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Investigation And Study Of Monomers And Polymers Based On Known Metal Induced Couplings Of Alkynes And Diynes

Jesse Quinn
Ryerson University

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**INVESTIGATION AND STUDY OF MONOMERS AND POLYMERS BASED ON
KNOWN METAL INDUCED COUPLINGS OF ALKYNES AND DIYNES**

by

**Jesse Quinn
B.Sc., Ryerson University, 2010**

A thesis

presented to Ryerson University

in partial fulfillment of the

requirements for the degree of

Master of Science

in the program of

Molecular Science

Toronto, Ontario, Canada, 2013

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INVESTIGATION AND STUDY OF MONOMERS AND POLYMERS BASED ON KNOWN METAL INDUCED COUPLINGS OF ALKYNES AND DIYNES

Jesse Quinn

Master of Science, Molecular Science, Ryerson University 2013

Abstract

Both reduced zirconocene ("Cp₂Zr") and zero valent lithium are known to induce coupling of alkynes to form dimers, oligomers, and polymers. Established work from Fagan *et al.*, Tilley *et al.*, and Eisch *et al.* was used as the basis for the synthesis of desired targets. First, the attempted syntheses of novel Group IV metallocenes from a zirconocene intermediate were studied. There was no conclusive data to state that 2,3,4,5-tetraphenylzirconacyclopentadiene will undergo metallacycle transfer with CrCl₃ and FeCl₃. The presence of zirconocene dichloride suggests that metallacycle transfer may have occurred, which warrants further investigation. Monomers, 1-bromo-4-hex-1-ynyl-benzene, 1-bromo-3-(phenylethynyl)benzene, and *p*-dihex-1-ynylbenzene, were synthesized successfully *via* Sonogashira coupling. Attempts to synthesize novel monomers *via* lithium and "Cp₂Zr" had mixed results. ¹H NMR acquisition of the hydrolyzed product from zirconocene-coupling of 1-bromo-3-(phenylethynyl)benzene appeared to be successful. Lastly, lithium and "Cp₂Zr" induced polymerization of novel monomers and known monomers were attempted. Metallacycle transfer from the zirconocene intermediate polymers to thiophene, thiopheneoxide, thiophenedioxide, and phosphole were attempted. However, limited characterization was completed. ¹H NMR acquisitions suggest polymer by the loss of resolution and broadening of resonance signals, but further characterization *via* GPC is required. Monomers, and polymers were characterized using various means such as ¹H, ¹³C, ³¹P, ¹¹⁹Sn NMR spectroscopy, UV-Vis spectroscopy, AIMS AccuTOF-DART mass spectrometry and GPC.

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List of Abbreviations

TOF-DART	Time of Flight-Direct Analysis in Real Time
BIPY	2,2'-Bipyridine
<i>n</i> -BuLi	<i>n</i> -Butyllithium
CB[5]	Cucurbituril ([5] refers to 5 glycoluril units)
CB[6]	Cucurbituril ([6] refers to 6 glycoluril units)
CB[7]	Cucurbituril ([7] refers to 7 glycoluril units)
CB[8]	Cucurbituril ([8] refers to 8 glycoluril units)
CI	Chemical Ionization
α -CD	Cyclodextrin (α - refers to 6-membered sugar ring molecule)
β -CD	Cyclodextrin (β - refers to 7-membered sugar ring molecule)
γ -CD	Cyclodextrin (γ - refers to 8-membered sugar ring molecule)
Cp	Cyclopentadienyl Ring
COD	1,5-Cyclooctadiene
DCM	Dichloromethane
DMAC	Dimethylacetamide
DMF	Dimethylformamide
EA	Elemental Analysis
EDG	Electron-Donating Group
EI	Electron Ionization
EtOH	Ethanol
Et ₃ N	Triethylamine
EWG	Electron-Withdrawing Group
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
H ₂ O	Water
HF	Hydrofluoric Acid
HPLC-MS	High Performance Liquid Chromatography
LUMO	Lowest Unoccupied Molecular Orbital
MeOH	Methanol
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance Spectroscopy

PDI	Polydispersity Index
Pen	Pentane
Pyr	Pyridine
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
Tol	Toluene
UV-Vis/UV	Ultraviolet-Visible Radiation/Ultraviolet Radiation

1 Introduction

Since the early 1990s major synthetic efforts have been extended towards producing materials (*e.g.* conductors, semiconductors, and insulators) that are based on the assembly of oligomers, macrocycles, and polymers that create well defined structures and present novel properties (*e.g.* magnetic, electrical, optical, catalytic, polarizability, small band gaps, or low lying LUMOs).¹⁻¹² Transition metal-mediated coupling reactions, which use rare metals like palladium, rhodium, or ruthenium are typically required to produce such materials.^{1,13} However, a new class of metal containing macromolecules including oligomers, macrocycles, and polymers that utilize Group *IVB* transition metals such as titanium, zirconium, and hafnium has been established.¹⁴⁻¹⁷ These novel metal containing macromolecules have attracted much attention due to their useful properties (*e.g.* magnetic, electrical, optical, and catalytic) that are created by the transition metal fragments within their structure.¹ These macromolecules incorporate stoichiometric amounts of transition metal moieties so that the final macromolecule provides a versatile pathway for post-modification to synthesize other structurally interesting and potentially useful macromolecules.^{1,14-17}

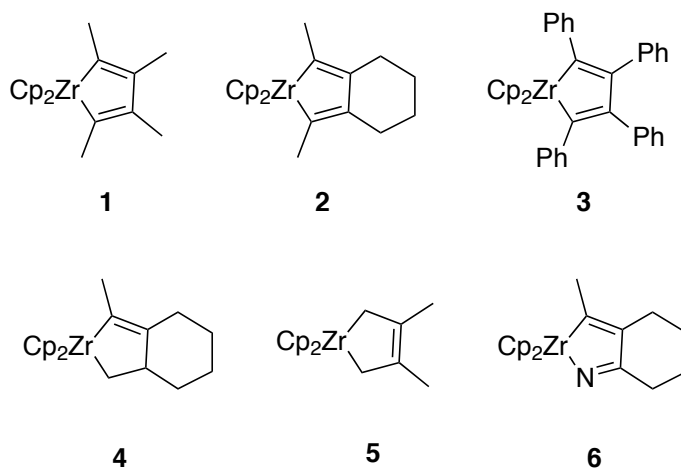
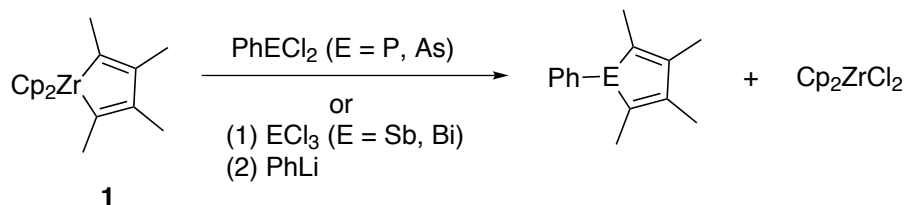


Figure 1: Zirconium metallacycles prepared by Nugent *et al.* for the preparation of a variety of main group heterocycles.¹⁸



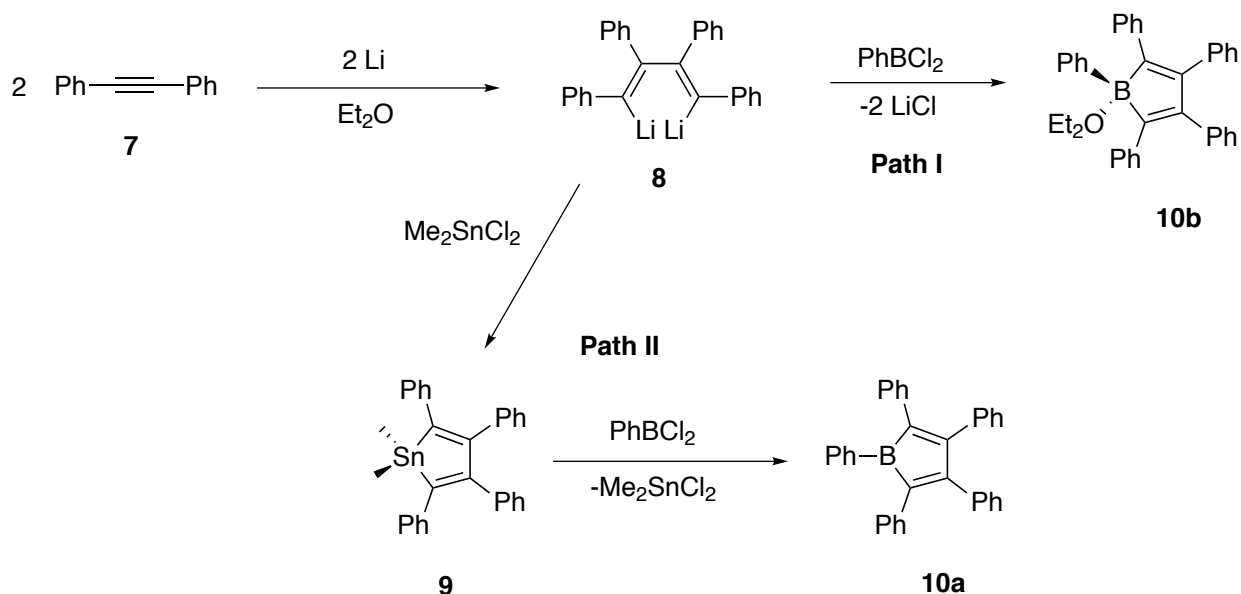
Scheme 1: Zirconium metallacycle (1) was used to prepare several main group heterocycles with 70% to 85% yield.¹⁸

Group *IVB* transition metal-based compounds such as zirconium metallacycles (see Figure 1) have been successfully used as intermediates in organic synthesis. They present a versatile pathway to synthesize main group heterocycles and metallacycles based on the coupling of alkenes and alkynes (see Scheme 1).^{19,20} Similarly, Group *IVB* metal-based compounds have been utilized as catalysts for the polymerization of olefins and alkynes (*i.e.* as Ziegler-Natta homogeneous catalysts).^{1,13,21–23} Alternatively, rare earth metals and other metallocenes (*e.g.* cobaltocene derivatives) have been studied for similar purposes.^{13,24,25}

Another type of alkyne coupling, which uses lithium metal, will also be discussed. Very little research has been established in this area.

1.1 Electrophilic substitution (metallacycle transfer)

While electrophilic substitution is by no means a new concept, Fagan *et al.*, and Tilley *et al.* have established a novel and versatile electrophilic substitution mechanism, also known as metallacycle transfer, utilizing zirconium metallacycles (see Scheme 1).^{1,18,19} The mechanism provides a useful synthetic route to main group heterocycles (Group *IIIA* to *VIA* elements) and metallacycles (Group *IVB* elements) which were once thought not possible or difficult to synthesize.¹⁹ Alternatively, Eisch *et al.* have studied the use of stannoles (**9**) as intermediates for metallacycle transfer to form synthetically challenging boroles (**10a**) (see **Error! Reference source not found.**).²⁶

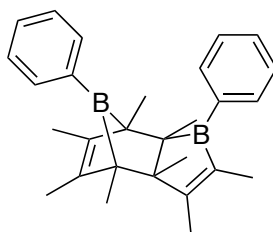


Scheme 2: Eisch *et al.* synthetic routes to form a borole. Unsolvated and etherate forms.²⁶

Eisch *et al.* were able to synthesize rare and highly reactive boroles *via* two methods. The first method (see Scheme 2 Path I) used a 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene reagent (**8**) as an intermediate, which reacted with PhBCl_2 to form a borole etherate (**10b**). The second method (see Scheme 2 Path II) used a stannole intermediate (**9**) that underwent metallacycle transfer with PhBCl_2 to create a unsolvated borole (**10a**).²⁶

1.1.1 A brief discussion of zirconium metallacycles and similar metallacycles

It was originally thought that Diels-Alder addition of acetylenes would be an useful reaction to form novel heterocyclic compounds.¹⁹ It was reported in 1988 by Mathey *et al.* (related to phospholes) and in 1990 by Dubac *et al.* (related to Group *VA* elements in general) that the Diels-Alder addition of acetylenes had low yields.^{27,28} It was in 1994 that Fagan *et al.* studied the metallacycle transfer approach from zirconium metallacycles (see Scheme 1) and reported that it was superior to the alternative Diels-Alder route. A variety of heteroles, incorporating Group *IIIA* to Group *VIA* elements, were synthesized with simplified procedures and yields from low to high (28% to 89%). However, a majority of synthesized targets had moderate to high yields (70% to 89%). Even the rare Diels-Alder borole dimer (**11**) of 1-phenyl-2,3,4,5-tetramethylborole was isolated at 68% *via* the metallacycle transfer approach (see Figure 2). Due to the limited number of synthetic routes to these boron systems, only Eisch *et al.* and Herberich *et al.* have successfully synthesized stable boroles, metallacycle transfer from zirconium metallacycles has promoted further research into Group *IVB* elements and other transition metal-based metallocenes to act as intermediates for similar reactions.^{19,29} For instance, reduced titanocene has been used to couple alkynes to form titanium metallacycles that can act as intermediates similar to zirconium metallacycles.^{21,30} Alternatively, a cobaltocene derivative (*e.g.* $\text{CoCp}(\text{PPh}_3)_2$) has been used to couple buta-1,3-diyne to form various oligomers and polymers.³¹⁻³³ In addition, polymerization of acetylenes *via* zirconocene dichloride and ethylaluminum dichloride has been studied.²² These metallocenes and more have been studied since 1995.¹³

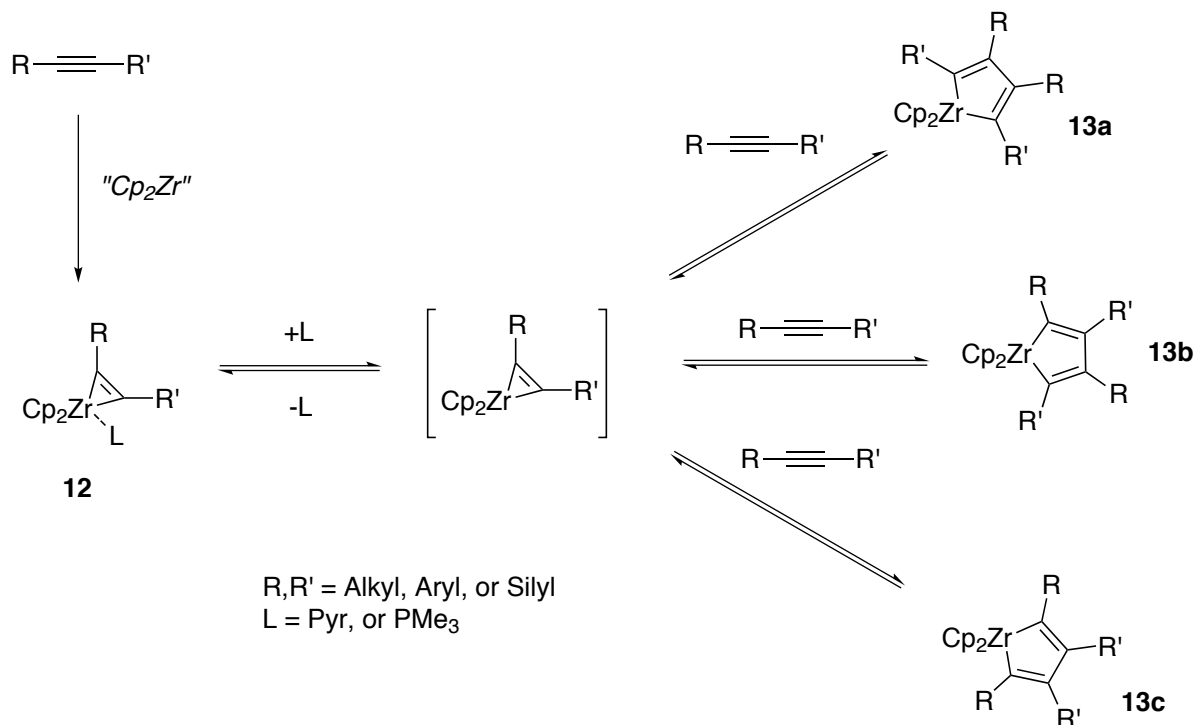


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Figure 2: Diels-Alder dimer of 1-phenyl-2,3,4,5-tetramethylborole.¹⁹

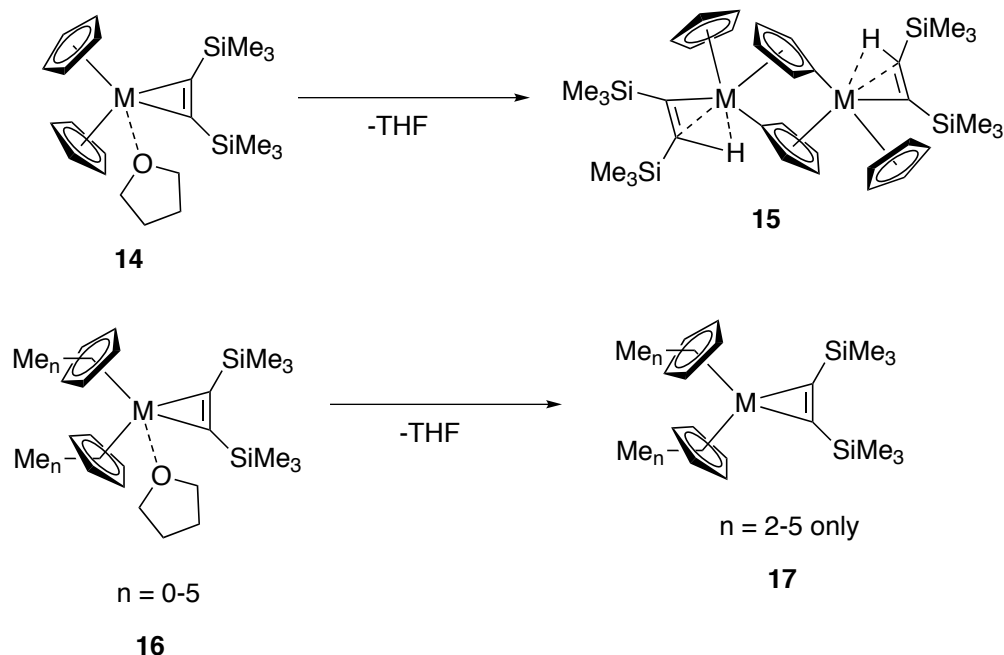
1.1.1.1 Zirconocene-coupling stability, mechanism, and reversibility of such couplings

In 2008, the mechanism of zirconocene-coupling of alkynes was studied. It was assumed that zirconocene-coupling of alkynes occurs in a stepwise fashion due to evidence that some zirconium metallacycles react with a Lewis base (*e.g.* pyridine or trimethylphosphine) to eliminate one equivalent of alkyne to form a base-stabilized zirconacyclopropene (**12**) (see Scheme 3).³⁴



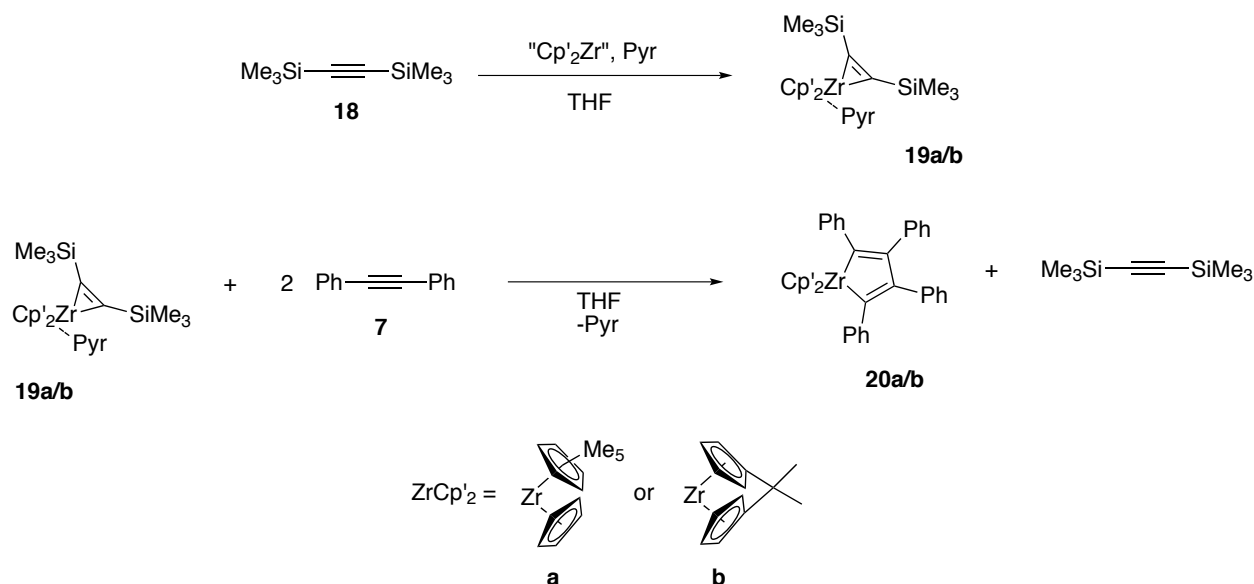
Scheme 3: Tilley *et al.* study of the regio-selective and reversible zirconocene-coupling mechanism.³⁴

Similarly, zirconium or titanium-based metallocenes with ancillary ligands like $C_5H_{5-n}Me_n$ ($n = 0 - 2$), have known η^2 -complexes with $C_2(SiMe_3)_2$ and are stabilized by solvents like THF (see Scheme 4). The lone pair of electrons on the oxygen of THF coordinates with the metallocene moiety (*i.e.* $M = Ti$, or Zr), which has been supported by both X-ray crystallography and NMR spectroscopy.^{35,36} For either metallocene moiety, the dimerized product (**15**) is easily obtained when the ancillary ligands have no methyl substituents present or when the ancillary ligands have few methyl substituents ($n = 1 - 2$) with the loss of THF. However, with methyl substituents ($n = 2 - 5$) present on the ancillary ligands a shielding effect from dimerization occurs and are stable without THF.^{35,37}



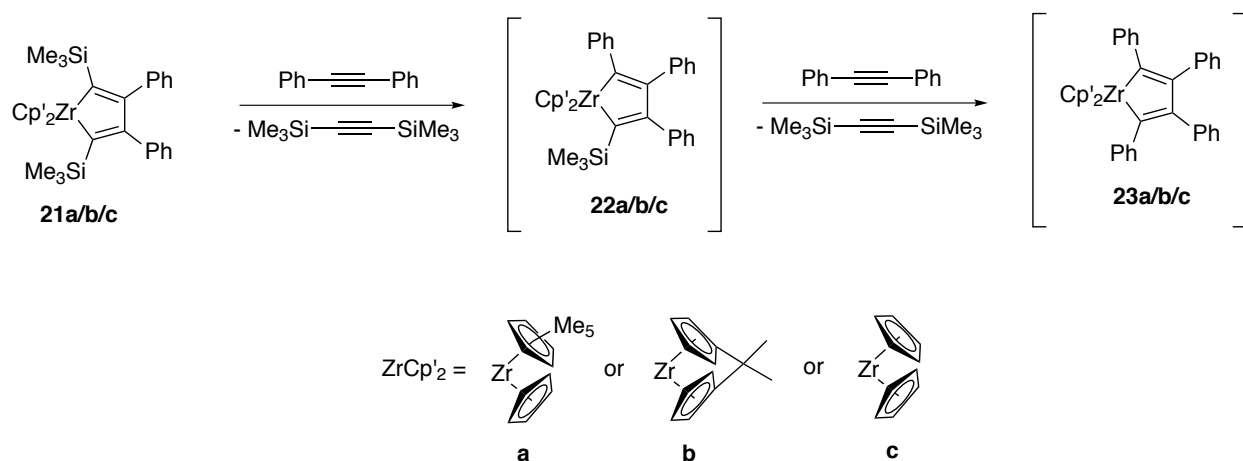
Scheme 4: Hiller *et al.* study of the metallacyclopropene (M = Ti, or Zr) stabilized by THF. Ancillary ligands that consist of methyl substituents (n = 2 - 5) were stable without THF. All other metallacycloprenes dimerized with the loss of THF.³⁵

Tilley *et al.* utilized several ancillary ligands to better understand the role of zirconocene moieties during coupling (see Scheme 5). The two ancillary ligands compared were Cp(η^5 -C₅Me₅) and Me₂C(η^5 -C₅H₄)₂. These two ancillary ligands were compared to probe the effects of sterically encumbered moieties on the coupling mechanistics and rates of coupling. The conclusion was that the coupling occurs in a stepwise fashion. In Scheme 5, the zirconacyclopropene (**19a**) reacts with two equivalents of diphenylacetylene (**7**) over a period of 24 hours when heated at 75°C during which time two intermediates formed before the final zirconacyclopentadiene product (**20a**). The two intermediates were observed by ¹H NMR spectroscopy. The first intermediate was Cp(η^5 -C₅Me₅)Zr(η^2 -PhC \equiv CPh)(Pyr) and the second Cp(η^5 -C₅Me₅)Zr(2,3-(Me₃Si)₂-4,5-Ph₂C₄). Reactions with the starting zirconacyclopropene (**19b**) and two equivalents of **7** at ambient temperature were converted cleanly in 30 minutes to the final zirconacyclopentadiene product (**20b**).³⁴



Scheme 5: Synthesis of zirconacycloprenes with various ancillary ligands and competitive reagents (*i.e.* diphenylacetylene (7**)).³⁴**

Further studies were accomplished to determine the alkyne substitution competitiveness of labile zirconacyclopentadienes (see Scheme 6) while still observing the rates of coupling and thoroughly characterizing the mechanism of different ancillary ligands. For instance, a labile zirconacyclopentadiene (**21c**) was found to readily undergo substitution with alkynes that were less sterically encumbered than the alkynes within the zirconacyclopentadiene (*i.e.* $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ (**18**)) when heated at 80°C for one hour. Similarly, the zirconacyclopentadiene (**21b**) underwent substitution within one hour at ambient temperature. In contrast, 50% of the zirconacyclopentadiene (**21a**) underwent substitution within one hour at 80°C and only after 14 hours was the substitution complete. Furthermore, it was determined by ¹H-NMR spectroscopy that a mixture of intermediates existed before the final zirconacyclopentadiene product (**23a**).³⁴ Therefore, the choice of ancillary ligand used will ultimately dictate the rate of substitution to a desired targeted product. In general, the less sterically bulky the ancillary ligand is the greater rate of substitution.



Scheme 6: Study of substitution of diphenylacetylene into silylated zirconacyclopentadienes.³⁴

The nature of the alkyne substituents, be it a terminal trimethylsilyl, *tert*-butyl, diphenylphosphino, or symmetrical alkynes, will determine the resulting coupled product. For instance, the first three types of terminal alkyne substituents listed above would adopt a α -position in the zirconacyclopentadiene. The more electron withdrawing substituents would adopt the β -position in the zirconacyclopentadiene (see Figure 3). While the last example using symmetrical alkynes would adopt any position. The end result would be a symmetrical zirconacyclopentadiene. In any case, it is quite difficult to characterize such mechanisms due to the high rates of dimerization, uncertainty in the exact structure of the zirconocene species that initiates coupling, and the limited life span of the zirconacycloprenes. Hence, the importance of isolating zirconacycloprenes and studying their reactions to specific situations.³⁴

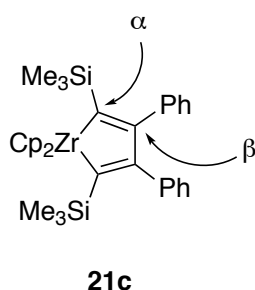


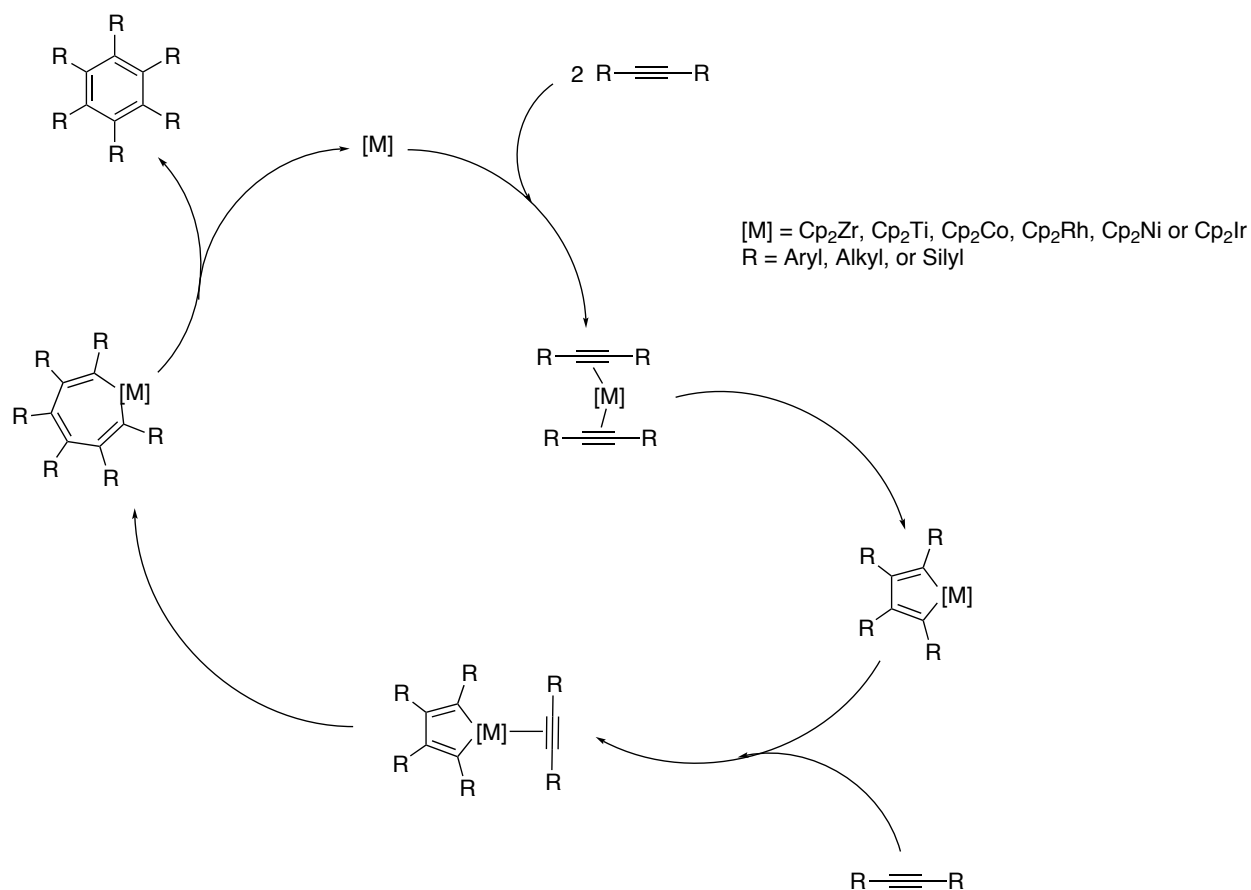
Figure 3: The α - and β -positions of substituents attached to a silylated zirconacyclopentadiene (21c).

The reversibility of this mechanism was demonstrated by trimethylsilyl, *tert*-butyl, and diphenylphosphino substituents on an alkyne where the less electron-withdrawing group was located in the α -position (see Figure 3). Additionally, if a ligand were present, it would likely stabilize the

zirconacyclopentadiene intermediates that formed. It was also believed that certain solvents like THF can adopt this role and stabilize these zirconacyclopentadiene intermediates.^{35,37} This idea was proven when isolating the Cp₂M (M = Ti, Zr) moieties in Scheme 4 and also when dealing with macrocyclization from zirconacyclopentadiene polymers using the solvents THF and benzene.^{1,35,37} However, macrocyclization and depolymerization will be discussed in a separate section. Furthermore, Tilley *et al.* demonstrated by using diphenylacetylene as a competitive alkyne for substitution into a silylated zirconacyclopentadiene (see Scheme 6) all three ancillary ligands, no matter the rate, were all able to reverse or "crack" the zirconacyclopentadiene and reform the zirconacyclopentadiene to begin coupling with diphenylacetylene (**7**) (a less sterically encumbered alkyne).³⁴

1.1.1.2 Alternative metallocyclopentadienes for stoichiometric or catalytic cycloaddition reactions and other organic reactions

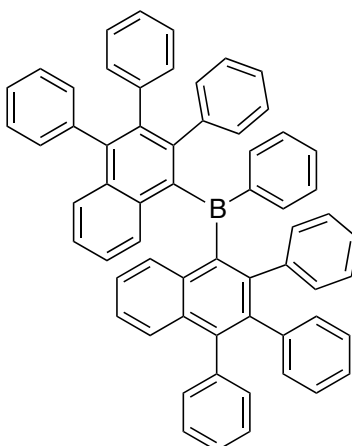
There are several alternative metallocenes to zirconocene dichloride that are being researched for the purposes of catalysts and coupling agents. There is the corresponding titanocene dichloride that has been reported to form titanocyclopentadienes with Me₃SiC≡CSiMe₃ (**18**).^{30,38,39} Alternatively, Nishihara *et al.* have utilized cobaltocene derivatives (*e.g.* CoCp(PPh₃)₂) as catalytic metallocenes for cycloaddition reactions (see Scheme 7). Likewise, Farona *et al.* utilized catalytic amounts of zirconocene dichloride and ethylaluminum dichloride with a similar mechanism to Scheme 7 to produce polyacetylenes.²² Rhodocene derivatives (*e.g.* Rh(η⁵-C₅Me₅)(PMe₃)) have been used for catalytic carbonylation of biphenylene.⁴⁰ Lastly, there also are many nickel and iridium metallocene derivatives that are used to form 2,2'-biphenyl complexes.¹³



Scheme 7: General scheme for cycloaddition with a metallocene and alkyne.¹³

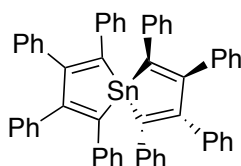
1.1.2 Lithium metal dimerized diarylacetylene

Eisch *et al.* demonstrated that 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**8**) will react with PhBCl₂ or Me₂SnCl₂ to create stable boroles or stannoles respectively (see Scheme 2). However, very little research has been established utilizing lithium metal to induce dimerization of acetylenes to ultimately produce main group heteroles, transition metalloles, and their polymer counterparts (*i.e.* utilizing rigid diynes).¹³ Eisch *et al.* did elaborate that utilizing lithium metal has some drawbacks. Most importantly, the Lewis acid (*i.e.* PhBCl₂) needs to be added as an ether solution or the borole that is generated must be in an ether solution. This allows for the formation of the borole etherate. Consequently, the borole etherate needs to be warmed to remove the solvated ether, but evidence suggests that the reaction mixture needs to be kept at a low temperature otherwise the PhBCl₂ can promote the isomerization of the **8** to form phenylbis(2,3,4-triphenyl-1-naphthyl)borane (**24**). Likewise, an equal ratio of Me₂SnCl₂ and **8** must be employed otherwise an excess of **8** favours the formation of a spiro-stannole (**25**). Instead, with the excess of Me₂SnCl₂, HCl can be generated which promotes the protodestannylation of the desired stannole to form the unwanted chlorodimethyl-(*E,E*)-(1,2,3,4-tetraphenyl-1,3-butadien-1-yl)tin (**26**).²⁶



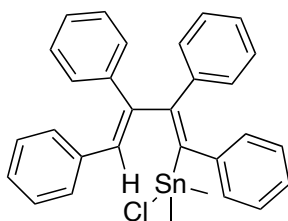
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Figure 4: The competitive product, phenylbis(2,3,4-triphenyl-1-naphthyl)borane (24), from the boration of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (8) if the reaction temperature is not kept low.²⁶



25

Figure 5: Suggested spirostannole (25) that is formed with excess 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (8) in the presence of Me_2SnCl_2 .²⁶

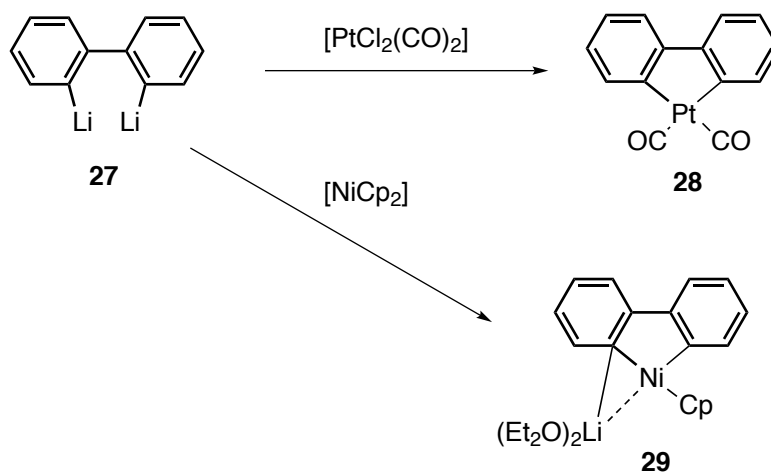


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Figure 6: Excess Me_2SnCl_2 in the presence of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (8) can lead to the generation of HCl that leads to the protodestannylation of the desired stannole to form chlorodimethyl-(*E,E*)-(1,2,3,4-tetraphenyl-1,3-butadien-1-yl)tin (26).²⁶

