Signature page

Biphenyl substituted Cyclopentadienyl Ligand Complexes

By
Ketnavi Ramgoolam

A Thesis Submitted to
Saint Mary's University, Halifax, Nova Scotia
in Partial Fulfillment of the Requirements for
the Degree of Bachelor of Science Degree with Honours in Chemistry

April 2019, Halifax, Nova Scotia

Approved:	Dr. Jason Masuda
	Supervisor
	Department of Chemistry

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Abstract

The synthesis of biphenyl substituted cyclopentadienyl ligands are described. The synthetic route is accomplished through the reaction of aryl lithium reagents with cobaltocenium salts, followed by oxidation of the intermediate cobalt(I) species to give the corresponding cyclopentadiene. Detailed information on their preparation, structural, and spectroscopic properties are described. A preliminary reaction towards the biphenyl substituted cyclopentadienyl ligand complexes yielding the corresponding alkali metal salt (K) is also described. Its structural and spectroscopic properties are described briefly.

March 20, 2019

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First of all, I would like to express my most sincere gratitude to my supervisor, Dr. Jason Masuda, for all of his time, efforts, teachings and guidance. Thank you for being a most wonderful and understanding human being. This project helped me in discovering my potential as a chemist and I had plenty of wonderful experiences and opportunities that I personally believe will forever shape and influence my professional life as well as my personal growth. Huge thanks to all of the past and current Masuda group members: Alex Veinot, Darcie Stack, Jennifer (Jenn) Wright, Bailey Mosher and Tanner George. A most special thanks to Jenn for always being so responsive to all of the questions & confusions I had and for always being so helpful. I would also like to thank Alyssa Doué for her assistance and technical support.

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List of Symbols & Abbreviations

°	degree
°C	degree Celsius
Å	Angstrom
Ar	aryl
β-	Beta-
Bu	butyl
COSY	COrrelation SpectroscopY
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
d	doublet
D	deuterium
dd	doublet of doublets
DEPTQ	Distortionless Enhancement by Polarisation Transfer Quaternaries
eq.	equivalent
Et	Ethyl
g	gram
h	hour
Hz	Hertz
in vacuo	under vacuum
iPr	isopropyl
J	coupling constant
M	molarity
m	multiplet (NMR spectroscopy)
Me	methyl
Mes	mesityl
mg	milligram
MHz	MegaHertz

mins	minutes
mL	millilitre
mmol	millimole
m.p.	melting point
NMR	nuclear magnetic resonance
NOESY	Nuclear Overhauser Effect Spectroscopy
Ph	phenyl
pKa	acidity measurement
q	quartet
r.t.	room temperature
s	singlet (NMR spectroscopy)
t	triplet
Biphenyl	1, 1'-biphenyl/phenylbenzene
Ter^{Dipp}	2,6-bis(2,6-diisopropylphenyl)phenyl
Ter^{Mes}	2,6-bis(2,4,6-trimethylphenyl)phenyl
Ter^{Ph}	2,6-di(phenyl)phenyl
THF	tetrahydrofuran
TMS	tetramethylsilane
δ	chemical shift
η	hapticity

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1.0 Introduction

1.1 Overview

Cyclopentadiene (Figure 1.1.1A) is an organic molecule with the molecular formula C_5H_6. It is readily deprotonated by strong bases such as alkali metal hydrides or amides to produce the cyclopentadienyl anion ($C_5H_5^-$, abbreviated as Cp in Figure 1.1.1B).[1] The unusual acidity of cyclopentadiene (pKa = 15) also allows the formation of this cyclopentadienyl anion.[2]
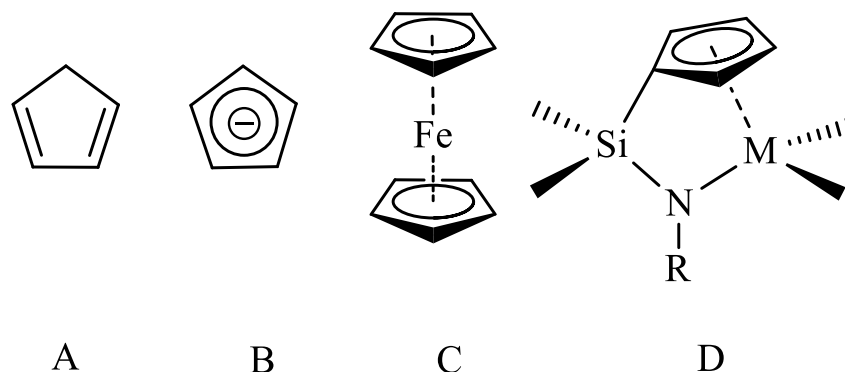
Figure 1.1.1. Cyclopentadiene, the cyclopentadienyl anion, Ferrocene and the cyclopentadienyl-amido complex (e.g. constrained geometry complex) as denoted by A, B, C and D respectively.

Back in 1951, Kealy and Pauson[3] successfully isolated the compound, dicyclopentadienyl iron, or as it is commonly known, ferrocene (Figure 1.1.1C) This was a huge breakthrough in the field of organometallic chemistry, as all previous and numerous works done regarding the reaction of Grignard reagents with anhydrous ferric chloride to isolate any organo-iron compounds or to produce any evidence of their formations had been unsuccessful.[3] They attributed this remarkable stability of ferrocene to the tendency of the cyclopentadienyl group to become aromatic by

acquisition of a negative charge.[3] Following this report of ferrocene, the elucidation of its structure and bonding was then done in 1952.[4] Thus, since then, cyclopentadienyl-metal complexes have contributed enormously to the field of organometallic chemistry and Cp ligands became one of the most important ligands used by inorganic chemists.

The deprotonation of cyclopentadiene which results into the formation of the cyclopentadienyl anion, gives a 6-electron aromatic π-system similar to that of benzene.[2] The cyclopentadienyl anions/ligands can donate up to 6 electrons to a transition metal forming Cp-transition metal complexes. Complexes of Cp ligands are known for most main group elements, all transition metals as well for the f-block elements.[5] The use of cyclopentadienyl ligands on metals in various catalytic processes have also proved to be very useful, particularly those incorporating chelating cyclopentadienyl-amido ligands (Figure 1.1.1D) bound to Group IV metals for olefin polymerisation reaction[6], as Cp ligands have a relatively low intrinsic reactivity that makes them excellent spectator ligands.[7] Cyclopentadienyl ligands are also very easily modified which enhances their steric and electronic effects. One such example is $C_5Me_5^-$ (Cp*[-]), a ligand that inorganic chemists often use because it provides an increased steric hindrance at the metal centre, enhanced electron donating abilities and improved solubility in organic solvents.[8,9,10]

This research was on the synthesis and the chelation of biphenyl substituted cyclopentadienyl ligand to metal ions. A chelating agent is a ligand that can form more than one bond to a single metal ion. In other words, a chelating agent is a multidentate ligand. The different ways of chelation that are believed to be achievable using the target ligand are showed by Figure 1.1.2.

L = Ligand
M = Metal
iPr = isopropyl

Chelated   Non-chelated
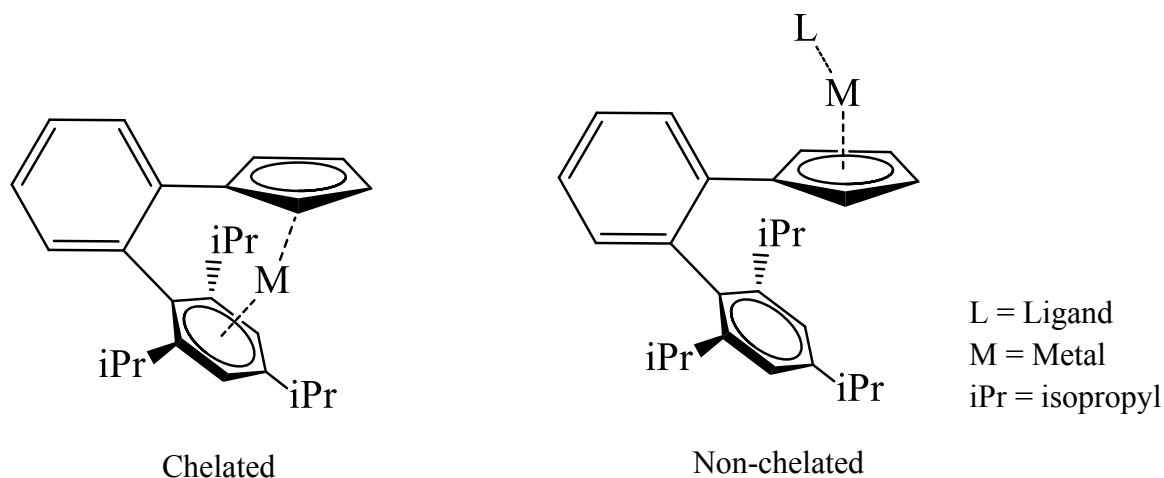
Figure 1.1.2. The different ways of chelation that are believed to be achievable by the metal ions.

In the literature, there are currently very limited examples and evidences of the research done on the isolation of these biphenyl substituted Cp ligands and their corresponding metal complexes. The very few examples that exist in the literature are those of the bulky cyclopentadienyl ligand precursor Ter[Ph]CpH (Scheme 1.1.1.) that was synthesised through a Pd-catalysed cross-coupling reaction (Stille reaction), alongside with a corresponding Zr complex which was also successfully isolated.[11]
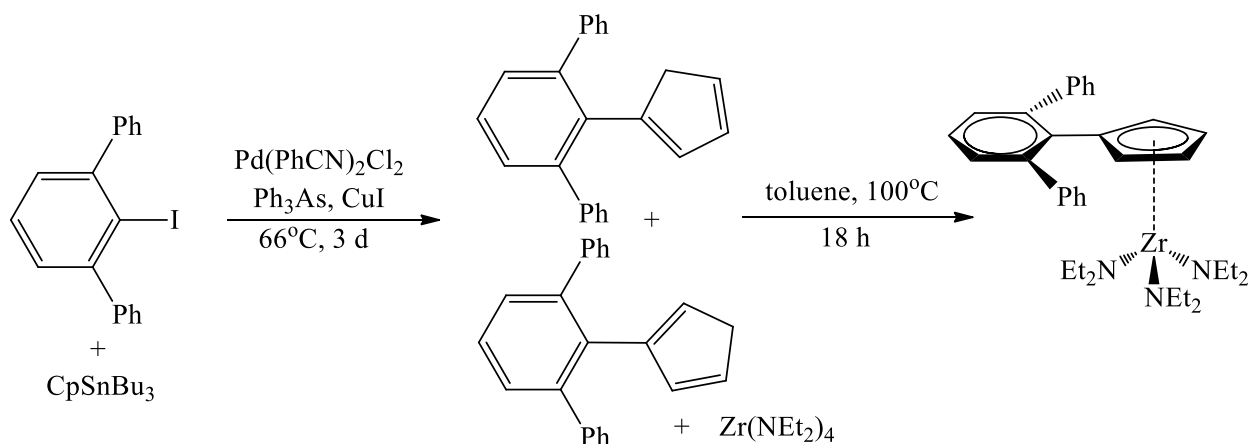
Scheme 1.1.1. Reaction of the cyclopentadienyl ligand precursor Ter[Ph]CpH, synthesised through a Pd-catalysed cross-coupling reaction, and its corresponding Zr complex that was successfully isolated.[11]

The best and most recent example so far of such a work is the isolation of the free *m*-terphenyl substituted Cp ligands and their corresponding metal complexes done by Veinot and Masuda.[1] It was expected that by expanding the library of known m-terphenyl substituted Cp ligands, a new class of hemilabile, bidentate cyclopentadienyl ligands would result that are capable of binding to metal centers through both cyclopentadienyl and aryl substituents.[1,5] In the same paper by Veinot and Masuda, entitled, "A Bulky m-Terphenyl Cyclopentadienyl Ligand and Its Alkali-Metal Complexes"[1], it was reported that attempts at using the Stille coupling for preparing the ligand to yield the corresponding Ter[Mes]-cyclopentadiene compound was unsuccessful because of the increased steric demands of the Ter[Mes] substituent.[1] Nevertheless, nucleophilic substitution reactions of unsaturated hydrocarbons such as benzene, are well known to produce the corresponding exo addition products when bound as ligands to cationic transition metals.[12] Therefore, taking the latter fact into consideration as well as using methodologies from other

synthetic strategies described previously in the literature,[13,14] an alternative synthetic approach was used to make the C-C bond between the m-terphenyl and cyclopentadiene. The organolithium reagent TerMesLi[15] was treated with cobaltocenium iodide to give the corresponding air-stable cobalt(I) cyclopentadiene complex having a 66% yield following recrystallization from cold pentane (Scheme 1.1.2.).[1] Therefore, the same methodology was used in this research involving the biphenyl substituted cyclopentadienyl ligand and it is described in the experimental sections.[1]
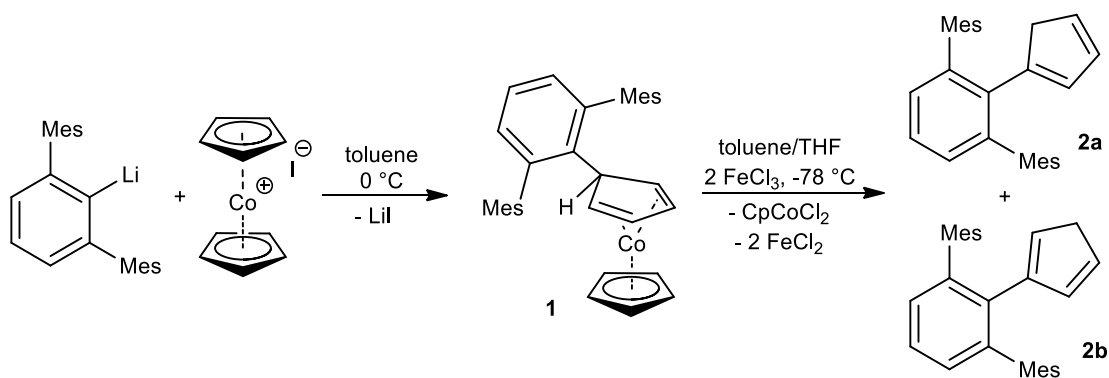
Scheme 1.1.2. Reaction of TerMesLi with cobaltocenium iodide to give the corresponding air-stable cobalt(I) cyclopentadiene complex and its subsequent oxidation gave the cyclopentadienyl ligand precursor Ter^{Mes}CpH, whereby 2a and 2b are the two different isomers that are possible, showing the two different ways through which the Ar-group could possibly bind to.[1]

Similarly, being a very bulky ligand, the aim of this research work was to investigate whether the biphenyl substituted cyclopentadienyl ligand would yield similar results to the free *m*-terphenyl substituted Cp ligands or not. The efficiency in terms of yield, cost, time and labour of using the biphenyl substituted cyclopentadienyl ligand over the *m*-terphenyl substituted cyclopentadienyl ligand as well was studied and compared so as to see which ligand was most suited for such a

reaction. Additionally, it was hypothesized that there could potentially be three different isomers (2a, 2b, 2c: Figure 1.1.3.) showing the three different positions of the aryl group and the hydrogen(s) on the cyclopentadiene fragment. Preliminary reactions with the cobaltocenium compound (Reaction 2.2.3) and the corresponding ^{1}H NMR spectroscopy that was carried out could not tell which isomer was formed. The X-ray crystallography that was also carried out however, showed that in the solid state, the isomer as showed by Figure 1.1.3. (2c) is isolated.

Figure 1.1.3. The three different isomers (2a, 2b, 2c) showing the three different positions of the aryl group and the hydrogen(s).

It is important to understand at the very onset of this project the meaning of the term a "bulky ligand". According to a review done on the classification of cyclopentadienyl ligands as being bulky[16], it was mentioned that only Cp ligands with three or more substituents larger than a methyl group were to be classified as "bulky Cp ligands". The use of these sterically hindered cyclopentadienyl ligands, as mentioned earlier, is based upon on how convenient these ligands are to prepare. Several synthetic routes for the synthesis of bulky Cp ligands have been described in the literature.[17,18,19] However, most of the time, in their search for new ligands, many organometallic chemists come up with their own developments and methodologies involving

bulky Cp ligands.[5] It has to be mentioned that because most sterically demanding cyclopentadienyl ligands are not commercially available for routine use, their synthesis as a precursor is therefore an important first step before doing any further coordination chemistry.[5]

The synthetic routes used to make typical unhindered Cp complexes work well with the bulkier ligands as well. The three reactions most frequently used are (i) salt metathesis, (ii) oxidative addition, and (iii) metalation/deprotonation according to the scheme below[5]:

i. $CpM + M'X \rightarrow CpM' + MX$

ii. $CpX + M^{m+}L_n \rightarrow CpM^{(m+2)+}L_{n-a}X + a\,L$

iii. $2\,CpH + 2\,M \rightarrow 2\,CpM + H_2$
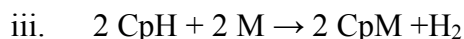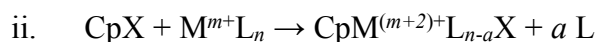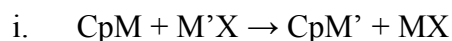
Scheme 1.1.3. The three reactions used to make typical unhindered Cp complexes are (i) salt metathesis, (ii) oxidative addition, and (iii) metalation/deprotonation.[5]

Salt metathesis is frequently used to prepare the majority of new Cp-metal complexes, while oxidative addition reactions are typically reserved for low oxidation state metals and require the bromine derivative of a highly substituted cyclopentadienyl ligand.[5,16] Regarding this project, methods (i) and (iii) are the two ways through which the complexes synthesized were supposed to be based upon.[5]

1.2 Uses of cyclopentadienyl ligands

A cyclopentadienyl complex is a metal complex with one or more cyclopentadienyl groups (C_5H_5, Cp).[20] Cyclopentadienyl ligands bind to metals in an η^5-bonding mode. Examples of biscyclopentadienyl complexes (metallocenes) such as ferrocene, a sandwich complex, have been mentioned in the overview section of this thesis. Chromocene ($CrCp_2$), cobaltocene ($CoCp_2$), and nickelocene ($NiCp_2$) are other common metallocenes which are also used.[20] Metallocenes are thermally stable and are thus used as catalysts in various types of reactions, for example, as catalysts for ethylene (olefin) polymerization.[20]

In most of the M–Cp complexes, all 5 carbon atoms of the Cp ligand are bound to the metal centre and this binding mode is known as η^5-coordination.[20] The M–Cp bonding arises from overlap of the five π molecular orbitals of the Cp ligand with the s, p, and d orbitals on the metal.[20] This π bonding is significant, hence these complexes are referred to as π-complexes. Almost all of the group 4 to 10 transition metals use this coordination mode.

