(3,5-dtbc)$_2$(py)$_2$ with Grignard Reagents: R = Bu, Ph, Bn

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques unless specified otherwise. All equipment was flame dried prior to use and kept under an argon atmosphere. In a 100 mL flask equipped with magnetic stirring and a reflux condenser, RMgCl (~3 mmol) was added to a suspension of Si(3,5-dtbc)$_2$(py)$_2$ (100 mg, 0.160 mmol) dissolved in 2.50 mL of the same solvent as the organometallic reagent (THF). The mixture was allowed to reflux for 24 h. After cooling to room temperature, 15 mL of hexanes were added to the crude reaction mixture followed by 5 mL water and the reaction mixture was allowed to stir for 5 minutes. The organic and aqueous layers were separated with a separatory funnel. The organic layer was washed with 5 mL water, then concentrated using a rotary evaporator. The crude reaction mixture was purified using preparative thin layer chromatography on a 2 mm × 20 cm × 20 cm silica gel plate using hexanes as eluent. The solid phase was extracted by allowing it to stir overnight in 40 mL of chloroform, decanting, and then washing with 40 mL of chloroform. The extraction was repeated one more time. For smaller scale reactions, chromatography on a 0.2

mm TLC plate followed by stirring the isolated fractions with 30 mL of chloroform overnight followed by washing with 30 mL of chloroform is sufficient. $SiPh_4$ was isolated using column chromatography over silica.

$SiBu_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 1.32 (8H, m, C**$\underline{H_2}$**), 1.26 (8H, m, C**$\underline{H_2}$**), 0.89 (12H, t, ^3J = 7.2 Hz, C**$\underline{H_3}$**), 0.50 (8H, m, Si-C**$\underline{H_2}$**); **^{13}C NMR** (150 MHz, $CDCl_3$): 26.87, 26.20, 13.79, 12.20; **GC-MS** (*m/z*): 95% pure; 199 (Bu_3Si^+, 35%), 143 (Bu_2SiH^+, 80%), 114 (5%), 101 (87%), 87 ($BuSiH_2^+$, 100%), 73 (70%), 60 (20%).

$SiPh_4$:[28] **^{1}H NMR** (600 MHz, $CDCl_3$): 7.61-7.57 (8H, m), 7.47-7.42 (4H, m), 7.41-7.36 (8H, m); **^{13}C NMR** (100 MHz, $CDCl_3$): 136.38, 134.20, 129.57, 127.85; **GC-MS** (*m/z*): 99% pure; 336 (Ph_4Si^+, 40%), 259 (Ph_3Si^+, 100%), 182 (Ph_2Si^+, 75%), 155 (15%), 129 (23%), 105 (35%), 79 (10%).

$SiBn_4$: **^{1}H NMR** (600 MHz, $CDCl_3$): 7.22 (8H, m, C**$\underline{H}$**), 7.11 (4H, m, C**$\underline{H}$**), 6.93 (8H, m, C**$\underline{H}$**), 2.10 (8H, m, Si-C**$\underline{H_2}$**); **^{13}C NMR** (150 MHz, $CDCl_3$): 138.87, 128.70, 128.37, 124.41, 21.42; **GC-MS** (*m/z*): 81% pure; 392 (Bn_3Si^+, 8%), 301 (Bu_3Si^+, 100%), 223 (18%), 145 (10%), 131 (9%), 121 ($BnSiH_2^+$, 28%), 105 (28%), 91 ($C_7H_6^+$, 23%), 65 (11%).

4.7 References

1. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, F. Ullmann: *Ullmann's Encyclopedia of Industrial Chemistry,*

VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany; Deerfield Beach, Fla, **1985**.

2. R. E. Kirk, D. F. Othmer, J. I. Kroschwitz, M. Howe-Grant: *Encyclopedia of Chemical Technology,* Wiley, New York, **1991**.
3. C. Eaborn: *Organosilicon Compounds*, Butterworths Scientific Publications, London, **1960**.
4. N. N. Greenwood, A. Earnshaw: *Chemistry of the Elements*, Butterworth-Heinemann, Boston, Mass., **1997**.
5. Sigma Aldrich: *www.sigmaaldrich.com*: last accessed April 15th, 2017.
6. E. G. Rochow: Tetramethyl Silicate: US2473260, **1949**.
7. W. E. Newton, E. G. Rochow: *Inorg. Chem.,* **1970**, *9*, 1071-1075.
8. E. G. Rochow: Catalytic Preparation of Alkoxy Derviatives of Silicon, Germanium, Tin, Thallium, and Arsenic: US3641077, **1972**.
9. W. B. Herdle, B. Kanner, D. L. Bailey: Tetraalkoxysilanes: US4289889, **1981**.
10. W. L. Magee, J. E. Telschow: Tetraalkyl Silicates: US4288604, **1981**.
11. U. Dittrich, F. Steding, R. Mueller: Continuous Method of Preparation of Chlorine-Free Tetraalkoxysilanes: DE19804731, **1999**.
12. Q. Xu, C. Xu, Z. Zhang, L. Li, X. Zhu, Y. Yang: Chlorine-Free Process for Preparation of Tetraalkoxysilanes: CN101041668, **2007**.
13. N. Fukaya, S. Choi, J. Choi, T. Horikoshi, K. Sato, H. Yasuda: Preparation of Tetraalkoxysilanes by Reacting Alcohols with Silicon Oxide in the Presence of Metal Alkoxide Acetals: WO2015170665, **2015**.
14. F. D. Mendicino: A Process for Preparing Trialkoxysilane/Tetraalkoxysilane Mixtures from Silicon and Alcohols: US4762939, **1988**.
15. T. Shimizu, T. Ogiwara: Preparation of Tetraalkoxysilanes: JP01135788, **1989**.

16. A. S. Gorshkov, P. A. Storozhenko: Process for Preparation of Alkoxysilanes by Catalytic Alkoxylation of Ground Silicon with Alcohols: RU2277537, **2006**.

17. A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Organometallics,* **1988**, *7*, 1165-1171.

18. A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Angew. Chem. Int. Ed.,* **1986**, *25*, 474-476.

19. T. Zoeller, L. Iovkova-Berends, C. Dietz, T. Berends, K. Jurkschat: *Chem. Eur. J.,* **2011**, *17*, 2361-2364.

20. T. A. Annan, D. G. Tuck: *Can. J. Chem.,* **1989**, *67*, 1807-1814.

21. J. V. Kingston, B. Vargheese, M. N. S. Rao: *Main Group Chem.,* **2000**, *3*, 79-90.

22. A. Doddi, J. V. Kingston, V. Ramkumar, M. Suzuki, M. Hojo, M. N. S. Rao: *Phosphorus, Sulfur, and Silicon and the Related Elements,* **2012**, *187*, 343-356.

23. P. Anastas, N. Eghbali: *Chem. Soc. Rev.,* **2010**, *39*, 301-312.

24. A. Tuulmets, A. Ploom, D. Panov, J. Jarv: *Synlett,* **2010**, 291-293.

25. C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young: *Chem. Rev.,* **1993**, *93*, 1371-1448.

26. A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Angew. Chem. Int. Ed.,* **1986**, *25*, 473-474.

27. S. Patai, Z. Rappoport, Y. Apeloig: *The Chemistry of Organic Silicon Compounds,* Wiley, Chichester, England, **1989**.

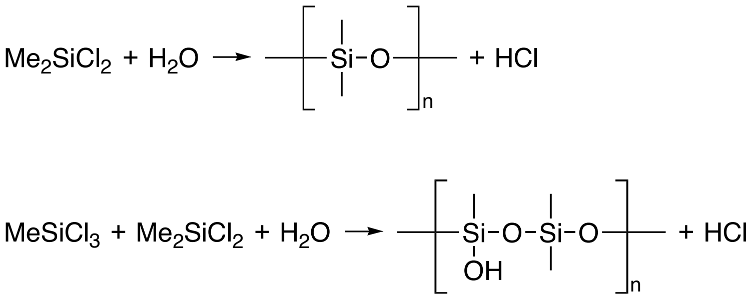
28. Y. Yamanoi, T. Taira, J. Sato, I. Nakamula, H. Nishihara: *Org. Lett.,* **2007**, *9*, 4543-4546.

Chapter 5: Reactivity Studies

5.1 Introduction

Difunctional silicon and tin compounds are of great industrial importance, because they lead to silicones (Si application), PVC stabilizers, and biocidal materials (Sn applications),[1, 2] which are critical to maintaining our current standard of living.

Silicones are very useful polymers with many applications ranging from insulating electrical equipment to biomaterials.[2, 3] The synthesis of silicone polymers relies heavily on $R_nSiX_{(4-n)}$ compounds.[1, 2] In general, a specific ratio of mono-, di-, and / or trifunctional chlorosilanes is hydrolyzed to yield a silicone polymer with the desired characteristics (Scheme 5.1). HCl is produced as a byproduct. The properties of silicone materials can be adjusted by varying the alkyl or aryl groups on the starting chlorosilane, by varying the polymerization method, by varying the amount of crosslinking, or by adding fillers such as silica.[1, 2] In this way, it is possible to produce silicone oils, elastomers, to rubbers with many different properties.[1, 2]



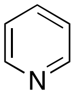
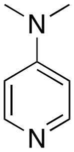
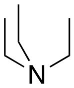
Scheme 5.1: Synthesis of silicone polymers from $Me_nSiCl_{(4-n)}$ (n = 1, 2) and water.

Functional organotin compounds have many industrial applications, mainly as biocidal materials and as PVC stabilizers.[1, 4] The most important biocide is ($cyclo$-C_6H_{11})$_3$SnOH, which protects plants and insects by attacking a wide variety of mites and acarides. Good fungicides, used to stop potato rot, are Ph_3SnOH and $Ph_3SnOCOMe$.[4] Me_2SnCl_2 and $MeSnCl_3$ are converted to $Me_2Sn(SCH_2CO_2(CH_2)_5{}^iPr)_2$ and $MeSn(SCH_2CO_2(CH_2)_5{}^iPr)_3$, which are utilized as poly(vinyl chloride) (PVC) stabilizers.[4] Dibutyltin dilaurate, $Bu_2Sn(O_2C(CH_2)_{11}H)_2$, dibutyltin maleate, $-[Bu_2SnO_2CCH{=}CHCO_2]-_n$, dibutyltin bis(isooctylmaleate), $Bu_2Sn(O_2CCH{=}CHCO_2(CH_2)_5{}^iPr)_2$, and dibutyltin bis(thioacetic acid isooctyl ester), $Bu_2Sn(SCH_2CO_2(CH_2)_5{}^iPr)_2$ are also used industrially as PVC stabilizers.[4] PVC stabilizers work by scavenging the chloride ions generated from the degradation of PVC by light and heat.

Difunctional silicon and tin compounds are produced by methods that rely heavily on HCl and Cl_2, and thus, their production poses safety risks and is a threat to the environment.[4] For these reasons, new routes to difunctional compounds of silicon, germanium, and tin that do not involve chlorine-based reagents are needed and this is the focus of this chapter. The synthesis of difunctional compounds will utilize the three complexes $E(3,5\text{-dtbc})_2(py)_2$ previously reported in this study. The influence of the nature of the nitrogenous ligand on the reactivity of $E(3,5\text{-dtbc})_2(L)_2$ in the synthesis of R_2EX_2 will be investigated. Therefore, a good synthetic route to six different complexes $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = NEt_3, DMAP) where the ligand was varied from pyridine to triethylamine (NEt_3) to 4-dimethylaminopyridine (DMAP) was investigated. The nine complexes, $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP), were then investigated as substrates in the synthesis of difunctional compounds by the reaction with a stoichiometric quantity of an organometallic reagent. The overall goal is to selectively synthesize R_2EX_2.

The three ligands, py, NEt_3, and DMAP, were chosen because they have a range in size and electronic characteristics, which may lead to different reactivity and product distributions when the complexes $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP) are reacted with an organometallic reagent. The pKa's[5] of the conjugate acids of the ligands in water, and the Tolman cone angles,[6, 7] arranged in increasing order, are shown in Table 5.1. Using py as a reference, DMAP is of a similar bulk but a stronger donor. NEt_3 is bulkier than both py and DMAP and is also a stronger donor. Three different routes for the synthesis of $E(3,5\text{-dtbc})_2(L)_2$, where L is DMAP or NEt_3 were explored: the direct reaction of a group 14 precursor with 3,5-dtbc and the ligand, the direct reaction of a group 14 metal with 3,5-dtbq and the ligand, or by ligand exchange of $E(3,5\text{-dtbc})_2(py)_2$ with either DMAP or NEt_3.

Table 5.1: pKas[5] and Tolman[6, 7] cone angles of pyridine, DMAP, and NEt_3.

	Ligand		
	 py	 DMAP	 NEt_3
pKa (conjugate acid in water)	5.4	9.7	10.7
Tolman cone angle	101°	101°	150°

Grignard reagents were selected as the organometallic reagent for this study because they are commonly used in the preparation of element-carbon bonds for E = Si, Ge, and Sn, and because a wide variety of Grignard reagents are available. The Grignard reagents selected were BuMgCl and PhMgCl, to represent a typical alkyl or aryl group and because they will produce products of low volatility which simplifies the isolation of the products. For this study, standardized reaction conditions were employed to allow comparisons between the reactions. Two eq of Grignard reagent were reacted with one equivalent of complex because the synthesis of difunctional compounds was targeted. This chapter begins with a discussion of the synthesis of the complexes which is followed by a discussion of their reactivity.

5.2 Results and Discussion

5.2.1 Synthesis of Complexes

The attempted synthesis of E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = NEt$_3$, DMAP) began with the reaction of SiO$_2$ with 2 eq of 3,5-dtbc and 2 eq of DMAP using ethanol as solvent and heating the mixture to reflux (Table 5.2, entry 1). It was hypothesized that ethanol might form a low concentration of Si(OEt)$_4$, which should react to form Si(3,5-dtbc)$_2$(DMAP)$_2$. However, no reaction with SiO$_2$ took place; the only product formed was a 1:1 salt between 3,5-dtbc and DMAP. The use of a higher boiling solvent, 1-hexanol, lead to decomposition of the starting materials (Table 5.2, entry 2). A similar reaction using GeO$_2$ as the starting oxide and employing toluene, a solvent with an intermediate boiling point, was also unsuccessful (Table 5.2, entry 3). Even following the same conditions used to synthesize Ge(3,5-dtbc)$_2$(py)$_2$ from 2 eq of 3,5-dtbc in refluxing pyridine, however using NEt$_3$ as the solvent, did not produce any products (Table 5.2, entry 4). Given the lack of success with silicon and germanium, our attention shifted to tin. The reactions of SnO$_2$ with 2 eq of 3,5-dtbc and 2 eq of DMAP in refluxing toluene or 1-hexanol were unsuccessful (Table 5.2, entries 5 and 6). Again, the reaction with the same stoichiometry of SnO$_2$ and 3,5-dtbc in refluxing NEt$_3$ did not produce the desired complex (Table 5.2, entry 7). The lack of success under standard thermal conditions prompted us to explore the reactions using mechanochemical conditions. However, the mechanical mixing of silicon metal, 2 eq of 3,5-dtbc, and 2 eq of DMAP gave no products (Table 5.2, entry 8).

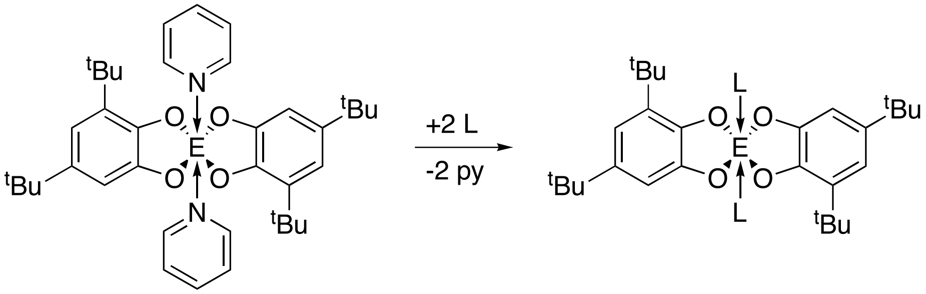
Similarly, when SiO_2 or SnO_2 were milled with 3,5-dtbc and DMAP, only the formation of (3,5-dtbc)•DMAP was observed (Table 5.2, entries 9 and 10).

Table 5.2: Attempted synthesis of E(3,5-dtbc)$_2$(L)$_2$.