Between 1959 and 1961 Leavitt *et al.* and Braye *et al.* reported that alkynes could be coupled by lithium metal and be used as intermediates to main group heterocycles and metallacycles. From their research

many elements ranging from Group *IB* to *VIA* were utilized. Unfortunately, very little characterization was given and may be considered arguable and such may not support the actual desired products.^{41–43} Likewise, in recent years several groups have utilized lithium metal-induced coupling of alkynes to synthesize heterocyclic compounds (*e.g.* phospholes).^{44–47}

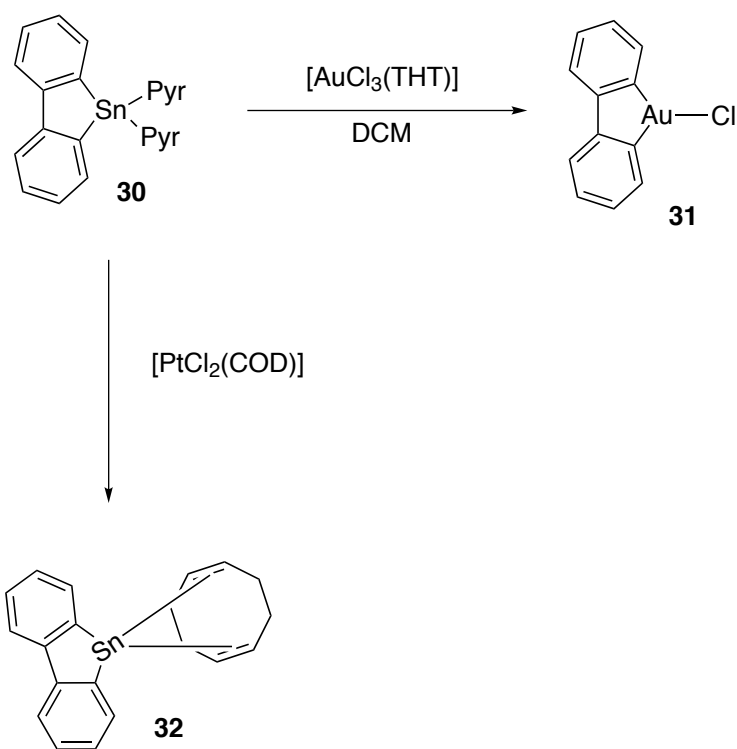


Scheme 8: Alternative reactions with dilithium reactants.^{48–50}

Alternatively to the direct coupling of alkynes with lithium, several research groups have utilized dilithiobiphenyls (**27**) to form various metallacycles (**28** and **29**), which have been confirmed by X-ray crystallography.^{48–50}

1.1.3 Stannoles

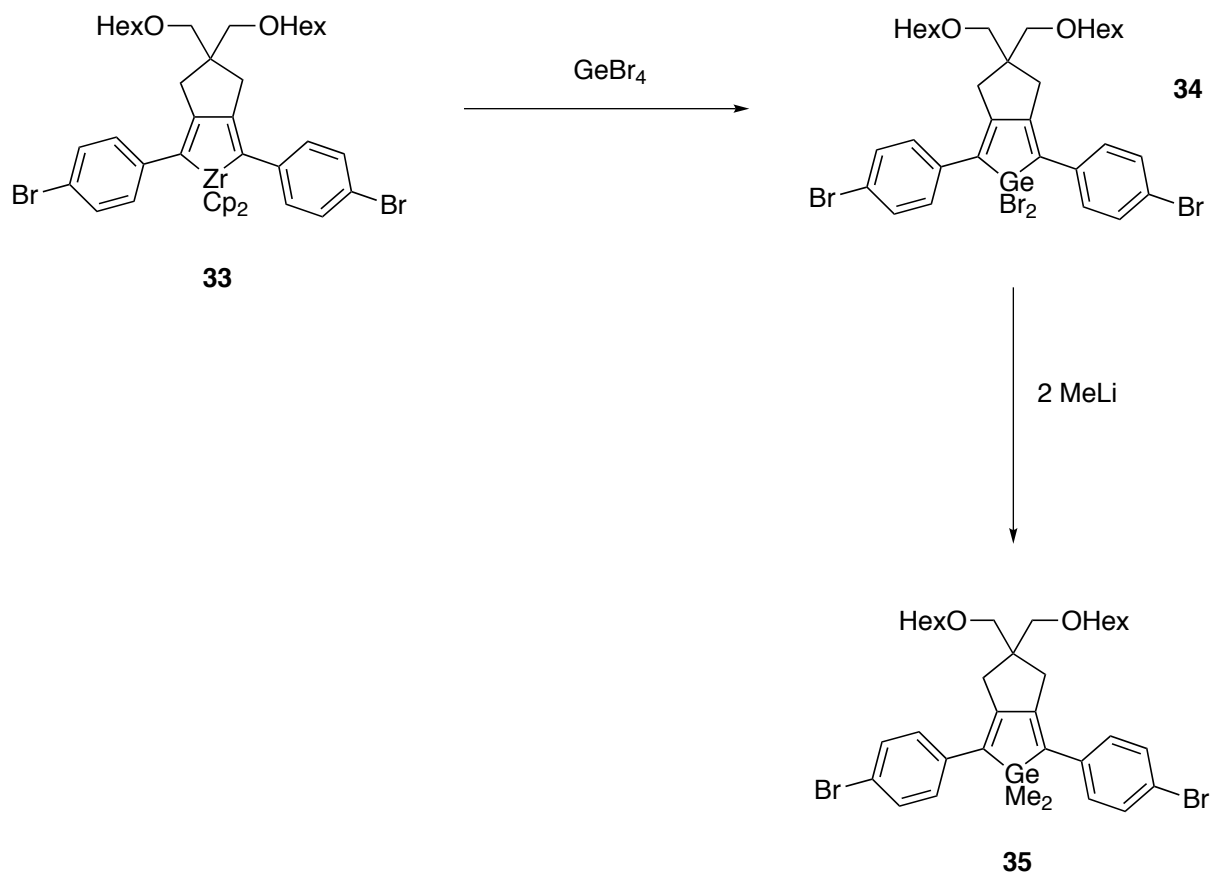
The synthesis of the stannole *via* the route Eisch *et al.* utilized does act as a viable alternative to Fagan *et al.* route.¹³ Eisch *et al.* provided concrete evidence that stannoles can act as intermediates to boroles.²⁶ The question that remains is if stannoles can also act as intermediates for other main group heterocycles, and metallacycles. Similarly to 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**8**), very little research has been established to determine the limits of stannoles as practical intermediates for metallacycle transfer.¹³ Of the research that does exist dibenzostannoles were used as intermediates. For instance, Uson *et al.* and Brune *et al.* were able use $[\text{AuCl}_3(\text{THT})]$ and $[\text{PtCl}_2(\text{COD})]$ complexes to form novel metalloles (**31** and **32**).^{13,51,52}



Scheme 9: Other known metallacycle transfers with stannoles.^{13,51,52}

1.1.4 A brief discussion of other heteroles

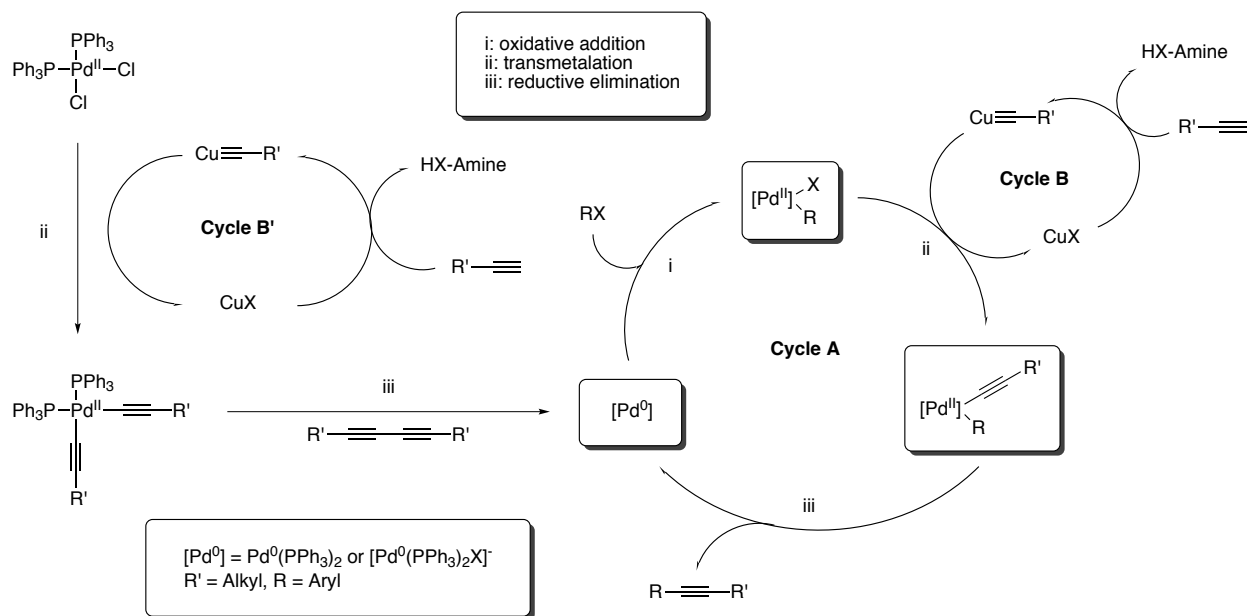
Fagan *et al.* have accumulated a considerable amount of information in regards to heteroles synthesis *via* metallacycle transfer from zirconacyclopentadiene intermediates (see Scheme 1). Of the many main group heteroles studied boroles, stannoles, siloles, germoles, and thiophenes remain the most studied.^{1,3,18,19,53} Boroles are known to be rare due to their ability to easily undergo substitution with oxygen, bases, and acids thus are considered highly reactive. However, Eisch *et al.* have demonstrated the synthesis of stable borole etherates and unsolvated boroles (see Scheme 2), but require certain temperature conditions. Unless the reaction temperature was kept low (25°C), isomerization of the borole to form phenylbis(2,3,4-triphenyl-1-naphthyl)borane (**24**) was possible.²⁶ Derivatives of these antiaromatic boroles (*e.g.* perfluoropentaphenylborole), while still reactivity with air or water, have given further insight into alkyne reactivity/selectivity when used for Diels-Alder (insertion) chemistry.⁵⁴ More importantly, perfluoropentaphenylboroles have been reportedly used as hydrogen activators (*i.e.* splitting of molecular hydrogen H₂). Thus, presenting a novel and environmentally friendly pathway for splitting H₂.⁵⁵ Stannoles represent a likely alternative to zirconacyclopentadiene metallacycle transfer as they readily undergo reactions that appear unfavourable to zirconacyclopentadienes. For instance, perfluoropentaphenylborole is synthesized readily from fluorinated stannole intermediates while corresponding reactions with fluorinated zirconacyclopentadiene intermediates are sluggish or do not occur. This is due to the fluorination of the zirconacyclopentadiene making them far less nucleophilic compared to non-fluorinated analogues.²⁹ Dibenzostannoles have been reported to undergo metallacycle transfer with [AuCl₃(THT)] and [PtCl₂(COD)] complexes (see Scheme 9), while analogous zirconacyclopentadienes have not even been synthesized.¹³ Siloles have been suggested to have small band gaps and low-lying LUMOs. Thus, macromolecules containing such rings could have interesting optoelectronic properties.² Tilley *et al.* have demonstrated that germoles can be synthesized in high yields, similar to siloles, and undergo post nucleophilic substitution (see Scheme 10).⁵⁶ Lastly, thiophenes are highly industrially used heteroles typically used in the form of poly(thiophenes). They have been used in electrochemical applications (*e.g.* energy storage, electrochromic devices, sensors, modified electrodes, electronic devices, and nonlinear optics).⁵⁷



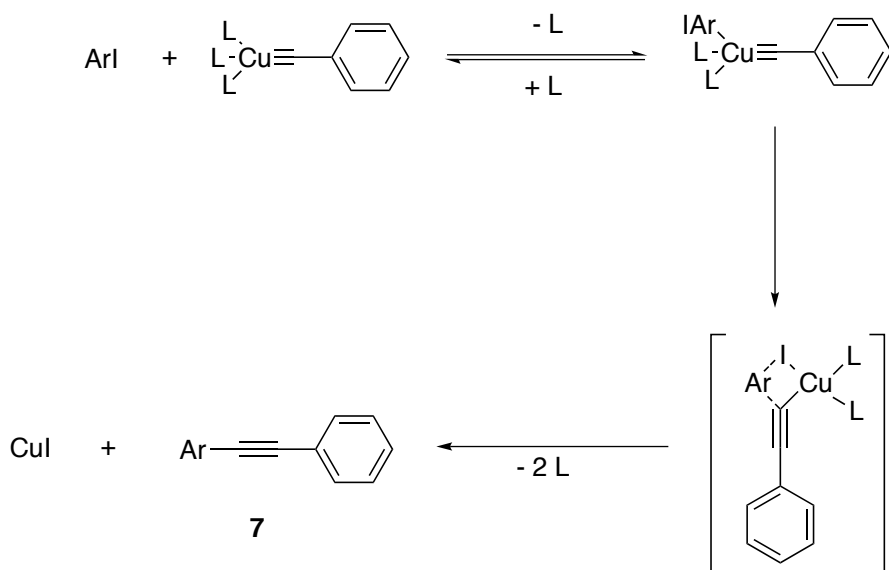
Scheme 10: Tilley *et al.* study of the nucleophilic substitution of germales.²

1.2 A brief history of Sonogashira coupling

Palladium-catalyzed $\text{sp}^2\text{-sp}$ coupling reaction between aryl, alkenyl halides/triflates and terminal alkynes have been reported separately by several groups (*i.e.* Heck *et al.*, Cassar *et al.*, and Sonogashira *et al.*) in 1975.^{58–60} Heck's methodology was developed on the known Mizoroki-Heck reaction for the palladium-catalyzed arylation or alkenylation of alkenes. It utilized diacetatobis(triphenylphosphine)palladium(II) complex as a catalyst and a basic amine, such as triethylamine or piperidine, acting as a solvent and base.^{59,60} Cassar's methodology involved the use of nickel(0) or palladium(0) triphenylphosphine complex acting as a catalyst with sodium methoxide as a base and DMF as a solvent.⁵⁸ Sonogashira's methodology (see Scheme 11) was to utilize a palladium source like dichlorobis(triphenylphosphine) palladium(II) as a catalyst with CuI as a co-catalyst combined in an amine solvent. These reactions were meant as an alternative to Castro-Stephens coupling (see Scheme 12), which typically have low yield and require stoichiometric amounts of CuI .^{61,62}



Scheme 11: A hypothesis of the Sonogashira coupling reaction and the potential side homo-coupling reaction (cycle B').⁶³



Scheme 12: A hypothesis of the Castro-Stephens coupling reaction to synthesize diphenylacetylene.⁶²

In 1975, both Sonogashira and Hagihara reported that the addition of a catalytic amount of CuI would greatly accelerate the reaction and decrease the harsh temperature condition required by the reaction (*i.e.* up to $100^\circ C$ was required). The use of cuprates were observed in Castro-Stephens coupling; thus

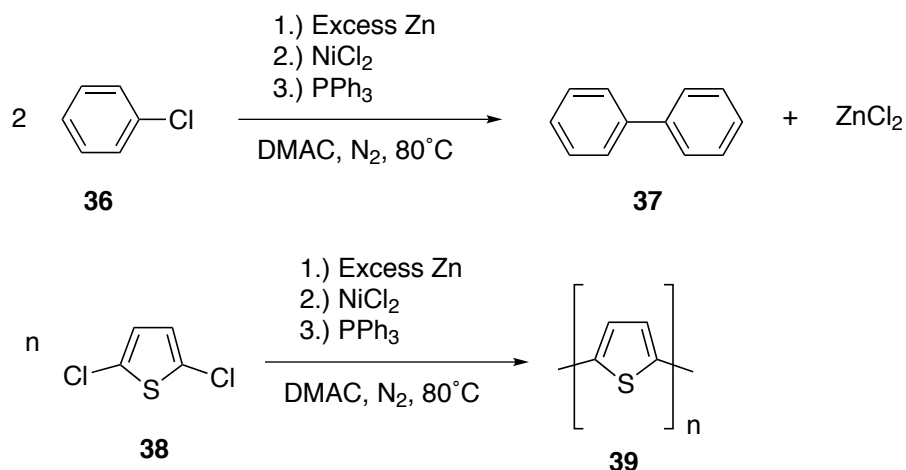
supporting the claim.⁶⁴ However, the addition of CuI as a co-catalyst has its drawbacks. CuI is an environmentally unfriendly reagent, difficult to recover, and generates cuprates (*i.e.* copper acetylides) that can easily generate homo-coupling products of the terminal alkyne (Glaser coupling) when oxidative agents (*i.e.* air) are present.^{60,64} Therefore, significant efforts have been made by many to create copper-free methodologies. Typically, these reactions utilize excess amine, or expensive metals (*e.g.* gold), which ultimately lessen the environmental or economical advantages of the methodology respectively.^{64,65}

The palladium/copper-catalyzed mechanism is still not fully understood. This is due to the difficulties of characterizing the combined role of the two metal catalysts. However, it is typically thought as two independent catalytic cycles (see Scheme 11). First the palladium begins with the catalytically active species $[Pd(0)L_2]$. The cycle is then initiated by the oxidative addition of the aryl, alkenyl halide/triflate, which is considered to be the rate-limiting step of both cycles. Oxidative addition barriers increase in the order of $RI < ROTf < RBr < RCl$ (*i.e.* R is an aryl, or alkenyl). The now newly formed $[Pd(II)R^1L_2X]$ adduct is then converted into a $[Pd(II)L_2R^1(CCR^2)]$ adduct after transmetallation with a cuprate, which is formed in the "copper cycle". This adduct undergoes reductive elimination, after *cis/trans*-isomerization, regenerating the catalytically active species $[Pd(0)L_2]$ and the hetero-coupled desired product.^{64,65}

1.3 A brief discussion of project relevant polymers

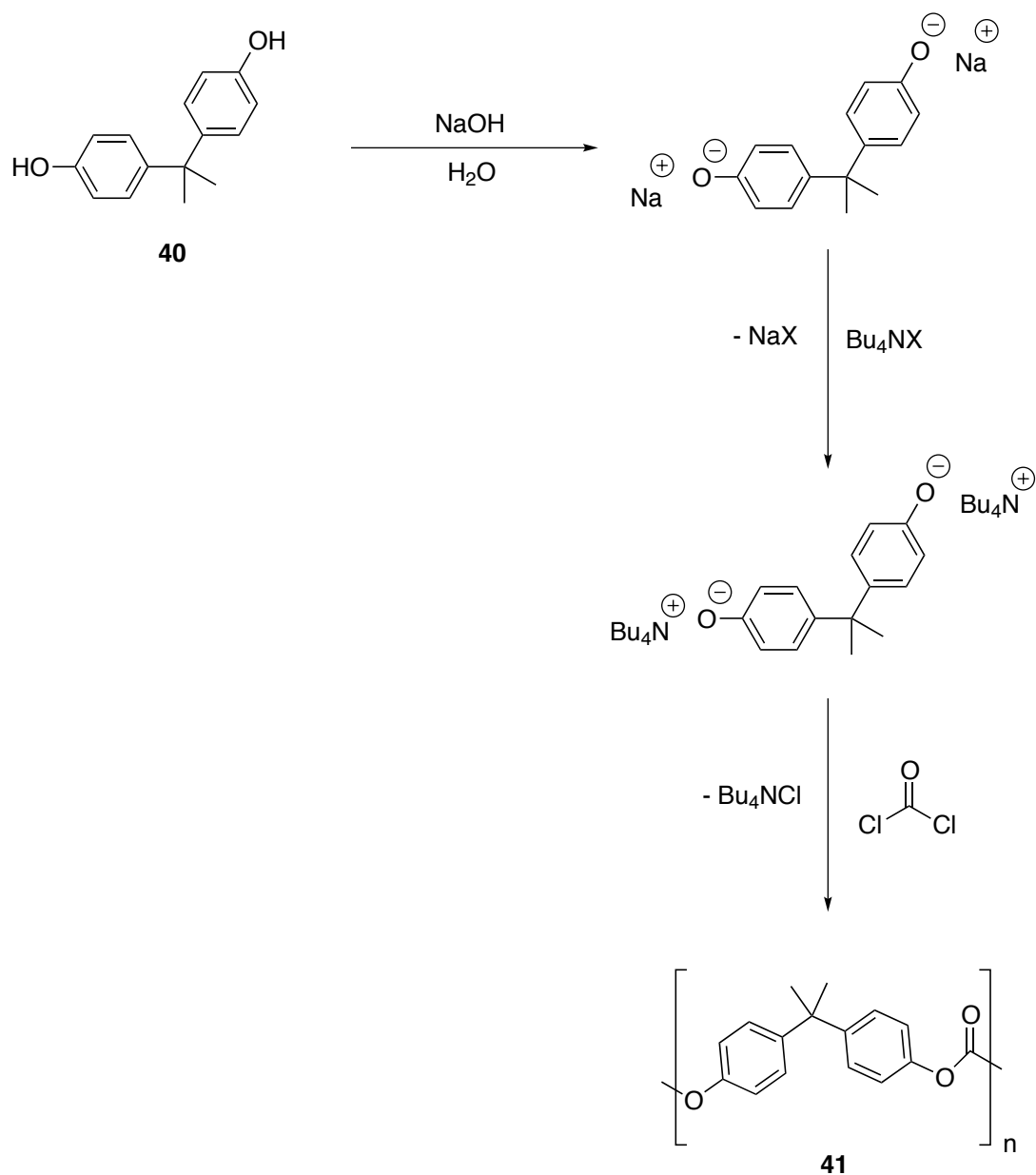
1.3.1 Dimerization and polymerization *via* nickel metal complexes

High molecular weight polymers synthesized from sp^2 -carbon- sp^2 -carbon bond formations are considered to be high interest (see Scheme 13 bottom). Such polymers will create novel and unique structures that are impossible to synthesize *via* known methods (*e.g.* Grignard reaction, or Sonogashira coupling). These routes are believed to be more economical than existing routes previously used to synthesize them.^{66,67}



Scheme 13: Colon *et al.* novel zero valent nickel coupling to form carbon-carbon bonds. Can be used to form simple compounds (top) and high molecular weight polymers (bottom).⁶⁶

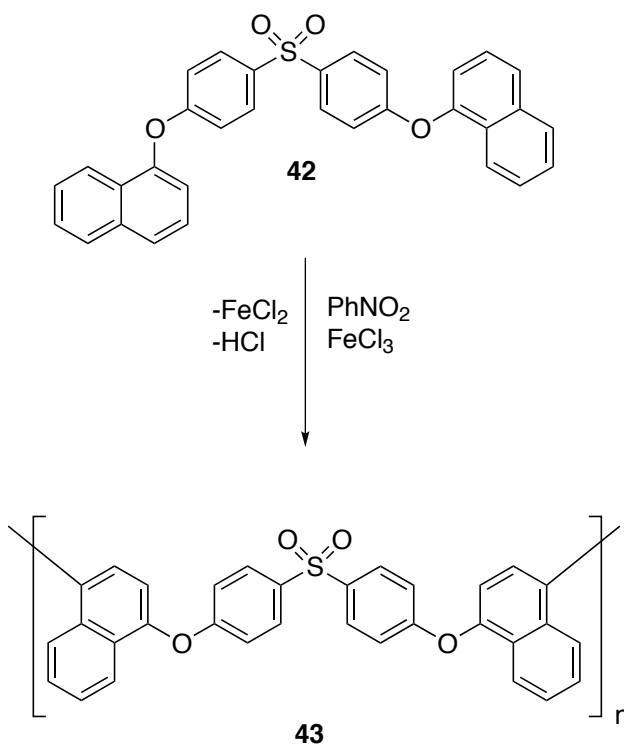
There are a substantial number of methods for the preparation of aromatic polymers. Unfortunately, majority implement a carbon-heteroatom formation (*i.e.* carbon-oxygen formation).⁶⁷ For example, aromatic polycarbonates (**41**) are synthesized using dihydric phenol (**40**) with phosgene (see Scheme 14), the oxidative polymerization of substituted phenols to form poly(phenyleneoxide), or the nucleophilic substitution of an activated aryl halide reacted with a phenoxide anion to form poly(arylether) derivatives.^{67,68}



Scheme 14: General synthesis of polycarbonates. Dihydric phenol is reacted with phosgene where a carbon-oxygen bond is formed and a polymer as a result.^{67,68}

Three high molecular polymer methodologies were established in the 1970s utilizing carbon-carbon bond formation (emphasis on sp^2 -carbon- sp^2 -carbon bond formation). The first methodology involves the preparation of electrophilic starting reagent (*e.g.* terephthaloyl chloride reacted with diphenyl ether).^{67,69} The second methodology involves the self-condensation polymerization of *p*-phenoxybenzoyl chloride in solution with BF_3/HF .^{67,69} The final methodology involves the oxidative coupling of 4,4'-di(1-

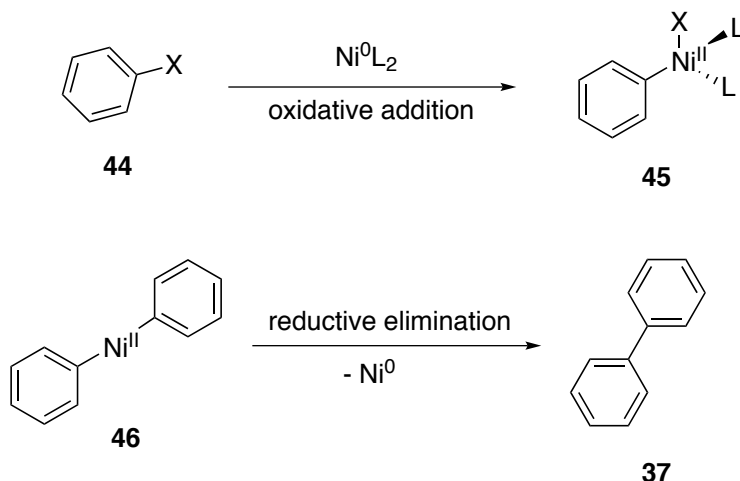
naphthoxy)diphenyl sulfone (**42**) or 4,4'-di(1-naphthoxy)benzophenone with ferric chloride.^{67,70} This reaction follows the Scholl reaction (see Scheme 15).



Scheme 15: The Scholl reaction with 4,4'-di(1-naphthoxy)diphenyl sulfone (42**) in nitrobenzene and ferric chloride catalyst.**⁷⁰

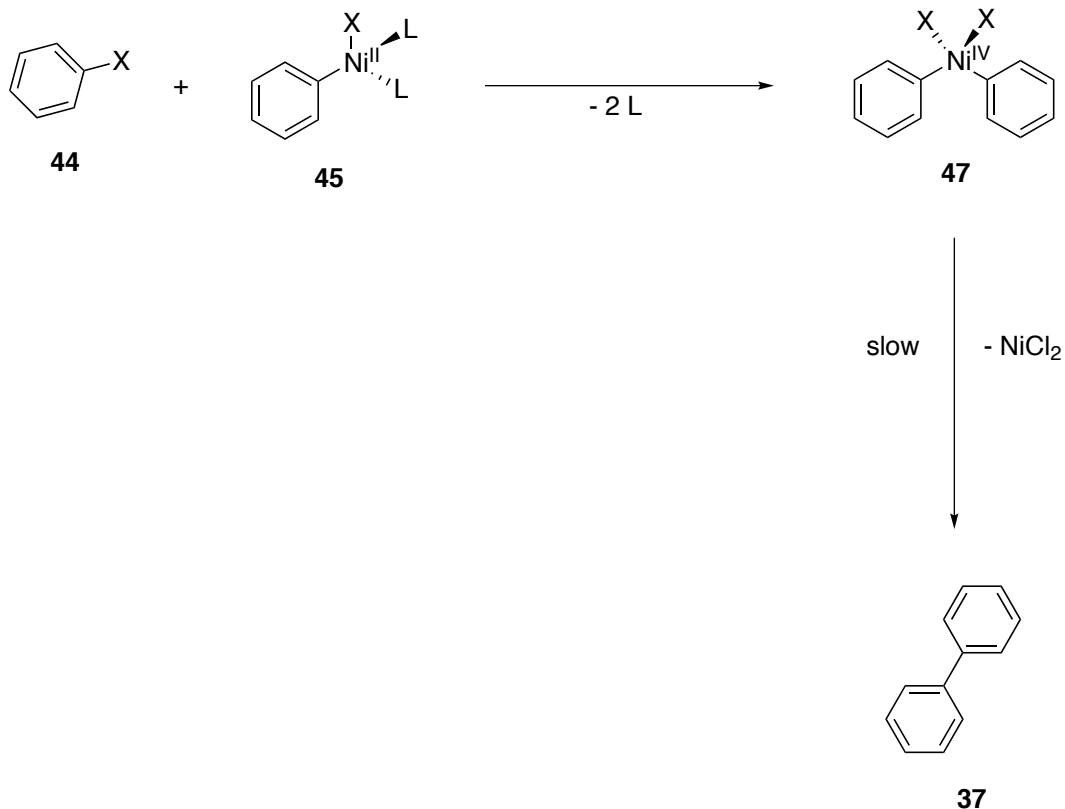
In all three cases there are drawbacks. The first two examples rely on an aliphatic carbon or an aromatic carbon limiting the type of organic compounds that can be used. Moreover, the second example relies on a strong acid such as HF. The last example requires stoichiometric amount of Lewis acid and is limited to Scholl capable systems (*e.g.* polycyclic aromatic compounds).^{66,67}

It was in 1986 when Colon *et al.* demonstrated the coupling of aryl chlorides by zero valent nickel (see Scheme 13 top) can be applied to form high molecular weight polymers (see Scheme 13 bottom).^{66,67}



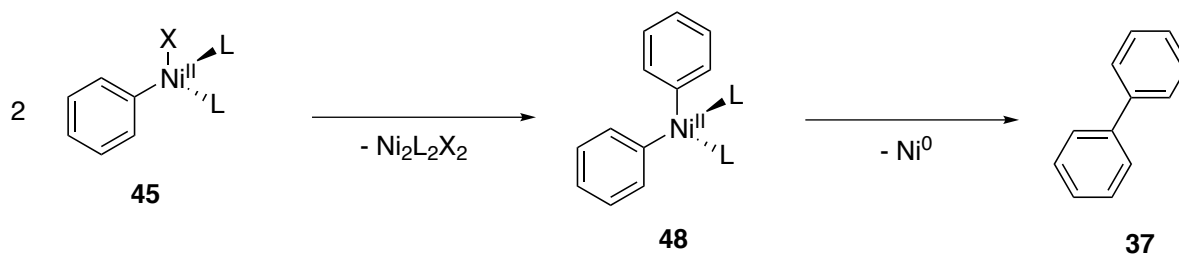
Scheme 16: Agreed zero valent nickel redox reactions.⁶⁶

The exact mechanism for this sp^2 -carbon- sp^2 -carbon bond formation has inspired some debate. However, there are two aspects that are typically agreed upon (see Scheme 16). First, the initial oxidative addition of aryl halide (**44**) to zero valent nickel to form the arylnickel(II) intermediate (**45**). Second, that the biaryl formation occurs by reductive elimination from a diarylnickel intermediate (**46**). The intermediate steps from **45** to the **46** and the oxidations within are controversial due to the diverse conditions and observations reported by various groups.^{66,71–76} For instance, Semmelhack *et al.* proposed that the intermediate **45** reacts with **44** to form diarylnickel(IV) (**47**) which undergoes reductive elimination as the slow step (see Scheme 17).^{66,71–73}



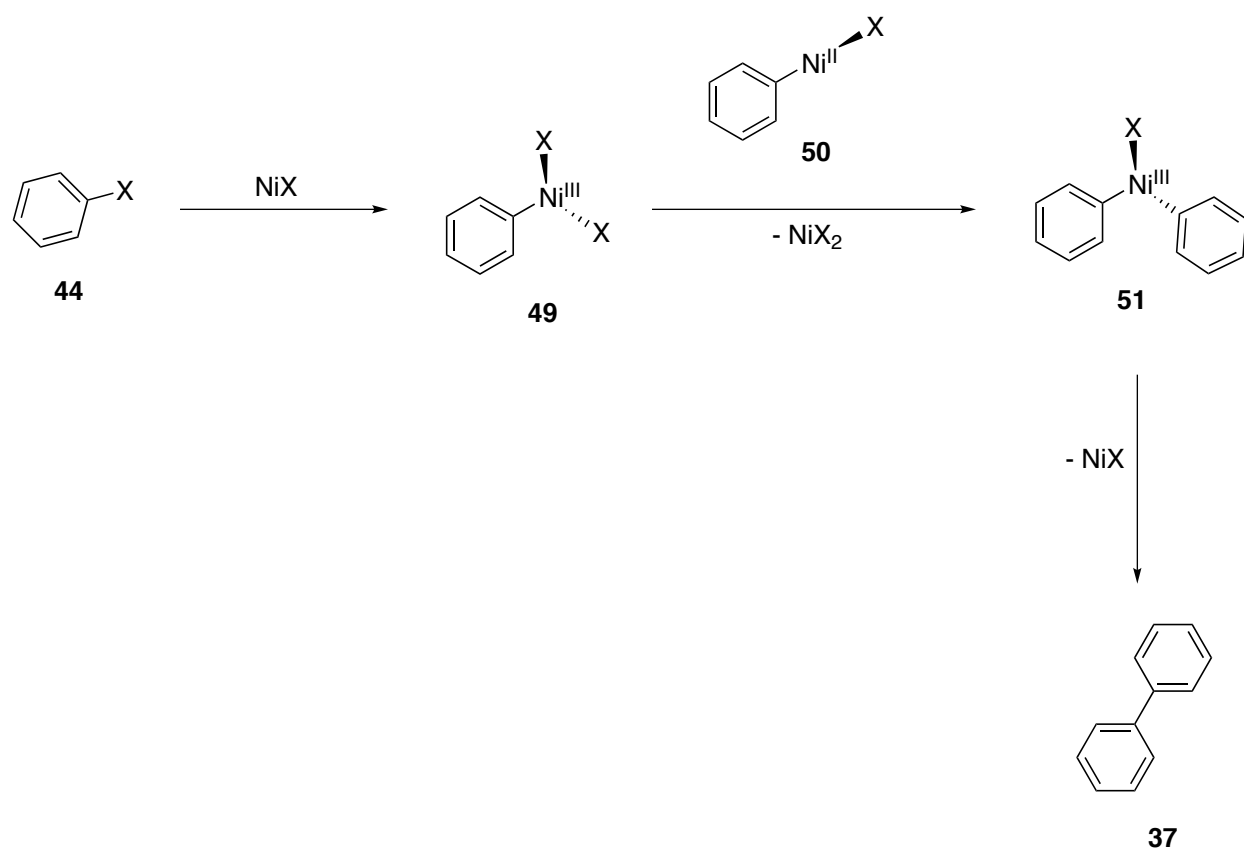
Scheme 17: Semmelhack *et al.* proposed steps. ^{66,71–73}

This proposal was based on the fact that the formation of biaryl (**37**) was slower than the disappearance of iodobenzene when reacted with $\text{Ni}(\text{COD})_2$. Thus, it is important to acknowledge the role of the nickel catalyst, metal co-catalyst, solvent, ligands, and aryl halide type. ^{66,71–73}