Derivatives of Cp_2TiCl_2 and Cp_2ZrCl_2 are the basis of some reagents in organic synthesis. Upon treatment with aluminoxane, these dihalides give catalysts for olefin polymerization.[20] A Ziegler–Natta catalyst, named after Karl Ziegler and Giulio Natta, is a catalyst used in the synthesis of polymers of 1-alkenes (alpha-olefins).[21] There are two broad classes of the Ziegler-Natta catalysts and they are differentiated by their solubility. Heterogeneous catalysts based on titanium compounds are used in polymerization reactions together with cocatalysts, and triethylaluminium, $Al(C_2H_5)_3$.[22] This class of catalyst dominates the industry. Homogeneous catalysts are usually based on complexes of Ti, Zr or Hf.[23] They are usually used in combination with a different

organoaluminum cocatalyst or methylaluminoxane.[23] These catalysts traditionally contain metallocenes but also feature multidentate oxygen- and nitrogen-based ligands.[23]

Ziegler–Natta catalysts are used to polymerize terminal alkenes.[20]

$$\text{n } CH_2{=}CHR \rightarrow {-}[CH_2{-}CHR]_n{-}$$
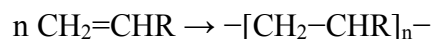
The transition metal catalyzed polymerization of olefins can be thought of as a reaction in which the carbon-carbon π-bond in α-olefins (1-alkenes) are cut and then remade as a carbon-carbon σ-bonds, linking the olefins together in long hydrocarbon chains known as polymers.[23] Polymers are the principal constituents of many common plastics. Some familiar plastics made via early transition metal catalyzed polymerization include high density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and others.[23]

The commonly accepted mechanism for the olefin polymerization reaction is shown below (Scheme 1.2.1).[24] An electron deficient metal center such as Cp_2ZrCl_2, coordinates to the π-bond of an olefin to form a weakly bound olefin complex. The bond is weak because there are no d-electrons to form a π-bond with.[24] The bounded olefin then inserts into a metal-carbon bond within the complex via a four-center transition state, forming new metal-carbon and carbon-carbon bonds. This process then repeats, extending the chain indefinitely.[24]
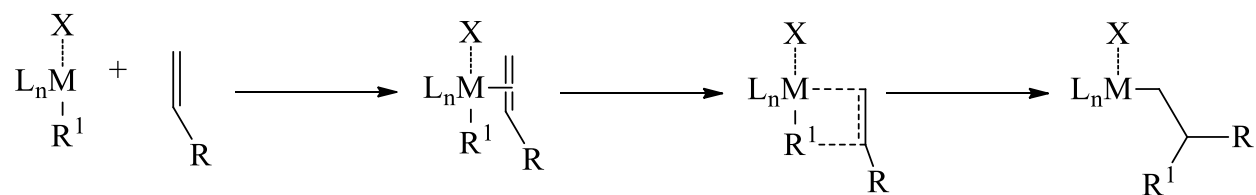
Scheme 1.2.1. Coordination of an electron deficient metal center such as Cp_2ZrCl_2, to the π-bond of an olefin to form a weakly bound olefin complex and ultimately forming new metal-carbon and carbon-carbon bonds.[24]

β-hydride elimination is a common process used to terminate chain growth. Catalysts with relatively strong M-C bonds give higher molecular weight polymers, while those with relatively weak M-H bonds give lower molecular weight polymers. β-hydride elimination leads to polymers with vinyl (R=H) or vinylidene (R=Me, Et, Pr) end groups.[24]
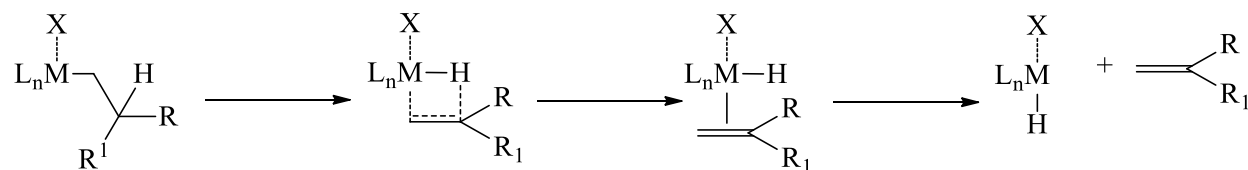
Scheme 1.2.2. Termination of chain growth by a β-hydride elimination reaction.[24]

1.3 Concepts for using bulky ligands

Cyclopentadienyl ligands incorporating bulky substituents are very useful because they allow for the accessibility to unusual molecular structures, spin states or reactivity.[5,25,26,27,28] Bulky ligands are used to control the steric properties of a metal center by providing kinetic and/or thermodynamic inertness to unstable species. Large substituents are used to protect reactive sites within the unstable species hence allowing their successful isolation.[27,26,28] These substituents act as a protective barrier, lowering the rate of decomposition through homomolecular collisions in solution or by preventing reaction with small molecules such as water or oxygen.[5]

Moreover, the use of bulky ligands shifts the balance of both the steric and electronic properties of molecules hence allowing them to attain a different molecular geometry.[5] This shift then allows the isolation of molecules/species that were otherwise unachievable or unstable if smaller ligands were to be used. Bulky ligands allow the isolation of these unstable species because these ligands are large enough to block low-lying vacant orbitals at the metal centre hence preventing reactivity.[5] Furthermore, sterically crowded cyclopentadienyl rings are more likely to experience reduced rotation about the metal centre due to repulsive forces between the bulky substituents bound to each ring.[5] Therefore, as it can be deduced from all the above listed reasons and concepts, cyclopentadienyl ligands are hugely beneficial to inorganic chemists.

2.0 Experimental

2.1 Experimental Procedures and Characterization

All manipulations in this research were mostly dealt with air sensitive materials and were mainly small-scale reactions in oven dried 20 mL vials, and they were carried out under an inert atmosphere of dry nitrogen using either standard Schlenk techniques or in a glove box unless otherwise required. Glassware was dried for a minimum of four hours prior to use in a 150 °C oven. Alumina and molecular sieves were pre-dried in an oven at 150 °C for one day prior to use. Celite and silica gel was dried by storing in a 150 °C oven for a minimum of three days prior to use. NMR solvents as well as other reagents or starting materials were purchased from specific suppliers or synthesized and stored over molecular sieves, when necessary, for a minimum of one day prior to use. NMR spectroscopy was recorded at 298 K on a 300 MHz spectrometer (Bruker) unless otherwise indicated and chemical shifts are reported in ppm. Coupling constants are reported in Hz as absolute values. Melting point was recorded on an Electrothermal MEL-Temp 3.0 using glass capillaries. Elemental analysis was performed by the Centre for Environmental Analysis and Remediation (CEAR) facility at Saint Mary's University using a Perkin Elmer 2400 II series Elemental Analyser. Deionised water was used in synthetic procedures unless otherwise indicated. Reactants such as 2,4,6-triisopropylbromide were purchased from suppliers and were used to synthesize the starting material Biphenyl-I in our laboratory. Bis(cyclopentadienyl)cobalt(III) hexafluorophosphate [Cp_2Co][PF_6] used for making the Co(I) compound (Scheme 2.3.3) was also synthesized in our laboratory following the optimization of an already known synthetic method of the latter.[29]

2.2 X-ray crystallography

Crystals were prepared for mounting by suspending them in paratone-N oil on a microscope slide under inert conditions. Crystals were attached to the tip of an appropriately sized MiTeGen loop with paratone-N oil and cooled to 125 K.[5] Measurements were made on a Bruker APEX2 CCD equipped diffractometer (30 mA, 50 mV) using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 125 K.[5] The initial orientation and unit cell were indexed[30] using a least-squares analysis of a random set of reflections collected from three series of 0.5° wide scans, 10 seconds per frame and 12 frames per series that were well distributed in reciprocal space.[5] For data collection, four ω-scan frame series were collected with 0.5° wide scans and 366 frames per series at varying φ angles ($\varphi = 0°, 90°, 180°, 270°$). The frame length was adjusted between 10 s and 60 s to provide an expected resolution limit below 0.8 Å.[5] The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT software,[31] which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarization effects. Data processing and a multi-scan absorption correction was applied using APEX3 software package.[31] Structures were solved using direct[31] or intrinsic methods[32] and all non-hydrogen atoms were refined anisotropically using the ShelXLE[33] graphical user interface and SHELXL[34]. Hydrogen atoms were included at geometrically idealized positions and were fixed (Ar-H, C-H, CH_2) or, in the case of methyl[5] groups, the dihedral angle of the idealized tetrahedral CH_3 fragment was allowed to refine and coupled with isotropic temperature factors. Figures were made using ORTEP-3 for Windows.[35]
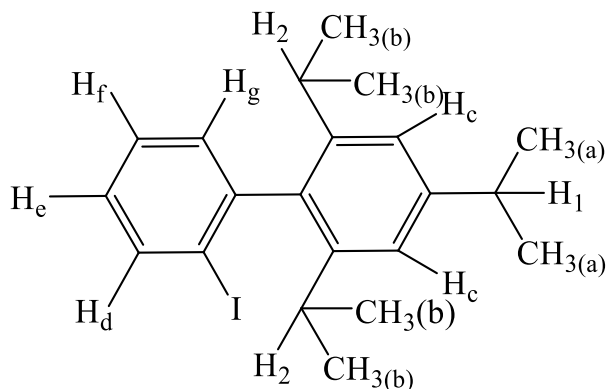
2.3.1 Synthesis of Biphenyl-I (1-Iodo-2-(2',4',6'-i-Pr$_3$C$_6$H$_2$)C$_6$H$_4$)
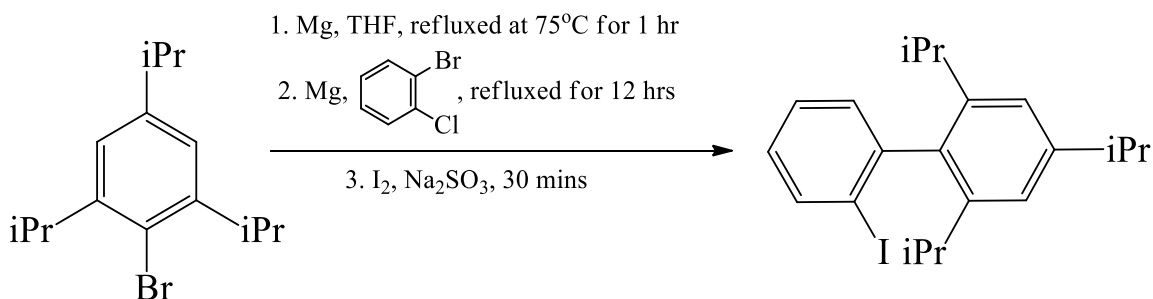
Following a similar procedure as previously reported in the literature[36], 1-Iodo-2-(2',4',6'-i-Pr$_3$C$_6$H$_2$)C$_6$H$_4$ (Biphenyl-I) was synthesized. Magnesium powder (10.72 g, 441 mmol) was placed in a 500 mL Schlenk flask in the oven (120 °C) overnight. The flask was then put under N$_2$ and it was sealed with a septum and 300 mL of dry THF was added via a syringe. A few crystals of iodine were added, a refluxed condenser was attached, and the mixture was heated to 75°C until the color of the solution changed from pale yellow to colorless. 2,4,6-triisopropylbromide (50.00 g, 177 mmol) was slowly added and the mixture was refluxed overnight. The next day, ortho-bromochlorobenzene (20.6.4 mL, 177 mmol) was added slowly and refluxing was continued for 12 h. Finally, the flask was cooled to 0 °C and iodine (67.20 g, 264.8 mmol) was added, and the solution was stirred at room temperature for 30 mins. Excess I$_2$ was quenched through addition of a saturated solution of Na$_2$SO$_3$ and the product was extracted with 50 mL of diethyl ether four times. The ether layer was dried with MgSO$_4$ and the mixture was filtered. The diethyl ether was removed from the filtrate *in vacuo* and the solid product was washed with hexane and dried on a frit under a vacuum to yield a pale yellow solid.

Yield: 50.66 g, 85% yield

¹H NMR (CDCl₃): δ 7.97 (dd, $^3J_{HH}$ = 9.00 Hz, $^4J_{HH}$ = 1.08 Hz, 1H, H_d), 7.40 (td, $^3J_{HH}$ = 7.47 Hz, $^4J_{HH}$ = 1.17 Hz, 1H, H_e), 7.22 (dd, $^3J_{HH}$ = 7.53 Hz, $^4J_{HH}$ = 1.68 Hz, 1H, H_g), 7.07 (s, 2H, H_c), 7.04 (td, $^3J_{HH}$ = 7.59 Hz, $^4J_{HH}$ = 1.68 Hz, 1H, H_f), 2.95 (sept, $^3J_{HH}$ = 6.90 Hz, 1H, H_1), 2.39 (sept, $^3J_{HH}$ = 6.90 Hz, 2H, H_2), 1.31 (d, $^3J_{HH}$ = 6.90 Hz, 6H, H_a), 1.21 ppm (d, $^3J_{HH}$ = 6.90 Hz, 6H, H_b), 1.01 ppm (d, $^3J_{HH}$ = 6.90 Hz, 6H, H_b).

¹³C{¹H} NMR (CDCl₃): δ 148.6, 145.9, 145.7, 139.2, 102.4, 138.8, 130.6, 128.2, 127.7, 120.8, 34.2, 30.7 ppm

2.3.2 Synthesis of Biphenyl-Li
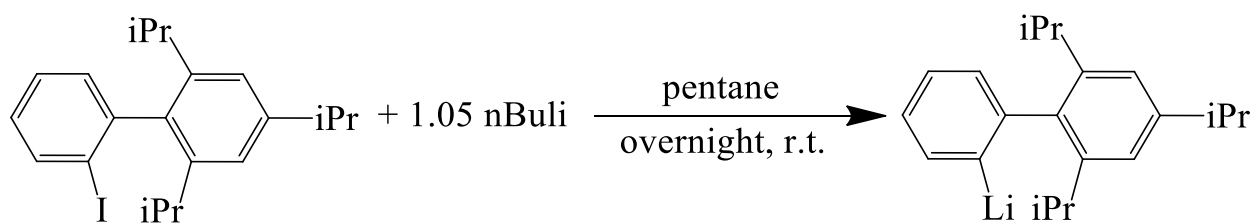
A 20 mL oven-dried Schlenk was equipped with a magnetic stir bar and 0.500 g (1.23 mmol, 1.0 eq.) of pale-yellow 1-Iodo-2-(2',4',6'-i-Pr₃C₆H₂)C₆H₄ were suspended in 10 mL of pentane to produce a pale-yellow mixture (or almost colorless). To this mixture, 0.517 mL of a pale yellow

coloured n-Butyllithium solution (2.5 M in hexanes, 2.58 mmol, 1.05 eq.) were added to produce a cloudy white coloured mixture. This mixture was left to stir overnight. The following day, the stir bar was removed, and the cloudy white coloured solids were allowed to settle at the bottom of the beaker, the colourless solvent layer was then decanted, and the resulting white solids were then washed with a minimal amount of cold pentane and dried *in vacuo* to yield a white powder.

Yield: 0.405 g, 98%

^{1}H NMR (THF-d$_8$): δ 7.39-7.44 ppm (m, 2H, Ar-H), 7.34-7.36 ppm (m, 1H, Ar-H), 7.16-7.19 ppm (m, 1H, Ar-H), 7.09 ppm (s, 2H, H$_c$), 2.95 ppm (sept, $^3J_{HH}$ = 6.90 Hz, 1H, H$_1$), 2.65 ppm (sept, $^3J_{HH}$ = 6.90 Hz, 2H, H$_2$), 1.31 ppm (d, $^3J_{HH}$ = 6.90 Hz, 6H, H$_a$), 1.10 ppm (d, $^3J_{HH}$ = 6.90 Hz, 12H, H$_b$).
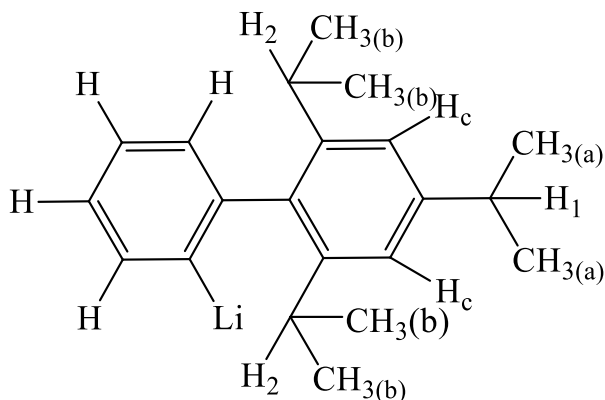
^{13}C{^{1}H} NMR (THF-d$_8$): δ 147.7, 146.2, 140.9, 137.2, 129.6, 127.7, 126.3, 120.1, 34.4, 22.2 ppm

It has to be mentioned that some ^{13}C peaks are obscured by the THF-d_8 solvent at δ 25.31 and 67.21 ppm.