Entry	**Group 14 Reagent**	**Eq of 3,5-dtbc / 3,5-dtbq**	**Eq of L**	**Reaction Conditions**	**Result**
1	SiO_2	2 eq 3,5-dtbc	2 eq DMAP	EtOH, Δ	salt (3,5-dtbc)•DMAP
2	SiO_2	2 eq 3,5-dtbc	2 eq DMAP	1-hexanol, Δ	unknown polymer
3	GeO_2	2 eq 3,5-dtbc	2 eq DMAP	toluene, Δ	no reaction
4	GeO_2	2 eq 3,5-dtbc	excess NEt_3	Δ	no reaction
5	SnO_2	2 eq 3,5-dtbc	2 eq DMAP	toluene, Δ	no reaction
6	SnO_2	2 eq 3,5-dtbc	2 eq DMAP	1-hexanol, Δ	no reaction
7	SnO_2	2 eq 3,5-dtbc	excess NEt_3	Δ	no reaction
8	Si	2 eq 3,5-dtbq	2 eq DMAP	milling	no reaction
9	SiO_2	2 eq 3,5-dtbc	2 eq DMAP	milling	(3,5-dtbc)•DMAP
10	SnO_2	2 eq 3,5-dtbc	2 eq DMAP	milling	(3,5-dtbc)•DMAP

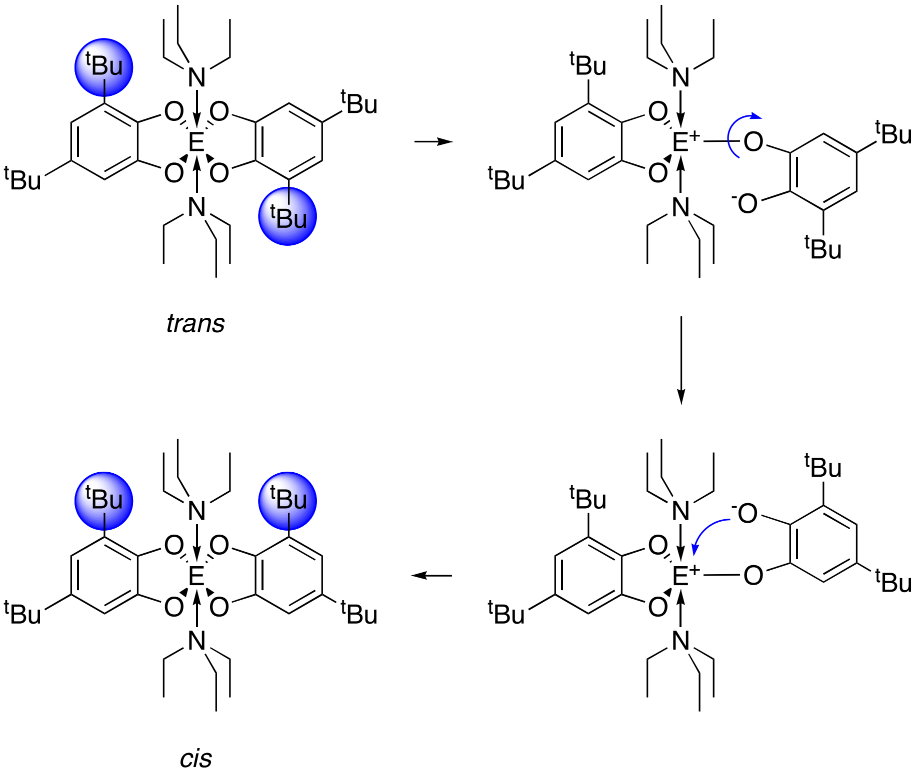
The Kocheshkov redistribution reaction is a well-known and reliable method for obtaining difunctional tin compounds starting from R_4Sn and SnX_4.[1] However, unlike $SnCl_4$, the complex Sn(3,5-dtbc)$_2$(py)$_2$ is stable and unreactive toward redistribution reactions. When 1 equivalent of Sn(3,5-dtbc)$_2$(py)$_2$ and 1 equivalent of either $SnBu_4$ or $SnPh_4$ were combined in toluene and refluxed for 6 days, no reaction took place. Under forcing conditions (tube furnace at 250 °C for 24 h), a black, intractable material was produced. While preliminary studies on Kocheshkov redistribution reactions of Sn(3,5-dtbc)$_2$(py)$_2$ did not yield positive results, there is potential for this method to work because many reaction conditions remain to be tested.

An exchange reaction takes place between Ge(3,5-dtbc)$_2$(py)$_2$ and excess py-d$_5$ to yield Ge(3,5-dtbc)$_2$(py-d$_5$)$_2$, as evidenced by ^{1}H NMR spectroscopy. This prompted the exploration of ligand exchange reactions with donors stronger than pyridine for the synthesis of E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = NEt$_3$, DMAP). Indeed, the reaction of E(3,5-dtbc)$_2$(py)$_2$ (E= Si, Ge, Sn) with DMAP or NEt$_3$ proceeded in good yield to give the ligand exchange products. Given the greater donor strength of DMAP compared to pyridine, only 2 eq of DMAP were required to produce E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = DMAP) in good yields from the pyridine derivatives (Scheme 5.2).



Scheme 5.2: Synthesis of E(3,5-dtbc)$_2$(L)$_2$ from E(3,5-dtbc)$_2$(py)$_2$ by ligand exchange (L = DMAP and L = NEt$_3$).

The ligand exchange reactions outlined in Scheme 5.2 produce the *cis* isomer as a minor product when L = NEt$_3$ and when E = Si and Sn. NEt$_3$ is the bulkiest of the three ligands used, and therefore, it may facilitate dissociation of one of the oxygen atoms of the bulky 3,5-dtbc ligands resulting in the formation of five-coordinate complexes, which can reassociate to give the *cis* isomer (Scheme 5.3). Presumably, the oxygen that detaches from the central element of the *trans*-complex is in the 2 position of the aromatic ring, as shown in Scheme 5.3, to minimize the steric repulsion between the bulky ^{t}Bu and NEt_3 groups. A large excess of NEt_3 was used in these reactions, while for L = DMAP only 2 eq were used, and this may have affected the rate of isomerization. It is also possible that the isomerization proceeds through a heptacoordinate intermediate. While the minor isomer of Ge(3,5-dtbc)$_2$(NEt_3)$_2$ was not observed, It also may have formed, but in quantities below the detection limit of ^{1}H NMR spectroscopy, which was the primary method used to characterize the reaction mixtures.



Scheme 5.3: Conversion mechanism of *trans*-E(3,5-dtbc)$_2$(NEt_3)$_2$ to *cis*-E(3,5-dtbc)$_2$(NEt_3)$_2$ through a five-coordinate zwitterionic intermediate.

5.2.2 Method of Analysis

To accurately and rapidly analyze the crude reaction mixtures produced in the reactions of complexes E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP) and the Grignard reagents, GC-MS was utilized. The reactions were conducted on a small scale (< 10 mg of products), and thus, GC-MS is well suited to separate and analyze the product mixtures.

To use GC-MS as a method to quantify analytes, relative response factors (RRFs) are important.[8, 9] An RRF is a constant between 0 and 1 that relates the analyte mass, analyte peak area, internal standard mass, and internal standard peak area according to equation 1 below:

$$(m_{ISTD} / A_{ISTD}) \times (RRF) = (m_i / A_i) \tag{1}$$

where m_{ISTD} is the mass of the internal standard, A_{ISTD} is the peak area of the internal standard in the chromatogram, m_i is the mass of the analyte, A_i is the peak area of the analyte in the chromatogram, and RRF is the relative response factor.[8] The ratio of analyte mass to analyte area is related to the ratio of the internal standard mass to the internal standard area by the RRF.[9] To be precise, quantification of each analyte by GC-MS must be done by first running an internal standard with a known mass of the analyte to solve for the RRF of that particular analyte. Then, knowing the RRF for each analyte, the research sample is run and the quantification of each analyte is done precisely. There are two major problems with this approach. First, it is very time consuming to determine RRFs for each analyte, especially because the RRF is different for an analyte for each different GC-MS instrument since the conditions used as well as the type of dectector influence the result.[8, 9] Secondly, to determine the RRF, enough analyte must be available, and the analyte must be stable enough to reliably analyze. Often, it is the case, that a byproduct forms and there is not enough of it present to isolate to determine the RRF.[8, 9] To overcome these problems, what is typically done, but is not completely accurate, is the RRFs of all analytes are assumed to be equal to 1. This method allows the rapid quantification of samples. Therefore, equation 1 transforms into equation 2:

$$(m_{ISTD} / A_{ISTD}) = (m_i / A_i) \tag{2}$$

which states that the ratio of internal standard mass to internal standard area is equal to the ratio of analyte mass to analyte area, or rearranging we get equation 3:

$$(A_i / A_{ISTD}) = (m_i / m_{ISTD}) \tag{3}$$

that shows that the area ratio between analyte and internal standard is equal to the mass ratio between analyte and internal standard. This means that just by knowing the area ratio between two analytes, the mass ratio between those analytes is also known. Combining the mass ratio of analytes with the total weight of all analytes, it is possible to calculate the weight of each analyte and also to calculate yields. This approach has been followed in calculating the yields of the products in each of the following reactions.

5.2.3 Results

Each complex E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = py, NEt$_3$, DMAP) was reacted with two eq of Grignard reagent (BuMgCl or PhMgCl) in refluxing THF for 24 h. After workup, the organic soluble products were analyzed by GC-MS and the results are shown in Table 5.3. Appreciable quantities of R$_2$E(3,5-dtbc-κ^2), R$_3$E(3,5-dtbc-κ^1) and ER$_4$ were only obtained for E = Ge, with the yields of these products for E = Si and Sn being zero or close to zero in all cases (Table 5.3).

Table 5.3: Product yields (%) from the reaction of E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = py, NEt$_3$, DMAP) with 2 eq of Grignard reagent.

		R					
		Bu			Ph		
E	L	Bu$_2$E(3,5-dtbc-κ^2)	Bu$_3$E(3,5-dtbc-κ^1)	Bu$_4$E	Ph$_2$E(3,5-dtbc-κ^2)	Ph$_3$E(3,5-dtbc-κ^1)	Ph$_4$E
Si	py	1	0	0	0	0	0
	NEt$_3$	0	0	0	0	0	0
	DMAP	0	0	0	0	3	0
Ge	py	13	21	16	1	15	35
	NEt$_3$	57	6	1	44	5	0
	DMAP	17	12	6	0	0	23
Sn	py	0	0	0	0	0	1
	NEt$_3$	0	0	0	0	0	1
	DMAP	0	0	0	0	0	0

For the reactions of E(3,5-dtbc)$_2$(L)$_2$ with 2 eq of Grignard reagent, the products R$_2$E(3,5-dtbc-κ^2), R$_3$E(3,5-dtbc-κ^1), and R$_4$E were identified and quantified using GC-MS. As an illustrative example, the chromatogram for the reaction of Ge(3,5-dtbc)$_2$(NEt$_3$)$_2$ with 2 eq of BuMgCl is shown in Figure 5.1. The major products of the reaction are Bu$_2$Ge(3,5-dtbc-κ^2) and Bu$_3$Ge(3,5-dtbc-κ^1) as evidenced by GC-MS. The mass spectra of the major products are shown in Figure 5.2 and Figure 5.3.

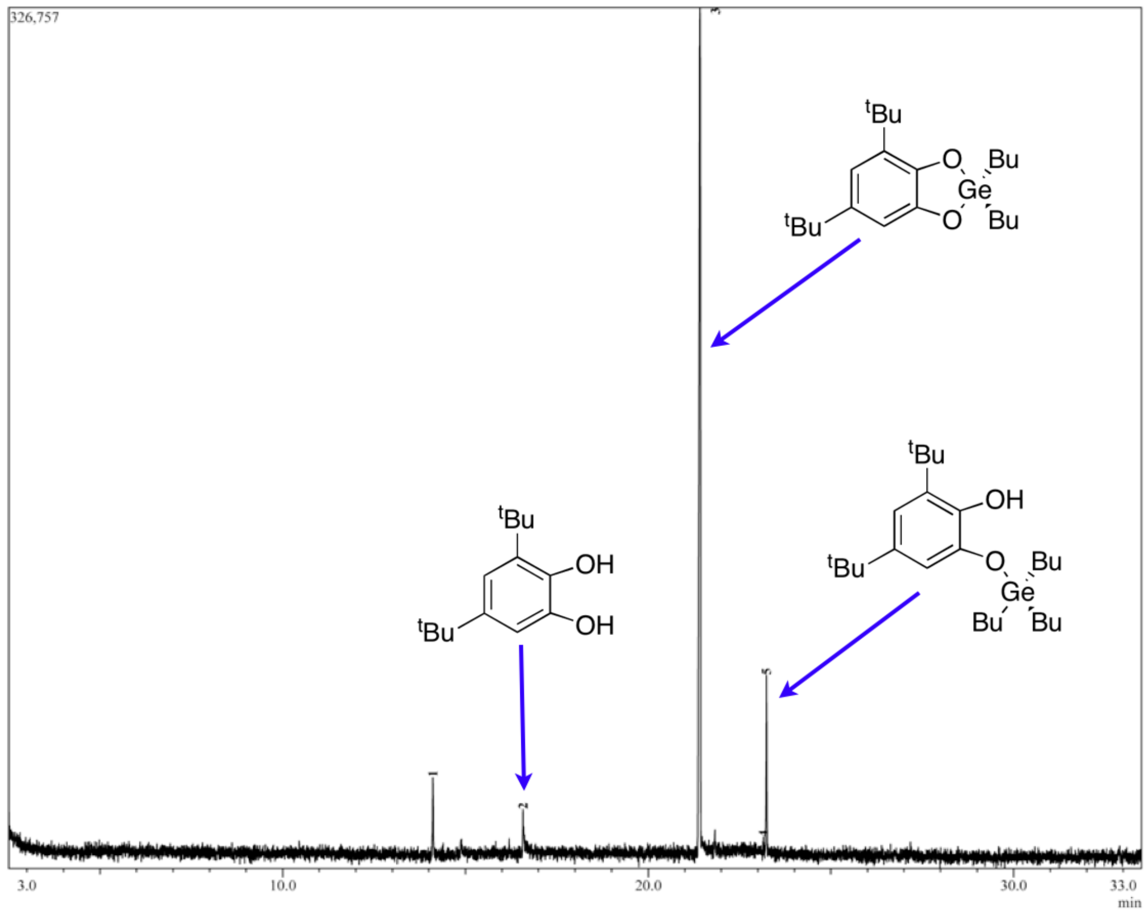


Figure 5.1: Chromatogram of the reaction of Ge(3,5-dtbc)$_2$(NEt$_3$)$_2$ with 2 eq of BuMgCl.

The signals which can be assigned to the molecular ions can be seen in the mass spectra of Bu$_2$Ge(3,5-dtbc-κ^2) (Figure 5.2) and Bu$_3$Ge(3,5-dtbc-κ^1) (Figure 5.3). For Bu$_2$Ge(3,5-dtbc-κ^2), the base peak at *m/z* = 393 is due to the loss of a methyl group from M^+ (Figure 5.2), and, for $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$, the base peak at *m/z* = 409 is due to the loss of a butyl group (Figure 5.3).

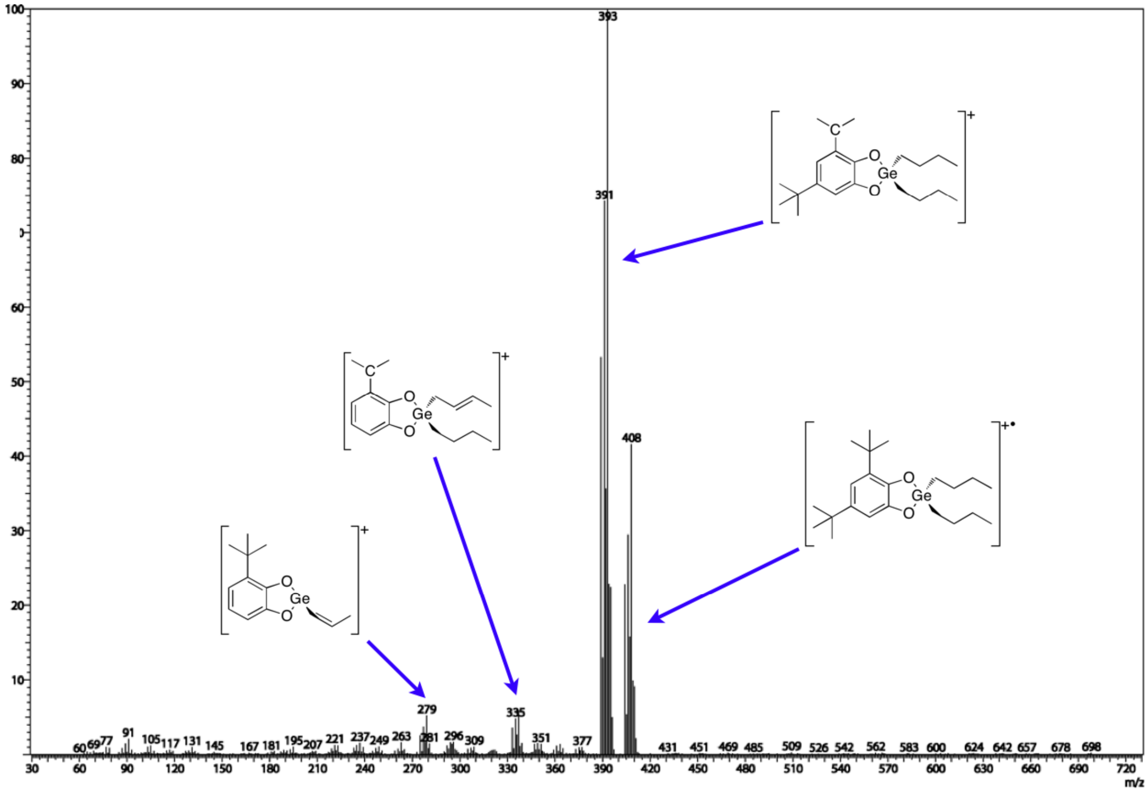


Figure 5.2: EI mass spectrum of $Bu_2Ge(3,5\text{-dtbc-}\kappa^2)$.

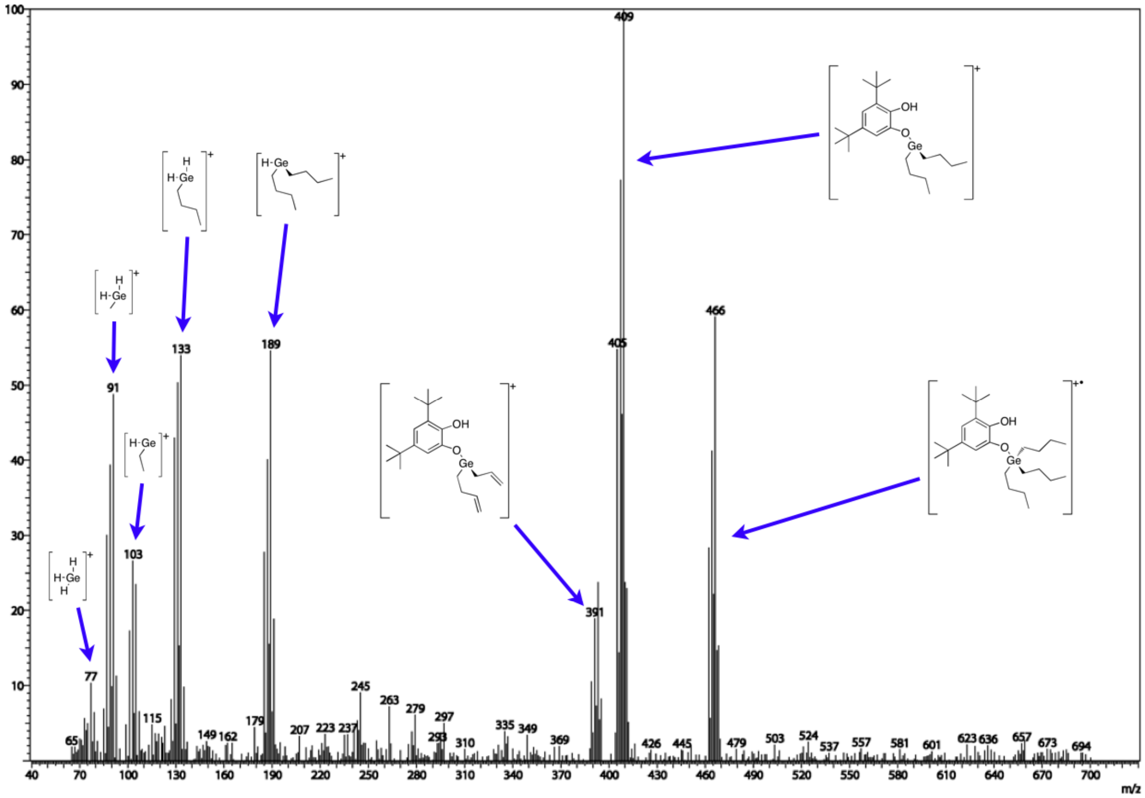


Figure 5.3: EI mass spectrum of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$.