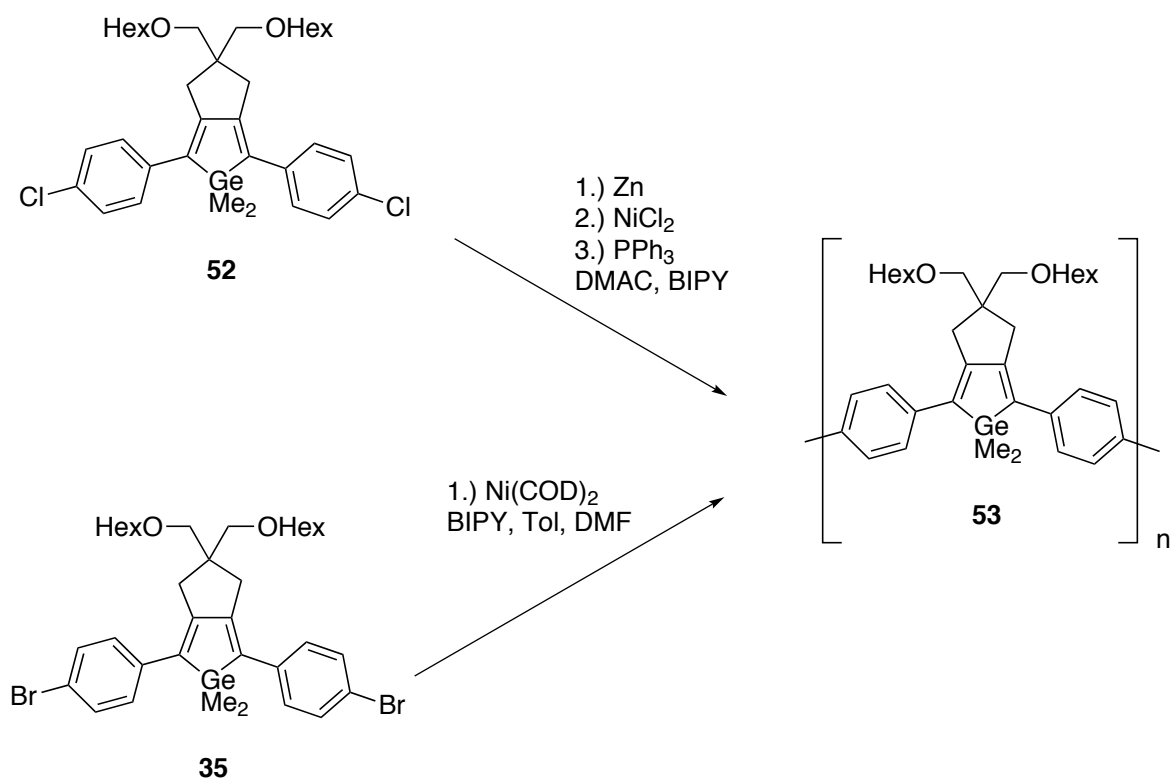


Scheme 18: Nakamura *et al.* and Parshall *et al.* proposed steps. ^{74,75}

Nakamura *et al.* and Parshall *et al.* proposed that **37** was formed from the metathesis of two equivalents of **45** (see Scheme 18) while Tsou *et al.* proposed nickel intermediates with oxidation states of +1 and +3 rather than +2 and +4 (see Scheme 19). ^{74–76}



Scheme 19: Tsou *et al.* proposed steps.⁷⁶

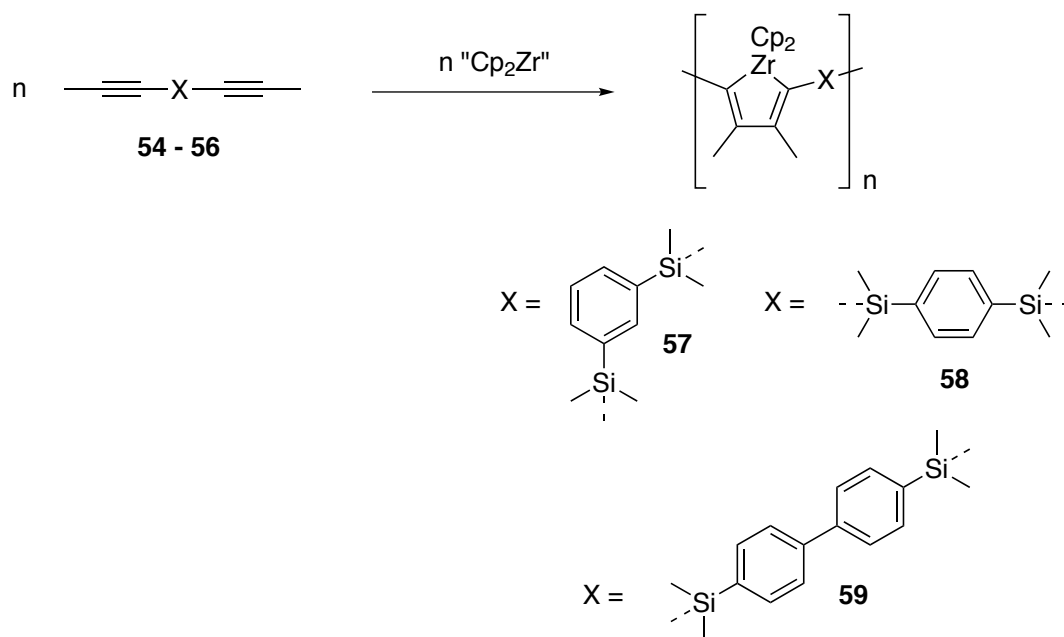


Scheme 20: Two routes to synthesize germole based polymers using zero valent nickel.²

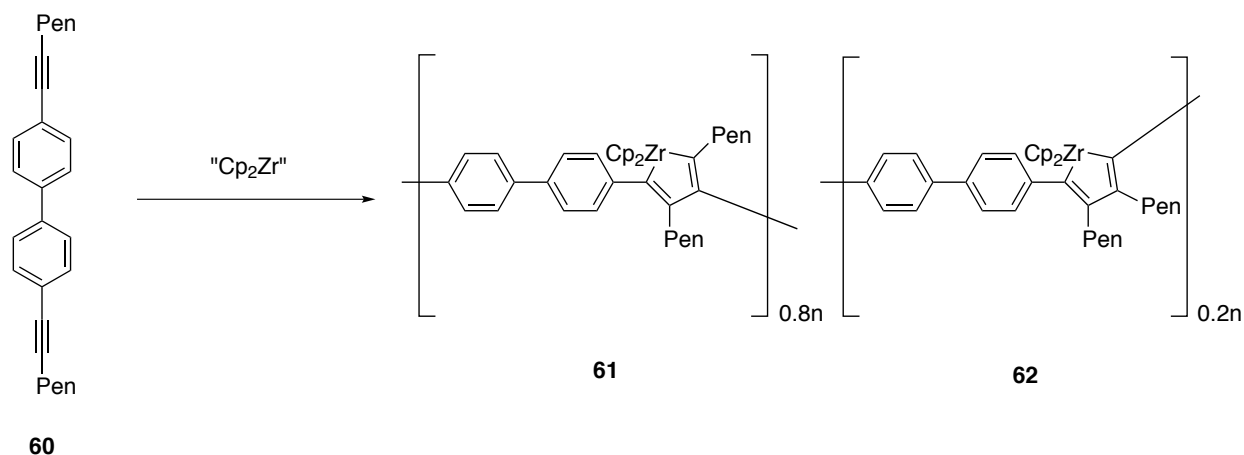
In 1999, Yamamoto *et al.* reported an improved sp²-carbon-sp²-carbon bond formation mechanism using a Ni(COD)₂ and bipyridine in a DMF/toluene solution over the more common Colon *et al.* method.^{67,77,78} Unfortunately, Ni(COD)₂ is used in excess of starting monomer. Fortunately, this route proved advantageous for Tilley *et al.* when polymerizing a germole monomer, see Scheme 20, increasing the molecular weight dramatically over the Colon *et al.* method.²

1.3.2 Zirconocene-Coupling of Diynes

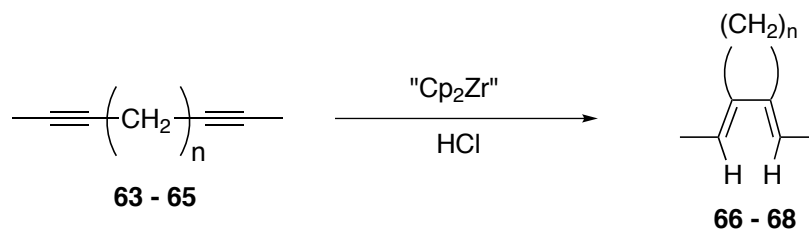
Identical to the zirconocene-coupling of alkynes (see Scheme 1), diynes can mechanistically work the same way (see Scheme 21). However, with the use of diynes there are several outcomes. If rigid spacer groups are used then polymers are the most likely outcome. In the event the spacer group is flexible, there is the potential chance of coupling the diyne to itself. With rigid spacer groups, the shape and properties of respective polymers can be controlled. In all cases, the silyl group adopts the α -position in the zirconacyclopentadiene ring while the electron withdrawing alkyne substituents adopt the β -positions. Unfortunately, these silylated products can easily undergo reverse zirconocene-coupling to give labile intermediates. This can be advantageous if synthesizing macrocycles.³⁴ Alternatively, Tilley *et al.* studied the regio-selectivity of 4,4'-(heptynyl)dibenzene (**60**) a non-silylated diyne (see Scheme 22). Polymerization occurred, but resulted in a distribution that had a ratio of 8:2 (symmetrical:asymmetrical configuration).³



Scheme 21: The generic zirconocene-coupling of diynes. Silylated spacer groups are shown. However, non-silylated spacer groups have been reported to work as well.^{1,3}

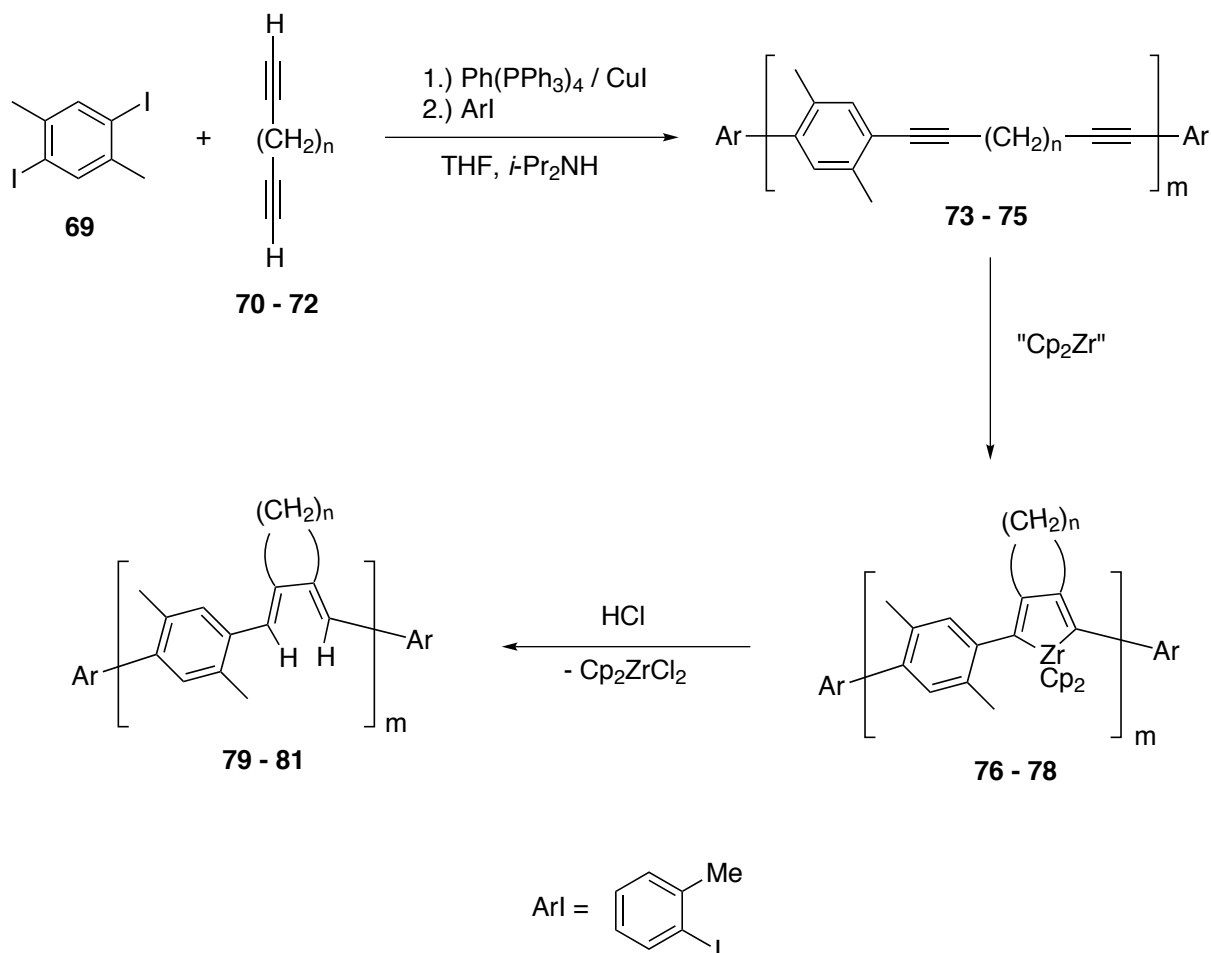


Scheme 22: Distribution of polymer formed from a non-silylated diyne (60**).³**



Scheme 23: A method of avoiding *cis-trans* formation when working with flexible diyne spacer groups where n = 2 - 4.³

Tilley *et al.* also studied the use of long chained methylene spacer groups incorporated into diynes (see Scheme 23). Due to the flexibility of the long methylene spacer groups (n = 2 - 4), the diynes coupled with themselves to form zirconacyclopentadiene rings, which were subsequently hydrolyzed to form **66** to **68** (see Scheme 23). Similarly, Tilley *et al.* incorporated **these diynes** into corresponding polymers *via* Sonogashira coupling (see Scheme 24).³ This method introduced aromatic hydrocarbons into the polymer backbone increasing conjugation. It was then possible to further increase this conjugation by performing zirconocene-coupling of the diynes within the poly(arylenediyne) (**73** to **75**) and then hydrolyzing it to form poly(arylenediene)s (**79** to **81**).³



Scheme 24: Synthesis of band gap tunable polymers *via* zirconocene-coupling of poly(arylenediyne)s to form poly(arylenedieneylene)s where $n = 2 - 4$.³

1.4 An introduction to macrocycles

Macrocycles have become important structural units or building blocks in supramolecular chemistry. The widespread interest in them are due to their ability to serve as highly selective hosts and receptors due to specific chemical interactions with other molecules and due to their controlled interior geometries or shapes. Macrocycles such as cyclodextrins or cucurbiturils pertain to such areas of research. They both have selective interiors that interact with other molecules *via* nonpolar interactions and Van der Waals interactions. Moreover, their interior geometries can be controlled *via* the amount of sugar chains incorporated, cyclodextrins, or glycoluril monomers incorporated, cucurbiturils. These properties make them useful in the pharmaceutical, cosmetic, and food industries as solubilizers and stabilizers.⁷⁹

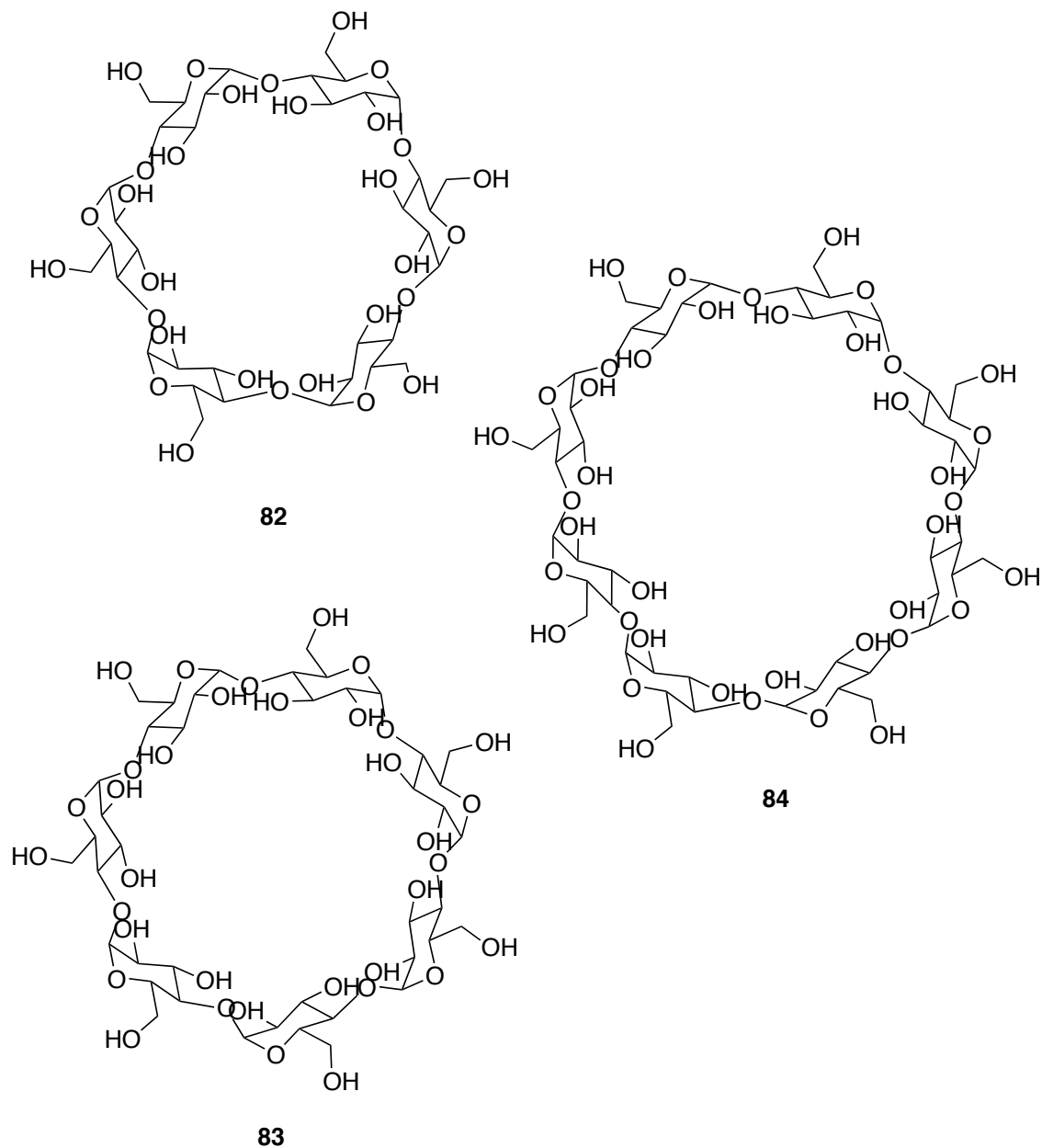


Figure 7: Various cyclodextrins: α -CD (82), β -CD (83), and γ -CD (84).^{79,80}

Cyclodextrin (α -, β -, or γ -CD) (see Figure 7) that incorporate many sugar chains have been used as host-guest complexes with hydrophobic molecules to form drug delivery vehicles. For instance, di-*n*-decyldimethylammonium chloride and cyclodextrin mixtures have been used as antifungal agents.⁸¹ Ziprasidone mesylate, an antipsychotic used in the treatment of schizophrenia and bipolar disorder, complexed with cyclodextrin have been used to increase absorption during the fasted state.⁷⁹ Modified γ -CD known as Sugammadex is being used a drug-specific sequestering agent. Sugammadex specifically

includes rocuronium, a chemical used in general anesthesia as an aminosteroid neuromuscular blocking drug (NMBD).⁸⁰

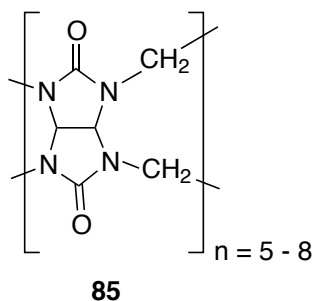
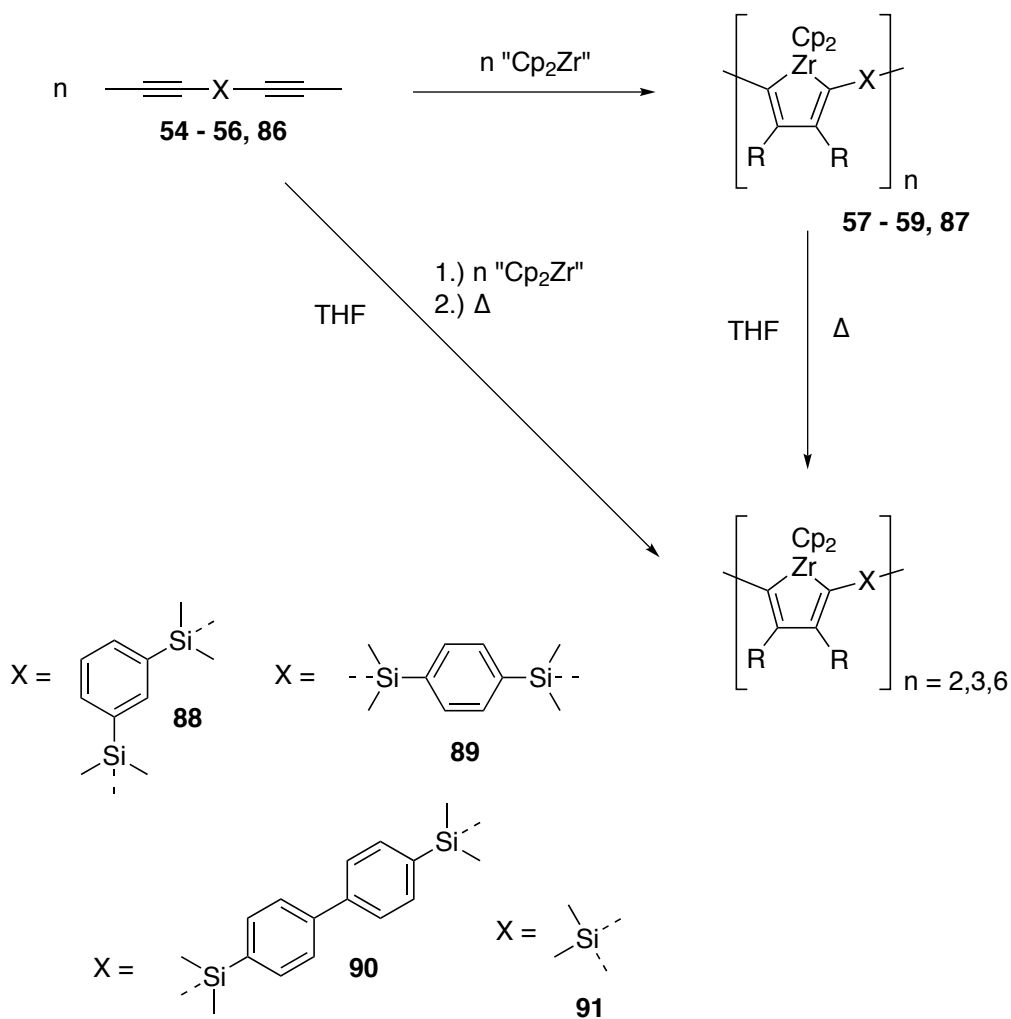


Figure 8: Various cucurbiturils where $n = 5 - 8$.⁸²

Cucurbit[n]uril (CB[5], CB[6], CB[7], and CB[8]) (see Figure 8) are extensively used in the pharmaceutical, cosmetic and food industries. In recent years, many have utilized the controlled complexation of additional CB[8] to reaction mixtures containing calix[5]arenes and alkylammoniums to form robust polymeric arrays of monomer units assembled by noncovalent interactions. Due to the noncovalent interactions that hold these monomeric arrays together, a certain capability coined as self-repairing or self-healing has been demonstrated, which also falls into a novel area of research known as smart materials. It is apparent that these polymers can easily assemble and disassemble *via* specific stimuli (*i.e.* heat, light, redox, etc.).⁸² Crown ethers, rotaxanes and cyclodextrins also possess such properties.⁸³⁻⁸⁷

1.4.1 Zirconocene-Coupling Reversibility Related to Macrocyclization

A novel and versatile pathway to synthesize macrocycles has been established in recent years (see Scheme 25). Tilley *et al.* have developed an alternative to traditional macrocyclization reactions.¹ Tilley *et al.* rely on a reversible self-assembly, yet high-yielding, macrocyclization of zirconacyclopentadiene rings from zirconocene and two alkynes.⁵⁶



Scheme 25: Two routes to synthesize macrocycles based on silylated polymers.¹

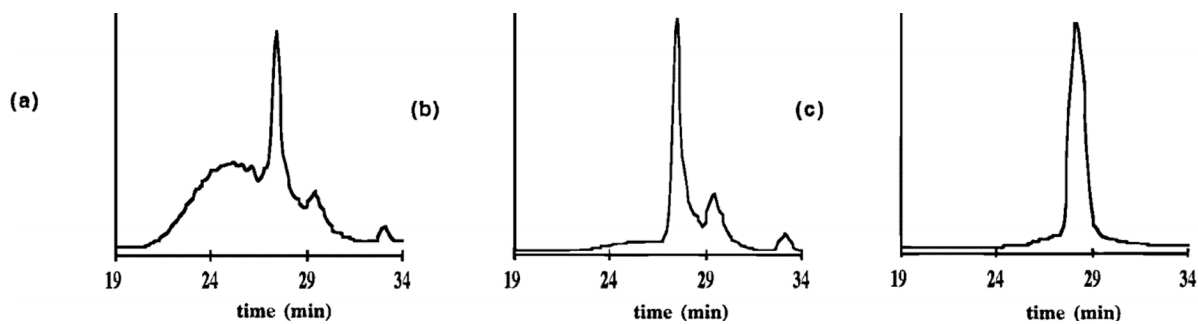
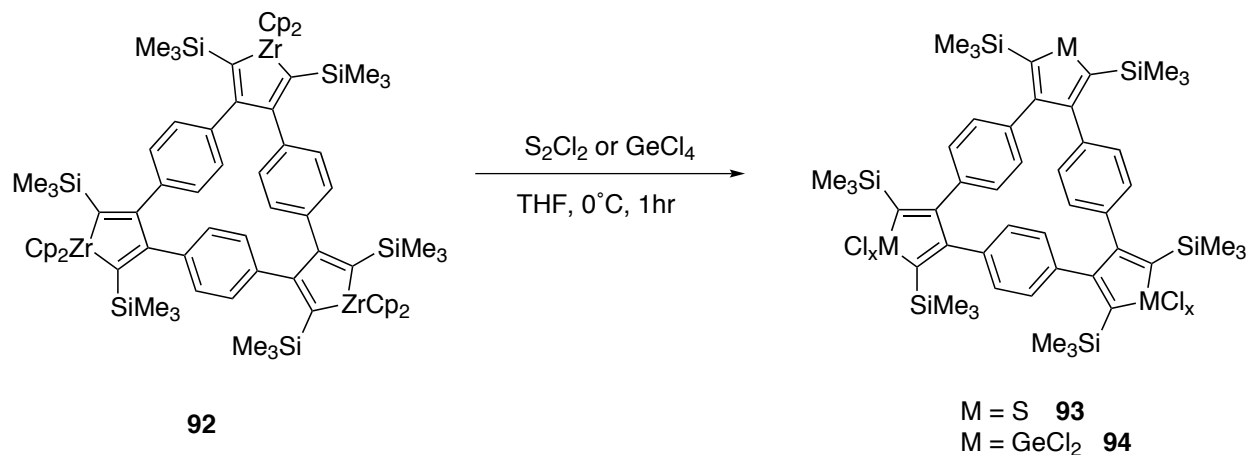


Figure 9: GPC results of macrocyclization (depolymerization) of [(1,4-Me₂SiC₆H₄SiMe₂)C₄Me₂ZrCp₂]₃ (58) where (a) is a benzene solution that has been refluxed for 24 hours, (b) refluxed benzene solution after 48 hours, and (c) refluxed THF solution after 12 hours.¹

It has been studied by Tilley *et al.* that certain sterically bulky terminal alkyne substituents like trimethylsilyl, *tert*-butyl, and diphenylphosphinos unequivocally adopt the α -position in the zirconacyclopentadiene ring. As a consequence, they promote the reverse propagation or depolymerization of the polymer.³⁴ This can be advantageous if macrocycles are intended. However, to synthesize a monomodal distribution of molecular weight macrocycles, solvents play an important role. For instance, Tilley *et al.* determined refluxing the silylated polymer in THF created a monomodal distribution while refluxing in benzene for the same silylated polymer created a polymodal distribution (see Figure 9). Thus, indicative of THF stabilizing the η^2 -complexed zirconacyclopentadiene that is formed as an intermediate (similar to Scheme 3 and Scheme 4).^{1,34} It must be noted though, it has not been reported by Tilley or by others the depolymerization of non-silylated polymers.

1.4.2 Zirconacyclopentadiene macrocycle and post modifications

The macrocycles synthesized *via* zirconocene coupling can be controlled for shape, size, geometry, functional groups, rigidity, symmetry, and other properties. This occurs with introduction of different diynes. Moreover, post modification to the macrocycle is similar to the linear polymer counter part. Thus, metallacycle transfer to main group atoms to form germoles, thiophenes, thiophene oxides, phospholes, and so on, are possible. Moreover, an air stable cyclophane can also be easily created using acids.^{56,88–90}



Scheme 26: The metallacycle transfer of trimethylsilyl α -positioned zirconacyclopentadiene (92) based macrocycles.⁵⁶

Tilley *et al.* have reported findings for various metallacycle transfers (see Scheme 26) from the zirconacyclopentadiene. Results vary with yields as low as 10% and as high as 93%.⁵⁶ Specific main group halides (*e.g.* GeCl_4) provide post modification abilities to the macrocycle *via* nucleophilic substitution of the chloride ligands. For instance, reactions of $(\text{Me}_3\text{Si})_2\text{S}$ or Me_3SiCN with

hexachlorotrigermoles have moderately high yields. This introduces exocyclic binding sites into these macrocycles creating novel building blocks for supramolecular chemistry.⁵⁶

There are apparent limitations for the substitution at the zirconium. For instance, if trimethylsilyl, SiMe₃, substituents are located at the α -position to zirconium on a zirconacyclopentadiene ring (see Scheme 26), the steric barrier is dramatically increased resulting in a decrease in the functionalization of the macrocycles *via* reactions at the zirconacyclopentadiene.⁵⁶ However, it is apparent that bulky, SiMe₃, substituents are required for the formation of macrocycles *via* zirconocene coupling.⁵³ Similarly, dimethylsilylated spacer groups in the α -position are required for the polymerization/macrocyclization of those particular monomers, but reduces the metallacycle transfer capabilities.¹

1.5 Optical properties of poly(phenylenediene)s

Tilley *et al* have studied the optical capabilities of the polymers shown in Figure 10. The poly(phenylenediene)s formed were studied in dilute deoxygenated THF solutions. The absorption and emission data is summarized in Table 1. From the absorption data collected it is apparent as the ring size decreases the absorption of the polymer becomes more red-shifted. It is also apparent that the substituents on the aryl ring affect absorptions. There is an auxochromic red shift of 52 to 76 nm for A polymers when compared to B polymers (see Table 1). In any case, it is possible to tune these polymers to absorb specific ranges of wavelengths; thus, demonstrating their optical properties and their potential usefulness as organic light emitting diodes.³

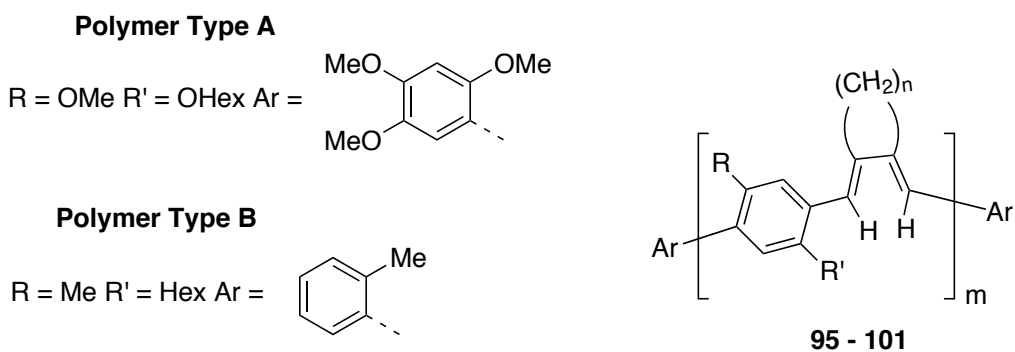


Figure 10: Band gap tunable poly(phenylenediene)s that Tilley *et al.* reported.³

Polymer	λ_{max} (nm)	λ_{max} (nm)	Colour
	Absorption	Emission	
A _{n=4}	368	489	Yellow
A _{n=3}	472	546	Red
A _{n=2}	524	619	Purple
B _{n=4}	316	437	Colourless
B _{n=3}	414	495	Orange
B _{n=2}	438	556	Red

Table 1: Optical properties of poly(phenylenedieneylene)s.³

1.6 Aim of Project

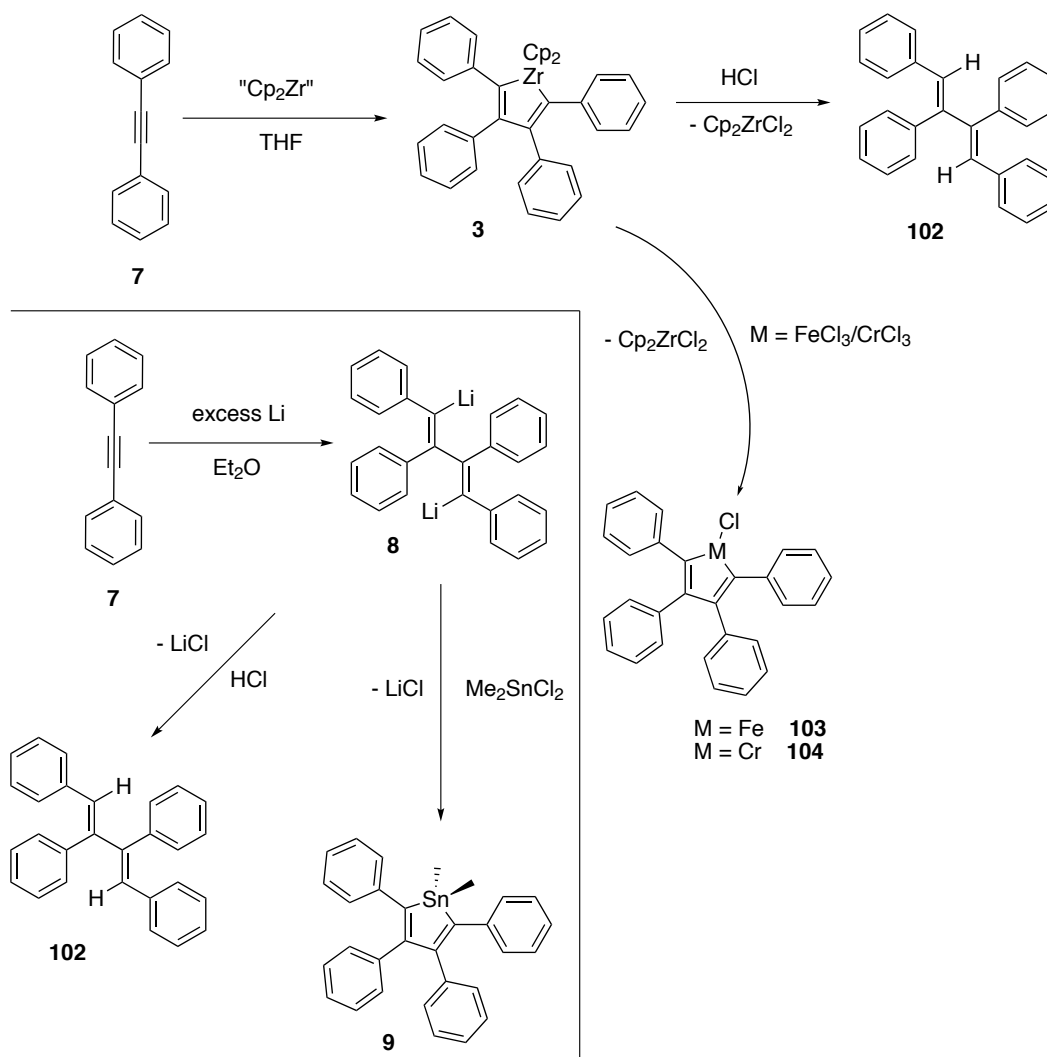
The aim of this project was to investigate and study the metal induced coupling (*i.e. via* lithium or zirconocene dichloride) of alkynes and diynes. Furthermore, to familiarize and expand our knowledge of metallacycle transfer and substitution capabilities of known zirconacyclopentadienes and related polymers. For instance, the attempted synthesis of a chromole and ferrole from 2,3,4,5-tetraphenylzirconacyclopentadiene. Alternatively, the attempted synthesis and post modification of Tilley *et al.* polymer analogs. A great deal of emphasis was placed on the metallacycle transfer to thiophene-based products. Thiophenes offer air and moisture stability due their aromaticity (*i.e.* two free lone pairs) and increased electrical properties for the same reason (versus antiaromatic boroles or nonaromatic zirconacyclopentadienes). Therefore, thiophenes and thiophene derivatives (*i.e.* thiophene oxides) proposed a useful target product. However, other main group atoms such as phosphorous were investigated.

2 Results and discussion

Within this chapter the synthesis and attempted synthesis with corresponding characterization related to metalloles, monomers, and polymers based on zirconocene-coupling and lithium coupling will be explored.

2.1 Synthesis of metallole precursors and attempts at synthesis of metalloles

Specific details to the synthesis with corresponding characterization (when possible) of 2,3,4,5-tetraphenylzirconacyclopentadiene (**3**) and 1,4-dithio-1,2,3,4-tetraphenyl-1,3-butadiene (**8**) and all subsequent reactions related to these two compounds will be presented within this section as seen in Scheme 27.



Scheme 27: Zirconocene-coupling and lithium metal-induced coupling reactions to synthesize various intermediate and final compounds.

