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Synthesis Attempts And Plausible Applications Of Dithiolated Ortho –Carboranyl Transition Metal Complexes And Synthesis Of Bulky Terphenyls

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SYNTHESIS ATTEMPTS AND PLAUSIBLE APPLICATIONS OF DITHIOLATED
ORTHO-CARBORANYL TRANSITION METAL COMPLEXES AND SYNTHESIS
OF BULKY TERPHENYLS

by

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For the Degree of Master of Science in

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DEDICATION

I dedicate this work to my parents and wife who always helped, inspired and motivated me in every step of my life to achieve my goals.

ACKNOWLEDGEMENTS

Firstly, I would like to express profound and sincere gratitude to my advisor Dr. Dmitry V. Persykhov for allowing me to pursue excellent research work in his lab. It is a privilege to get his guidance, support and exceptional supervision throughout my graduate career, without which I would not have been able to complete the difficult journey of this graduate program. The knowledge, skills, and motivation that I learned from him will always help me move forward in the future.

I would like to express my heartfelt gratitude to Dr. Aaron K. Vannucci and Dr. Thomas Makris for serving as my committee members. Their constructive criticism and feedback helped me to be a better researcher. I would also like to thank my professors and administrative staff for their invaluable academic and administrative support.

Lastly, I would like to extend special thanks to Dr. Onn Wong and all other group members for their help, suggestions and guidance in the lab.

ABSTRACT

The reaction of coordination compounds of palladium, rhodium, ruthenium and nickel with thiolated *ortho*-carborane derivatives- 1,2-dimercapto-*o*-carborane (1,2-(HS)₂-1,2- C₂B₁₀H₁₀) and 9,12- dimercapto-*o*-carborane (9,12-(HS)₂-1,2- C₂B₁₀H₁₀) and with carbonyl dicarboxylate has been studied. To further investigate the chemistry of *o*-carboranyl dithiolate, both of the reported literature dithiols have been employed to study the reactivity with some of the above mentioned transition metal coordination compounds. The 1,2-dimercapto-*o*-carborane reacts with bis(triphenylphosphine)palladium(II) chloride [PdCl₂(PPh₃)₂] to form a square planar bis(triphenylphosphine)palladium(II) carboranyl dithiolate (PdC₂B₁₀S₂(PPh₃)₂) complex. With the inspiration from the reactivity of the dithiols and versatility of carboranyldithiolate ligand in organometallic chemistry, new avenue of carboranyltetrathiolate coordination could be envisioned. The synthesis of 1,2,9,12- tetramercapto- *ortho*-Carborane has also been attempted.

Extremely sterically demanding *m*-terphenyl amines are excellent ligands because of the ease in forming main group complexes in low coordination numbers but also provide a large area to study the reactivity between their nitrogen atom containing steric pocket and transition metal. Two well-known literature routes for the synthesis of *m*-terphenyl aniline has thoroughly been discussed within this paper in chapter 2. Additionally, terephenyl iodide (2'-iodo-3,3'',5,5''-tetramethyl-1,

1',3',1"-terphenyl) has been synthesized following one of the reported synthetic route (Scheme 2.2, route A) and has paved a future foundation for our anticipated cyclization of the *m*-terphenyl aniline via borylation. Several attempts to synthesize *m*-terphenyl aniline has also been discussed within this paper as well.

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CHAPTER 1

INTRODUCTION ON CARBORANES

The hexacoordination environment among carbon, boron and hydrogen atoms in icosahedral dicarba-*closo*-dodecarborane or simply carborane has attracted extensive attention and voluminous study that has been going on since its discovery in 1963. Leading from much easier C-H vertex derivatization to B-H vertex activation, this boron rich cluster compound has been functionalized in several ways. One of the most prodigious study so far is the functionalization of the cluster vertices by employing transition metals. Recent studies have focused on the *ortho*-carborane and its derivative based compounds in order to explore the effects of the carboranyl unit on the numerous properties of these compounds. Noticeable research efforts have been focused on these cluster compounds because of their important applications in biological and pharmaceutical fields and in material science¹.