In addition, $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ was isolated from some of the reactions of $Ge(3,5\text{-dtbc})_2(L)_2$ with 2 eq of BuMgCl and identified using NMR spectroscopy. Both the ^1H NMR (Figure 5.4) and ^{13}C NMR spectra (Figure 5.5) revealed that only one of two possible structural isomers (isomer A and B in Figure 5.6) was isolated.

The ^{13}C-^1H HSQC spectrum (Figure 5.7) of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ shows that the two signals at 114.41 ppm and either 111.91 ppm or 111.88 ppm in the ^{13}C dimension correlate to the two signals at 6.79 ppm and 6.63 ppm in the ^1H dimension which were assigned to the aromatic hydrogens on the basis of the chemical shift and the coupling constant (2.2 Hz). The ^{13}C-^1H HMBC spectrum (Figure 5.8) of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ shows that the signal at 6.16 ppm in the ^1H

dimension and assigned to the -O**H** correlates to three signals at 143.73 ppm, 140.54 ppm, and 133.84 ppm in the ^{13}C dimension. Thus, the carbons giving rise to these signals must be within 2 – 3 bonds of the hydroxylic hydrogen. Notably, these signals can be assigned to quaternary carbons as no correlations to these signals were observed in the ^{13}C-^{1}H HSQC spectrum and of the two possible structural isomers of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$, only isomer A (Figure 5.6) fits the data. Isomer B (Figure 5.6) has a carbon atom bonded to a hydrogen atom as one of the three carbon atoms in close proximity to the -O**H** proton. Notably, isomer A is less sterically strained than isomer B, and can reasonably be expected to be the major product.

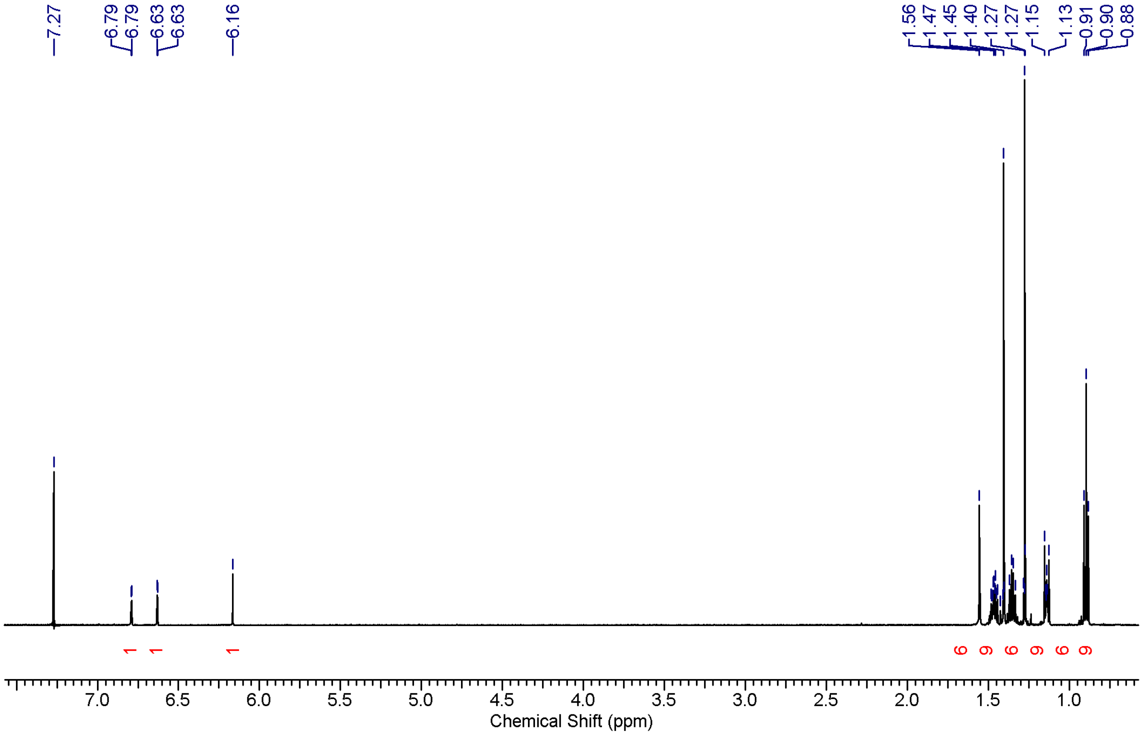


Figure 5.4: ^{1}H NMR spectrum (600 MHz) of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ in $CDCl_3$.

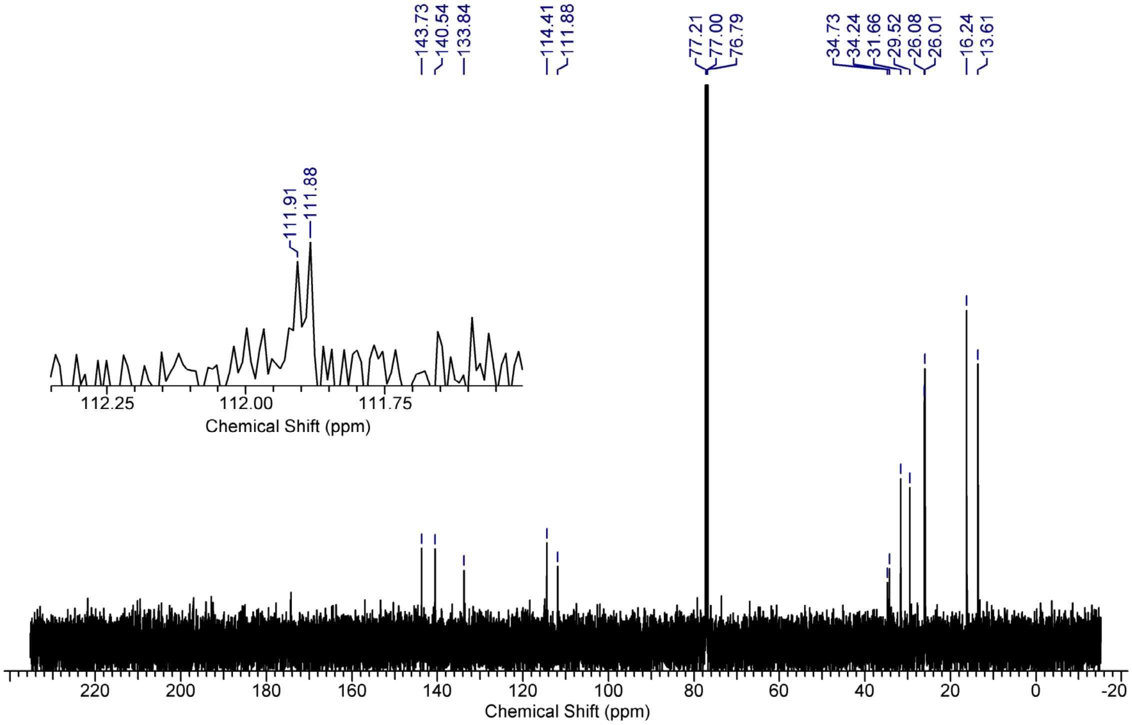
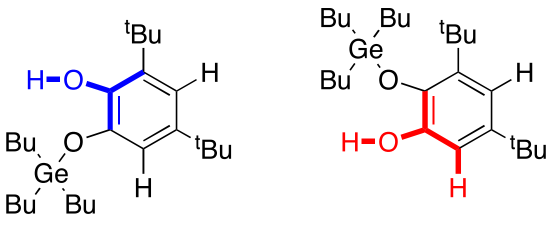


Figure 5.5: $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ in $CDCl_3$, inset: 112.25 ppm – 111.75 ppm.



Isomer A

Isomer B

Figure 5.6: The two possible structural isomers of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$.

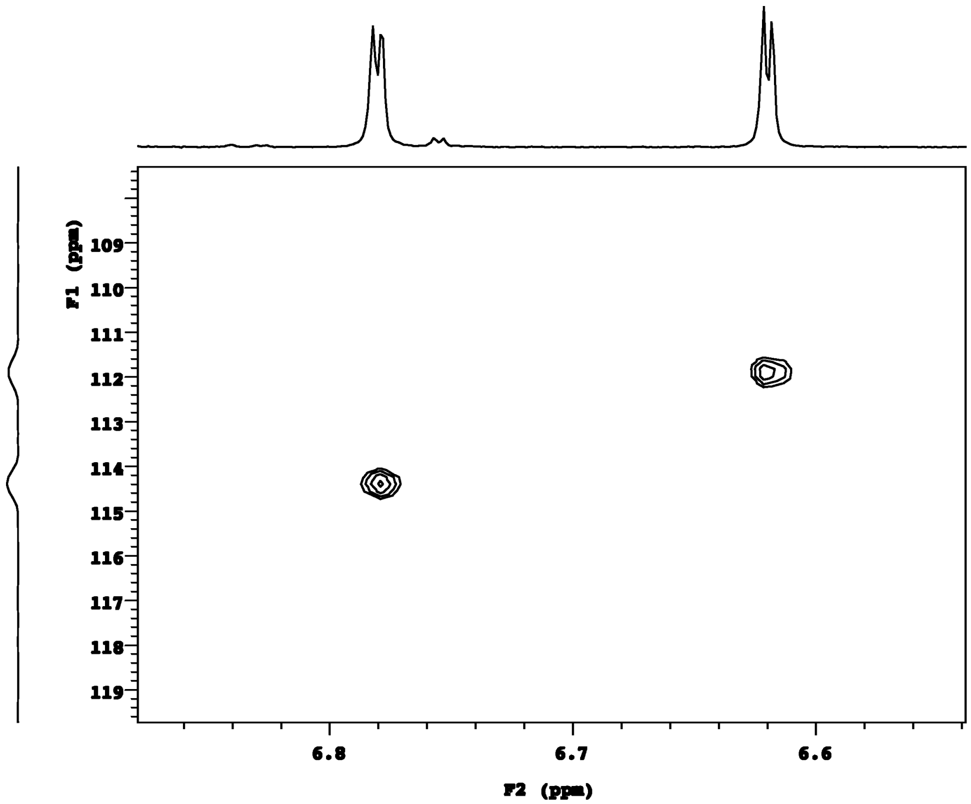


Figure 5.7: ^{13}C-^{1}H gHSQC spectrum of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ in $CDCl_3$.

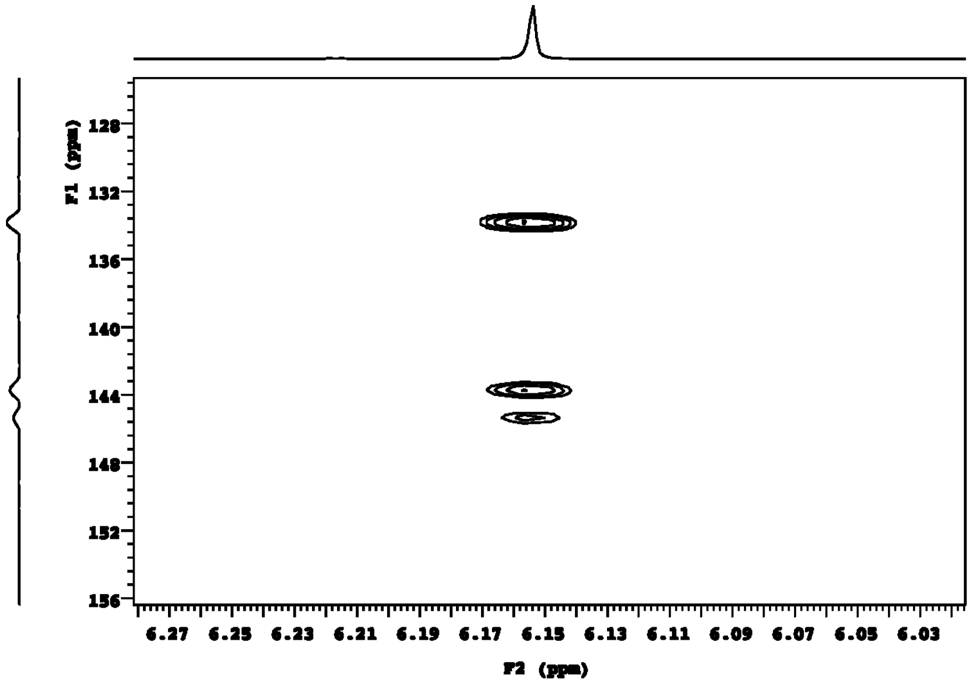


Figure 5.8: ^{13}C-^{1}H HMBC spectrum of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ in $CDCl_3$.

In the reaction of Ge(3,5-dtbc)$_2$(L)$_2$ with 2 eq of BuMgCl, approximately equal quantities of Bu$_2$Ge(3,5-dtbc-κ^2), Bu$_3$Ge(3,5-dtbc-κ^1), and GeBu$_4$, were produced for L = py and L = DMAP, however, for L = NEt$_3$, the major product was Bu$_2$Ge(3,5-dtbc-κ^2) (Figure 5.9). The yields of Bu$_3$Ge(3,5-dtbc-κ^1) and GeBu$_4$ were approximately double when L = py compared to L = DMAP.

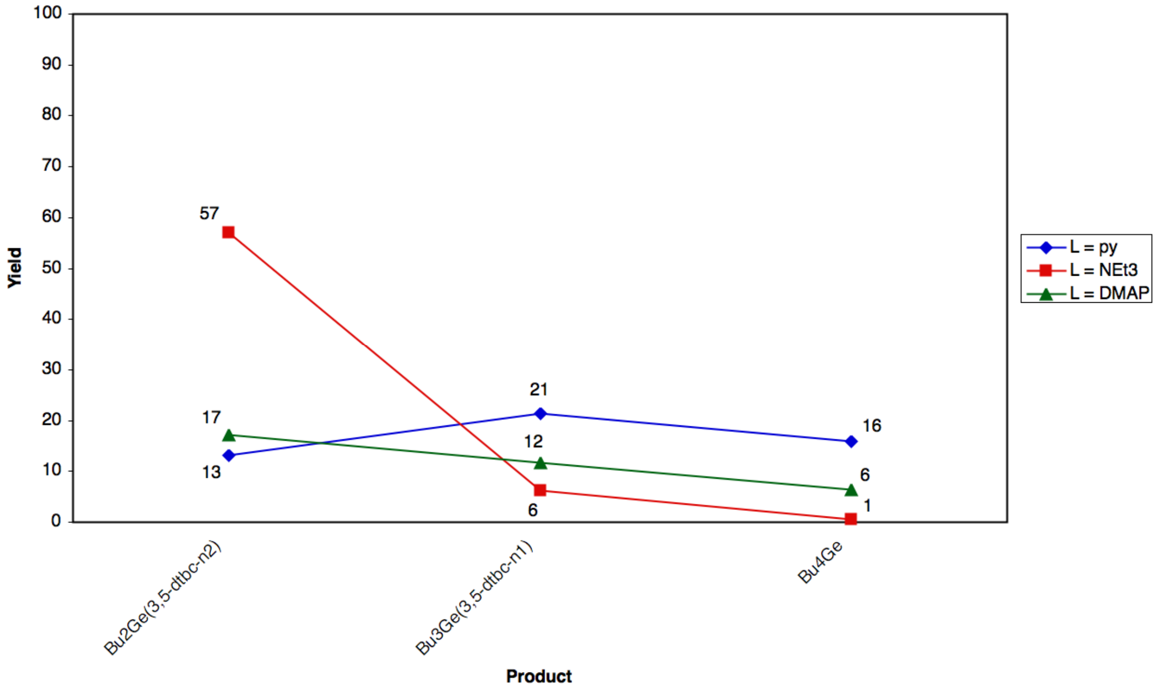


Figure 5.9: Product yields vs. product distribution for the reaction of Ge(3,5-dtbc)$_2$(L)$_2$ + 2 BuMgCl.

In the reaction of Ge(3,5-dtbc)$_2$(L)$_2$ with 2 eq of PhMgCl (Figure 5.10), the same trend was observed when L = NEt$_3$: the main product was Ph$_2$Ge(3,5-dtbc-κ^2). For L = py and L = DMAP similar product distributions were obtained, with the major product in both cases being GePh$_4$ (Figure 5.10).