2.1.1 Synthesis of 2,3,4,5-tetraphenylzirconacyclopentadiene (**3**) and derivatives (**102** to **104**)

The successful synthesis of 2,3,4,5-tetraphenylzirconacyclopentadiene (**3**) was based on the modification of two methods previously reported by Fagan *et al.*¹⁹ (method 1) and Negishi *et al.*⁹¹ (method 2). Method 1 was attempted first and only trace amounts of product were isolated. The method stated that *n*-BuLi should be added after diphenylacetylene and zirconocene dichloride were already dissolved with THF and cooled to -78°C.¹⁹

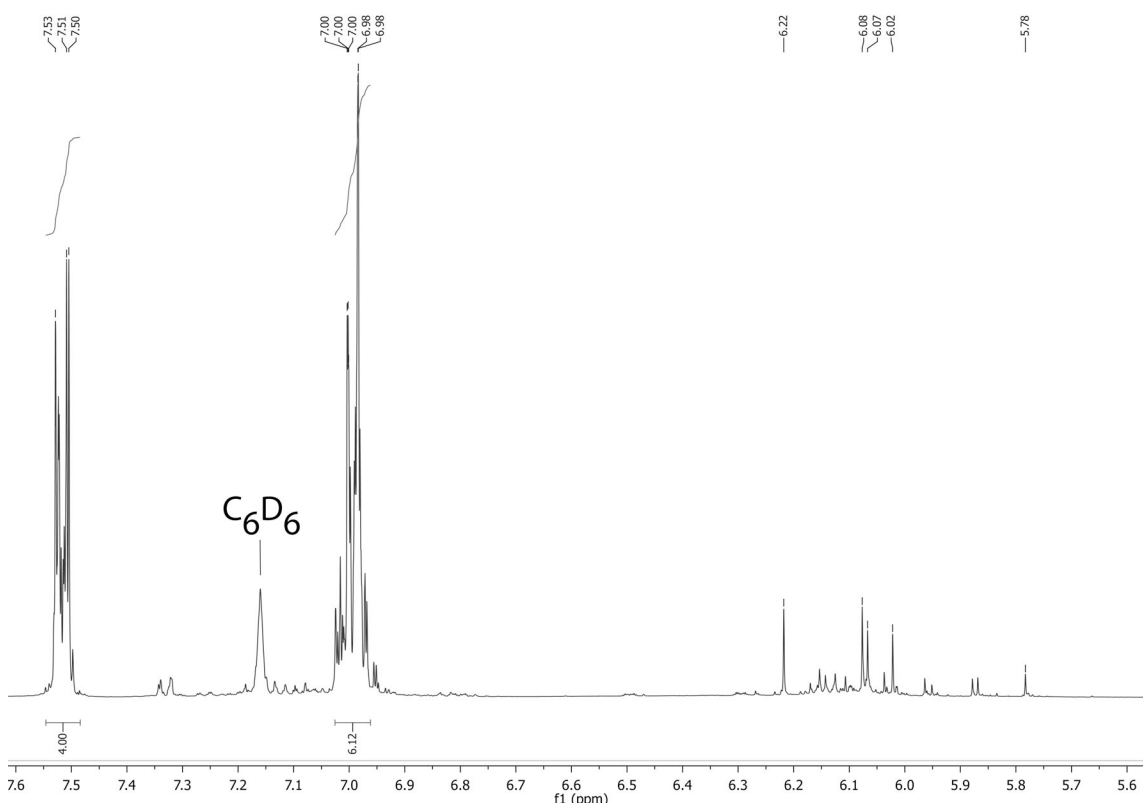


Figure 11: A ¹H NMR spectrum of a reaction mixture, focused within the aromatic region, that followed the method reported by Fagan *et al.*¹⁹

After performing ¹H NMR analysis (see Figure 11) on the reaction mixture of method 1 only trace amounts of **3** were observed suggested by the singlet resonance signal at $\delta = 6.02$ ppm, which was close to the literature value of $\delta = 6.01$ ppm for **3**.¹⁹ Unfortunately, unreacted diphenylacetylene, which has multiplet resonance signals at $\delta = 7.51$ and 7.00 ppm were also observed.⁹² Moreover, several resonance signals were observed within $\delta = 6.22$ and 5.78 ppm. Majority of the signals were believed to be zirconole intermediates (*e.g.* η^2 -coordination) due to the singlet splitting pattern, characteristic of

cyclopentadienyl rings, and the chemical shifts expected for such species.³⁴ Further analysis by ¹³C NMR and 2D NMR spectroscopy is required to help assign the doublet resonance signals at $\delta = 6.08$ ppm, the multiplet resonance signals that overlap in that region, and confirm suspicion of zirconole intermediates. There was no unreacted zirconocene dichloride observed supported by the lack of a singlet resonance signal at $\delta = 5.90$ ppm.⁹³

Negishi *et al.* (method 2) described the mechanism by which zirconocene dichloride becomes reactive.⁹¹ Negishi *et al.* demonstrated *via in situ* ¹H NMR spectroscopy study that with the addition of *n*-BuLi to a solution of zirconocene dichloride in THF that *n*-BuLi reduces zirconocene into a highly reactive species (*i.e.* typically shown in literature as "Cp₂Zr"). The decomposition of *n*-Bu₂ZrCp₂ into "Cp₂Zr" was considered the rate-determining step. With the addition of alkyne to the reactive "Cp₂Zr" species the zirconacyclopentadiene was readily made. Butane and 1-butene were reported as by-products.⁹¹

By utilizing the chemicals suggested by Fagan *et al.* and by introducing diphenylacetylene after *n*-BuLi, as suggested by Negishi *et al.*, **3** was successfully synthesized in high yields (80%). Unfortunately, **3** was quite air and moisture sensitive and had a short life span even when kept under argon at a temperature of -20°C. After further research an identical method to ours was found, which was used by Le Floch *et al.*, but yields were not reported as it was used *in situ* to form a phosphole.⁹⁴

Alternatively methods to synthesize **3** were studied and in some cases attempted. For instance, Rausch *et al.*, reported that Cp₂Zr(CH₃)₂ in the presence of UV electromagnetic radiation could induce photolytically the formation of "Cp₂Zr", which would then react with alkynes. Although considered an elegant reaction by Rausch *et al.* for the preparation of metallocenes there were several disadvantages. Rausch *et al.* reported 35% to 50% yields for **3** and that the photolytic reaction was solvent dependent.⁹⁵ Due to low yields and solvent restrictions this reaction was passed. Farona *et al.* reported the synthesis of **3** was possible using magnesium in excess, a stoichiometrically equal amount of HgCl₂, and excess amount of diphenylacetylene in respect to zirconocene dichloride.²⁰ Unfortunately, after several attempts no **3** was isolated. After consulting with Dr. Farona it was then concluded that the *n*-BuLi route was the most viable option (see Figure 12).

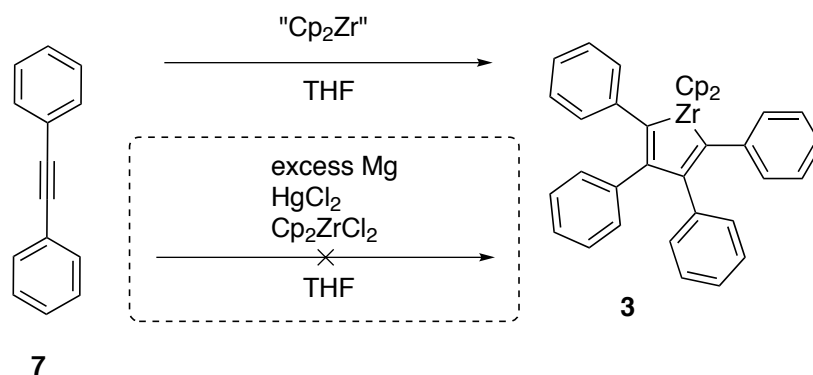


Figure 12: Attempted zirconocene related reactions to synthesize compound 3.

Compound **3** is sensitive to oxygen and readily forms insoluble oxides. Therefore, a small aliquot of a solution of **3** was hydrolyzed with aqueous 1 M HCl in a Schlenk flask under argon to produce a more manageable product that would indirectly provide sufficient evidence that **3** was synthesized.

The transition metal based salts, $\text{CrCl}_3(\text{THF})_3$ and FeCl_3 in THF, were added at a 1:1 mole ratio to two independent solutions of **3** as an attempt to synthesize a chromole (**104**) and ferrole (**103**).

2.1.1.1 Characterization of compound 3 and derivatives (**102** to **104**)

The ruby crystals of **3** that were isolated from the procedure above were characterized using ^1H NMR analysis in C_6D_6 (see Figure 13). The ^1H NMR analysis showed a cluster of multiplet resonance signals and a doublet resonance signal integrating in *ca.* 20:10 ratio. No unreacted diphenylacetylene multiplet resonance signals ($\delta = 7.51$ and 7.00 ppm) were observed.⁹² A rather large benzene resonance signal was observed at $\delta = 7.16$ ppm. The cluster of multiplet resonance signals observed within $\delta = 7.10$ to 6.66 ppm range showed an integral of 20 protons and were consistent with the aromatic protons which have been assigned as *b* to *g* in Figure 13. Examination of the molecular structure of **3** would suggest that protons *b* and *d* and protons *e* to *g* should have overlapping monosubstituted benzene splitting patterns. The magnetically inequivalent carbon atoms in the attached carbon-carbon double bond and the anisotropic effect thereof would cause the overlap. If the carbon atoms in the carbon-carbon double bond were magnetically equivalent a single monosubstituted benzene-splitting pattern with an integral representative of four phenyl substituents rather than two would be observed. Unfortunately, the aromatic substituents have more complicated splitting patterns involving not only $^3J_{ortho}$ coupling, but also $^4J_{meta}$ coupling and possibly $^5J_{para}$ coupling.

Expansion of the aromatic region shows several overlapping resonance signals and resonance signals that appear as doublets with second-order interactions that were not expected and made the analysis of the spectrum more difficult. The doublet resonance signal observed at $\delta = 6.01$ ppm showed an integral of 10 protons and was consistent with the cyclopentadienyl protons which have been assigned as environment *a*. The downfield shift ($\delta = 5.90$ to 6.01 ppm) observed for the cyclopentadienyl protons was expected due to the loss of two chlorides and with the incorporation into a cyclopentadiene ring. Similar to phenyl protons, it was expected that the cyclopentadienyl protons would have a singlet splitting pattern due to magnetically equivalent protons. However, a second resonance signal was observed overlapping the expected singlet resonance signal. This may have occurred due to magnetically inequivalent protons in the cyclopentadienyl ring due differing conformations and anisotropic effects from the phenyl substituents. Some residual zirconocene dichloride was believed to be present, but due to the identical deviations observed from $\delta = 5.90$ ppm for zirconocene dichloride, the assignments for resonance signals $\delta = 5.87$ and 5.93 ppm require further investigation. Although, the ^1H NMR spectrum of **3** is in agreement with literature further analysis by X-Ray crystallography is still required.¹⁹

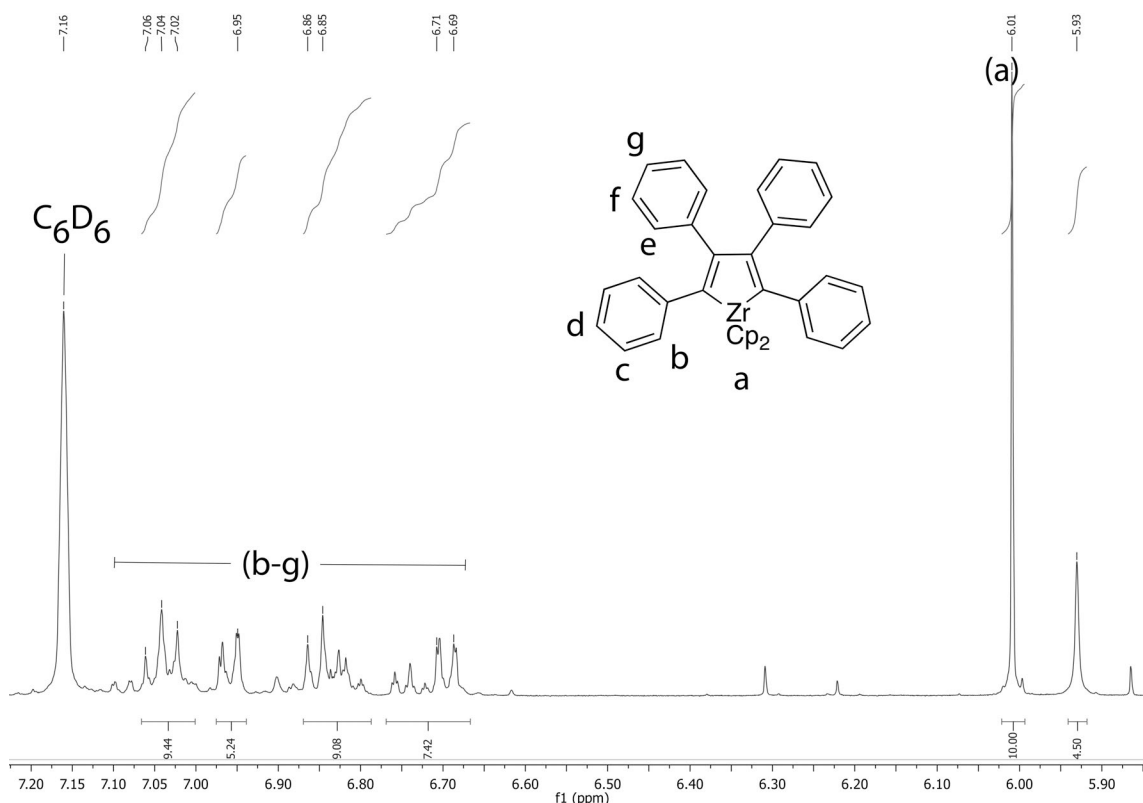


Figure 13: A ^1H NMR spectrum of compound **3 focused within the aromatic region.**

1,2,3,4-tetraphenyl-1,3-butadiene (**102**) was characterized by ^1H and ^{13}C NMR analysis in CDCl_3 (see Figure 14 and Figure 15). The ^1H NMR analysis showed three clusters of multiplet resonance signals and a singlet resonance signal integrating in *ca.* 10:6:4:2 ratio. The overlapping multiplet resonance signals observed within $\delta = 7.43$ to 7.30 ppm range showed an integral of 10 protons and were consistent with the aromatic protons which have been assigned as environments *b* to *d*. Similar to the above molecular structure examination of **3**, six unique aromatic protons environments should have overlapping splitting patterns characteristic of monosubstituted benzene. However, more widely spaced resonance signals are expected from environments *g* to *f* relative to the spacing of resonance signals associated with environments *b* to *d* as a result of the magnetic inequivalency of the carbon atoms in the carbon-carbon double bonds of the butadiene moiety and the related anisotropic effects. The loss of the Cp_2Zr and the gain of two protons on the carbon-carbon double bonds would also help explain the difference in spectra observed for **102** compared to **3**. The shift and relative integration (six protons) of overlapping multiplet resonance signals observed within $\delta = 7.05$ to 7.00 ppm range are consistent with those expected from environments *e* and *f* ppm. The resonance signal associated with aromatic proton environment *g* ($\delta = 6.77$ to 6.71 ppm, relative integration of four) was expected to be shifted the furthest upfield due to the phenyl groups being located in position 2 and 2' along the butadiene moiety. Expansion of the region reveals doublet of doublets splitting pattern, which further supports the assigned environment for protons *g*.

Coupling constants with magnitudes characteristic of $^4J_{\text{meta}}$ coupling (*ca.* 4 Hz) and $^3J_{\text{ortho}}$ coupling (*ca.* 8 Hz) were observed throughout the aromatic region, as well, in all similarly structured compounds within 2.1. The singlet resonance signal observed at $\delta = 6.31$ ppm showed an integral of two protons and was consistent with the protons bound to the butadiene moiety in environment *a*. These protons were the most readily identifiable signal in the ^1H NMR spectrum of **102** as a singlet resonance signal was expected slightly upfield from the aromatic region. The singlet resonance signal observed at $\delta = 7.26$ ppm is characteristic of chloroform. The resonance signals observed were in agreement with literature.⁹⁶

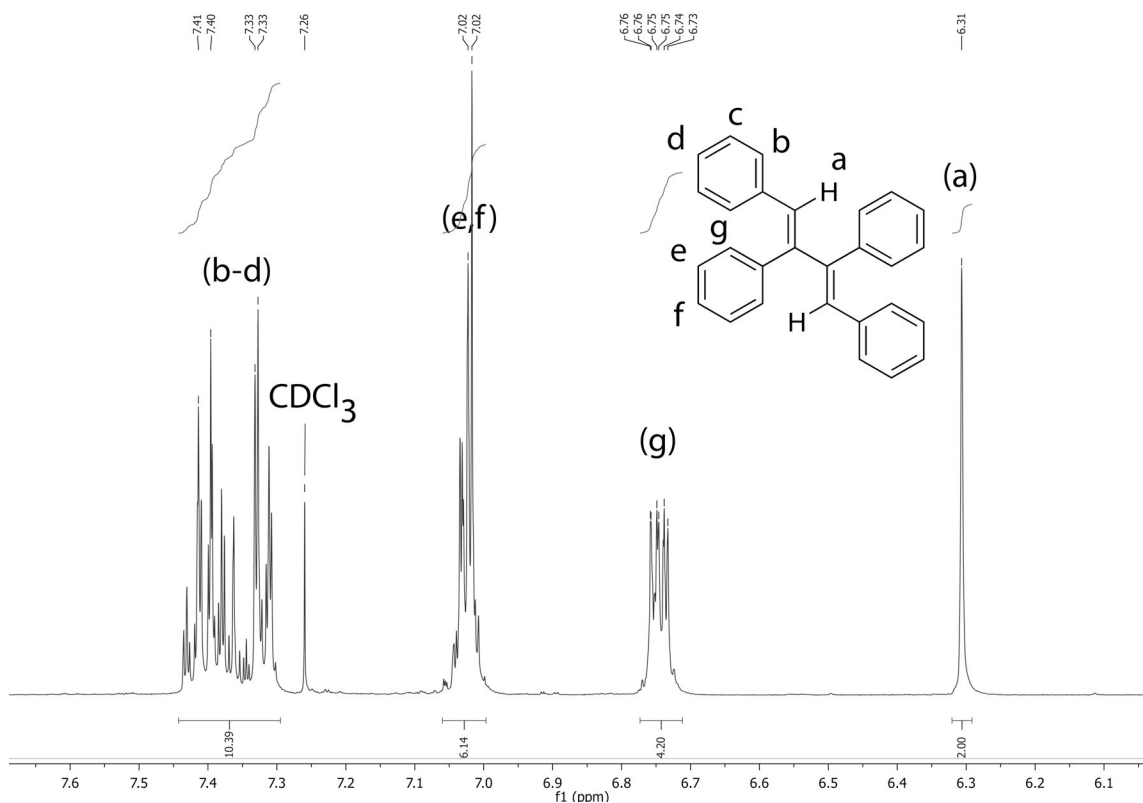


Figure 14: A ^1H NMR spectrum of compound **102 focused within the aromatic region.**

The ^{13}C NMR analysis of **102** had the appropriate amount of observed chemical environments (10). Unfortunately, resonance signals associated with both alkenes and aromatics can fall within the $\delta = 140$ to 100 ppm range of a ^{13}C NMR spectrum.

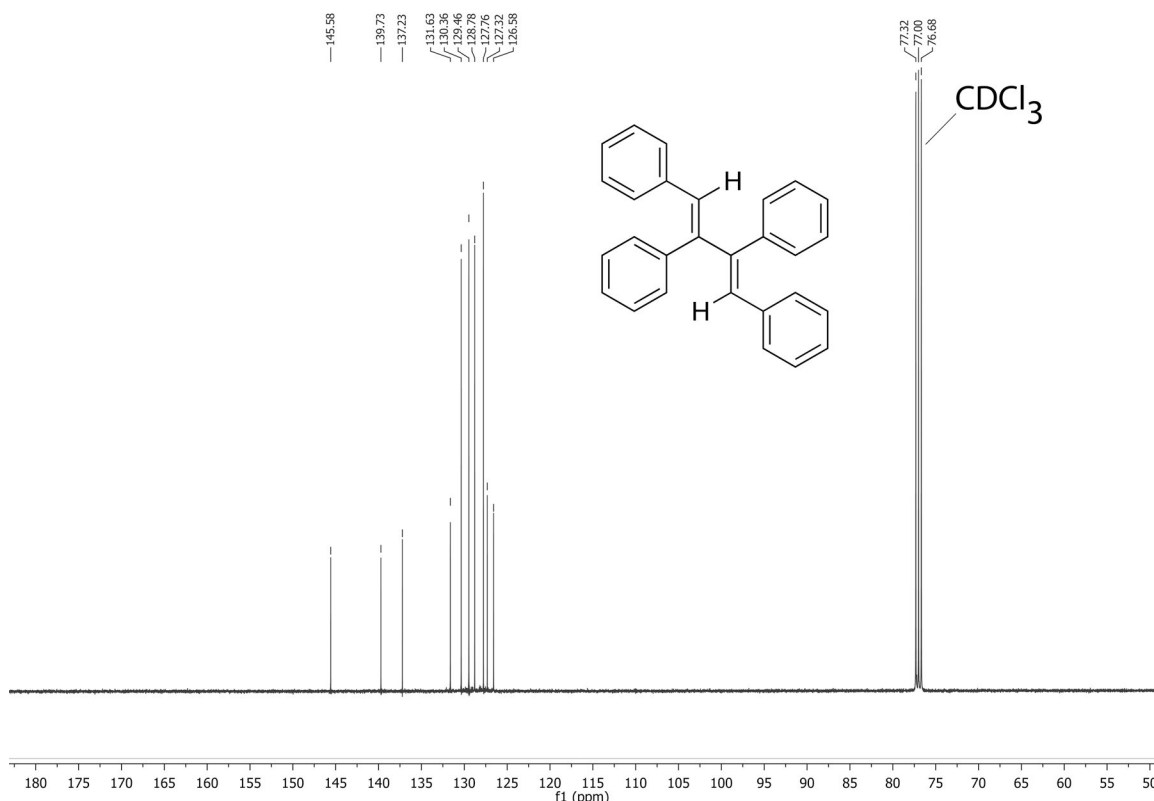


Figure 15: A ^{13}C NMR spectrum of compound **102** focused within the aromatic region.

2.1.1.2 Characterization of the brown oil from the attempted synthesis of **103**

The crude brown oil from the reaction mixture of the attempted synthesis of compound **103** was characterized by ^1H NMR analysis in C_6D_6 (see **Error! Reference source not found.**). The ^1H NMR spectrum suggested the formation of zirconocene dichloride (*i.e.* $\delta = 5.88$ ppm). The singlet resonance signal at $\delta = 7.16$ ppm is characteristic of benzene. The singlet resonance signals at $\delta = 7.52$ and 6.99 ppm match diphenylacetylene. However, diphenylacetylene (**7**) should have a complex pattern of overlapping multiplet resonance signals while only two singlet resonance signals are present in the spectrum. NMR artifacting due to improper shimming could account for the loss of resolution and broadening of these resonance signals and others observed.⁹⁷ Nonetheless, the presence of diphenylacetylene and zirconocene dichloride would suggest that **3** decomposed into starting reactants as **3** was confirmed before the reaction took place. There was also slight toluene contamination suggested by the resonance signal at $\delta = 2.11$ ppm. The corresponding toluene resonance signals ($\delta = 7.13$ and 7.02 ppm) were overlapped with **7** and benzene but represent very little of the integral shown.

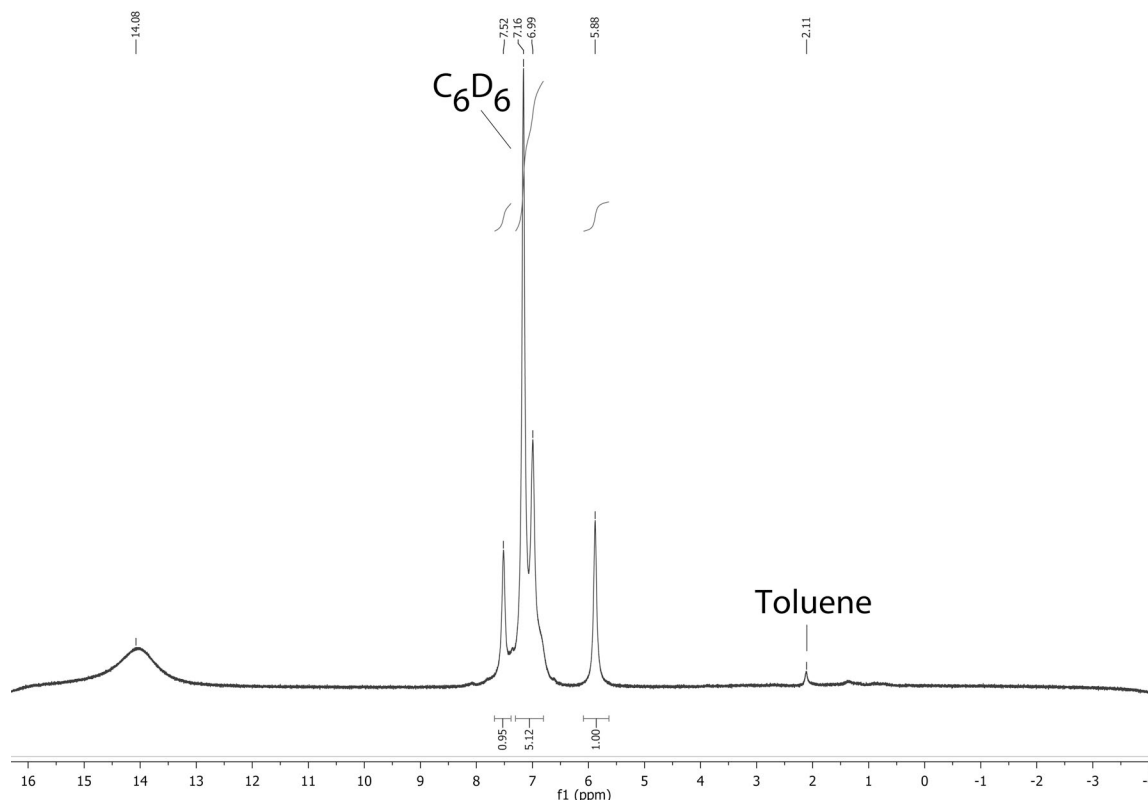


Figure 16: A ^1H NMR spectrum of the brown oil from the attempted synthesis of 103.

2.1.1.3 Characterization of the crystals isolated from the attempted synthesis of 104

The crude green crystals isolated from the reaction mixture of the attempted synthesis of compound **104** were characterized by ^1H NMR analysis in C_6D_6 (see Figure 38). Unfortunately, the characteristic resonance signal for the Cp groups $\delta = 6.02$ ppm indicated the presence of significant amounts of unreacted **3**. However, the resonance signal at $\delta = 5.87$ ppm is consistent with the formation of zirconocene dichloride during the reaction.⁹³ The formation of zirconocene dichloride suggests that metallacycle transfer with $\text{CrCl}_3(\text{THF})_3$ may have occurred, as there was no other source of chlorides available. The singlet resonance signal at $\delta = 7.16$ ppm is characteristic of benzene.

Qualitatively, the colour change from purple to green that was observed during the attempted synthesis of **104** would suggest that moisture was present and had coordinated with CrCl_3 . $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ appears as a dark green colour. Further investigation in the actual reaction-taking place should be pursued. Studies *via* variable temperature ^1H NMR spectroscopy may give further insight into the mechanism of **3** in the presence of CrCl_3 .

X-Ray crystallographic analysis of crystals isolated from the reaction mixture revealed the presence of either decomposition products or reaction by-products, as the data was consistent with those previously reported for both **102** and zirconocene dichloride were observed. As **102** was not observed in Figure 17, the crude green crystals that were isolated could have reacted and changed composition.

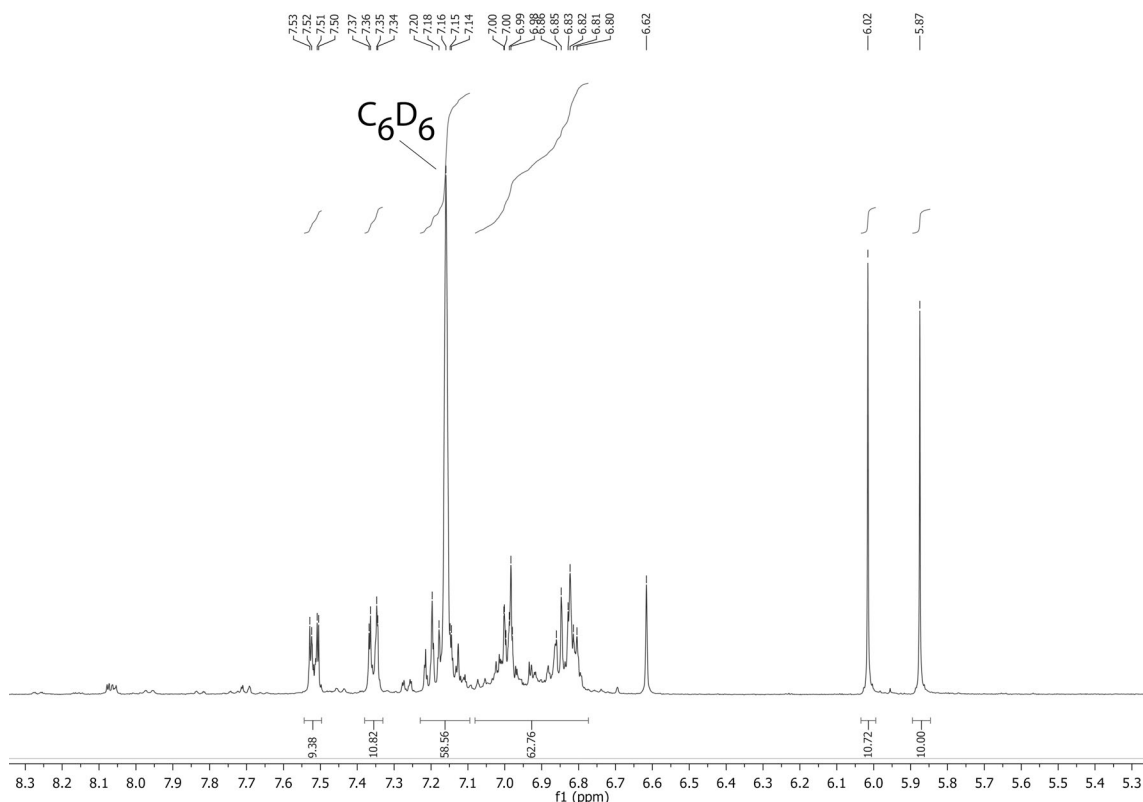


Figure 17: A ^1H NMR spectrum of the green crystals in the aromatic region from the attempted synthesis of **104.**

2.1.2 Synthesis of 1,4-dithio-1,2,3,4-tetraphenyl-1,3-butadiene (**8**) and derivatives (**9**, and **102**)

The synthesis of 1,4-dithio-1,2,3,4-tetraphenyl-1,3-butadiene (**8**) followed a method reported by Eisch *et al.*¹⁶ According to Eisch *et al.* several competing mechanisms can occur such as the formation of 1,2-diphenylethenes or 1,2,3-triphenylnaphthalene.¹⁶

A solution of **7** and lithium wire (six equivalent excess) in Et_2O were stirred at room temperature for several hours under argon. After several hours a red solution formed with yellow precipitate. The reaction mixture was left to stir for 30 minutes after the initial appearance of yellow precipitate. The amount of yellow precipitate would increase by keeping the lithium in longer; unfortunately, there was the risk of

terminating the reaction if lithium remained in the reaction mixture for too long, which would result in the disappearance of the yellow precipitate and the reaction mixture turning black. After 30 minutes the removal of lithium was accomplished by decanting the reaction mixture into a new dried Schlenk flask. After the lithium pieces were removed, the solution was stirred for another 30 minutes.

Characterization of the organolithium compound could not be performed in a standard NMR tube as it would immediately hydrolyze. Isolation of the yellow precipitate (**8**) was accomplished by filtering it within a nitrogen-filled glove box. However, the risk of decomposition of the product by nitrogen was great. All subsequent reactions were completed *in situ*.

Indirect evidence of the formation of **8** was obtained from the synthesis of 1,2,3,4-tetraphenyl-1,3-butadiene, **102**, *via* the hydrolyzation of a small aliquot of a solution of **8** with aqueous 1 M HCl in a Schlenk flask. Recrystallization with DCM/EtOH produced white crystals of **102**.

Synthesis of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (**9**) was accomplished by following a reported method by Eisch *et al.*¹⁶ A Schlenk flask containing a solution of **8** was directly added to an equally stoichiometric amount of dimethyltin dichloride in THF. With the addition of **8** to the dimethyltin dichloride solution it began to change from red to a clear yellow solution. The reaction mixture was allowed to stir for two hours before removing the solvent and any volatiles. The yellow/white powder was washed with EtOH. Recrystallization with DCM/EtOH yielded low to moderate yield (maximum 20%). The order in which reactants were added to the reaction mixture played a critical role in controlling the composition of the products. When dimethyltin dichloride in THF was added to a solution of **8**, spirostannole would form as the major product. Similarly, if solution of **8** was added too quickly to the dimethyltin dichloride in THF, there was an increased possibility for the formation of spirostannole as the major product. The consideration of spirostannole as the major product in each of these cases was based on ¹H NMR analysis by Eisch *et al.*²⁶ However, no supporting information based on NMR spectroscopy were provided by Eisch *et al.* only melting point (275 - 277°C). Zavistoski *et al.* only provided elemental analysis and melting point (263°C).⁹⁸

2.1.2.1 Characterization of compound **8** and derivatives (**9**, and **102**)

1,2,3,4-tetraphenyl-1,3-butadiene (**102**) was characterized by ¹H and ¹³C NMR analysis in CDCl₃ (see Figure 14 and Figure 15). The results were identical to the hydrolyzation of **3** and the ¹H NMR spectrum was in agreement with literature.⁹⁶

1,1-dimethyl-2,3,4,5-tetraphenylstannole (**9**) was characterized using ^1H and ^{119}Sn NMR analysis in CDCl_3 (see Figure 18 and Figure 41 top). The ^1H NMR analysis showed four multiplet resonance signals in the aromatic region and a singlet resonance signal with tin satellites integrating in *ca.* 20:6 ratio. The multiplet resonance signals within $\delta = 7.08$ to 6.76 ppm range integrated for 20 protons and were consistent with the aromatic protons in environments *b* to *g*. The singlet resonance signal observed at $\delta = 0.62$ ppm integrated for six protons and was consistent with the methyl protons in environment *a*. These assignments were in agreement with literature.²⁶ When compared to the corresponding signal in dimethyltin dichloride the methyl resonance signal in **9** has shifted upfield to $\delta = 0.62$ ppm from $\delta = 1.21$ ppm. This was expected from the loss of two EWGs (i.e. chlorides) and with the addition of two EDGs (i.e. alkenes). There was also resonance signals from chloroform ($\delta = 7.26$ ppm) and contamination from silicone grease ($\delta = 0.07$ ppm), water ($\delta = 1.54$ ppm), and ethanol ($\delta = 3.72$ and 1.25 ppm).

The ^1H NMR analysis of the reaction mixture suggested the formation of spirostannole due to the detection of multiplet resonance signals in the aromatic region ($\delta = 7.53$ and 7.34 ppm) that showed an integral proton ratio of 1:1.5. The downfield shift of the signals compared to **9** can be explained by the significant amount of aromatic substituents present and the stronger anisotropic effect caused by the carbon-carbon double bonds that are all directly attached to a tin.