2.3.3 Synthesis of BiphenylCpH(CoCp)
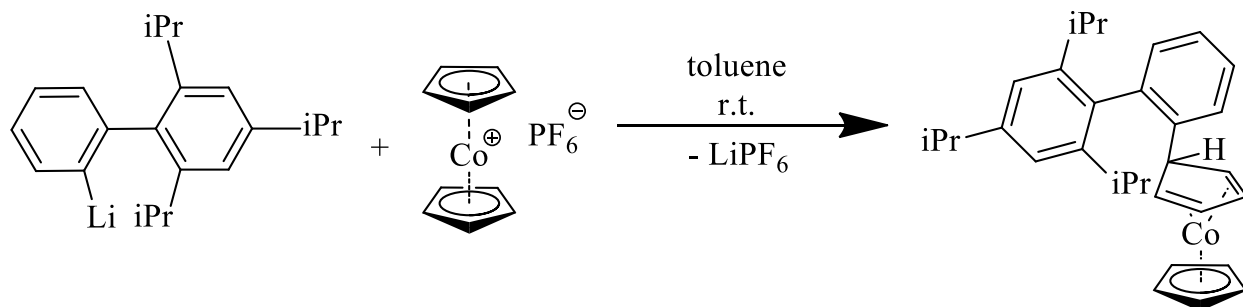
In a 20 mL oven-dried scintillation vial, 0.405 g (1.41 mmol, 1.0 eq.) of the white Biphenyl-Li powder were dissolved in 10 mL of toluene to produce a very pale yellow mixture. In a separate 20 mL Schlenk flask, 0.473 g (1.41 mmol, 1.0 eq.) of bright yellow coloured bis(cyclopentadienyl)cobalt(III) hexafluorophosphate [Cp$_2$Co][PF$_6$] was measured and was suspended in 7 mL of toluene, producing a bright yellow coloured mixture. The very pale yellow coloured Biphenyl-Li mixture was added dropwise to the bright yellow coloured [Cp$_2$Co][PF$_6$] suspension to quickly produce a dark red-orange coloured mixture. The mixture was left to stir overnight. The following day, an aliquot was removed for ^{1}H NMR spectroscopy, which indicated that the reaction was complete. The reddish-orange coloured mixture was filtered through Celite to yield a cherry red coloured solution. Removal of the solvent *in vacuo* yielded the crude product as a dark red coloured solid. Crystallization was achieved by two different methods. The dark red coloured solid was dissolved in toluene and filtered again over Celite and the filtrate was allowed to evaporate, in the glovebox, in order to crystallize the solids. Secondly, the red colored solid was dissolved in pentane and stored in a freezer at -35 °C overnight. The red coloured liquid layer was decanted from the red coloured crystals, and the crystals were washed three times with ca. 1 mL portions of cold pentane.

Yield: 0.535 g, 89%

EA: Calc for $C_{31}H_{37}Co$, 0.33 C_7H_8: C: 80.17 %, H: 8.02 %, N: 0.00 %. Found: C: 80.23 %, H: 7.97 %, N: 0.03 %.

m.p. (°C): 112.4 ºC – 114.0 ºC

¹H NMR (CDCl₃): δ 6.86-7.26 ppm (m, 6H, Ar-H), 5.26 ppm (s, 2H, BiphenylCp-H), 4.61 ppm (s, 5H, H_{Cp}), 3.57 ppm (s, 1H, BiphenylCp-H), 2.65 ppm (s, 2H, BiphenylCp-H), 6.88 ppm (s, 2H, H_c), 3.00 ppm (sept, $^3J_{HH}$ = 6.90 Hz, 1H, H_1), 2.32 (sept, $^3J_{HH}$ = 6.90 Hz, 2H, H_2), 1.38 (d, $^3J_{HH}$ = 6.90 Hz, 6H, H_a), 1.19 ppm (d, $^3J_{HH}$ = 6.90 Hz, 6H, H_b), 0.98 ppm (d, $^3J_{HH}$ = 6.90 Hz, 6H, H_b).
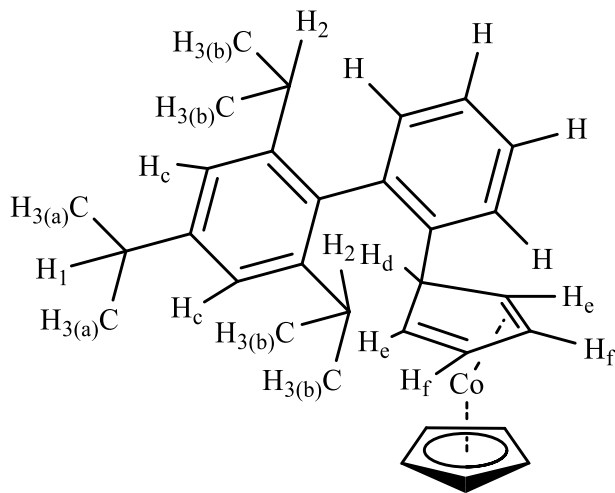
¹³C{¹H} NMR (CDCl₃): δ 147.9, 146.3, 143.4, 139.5, 138.4,138.1, 129.6, 129.4, 128.5, 128.1, 127.5, 125.0, 121.4, 56.7, 48.3, 37.9, 30.4, 30.3, 25.1, 24.2, 23.2 ppm

The BiphenylCo(I) intermediate is structurally different in solution, as indicated by the methylene resonance at 3.57 ppm in the ^{1}H NMR spectrum. It was hypothesized that there could potentially be three different isomers showing the three different positions of the aryl group and the hydrogen(s) on the cyclopentadiene fragment.

2.3.4(I) Attempted synthesis of BiphenylCpH
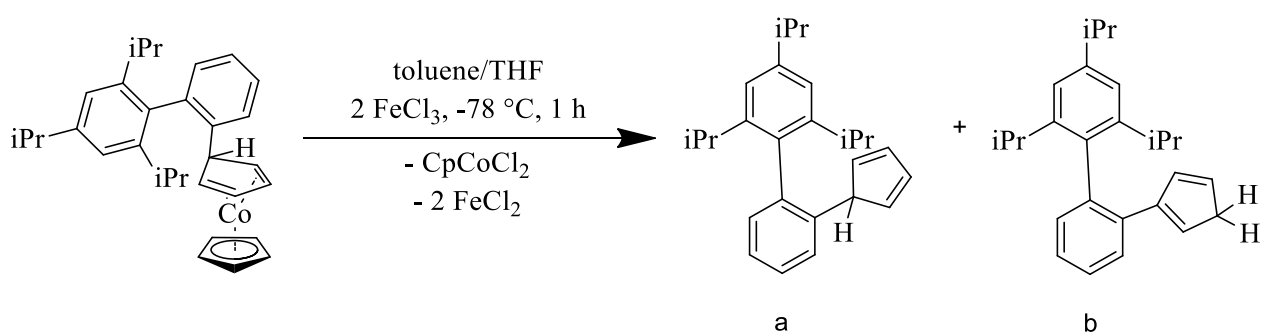
The BiphenylCo(I) intermediate (0.535 g) obtained from the previous reaction was dissolved in 20 mL toluene and the mixture was transferred to an oven-dried 50 mL Schlenk flask. In a 20 mL scintillation vial, 0.370 g (2.28 mmol, 2.00 eq.) of dark green coloured FeCl$_3$ was measured out, and carefully dissolved in 10 mL of THF to produce a green colored solution. The green coloured solution of FeCl$_3$ was transferred to the 10 mL syringe and the tip of the needle was sealed with a rubber septum. The Schlenk flask and syringe were then removed from the glove box and the Schleck flask was connected to a Schlenk line before cooling the red coloured solution of the BiphenylCo(I) intermediate to ca. -78 °C using a liquid nitrogen-acetone bath. Once cold, the green coloured solution of FeCl$_3$ was added dropwise to immediately produce a bluish-green coloured mixture. The mixture was left to stir at between -65 and -75 °C for one hour and the temperature of the cold bath was monitored using a thermocouple. While cold, the blue green coloured mixture was transferred via cannula transfer to a -35 °C column containing ca. 150 mL of silica gel and

toluene and eluted through the column using toluene in air. The initial bright yellow coloured fraction was collected into a 250 mL round bottom flask (ca. 150 mL of toluene was used to isolate the product) while the slower eluting blue and red coloured fractions were discarded. The solvent was removed by the rotary evaporator to yield a navy blue coloured paste. This reaction therefore did not produce the desired product. It was determined that the resulting product, which was paste-like in texture and oily looking navy blue in color, contained a lot of paramagnetic impurities in it as showed by the ^{1}H NMR spectrum of the product. This reaction was extremely temperature sensitive and had to be carried out at approximately -78 °C at all times and eluted at the same temperature in air. The -35 °C column was too high in temperature for this reaction and therefore this resulted into the decomposition of the product.

2.3.4(II) Attempted synthesis of BiphenylCpH
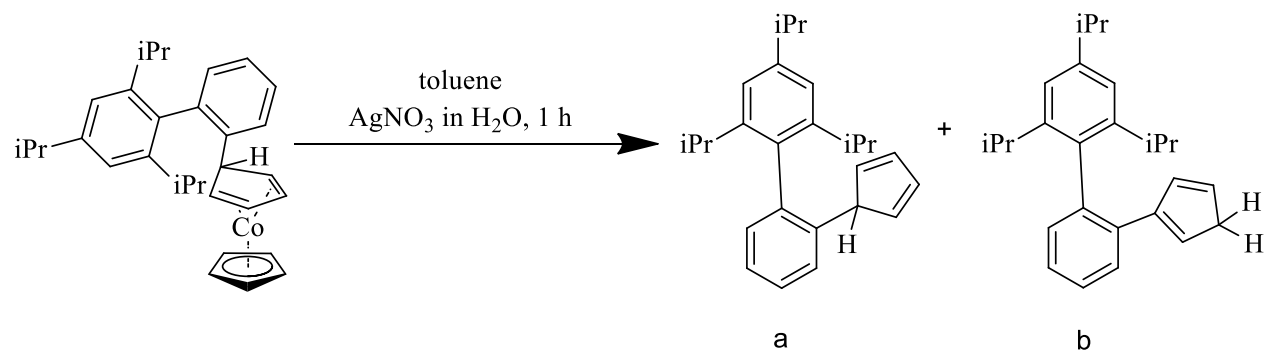
In a 50 mL glass round-bottom flask was added 0.200 g of BiphenylCo(I) intermediate and this was dissolved in about 10 mL of Toluene. A dark-red solution was obtained. 0.074 g of silver nitrate (AgNO₃) was dissolved in about 10 mL of water and this formed a colourless solution. This solution was then added dropwise to the BiphenylCo(I) solution and the mixture was allowed to stir at room temperature for approx. 1 hour. As the reaction proceeded, the dark red colour turned to a reddish-brown one with dark-blue spots that were spread out through the entire solution. After

1 h, the reaction mixture was filtered through a plug of Celite which was then washed twice with 2-5 mL of more pentane in order to get wash off any product that may had been left behind on the Celite. The resulting solution was then put into a separatory funnel. Two different layers were obtained. The bottom layer (aqueous layer) was light pink in colour and the top layer (organic layer) was a reddish-orange colour. The organic layer was collected, and the aqueous layer was extracted twice more with pentane. The combined organic fractions were dried over $MgSO_4$ for around 10 mins and then the suspension was gravity filtered. The resulting solution was then dried on a rotary evaporator which yield reddish-orange paste-like product. This reaction therefore did not produce the desired product. ^{1}H NMR spectroscopy showed that the isolated material was mostly the unreacted BiphenylCo(I) intermediate as showed by the peaks at 3.94, 4.43 and 5.14 ppm integrating to 2, 5, and 1 protons respectively.
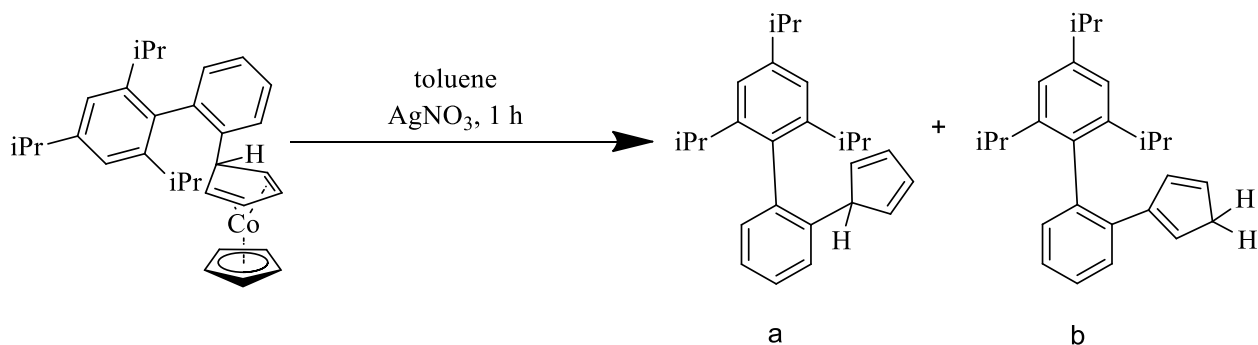
2.3.4(III) Attempted synthesis of BiphenylCpH

In a 50 mL glass round-bottom flask was added 0.200 g of BiphenylCo(I) intermediate and this was dissolved in about 10 mL of toluene. A dark-red solution was obtained. 0.074 g of solid silver nitrate ($AgNO_3$) was then added to the BiphenylCo(I) intermediate solution and the mixture was allowed to stir at room temperature for approx. 1 hour. As the reaction proceeded, the dark red colour turned to a reddish-brown one After 1 h, the reaction mixture was filtered through a plug

of Celite which was then washed twice with 2-5 mL of toluene in order to wash off any product that may had been left behind on the Celite. The resulting solution was then left to evaporate to yield reddish-brown paste-like product. This reaction therefore did not produce the desired product. ^{1}H NMR spectroscopy showed that the isolated material was mostly the unreacted BiphenylCo(I) intermediate as showed by the peaks which were still prominent at around 3.91 ppm, 4.43 ppm and 5.14 ppm integrating to 2, 5 and 1 protons respectively.

2.3.4(IV) Synthesis of BiphenylCpH
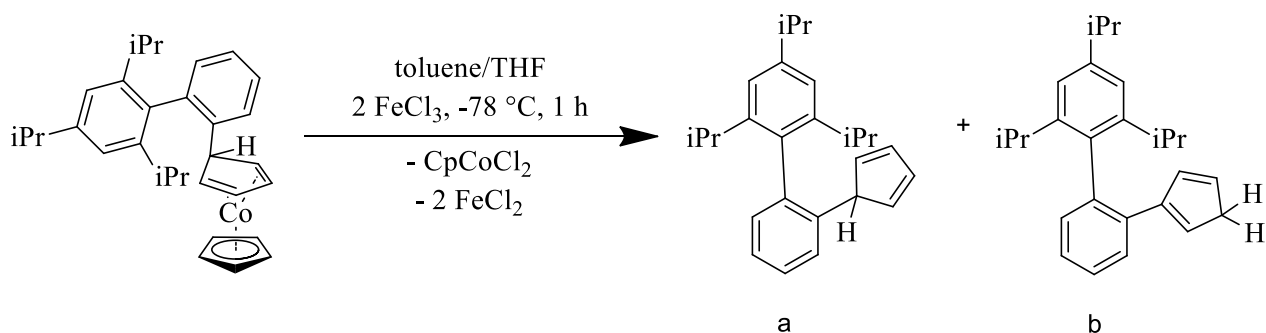
Following the similar procedure as in Reaction 2.3.3, BiphenylCo(I) intermediate was synthesized from Biphenyl-Li and [Cp$_2$Co][PF$_6$]. The resulting BiphenylCo(I) intermediate (0.527 g) obtained from this reaction was dissolved in 20 mL toluene and the mixture was transferred to an oven-dried 50 mL Schlenk flask. In a 20 mL scintillation vial, 0.365 g (2.25 mmol, 2.00 eq.) of dark green coloured FeCl$_3$ was measured out, and carefully dissolved in 10 mL of THF to produce a green colored solution. The green coloured solution of FeCl$_3$ was transferred to the 10 mL syringe and the tip of the needle was sealed with a rubber septum. The Schlenk flask and syringe were then removed from the glove box and the Schleck flask was connected to a Schlenk line before cooling the red coloured solution of the BiphenylCo(I) intermediate to ca. -78 °C using an acetone-dry ice bath. Once cold, the green coloured solution of FeCl$_3$ was added dropwise to immediately produce

a bluish-green coloured mixture. The mixture was left to stir at between -70 and -78 °C for one hour and the temperature of the cold bath was monitored using a thermocouple. While cold, the blue green coloured mixture was transferred via cannula transfer to a column setup as shown by Figure 2.3.4(IV) containing ca. 100 mL of silica gel and toluene and eluted through the column using toluene in air. The initial light yellowish-beige coloured fraction was collected into a 250 mL round bottom flask (ca. 150 mL of toluene was used to isolate the product) while the slower eluting blue and red coloured fractions were discarded. Yellowish-beige solids were isolated upon removal of the solvent on the rotary evaporator.

Top of column containing the reaction mixture.

Container filled with dry ice.

Black rubber support which the container sits on.

Column filled with dried silica gel in toluene.