The electron deficient boron atoms limit the cage properties of carboranes and are directly associated with the cluster geometry. The hydrophobicity of the boron-hydrogen units (B-H) and comparatively acidic C-H units determine the intermolecular interactions.

1.1. Geometry

Polyhedral boranes exist in several molecular architectures having *closo*, *nido*, *arachno* and *hypo* structures. Among these boranes, dicarba-*closo*-carboranes ($C_2B_{10}H_{12}$) mimic a slightly distorted icosahedral geometry. These cluster compounds are obtained from the dodecaborane anion $[B_{12}H_{12}^{2-}]$ by substituting two B-H units with C-H units. They organize into three isomeric forms namely- *ortho*, *meta* and *para* isomers (Figure 1) with the first two isomers having C_{2v} and the third possessing D_{5d} symmetry.² *Ortho*-carborane ($1,2-C_2B_{10}H_{12}$) undergoes thermal isomerization into *meta*-carborane ($1,7-C_2B_{10}H_{12}$) and *para*-Carborane ($1,12-C_2B_{10}H_{12}$) in inert atmosphere.³⁻⁵ Table 1.1 shows the average inter-atomic distances in *ortho*-carborane.⁶ Table 1.2 summarizes the geometric parameters of the isomers.^{7,8}

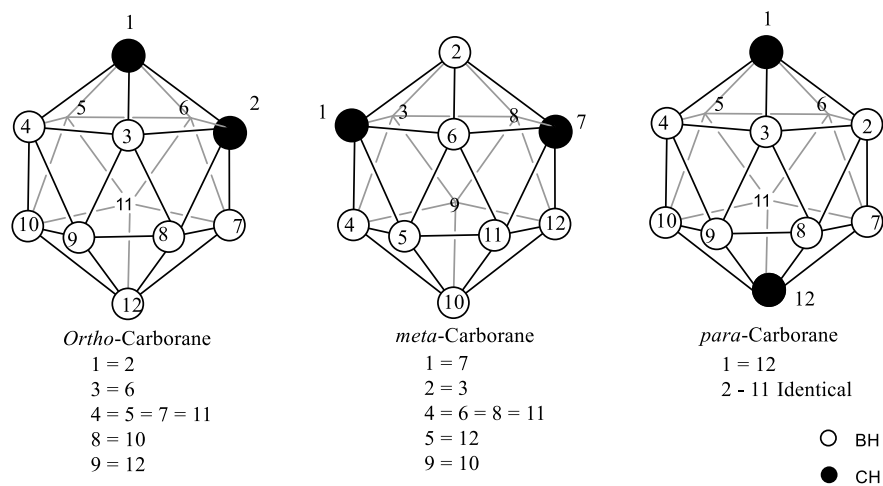


Figure 1.1. Isomers of carboranes with IUPAC numbering of the vertices¹¹

Table 1.1 Bond lengths found in *ortho*-carborane

Bond Distances Found in <i>Ortho</i> -Carborane	
Bond	Distance (Å)
C-C	1.62-1.71
B-C	1.70-1.75
B-B	1.70-1.79

Table 1.2. Geometric parameters of Carboranes

Parameters	Carboranes		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
<i>Symmetry</i>	C_{2v}	C_{2v}	D_{5d}
C –C distance (Å)	1.62	2.61	3.06
H – C –C – H angle (degree)	~ 52	~ 115	180
S_{IC}	0.1	0.1	0.13
V_{vdW} (Å ³)	148	143	141

Among the three isomers of carboranes, the C–C distance of *ortho*-carborane has been studied the most. The C–C distance is the shortest among the three isomers in unsubstituted cluster. This distance increases with attachment of substituent groups because of steric and electronic effects. Additionally, the anionic substituents and π donors increase the C–C distance.^{8,10} Figure 1.2 shows the change in C–C distance vs substituent groups.⁹