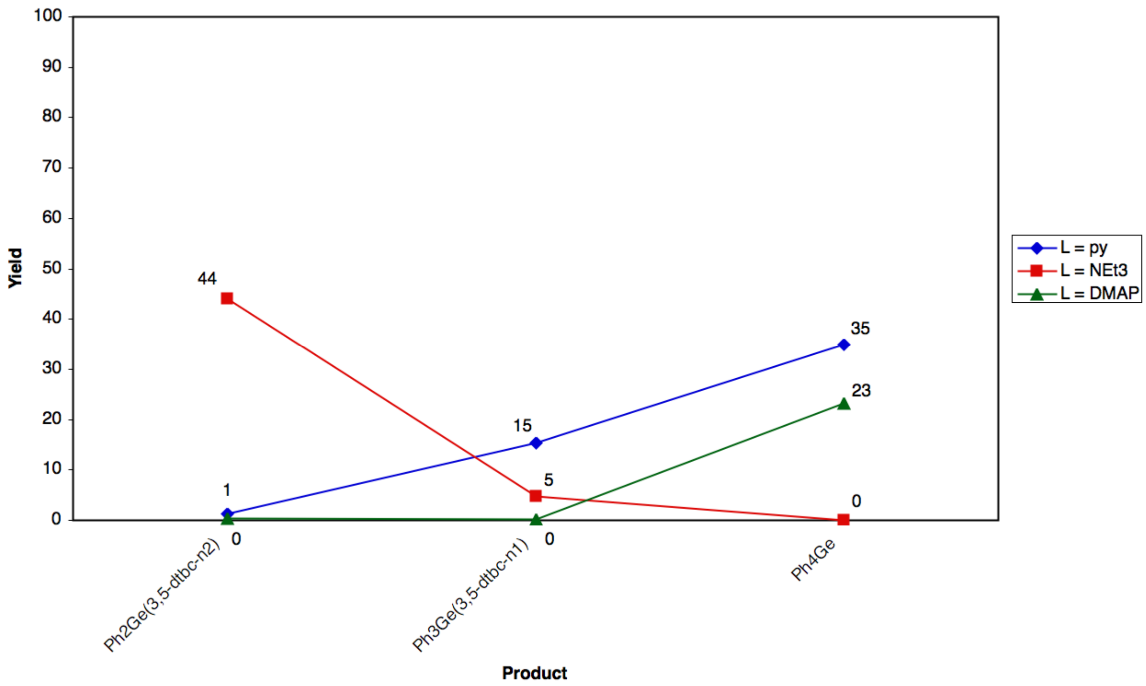
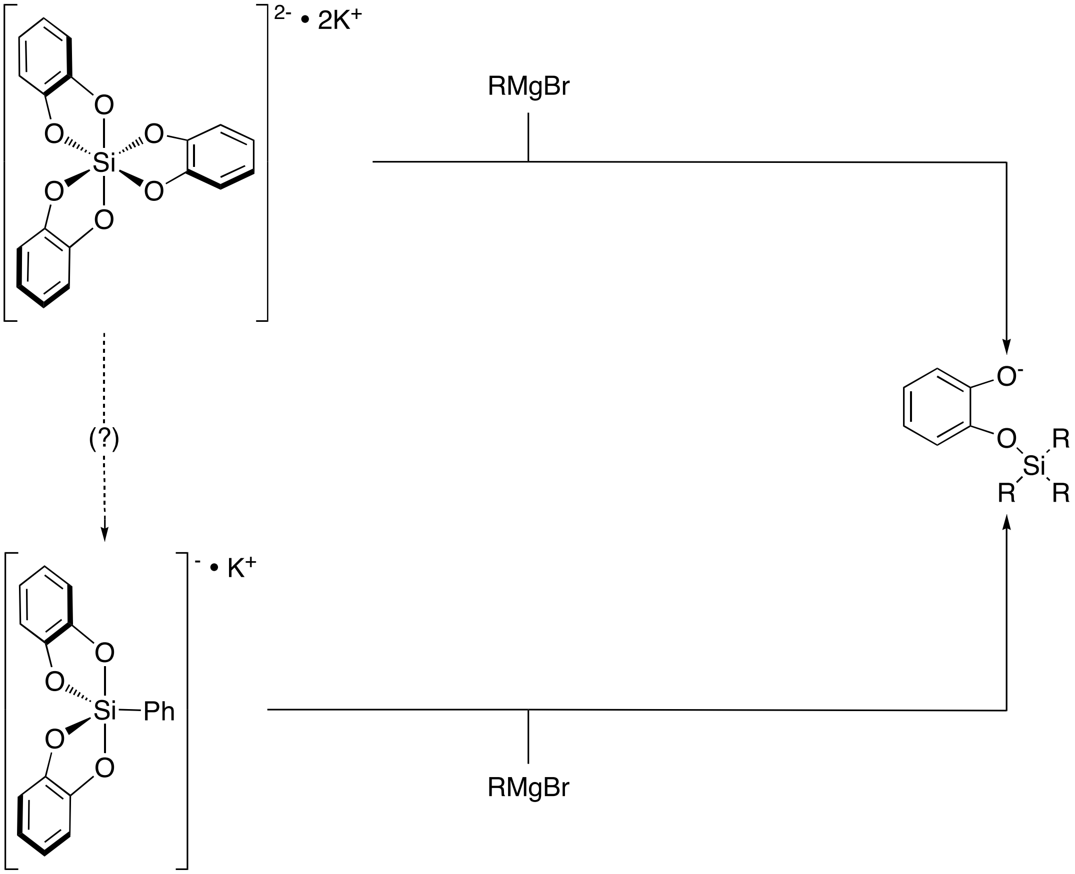


Figure 5.10: Product yields vs. product distribution for the reaction of Ge(3,5-dtbc)$_2$(L)$_2$ + 2 PhMgCl.

5.2.4 Mechanistic Considerations

Corriu *et al.* found that the complexes [E(o-$C_6H_4O_2$)$_3$$^{2-}$•2K$^+$] (E = Si, Ge), react with organometallic reagents in a similar manner in comparison to the reactivity of E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP).[10, 11] The product of the reaction between [Si(o-$C_6H_4O_2$)$_3$$^{2-}$•2K$^+$] and RMgBr was R_3Si(o-$C_6H_5O_2$-η^1) when R = alkyl, and was SiR_4 for all other types of Grignard reagents, e.g. R = Ph, allyl, vinyl, alkynyl, and was independent of the number of eq of Grignard reagent used.[12] Evidently, when the Grignard reagent has an sp^2 hybridized R group (e.g. R = Ph, allyl, vinyl, alkynyl), the outcome of the reaction of [Si(o-$C_6H_4O_2$)$_3$$^{2-}$•2K$^+$] with RMgBr is a higher level of substitution than when R is an sp^3 hybridized group (alkyl). This can be rationalized since an sp^2 C is more electronegative than an sp^3 C, and thus, the silicon is more electrophilic. The reactivity of $[Ge(o\text{-}C_6H_4O_2)_3{}^{2-}\bullet 2K^+]$ towards Grignard reagents differed from the silicon analog: all Grignard reagents produced GeR_4 as the major product. Again, the product obtained was independent of the number of eq of Grignard reagent used.[11] By varying the ligand in the complex from catecholato to butanolato, Corriu found that $[Ge(C_4H_8O_2)_3{}^{2-}\bullet 2K^+]$ produces R_3GeX as the major product independent of the number of eq of Grignard reagent used.[13] These findings support the hypothesis put forward by Corriu that, in the substitution reactions of hypercoordinate complexes using Grignard reagents, the rate constant of each subsequent substitution step increases.[12] Furthermore, when either $[Si(o\text{-}C_6H_4O_2)_3{}^{2-}\bullet 2K^+]$ or $[PhSi(o\text{-}C_6H_4O_2)_2{}^{-}\bullet K^+]$ were reacted with Grignard reagents under identical conditions, the product yields were identical after the same amount of reaction time, indicating that a pentacoordinate intermediate cannot be involved in the reactions (Scheme 5.4).[12] For these reasons, Corriu favors the formation of a heptacoordinate intermediate. From Corriu's work, it is clear that hypercoordinate complexes can act as excellent electrophiles toward Grignard reagents despite seemingly being sterically congested, and that the electrophilicity of the central metal atom plays an important role in the mechanism.



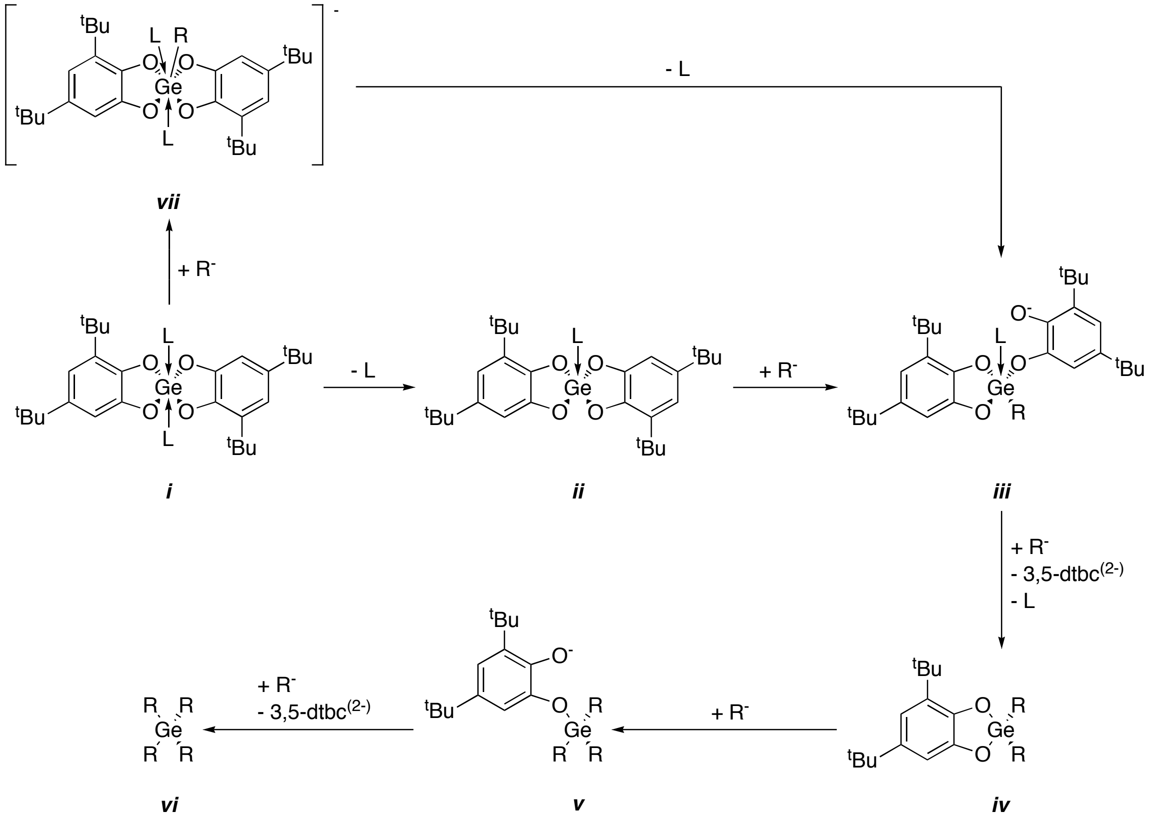
Scheme 5.4: Summary of comparative kinetic studies performed by Corriu.

The relevant experimental results from the current study can be summarized as follows:

1. An exchange reaction takes place between $Ge(3,5\text{-dtbc})_2(py)_2$ and excess py-D_5 to yield $Ge(3,5\text{-dtbc})_2(py\text{-}D_5)_2$.
2. In the ligand exchange reactions involving NEt_3, isomerization is seen for $E(3,5\text{-dtbc})_2(py)_2$ when E = Si and Sn.
3. For $E(3,5\text{-dtbc})_2(L)_2$ where E = Si and Sn, and L = py, NEt_3, and DMAP, essentially no reaction takes place with 2 eq of Grignard reagent, however, with 20 eq of Grignard reagent, ER_4 is formed when L = py.

4. $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ is observed in greatest yield when L = NEt_3 for $Ge(3,5\text{-dtbc})_2(L)_2$.
5. In general, yields of organogermanes are greater for L = py compared to DMAP for $Ge(3,5\text{-dtbc})_2(L)_2$, but are not selective.

A proposed mechanism for the reaction of $E(3,5\text{-dtbc})_2(py)_2$ with Grignard reagents is shown in Scheme 5.5. The formation of $R_2E(3,5\text{-dtbc-}\kappa^2)$, $R_3E(3,5\text{-dtbc-}\kappa^1)$, and ER_4 are the result of a series of substitutions of 3,5-dtbc ligands with the organic group. In general, there are two possible pathways: an assosiative pathway through the heptacoordinate intermediate ***vii***, and a dissociative pathway through the pentacoordinate intermediate ***ii***. Notably, in the reaction of $[Si(o\text{-}C_6H_4O_2)_3^{2-}\bullet 2K^+]$, Corriu proposed that a heptacoordinate intermediate is involved on the basis of a comparative kinetic study.[12] He also noted that the number of eq of the Grignard reagent did not influence the level of substitution, and thus, proposed that the rate constants increased with increasing substitution by the organic substituents. Given that the reaction of two eq of RMgCl with $Ge(3,5\text{-dtbc})_2(NEt_3)_2$ produces $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ as the major product, we propose that a pentacoordinate intermediate is involved, at least in the case where the complex is $Ge(3,5\text{-dtbc})_2(NEt_3)_2$ (Scheme 5.5). The preferential formation of the pentacoordinate product indicates that the steps from ***i*** to ***ii***, and from ***ii*** to ***iii***, must be rapid, and thus, lead only to $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ in the presence of two eq of RMgCl. This proposal is in contrast to Corriu's hypothesis. The steric bulk of NEt_3 may increase the rate of the conversion of ***i*** to ***ii*** compared to that of ***i*** to ***vii***.



Scheme 5.5: Proposed mechanism of formation of $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ (***iv***), $R_3Ge(3,5\text{-dtbc-}\kappa^1)$ (***v***), and GeR_4 (***vi***) from $Ge(3,5\text{-dtbc})_2(L)_2$ and 2 eq of Grignard reagents.

Furthermore, $Ge(3,5\text{-dtbc})_2(py)_2$ is less electrophilic compared to the tri(catecholato) derivatives. In contrast, given that mono-, di-, and trifunctional germanes are observed in the reactions of Grignard reagents with $Ge(3,5\text{-dtbc})_2(py)_2$ and $Ge(3,5\text{-dtbc})_2(DMAP)_2$, an associative mechanism, with an initial slow step is most likely operative. At some point, the two pathways will converge to a common intermediate. Pyridine occupies less volume than DMAP and this may explain why the products are formed in greater yield when the pyridine complexes are used. In all cases (L = py, NEt_3, DMAP), there is a possibility that both pathways are operating, but at different rates.

The reactions of Ge(3,5-dtbc)$_2$(L)$_2$ with 2 eq of BuMgCl (Figure 5.9) or PhMgCl (Figure 5.10) may be more facile than the corresponding silicon and tin complexes because the Ge-O bond is much weaker ($\approx$ 350 kJ•mol^{-1}) than the Si-O bond ($\approx$ 450 kJ•mol^{-1}) or Sn-O bond ($\approx$ 550 kJ•mol^{-1}).[2, 14] E(3,5-dtbc)$_2$(py)$_2$ (E = Si and E = Sn) do react with 20 eq of Grignard reagent to give good yields of ER_4, and thus, it is perplexing that no reaction took place for these complexes when 2 eq of Grignard reagent were used. The most likely explanation is that the rate of reaction of these complexes depends of the concentration of Grignard reagent, and that by reducing the concentration of the Grignard reagent by a factor of 10, the reaction rate reduces almost to a halt. This implies that the silicon and tin complexes may react through an associative mechanism.

5.3 Conclusions

The synthesis of E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = NEt_3, DMAP) was found to proceed only from E(3,5-dtbc)$_2$(py)$_2$ (E= Si, Ge, Sn) by ligand exchange, and not by the synthesis of the complexes from EO_2 or E. The nine complexes E(3,5-dtbc)$_2$(L)$_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP) were reacted with 2 eq of Grignard reagents, using BuMgCl as a prototypical alkyl Grignard reagent and PhMgCl as a prototypical aromatic Grignard reagent. The silicon and tin complexes formed unknown insoluble products. For the germanium analog, the complexes with pyridine and DMAP ligands functioned similarly, although the yields of products from the pyridine complexes were higher. For NEt_3, the yields of $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ were significantly higher than the yields of $R_3Ge(3,5\text{-dtbc-}\kappa^1)$ and R_4Ge, and this can be traced back to the effects of the larger steric bulk of NEt_3 compared to pyridine and DMAP. The complex $Ge(3,5\text{-dtbc})_2(NEt_3)_2$ has shown promise for becoming a useful starting material for making difunctional germanes $R_2Ge(3,5\text{-dtbc-}\kappa^2)$ or R_2GeX_2, and is soluble in THF, making the preparation of solutions convenient. $Ge(3,5\text{-dtbc})_2(NEt_3)_2$ is better for making difunctional germanes compared to GeX_4 (X = Cl, Br) because no HCl or Cl_2 is involved in the synthesis of the Ge^{IV} precursor, and therefore, many of the principles of green chemistry have been applied, and the process is safer for humans and the environment. The mechanisms operating for the reactions of $Ge(3,5\text{-dtbc})_2(L)_2$ (L = py, NEt_3, DMAP) with 2 eq of Grignard reagent were shown to be dissociative for L = NEt_3, and associative for L = py and L = DMAP. The ideas presented here can be used as a basis for more detailed mechanistic studies.

5.4 Experimental Procedures

5.4.1 General Experimental Procedures

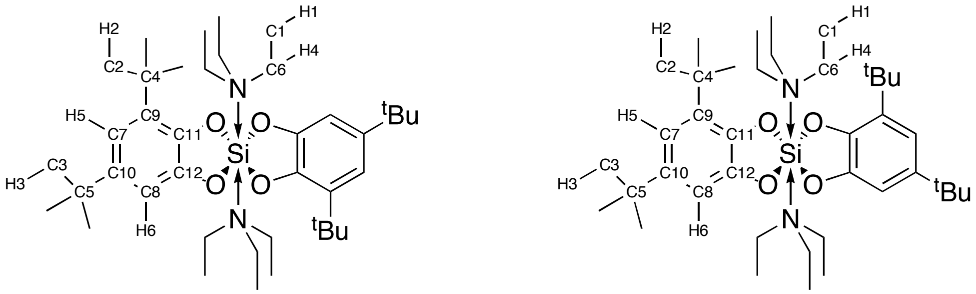
Chemicals and solvents were purchased from Sigma Aldrich, Alfa Aesar or Gelest, and used as received without further purification. Solvents for Grignard reactions were dried and purified using a PureSolv MD 7 from

Innovative Technology. ^{1}H NMR and ^{13}C NMR spectra were acquired using an Inova 400 MHz or an Inova 600 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to: ^{1}H: 7.27 ppm; ^{13}C: 77.00 ppm. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Gas chromatography – mass spectrometry (GC-MS) spectra were obtained on a GCMS-QP2010S instrument with a GC-2010 gas chromatograph at an ionizing voltage of 70 eV (EI), with a quadrupole mass filter, and a DB-5MS 30 m x 0.25 μm column from J & W Scientific utilizing the following temperature program: 3 min at 65 °C; 17 min constant heating rate of 15 °C / min; 5 min at 320 °C. Mass spectral data are reported in mass-to-charge units, m/z, with ion identity and peak intensities (%) in parentheses. The data listed for germanium are for the ^{74}Ge isotope. ESI-MS data were obtained on a Bruker micrOTOF 11 instrument. Melting point data are uncorrected.