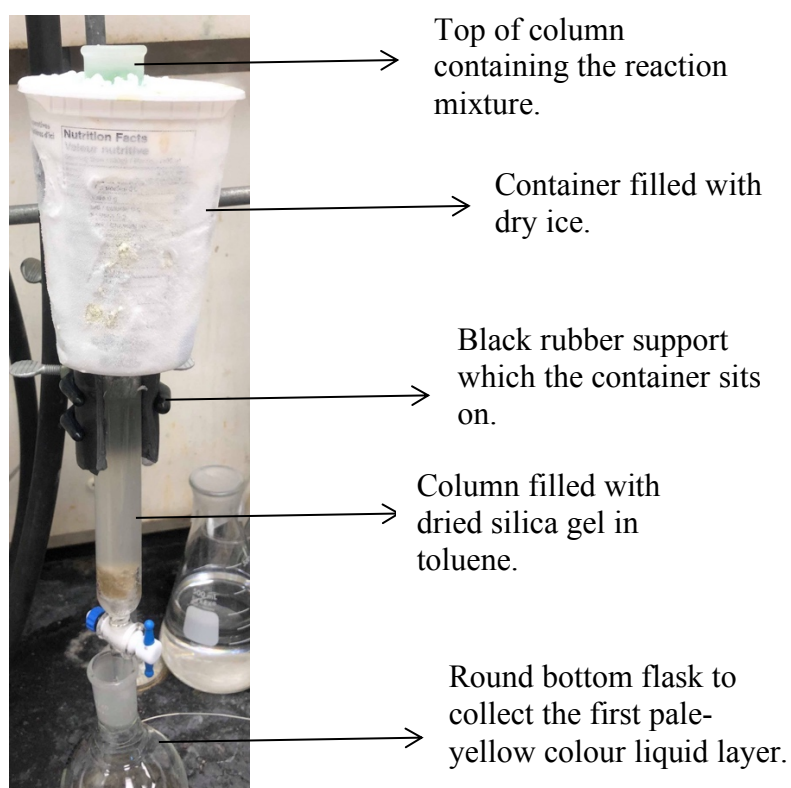Round bottom flask to collect the first pale-yellow colour liquid layer.

Figure 2.3.4(IV). Cold column chromatography setup for the isolation of the BiphenylCpH.

Yield: 0.1467 g, 24%

The ^{1}H NMR spectrum was too complex to be fully assigned and interpreted without other NMR experiments but it served as proof that BiphenylCpH was successfully synthesized as confirmed by the peaks at 6.02 - 7.10 ppm. An attempt at purifying and removing all of the residual solvent in the BiphenylCpH solids was made by dissolving the solids in a minimum amount of benzene. The resulting solution was then heated on a rotary evaporator at 60 °C for half an hour. Subsequent ^{1}H NMR spectroscopy of the resulting product as showed by Figure A9 in Appendix A, was very complex and quite different from the initial spectrum. It was deduced that this could be an indication of the potential [4 + 2] Diels-Alder dimerization (cycloaddition) product that could have potentially been formed after heating the BiphenylCpH at 60 °C.

2.3.5 Attempted synthesis of K(BiphenylCp)
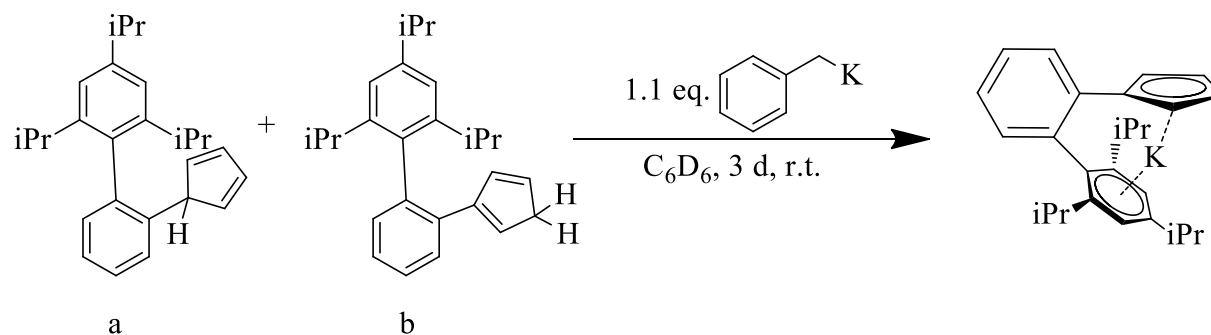
In a 20 mL oven-dried vial was added 0.025 g of BiphenylCpH and this was dissolved in about 1 mL of deuterated benzene. A pale-yellow solution was obtained. The BiphenylCpH solution was then added to the 0.010 g of benzyl potassium solids (dark orange) weighed out in a separate 20 mL oven-dried vial and the mixture was allowed to stir at room temperature in the glovebox for approx. 3 days. An initial dark reddish-orange solution was obtained. As the reaction proceeded,

the dark reddish-orange colour turned into a dark brown colour. The resulting solution was filtered through kimwipe paper in a pipette and the ^{1}H NMR spectrum was obtained which was a very complex looking one. This reaction therefore did not produce the desired product. ^{1}H NMR spectroscopy showed that the isolated material was mostly the unreacted BiphenylCpH.
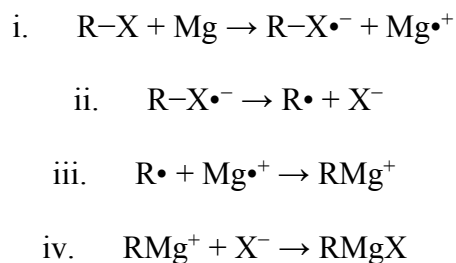
3.0 Results and Discussion

3.1 Synthesis of Biphenyl-I

Grignard reagents are formed by the reaction of magnesium metal with alkyl, alkenyl or aryl halides.[37,38] These alkyl, alkenyl or aryl magnesium halides are called Grignard Reagents after the French chemist, Victor Grignard, who discovered them and received the Nobel Prize in 1912 for this work.[37] Grignard Reagents are very good nucleophiles and they react with electrophiles such as carbonyl compounds and epoxides.[37] They are also very strong bases and react with acidic hydrogens.[37] As stated earlier, Grignard reagents are made through the addition of magnesium metal to alkyl, alkenyl or aryl halides. The halide can be Cl, Br, or I. In the Grignard reaction as shown by the reaction Scheme 3.1.1, the magnesium metal inserts itself between the carbon and the halide forming the Grignard reagent. THF is a most common solvent used for the preparation of Grignard reagents.[37]
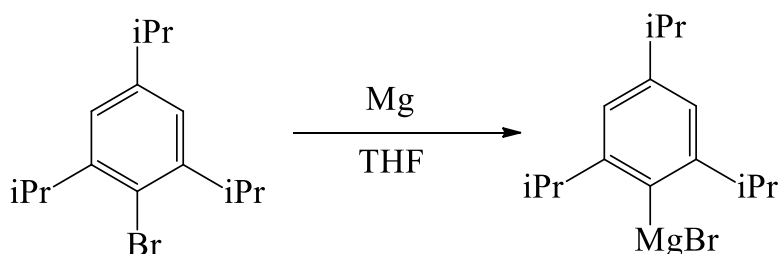

Scheme 3.1.1. Grignard reaction where the magnesium metal inserts between the carbon and the halide forming the Grignard reagent**.**

The mechanism of formation of a Grignard reagent involves radical intermediates.[39] Grignard formation however, is a non-chain radical mechanism. The first step, as shown by Scheme 3.1.2, involves the transfer of one electron from Mg, which has two electrons in its valence shell to the carbon-halogen bond and this is the rate-determining step.[38] This results into Mg^{+1}, which is a radical and this radical then couples with the alkyl radical which was also formed as shown by Scheme 3.1.2.[38,39] THF is an especially good solvent for the formation of Grignard reagents because it is aprotic.[37] Water or alcohols would protonate and thus destroy the Grignard reagent as the Grignard carbon is highly nucleophilic resulting into the formation of a hydrocarbon.[38]

i. $R-X + Mg \rightarrow R-X\bullet^- + Mg\bullet^+$

ii. $R-X\bullet^- \rightarrow R\bullet + X^-$

iii. $R\bullet + Mg\bullet^+ \rightarrow RMg^+$

iv. $RMg^+ + X^- \rightarrow RMgX$

Scheme 3.1.2. Radical mechanism for the formation of Grignard Reagents[38,39].

A one-pot reaction is carried out for the synthesis of the starting material Biphenyl-I, and this reaction starts with the formation of a Grignard reagent as shown by Scheme 3.1.1. The next step involved the aryne (benzyne) formation. This process is clearly illustrated by Scheme 3.1.3. below. The loss of MgBrCl from the benzene ring results into the benzyne intermediate.
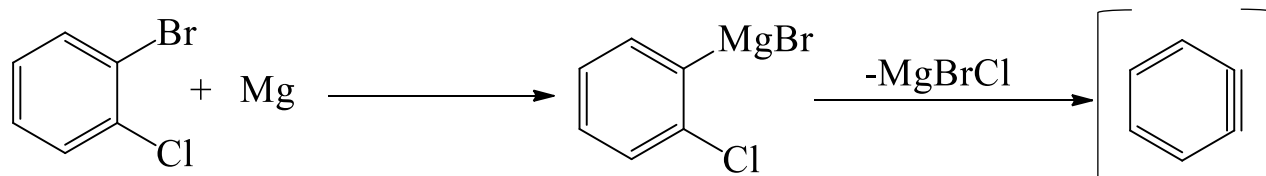
Scheme 3.1.3. Benzyne formation through the loss of MgBrCl.

The formation of aryl-aryl bonds is an important concept in organic as well as in inorganic synthesis, and a lot of methods are available for this formation.[40] The Ullmann, the Pschorr and Gomberg Bachmann-Hey reactions, and the benzidine rearrangement are some of the venerable methods that are used, often with improved modifications.[40] Newer methods involve mainly oxidative coupling of arenes, aryl halides, phenols, and other aromatic derivatives, using as reagents transition metals, chemical oxidants, or electrochemical methods.[40] Photochemical aryl-aryl bond formation is also widely used.[40,41] Another method for aryl-aryl bond formation is the nucleophilic addition of aryllithiums or other aryl organometallics such as Grignard reagents to arynes and this was discovered by Wittig, Huisgen, and co-workers.[40,42] It was a key reaction in the early recognition of benzyne as a reactive intermediate.[40,42] The yield of biaryls by this route can sometimes be quite high, as in the following example below.[42]


E = H, I, Br
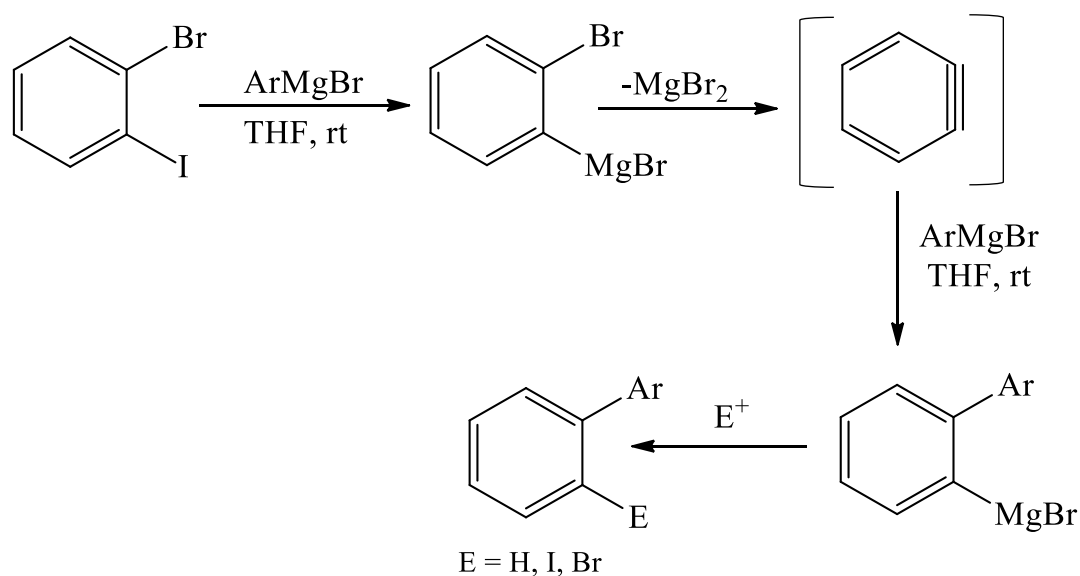
Scheme 3.1.4. Addition of aryl Grignard reagents to arynes.[42]

The addition of aryl Grignard reagents to arynes as a controlled method for terphenyl synthesis was investigated by Hart and co-workers.[40] The first step consisted of a halogen–magnesium

exchange of an o-bromo-iodoarene derivative with one equivalent of an aryl Grignard reagent, affording the 2-bromoaryl Grignard (Scheme 3.1.4).[42] This organometallic intermediate can easily eliminate $MgBr_2$ to give the reactive aryne, which undergoes addition with a second equivalent of aryl Grignard to give the novel 2-biaryl Grignard.[42] The Grignard reagent is therefore used in excess. Quenching with iodine gave the dissymmetrical biaryl.[42]

This same idea and concept laid behind the synthesis of the Biphenyl-I during the course of this project. Following the formation of the benzyne intermediate as described by Scheme 3.1.3, this benzyne owing to the fact that it is a very unstable molecule and thus extremely reactive, will react instantaneously with an equivalent of the Grignard reagent. This is so because this whole reaction is carried in one-pot as mentioned earlier. There is always a continuous availability of the Grignard reagent to react instantly with any benzyne intermediates being formed as illustrated by Scheme 3.1.5.
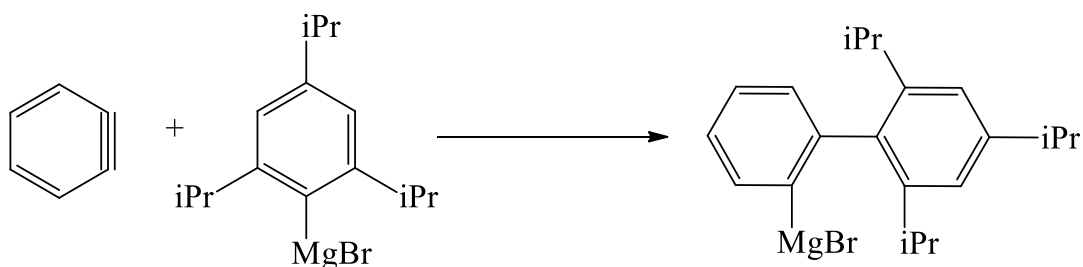
Scheme 3.1.5. The benzyne intermediate reacting with one equivalent of the Grignard reagent forming the aryl-aryl bond in this one-pot reaction.

Subsequently, reaction with iodine and then quenching with Na_2SO_3 gives the dissymmetrical biaryl as in the previously stated example as showed by Scheme 3.1.4. Scheme 3.1.6. below shows the I_2 which acts as an electrophile, to give the desired product, Biphenyl-I in an 85% yield.
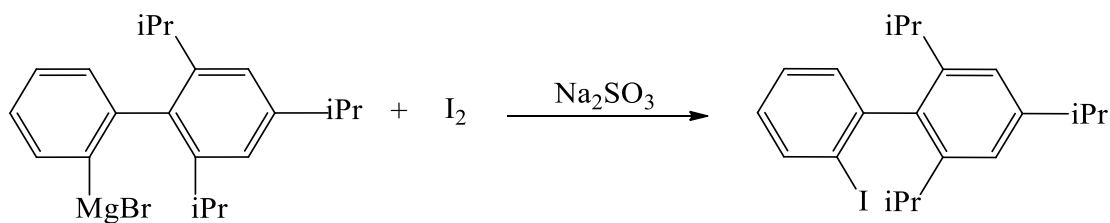
Scheme 3.1.6. Reacting with iodine and then quenching with Na_2SO_3 which gives Biphenyl-I.

Carbon-carbon bond formation reactions are some of the most important processes in chemistry that provide key steps in the building of more complex molecules from simple precursors.[43] Over the last several decades, reactions for carbon-carbon bond formation between molecules with saturated sp^3 C-atoms have been developed.[43] However, there were no simple and general methods for carbon-carbon formation between unsaturated groups such as vinyl, aryl, and alkynyl moieties, until the discovery and development of metal mediated cross-coupling reactions in the 1970s. Coupling reactions are useful for generating carbon-carbon bonds.[43] Palladium-catalyzed coupling reactions comprise a family of cross-coupling reactions that employ palladium complexes as catalysts.[44] It has applications in homogeneous catalysis. In 2010, the Nobel Prize in Chemistry was awarded to Richard F. Heck, Eiichi Negishi and Akira Suzuki for their work on palladium-catalyzed cross couplings in organic synthesis.[44]

The characterization of this compound was done by obtaining the ^1H, ^{13}C, COSY and Dept-Q spectroscopy data of the pure product sample. This compound is already known in the literature and all the peaks and coupling constants values were matching to those in the literature. The most prominent and relevant peaks were from the –CH_3 of the isopropyl groups and they were at 1.31 ppm, 1.21 ppm, and 1.01 ppm each integrating to 6 protons. The literature values for these peaks were 1.32 ppm, 1.23 ppm and 1.02 ppm respectively. The methine peaks were at 2.95 ppm which

integrated to 1 proton and 2.39 ppm which integrated to 2 protons and the literature values for these methine were at 2.97 ppm and 2.34 ppm each integrating to 1 proton and 2 protons respectively. The peaks in the aromatic region as well corresponded to those as reported in the literature and there were no other peaks present in the spectrum. Therefore, the Biphenyl-I synthesized in this project was deduced to be pure.
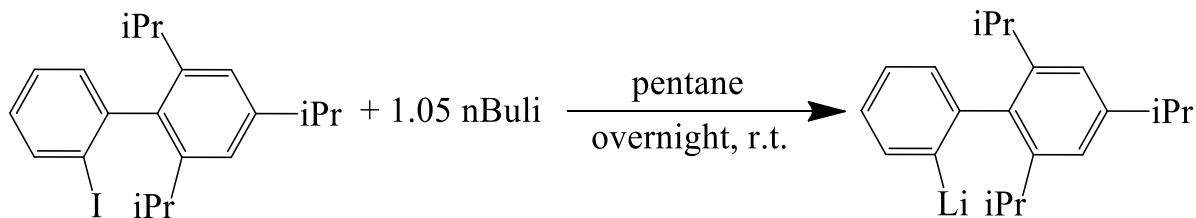
3.2 Synthesis of Biphenyl-Li

Organolithium reagents are organometallic compounds that contain carbon-lithium bonds. They are important reagents in organic synthesis, and they are used to transfer the organic group or the lithium atom to the substrates in synthetic steps, through nucleophilic addition or simple deprotonation.[45] Organolithium reagents have various use in industries for anionic polymerization and they have also been applied in asymmetric synthesis in the pharmaceutical industry.[46] The C-Li bond is highly ionic because of the large difference in electronegativity between the carbon atom and the lithium atom and this is also why organolithium reagents are good nucleophiles and strong bases.[46]

The synthesis of Biphenyl-Li consisted of reacting the previously synthesized Biphenyl-I with n-Butyllithium. Lithium-halogen exchange is a metathesis reaction between an organohalide and organolithium species discovered by Gilman and Wittig in the late 1930s.[47] n-Butyllithium is known to react with a few organic bromides and iodides by undergoing an ion exchange reaction to form the corresponding organolithium derivative as shown by the equation below:

$$C_4H_9Li + RX \rightarrow C_4H_9X + RLi \ (X = Br, I)$$
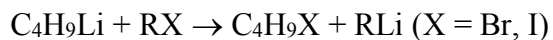
Scheme 3.2.1. Reaction of n-Butyllithium with an organic halide RX (X = Br, I) to form the corresponding organolithium derivative.