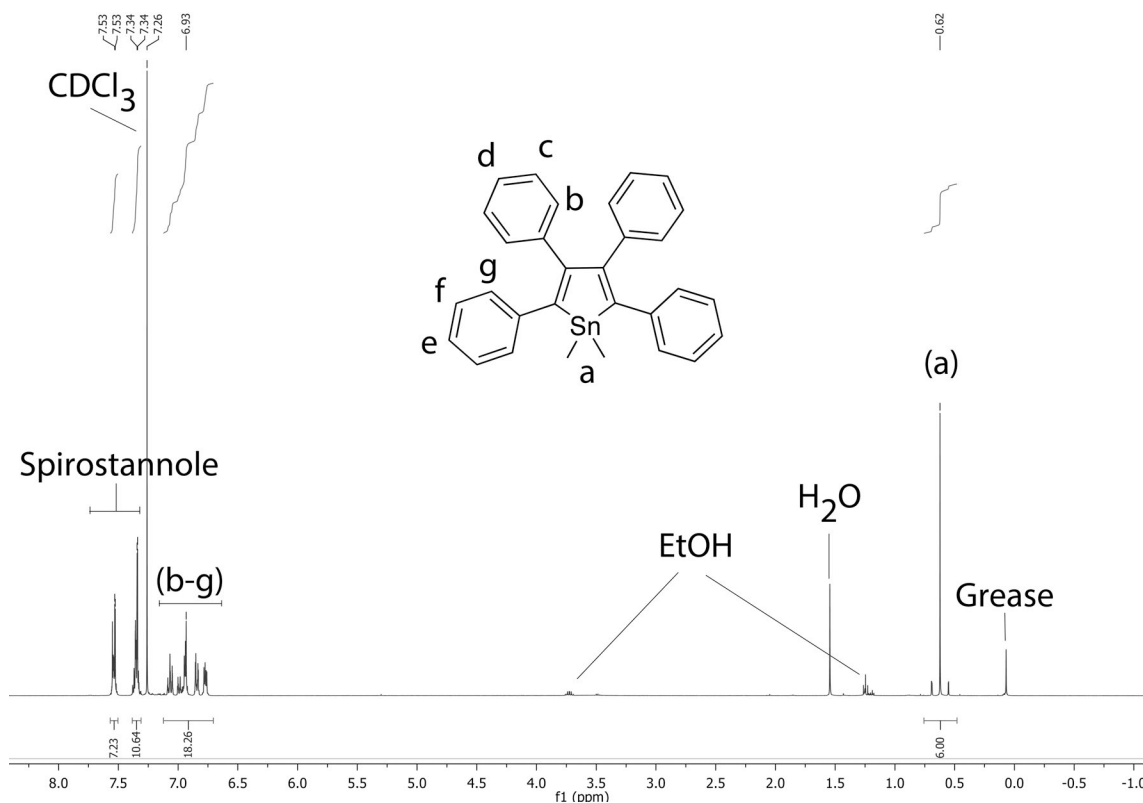


Figure 18: A ^1H NMR spectrum of compound **9** with contamination from suggested spirostannole (multiplet signals at $\delta = 7.53$ and 7.34 ppm).

^{119}Sn NMR analysis of pure **9** (obtained through recrystallization) had a resonance signal at $\delta = 52.84$ ppm (see Figure 19 top) that was located significantly upfield from the resonance signal of the starting material, dimethyltin dichloride ($\delta = 142.38$ ppm), which had been completely consumed during the reaction. With the loss of two chlorides and the gain of two alkenes this upfield shift was expected.

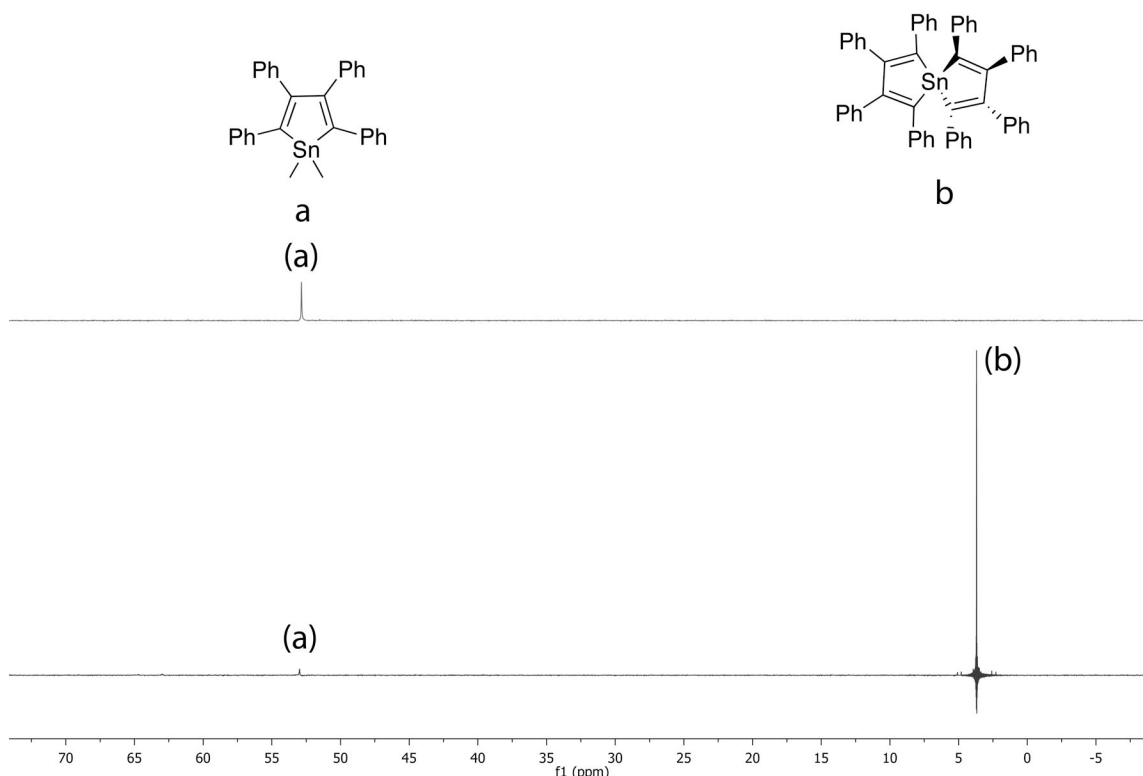
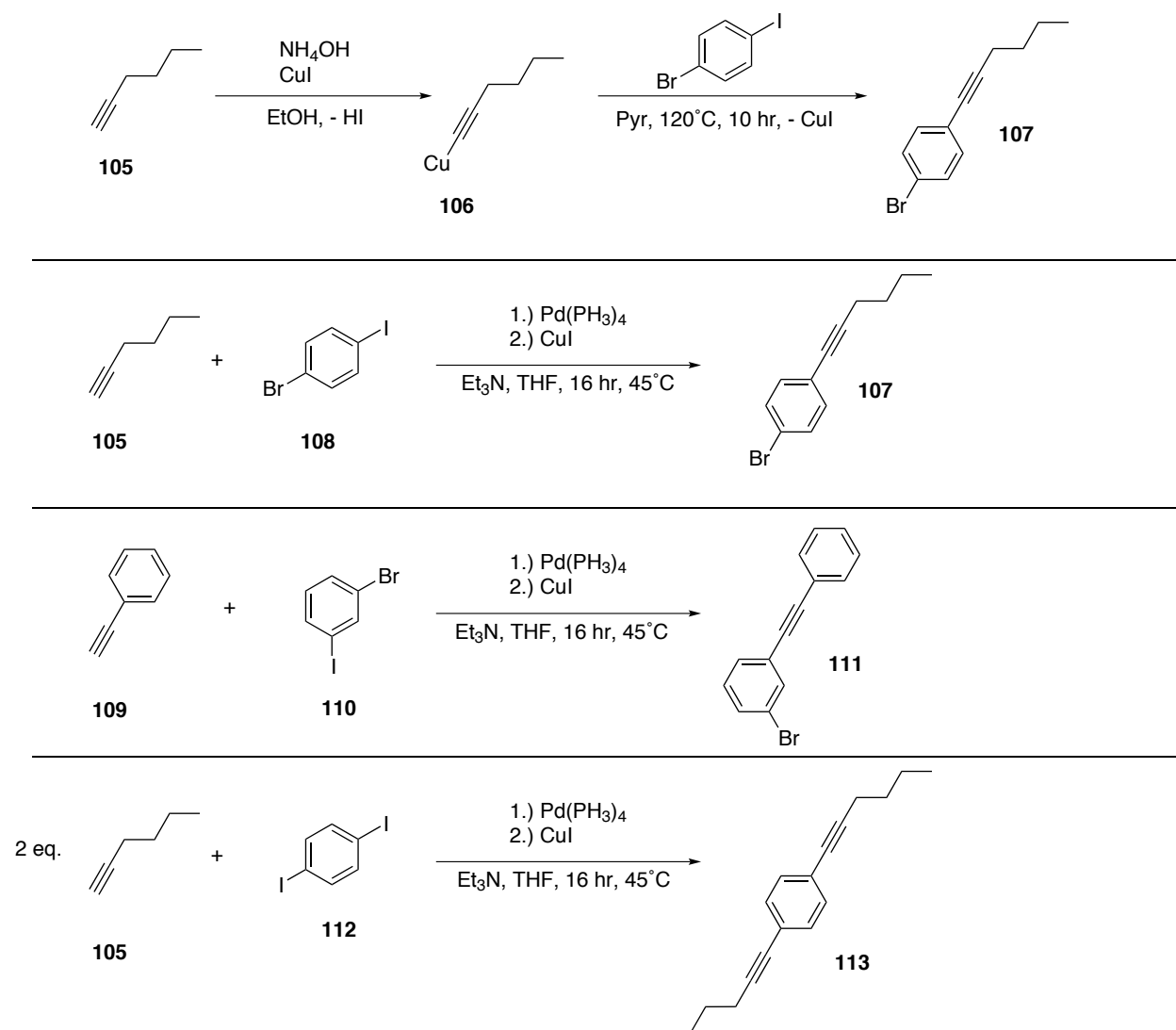


Figure 19: ^{119}Sn NMR spectra of pure compound **9** (top) and suggested spirostannole with compound **9** (bottom). The pure compound **9** was obtained through recrystallization. However, the bottom spectrum has no association with the ^1H NMR spectrum discussed previously.

However, if the reactants were added in the opposite order, as described above, an additional resonance signal at $\delta = 3.69$ ppm was also observed (see Figure 19 bottom). This resonance signal at $\delta = 3.69$ ppm potentially indicates the presence of the spirostannole reported by Eisch *et al.*²⁶ and Zavistoski *et al.*⁹⁸ The presence of two more EWGs (alkene substituents) on the spirostannole versus the two EDGs (methyl substituents) on **9** would upfield shift the spirostannole in respect to **9**. Unfortunately, tetraalkyltins can fall anywhere between 600 and 0 ppm on a ^{119}Sn NMR spectrum and no literature values exist for this specific compound; therefore, the suggested spirostannole could not be confirmed.⁹⁹

2.2 Synthesis of monomers *via* Castro-Stephens and Sonogashira coupling

A summary of Castro-Stephens and Sonogashira compounds (**106**, **107**, **111**, and **113**) will be presented within this section as seen in Scheme 28.



Scheme 28: Completed Castro-Stephens and Sonogashira couplings.

2.2.1 Synthesis of compounds **106**, **107**, **111**, and **113**

Cuprous *n*-Butylacetylide (**106**) was synthesized following a method reported by Castro *et al.*^{61,62} The yield was moderately high (79%). Another method, reported by Whiteley *et al.*, gave higher yields (89%).¹⁰⁰ The life span of the product would vary, but on average had a shelf life of one week before

turning brown. Attempts to increase the shelf life were pursued. Storing **106** under vacuum, nitrogen, or argon, all resulted with the same average life span of one week.

1-bromo-4-hex-1-ynyl-benzene (**107**) was synthesized following two methods. The first method based on Castro *et al.*^{61,62} reported synthesis of similar compounds produced a low yield (8%) for **107**. The second method based on Sonogashira *et al.*⁶³ produced a much higher yield (85%). Similarly, **111** and **113** also had moderate to high yields (86% to 87%) following Sonogashira *et al.* methodology.⁶³

2.2.1.1 Characterization of compounds 106, 107, 111, and 113

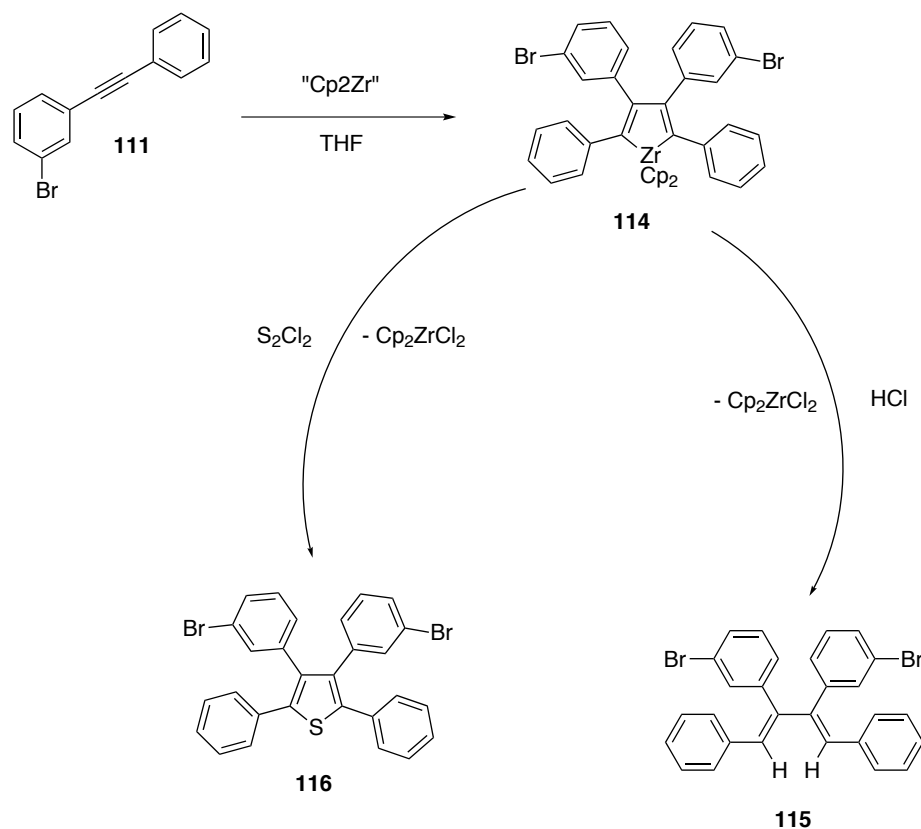
NMR analysis for **106** was made difficult as **106** was insoluble in all available deuterated solvents. The ¹H and ¹³C NMR analysis for **107**, **111**, and **113** were performed in CDCl₃ and in agreement with literature.^{101–103} Compound **107** was further characterized by AIMS AccuTOF-DART mass spectrometry.

Compound **107** was reportedly used in a zirconocene-coupling reaction. A Japanese patent exists by Tamotsu Takahashi that has utilized **107**, but very little detail was given in the patent.¹⁰⁴

The synthesis of **113** was to act as an alternative monomer for diyne zirconocene-coupling polymerization. Tilley *et al.* utilized 4,4'-di(hept-1-yn-1-yl)-1,1'-biphenyl, a slightly longer chained monomer, with success.¹⁰⁵

2.3 Attempted synthesis of novel monomers using 1-bromo-3-(phenylethynyl)benzene (**111**) as starting material for zero valent nickel polymerization

A summary of reaction products isolated from the attempted syntheses of compounds **114** to **116** will be presented within this section as seen in Scheme 29.



Scheme 29: Attempted reactions to synthesize novel monomers for zero valent nickel polymerization.

2.3.1 Attempted synthesis of 3,4-bis(3-bromophenyl)-2,5-diphenylzirconacyclopentadiene (**114**) and derivatives (**115** and **116**)

The attempted synthesis of 3,4-bis(3-bromophenyl)-2,5-diphenylzirconacyclopentadiene (**114**) was based on the modified method utilized in all zirconocene based reactions described in 2.1.1. A Schlenk flask containing zirconocene dichloride and THF was cooled to -98°C (toluene/liquid nitrogen slush bath). A hexanes solution of *n*-BuLi was added dropwise to the cooled reaction. The solution began to turn yellow. After 30 minutes a solution of **111** in THF was added. After another 30 minutes the reaction mixture was warmed to room temperature by removing the slush bath. The solution began to turn red. All subsequent reactions were completed *in situ* due to failed attempts to isolate. After solvent removal

and addition of recrystallization solvents (toluene/hexanes) to produce suitable crystals for X-Ray analysis, discolouration and formation of insoluble products occurred almost instantaneously.

A reaction mixture was prepared as described above. An aqueous 6 M HCl solution was added dropwise to the reaction mixture. The red solution turned clear yellow. After stirring for two hours the solvent and any volatiles were removed by vacuum. After an extractive workup (ethyl acetate, NaHCO₃, and NaCl) and removal of the solvent, the solid that remained was recrystallized in a DCM/hexanes mixture to form clear crystals.

Another reaction mixture was prepared as described above. Sulfur monochloride was added dropwise to the reaction mixture. The solution turned from red to brown-orange. After stirring for two hours the solvent and any volatiles were removed by vacuum. After an extractive workup (5% H₂SO₄, ethyl acetate, NaHCO₃, and NaCl) and removal of the solvent, the orange-brown residue was purified by flash chromatography (hexanes) to produce a viscous yellow liquid. Attempts to recrystallize this compound in DCM/hexanes failed. A viscous yellow liquid was all that remained from recrystallization.

Compounds attempted in these syntheses should not have any preference for α - or β - positioning of alkyne substituents due to similar electron withdrawing properties of each substituent and when silicon based substituents are not present. A distribution (symmetrical:asymmetrical 2:8 ratio) was observed by Tilley *et al.* for carbon based alkyne 4,4'-di(hept-1-yn-1-yl)-1,1'-biphenyl after polymerization *via* zirconocene-coupling.¹⁰⁵ However, the proposed structure for **114** and derivatives (**115** and **116**) were based on the symmetrical configuration due to **115** results.

2.3.1.1 Characterization of reaction products from the attempted syntheses of **114** to **116**

As mentioned above, attempts to isolate **114** using toluene/hexanes failed. Furthermore, characterization of the reaction mixture *via* ¹H NMR spectroscopy failed due to immediate conversion of reaction mixture to insoluble products.

The clear crystals were characterized using ¹H and ¹³C NMR analysis in CDCl₃ (see Figure 20 and Figure 21). The ¹H NMR analysis showed one multiplet resonance signal, three overlapping multiplet resonance signals, and a singlet resonance signal integrating in *ca.* 4:4:6:4:2 ratio. Examination of the molecular structure would suggest a monosubstituted benzenoid ring splitting pattern, a *meta*-disubstituted benzenoid ring-splitting pattern, and a singlet. The singlet resonance signal observed at δ = 6.31 ppm (integrating for two protons) was consistent with the protons bound to

the butadiene moiety in environment *a*. These protons were the most readily identifiable signal in the NMR spectrum of **115** as a singlet resonance signal was expected slightly upfield from the aromatic region.

Unlike what had been observed in the compound **102**, second-order interactions impeded coupling constant extraction for all multiplet resonance signals. However, observed relative integrations and expected chemical shifts helped assign the multiplet resonance signals. The multiplet resonance signals observed within $\delta = 7.53$ to 6.77 ppm range showed the expected integrations and were consistent with the aromatic protons in environments *b* to *h*. Proton environments were assigned based on their relative position to the butadiene moiety. Several smaller multiplet resonance signals and singlet resonance signals overlapped by **115** were observed.

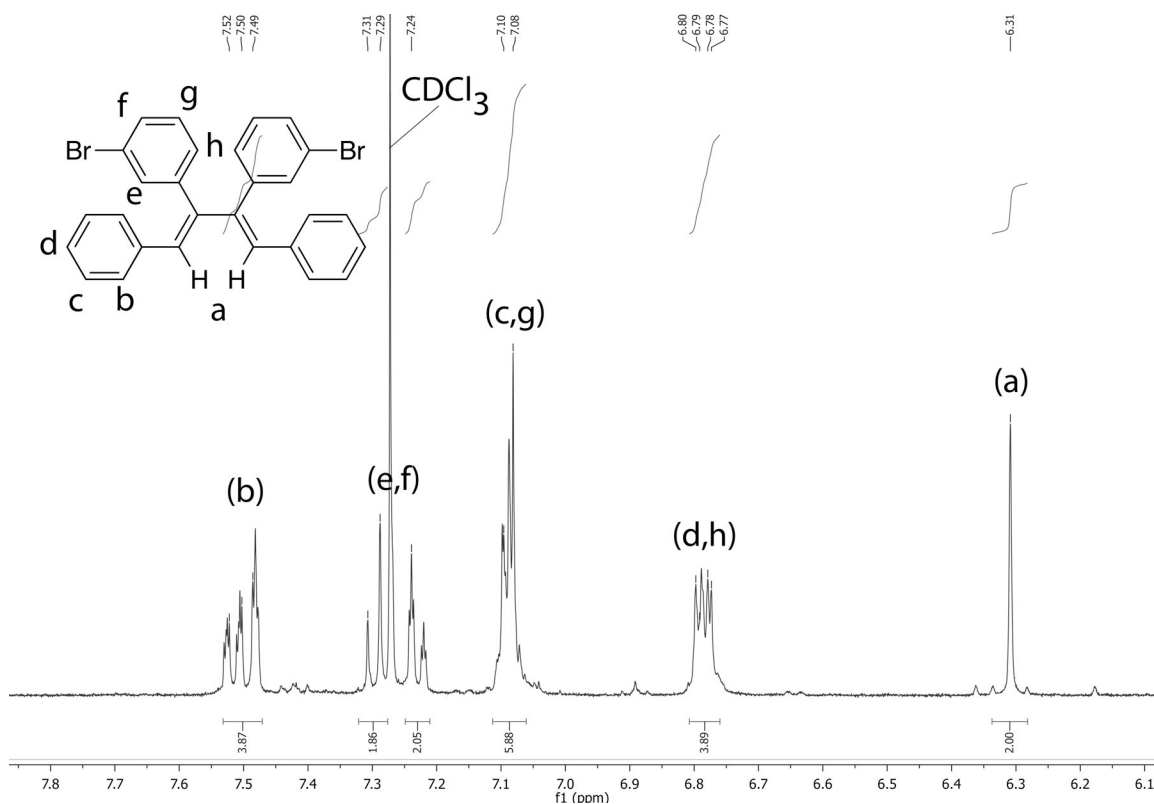


Figure 20: A ¹H NMR spectrum of suggested compound 115.

The ¹³C NMR assignments were considered arguable due to the amount of similar chemical environments within the aromatic region. However, the correct amount of chemical environments (12) were observed.

If indeed **115** was synthesized it would provide further insight into carbon based alkyne preferences.

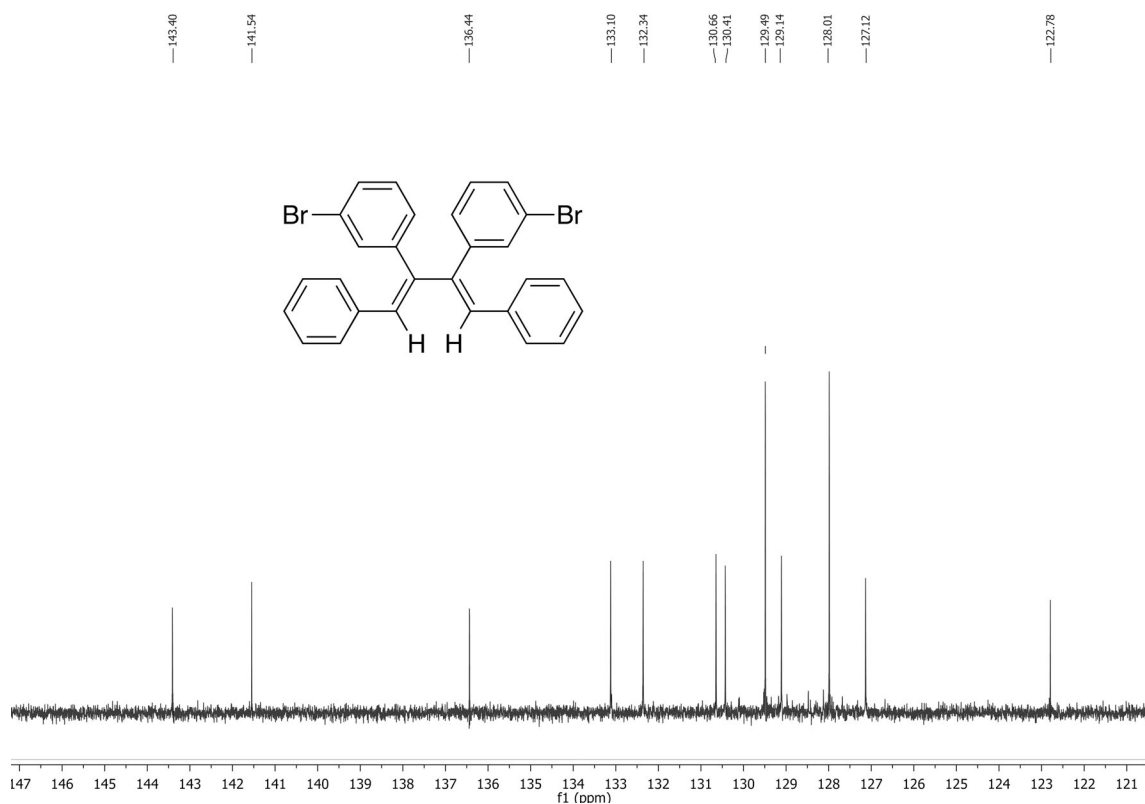


Figure 21: A ^{13}C NMR spectrum of suggested compound 115.

The viscous yellow liquid was characterized using ^1H and ^{13}C NMR analysis in CDCl_3 (see Figure 22 and Figure 23). ^1H NMR analysis showed a cluster of multiplet resonance signals within $\delta = 7.46$ to 6.89 ppm range. Examination of the molecular structure of **116** would suggest complicated multiplets in the aromatic region as observed for **115**.

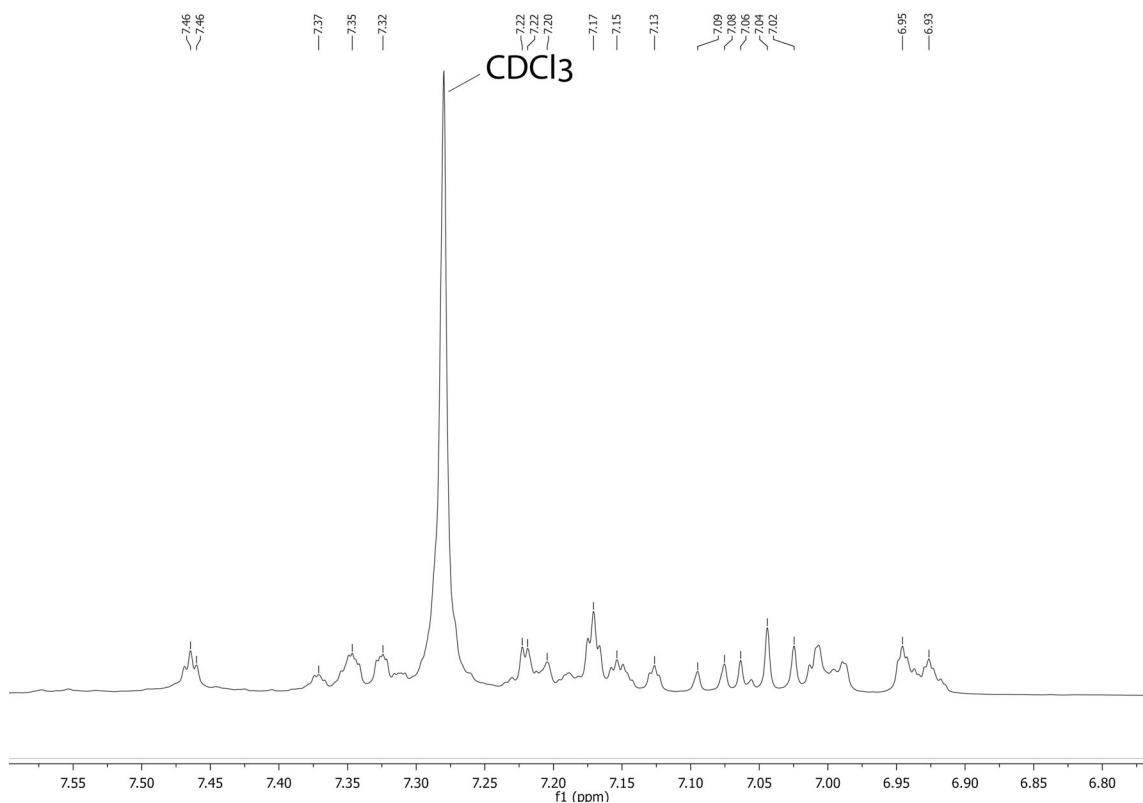


Figure 22: A ^1H NMR spectrum of the viscous yellow liquid from the attempted synthesis of 116.

The ^{13}C NMR analysis of the viscous yellow liquid suggests the presence of an aromatic compound due to the resonance signals that were observed within the aromatic range of 140 to 120 ppm. When compared to **115**, the resonance signals $\delta = 143.50$ and 141.54 ppm were absent. Unfortunately, low yields were expected based upon reported values from Fagan *et al.* for similar compounds (*e.g.* 55% yield with diphenylacetylene).¹⁹ Potential by-products were not discussed by Fagan *et al.* 2,3,4,5-tetraphenylthiophene oxide was reported to have resonance signals ranging from $\delta = 145.29$ to 128.05 ppm. The differences in resonance signals could be attributed to the presence of bromides on some of the benzenoid substituents.¹⁹

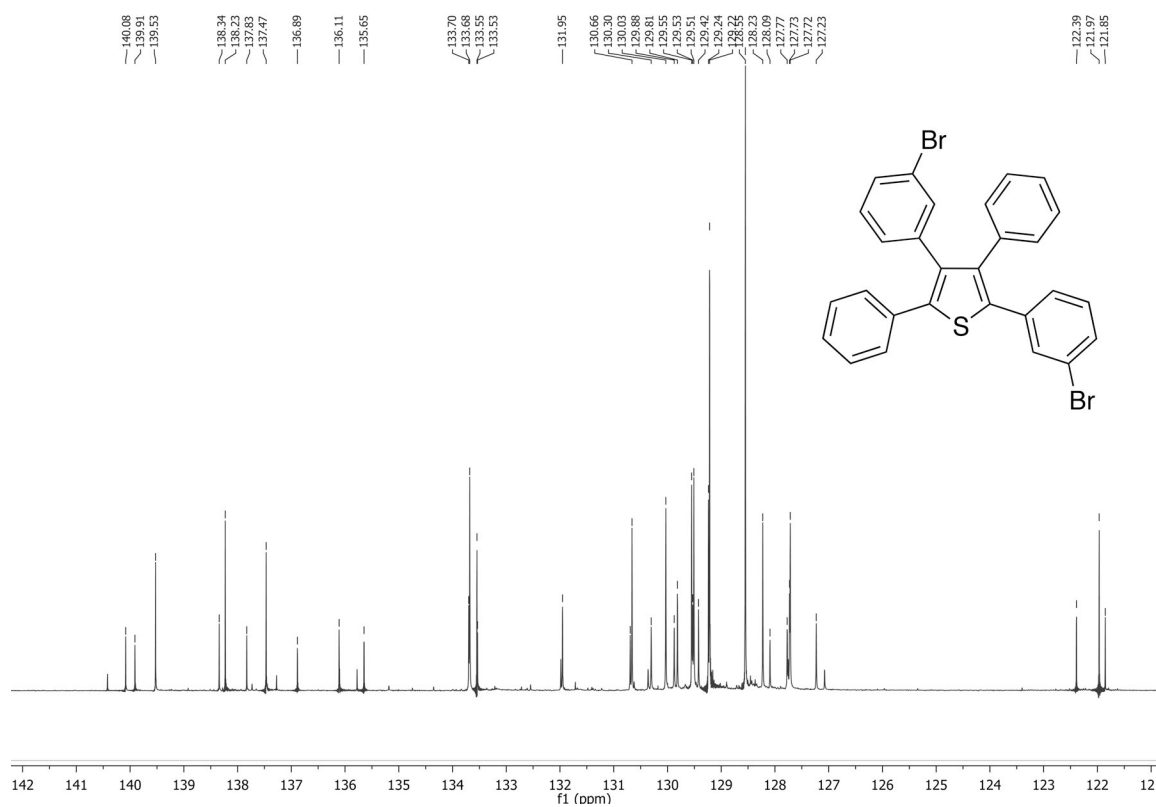
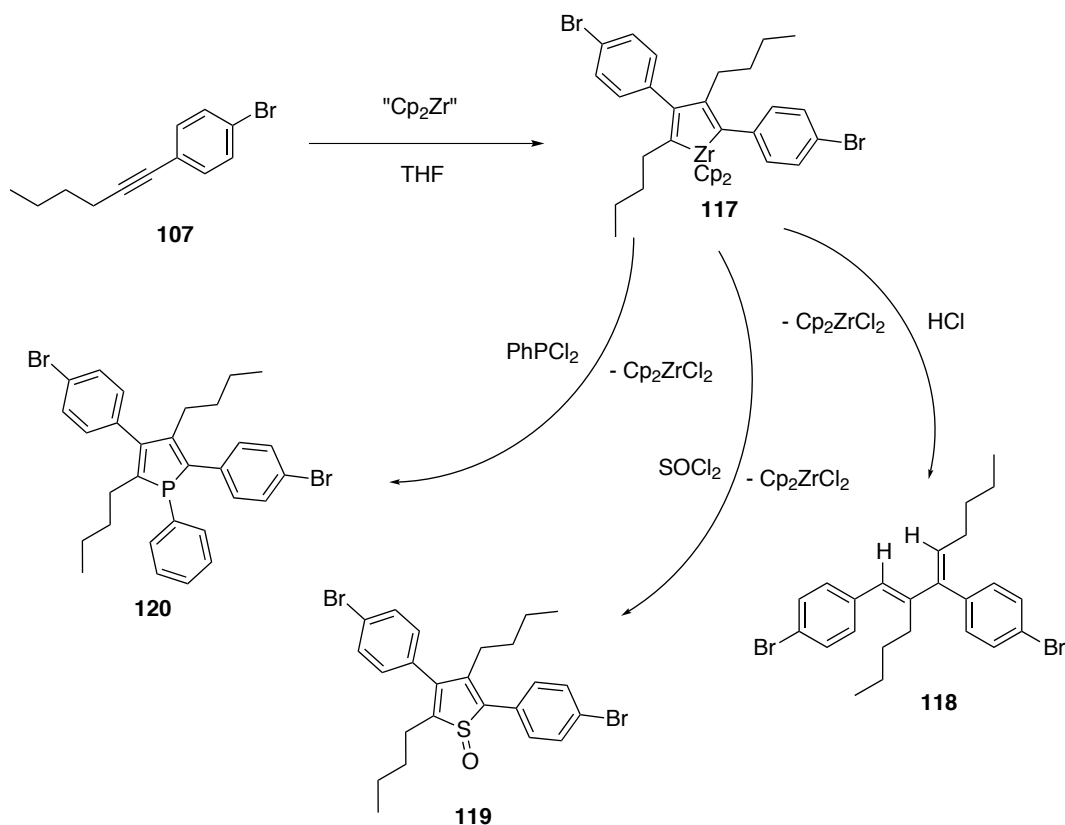


Figure 23: A ^{13}C NMR spectrum of the viscous yellow liquid from the attempted synthesis of 116.

2.4 Attempted synthesis of novel monomers using 1-bromo-4-(hex-1-ynyl)benzene (**107**) as starting material for zero valent nickel polymerization

A summary of reaction products isolated from the attempted syntheses of compounds **117** to **120** will be presented within this section as seen in Scheme 30.



Scheme 30: Attempted reactions to synthesize novel monomers for zero valent nickel polymerization.

2.4.1 Attempted synthesis of 2,4-bis(4-bromophenyl)-3,5-dibutylzirconacyclopentadiene (**117**) and derivatives (**118** to **120**)

The attempted synthesis of 2,4-bis(4-bromophenyl)-3,5-dibutylzirconacyclopentadiene (**117**) was based on the modified method utilized in all zirconocene based reactions described in 2.1.1. A Schlenk flask containing zirconocene dichloride and THF was cooled to -98°C (toluene/liquid nitrogen slush bath). A hexanes solution of $n\text{-BuLi}$ was added dropwise to the cooled reaction. The solution began to turn yellow. After 30 minutes a solution of **107** in THF was added. After another 30 minutes the reaction mixture was warmed to room temperature by removing the slush bath. The solution began to turn red. All

subsequent reactions were completed *in situ* due to failure to isolate without formation of insoluble products.

A reaction mixture was prepared as described above. After one hour of stirring an aqueous 6 M HCl solution was added dropwise. The red solution turned clear yellow. After stirring for two hours the solvent and any volatiles were removed by vacuum. After an extractive workup (5% HCl, ethyl acetate, NaHCO₃, and NaCl) and removal of the solvent, a light yellow liquid remained.

A reaction mixture was prepared as described above. At which point, dichlorophenylphosphine in slight excess to zirconocene dichloride was added dropwise. After stirring for 2 hours the solvent and any volatiles were removed by vacuum. In a nitrogen filled glovebox, the product was extracted from a brown residue with minimal hexanes, and the extract was filtered (medium-fast filter paper). The filtrate, brown liquid, was then vacuum dried for several days leaving a brown liquid.

A reaction mixture was prepared as described above. At which point, thionyl chloride in slight excess to zirconocene dichloride was added dropwise. After stirring for 2 hours the solvent and any volatiles were removed by vacuum. After an extractive workup (5% H₂SO₄, ethyl acetate, NaHCO₃, and NaCl) and removal of the solvent, the product was extracted from a orange residue with minimal hexanes, and the extract was filtered (medium-fast filter paper). The filtrate, orange liquid, was then vacuum dried for several days leaving a orange liquid.