5.4.2 General Experimental Procedure for Ligand Exchange Reactions

Excess ligand (either 2.1 eq of DMAP dissolved in methanol, or 250 eq of NEt_3) and $E(3,5\text{-dtbc})_2(py)_2$ (1 eq) were added to a 100 mL flask equipped with a magnetic stir bar to give a white suspension which was stirred for 24 h at room temperature (Scheme 5.2) (except for in the synthesis of $Si(3,5\text{-dtbc})_2(DMAP)_2$, where a clear, light yellow solution forms). The phases were separated by centrifugation and the liquid phase removed by decantation, then the solid was dried under vacuum for one hour, yielding E(3,5-dtbc)$_2$(L)$_2$ (except in the synthesis of Si(3,5-dtbc)$_2$(DMAP)$_2$ where the product was isolated by rotatory evaporation of the solvents).

5.4.3 Si(3,5-dtbc)$_2$(NEt$_3$)$_2$



major isomer

minor isomer

Figure 5.11: Isomers of Si(3,5-dtbc)$_2$(NEt$_3$)$_2$.

Average yield = 77%; m.p. = 163 – 164 °C (dec.); major isomer: **^{1}H NMR** (600 MHz, CDCl$_3$): 6.70 (2H, d, ^4J = 2.1 Hz, H6/5), 6.64 (2H, d, ^4J = 2.1 Hz, H5/6), 2.84 (12H, q, ^3J = 7.2 Hz, H4), 1.42 (18H, s, H3/2), 1.27 (18H, s, H2/3), 1.15 (18H, t, ^3J = 7.2 Hz, H1); **^{13}C NMR** (150 MHz, CDCl$_3$): 148.17 (C12/11), 145.12 (C11/12), 139.20 (C10/9), 132.28 (C9/10), 112.53 (C8/7), 105.85 (C7/8), 46.14 (C6), 34.35 (C5/4), 34.29 (C4/5), 31.89 (C3/2), 29.52 (C2/3), 10.21 (C1); minor isomer: **^{1}H NMR** (600 MHz, CDCl$_3$): 6.61 (2H, d, ^4J = 1.7 Hz, H6/5), 6.58 (2H, d, ^4J = 1.7 Hz, H5/6), 2.84 (12H, q, ^3J = 7.2 Hz, H4), 1.38 (18H, s, H3/2), 1.24 (18H, s, H2/3), 1.15 (18H, t, ^3J = 7.2 Hz, H1); **^{13}C NMR** (150 MHz, CDCl$_3$): 149.84 (C12/11), 143.87 (C11/12), 140.47 (C10/9), 132.34 (C9/10), 111.05 (C8/7), 105.48 (C7/8), 46.14 (C6), 34.41 (C5/4), 34.35 (C4/5), 31.89 (C3/2), 29.83 (C2/3), 10.21 (C1); 2 : 1 mixture of isomers: **ESI-MS** (*m/z*): 689.5 (3%, $[C_{40}H_{70}N_2O_4Si \cdot H_2O]^+$), 399.2 (100%, $[C_{23}H_{31}O_4Si]^+$), 242.3 (70%, $[C_{12}H_6O_4Si]^+$), 186.2 (5%).

5.4.4 $Si(3,5\text{-dtbc})_2(DMAP)_2$

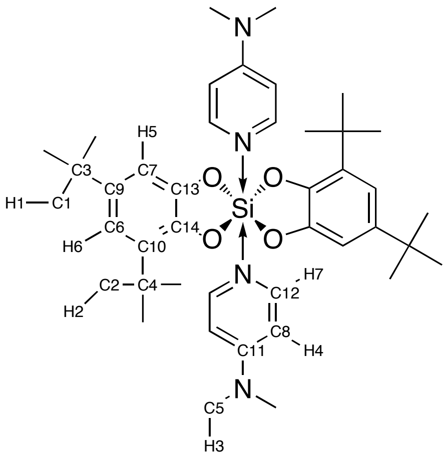


Figure 5.12: $Si(3,5\text{-dtbc})_2(DMAP)_2$.

Average yield = 81%; m.p. = 147 – 148 °C (dec.); **^{1}H NMR** (600 MHz, $CDCl_3$): 8.20 (4H, m, H7), 6.87 (2H, d, ^4J = 2.3 Hz, H6/H5), 6.80 (2H, d, ^4J = 2.3 Hz, H5/H6), 6.59 (4H, m, H4), 3.11 (12H, s, H3), 1.43 (18H, s, H2/H1), 1.27 (18H, s, H1/H2); **^{13}C NMR** (150 MHz, $CDCl_3$): 154.69, 148.23, 144.03, 141.89, 141.24, 134.64, 114.32, 110.25, 106.63, 39.11, 34.80, 34.26, 31.65, 29.62; **ESI-MS** (*m/z*): 415.2 (10%), 399.2 (100%, $[C_{23}H_{31}O_4Si]^+$), 242.3 (15%, $[C_{12}H_6O_4Si]^+$), 186.2 (5%).

5.4.5 $Ge(3,5\text{-dtbc})_2(NEt_3)_2$

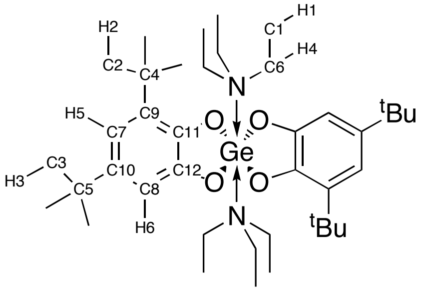


Figure 5.13: Ge(3,5-dtbc)$_2$(NEt$_3$)$_2$.

Average yield = 88%; m.p. = 210 – 211 °C (dec.); **^{1}H NMR** (600 MHz, CDCl$_3$): 6.70 (2H, d, ^4J = 1.8 Hz, H6/5), 6.64 (2H, bs, H5/6), 2.85 (12H, q, ^3J = 7.0 Hz, H4), 1.42 (18H, s, H3/2), 1.25 (18H, s, H2/3), 1.15 (18H, t, ^3J = 7.0 Hz, H1); **^{13}C NMR** (150 MHz, CDCl$_3$): 200.6 (C12/11), 165.1 (C11/12), 139.4 (C10/9), 132.9 (C9/10), 112.5 (C8/7), 106.6 (C7/8), 46.2 (C6), 34.6 (C5/4), 34.3 (C4/5), 31.8 (C3/2), 29.6 (C2/3), 9.9 (C1); **ESI-MS** (*m/z*): 1366.8 (10%), 735.5 (100%), 319.3 (40%).

5.4.6 Ge(3,5-dtbc)$_2$(DMAP)$_2$

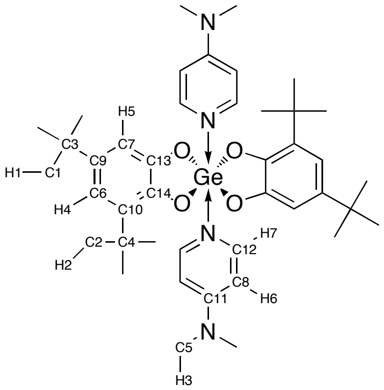
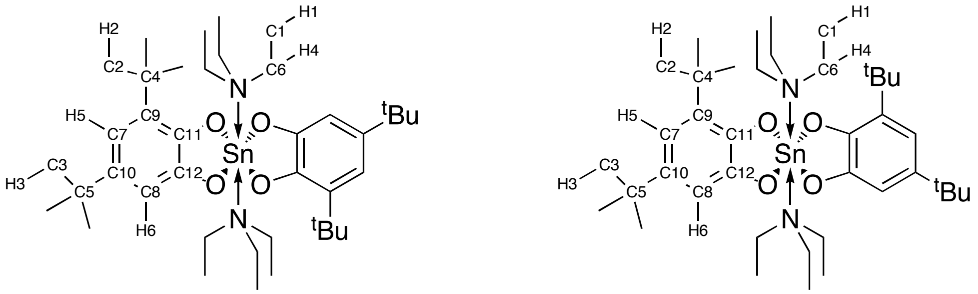


Figure 5.14: Ge(3,5-dtbc)$_2$(DMAP)$_2$.

Average yield = 77%; m.p. = 344 – 346 °C (dec.); **^{1}H NMR** (600 MHz, D$_3$COD): 8.07 (4H, m, H7), 6.80 (6H, m, H6 & H5/H4), 6.62 (2H, d, ^4J = 2.2 Hz, H4/H5), 3.13 (12H, s, H3), 1.44 (18H, s, H2/H1), 1.26 (18H, s, H1/H2); **ESI-MS** (*m/z*): 2026.0 (20%), 1629.7 (5%), 1357.6 (10%), 1157.4 (10%), 759.4 (30%), 659.3 (15%), 591.2 (100%), 245.2 (20%).

5.4.7 Sn(3,5-dtbc)$_2$(NEt$_3$)$_2$



major isomer

minor isomer

Figure 5.15: Isomers of Sn(3,5-dtbc)$_2$(NEt$_3$)$_2$.

Average yield = 67%; m.p. = 167 – 168 °C (dec.); major isomer: ^{1}**H NMR** (600 MHz, CDCl$_3$): 6.50 (2H, s, H6/5), 6.39 (2H, s, H5/6), 3.05 (12H, s, H4), 1.26 (18H, s, H3/2), 1.21 (18H, s, H2/3), 1.12 (18H, s, H1); ^{13}**C NMR** (150 MHz, CDCl$_3$): 148.60 (C12/11), 148.43 (C11/12), 135.71 (C10/9), 133.76 (C9/10), 110.66 (C8/7), 108.05 (C7/8), 45.43 (C6), 34.76 (C5/4), 33.96 (C4/5), 31.90 (C3/2), 29.67 (C2/3), 8.79 (C1); minor isomer: ^{1}**H NMR** (600 MHz, CDCl$_3$): 6.63 (2H, s, H6/5), 6.42 (2H, s, H5/6), 3.05 (12H, s, H4), 1.38 (18H, s, H3/2), 1.26 (18H, s, H2/3), 1.12 (18H, s, H1); ^{13}**C NMR** (150 MHz, CDCl$_3$): 149.50 (C12/11), 148.08 (C11/12), 135.48 (C10/9), 133.76 (C9/10), 112.18 (C8/7), 107.45 (C7/8), 45.43 (C6), 34.76 (C5/4), 33.96 (C4/5), 31.90 (C3/2), 29.67 (C2/3), 8.79 (C1);

ESI-MS (*m/z*): 1339.7 (5%), 985.6 (100%), 884.5 (5%), 399.2 (40%), 242.3 (5%), 181.2 (5%).

5.4.8 $Sn(3,5\text{-dtbc})_2(DMAP)_2$

Average yield = 90%; m.p. = 348 – 350 °C (dec.); **ESI-MS** (*m/z*): 1485.6 (5%), 1363.6 (7%), 1142.4 (4%), 985.5 (4%), 927.5 (10%), 863.5 (4%), 805.4 (25%), 399.2 (100%), 181.2 (50%); **NMR**: Solution NMR was not possible because the compound is insoluble in all solvents; **Elemental Analysis** calcd for $C_{42}H_{60}N_4O_4Sn$: C, 62.77; H, 7.53; N, 6.97; found: C, 62.50; H, 7.62; N, 6.99.

5.4.9 Preparation of Organic Compounds

All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques unless specified otherwise. All equipment was flame dried prior to use and kept under an argon atmosphere. In a 100 mL flask equipped with magnetic stirring and a reflux condenser, R-MgCl (~0.3 mmol, 2 eq) was added to a suspension of $E(3,5\text{-dtbc})_2(L)_2$ (~100 mg, ~0.15 mmol, 1 eq) dissolved in 3.85 mL of the same solvent as the organometallic reagent (THF). The mixture was allowed to reflux for 24 h. After cooling to room temperature, 15 mL of pentane was added to the crude reaction mixture followed by 5 mL water and the reaction mixture was allowed to stir for 5 minutes. The organic layer was washed with 5 mL water, then concentrated using a rotary evaporator. The crude weight was measured and the crude products were dissolved in 2 mL chloroform for analysis by GC-MS. The area integration of the GC-MS was taken to be the mass ratio of compounds in the crude mixture, which was then converted to moles and yields were calculated.

5.4.10 Bu$_3$Ge(3,5-dtbc-κ^1): ^{1}**H NMR** (600 MHz, CDCl$_3$): 6.79 (1H, d, ^4J = 2.2 Hz, Ar**H**), 6.63 (1H, d, ^4J = 2.2 Hz, Ar**H**), 6.16 (1H, s, O**H**), 1.50-1.43 (6H, m, C**H**$_2$), 1.40 (9H, s, C(C**H**$_3$)$_3$), 1.38-1.32 (6H, m, C**H**$_2$), 1.27 (9H, s, C(C**H**$_3$)$_3$), 1.16-1.12 (6H, m, C**H**$_2$), 0.90 (9H, t, ^3J = 7.3 Hz, C**H**$_3$); ^{13}**C NMR** (150 MHz, CDCl$_3$): 143.73, 140.54, 133.84, 114.41, 111.91, 111.88, 34.73, 34.24, 31.66, 29.52, 26.08, 26.01, 16.24, 13.61; **GC-MS** (*m/z*): 466 (Bu$_3$Ge(3,5-dtbc-κ^1)$^+$, 60%), 409 (100%), 391 (20%), 245 (13%), 189 (Bu$_2$GeH$^+$, 55%), 133 (BuGeH$_2^+$, 55%), 103 (26%), 91 (48%), 77 (10%).

5.5 References

1. R. E. Kirk, D. F. Othmer, J. I. Kroschwitz, M. Howe-Grant: *Encyclopedia of Chemical Technology*, Wiley, New York, **1991**.

2. N. N. Greenwood, A. Earnshaw: *Chemistry of the Elements,* Butterworth-Heinemann, Boston, Mass., **1997**.

3. D. M. P. Mingos, R. H. Crabtree: *Comprehensive Organometallic Chemistry III*, Elsevier, Amsterdam; London, **2007**.

4. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, F. Ullmann: *Ullmann's Encyclopedia of Industrial Chemistry*, VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany; Deerfield Beach, Fla, **1985**.

5. E. Vedejs: *Lewis Base Catalysis in Organic Synthesis*, **2016**.

6. P. Siega, L. Randaccio, P. A. Marzilli, L. G. Marzilli: *Inorg. Chem.,* **2006**, *45*, 3359-3368.

7. J. A. Bilbrey, A. H. Kazez, J. Locklin, W. D. Allen: *J. Comput. Chem.,* **2013**, *34*, 1189-1197.

8. J. de Saint Laumer, S. Leocata, E. Tissot, L. Baroux, D. M. Kampf, P. Merle, A. Boschung, M. Seyfried, A. Chaintreau: *J. Sep. Sci.,* **2015**, *38*, 3209-3217.

9. A. Undri, M. Abou-Zaid, C. Briens, F. Berruti, L. Rosi, M. Bartoli, M. Frediani, P. Frediani: *J. Anal. Appl. Pyrolysis,* **2015**, *114*, 208-221.

10. A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Organometallics,* **1988**, *7*, 1165-1171.

11. G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Organometallics,* **1988**, *7*, 787-789.

12. C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young: *Chem. Rev.,* **1993**, *93*, 1371-1448.

13. G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye: *Organometallics,* **1991**, *10(5)*, 1510-1515.

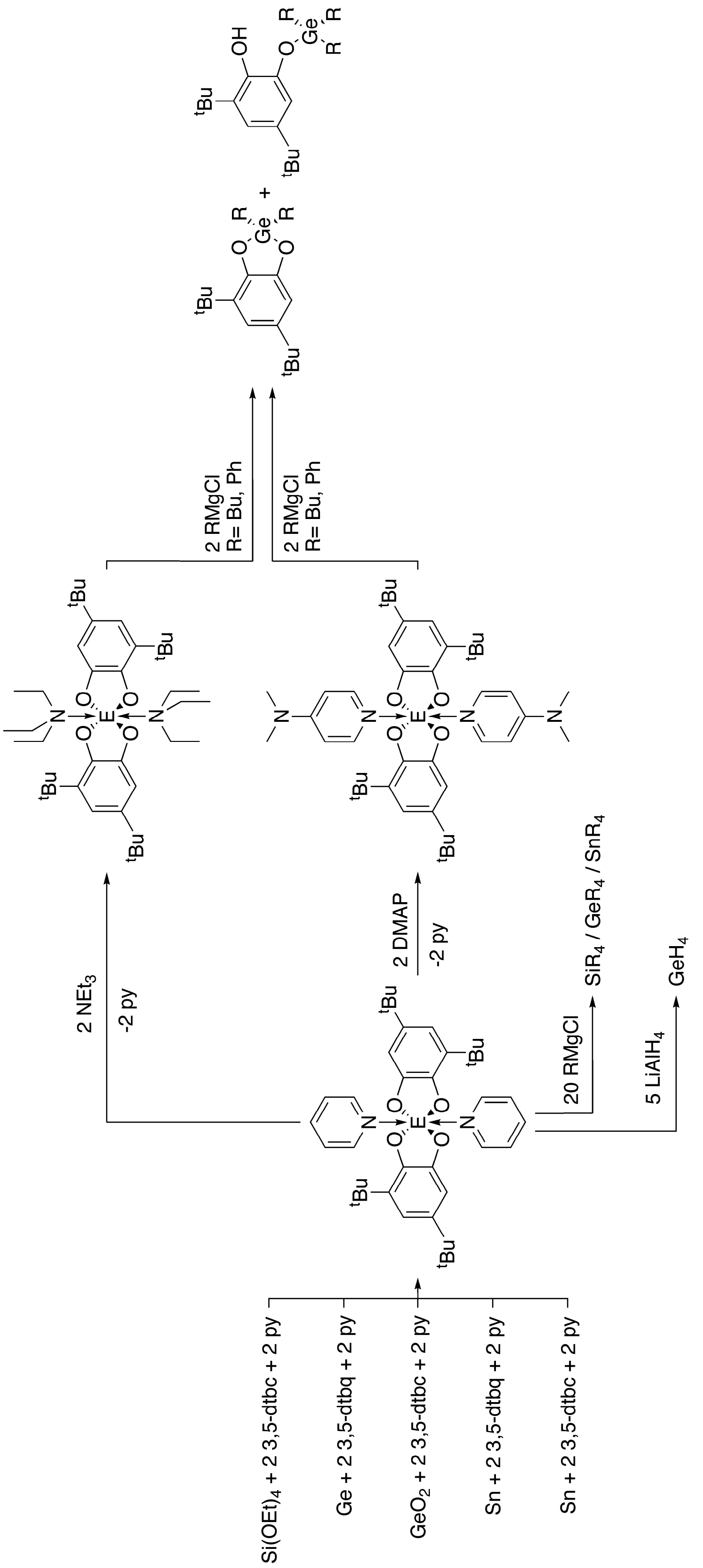
14. Y. Luo: *Comprehensive Handbook of Chemical Bond Energies,* CRC Press, Boca Raton, **2007**.