This reaction is useful for preparation of several types of RLi compounds such as aryllithium and some vinyllithium reagents. In the case of this research work, Biphenyl-I was reacted with n-Butyllithium to yield the corresponding Biphenyl-Li product as shown by Scheme 2.3.2. This reaction was carried out in pentane as Biphenyl-I is very soluble in it. However, the presence of n-Butyl iodide in the reaction mixture significantly decreased the utility of this method, as the n-Butyl iodide can react with the RLi reagent formed, thus resulting in low yields. It should be also mentioned that this particular reaction is very stoichiometrically selective. For the first few attempts at this reaction, the wrong volume of n-Butyllithium was added to the Biphenyl-I in pentane reaction mixture and the ^{1}H NMR spectroscopy for the product was very confusing. There was a lot of peaks which resulted from the unreacted Biphenyl-I at around 1.0 - 2.5 ppm in the ^{1}H NMR spectrum which was in deuterated benzene. This was an indication that the ratio of Biphenyl-I to n-Butyllithium was not correct, and so various reactions with continuously increasing volumes of n-Butyllithium used were carried out, but the results were still the same. However, a quick check at the stoichiometric calculations confirmed that the wrong stoichiometry was being used. The correct volume of n-Butyllithium was determined and the reaction was carried out again which yielded the desired product as white solids. ^{1}H NMR spectroscopy of the product confirmed the almost full conversion of Biphenyl-I to Biphenyl-Li.

Scheme 3.2.2. Synthesis of Biphenyl-Li.

The rate of lithium halogen exchange is extremely fast. It is usually faster than nucleophilic addition.[48] Lithium-halogen exchange is very useful in preparing new organolithium reagents. Exchange rates usually follow the trend I > Br > Cl.[48] Alkyl- and arylfluoride are generally unreactive toward organolithium reagents.[48] Lithium halogen exchange is kinetically controlled, and the rate of exchange is primarily influenced by the stabilities of the carbanion intermediates ($sp > sp^2 > sp^3$) of the organolithium reagents.[49,50] For example, the more basic tertiary organolithium reagents (usually n-butyllithium, sec-butyllithium or tert-butyllithium) are the most reactive, and will react with primary alkyl, vinyl or aryl halide (usually bromide or iodide) to form the more stable organolithium species.[50] Therefore, lithium halogen exchange is most frequently used to prepare vinyl-, aryl- and primary alkyllithium reagents.

The characterization of this compound was done by obtaining the ^1H, ^{13}C and ^1H-^1H COSY spectroscopy of the pure product sample. The most prominent and relevant peaks were from the – CH_3 of the isopropyl groups and they were at 1.31 ppm and 1.10 ppm each integrating to 6 and 12 protons respectively having a coupling constant (J) of 6.90 Hz, the same as the Biphenyl-I. The methine peaks were at 2.95 ppm and 2.65 ppm each integrating to 1 proton and 2 protons respectively. The peaks in the aromatic region could not be identified and assigned as they were

too complex and very broad. They were reported as being peaks from the Ar-H as multiplets and intergrated 2, 1 and 2 protons respectively. Attempts at assigning the corresponding peaks to each proton in the aromatic region can be done by obtaining the NOESY, Dept-Q, Dept-45 and Dept-135 NMR spectroscopic data of the sample. From the ^{1}H NMR spectroscopic data that was obtained, it was deduced that the Biphenyl-Li synthesized as a colourless powder in this project, was pure and good for further use.

3.3 Synthesis of BiphenylCo(I) intermediate with Cobaltocenium Salts

In metallocene chemistry, ferrocene and its derivatives represent by far the most important class of compounds, due to their advantageous chemical and physical properties such as air stability, reversible redox chemistry, well-developed synthetic chemistry, useful material properties in homogeneous catalysis, amongst others. In comparison, much less is known of the isoelectronic cobaltocenium salts, although they have some analogous advantageous properties such as high chemical stability and reversible redox chemistry.[51] In contrast to neutral ferrocenes with their 18 valence electrons, the isoelectronic cobaltocenium salts with 18 valence electrons are positively charged and therefore water-soluble which makes them a potentially useful feature for applications in green chemistry.[51] On the other hand, the cationic cobaltocenium core makes functionalized cobaltocenium salts much more difficult to synthesize and they are very few in number in comparison to ferrocene derivatives.[51] Historically, the parent cobaltocene[52] was prepared shortly after the discovery of ferrocene and functionalized cobaltocenium salts have been known since 1970 from the pioneering work of Sheats and Rausch.[53]

Nucleophilic substitution reactions on unsaturated hydrocarbons such as ethylene, butadiene, benzene produce the corresponding exo-addition products when bound as ligands to cationic transition metal complexes.[12,13,14] Cyclopentadienyl ligands also take part in nucleophilic substitution reactions and a commonly observed reaction in cobalt reaction chemistry is the nucleophilic substitutions on the cyclopentadienyl ligands of cobaltocenium cations, $[Cp_2Co]^+$ (Figure 3.3.1).[14]
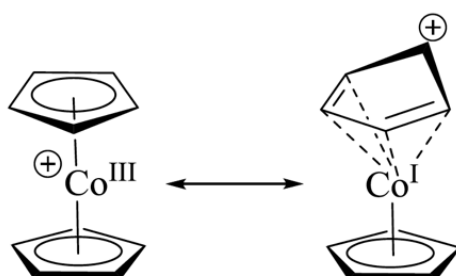

Figure 3.3.1. Electromeric structures of cyclopentadienium Cobalt(III) - left and cyclopentadienyl Cobalt(I) - right .[5,14]

Nucleophilic substitution reactions to cobaltocenium cations were first reported in 1961[54], and can be understood when the electromeric structures of the cobaltocenium cation are considered (Figure 3.3.1). The cobaltocenium cation is considered as a Co^{III} complex substituted by two anionic cyclopentadienyl ligands, or as a $CpCo^I$ stabilised cyclopentadienyl cation, $(C_5H_5)^+$.[5,14] With the $CpCo^I$ cation, no redox chemistry occurs at the cobalt centre and therefore nucleophilic substitution can occur at the cyclopentadienyl ring due to the highly electrophilic character and anti-aromaticity of the cyclopentadienyl cation.[5] Another description is that a nucleophilic attack occurs at one of the η^5-bonded Cp rings, converting the ligand to an η^4 -bonded cyclopentadiene ligand while the Co(III) centre is reduced to Co(I).[5] Subsequent oxidation of the corresponding

Co[I] complex to Co[III] then liberates the substituted cyclopentadienyl derivative following purification.[5]

The reaction of the organolithium reagent Biphenyl-Li with [Cp$_2$Co][PF$_6$] yielded the corresponding air stable cobalt(I) (η^5-cyclopentadienyl)(η^4-cyclopentadiene) compound which was isolated as 85% following crystallisation from pentane (Scheme 3.3.1).[14] Toluene was chosen as the solvent for this reaction over benzene because of its lower freezing point, which is beneficial for recrystallisation, and a slightly better solubility of the starting materials.
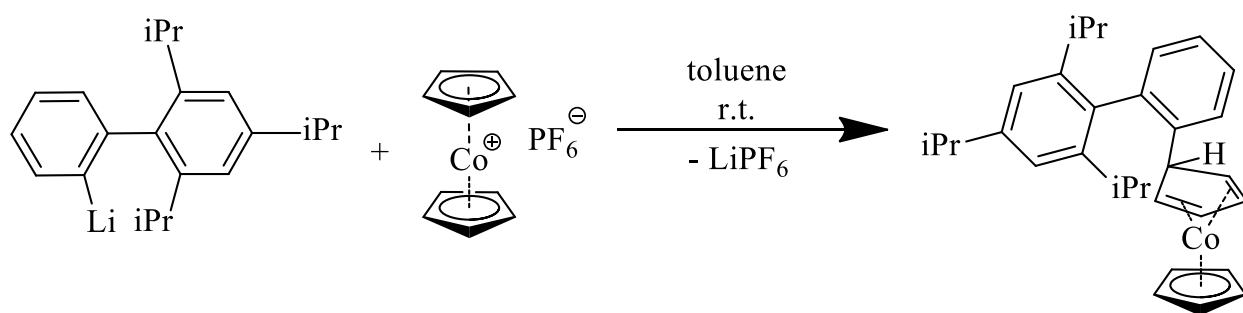
Scheme 3.3.1. Synthesis of BiphenylCo(I) intermediate.

Crystals of the cobalt(I) compound for single crystal X-ray diffraction studies were grown by evaporation of a toluene solution. The structure of the Co(I) compound was found to be similar to related structures.[1,14] The angle between the plane 1 made up by the butadienyl fragment (C7-C10) and the plane 2 (C6 C7 C10) is 34.071 (17)°. The angle between benzene ring (C11 C12 C13 C14 C15 C16) and the trip-benzene ring (C17 C18 C19 C20 C21 C22) is 82.943 (10)°. This makes the trip-aryl ring not perfectly perpendicular to the benzene ring.
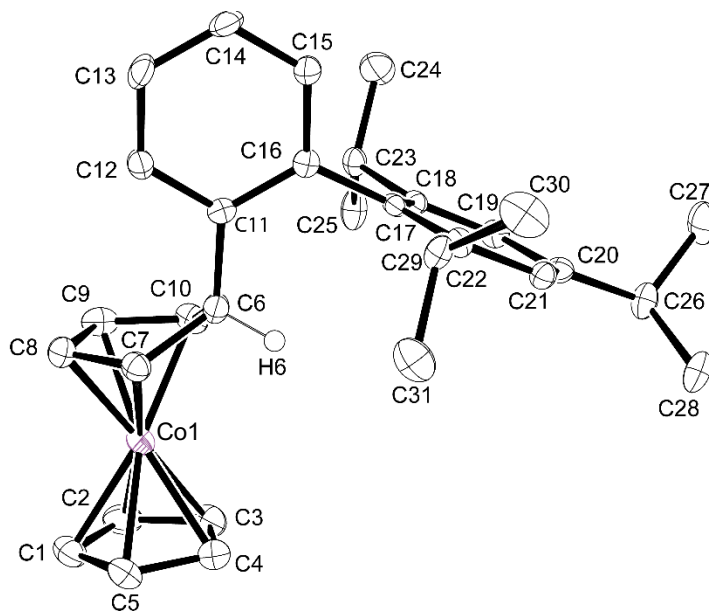
Figure 3.3.2. Molecular structure of the BiphenylCo(I) compound. Hydrogen atoms (except H6) have been removed for clarity. Selected bond lengths (Å) and angles (°) Co1-C10 2.021(3), Co1-C9 1.955(4), Co1-C8 1.970(3), Co1-C7 2.040(3).

Interestingly the molecular structure of BiphenylCo(I) compound has matching bond lengths within 3σ of each other to those as reported in the literature. One such particular compound is the Ter[Mes]Co(I) made by Veinot and Masuda.[1,5] The molecular structure of this Co(I) compound (Figure 3.3.3) was found to be similar to to the Biphenyl cobalt(I) complex synthesized over the course of this project. Veinot and Masuda described the Ter[Mes]Co(I) as featuring a cobalt atom 1.6745(11) Å from the Cp centroid and 1.6045(11) Å from the plane defined by C6-C9.[1,5] The plane made up by the butadienyl fragment (C6-C9) is tilted 6.49(12)° away from the η⁵-Cp fragment.[5] The sp³-hybridized C10 lies 0.597(3) Å above the butadiene plane causing the cyclopentadiene ring to pucker, and exhibits an angle of 34.74(17)° between the C6 C10-C9 and

C6-C7-C8-C9 planes.[5] The flanking mesityl groups are nearly parallel and twist out of the plane of the central aryl ring by 82.86(7)° and 80.72(6)°.[1,5]
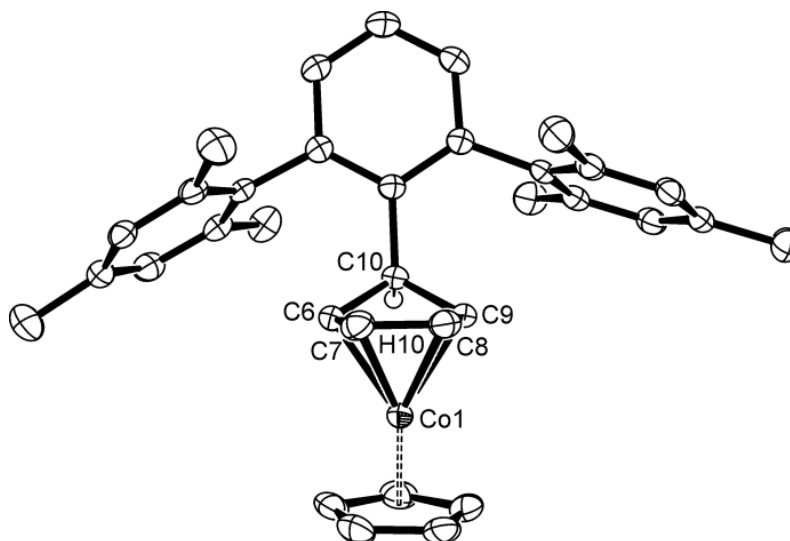

Figure 3.3.3. Molecular structure of Ter^{Mes}Co(I). Ellipsoids are shown at the 50 % probability level. Hydrogen atoms (except H10) have been removed for clarity. Selected bond lengths (Å) and angles (°) (note Cpc denotes the ring centroid): Co1-C6 2.0023(17), Co1-C7 1.9627(19), Co1-C8 1.9649(19), Co1-C9 2.0181(17), Co1-Cpc 1.6745(11).[1,5]

It has to be mentioned that the BiphenylCo(I) intermediate is structurally different in solution (Figure 3.3.4), as indicated by the methylene resonance at 3.57 ppm in the ^{1}H NMR spectrum, which was confirmed to be part of the cyclopentadiene ring by examination of the preliminary correlations in the ^{1}H-^{1}H COSY NMR spectroscopy. It was hypothesized that there could potentially be three different isomers (2a, 2b, 2c: Figure 3.3.4.) showing the three different positions of the Aryl-group and hydrogen(s) on the cyclopentadiene fragment. Preliminary reactions with the cobaltocenium compound (Reaction 2.2.3) and the corresponding ^{1}H NMR

spectroscopy that was carried out could not tell which isomer was formed. The X-ray crystallography that was also carried out however, showed that in the solid state, the isomer as showed by Figure 3.3.4. (2c) was isolated. It is hypothesized that the isomer that would be isolated in the liquid state (solution for NMR) and solid state (crystals for X-ray crystallography) most likely would accommodate the significant steric demand of the Biphenyl ligand bound to the cyclopentadiene fragment.[5]
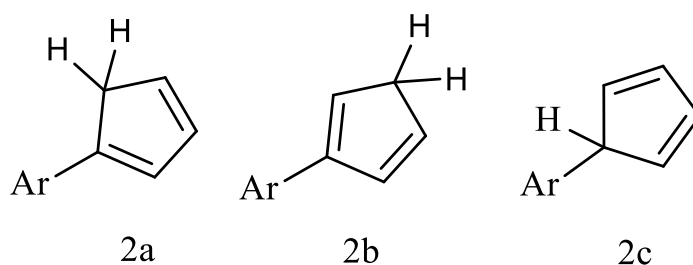

Figure 3.3.4. Possible isomers of the cyclopentadiene attached to the BiphenylCo(I) intermediate. The methine isomer has been confirmed in the solid state by X-ray crystallography.

The characterization of this compound was done by obtaining the ^{1}H, ^{13}C and ^{1}H-^{1}H COSY spectroscopy of the pure product sample. The most prominent and relevant peaks were from the – CH$_3$ of the isopropyl groups and they were at 1.38 ppm, 1.19 ppm and 0.98 ppm each integrating to 6 protons respectively having a coupling constant (*J*) of 6.90 Hz, the same as the Biphenyl-I and Biphenyl-Li. The methine peaks were at 3.00 ppm and 2.32 ppm each integrating to 1 proton and 2 protons respectively. The peaks in the aromatic region could not be identified and assigned as they were too complex and very broad. They were reported as being peaks from the Ar-H as multiplets. The H$_{cp}$ peak was at 4.61 ppm as a sharp singlet integrating to 5 protons.

Thin layer chromatography was also carried out by dissolving the BiphenylCo(I) intermediate in a minimum amount of pentane, in order to deduce which solvent was the best suited to dissolve and carry out the filtration of the BiphenylCo(I) intermediate in. It was observed that the upon spotting the TLC with the BiphenylCo(I) intermediate solution in pentane or toluene or a mixture of both, there was a quick and sudden change from the reddish-orange colour of the BiphenylCo(I) intermediate to a dark blue coloration. It was believed that the silica gel might be possibly abstracting the Co(I) from the BiphenylCo(I) intermediate to result into the desired product which was the BiphenylCpH. Further investigations however, concluded that this was not the case and the BiphenylCo(I) intermediate was getting decomposed on the TLC plate.