Compounds attempted in these syntheses should not have any preference for α - or β - positioning of alkyne substituents due to similar electron withdrawing properties of each substituent and when silicon based substituents are not present. A distribution (symmetrical:asymmetrical 2:8 ratio) was observed by Tilley *et al.* for carbon based alkyne 4,4'-di(hept-1-yn-1-yl)-1,1'-biphenyl after polymerization *via* zirconocene-coupling.⁸⁵ However, the proposed structure for **117** and derivatives (**118** to **120**) were based on the asymmetrical configuration.

2.4.1.1 Characterization of reaction products from the attempted syntheses of **117** to **120**

Attempts to produce suitable crystals of **117** for X-Ray analysis failed with the immediate formation of insoluble products. Similarly, characterization attempts of **117** *via* NMR spectroscopy failed with the immediate formation of insoluble products and discolouration (i.e. loss of red colour). Therefore, **117** was used *in situ* to minimize any chance of discolouration and formation of insoluble products.

The isolated yellow liquid that remained from the reaction mixture of the attempted synthesis of **118** was characterized using ^1H , ^{13}C NMR spectroscopy in CDCl_3 (see Figure 24 and Figure 25) and mass spectrometry (see Figure 26). The ^1H NMR analysis showed identical resonance signals to that of **107**. Further investigation is required to determine if **117** decomposed or if **107** simply did not react with “ Cp_2Zr ”. It was quite possible that the long chain substituent hindered coupling and slowed the rate of coupling or reversed the coupling. In future, the reaction time should be increased to test this theory. *In situ* ^1H NMR acquisitions should also be conducted to study the reaction of **107** in the presence of “ Cp_2Zr ”.

Qualitatively, the reaction mixture for **117** appeared as a ruby red solution before the introduction of aqueous HCl . Further examination of the NMR acquisition shows noticeable smaller resonance signals throughout that do not correspond with any known solvent.

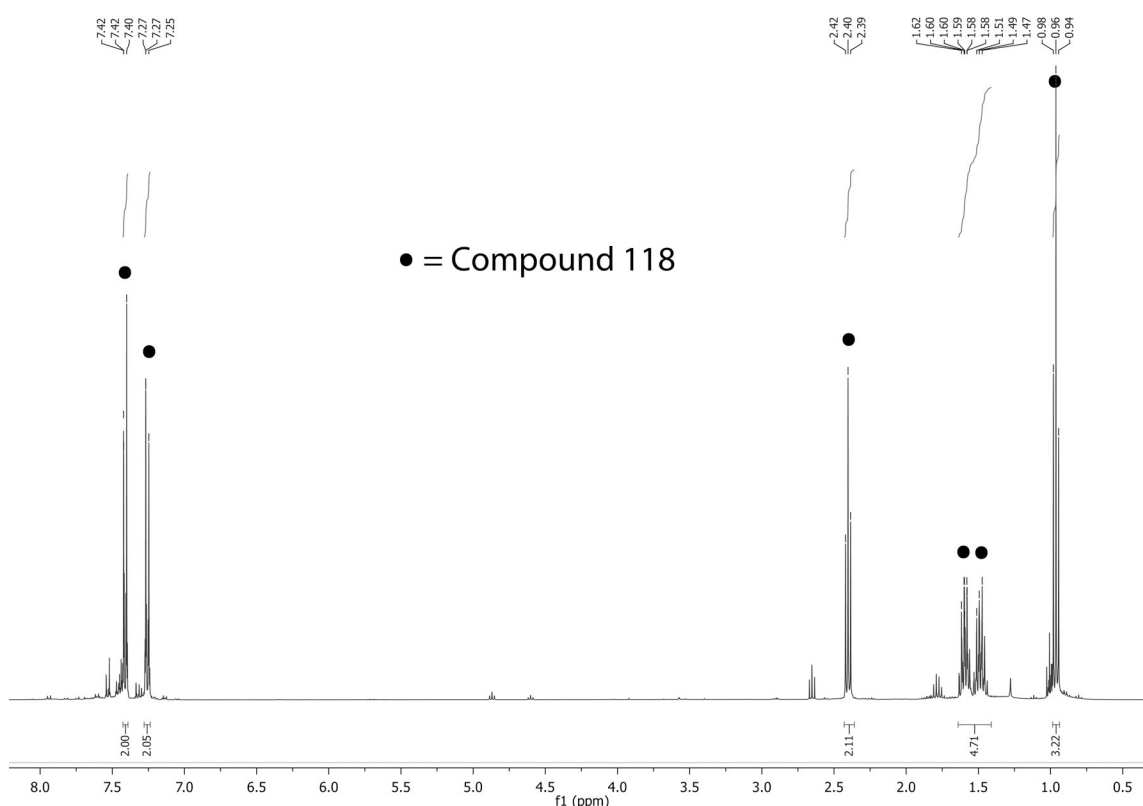


Figure 24: A ^1H NMR spectrum of the yellow liquid from the attempted synthesis of **118.**

Similar to the ^1H NMR analysis, the ^{13}C NMR analysis showed identical resonance signals to that of **107**. Resonance signals between $\delta = 135$ and 130 , at 47 , and 17 ppm were observed.

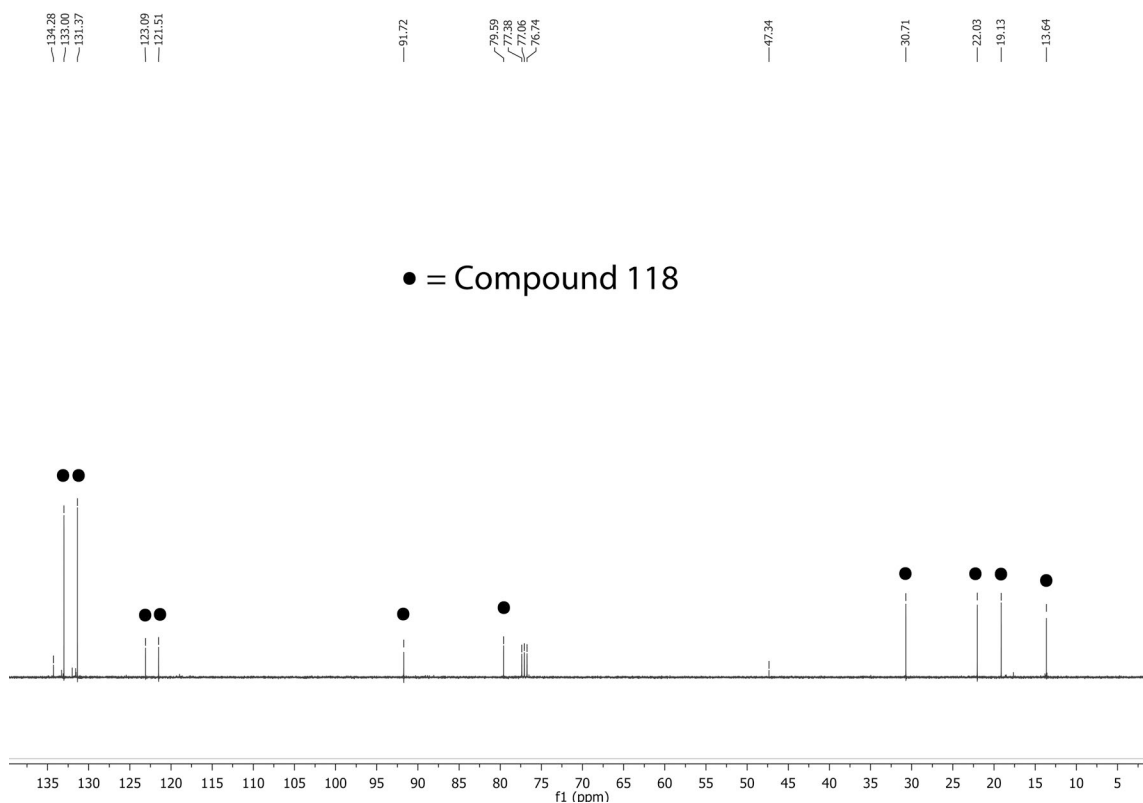
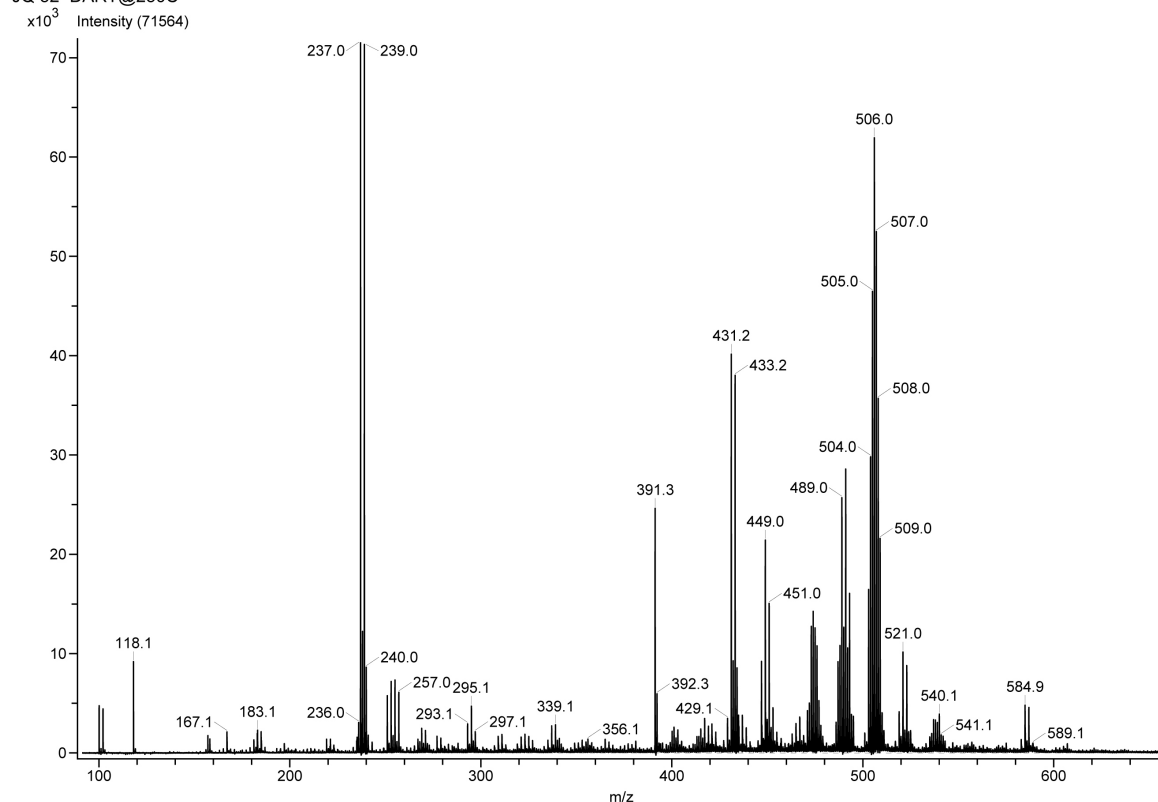


Figure 25: A ^{13}C NMR spectrum of the yellow liquid from the attempted synthesis of 118.

The mass spectrum showed M+H and M+H+2 signals at 237 m/z and 239 m/z corresponding to **107**, but also higher molecular weight compounds that had M, M+2, and M+4 patterns, that suggest polymerization took place. Further investigation by GPC is required. Also, an alternative type of ionization techniques (*i.e.* EI or CI) is suggested to compare against AIMS AccuTOF-DART mass spectrometry results.

Acq. Data Name: 120515_0187
Average(MS[1] Time:2.46..2.55)-1.0*Average(MS[1] Time:0.42..0.54)
JQ 52 DART@250C

5/15/2012 2:12:33 PM



ION MODE: POSITIVE

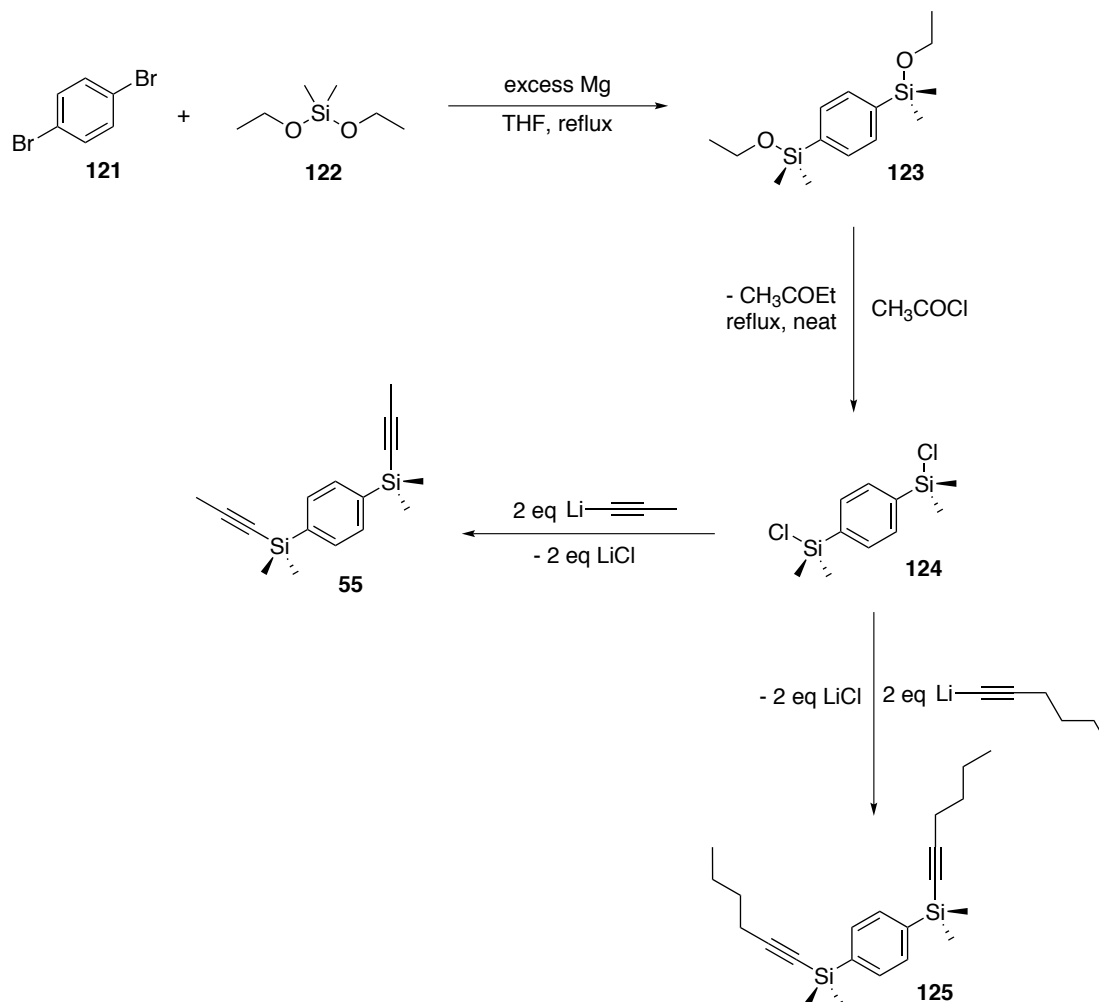
Figure 26: A mass spectrum of the light yellow liquid. The mass spectrum appears to have starting material compound 8 with unknown compound(s).

Similar to outcome of the attempted synthesis of **118**, the attempted synthesis of **119** and **120** resulted in significant amount of **107** and the mass spectrum for each reaction showed M, M+2, and M+4 patterns for higher molecular weight compounds.

Further characterization *via* HPLC-MS is suggested for all reaction products due to its high sensitivity and selectivity when used on complex mixtures.

2.5 Synthesis of Tilley *et al.* diynes

A summary of Tilley *et al.* diyne synthesis will be presented within this section. Characterization will be provided for the derivative compound.



Scheme 31: Synthesis of Tilley *et al.* polymer precursor and derivative.

2.5.1 Synthesis of compounds 55, and 123 to 125

1,4-bis(ethoxydimethylsilyl)benzene (123) and subsequent compounds derived from 123 were synthesized following methods reported by Tilley *et al.*¹ However, the derivative diyne (125) was synthesized using 1-hexyne rather than 1-propyne or *n*-BuLi and 1-bromopropene. Yields varied for each compound (52% to 89%).

2.5.1.1 Characterization of compounds 55, and 123 to 125

The ^1H and ^{13}C NMR analysis for **55**, **123**, and **124** were performed in CDCl_3 and in agreement with literature.¹

Compound **125** was characterized using ^1H , and ^{13}C NMR analysis in C_6D_6 (see Figure 79 and 80). ^1H NMR analysis showed five distinct resonance signals integrating at *ca.* 4:4:8:6:12 ratio. The singlet resonance signal observed at $\delta = 7.84$ ppm (integrating for four protons) was consistent with the aromatic protons in environment *a*. Coupling constants with magnitudes characteristic of $^3J_{\text{H-H}}$ coupling were observed throughout the methylene and methyl regions. Patterns of three resonance signals (triplet, overlapping multiplets, and triplet) integrating in the 4:8:6 ratio characteristic of the *n*-butyl group made up of environments *b* to *e*. The signals for protons in the methylene environment *b* were expected to be shifted furthest downfield due to their proximity to the alkyne moiety. The gradual upfield shift observed for resonance signals of the different protons along the *n*-butyl chain are expected as the environments will become more shielded the further they are away from the alkyne. The singlet resonance signal observed at $\delta = 0.34$ ppm showed an integral of 12 protons and was consistent with the methyl protons which have been assigned as *f*.

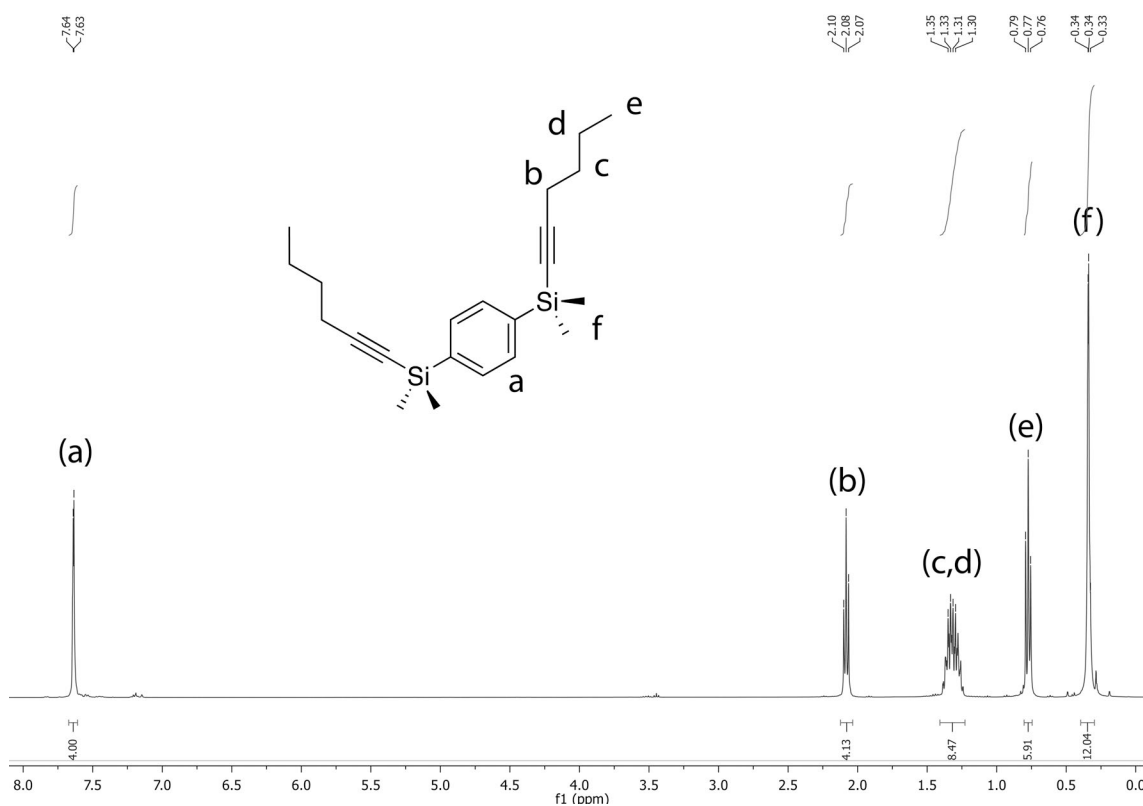


Figure 27: A ^1H NMR spectrum of compound **125**.

The ^{13}C NMR analysis showed nine resonance signals. The resonance signals were assigned as the following environments $\delta = 138.60(a)$, $133.03(b)$, $109.23(c)$, $82.18(d)$, $30.71(e)$, $21.90(f)$, $19.59(g)$, $13.52(h)$, and $-0.60(i)$ ppm.

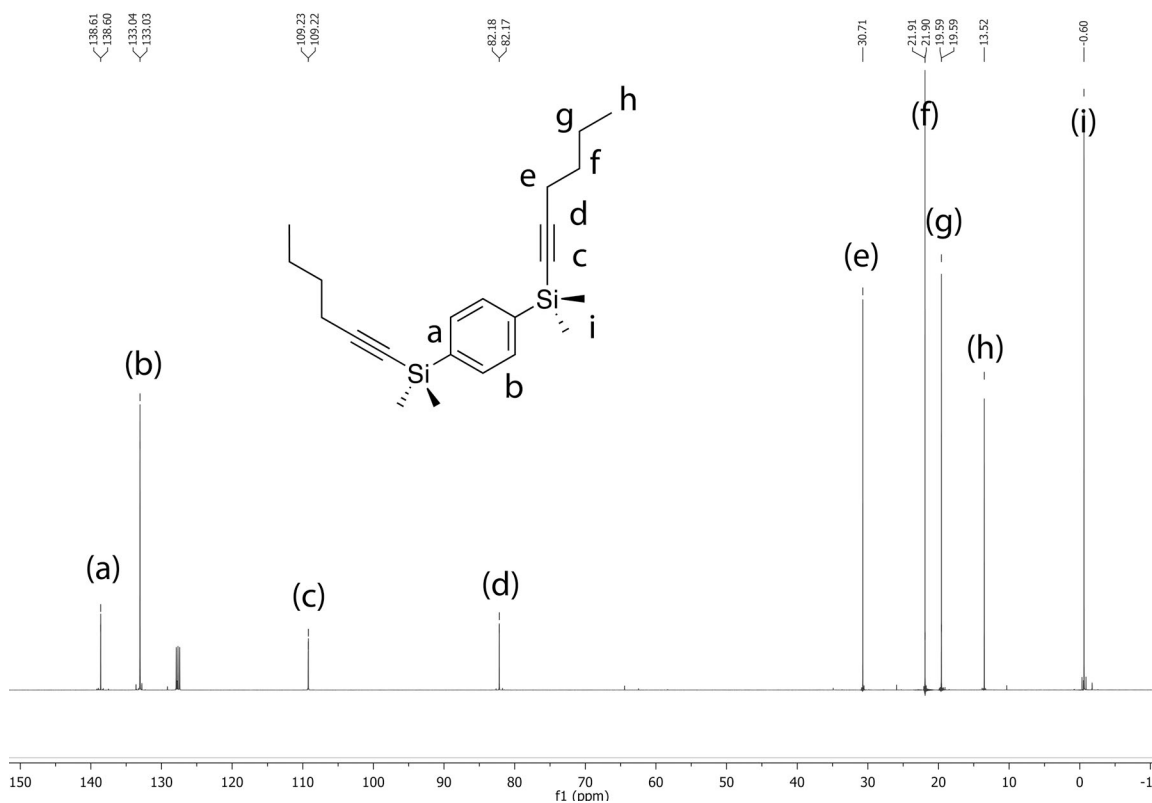
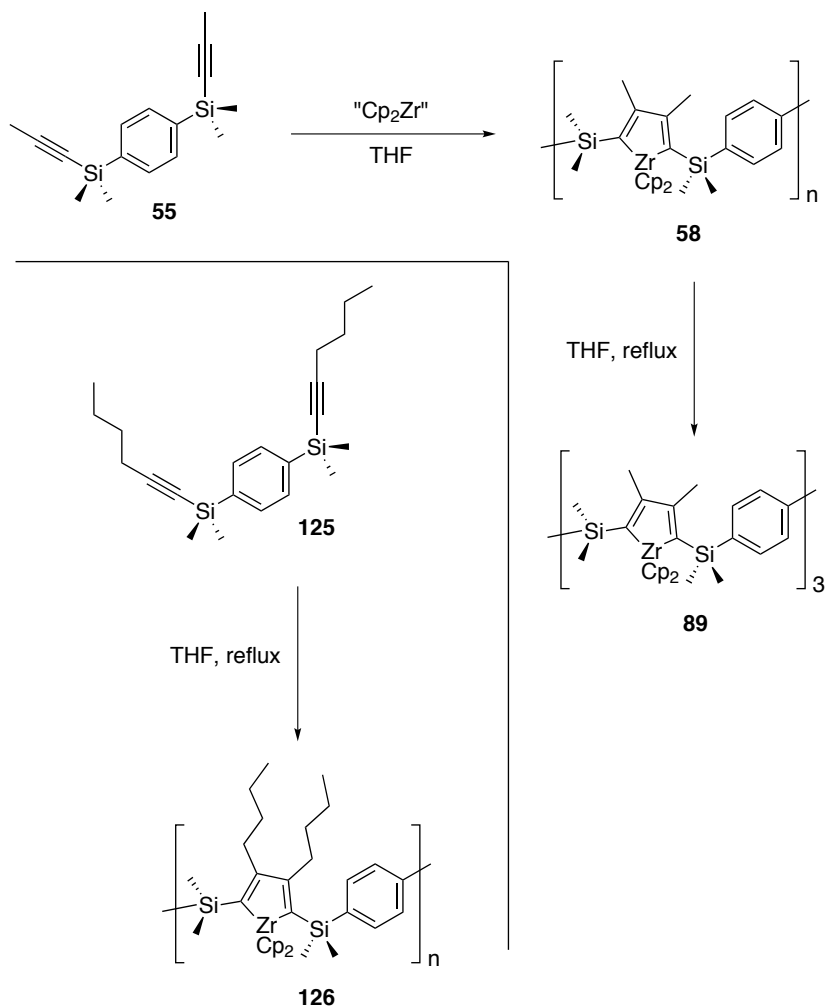


Figure 28: A ^{13}C NMR spectrum of compound 125.

2.6 Syntheses of silyl based zirconacyclopentadiene polymers

Polymers **22** to **24**, seen in Scheme 32, were attempted following a modified procedure. As mentioned previously (2.1.1), the formation of “Cp₂Zr” was more likely with zirconocene dichloride and *n*-BuLi without the presence of any competing diyne.



Scheme 32: Attempted syntheses of silyl based zirconacyclopentadiene polymers.

2.6.1 Attempted syntheses of polymers **58**, **89**, **125**, and **126**

A three neck round bottom flask with zirconocene dichloride and THF was cooled to -98°C (toluene/liquid nitrogen slush bath). With the dropwise addition of *n*-BuLi the reaction mixture became dark yellow-brown in appearance. The reaction mixture stirred for 30 minutes before removing the slush bath to warm the reaction mixture to room temperature. A one neck round bottom flask containing **55** and THF were added dropwise to the "Cp₂Zr" solution. After which, the dark yellow-brown

reaction mixture was stirred for 48 hours. After 48 hours any volatiles and solvent were removed by vacuum. A brown solid remained. Minimal toluene was added. The viscous [(1,4-Me₂SiC₆H₄SiMe₂)C₄Me₂ZrCp₂]_n (**58**) toluene solution was added dropwise into a vigorously stirring *n*-hexane sealed round bottom flask. An orange precipitate was allowed to settle. All solvent was decanted. The orange solid that remained was washed several times with *n*-hexane.

Attempts to depolymerize **58** by refluxing in THF or manipulating concentrations resulted with low yields of yellow crystals. In each case, an insoluble product was made. A 100 mL THF solution of **58** was heated at reflux for 24 hours, and then the solution was concentrated to 30 mL and added to 70 mL of *n*-hexanes. The resulting solution was left to give the product as yellow crystals in various yields of 1% to 30%.

Attempted synthesis of [(1,4-Me₂SiC₆H₄SiMe₂)C₄Bu₂ZrCp₂]_n (**126**) followed an identical procedure to **58**. However, a solution of **125** in THF was added dropwise rather than a solution of **55** to the reaction vessel. After 48 hours of reaction time all volatiles and solvent were removed by vacuum. A brown solid remained. Minimal toluene was added. The viscous **126** toluene solution was added dropwise into a vigorously stirring *n*-hexane sealed round bottom flask. An orange precipitate was allowed to settle. All solvent was decanted. The orange solid that remained was washed several times with *n*-hexane. It was apparent that a substantial amount of **126** was still slightly dissolved (*i.e.* cloudy solution) in the *n*-hexane. This could be due to the side butyl chains and/or smaller molecular weights (*i.e.* oligomers). Recovery was possible by using a centrifuge.

2.6.1.1 Characterizations of polymers **58**, **89**, **125**, and **126**

The product **58** was characterized by ¹H, ¹³C NMR analysis in C₆D₆ and UV-Vis. The results were identical to literature.¹

According to Tilley *et al.* there should be no change observed in the chemical shifts of the resonance signals for the trimer compared with those for the polymer.¹ The ¹H NMR analysis (see Figure 29) of the attempted macrocyclization had the expected resonance signals at $\delta = 7.87$, 6.10, 1.80, and 0.32 ppm for **89**. A characteristic resonance signal for benzene was observed at $\delta = 7.16$ ppm. There were also several new resonance signals, for example, $\delta = 7.78$ ppm and the multiplet resonance signals at $\delta = 1.53$ ppm. If macrocyclization did not occur, the formation of linear oligomers could explain the unknown resonance signals. Refluxing the polymer in THF may have stabilized random zirconole intermediates as suggested in 1.1.1.1.

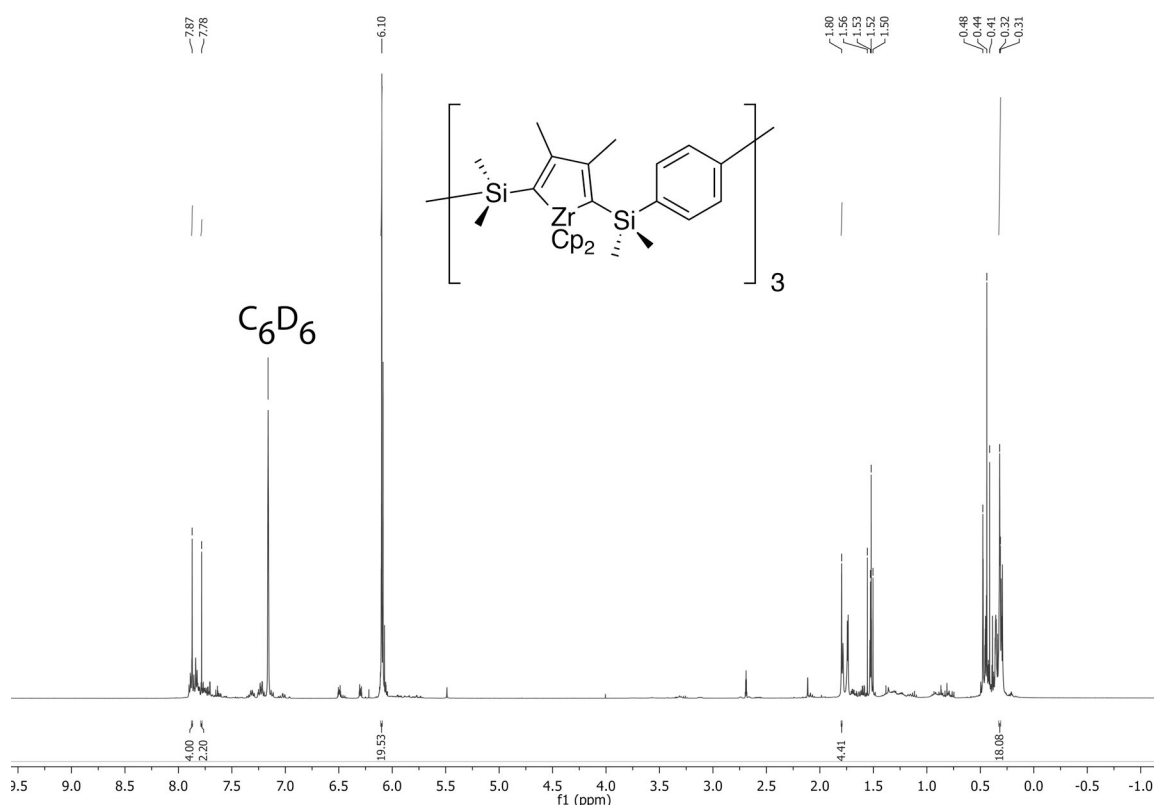


Figure 29: A ^1H NMR spectrum of an attempted macrocyclization of **58 with some solvent/unknown by product contamination.**

The orange product (**126**) was characterized by ^1H NMR analysis (see Figure 85) only. ^1H NMR analysis showed six distinct resonance signals that should integrate at *ca.* 4:10:4:8:6:12 ratio. Due to the similarities in the main chain for the two polymer systems, the chemical shifts for the singlet resonance signals generated by protons from the aromatic, cyclopentadienyl and dimethylsilyl moieties (in environments *a*, *b* and *g*) in **126** were nearly identical to those of the corresponding protons in **58** ($\delta = 7.90$, 6.08 and 0.37 ppm, respectively). Presence of the two butyl chains is supported by the broad resonance signals observed at $\delta = 0.85$ ppm (associated with the terminal methyl groups in environment *a*) and 1.23 ppm (most likely the result of overlapping resonance signals from protons in the methylene environments *d* and *e*). In addition, the triplet resonance signal from protons the methylene group *c* is observed slightly downfield at $\delta = 2.11$ ppm.

However, with solvent contamination from *n*-hexane, the relative integration values for the methylene and methyl regions of the spectrum were increased above their expected values. The loss of signal resolution and increased broadening of resonance signals is potentially of polymer formation. Further

study of **126** by GPC is required to confirm whether polymers, macrocycles, or linear oligomers were formed in this study.

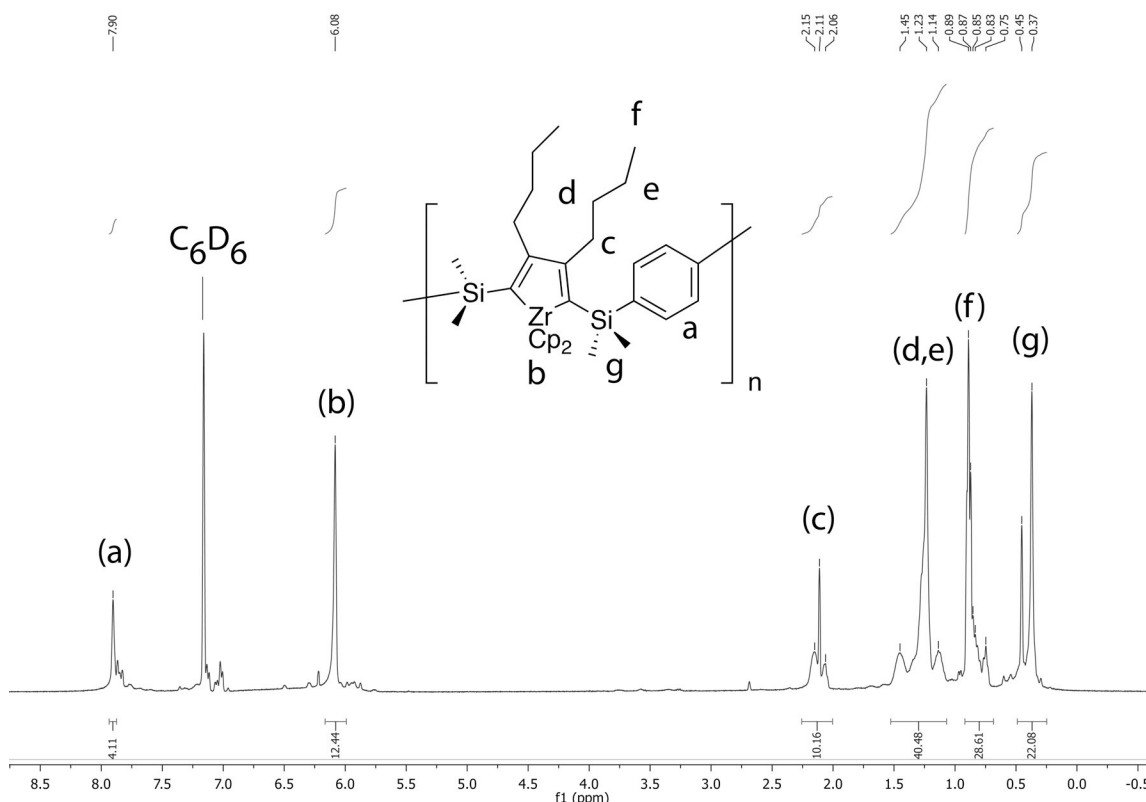


Figure 30: A ^1H NMR spectrum of polymer 24 with some *n*-hexane contamination.