Chapter 6: Summary, Conclusions, and Future Work

6.1 Summary

In summary, this thesis describes the synthesis of hypercoordinate complexes $E(3,5\text{-dtbc})_2(py)_2$ (E = Si, Ge, Sn) from $Si(OEt)_4$, Ge or GeO_2, or Sn, respectively. The complex $Si(3,5\text{-dtbc})_2(py)_2$ was synthesized from $Si(OEt)_4$ and 3,5-dtbc, using pyridine as the solvent. The complex $Ge(3,5\text{-dtbc})_2(py)_2$ was synthesized from germanium metal using 3,5-dtbq as an oxidant and pyridine as the auxiliary ligand under liquid-assisted grinding (LAG) conditions, and also from germanium dioxide using 3,5-dtbc and pyridine as the solvent. The complex $Sn(3,5\text{-dtbc})_2(py)_2$ was synthesized by the oxidation of tin metal with 3,5-dtbq using pyridine as the solvent, and also by the oxidation of tin metal with 3,5-dtbc with oxygen bubbling through the mixture and pyridine as the solvent (Scheme 6.1).

The complexes $E(3,5\text{-dtbc})_2(py)_2$ (E = Si, Ge, Sn) produced tetraorganosilanes / tetraorganogermanes / tetraorganostannanes in good to excellent yields and excellent purities, in most cases, when reacted with 20 eq of Grignard reagent. The complex $Ge(3,5\text{-dtbc})_2(py)_2$ also produced a high-purity stream of GeH_4, extensively used in the fabrication of electronic devices,[1, 2] when reacted with $LiAlH_4$ using dibutyl ether as the solvent. The tetraorganostannanes produced from $Sn(3,5\text{-dtbc})_2(py)_2$ can be converted to functional stannanes using the Kocheshkov redistribution reaction.[3]



Scheme 6.1: Synthetic overview of this project.

The complexes $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = NEt_3, DMAP) were synthesized from $E(3,5\text{-dtbc})_2(py)_2$ (E = Si, Ge, Sn) by ligand exchange using excess triethylamine or stoichiometric DMAP. All attempts to synthesize these complexes by direct methods from group 14 precursors did not yield any products.

Of the complexes $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP), only $Ge(3,5\text{-dtbc})_2(NEt_3)_2$ and $Ge(3,5\text{-dtbc})_2(DMAP)_2$ yielded di- and mono-functional compounds $R_2E(3,5\text{-dtbc-}\kappa^2)$ and $R_3E(3,5\text{-dtbc-}\kappa^1)$ (for E = Ge, R = Bu, Ph) when reacted with 2 eq of Grignard reagent. More studies are required to determine if conditions exist which will lead to the corresponding mono- and difunctional compounds of silicon, germanium, and tin selectively.

6.2 Conclusions

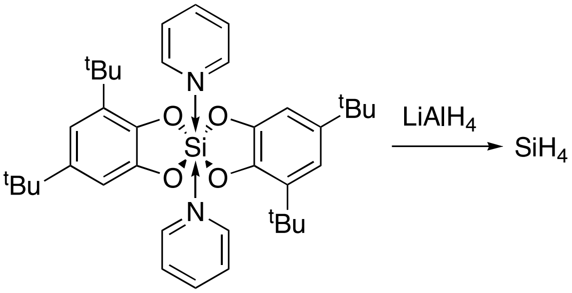
The synthesis of the complexes $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP) conducted in this study, and their application to the synthesis of tetraorganosilanes, tetraorganogermanes, GeH_4, mono- and di-functional organogermanes, and tetraorganostannanes adheres to the Principles of Green Chemistry (POGC), especially POGC points 1: prevention, 3: less hazardous chemical synthesis, 4: designing safer chemicals, and 12: inherently safer chemistry.[4] Less HCl / Cl_2 was used, especially in the functionalization of silicon, germanium, and tin. Less hazardous synthetic methods were employed by using chemicals safer (lower LD_{50} values) than HCl and Cl_2: 3,5-dtbc, 3,5-

dtbq, py, NEt_3, DMAP, $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP). Safer chemicals were designed: the complexes $E(3,5\text{-dtbc})_2(L)_2$ (E = Si, Ge, Sn; L = py, NEt_3, DMAP). Inherently safer chemistry for accident prevention was employed, with overall safer processes, by replacing $SiCl_4$ with $Si(OEt)_4$, leading to the complex $Si(3,5\text{-dtbc})_2(py)_2$, replacing $GeCl_4$ with GeO_2, leading to the complex $Ge(3,5\text{-dtbc})_2(py)_2$, and replacing $SnCl_4$ with Sn, leading to the complex $Sn(3,5\text{-dtbc})_2(py)_2$. Currently, industry relies on improving engineering to improve a process, and not as much on improving the underlying chemistry involved in that process. In this thesis, the chemistry of some processes has been examined and better alternatives offered. In particular, the concepts developed in this thesis offer a cleaner alternative to the current industrial processes used for germanium and tin refining, and present a potential method to recycle germanium and tin scrap, which is very important for critical elements.[5] Also demonstrated was a proof of concept for the cleaner and more environmentally friendly processes from ores to organic compounds of silicon, germanium, and tin. The concepts in this thesis can potentially find applications in the cleaner processing of other elements (e.g. Ga, Zn) as well.

6.3 Future Work

Three concepts that the system developed in this study can potentially be applied to are: 1) the synthesis of pure silane, SiH_4, 2) functionalization of silicon, germanium, and tin precursors E and EO_2 (E = Si, Ge, Sn) to generate complexes that lead to mono-, di-, or trifunctional compounds and 3) functionalization of SiO_2.

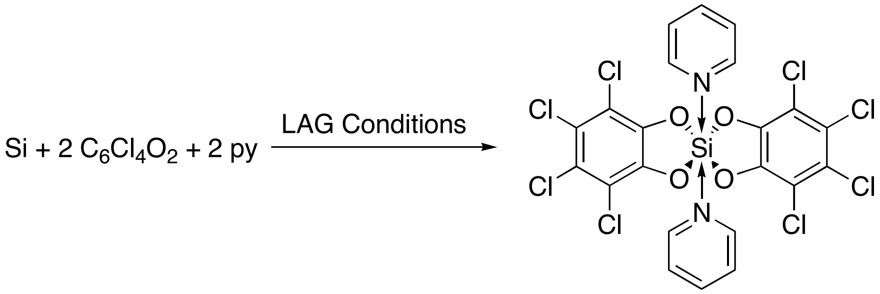
Silicon, pure to at least 99.999999%, is currently manufactured industrially by the chemical vapor deposition of SiH_4,[3, 6] which is generated in situ by the thermal rearrangement of $SiHCl_3$.[3, 6] To reduce the quantity of chlorine in the production of purified silicon, the reaction of Si(3,5-dtbc)$_2$(py)$_2$ with $LiAlH_4$ is proposed (Scheme 6.2), to generate silane.



Scheme 6.2: Synthesis of SiH_4 from Si(3,5-dtbc)$_2$(py)$_2$.

In the functionalization of silicon and tin using the system developed in this study, there are two main variables to explore in the structure of the complexes E(bis-diol)$_2$(L)$_2$: 1) the bis-diol ligand, and 2) the donor ligand (L). Adjusting the steric and electronic properties of the bis-diol may lead to favorable results. The combination of silicon metal with 3,5-dtbq and pyridine under liquid-assisted grinding (LAG) conditions did not produce any products. To overcome this lack of reactivity, the use of a stronger oxidant, $C_6Cl_4O_2$, successfully used by Tuck for the oxidation of tin metal to organometallic compounds,[7, 8] should be explored not only for reactions with tin, but also for reactions with silicon

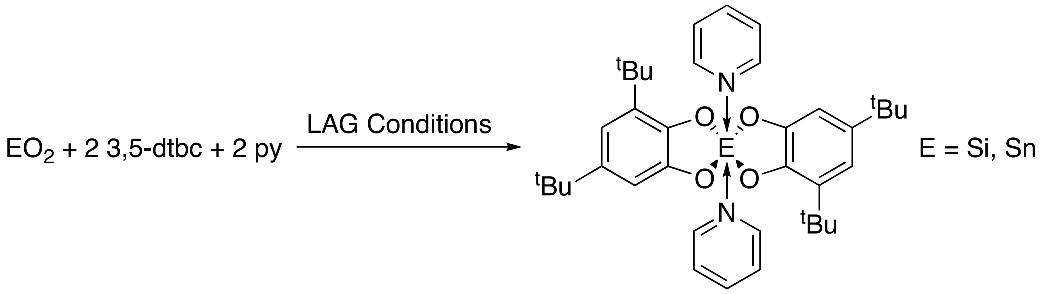
(Scheme 6.3). The complex $Si(C_6Cl_4O_2)_2(py)_2$ could be applied to the synthesis of tetraorganosilanes, mono- or di-functional silanes, and SiH_4.



Scheme 6.3: Synthesis of $Si(C_6Cl_4O_2)_2(py)_2$ from silicon metal and $C_6Cl_4O_2$.

The results obtained from this project suggest that the donor ligand plays an important role in the product distribution of the reaction of complexes E(3,5-dtbc)$_2$(L)$_2$ with organometallic reagents. For E = Ge, it was found that the most useful functionalization of complexes E(3,5-dtbc)$_2$(L)$_2$ came from L = NEt_3, and that the steric bulk of the ligand plays a greater role than the donor ability. Ligands bulkier than NEt_3 should be investigated to determine their influence on the product distributions of the reactions of complexes with organometallic reagents. Variation of the bis-diol ligand may alter the product distribution of the reactions of the complexes with organometallic reagents since by varying the bis-diol ligand, the reactivity of the complexes will be altered. Halogenated catecholato ligands (e.g.- $C_6Cl_4O_2^{2-}$) and butanolato ligands (e.g.- $C_4H_8O_2^{2-}$) are potential candidates because they are more electron-withdrawing and less-electron withdrawing than 3,5-dtbc, respectively. Variation of the organometallic reagent may produce useful results as well. While in this study Grignard reagents were used, there are many other organometallic reagents to explore such as organocuprates, organolithium reagents, and organozinc reagents.

While Corriu *et al.* found a method to functionalize silicon dioxide (SiO_2),[9] it relies on the formation of the salts of the catechols and significant quantities of organic solvents. The reaction of silicon dioxide with stoichiometric quantities of 3,5-dtbc and pyridine, using LAG condtions, to produce Si(3,5-dtbc)$_2$(py)$_2$, is proposed because it would be environmentally more benign to functionalize silicon dioxide (Scheme 6.4), as it requires much lower volumes of solvents. Furthermore, the proposed route has a better atom economy than Corriu's synthesis, so it would be more practical on an industrial scale. The above concept can also be extended to SnO_2 to produce Sn(3,5-dtbc)$_2$(L)$_2$ under LAG conditions. The first reactions to optimize should be the stoichiometric reactions of EO_2 (E = Si, Sn) with 2 eq of 3,5-dtbc and 2 eq of pyridine to yield E(3,5-dtbc)$_2$(py)$_2$, because these reactions have excellent atom economy and low quantities of waste. Variables to investigate include reaction time, the addition of various LAG solvents, and the addition of catalytic reagents such as salts.



Scheme 6.4: Synthesis of E(3,5-dtbc)$_2$(py)$_2$ (E = Si, Sn) from SiO_2 or SnO_2, 3,5-dtbc, and py.

6.4 References

1. R. Russotti: Method of Synthesis of Gaseous Germane: US4668502, **1987**.

2. H. P. Withers, P. B. Henderson: Production and Purification of Germane: US20050191854, **2005**.

3. W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville, F. Ullmann: *Ullmann's Encyclopedia of Industrial Chemistry,* VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany; Deerfield Beach, Fla, **1985**.

4. P. Anastas, N. Eghbali: *Chem. Soc. Rev.,* **2010**, *39*, 301-312.

5. C. Licht, L. T. Peiró, G. Villalba: *J. Ind. Ecol.,* **2015**, *19*, 890-903.

6. R. E. Kirk, D. F. Othmer, J. I. Kroschwitz, M. Howe-Grant: *Encyclopedia of Chemical Technology*, Wiley, New York, **1991**.

7. T. A. Annan, B. R. McGarvey, A. Ozarowski, D. G. Tuck, R. K. Chadha: *J. Chem. Soc., Dalton Trans.,* **1989**, 439-446.

8. T. A. Annan, D. G. Tuck: *Can. J. Chem.,* **1989**, *67*, 1807-1814.

9. C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young: *Chem. Rev.,* **1993**, *93*, 1371-1448.

Chapter 7: Apppendix

7.1 Appendix to Chapter 2

Figure 7.1: Submitted cover art for the publication “A Chlorine-Free Protocol for Processing Germanium”.

7.2 Appendix to Chapter 3

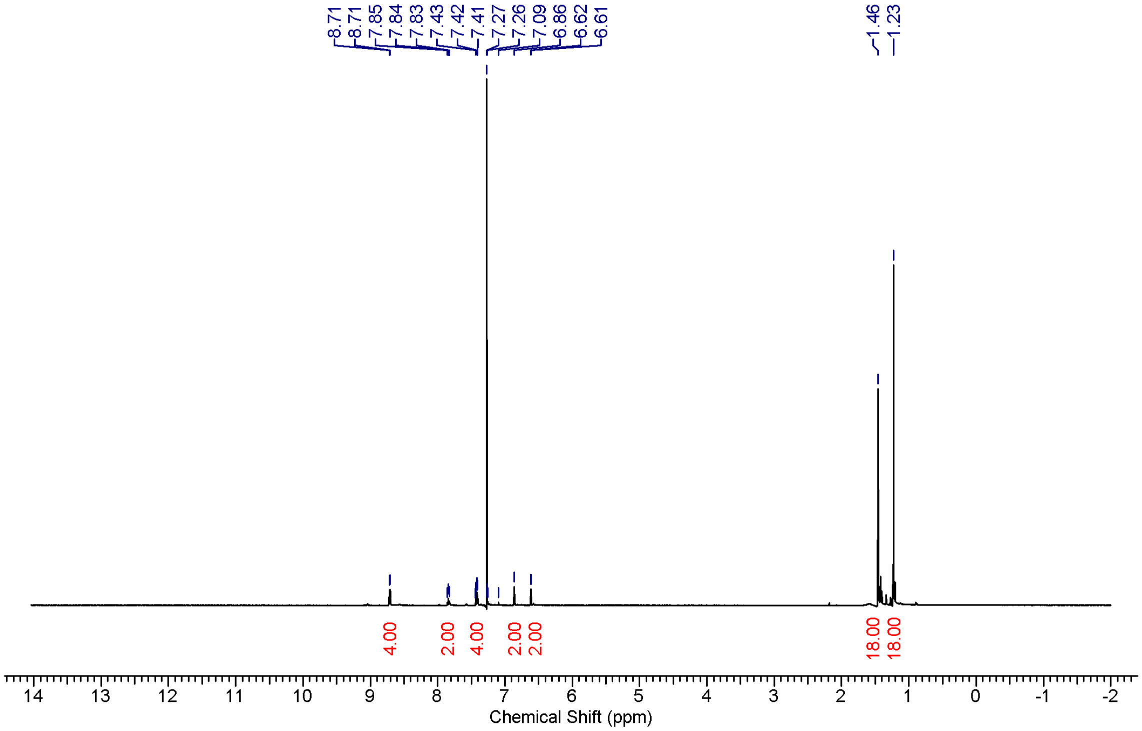


Figure 7.2: ^{1}H NMR spectrum (600 MHz) of Sn(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$.