3.4 Synthesis of BiphenylCpH

3.4.1 Unsuccessful oxidation with FeCl$_3$

The first attempt at the oxidation of the BiphenylCo(I) intermediate with two eq. of FeCl$_3$ was unsuccessful. The BiphenylCo(I) and FeCl$_3$ reaction mixture was left to stir between -65 and -75 °C for one hour and the temperature of the cold acetone-liquid nitrogen bath was monitored using a thermocouple. While cold, the blue green coloured mixture was transferred via cannula transfer to a -35 °C column containing approximately 150 mL of silica gel and toluene and eluted through the cold column using toluene in air. This reaction should be carried out at a temperature of approximately -78 °C and subsequently eluted through a cold column at approximately -78 °C also. Otherwise, the product would not be isolable. The resulting product, which was oily and paste-like in texture and looking navy blue in color, contained a lot of paramagnetic impurities as deduced by its ^{1}H NMR spectrum. This reaction was extremely temperature sensitive and had to be carried out at a temperature of approximately -78 °C at all times and eluted at the same

temperature in air. The -35 °C column was too high in temperature for this reaction and therefore this resulted into the product not being isolable, hence decomposed.
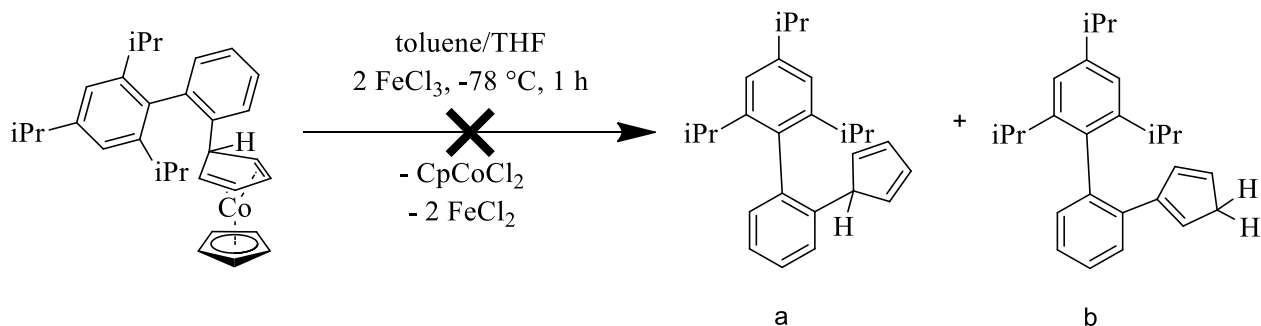
Scheme 3.4.1. Unsuccessful oxidation with two equivalents of FeCl$_3$ of the BiphenylCo(I) intermediate.
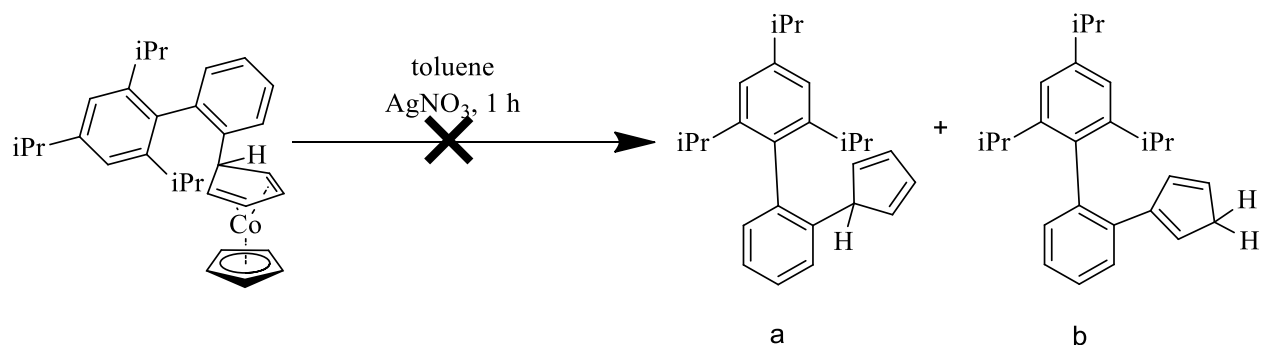
3.4.2 Reaction with AgNO$_3$

Following the unsuccessful oxidation with FeCl$_3$, an alternative method towards the synthesis of the BiphenylCpH was tried. This method was successful when it was tried with the Ter^{Mes}Co(I) intermediate and thus it was expected that it would work with the BiphenylCo(I) intermediate as well. It consisted of reacting the BiphenylCo(I) intermediate with a 1:1 ratio of AgNO$_3$ in water, extracting the organic layer, drying it with MgSO$_4$ and removing the solvent on a rotary evaporator. This was a redox reaction and it was believed that the silver (Ag) would abstract the metal (Co(I)) off the BiphenylCo(I) intermediate leaving behind the free BiphenylCpH ligand. The ^{1}H NMR spectroscopy however, showed that this was not the case since there almost no change in the ^{1}H NMR spectroscopy of the product when compared to that of the BiphenylCo(I) intermediate. The H$_{Biphenyl-Cp}$ peaks were still prominent at around 3.91 ppm, 4.43 ppm and 5.14 ppm integrating to 2, 5 and 1 protons respectively.
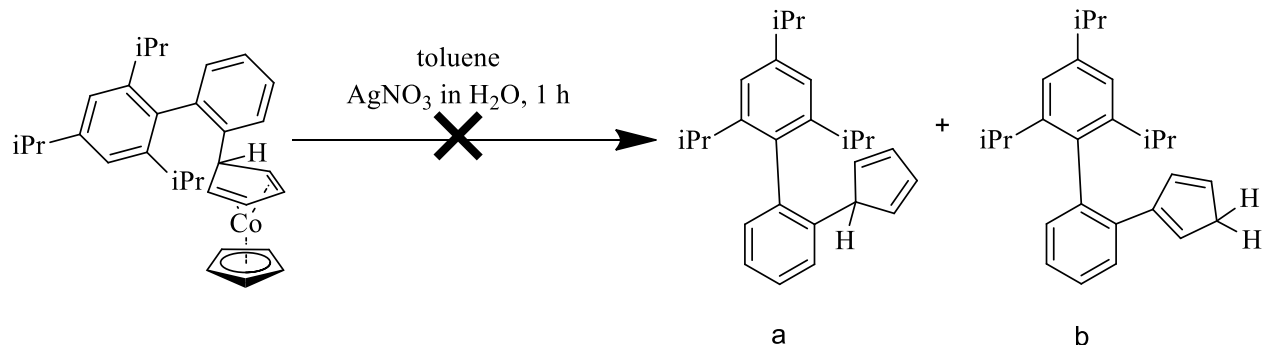
Scheme 3.4.2. Reaction of the BiphenylCo(I) intermediate with AgNO₃ in water.

A second reaction was then carried out with consisted of adding the AgNO₃ solids directly into the BiphenylCo(I)-toluene solution and allowing the mixture to stir for 1 h. Following the work up, the resulting solution was allowed to stand in the fume hood for a week until all of the solvent was evaporated. After one week, it was expected that crystals would be formed, however, a paste-like oily brown layer was left behind. The ^{1}H NMR spectrum of this resulting product confirmed that this second method as well did not work since there was no change in its ^{1}H NMR spectrum. This route towards making the BiphenylCpH was then deduced to be not working for the Biphenyl substituted ligands and as of now the reason why it did not work with them is not known.
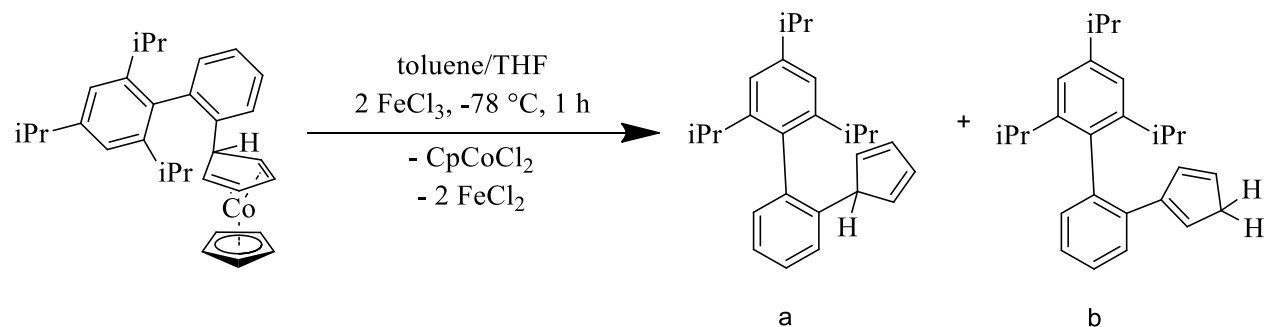

Scheme 3.4.3. Reaction of the BiphenylCo(I) intermediate with AgNO₃.

3.4.3 Successful oxidation with FeCl₃

Oxidation of the BiphenylCo(I) intermediate with two equivalents of $FeCl_3$, followed by column chromatography (silica gel, toluene) to remove all metal containing by-products yielded the desired cyclopentadienyl ligand precursor by constant monitoring and maintaining both the reaction mixture and the column at a temperature of -78 °C. The ¹H NMR spectroscopy of the product showed that two isomers of the BiphenylCpH were formed as indicated by the peaks at 2.63 and 2.84 ppm respectively. The ¹H NMR spectrum was however too complex to be fully assigned and interpreted but it served as proof that BiphenylCpH was successfully synthesized as confirmed by the peaks at 6.02 - 7.10 ppm. It has to be mentioned that this particular oxidation of the BiphenylCo(I) intermediate as opposed to the first time that it was carried out, was different in the sense that, during the first trial at this oxidation reaction, a cold column was used which was at -35 °C.

For the second trial at this oxidation reaction, however, the temperature of the reaction mixture was very carefully monitored, and the column was cooled to -78 °C by using dry ice in a set up as showed by Figure 2.3.4(IV). in the experimental sections. The column and hence the reaction mixture had to be maintained at a temperature of -78 °C constantly. Otherwise, a higher temperature than this would result into the product not being isolable. Thus, the toluene that was used to elute the product had to be cold as well. An attempt at purifying and removing all of the residual solvent in the BiphenylCpH solids was made by dissolving the solids in a minimum amount of benzene. The resulting solution was then heated on a rotary evaporator at 60 °C for half an hour. Subsequent ¹H NMR spectroscopy of the resulting product as showed by Figure A10 in

Appendix A, was very complex and quite different from the initial spectrum. It was deduced that this could be an indication of the [4 + 2] Diels-Alder dimerization (cycloaddition) product that could have been potentially formed after heating the BiphenylCpH at 60 °C.

Scheme 3.4.4. Successful oxidation with two equivalents of FeCl₃ with the BiphenylCo(I) intermediate carried out at a temperature of -78 °C.

3.5 Alkali metal complex of the BiphenylCp anion

The crude monomeric mixture of the two isomers of the BiphenylCpH can be transformed into the corresponding alkali metal salt when combined with the appropriate alkali metal transfer reagent. The resulting product could not be identified by ^{1}H NMR spectroscopy due to the fact that the mixture of the two isomers of the BiphenylCpH was deduced to have potentially underwent a [4 + 2] Diels-Alder cycloaddition.
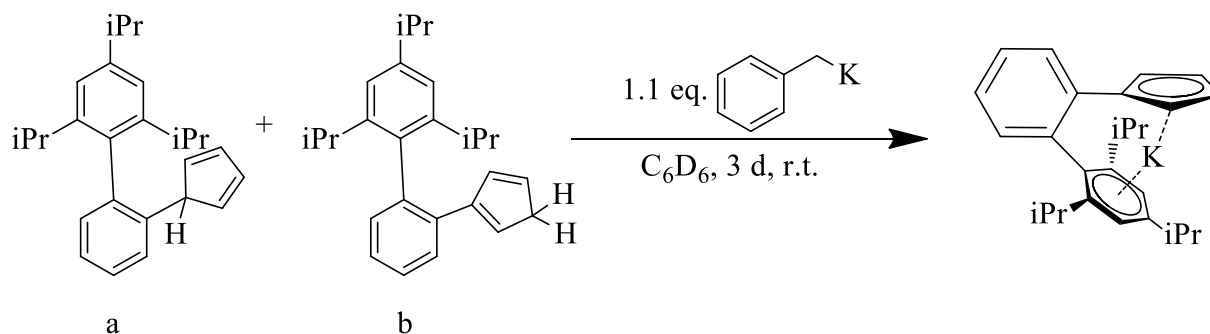
Scheme 3.5.1. Formation of the corresponding alkali metal salt by reaction of the mixture of the two different isomers of the BiphenylCpH with benzyl potassium.

3.6 Conclusion

Through a one-pot Grignard reaction, the synthesis of Biphenyl-I (starting material) was achieved. ^{1}H NMR spectroscopy concluded that the product was pure and was similar to the one which was synthesized in the literature. The next step consisted of making the organolithium reagent, Biphenyl-Li, by reacting the Biphenyl-I with n-Butyllithium. This reaction was also successful as confirmed by the ^{1}H NMR spectroscopy of the product. Nucleophilic substitution reaction to yield the cobaltocenium salts was the next reaction that was carried out. This was achieved by reacting the organolithium reagent Biphenyl-Li with bis(cyclopentadienyl)cobalt(III) hexafluorophosphate $[Cp_2Co][PF_6]$ which led to the formation of the BiphenylCo(I) intermediate, which when reacted with $FeCl_3$ should liberate the cyclopentadienyl precursors following column chromatography of the reaction mixture. However, the latter step was quite difficult to achieve as it is very temperature sensitive, requiring a temperature of -78 °C most of the time. Preliminary oxidation reaction with $FeCl_3$ resulted into the product getting decomposed. Attempts at synthesizing the BiphenylCpH was also tried by reacting the BiphenylCo(I) intermediate with $AgNO_3$. The ^{1}H NMR spectroscopy

of the product when compared with the BiphenylCo(I) intermediate was almost similar confirming that this reaction did not work. Finally, by maintaining and monitoring the temperature of the oxidation reaction mixture at -78 °C and subsequently eluting the product by cold column chromatography, BiphenylCpH was successfully isolated. Heating the BiphenylCpH on a rotary evaporator at 60 °C in an attempt to remove all the solvent, however resulted into which we suspected to be the [4 + 2] cycloaddition product following the analysis of the ^{1}H NMR spectroscopy. An attempt at the synthesis of the potassium salts was nevertheless attempted which did not yield great results as expected, and hence the molecular structure could not be established but it is expected that the BiphenylCp anion is capable of bonding through both Cp and aryl interactions.

Lastly, the most important result of this project was that the synthetic route which was used to make the Ter[Mes]Co(I) and Ter[Dipp]Co(I) intermediates was successfully applied to the synthesis of the BiphenylCo(I) intermediate. This result is significant because it shows the versatility of this method with respect to tolerating a variety of steric demands and demonstrates that the steric and electronic properties can be tailored to match almost any situation with only a few common reagents.[5]

3.7 Future Work

This project will likely serve as the foundation for future developments as it very open-ended. There is a lot of potential to further develop organometallic complexes of both main group and transition metal elements that incorporate the BiphenylCp anion, and there is also the potential to develop new cyclopentadienyl ligands incorporating bulkier, or electronically different Biphenyl substituents.[5]

Future works include completing all of the outstanding characterisation data (covered during the Results and Discussion section). The transformation of the BiphenylCpH into the corresponding alkali metal salts (Figure 3.7.1) upon combination with the appropriate alkali metal transfer reagent are planned in the future.
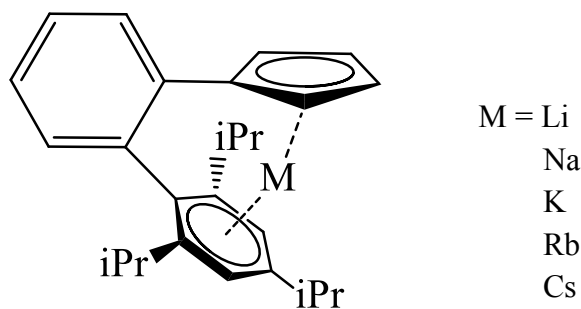
Figure 3.7.1. Targeted alkali metal complexes of the BiphenylCp anion.

Exploring the coordination chemistry of these new targeted synthesized ligands, will be the next step following the successful isolation of all the alkali metal salts complexes.