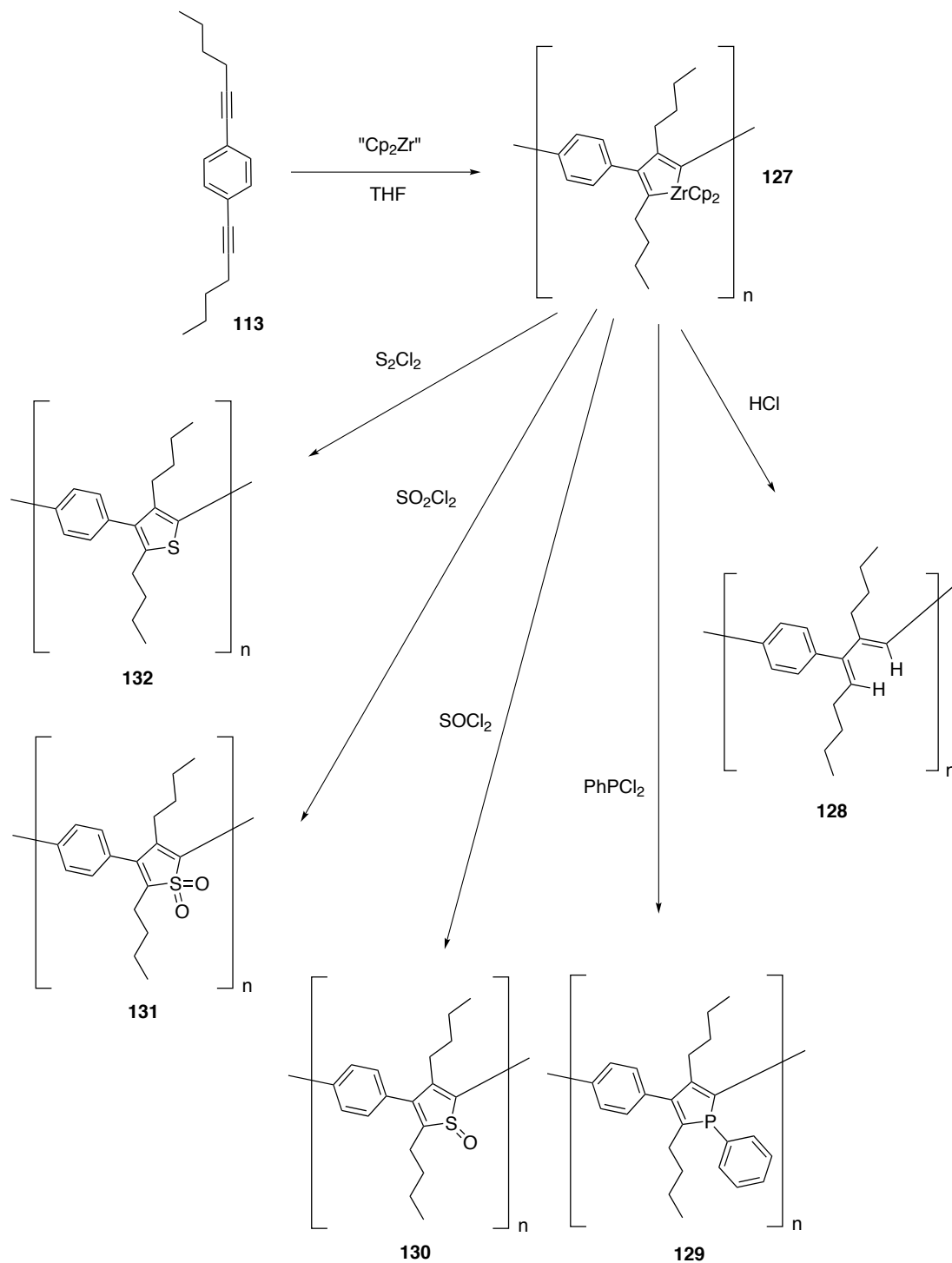
^{13}C NMR spectroscopy was attempted at various concentrations; however, no signal was observed after 12 hours of data acquisition when using C_6D_6 as the solvent. Due to poor solubility of the target polymer, longer data collection times may be required. Alternately, the use of different solvents, such as *d*-THF, may improve solubility. Increasing the concentration of the NMR sample would make the sample too viscous and/or form precipitate.

2.7 Attempted synthesis of carbon based zirconacyclopentadiene polymers

A discussion of synthesis and characterization of carbon based zirconacyclopentadiene polymers will be presented within this section as seen in Scheme 33.

Compounds attempted in these syntheses should not have any preference for α - or β - positioning of alkyne substituents due to similar electron withdrawing properties of each substituent and when silicon based substituents are not present. A distribution (symmetrical:asymmetrical 2:8 ratio) was observed by

Tilley *et al.* for carbon based alkyne 4,4'-di(hept-1-yn-1-yl)-1,1'-biphenyl after polymerization *via* zirconocene-coupling.¹⁰⁵ However, the proposed structure for **127** and derivatives (**128** to **132**) were based on the asymmetrical configuration.



Scheme 33: Attempted synthesis of polymers 127 to 132.

2.7.1 Attempted synthesis of polymer 127 and derivatives (128 to 132)

A one neck round bottom containing **113** and THF were added dropwise to a freshly prepared “Cp₂Zr” solution. After which, the dark-yellow reaction mixture was stirred for 36 hours. At which point, all volatiles were removed *in vacuo* and a brown residue remained. The brown residue was washed and filtered with minimal hexanes. Hexanes were then removed by vacuum to afford a brown residue. Further purification was attempted using pentane as a nonsolvent, identical procedure used by Tilley *et al.* for all related polymers, but preliminary ¹H NMR analysis suggested hydrolyzed product. For this reason, no further purification was attempted and used *in situ*.

All subsequent reactions were placed in Table 2: Summary of all subsequent reactions to suggested polymer 127.

to simplify procedure. Purification was performed on all products using methanol as a nonsolvent.

Polymer #	Reagent	Reaction Time	Product Description
128	HCl	2 hours	Yellow Solid
129	PhPCl ₂	5 days	Red Solid
130	SOCl ₂	12 hours	Brown Solid
131	SO ₂ Cl ₂	12 hours	White Solid
132	S ₂ Cl ₂	12 hours	Yellow Solid

Table 2: Summary of all subsequent reactions to suggested polymer 127.

2.7.2 Characterization of Reaction Products

¹H NMR analysis was performed of each of the isolated polymeric material to determine whether a successful metathesis reaction had taken place and to confirm that the Cp₂Zr moiety had been removed from the polymer main chain. In each case, resonance signals with chemical shifts typical of those expected for the butyl chains and *para*-disubstituted benzene rings have been assigned to the corresponding environments as indicated in Figure 31 to Figure 34. Unfortunately, there is evidence of solvent impurities present in each of the spectra. UV analysis for each compound was consistent with the presence of conjugated systems.

¹H NMR analysis of the brown residue isolated from the attempted synthesis of **127** revealed a broad resonance signal characteristic of the cyclopentadienyl protons (environment *a*) at $\delta = 6.13$ ppm. Treatment of **127** with HCl resulted in the formation of zirconocene dichloride as indicated by the

upfield shift of the Cp protons to $\delta = 5.99$ ppm. Unfortunately, no well resolved resonance signals with chemical shifts expected for protons environments *b* and *k* were observed, so it is not clear whether the target polymer **128** was formed (see Figure 32).

After treatment of **127** with PhPCl_2 ($\delta = 5.92$ ppm, see Figure 33), **129**, the NMR spectrum was nearly identical to that of **128** (see Figure 32) suggesting that the material may have hydrolyzed. It is not clear whether or not the phosphole moiety had formed prior to hydrolysis.

Upfield shifts were observed for the Cp protons after treatment of **127** with thionyl chloride ($\delta = 5.91$ ppm, see Figure 34), **130**, indicating that zirconocene dichloride had formed in this reaction and that the target compound may have been formed.

In contrast, ^1H NMR analysis of the reaction products formed after treatment of **127** with either sulfur monochloride, **132**, or sulfuryl chloride, **131**, revealed that the Cp protons had shifted down field to $\delta = 6.49$ ppm (see Figure 36**Error! Reference source not found.**) and 6.44 ppm respectively (see Figure 35**Error! Reference source not found.**). As there was no evidence that zirconocene dichloride had been formed, it is difficult to say whether or not the Zr atoms had been removed for the polymer chain.

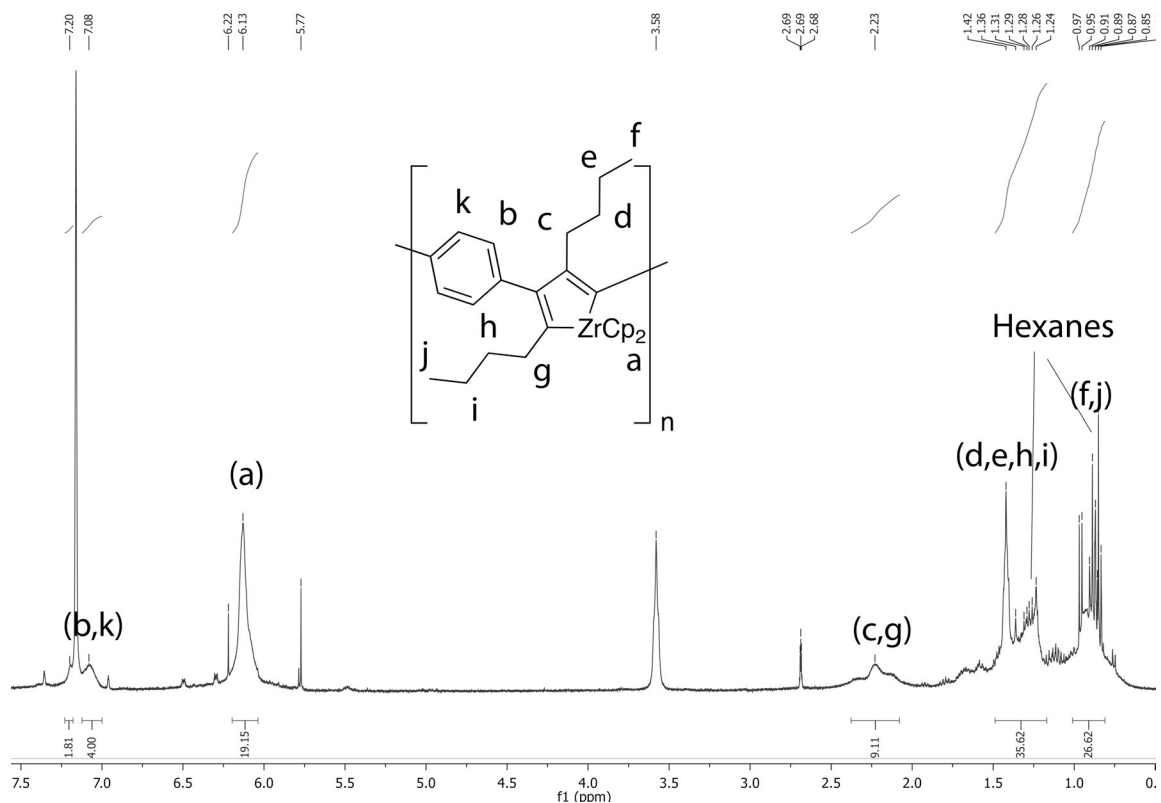


Figure 31: A ^1H NMR spectrum of the brown residue from the attempted synthesis of polymer 127.

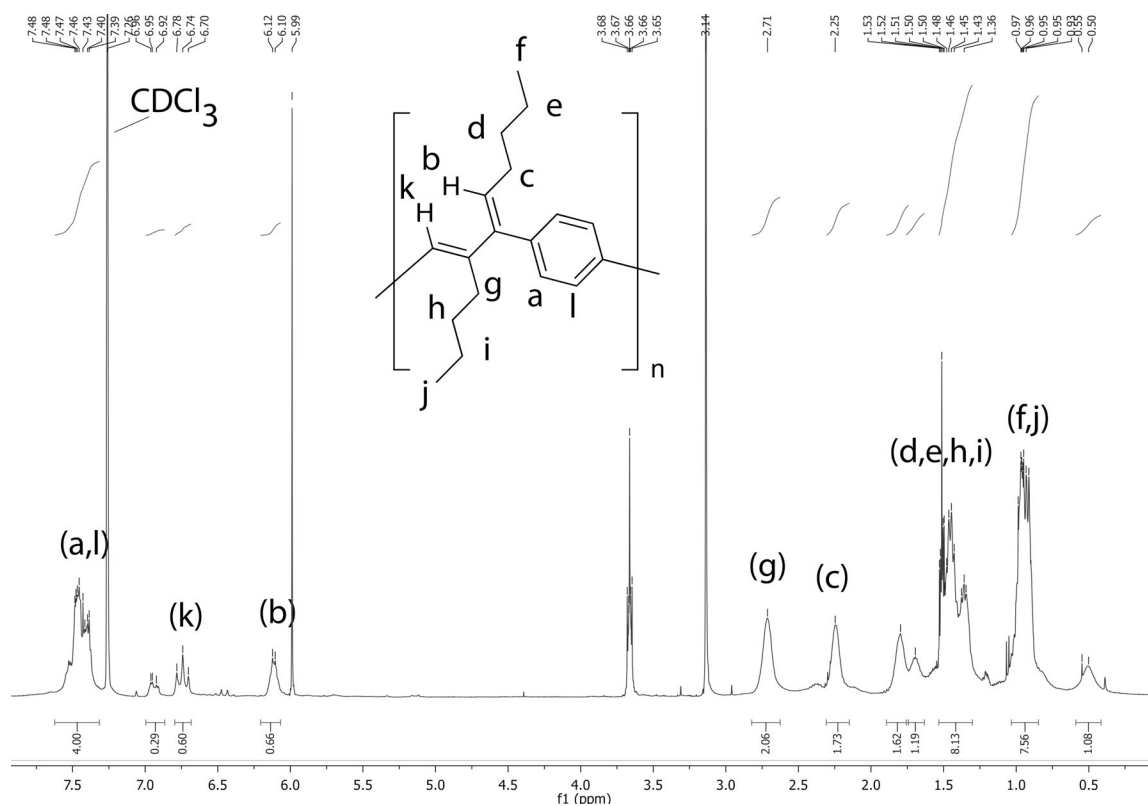


Figure 32: A ^1H NMR spectrum of the yellow solid from the attempted synthesis of polymer 128.

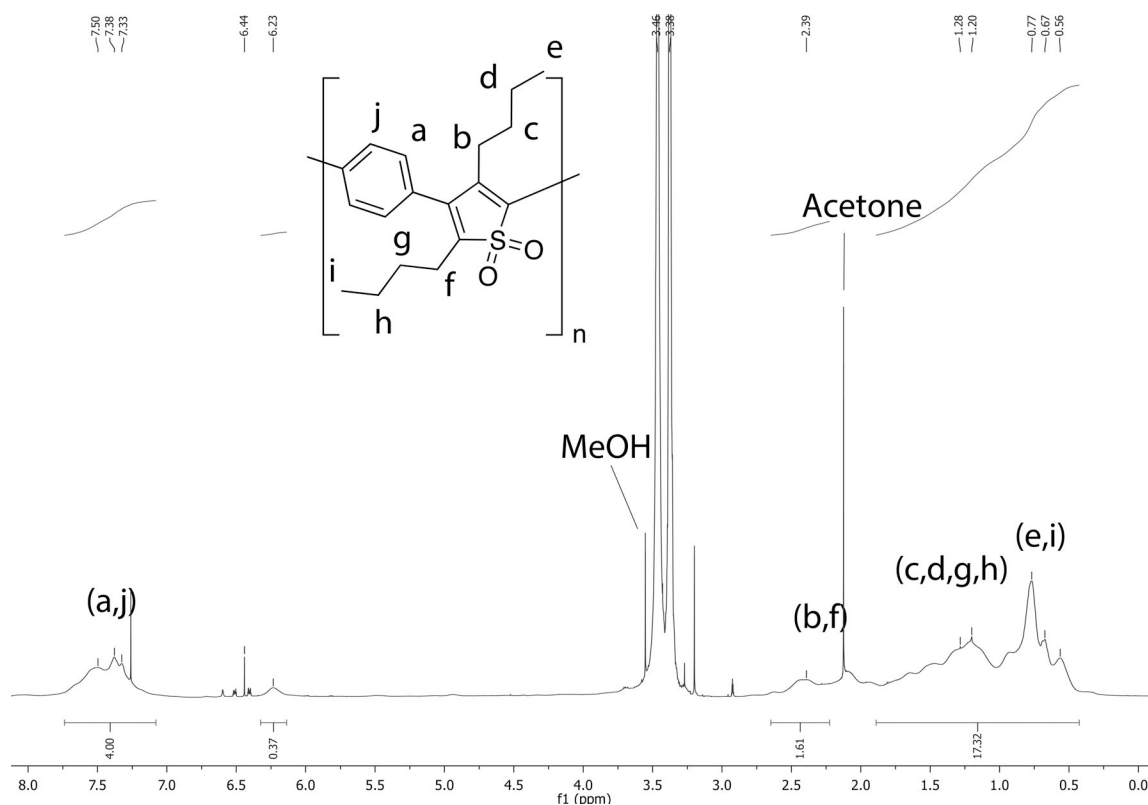


Figure 35: A ^1H NMR spectrum of the white solid from the attempted synthesis of polymer 131.

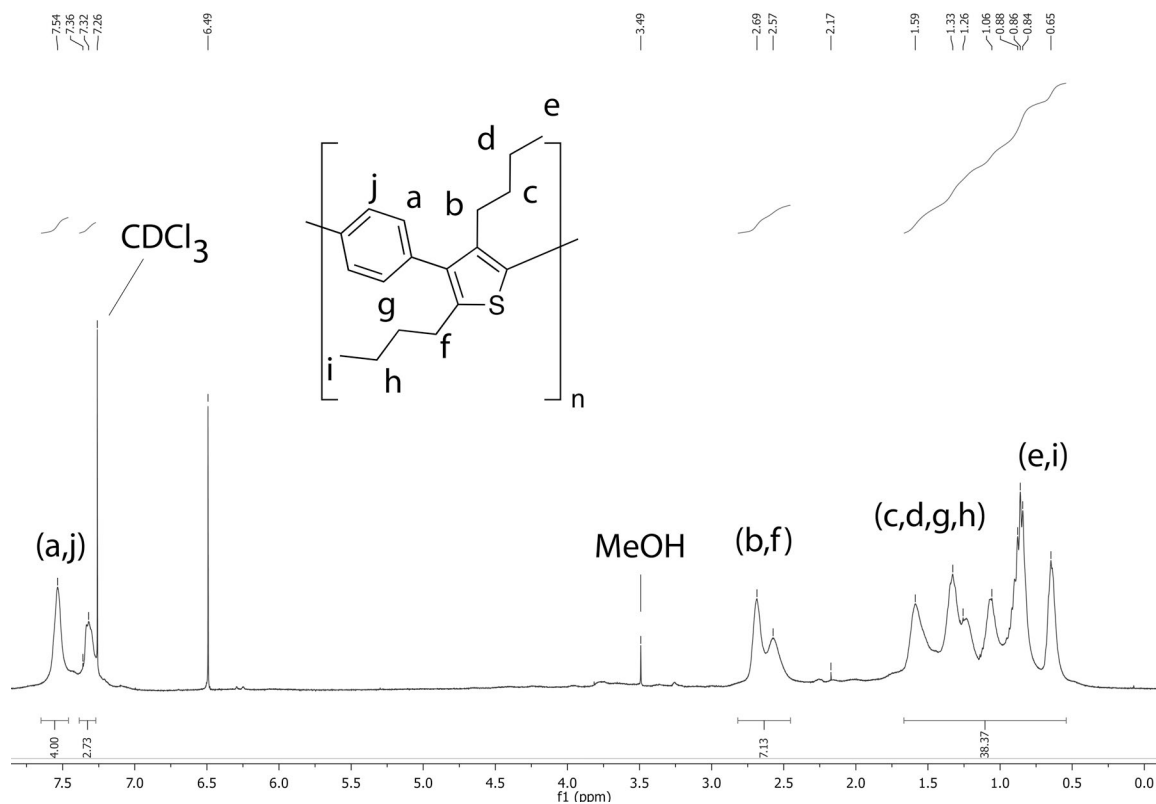


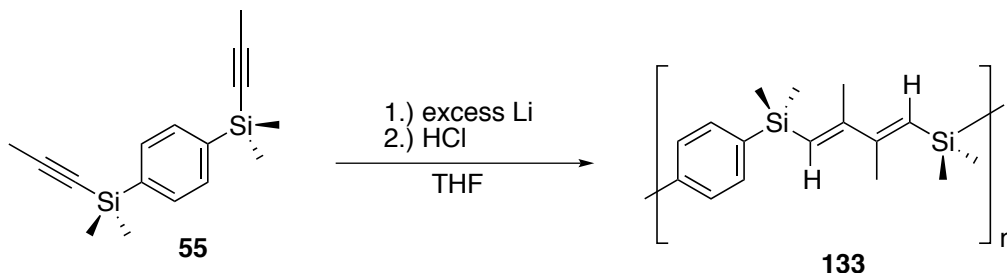
Figure 36: A ^1H NMR spectrum of the yellow solid from the attempted synthesis of polymer 132.

Further characterization by GPC for all reaction products will determine if they are polymers. As well, further purification may increase the likelihood of cleaner NMR spectra. Another suggestion would be that a higher frequency than 400 MHz for ^1H NMR experiments be used on all reaction products to increase resolution of resonance signals so that proper assignments may be made.

^{13}C NMR analysis was attempted at various concentrations on all suggested polymers; however, no signals were observed after 12 hours of data acquisition. Longer times may be required due to the low sensitivity of ^{13}C NMR. Alternatively, *d*-THF may improve solubility. Over 12 hours significant colour change occurred to the sample while the NMR tube lid was wrapped with Teflon to prevent air contamination.

2.8 Attempted synthesis of $[1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2]_n$ via lithium coupling of diynes

A discussion of the synthesis and characterization of $[1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2]_n$ (**133**). If **133** was synthesized it would provide an alternative method to zirconocene-coupling of diynes.



Scheme 34: Reaction pathway for $[1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2]_n$ (**133**).

2.8.1 Attempted synthesis of $[1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2]_n$ (**133**)

A Schlenk flask containing a solution of **55**, and lithium in six equivalent excess in THF was left to stir overnight. The reaction mixture was decanted into a new Schlenk flask. An aqueous 6 M HCl solution was added dropwise. After several hours of stirring the solution was concentrated and added to a vigorously stirring solution of methanol. A fine white powder formed.

2.8.1.1 Characterization of the fine white powder

The fine white powder was characterized by ^1H NMR analysis (see Figure 37) only. ^1H NMR analysis did not match literature.¹ The resonance signals should have integrated at *ca.* 4:2:6:12 ratio. Instead, the

resonance signal integration was *ca.* 4:24 ratio. As well, the loss of resolution, overlapping, and broadening of signals does not support the formation of **133**.

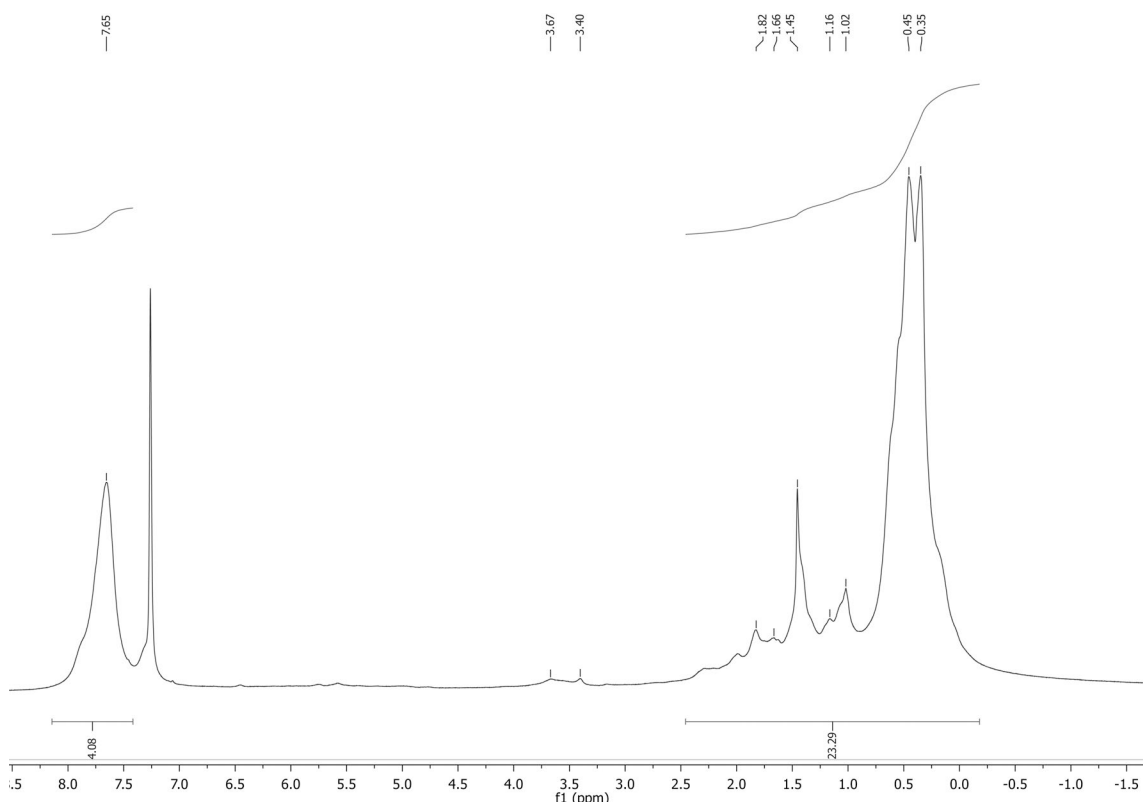


Figure 37: A ^1H NMR spectrum of the fine white powder from the attempted synthesis of [1,4- $\text{Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2$] $_n$ (**133**).

2.9 Future work and considerations

In future, further characterization by ^{13}C NMR, and 2D NMR (COSY, HSQC, and HMBC) spectroscopy of compounds discussed in 2.1, 2.3, and 2.4 is required. GPC (PDI), UV-Vis (band gap energy), elemental analysis (polymer composition), and cyclic voltammetry (polymer conductivity) is required for polymers discussed in 2.6, 2.7, and 2.8. On another note, synthesis of more carbon based diynes *via* Sonogashira coupling (see 2.2) for novel polymer synthesis would be valuable. Lastly, further study on the metallacycle transfer from zirconocene intermediates to main group atoms in polymers is needed.

3 Materials and methods

All reactions were carried out under nitrogen, argon or vacuum atmosphere using Schlenk techniques or a glovebox. Rubber septa were used to enable isolated transfers of liquid solutions *via* needle to needle and/or syringe and needle. All chemicals used were distributed by Sigma-Aldrich or Strem Chemicals Inc. Tetrahydrofuran and methanol were taken from a solvent purification system or supplier bottle, dried and distilled with sodium/benzophenone ketyl or CaH_2 . Hexanes and toluene were taken from a solvent purification system and used as dispensed. Dimethyldiethoxysilane (Sigma-Aldrich), 1,4-dibromobenzene (Sigma-Aldrich), magnesium (Sigma-Aldrich), acetyl chloride (CH_3COCl) (Sigma-Aldrich), 1-bromo-1-propene (Sigma-Aldrich), zirconocene dichloride (Cp_2ZrCl_2) (Strem), *n*-butyllithium in hexanes (Sigma-Aldrich), sulfur monochloride (Sigma-Aldrich), thionyl chloride (Sigma-Aldrich), sulfuryl chloride (Sigma-Aldrich), and dichlorophenylphosphine (Sigma-Aldrich) were used as supplied.

NMR spectra were recorded in benzene-*d*₆ (C_6D_6) or chloroform-*d* (CDCl_3) on a Bruker Avance II 400 spectrometer at various frequencies. The UV-Vis spectra were recorded in THF on a Perkin Elmer Lambda 20 UV-Vis spectrometer. AIMS AccuTOF-DART-MS analysis was recorded at various temperatures by the University of Toronto, Chemistry Department. GPC analysis was carried out using GPC Viscotek GPCMax VE2001 in THF.

The syntheses described within are modified procedures based on the work of Tilley *et al.*, Fagan *et al.*, Eisch *et al.*, Castro *et al.*, and Sonogashira *et al.*^{1,18,19,26,62,63}

3.1 Preparation of FeCl_3 and CrCl_3 for metallacycle transfer

3.1.1 Synthesis of $[\text{CrCl}_3(\text{THF})_3]$

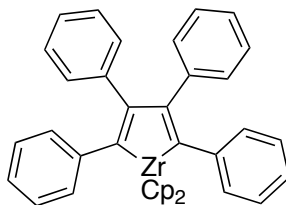
CrCl_3 (20.0 g, 126.3 mmol) was placed in a Soxhlet thimble with zinc dust. 150 mL THF was placed in a 250 mL round bottom attached to the bottom of the Soxhlet apparatus. A reflux condenser was attached to the top of the Soxhlet apparatus. The Soxhlet extractor was then placed under dynamic argon and the THF was refluxed. After several hours the purple CrCl_3 became solvated and exited the Soxhlet apparatus into the 250 mL round bottom below. Once most of the CrCl_3 was solvated the round bottom was removed and placed under vacuum to remove THF. Bright purple $[\text{CrCl}_3(\text{THF})_3]$ crystals were collected (41.21 g, 90%).

3.1.2 Further drying of anhydrous FeCl₃

Anhydrous FeCl₃ (20.0 g, 123.3 mmol) was placed into a 250 mL three neck round bottom with an attached reflux condenser. Thionyl chloride (50 mL, 256.6 mmol) was added *via* syringe under argon. The reaction mixture was refluxed for 4 hours. All volatiles including thionyl chloride were removed *via* vacuum to form anhydrous FeCl₃. Any residual hydrated FeCl₃ should not exist. Dark green/black crystals were collected.

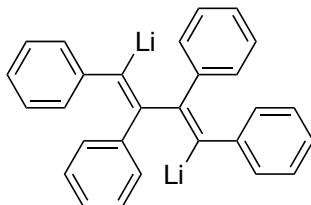
3.2 Synthesis of metallole precursors and attempts at synthesis of metalloles

3.2.1 Synthesis of 2,3,4,5-tetraphenylzirconacyclopentadiene (3)



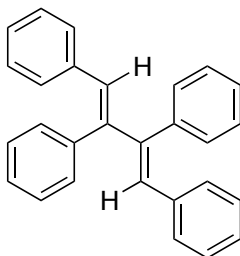
A 250 mL Schlenk flask equipped with a magnetic stirring bar and rubber septum was charged with zirconocene dichloride (2.3 g, 7.8 mmol) in a nitrogen-filled glovebox. The Schlenk flask was then removed from the glove box and attached *via* the barbed glass inlet on the Schlenk flask to an argon Schlenk line. 27 mL THF was then added *via* syringe. The flask was cooled to -78°C (dry ice-acetone bath) and *n*-BuLi (9.8 mL, 15.7 mmol, 1.6 M) in hexanes was added dropwise *via* syringe to the cooled reaction mixture. After the addition was complete, the reaction mixture was stirred at -78°C for 30 minutes. Then a solution of diphenylacetylene (3.1 g, 17.2 mmol) in minimal THF was added dropwise. The reaction was stirred for another 30 minutes. The flask was then allowed to warm by removing the dry ice-acetone bath, and the reaction mixture was stirred at room temperature for 2.5 hours at which point the mixture was dark red. For subsequent reactions, either the red solution can be used *in situ* or the product can be isolated and then used. To isolate, the THF was removed *via* vacuum. Minimal toluene was added. All precipitate was allowed to settle and toluene was decanted and filtered. *n*-hexane was added to the minimal toluene solution and then cooled to form bright red/ruby crystals. Yield (3.6 g, 80%). ¹H NMR (400 MHz, C₆D₆): δ_H = 7.10 - 6.66 (m, 20H, C₆H₄), 6.01 (s, 10H, C₅H₅) ppm.

3.2.2 Synthesis of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**8**)



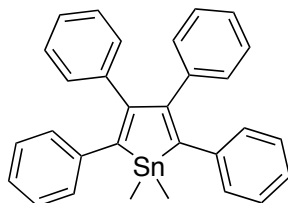
A 100 mL Schlenk flask equipped with a magnetic stirring bar and rubber septum was charged with diphenylacetylene (2.6 g, 14.6 mmol) and solid lithium metal pieces (607 mg, 87.5 mmol) under argon. The lithium metal pieces were prewashed with hexanes to remove any mineral oil. 30 mL Et₂O was then added *via* syringe. The reaction mixture was stirred for 2 hours or as soon as yellow precipitate forms. After which, the unreacted pieces of lithium metal were removed and allowed to stir for an extra 30 minutes. Any subsequent reactions with **2** were used *in situ*. However, the yellow product can be isolated if filtered in a nitrogen filled glovebox. Yields vary from (50% to 79% based on diphenylacetylene).

3.2.2.1 Synthesis of 1,2,3,4-tetraphenyl-1,3-butadiene (**102**)



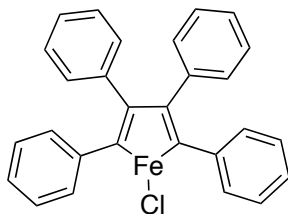
A small amount of **3** and **8** in separate vials in minimal THF were hydrolyzed using a 1 M HCl solution. The white hydrolyzed product can be recrystallized in a DCM/EtOH mix. ¹H NMR (400 MHz, CDCl₃) δ_H = 7.43 - 7.30 (m, 10H), 7.05 - 7.00 (m, 6H), 6.77 - 6.71 (m, 4H), 6.31 (s, 2H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ_C = 145.58, 139.73, 137.23, 131.63, 130.36, 129.46, 128.78, 127.76, 127.32, 126.58 ppm.

3.2.3 Synthesis of 1,1-dimethyl-2,3,4,5-tetraphenylstannocyclopentadiene (9)



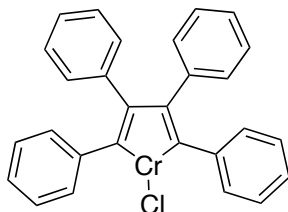
A 100 mL Schlenk Flask equipped with a magnetic stirring bar and rubber septum under argon containing a solution of **8** (2.88 g, 7.8 mmol) in Et₂O. Dimethyltin dichloride (1.7 g, 7.8 mmol) in minimal THF was added dropwise *via* syringe. The dark red solution gradually changed to a yellow and left to stir for 2 hours. The solvent and volatiles were removed by vacuum. The residue was washed several times with minimal (5 to 10 mL) EtOH to remove residual tin halides and LiCl. The crude product was purified by recrystallization using DCM and minimal EtOH. Yield (0.39 g, 10%). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.10 - 6.76 (m, 20H, C₆H₆), 0.63 (s, 6H, ²*J*_{Sn-H} = 28 Hz, CH₃) ppm. ¹¹⁹Sn NMR (149 MHz, CDCl₃) δ_{Sn} = 53.12 ppm.

3.2.4 Attempted Synthesis of 1-chloro-2,3,4,5-tetraphenylferrole (103)



A 250 mL Schlenk flask equipped with a magnetic stirring bar and rubber septum under argon containing a solution of **3** in THF with the amounts described previous (3.2.1) was cooled to -78°C (dry ice-acetone bath). Anhydrous FeCl₃ (1.3 g, 7.8 mmol) in minimal THF was added *via* syringe. The dark red solution changed to a dark brown. ¹H NMR analysis suggests the formation of poly(diphenylacetylene). λ_{max} = 280 nm.

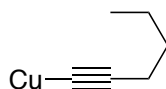
3.2.5 Attempted Synthesis of 1-chloro-2,3,4,5-tetraphenylchromole (104)



A 250 mL Schlenk flask equipped with a magnetic stirring bar and rubber septum under argon containing a solution of **3** in THF with the amounts described previous (3.2.1) was cooled to -78°C (dry ice-acetone bath). $\text{CrCl}_3(\text{THF})_3$ (2.9 g, 7.8 mmol) in minimal THF was added *via* syringe. The dark red solution changed to a dark green. ^1H NMR analysis suggests the formation of **104** and the existence of **3**. In some synthesis attempts, broad signals were observed *via* ^1H NMR spectroscopy and viscous oil formed suggesting possible polymerization took place. $\lambda_{\text{max}} = 280 \text{ nm}$.

3.3 Preparation of monomers *via* Castro-Stephens coupling

3.3.1 Synthesis of cuprous *n*-butylacetylide *via* CuI only (106)



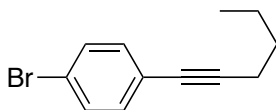
1-hexyne (2.4 g, 29.2 mmol) was added to a 250 mL Schlenk flask with a magnetic stirring bar and rubber septum. 100 mL EtOH was added *via* syringe to the 250 mL Schlenk flask. Cuprous iodide (5.6 g, 29.4 mmol) was added to 40 mL of aqueous ammonium hydroxide in a 250 mL beaker. The cuprous iodide solution (blue) was added to the 100 mL EtOH solution *via* syringe. The reaction mixture was stirred for 30 minutes and then allowed to stand for 15 minutes. The bright greenish-yellowish precipitate was filtered off and washed three times each with water, ethanol, and diethyl ether. The bright canary yellow solid was dried under vacuum for two days. Yield (3.3 g, 79%).