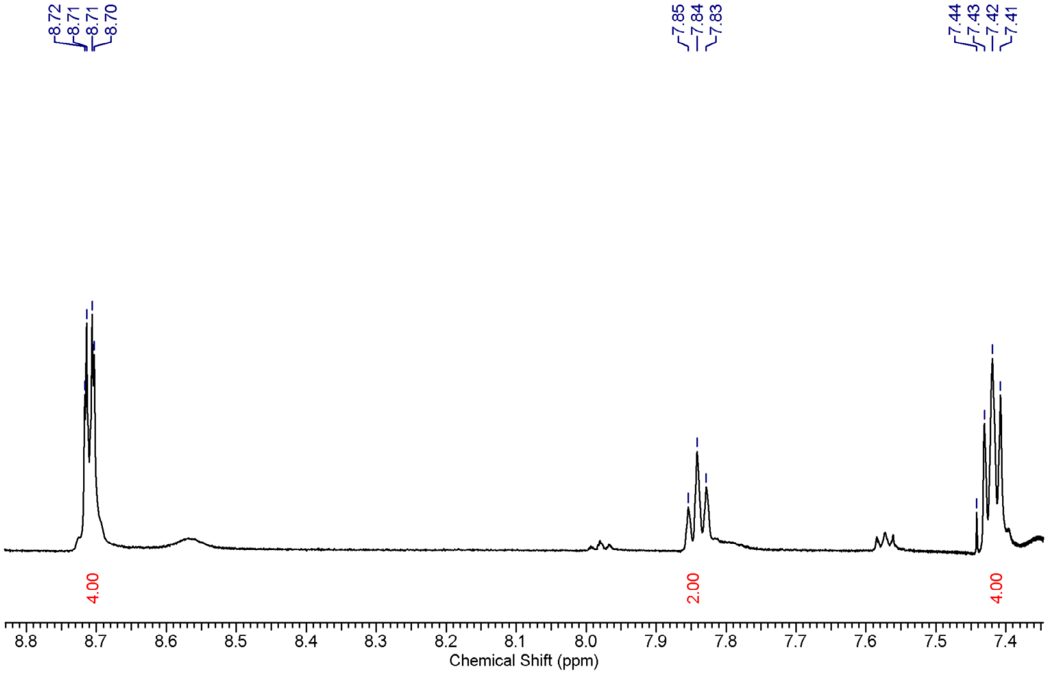


Figure 7.3: ^{1}H NMR spectrum (600 MHz) of Sn(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$ from 8.80 – 7.30 ppm.

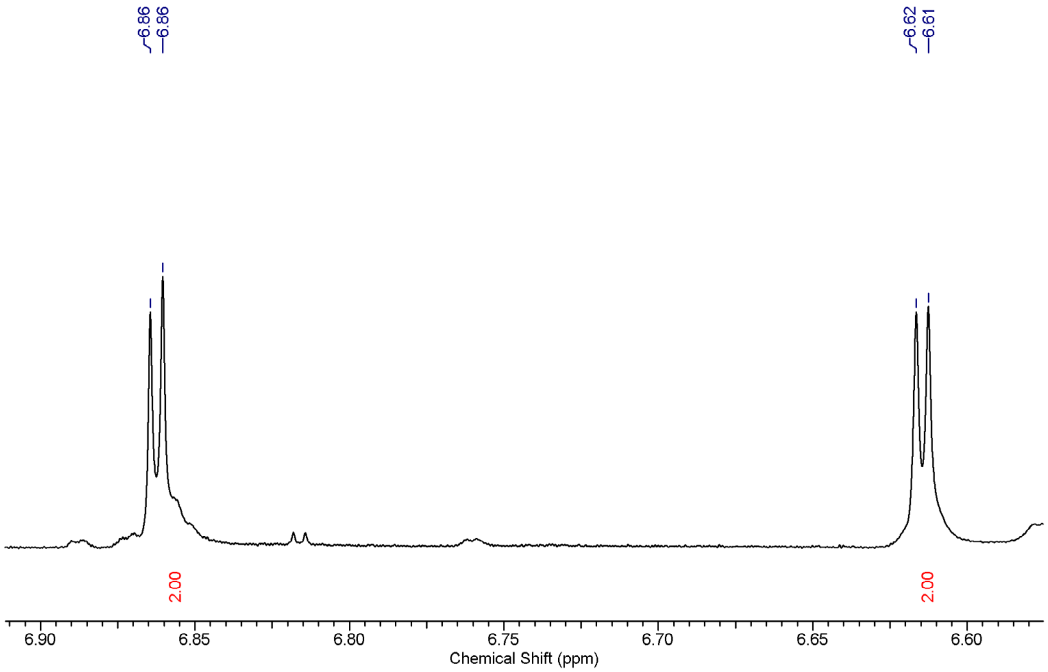


Figure 7.4: ^{1}H NMR spectrum (600 MHz) of Sn(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$ from 6.90 – 6.60 ppm.

Table 7.1: ^{13}C{^{1}H} NMR Shifts (CDCl$_3$) of GeR$_4$ vs. SnR$_4$.

^{13}C NMR Shifts (CDCl$_3$) of GeR$_4$ vs. SnR$_4$		
ER$_4$	E = Ge	E = Sn
EBu$_4$	27.52, 26.68, 13.80, 12.45	29.27, 27.41, 13.72, 8.75
EPh$_4$	136.08, 135.38, 129.08, 128.25	137.89, 137.22, 129.12, 128.62
EBz$_4$	139.80, 128.38, 128.28, 124.28, 21.50	141.46, 128.54, 127.41, 123.60, 18.82
EHx$_4$	33.41, 31.60, 25.24, 22.68, 14.15, 12.82	34.15, 31.52, 26.97, 22.67, 14.15, 9.10
E(CH$_2$CH=CH$_2$)$_4$	135.05, 113.16, 19.04	136.56, 111.07, 16.13
ETol$_4$	138.69, 135.31, 132.99, 128.98, 21.45	138.76, 137.14, 134.43, 129.37, 21.49
E^{s}Bu$_4$	—	29.30-29.00 (m), 22.95-22.70 (m), 18.50-18.20 (m), 14.55-14.15 (m)

Table 7.2: $^{119}Sn\{^1H\}$ NMR Shifts of SnR_4 Compounds.

^{119}Sn NMR Shifts ($CDCl_3$) of SnR_4		
SnR_4	Literature Value	This Work
$SnBu_4$	δ ^{119}Sn = -11.5 ppm (relative to δ ^{119}Sn $SnMe_4$ = 0 ppm), $J_{Sn\text{-}H}$ = 48.3 Hz[1]	-11.6 ($J_{Sn\text{-}H}$ = 49.3 Hz)
$SnPh_4$	δ ^{119}Sn = -129.6 ppm[2]	-129.5 ($J_{Sn\text{-}H}$ = 14.0 Hz)
$SnBn_4$	—	-36.0 ($J_{Sn\text{-}H}$ = 61.5 Hz)
$SnHx_4$	—	-12.2 ($J_{Sn\text{-}H}$ = 50.0 Hz)
Sn $(CH_2CH{=}CH_2)_4$	δ ^{119}Sn = -48 ppm, $J_{Sn\text{-}H}$ = 63 Hz[3]	-46.7 ($J_{Sn\text{-}H}$ = 61.9 Hz, 41.5 Hz, 21.5 Hz)
$SnTol_4$	δ ^{119}Sn = -123.0 ppm, $J_{Sn\text{-}C}$ = 536.6, 52.4, 38.2, 12.7 Hz[4]	-123.6 ($J_{Sn\text{-}H}$ = 46.6 Hz, 12.7 Hz)
$Sn^{s}Bu_4$	—	-44.5, -44.7, -45.0
$SnMes_4$	—	—

7.3 Appendix to Chapter 4

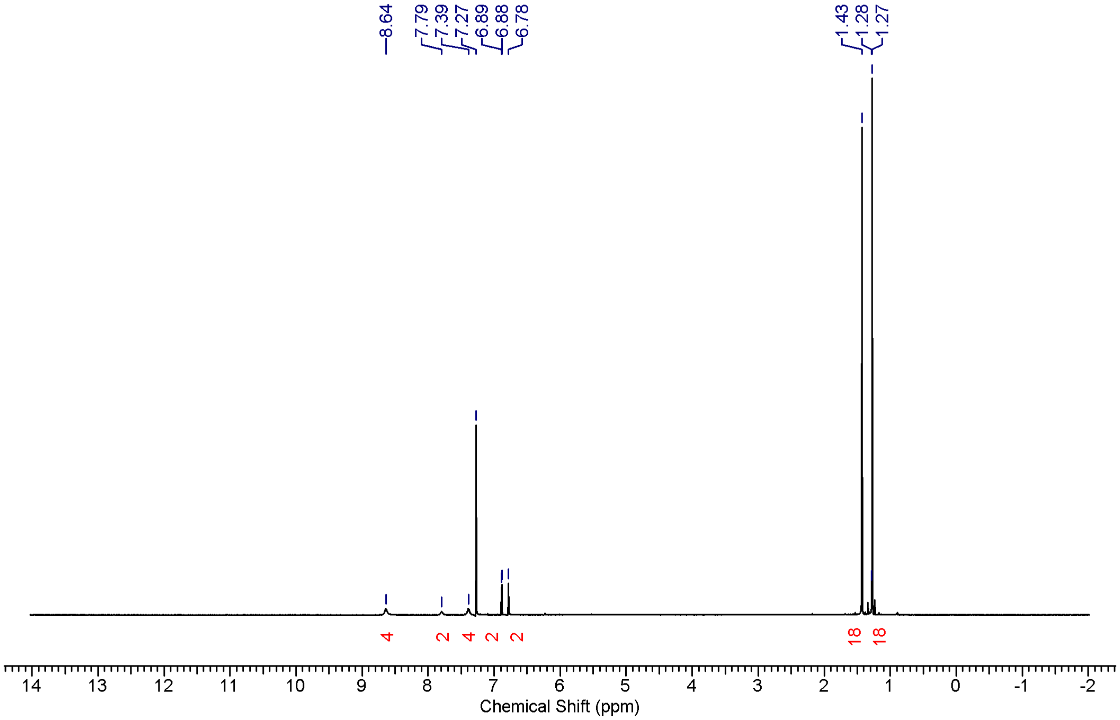


Figure 7.5: ^{1}H NMR spectrum (600 MHz) of Si(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$.

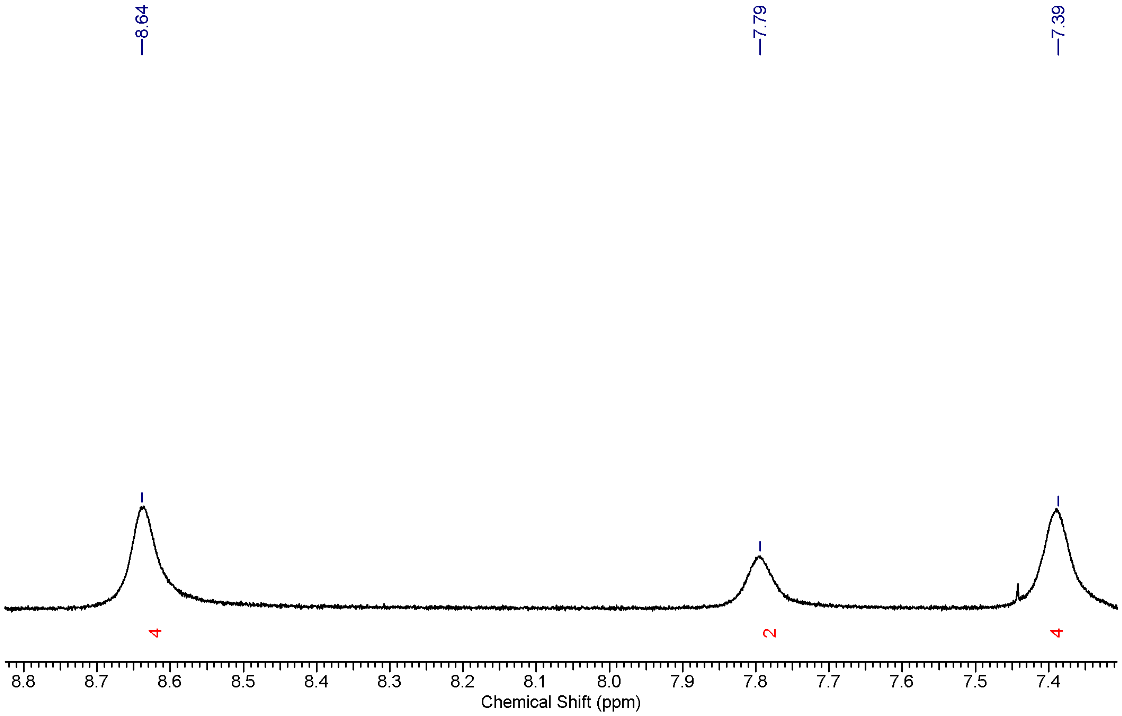


Figure 7.6: ^{1}H NMR spectrum (600 MHz) of Si(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$ from 8.80 ppm – 7.30 ppm.

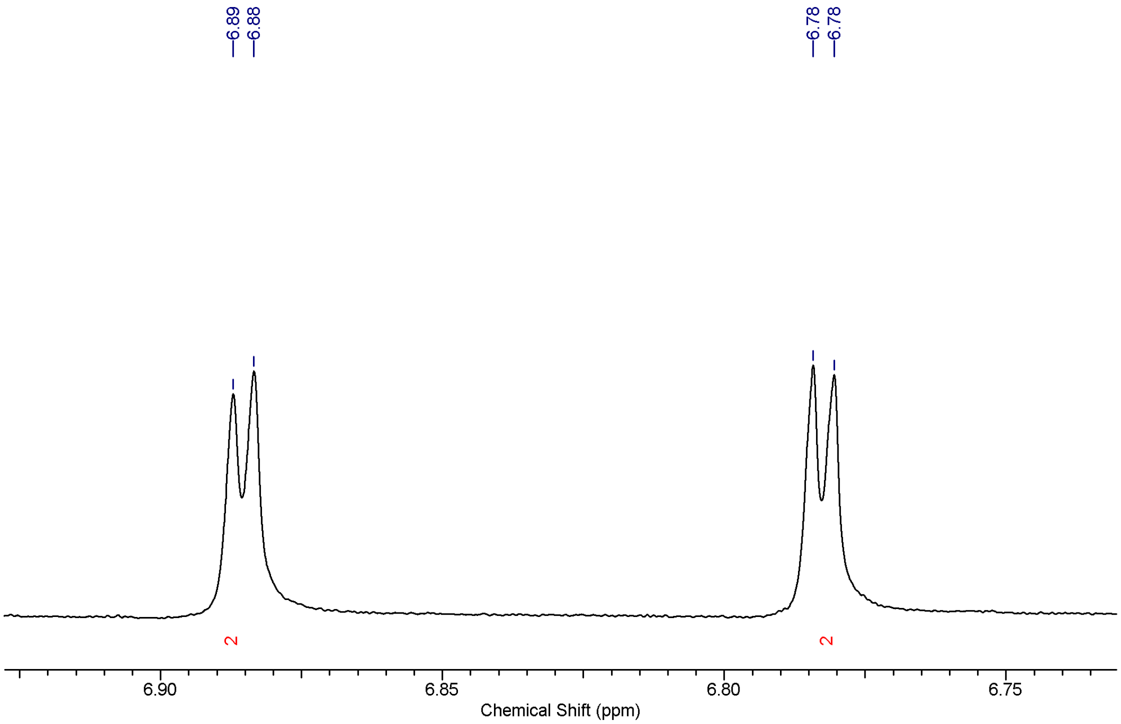


Figure 7.7: ^{1}H NMR spectrum (600 MHz) of Si(3,5-dtbc)$_2$(py)$_2$ in $CDCl_3$ from 6.90 ppm – 6.75 ppm.

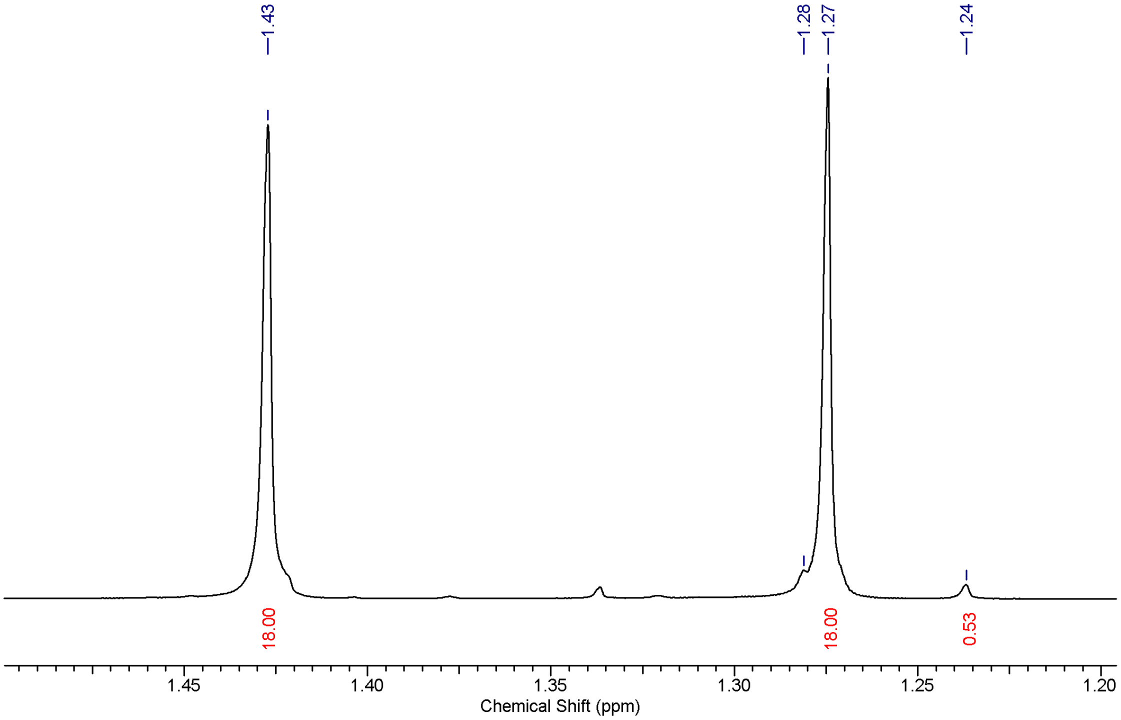


Figure 7.8: ^{1}H NMR spectrum (600 MHz) of Si(3,5-dtbc)$_2$(py)$_2$ in $CDCl_3$ from 1.50 ppm – 1.20 ppm.