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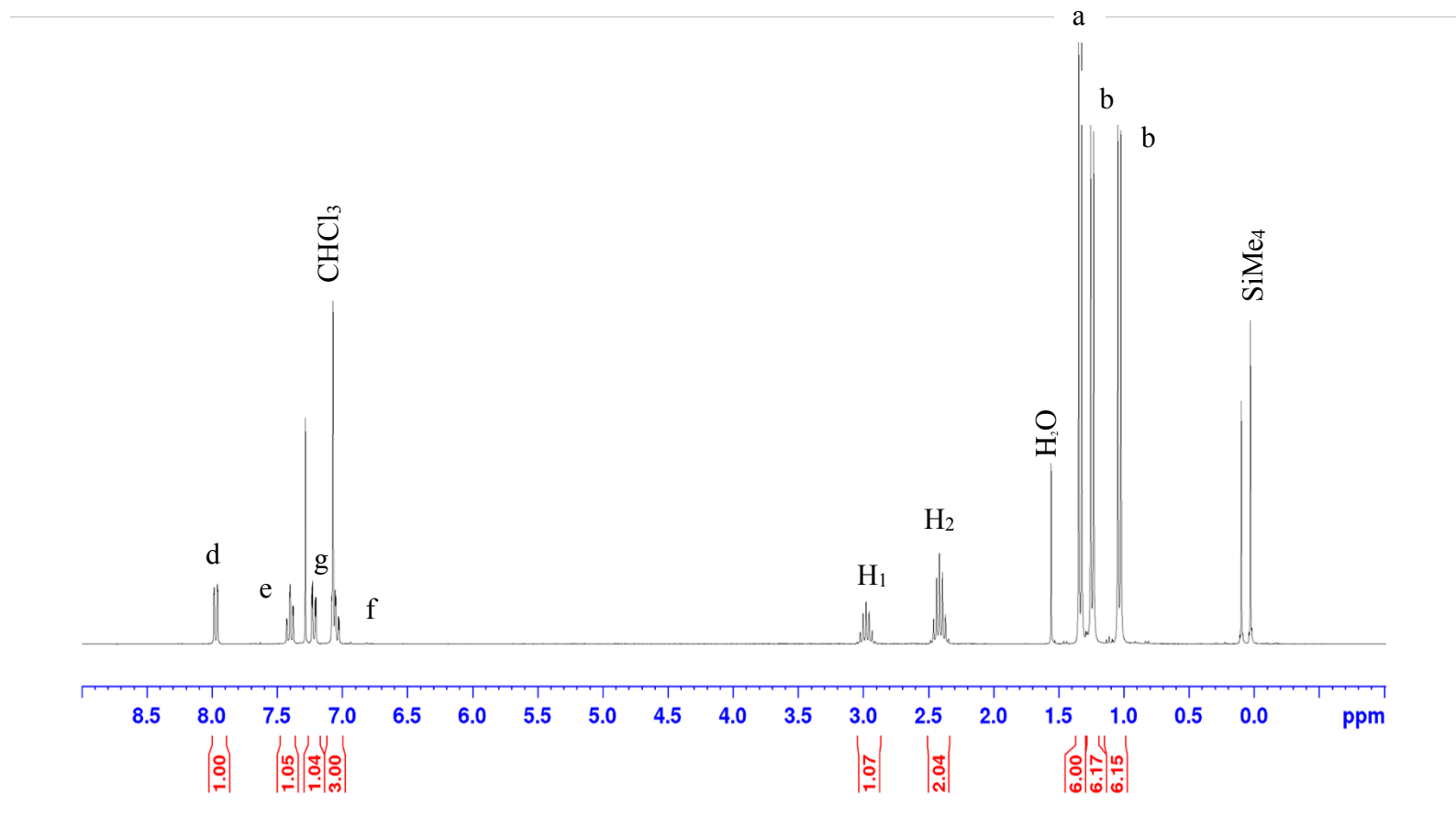
Figure A1. ^{1}H NMR spectrum for Biphenyl-I.
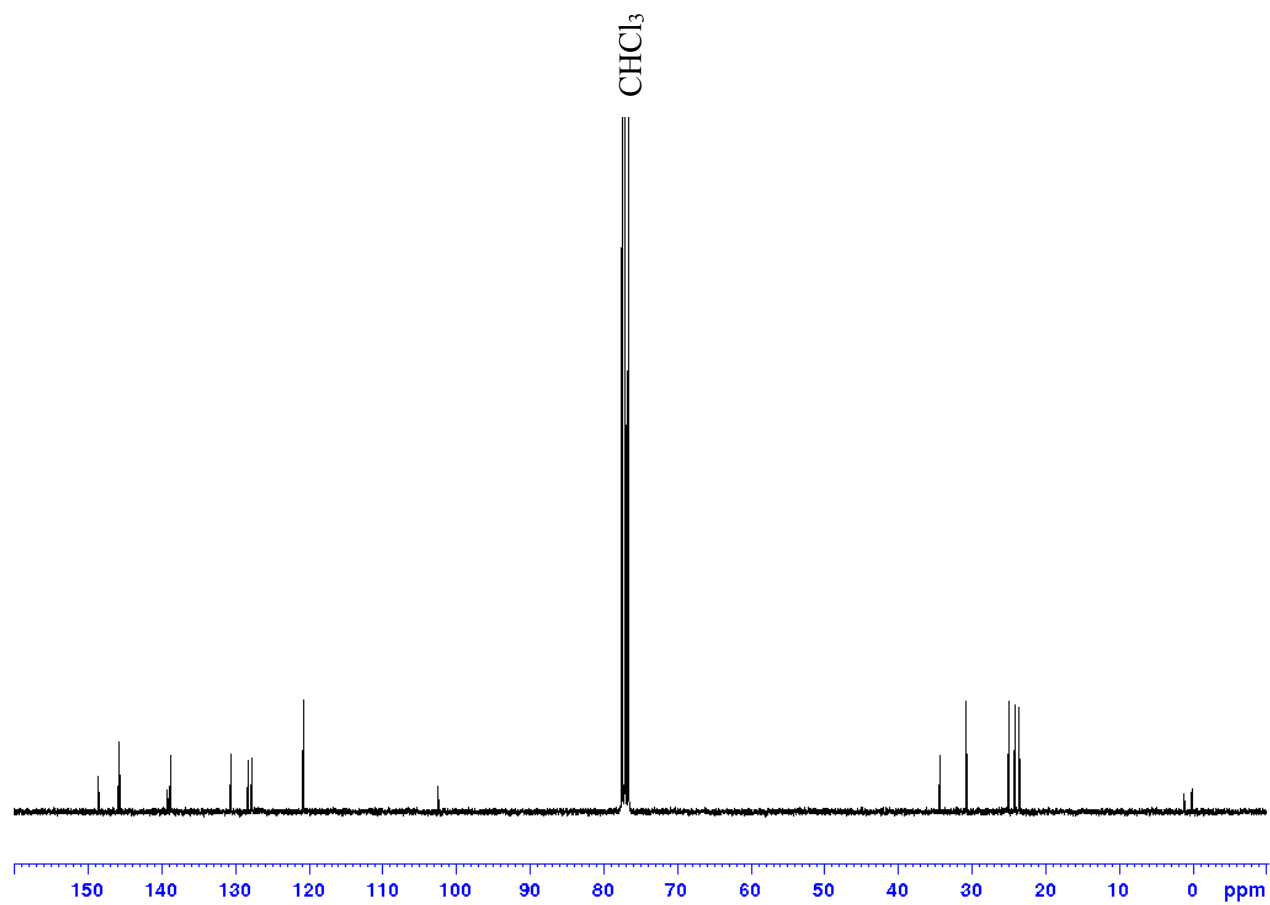
Figure A2. ^{13}C NMR spectrum for Biphenyl-I.
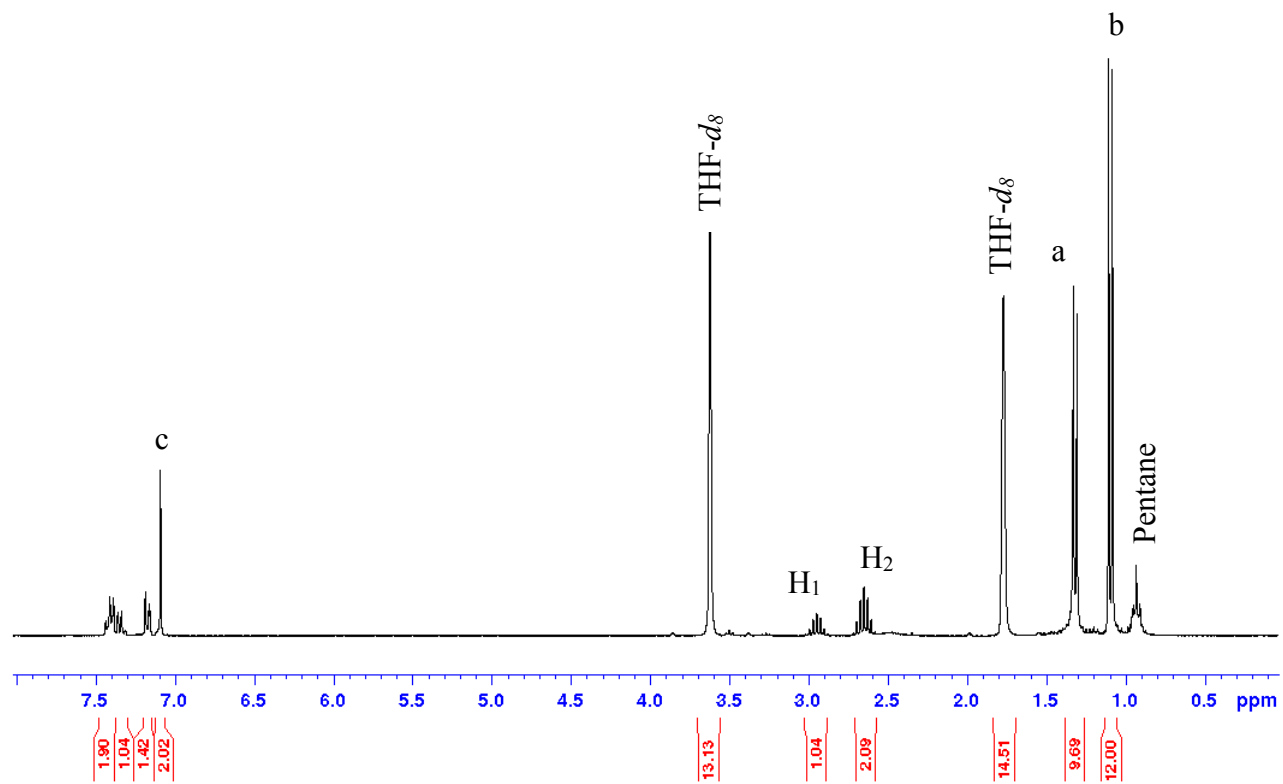
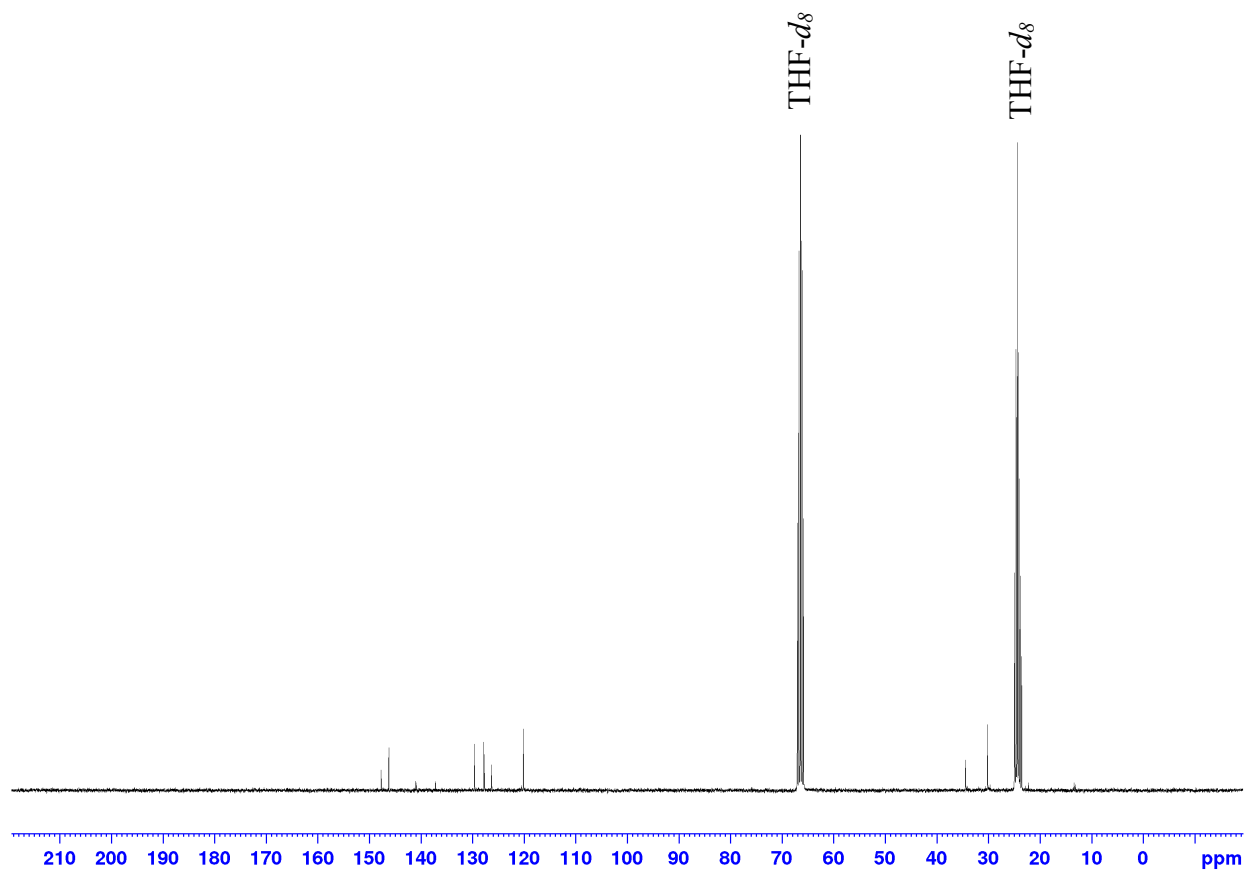**Figure A3.** ^{1}H NMR spectrum for Biphenyl-Li.

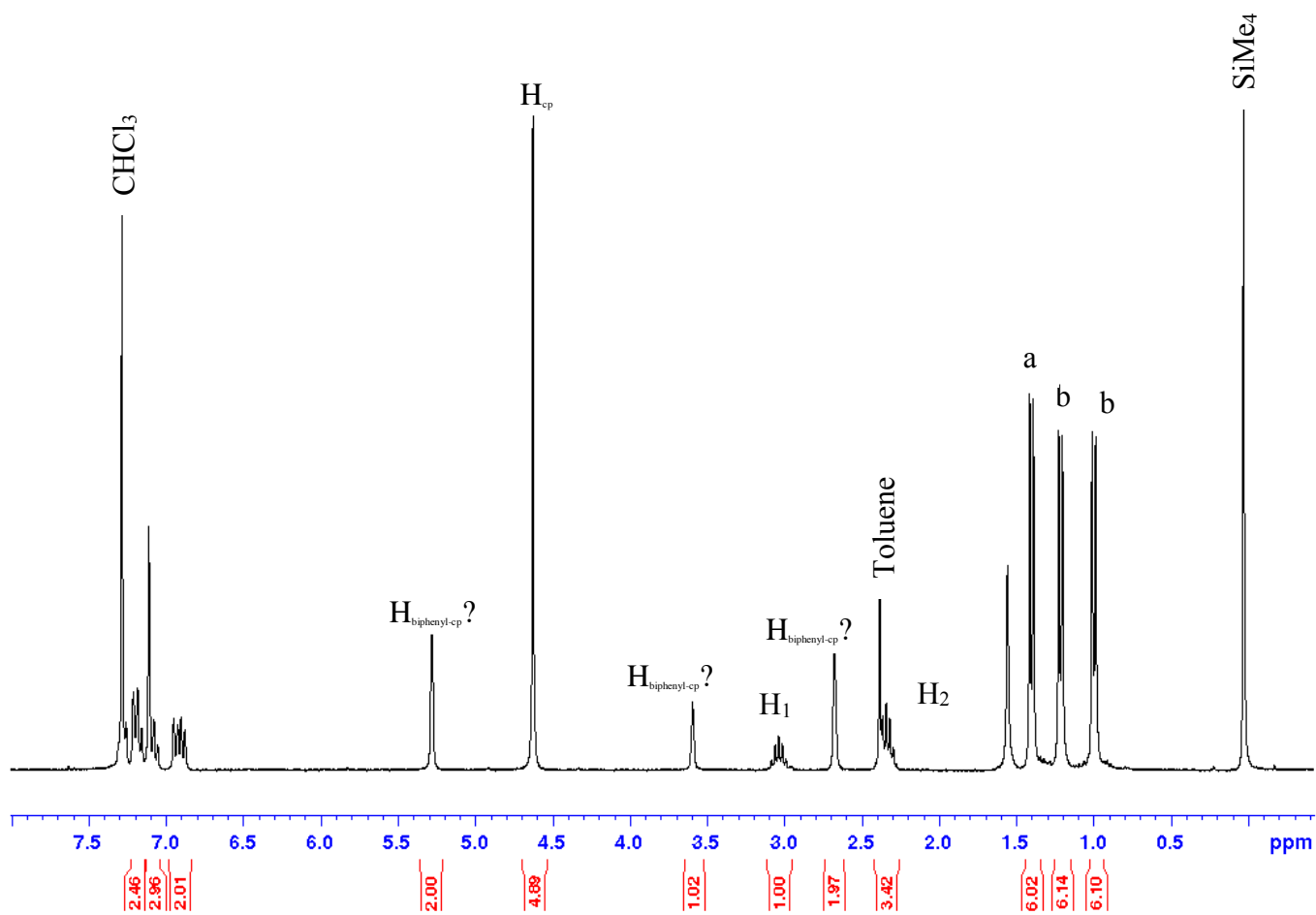**Figure A4.** ^{13}C NMR spectrum for Biphenyl-Li.