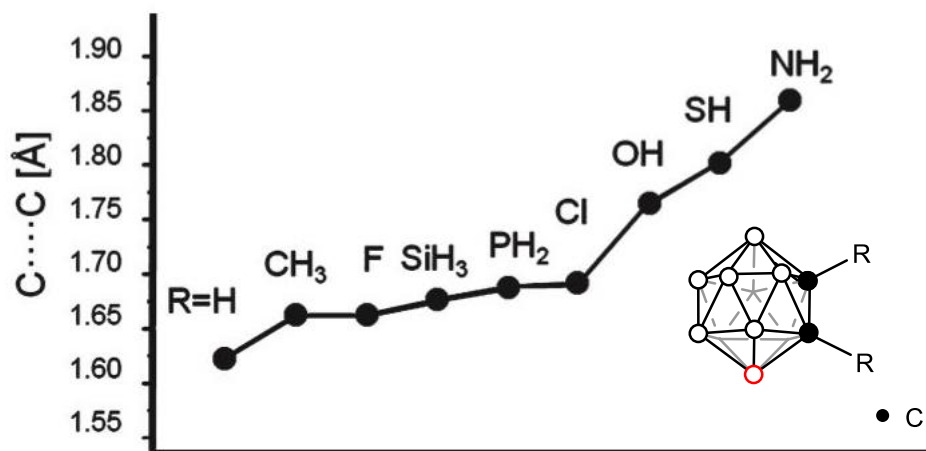


Figure 1.2. Calculated C–C distances of symmetrically disubstituted *ortho*-carboranes

1.2. Electronic Structure

Since the electrons in the cluster are delocalized three-dimensionally, carboranes are often considered as three-dimensional aromatic super analogue of benzene. They exhibit *closo* structure with 26 e⁻ for 12 vertices as dictated by $2n + 2$ skeletal electrons. The Mulliken and the natural population analysis (NPA) best describe the electronic structure.⁸ The latter technique is more convincing (Table 1.3).⁸

The inductive and resonance effects in the cluster are due to differences in electron densities of the various vertex positions.⁶ The inductive effect is more dominant than the resonance effect. The studies on calculation of electron densities on various positions show that all the cluster carbon atoms exert an electron withdrawing effect on attached substituents. Because of this, they decrease in the order *ortho* – to *meta* – to *para* - isomer.¹¹

Table 1.3. NPA charges for unsubstituted isomers of carboranes

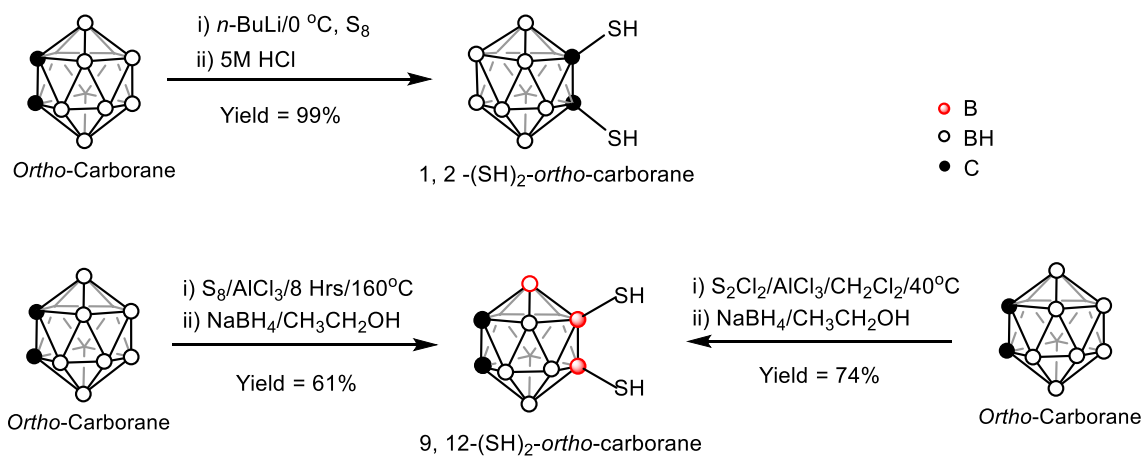
<i>o</i> -C ₂ B ₁₀ H ₁₂		<i>m</i> -C ₂ B ₁₀ H ₁₂		<i>p</i> -C ₂ B ₁₀ H ₁₂	
C _{1/2}	-0.496	C _{1/7}	-0.639	C	-0.664
H _{1/2}	0.300	H _{1/7}	0.299	H _C	0.299
B _{3/6}	0.158	B _{3/2}	0.149	B	0.005
H _{3/6}	0.054	H _{3/2}	0.066	H _B	0.068
B _{4/5/7/11}	0.000	B _{4/6/8/11}	-0.021		
H _{4/5/7/11}	0.069	H _{4/6/8/11}	0.073		
B _{8/10}	-0.165	B _{5/12}	0.058		
H _{8/10}	0.078	H _{5/12}	0.056		
B _{9/12}	-0.139	B _{9/10}	-0.176		
H _{9/12}	0.073	H _{9/10}	0.080		