3.3.1.1 Synthesis of cuprous *n*-butylacetylide *via* *n*-BuLi and CuI (106)

1-hexyne (3.0 g, 36.5 mmol) was added to a 100 mL Schlenk flask with a magnetic stirring bar and rubber septum in a nitrogen-fill glovebox. The Schlenk flask was then removed from the glove box and attached *via* the barbed glass inlet on the Schlenk flask to an argon Schlenk line. 50 mL Et_2O was added

via syringe to the 100 mL Schlenk flask. The reaction flask was then cooled to -78°C (dry ice-acetone bath) and *n*-BuLi (22.8 mL, 36.5 mmol, 1.6 M) in hexanes was added *via* syringe. A white suspension formed. The reaction was stirred for 1 hour and then CuI (7.0 g, 36.5 mmol) in Et₂O was added. The reaction mixture was then stirred for 1 hour. The dry ice-acetone bath was then removed and the reaction mixture allowed to warm to room temperature. The white suspension quickly became a thick yellow suspension. The yellowish precipitate was filtered off and washed three times each with water, ethanol, and diethyl ether. The bright canary yellow solid was dried under vacuum for two days. Yield (4.4 g, 83%).

3.3.2 Synthesis of 1-bromo-4-hex-1-ynylbenzene (107)



Cuprous *n*-butylacetylide (406.0 mg, 2.8 mmol), *p*-bromiodobenzene (735.5 mg, 2.6 mmol), and 50 mL pyridine were added to a 100 mL Schlenk flask fitted with a reflux condenser. The reaction mixture was then heated to 120°C for 24 hours. The yellow canary slurry slowly dissolved and turned dark red. The solution was then cooled to room temperature and the reaction mixture was extracted using 50 mL EtOAc. 50 mL of 0.1 M HCl was added to a 500 mL separation funnel containing the 100 mL reaction solution. The aqueous phase was collected first and then the organic phase. The aqueous phase was then extracted two more times with EtOAc. A 50 mL solution of NaHCO₃ was then added to the combined EtOAc solution and extracted once more. Finally, a saturated brine solution was used to extract the EtOAc solution. The solvent from the mother solution was then removed by vacuum. The remaining liquid was distilled (110°C at *ca.* 0.002 Torr) to give a yellow liquid. Yield (49.3 mg, 8%). ¹H NMR (400 MHz, CDCl₃) δ_{H} = 7.41 (d, 2H, ³*J*_{H-H} = 8.5 Hz), 7.25 (d, 2H, ³*J*_{H-H} = 8.5 Hz), 2.39 (t, 2H, ³*J*_{H-H} = 7.0 Hz), 1.63 – 1.42 (m, 4H), 0.95 (t, 3H, ³*J*_{H-H} = 7.0 Hz) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ_{C} = 133.04, 131.41, 123.19, 121.58, 91.70, 79.71, 30.81, 22.12, 19.20, 13.70 ppm.

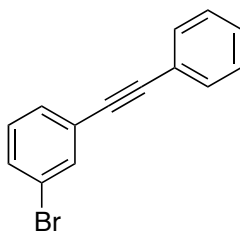
3.4 Preparation of monomers via Sonogashira coupling

3.4.1 Synthesis of 1-bromo-4-hex-1-ynylbenzene (107)

p-bromiodobenzene (5.6 g, 19.7 mmol), 1-hexyne (2.0 g, 24.3 mmol), and Pd(PPh₃)₄ (69.0 mg, 0.06 mmol) were added to a 250 mL Schlenk flask. 25 mL THF was subsequently added and gradually dissolved the catalyst. With the solution colour of red, 25 mL Et₃N was added. With immediate addition of cuprous iodide (370.0 mg, 1.9 mmol) the solution darkened to a black colour. The reaction

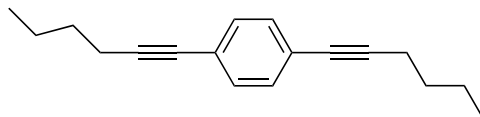
mixture was stirred and heated to 45°C for 16 hours. The solvent was removed by vacuum. The remaining liquid was then extracted in a similar fashion mentioned above (3.3.2). Hexanes added, and purified *via* column chromatography on SiO₂ (hexanes, R_f = 0.40) to produce a yellow/orange liquid. Yield (3.97 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.41 (d, 2H, $^3J_{H-H}$ = 8.5 Hz), 7.25 (d, 2H, $^3J_{H-H}$ = 8.5 Hz), 2.39 (t, 2H, $^3J_{H-H}$ = 7.0 Hz), 1.63 – 1.42 (m, 4H), 0.95 (t, 3H, $^3J_{H-H}$ = 7.0 Hz) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ_C = 133.04, 131.41, 123.19, 121.58, 91.70, 79.71, 30.81, 22.12, 19.20, 13.70 ppm. MS (TOF-DART-MS) 239.00, 237.00 m/z .

3.4.2 Synthesis of 1-bromo-3-(phenylethynyl)benzene (111)



m-bromiodobenzene (11.46 g, 40.5 mmol), phenylacetylene (5.74 g, 56.2 mmol), and Pd(PPh₃)₄ (400.0 mg, 0.35 mmol) were added to a 250 mL Schlenk flask. 60 mL THF was subsequently added and gradually dissolved the catalyst. With the solution colour of red, 60 mL Et₃N was added. With immediate addition of cuprous iodide (300.0 mg, 1.6 mmol) the solution darkened to a black colour. The reaction mixture was stirred and heated to 45°C for 16 hours. The solvent was removed by vacuum. The remaining liquid was then extracted in a similar fashion mentioned above (3.3.2). Hexanes added, and purified *via* column chromatography on SiO₂ (hexanes) to produce a clear liquid. Yield (9.06 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.73 (t, 1H, $^4J_{H-H}$ = 4 Hz), 7.60-7.53 (m, 2H), 7.51-7.47 (m, 2H, $^4J_{H-H}$ = 4 Hz), 7.41-7.36 (m, 3H), 7.23 (t, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ_C = 134.34, 131.71, 131.38, 130.15, 129.79, 128.64, 128.43, 125.35, 122.79, 122.21, 90.73, 87.84 ppm.

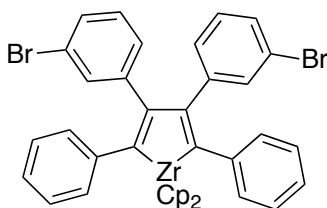
3.4.3 Synthesis of *p*-dihex-1-ynylbenzene (113)



p-diiodobenzene (5.6 g, 19.7 mmol), 1-hexyne (2.0 g, 24.3 mmol), and Pd(PPh₃)₄ (69.0 mg, 0.06 mmol) were added to a 250 mL Schlenk flask. 25 mL THF was subsequently added and gradually dissolved the catalyst. With the solution colour of red, 25 ml Et₃N was added. With immediate addition of cuprous iodide (370.0 mg, 1.9 mmol) the solution gradually darkened to a black colour. The reaction mixture was stirred and heated to 45°C for 16 hours. The solvent was removed by vacuum. The remaining liquid was then extracted in a similar fashion mentioned above (3.3.2). Hexanes added, and purified *via* column chromatography on SiO₂ (hexanes) to produce a yellow/orange liquid. Yield (3.97 g, 86%). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.33 (s, 4H), 2.44 (t, 4H, ³*J*_{H-H} = 8.0 Hz) 1.65 - 1.48 (m, 8H, ³*J*_{H-H} = 8.0 Hz), 1.00 (t, 6H, ³*J*_{H-H} = 8.0 Hz) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃) δ_C = 131.30, 123.22, 91.76, 80.40, 30.82, 22.02, 19.15, 13.59 ppm.

3.5 Attempted synthesis of novel monomers for zero valent nickel polymerization

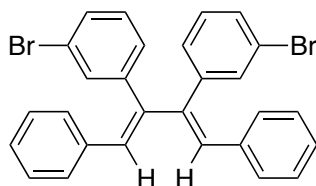
3.5.1 Attempted synthesis of 3,4-bis(3-bromophenyl)-2,5-diphenylzirconacyclopentadiene (114)



A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.64 g, 5.6 mmol), and THF (25 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) in hexanes was dropwise added. The solution began to turn yellow. The reaction was stirred for 30 minutes. Then a solution of **111** (2.89 g, 11.25 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after several hours of stirring. All subsequent reactions used this compound *in situ*. Direct characterization on this compound was not attempted as the compound, like all zirconocene based

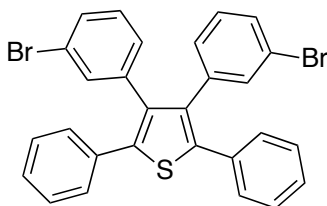
compounds studied in this research, have immediately hydrolyzed or become insoluble oxide based compounds.

3.5.1 Attempted synthesis of 3,3'-((1*E*,3*E*)-1,4-diphenylbuta-1,3-diene-2,3-diyl)bis(bromobenzene) (115)



A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.64 g, 5.6 mmol), and THF (25 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) in hexanes was dropwise added. The solution began to turn yellow. The reaction was stirred for 30 minutes. Then a solution of **111** (2.89 g, 11.25 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after one hour of stirring. An aqueous 6 M HCl solution was added dropwise. After stirring for two hours the solvent and any volatiles were removed by vacuum. After an extractive workup (ethyl acetate, NaHCO_3 , NaCl) and the removal of solvent by vacuum. A mixture of DCM/hexanes formed clear crystals. Yield (2.16 g, 75%). ^1H NMR (400 MHz, CDCl_3) $\delta_{\text{H}} = 7.53 - 7.47$ (m, 4H), 7.30 - 7.24 (m, 4H), 7.11 - 7.06 (m, 6H), 6.81 - 6.76 (m, 4H), 6.31 (s, 2H) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) $\delta_{\text{C}} = 143.40, 141.54, 136.44, 133.10, 132.34, 130.66, 130.41, 129.49, 129.14, 128.01, 127.12, 122.78$ ppm.

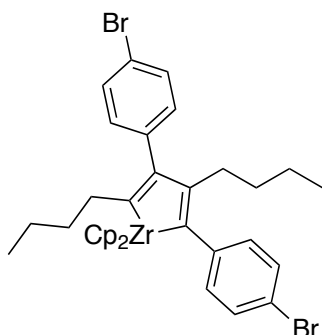
3.5.2 Attempted synthesis of 3,4-bis(3-bromophenyl)-2,5-diphenylthiophene (116)



A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.64 g, 5.6 mmol), and THF (25 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) in hexanes was dropwise added. The solution began to turn yellow. The

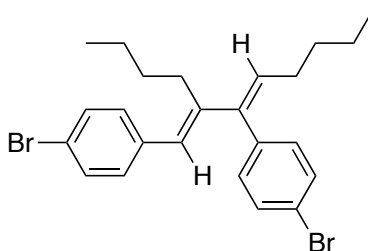
reaction was stirred for 30 minutes. Then a solution of **111** (2.89 g, 11.25 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after one hour of stirring. Once several hours past, sulfur monochloride (0.945 g, 7.00 mmol) was dropwise added and allowed to stir at room temperature for 1 hour. The solvent was then removed by vacuum. After an extractive workup (5% H₂SO₄, ethyl acetate, NaHCO₃, NaCl) and the removal of solvent by vacuum, the brown residue was purified *via* flash chromatography on SiO₂ (hexanes, R_f = 0.26) to produce a viscous yellow liquid. Attempts to recrystallize with DCM/hexanes failed. Crude mass (3.10 g). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.46 - 6.89 (m, 18H) ppm. Carbon could not be assigned, as it is apparent that three species may exist with similar structures.

3.5.2 Attempted synthesis of 2,4-bis(4-bromophenyl)-3,5-dibutylzirconacyclopentadiene (**117**)



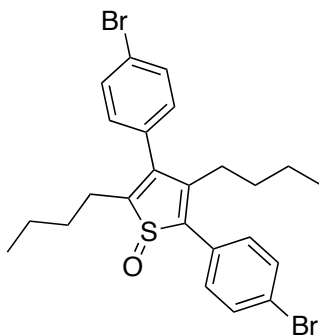
A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.92 g, 6.58 mmol), and THF (30 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) in hexanes was dropwise added. The solution began to turn yellow. The reaction was stirred for 30 minutes. Then a solution of **107** (3.12 g, 13.16 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after several hours of stirring. All subsequent reactions used this compound *in situ*. Direct characterization on this compound was not attempted as the compound, like all zirconocene based compounds studied in this research, have immediately hydrolyzed or become insoluble oxide based compounds.

3.5.3 Attempted synthesis of 4,4'-((1*E*,3*Z*)-2-butylocta-1,3-dienediyl)bis(bromobenzene) (118)



A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.92 g, 6.58 mmol), and THF (30 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) in hexanes was dropwise added. The solution began to turn yellow. The reaction was stirred for 30 minutes. Then a solution of **107** (3.12 g, 13.16 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after several hours of stirring. Hydrolyzation of compound was attempted with 6 M HCl. After an extraction using ethyl acetate and NaHCO_3 and all solvents removed by vacuum. ^1H , ^{13}C NMR spectroscopy and AIMS AccuTOF-DART mass spectrometry were performed on the light yellow liquid. Starting material was observed. However, AIMS AccuTOF-DART mass spectrometry suggests various high weight molecules were present in the sample with M^+ , $\text{M}+2$, $\text{M}+4$ signals.

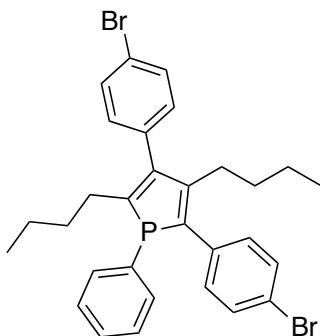
3.5.4 Attempted synthesis of 2,4-bis(4-bromophenyl)-3,5-dibutylthiophene 1-oxide (119)



A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.92 g, 6.58 mmol), and THF (30 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) was dropwise added. The solution began to turn yellow. The reaction

was stirred for 30 minutes. Then a solution of **107** (3.12 g, 13.16 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after several hours of stirring. Thionyl chloride (0.783 g, 6.58 mmol) was added directly into the reaction mixture. An immediately colour change was observed. The red solution became brownish. The reaction mixture was stirred for several hours. The solvent was then removed by vacuum. Minimal hexanes were used to wash/filter the dark orange liquid. Afterwards, the dark orange liquid filtrate was dried under vacuum. ^1H , and ^{13}C NMR spectroscopy and AIMS AccuTOF-DART mass spectrometry were performed on the dark orange liquid. Starting material was observed. However, AIMS AccuTOF-DART mass spectrometry suggests various high weight molecules were present in the sample with M^+ , $M+2$, $M+4$ signals.

3.5.3 Attempted synthesis of 2,4-bis(4-bromophenyl)-3,5-dibutyl-1-phenyl-phosphole (120)

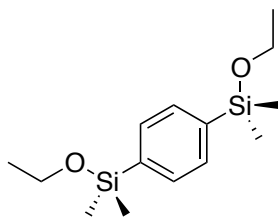


A 100 mL Schlenk flask was loaded with zirconocene dichloride (1.92 g, 6.58 mmol), and THF (30 mL) under argon. The reaction mixture was cooled to -98°C (toluene/liquid nitrogen slush bath) and *n*-BuLi (7.03 mL, 11.25 mmol) was dropwise added. The solution began to turn yellow. The reaction was stirred for 30 minutes. Then a solution of **107** (3.12 g, 13.16 mmol) in minimal THF was added dropwise. After 30 minutes the reaction mixture was allowed to warm to room temperature. The solution eventually became red after several hours of stirring. Dichlorophenylphosphine (1.18 g, 6.58 mmol) was added directly into the reaction mixture. The red solution became brownish. The reaction mixture was stirred for several hours. The solvent was then removed by vacuum. Minimal hexanes were used to wash/filter the brown liquid. Afterwards, the brown liquid filtrate was dried under vacuum. ^1H , ^{13}C , and ^{31}P NMR spectroscopy and AIMS AccuTOF-DART mass spectrometry were performed on the brownish liquid. Starting material was observed and no phosphorous signals were observed. However,

AIMS AccuTOF-DART mass spectrometry suggests various high weight molecules were present in the sample with M+, M+2, M+4 signals.

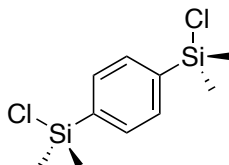
3.6 Synthesis of Tilley *et al.* polymer precursors

3.6.1 Synthesis of 1,4-bis(ethoxydimethylsilyl)benzene (123)



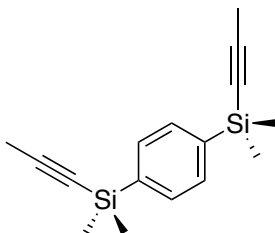
A 500 mL round-bottom flask charged with dimethyldiethoxysilane (31.8 mL, 27.5 g, 186 mmol) and magnesium (5.05 g, 208 mmol). A 100 mL Schlenk flask charged with 1,4-dibromobenzene (21.9 g, 93.0 mmol). Both were measured within a nitrogen-filled glove box. Approximately 50 mL THF was added to both flasks *via* needle and syringe. Both were stirred. The 500 mL round-bottom flask was fitted with a reflux condenser and, using a needle and syringe, the 1,4-dibromobenzene solution was added dropwise to the reaction mixture. After several drops of 1,4-dibromobenzene solution was added, the reaction mixture was heated to 30°C using an oil bath. The solution turned yellow and the reaction flask was hot to the touch once initiated. The reaction flask was allowed to cool to 30°C before adding the remaining 1,4-dibromobenzene solution dropwise. The mixture was refluxed 16 hours. The reaction flask was then removed from the oil bath and allowed to cool to room temperature. The solvent was then removed by vacuum. The greyish-white solid was washed with hexanes and filtered using a 1000 mL frit, into another 500 mL round-bottom flask. The volatile material and solvent was removed by vacuum and the yellow liquid was distilled at 80°C to produce a colourless liquid. Yield (13.6 g, 52%). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.65$ (s, 4H, C_6H_4), 3.56 (q, 4H, $^3J_{\text{H-H}} = 7.0$ Hz, OCH_2CH_3), 1.11 (t, 6H, $^3J_{\text{H-H}} = 7.0$ Hz, OCH_2CH_3), 0.35 (s, 12H, SiMe_2). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) $\delta_{\text{C}} = 139.66, 132.96, 58.43, 18.48, -1.78$ ppm.

3.6.2 Synthesis of 1,4-bis(chlorodimethylsilyl)benzene (**124**)



A 100 mL three-neck round-bottom flask was charged with **123** (13.6 g, 93 mmol) and CH_3COCl (33 mL, 36.5 g, 465 mmol). The flask was refluxed for 24 hours using an oil bath. After refluxing the oil bath was removed and the reaction flask was cooled to room temperature. The solvent was removed by vacuum. A pink to white solid remained. The white solution was purified *via* distillation under *ca.* 0.002 Torr and maximum heat settings from a heat gun, which was applied to the reaction flask and the distillation bridge. White crystals were formed. Yield (11.3 g, 89%). ^1H NMR (400 MHz, CDCl_3) $\delta_{\text{H}} = 7.61$ (s, 4H, C_6H_4), 0.54 (s, 12H, SiMe_2). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) $\delta_{\text{C}} = 138.51, 132.70, 1.61$ ppm.

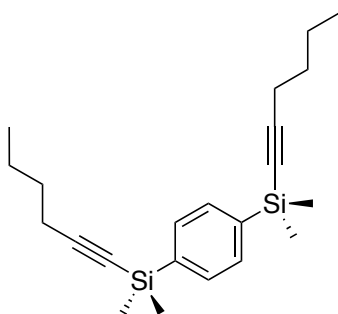
3.6.3 Synthesis of 1,4-bis(dimethyl(1-propynyl)silyl)benzene (**55**)



A 2000 mL round-bottom Schlenk flask was charged with 1-bromo-1-propene (18.9 mL, 26.86 g, 222 mmol) and 600 mL THF. The round-bottom Schlenk flask was cooled using a toluene/liquid nitrogen slush bath (-98°C) and *n*-BuLi (277.5 mL, 444 mmol) in hexanes was added slowly using a needle and syringe. The orange-white solution was left to react for 30 minutes before cooled to room temperature (with the removal of slush bath). While warming to room temperature, the solution turned yellow. A 150 mL round-bottom flask was charged with **124** (29.25 g, 111 mmol) with 90 mL THF. Using a needle and syringe, the fully dissolved **124** was added to the 1-bromo-1-propene and *n*-BuLi mixture. The dropwise addition of **124** slowly changed the mother reaction mixture darker yellow. The solution was stirred for 48 hours. The solvent was removed by vacuum and distilled under full vacuum and maximum heat settings from a heat gun on the reaction flask and the distillation bridge. The product was a light yellow

solution with eventually turned into clear crystals. Yield (22.9 g, 76%). ^1H NMR (400 MHz, C_6D_6): δ_{H} = 7.87 (s, 4H, C_6H_4), 1.65 (s, 6H, CH_3), 0.53 (s, 12H, SiMe_2) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ_{C} = 138.67, 133.21, 104.81, 81.85, 4.43, -0.73 ppm.

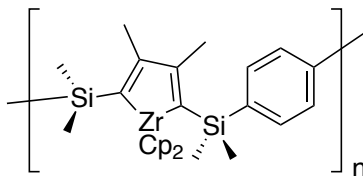
3.6.4 Synthesis of 1,4-bis(dimethyl(1-hexynyl)silyl)benzene (**125**)



A 2000 mL round-bottom Schlenk flask was charged with 1-hexyne (18.24 g, 222 mmol) and 600 mL THF. The round-bottom Schlenk flask was cooled using a toluene/liquid nitrogen slush bath (-98°C) and *n*-BuLi (138.8 mL, 222 mmol) in hexanes was added slowly using a needle and syringe. The orange-white solution was left to react for 30 minutes before cooled to room temperature (with the removal of slush bath). While warming to room temperature, the solution turned yellow. A 150 mL round-bottom flask was charged with **124** (29.25 g, 111 mmol) with 90 mL THF. Using a needle and syringe, the fully dissolved **124** was added to the 1-hexyne and *n*-BuLi mixture. The dropwise addition of **124** slowly changed the mother reaction mixture darker yellow. The solution was stirred for 48 hours. The solvent was removed by vacuum and distilled under *ca.* 0.002 Torr and maximum heat settings from a heat gun on the reaction flask and the distillation bridge. The product was a light yellow solution with eventually turned into clear crystals. Yield (25.69 g, 70%). ^1H NMR (400 MHz, C_6D_6) δ_{H} = 7.84 (s, 4H, C_6H_4), 2.18 (t, 4H, $\text{C}\equiv\text{CCH}_2$), 1.35 - 1.30 (m, C 8H, $\text{CH}=\text{CH}_2$), 0.77 (t, 6H, $\text{CH}=\text{CH}_3$), 0.34 (s, 12H, SiMe_2) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) δ_{C} = 138.60, 133.03, 109.23, 82.18, 30.71, 21.90, 19.59, 13.52, -0.60 ppm.

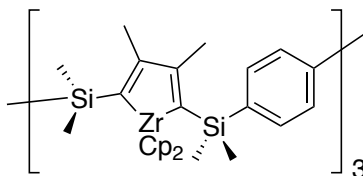
3.7 Syntheses of silyl based zirconacyclopentadiene polymers

3.7.1 Synthesis of [(1,4-Me₂SiC₆H₄SiMe₂)C₄Me₂ZrCp₂]_n (**58**)



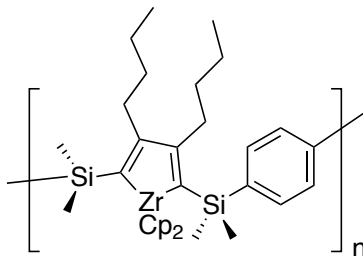
A 250 mL three-neck round-bottom charged with zirconocene dichloride (13.66 g, 47 mmol) with 50 mL THF. The light yellow-brown solution was cooled using a toluene/liquid nitrogen slush bath (-98°C) and *n*-BuLi (58.0 mL, 93 mmol) in hexanes was added slowly using a needle and syringe. The now dark yellow-brown solution was left to react for 30 minutes before warmed to room temperature (by removing slush bath). Another 250 mL one-neck round-bottom flask was charged with **55** (12.55 g, 47 mmol) and 30 mL THF. The **55** solution was added dropwise into the zirconocene dichloride and *n*-BuLi reaction mixture. The dark yellow-brown solution was allowed to stir for 48 hours. After 48 hours the solvent was removed by vacuum. Minimal toluene was added to dissolve the brown solid. Using a needle and syringe, the dissolved product was added to a 500 mL one-neck round-bottom flask containing 200 mL *n*-hexane and a magnetic stir bar. As the brown product was added to *n*-hexane, bright yellow-orange, sticky precipitate began to form and landed at the bottom of the flask. After the addition of polymer-toluene the stirrer was stopped. All orange precipitate was allowed to settle. The solvent was then decanted. The orange solid that remained was washed with *n*-hexane several times. The product was a yellow powder. Yield (17.9 g, 78%). ¹H NMR (400 MHz, C₆D₆) δ_H = 7.87 (s, 4H, C₆H₄), 6.10 (s, 10H, C₅H₅), 1.78 (s, 6H, C₄Me₂), 0.35 (s, 12H, SiMe₂) ppm. ¹³C {¹H} NMR (100 MHz, C₆D₆) δ_C = 198.95, 149.28, 142.47, 133.60, 111.38, 27.32, 1.94 ppm. λ_{Max} = 226 nm.

3.7.2 Synthesis of [(1,4-Me₂SiC₆H₄SiMe₂)C₄Me₂ZrCp₂]₃ (**89**)



A 100 mL THF solution of polymer **58** (5.00 g) was heated at reflux for 24 h, and then the solution was concentrated to 30 mL and added to 70 mL of *n*-hexanes. The resulting solution was left to give the product as yellow cubic crystals in various yields of 1% to 30% (0.05 g to 1.5 g). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.87$ (s, 4H, C_6H_4), 6.10 (s, 10H, C_5H_5), 1.80 (s, 6H, C_4Me_2), 0.32 (s, 12H, SiMe_2) ppm.

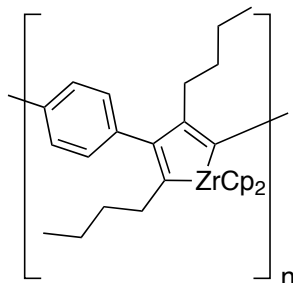
3.7.2 Synthesis of $[(1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2)\text{C}_4\text{Bu}_2\text{ZrCp}_2]_n$ (**126**)



A 250 mL three-neck round-bottom charged with zirconocene dichloride (13.66 g, 47 mmol) with 50 mL THF. The light yellow-brown solution was cooled using a toluene/liquid nitrogen slush bath (-98°C) and *n*-BuLi (58.0 mL, 93 mmol) in hexanes was added slowly using a needle and syringe. The now dark yellow-brown solution was left to react for 30 minutes before warmed to room temperature (by removing slush bath). Another 250 mL one-neck round-bottom flask was charged with **125** (15.54 g, 47 mmol) and 30 mL THF. The **125** solution was added dropwise into the zirconocene dichloride and *n*-BuLi reaction mixture. The dark yellow-brown solution was allowed to stir for 48 hours. After 48 hours the solvent was removed by vacuum. Minimal toluene was added to dissolve the brown solid. Using a needle and syringe, the dissolved product was added to a 500 mL one-neck round-bottom flask containing 200 mL *n*-hexane and a magnetic stir bar. As the brown product was added to hexane, bright yellow-orange, sticky precipitate began to form and landed at the bottom of the flask. After the addition of polymer-toluene the stirrer was stopped. All orange precipitate was allowed to settle. The solvent was then decanted. The orange solid that remained was washed with *n*-hexane several times. The product was a yellow powder. Yield (14.64 g, 50%). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.90$ (s, 4H, C_6H_4), 6.08 (s, 10H, C_5H_5), 2.11 (t, 4H CH_2CH_2), 1.53 - 1.07 (m, 8H, CH_2CH_2), 0.87 (t, 6H, CH_2CH_3), 0.45 (s, 12H, SiMe_2) ppm.

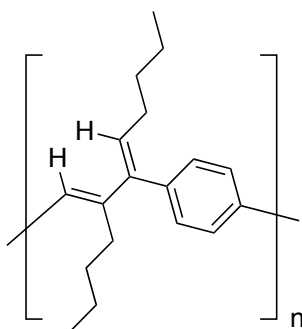
3.8 Attempted synthesis of carbon based zirconacyclopentadiene polymers

3.8.1 Attempted synthesis of $[(1,4\text{-C}_6\text{H}_4)\text{C}_4\text{Bu}_2\text{ZrCp}_2]_n$ (**127**)



A 100 mL Schlenk flask was charged with zirconocene dichloride (2.66 g, 9.11 mmol), and 20 mL THF under argon. The flask was cooled to -98°C (toluene/liquid nitrogen) and a hexane solution of 1.60 M *n*-BuLi (11.39 mL, 18.22 mmol) was then added dropwise. The reaction mixture was stirred for 30 minutes before warming to room temperature. A solution of **113** (2.17 g, 9.18 mmol) in minimal THF was added dropwise then stirred for 36 hours to afford a viscous red solution. The solvent was then removed by vacuum. The brown residue was washed and filtered with hexanes (*ca.* 30 mL). A brown solid was isolated. Yield (3.2 g, 76%). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.08$ (br), 6.13 (br), 2.23 (br), 1.26 (br), 0.87 (br) ppm. As well, hexanes solvent signals overlap butyl substituents.

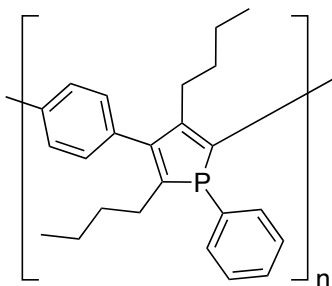
3.8.2 Attempted synthesis of $[1,4\text{-C}_6\text{H}_4\text{C}_4\text{Bu}_2\text{H}_2]_n$ (**128**)



A 100 mL Schlenk flask was charged with a solution of **127** (1.00 g, 2.17 mmol) under argon. 6 M aqueous HCl solution (5 mL) was added to the flask and the resulting mixture was stirred for 2 hours at room temperature. The reaction mixture was then added to a vigorously stirring quantity of methanol (*ca.* 150 mL), resulting in the formation of a yellow precipitate, which was collected by filtration, and washed

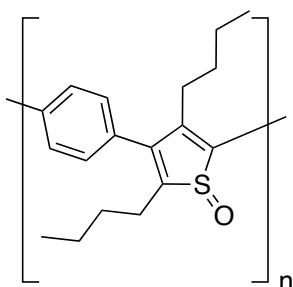
with methanol (3 x 20 mL) and then dried under vacuum for several hours. A yellow solid was isolated. Yield (410 mg, 79%). ^1H NMR (400 MHz, CDCl_3) $\delta_{\text{H}} = 7.08$ (br), 6.13 (br), 2.23 (br), 1.26 (br), 0.87 (br) ppm. $\lambda_{\text{max}} = 298$ nm.

3.8.3 Attempted synthesis of $[(1,4\text{-C}_6\text{H}_4)\text{C}_4\text{Bu}_2\text{P}(\text{C}_6\text{H}_5)]_n$ (**129**)



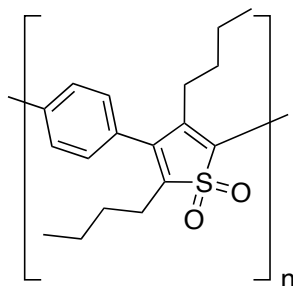
A 100 mL Schlenk flask was charged with a solution of **127** (2.3 g, 4.99 mmol) under argon. Then, dichlorophenylphosphine (1.00 g, 5.59 mmol) was added, and the mixture was stirred for 5 days. The solution was then concentrated and added to 100 mL methanol. A red precipitate was collected by filtration, and washed with methanol and dried under vacuum. Yield (1.28 g, 74%). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.35$ (br), 2.61 (br), 1.60 (br), 0.85 (br) ppm. $\lambda_{\text{max}} = 301$ nm.

3.8.4 Attempted synthesis of $[(1,4\text{-C}_6\text{H}_4)\text{C}_4\text{Bu}_2\text{SO}]_n$ (**130**)



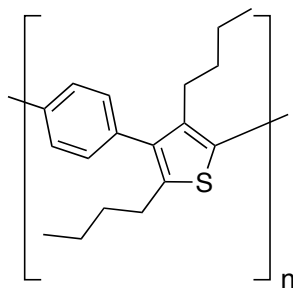
A 100 mL Schlenk flask was charged with a solution of **127** (2.3 g, 4.99 mmol) under argon. Then, thionyl chloride (1.00 g, 8.41 mmol) was added, and the mixture was stirred for 12 hours. The solution was then concentrated and added to 100 mL methanol. A brown precipitate was collected by filtration, and washed with methanol and dried under vacuum. Yield (1.52 g, 60%). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.49$ (br), 2.69 (br), 1.42 (br), 0.82 (br) ppm. $\lambda_{\text{max}} = 259$ nm.

3.8.5 Attempted synthesis of $[(1,4\text{-C}_6\text{H}_4)\text{C}_4\text{Bu}_2\text{SO}_2]_n$ (131)



A 100 mL Schlenk flask was charged with a solution of **127** (2.3 g, 4.99 mmol) under argon. Then, sulfuryl chloride (1.00 g, 7.09 mmol) was added, and the mixture was stirred for 12 hours. However, it must be noted that with the addition of sulfuryl chloride the reaction mixture became extremely exothermic. At times, with the addition the solvent would boil. Similarly, a gummy like material would crash out and redissolve. The solution was then concentrated and added to 100 mL methanol. A yellow/white precipitate was collected by filtration, and washed with methanol and dried under vacuum. Yield (1.21 g, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.50 (br), 2.61 - 0.44 (br) ppm. λ_{max} = 226 nm.

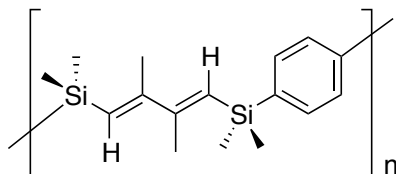
3.8.6 Attempted synthesis of $[(1,4\text{-C}_6\text{H}_4)\text{C}_4\text{Bu}_2\text{S}]_n$ (132)



A 100 mL Schlenk flask was charged with a solution of **127** (2.3 g, 4.99 mmol) under argon. Then, sulfur monochloride (1.00 g, 7.41 mmol) was added, and the mixture was stirred for 12 hours. The solution was then concentrated and added to 100 mL methanol. A yellow precipitate was collected by filtration, and washed with methanol and dried under vacuum. Yield (269 mg, 30%). ¹H NMR (400 MHz, CDCl₃) δ_H = 7.54 (br), 2.69(br), 1.59 - 0.65 (br) ppm. λ_{max} = 302 nm.

3.9 Attempted synthesis of $[1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2]_n$ via lithium coupling of diynes

3.9.1 Attempted synthesis of $[1,4\text{-Me}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{C}_4\text{Me}_2\text{H}_2]_n$ (133)



A 100 mL Schlenk flask was charged with **55** (1.5 g, 5.56 mmol), lithium (232 mg, 33.36 mmol), and THF (20 mL) under argon. The reaction was left stirring overnight. The reaction mixture was then decanted from the solid lithium pieces. An aqueous 6 M HCl solution (7 mL) was added and allowed to stir for 2 hours. Solvents were then concentrated and added to 100 mL methanol. A fine white powder/suspension formed. After centrifuging a fine white powder was collected. Yield (0.45 g, 30%). ^1H NMR (400 MHz, C_6D_6) $\delta_{\text{H}} = 7.65$ (br), 2.45 - (-0.08) (br) ppm.

4 Conclusion

The synthesis of Group IV (Fe and Cr), compound **103** and **104**, based metallocenes from zirconocene intermediates, compound **3**, still require further attention. There were signs, for instance, the formation of starting material zirconocene dichloride, that suggest that metallacycle transfer with FeCl_3 and CrCl_3 worked. Attempts to synthesize compound **5** and **6** should also be attempted *via* compound **8** and **9**. However, compound **9** has proven to be quite difficult to acquire in sufficient amounts for such reactions.

Sonogashira coupling has proven to be an advantageous method to synthesize alkynes (**107** and **111**) and diynes (**113**) useful for both novel monomer formation (**115**) and novel polymers (**127** to **132**). Castro-Stephens coupling worked, but yielded much lower results when compared to Sonogashira- coupling.

Tilley *et al.* polymer **58** has been synthesized and a butyl analog, polymer **126**, but offer limited metallacycle transfer capabilities as studied by Jennifer Nguyen of the Dr. McWilliams group. Macrocyclization of these polymers are possible, but are difficult to acquire. The polymers **127** to **132** require further study and characterization, but initial results are promising. Induced coupling *via* lithium of compound **55** to produce suggested polymer **133** also presents some interesting initial findings. It may be possible to polymerize diynes *via* lithium.

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