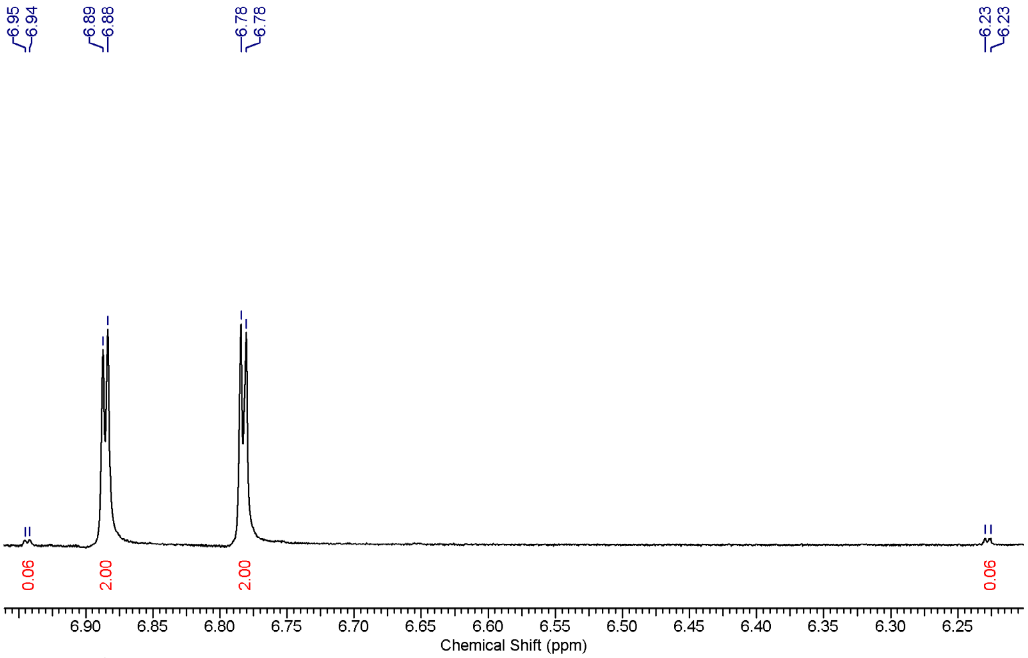


Figure 7.9: ^{1}H NMR spectrum (600 MHz) of Si(3,5-dtbc)$_2$(py)$_2$ in CDCl$_3$ from 7.00 ppm – 6.20 ppm.

7.4 Appendix to Chapter 5

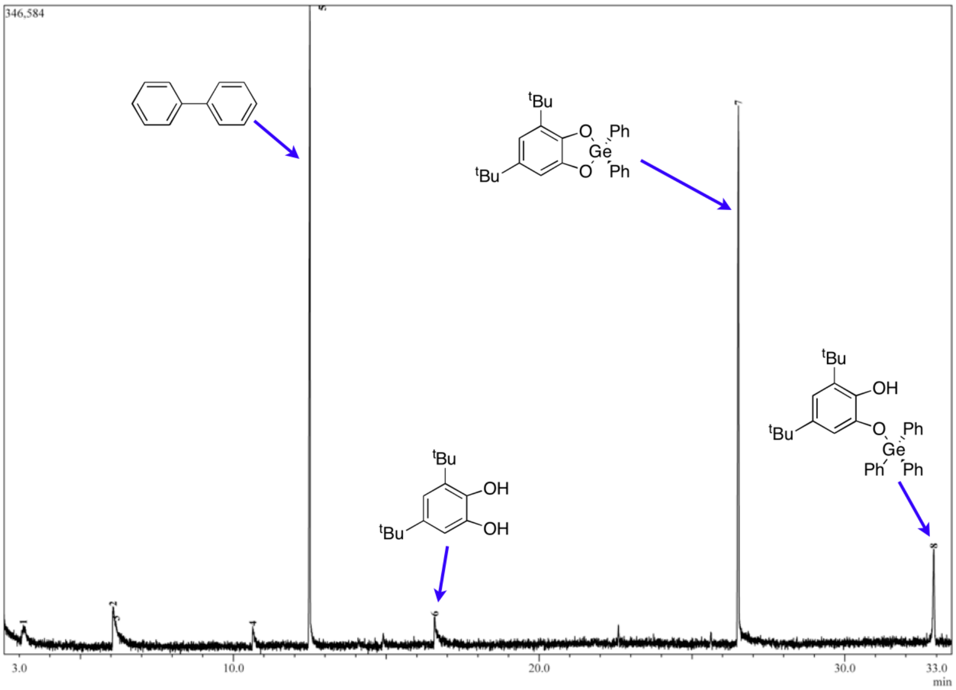


Figure 7.10: Chromatogram of the reaction of Ge(3,5-dtbc)$_2$(NEt$_3$)$_2$ with 2 eq of PhMgCl.

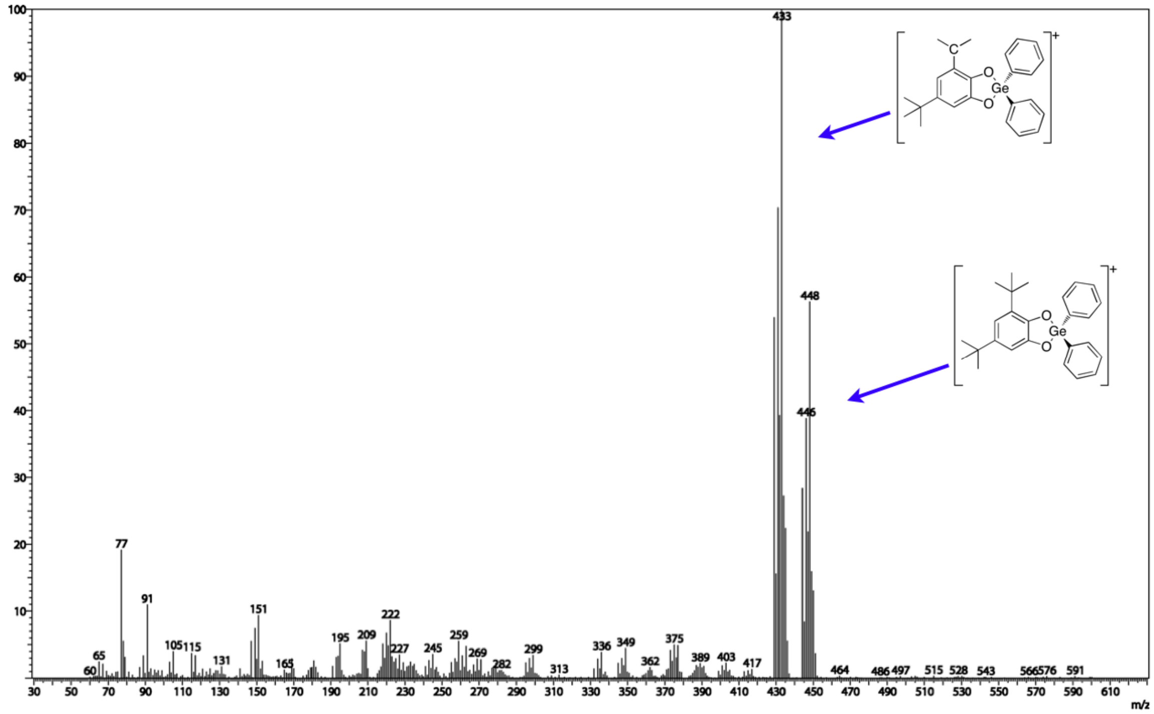


Figure 7.11: EI Mass spectrum of $Ph_2Ge(3,5\text{-dtbc-}\kappa^2)$.

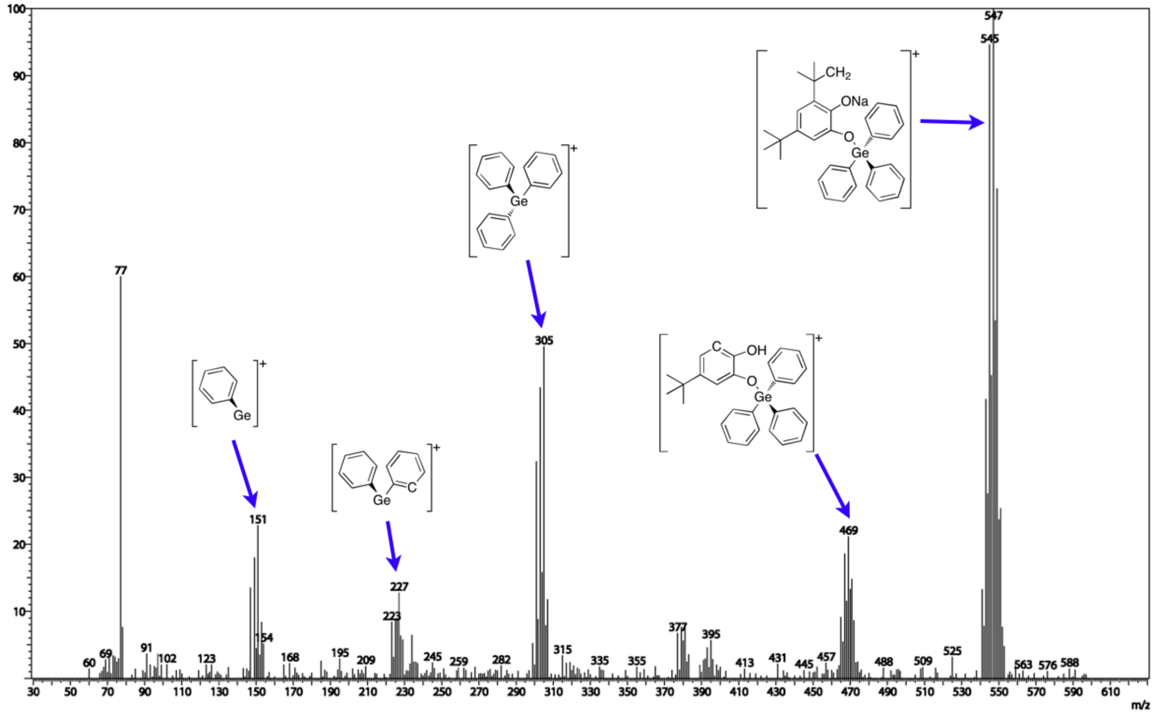


Figure 7.12: EI Mass spectrum of $Ph_3Ge(3,5\text{-dtbc-}\kappa^1)$.

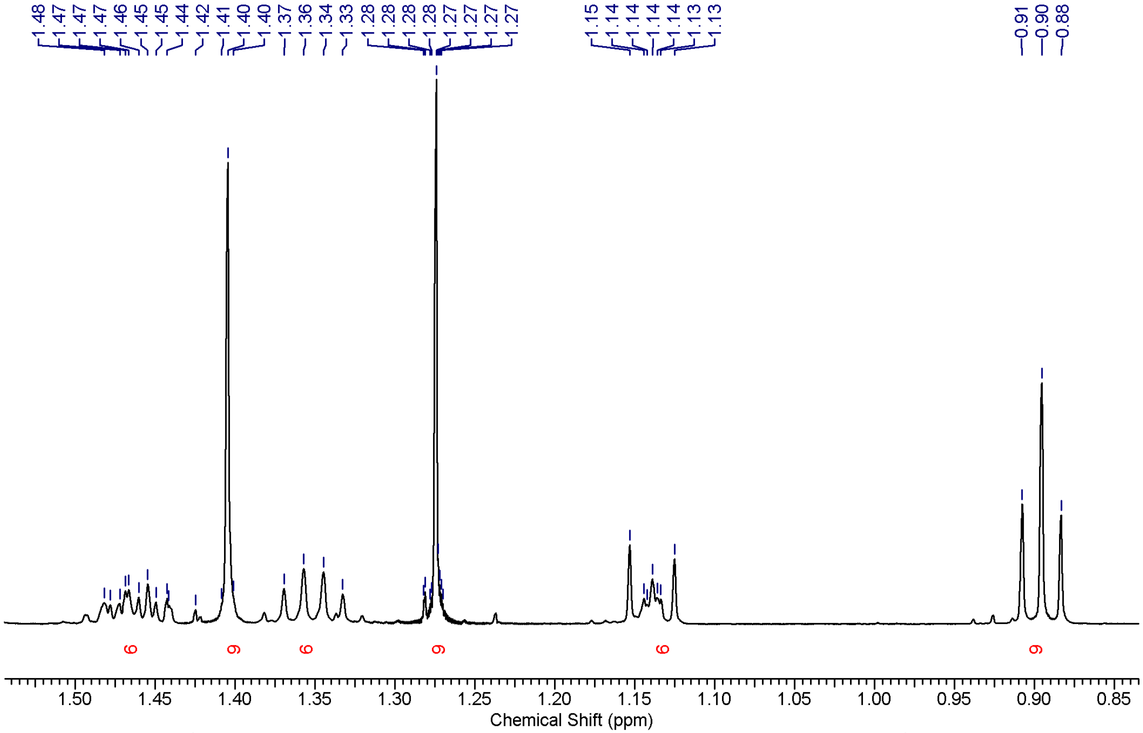


Figure 7.13: ^{1}H NMR spectrum (600 MHz) of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ from 1.55-0.85 ppm in $CDCl_3$.

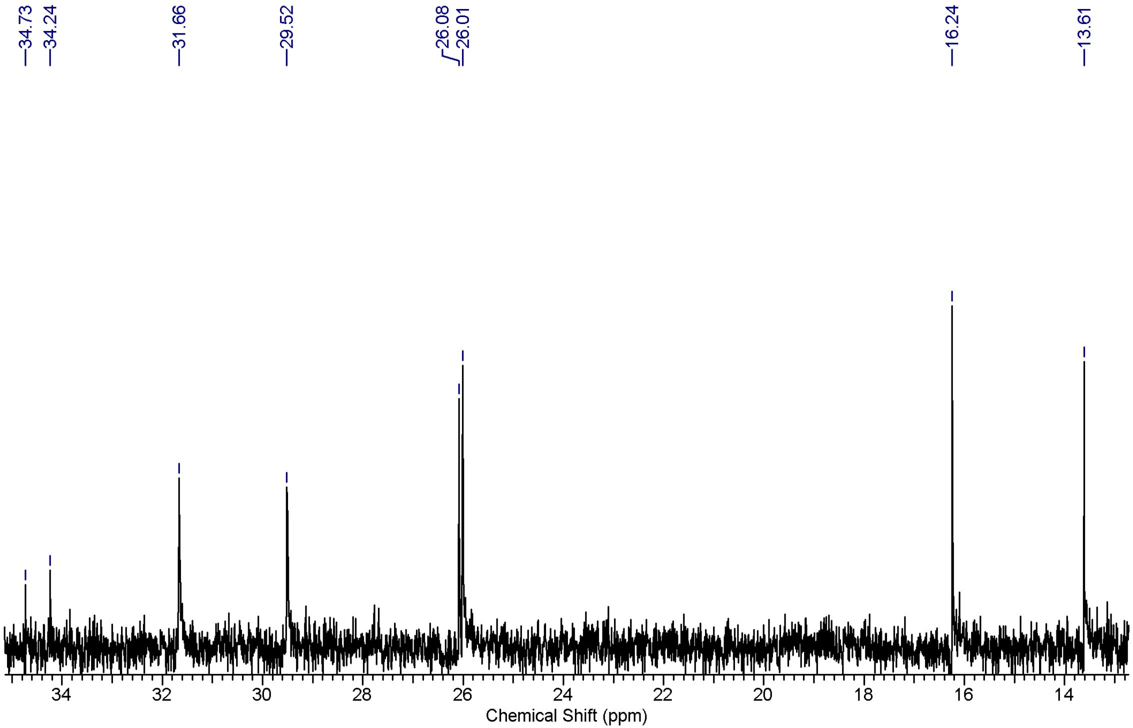


Figure 7.14: $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of $Bu_3Ge(3,5\text{-dtbc-}\kappa^1)$ from 35.0-13.0 ppm in $CDCl_3$.

7.5 References

1. W. F. Howard Jr., R. W. Crecely, W. H. Nelson: *Inorg. Chem.,* **1985**, *24*, 2204-2208.

2. A. Khan, R. A. Gossage, D. A. Foucher: *Can. J. Chem.,* **2010**, *88*, 1046-1052.

3. Y. Naruta, Y. Nishigaichi, K. Maruyama: *Tetrahedron,* **1989**, *45*, 1067-1078.

4. I. Wharf: *Inorg. Chim. Acta,* **1989**, *159*, 41-48.

7.6 Curriculum Vitae

Michael J. Krause

Education

- Ph.D. University of Western Ontario (2017), “A Chlorine-Free Protocol for Processing Silicon, Germanium, and Tin”, supervised by Dr. Kim M. Baines.
- M.Sc. University of Guelph (2011), “Sterically Demanding Ethylenediamines and Polyamines for the Stabilization of Main Group Elements in Low Coordination Numbers”, supervised by Dr. Michael K. Denk.
- Hon. B.Sc. University of Toronto (2003), Chemistry major, Mathematics minor.

Publications and Presentations

- M. Glavinović, M. Krause, L. Yang, J.A. McLeod, L. Liu, K.M. Baines, T. Friščić, and J.-P. Lumb: A Chlorine-Free Protocol for Processing Germanium: *Sci. Adv.*, **2017**, *3*, e1700149.
- Michael K. Denk, Mike J. Krause, Debyani F. Niyogi and Nachhattarpal K. Gill: *Tetrahedron*, **2003**, *59*, 7565-7570 (Reaction of 1,2-dibromoethane with primary amines: formation of N,N′-disubstituted ethylenediamines $\mathrm{RNH\text{-}CH_2CH_2\text{-}NHR}$ and homologous polyamines $\mathrm{RNH\text{-}[CH_2CH_2NR]_n\text{-}H}$).

- 14th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead (Inverary Resort, Baddeck, Nova Scotia, 2013): "Synthesis of Bis N – Heterocyclic Carbene Germanium Dichloride Complexes from Bis N – Heterocyclic Carbenes" (poster).
- 42nd Inorganic Discussion Weekend (University of Guelph, 2009): "Stabilization of Low Coordination Numbers with Polyamines" (poster).

Teaching Experience

Teaching Assistant: instructed and supervised first year general chemistry laboratories (four semesters) and second year organic chemistry laboratories (9 semesters).

Research Related Skills

- Experience manipulating air sensitive compounds using both a glove box and Schlenk line.
- Characterization of compounds by IR spectroscopy, mass spectrometry, and NMR spectroscopy.
- Compounded formulas from 10 mg scale to 1 kg scale to 100 kg scale.
- Designed, manufactured and repaired laboratory glassware.