1.3. Acidity

Several methods have been applied for the determination of pK_a of slightly acidic carbon atom protons of carboranes. The acidity of protons decreases in the order of *ortho*-, *meta*- and *para* – carborane.¹² These protons can easily be deprotonated by organometallic bases like *n*-BuLi forming a carboranyl nucleophile. The acidity is greatly affected by the substituents at boron or carbon vertices of the clusters. For example, halogen atoms substituted clusters have drastically increased acidity of the C-H units.^{13,14} The *ortho*-carborane carboxylic acid explains more clearly that the reactivity of functional substituents can be altered by the selection of vertex position similar to hydrophobicity.

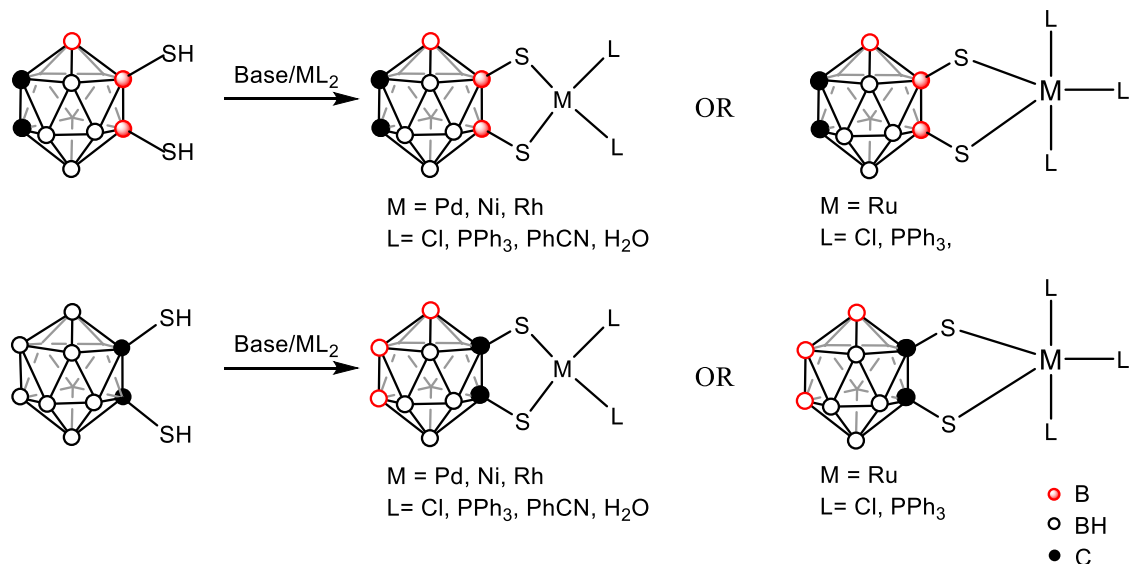
1.4. Thiols of Carborane

C-H vertex functionalized carborane thiols¹⁵ was discovered along with the discovery of carboranes in 1960s. The well-known B-mercaptocarboranes require some extreme conditions to activate the B-H bond of the carborane cage. Additionally, B-H vertex functionalization via thiol group became more rational by calculation of charge distribution on icosahedral carborane cluster atoms by the means of HS-derivatives¹¹. Mono- or multi-thiolated *o*-carborane is a versatile ligand in transition metal chemistry.¹⁵⁻¹⁷ Extended research has shed light on the reactivity of 1,2-*o*-carboranedithiol while rigorous investigation of 9,12-*o*-carboranedithiol chemistry is also expanding these days. Synthesis of the required carboranedithiols for the purpose of our study is shown in the scheme 1.1. Most recently, 8,9,12-*ortho*-carboranetetrathiol has been synthesized and its organometallics and electrochemistry has also been studied.¹⁷