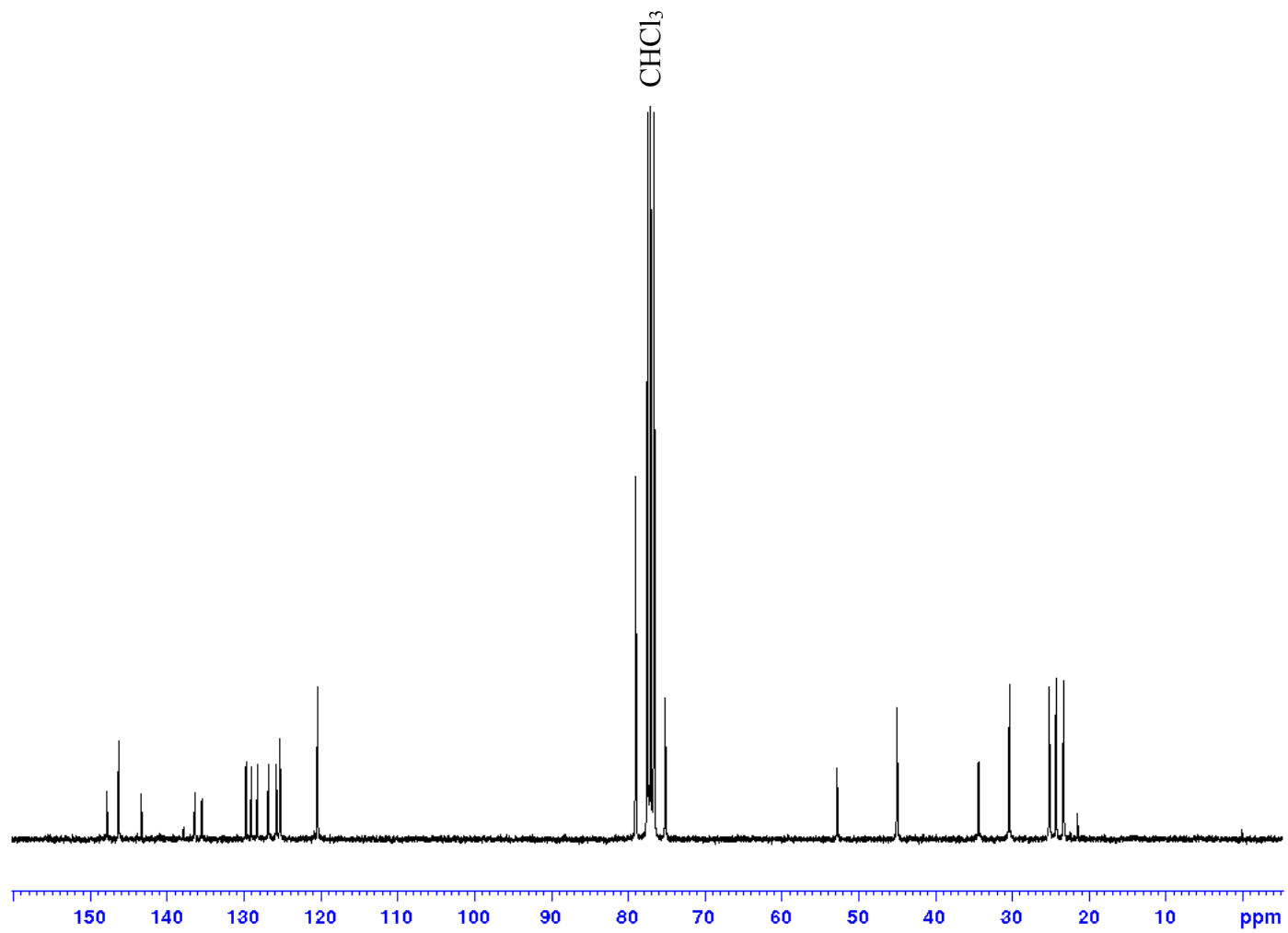**Figure A5.** ^{1}H NMR spectrum for BiphenylCo(I) intermediate-Pure crystals.

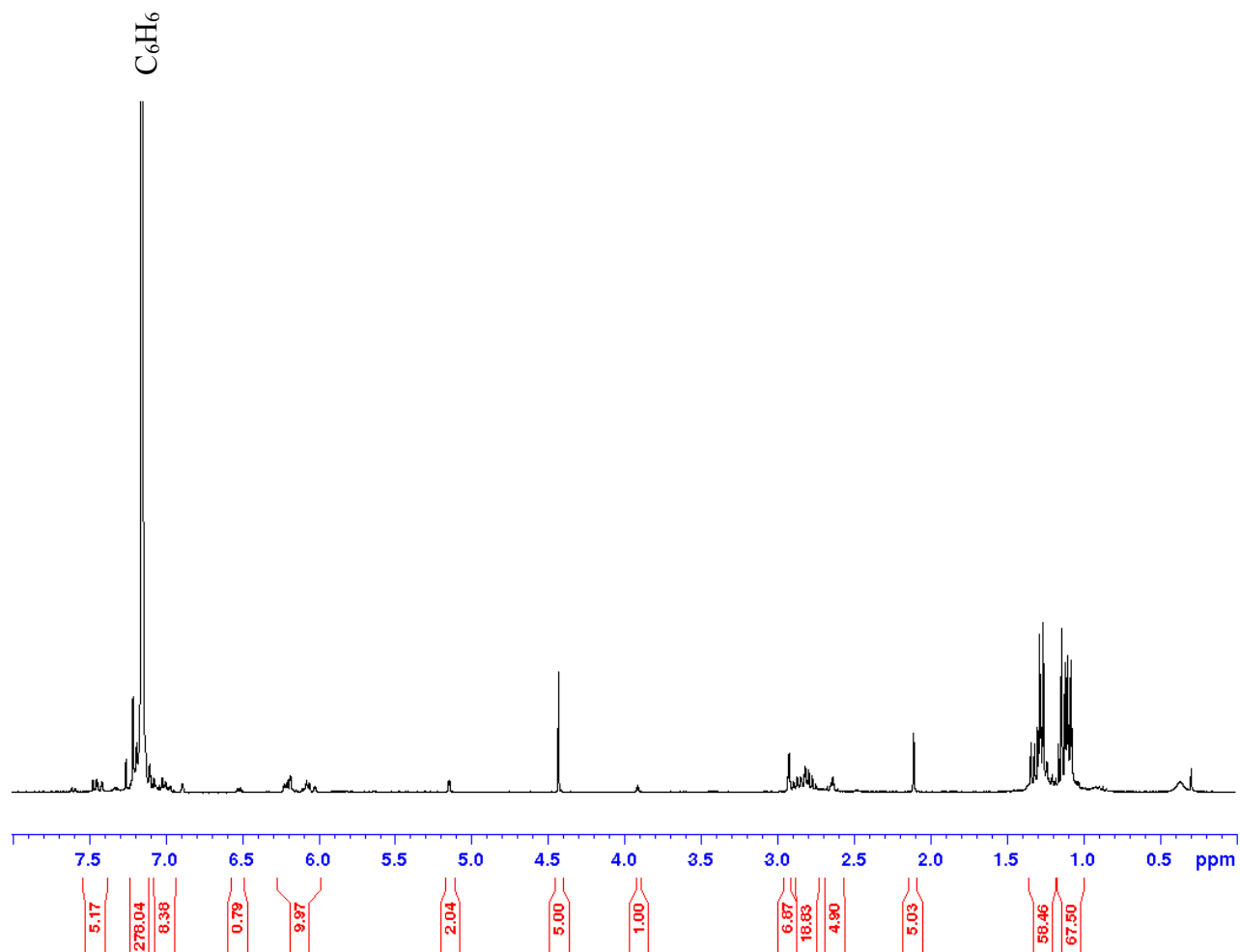**Figure A6.** ^{13}C NMR spectrum for BiphenylCo(I) intermediate-Pure crystals.

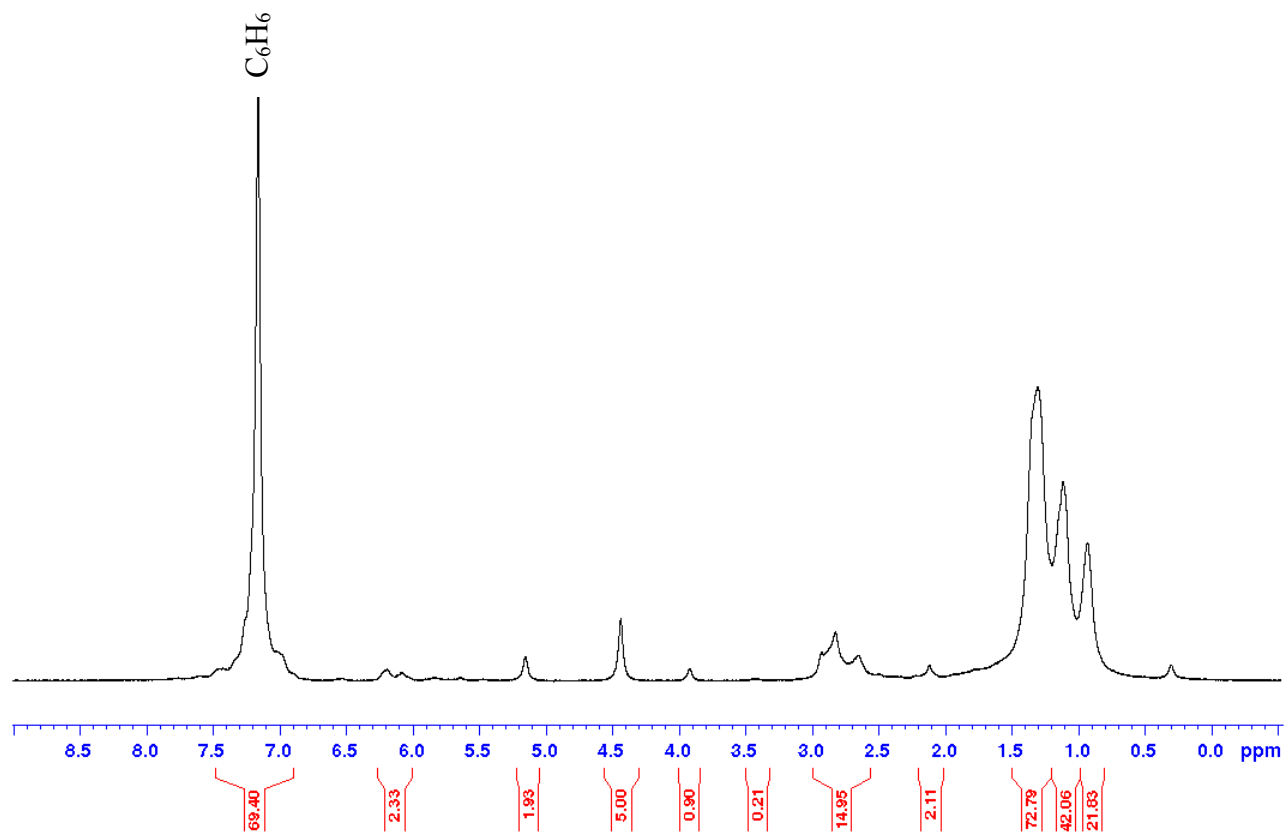**Figure A7.** ^{1}H NMR spectrum for attempted synthesis of BiphenylCpH by using AgNO$_3$.

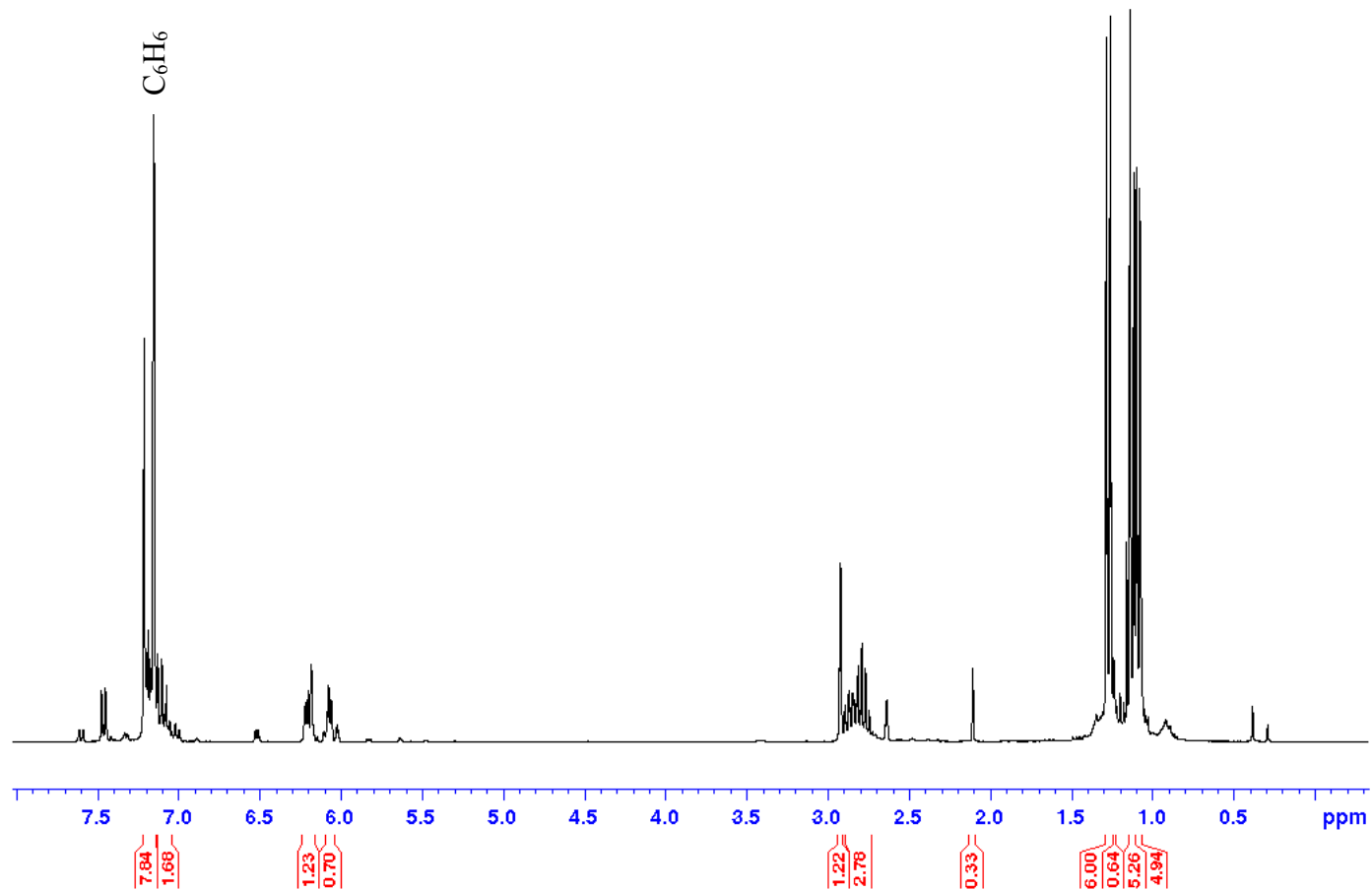**Figure A8.** ^{1}H NMR spectrum for attempted synthesis of BiphenylCpH by using AgNO$_3$.

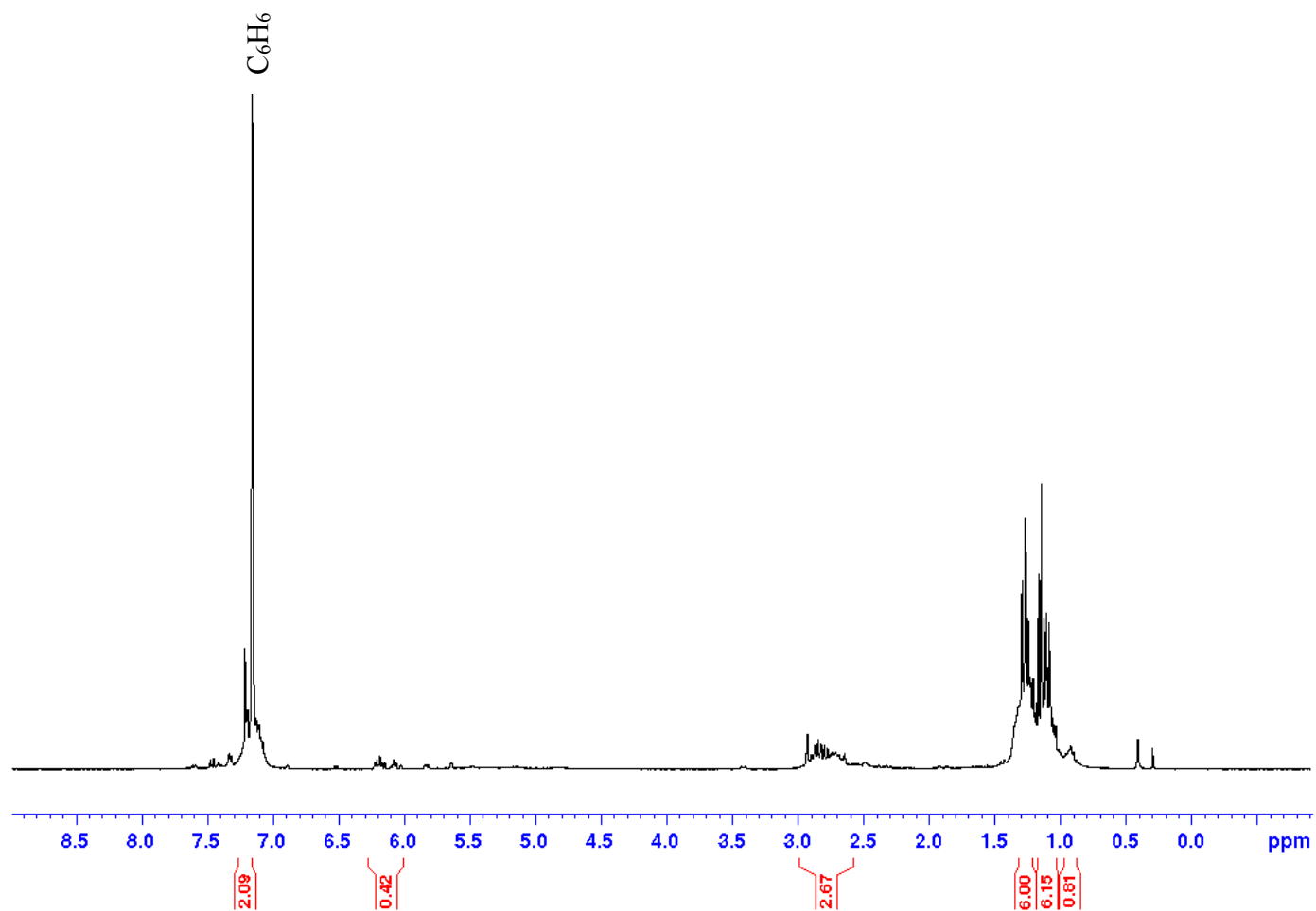**Figure A9.** ^{1}H NMR spectrum for BiphenylCpH.

Figure A10. ^{1}H NMR spectrum for the potential BiphenylCpH [4 + 2] cycloaddition product.