Scheme 1 .1. Synthesis of *ortho*-carboranedithiols^{11,18}

The thiol groups of 1,2-*ortho*-carboranedithiol ($pK_1 = 4.47$, $pK_2 = 8.87$) are acidic while that of 9,12- vertices attached thiol groups ($pK_1 = 5.5$, $pK_2 = 10.47$) exhibit less acidic nature.¹⁹ Considering the above mentioned fact, different binding modes of these dithiols is expected. Metallodithiolene complexes have been extensively studied because numerous applications arising from their redox, magnetic and optical properties.²⁰ The *o*-carboranyl dithiolato ligand involved as an organometallic complex has become an interesting area of study of related organometallic complexes. From a mononuclear 16-electron Cyclopentadienyl-cobalt(III)-dithiolate complex, to multimetallic clusters of cobalt, molybdenum, iron, rhodium, iridium, it has already been well established in literature to validate the versatility of the *o*-carboranyl dithiolato ligand while the study of interesting chemistry of the B-substituted dithiolato ligand still remains limited.²¹ Hence, the stimulus to explore the comparative coordination properties of these two carboranedithiols with palladium, nickel, ruthenium and rhodium metals would be interesting. The interest in employing palladium and nickel is their ability to form square planar complexes while the use of ruthenium and rhodium coordination compounds allows investigating if these thiols form complexes with octahedral environment. Scheme 1.2 shows the anticipated organometallic chemistry of the two dithiols of *ortho*-carborane.



Scheme 1.2. Coordination of o-carboranedithiols with some transition metals

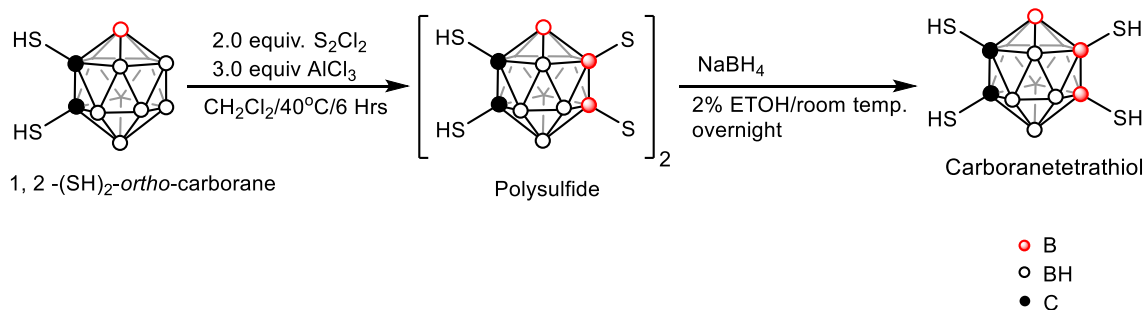
Palladium in +2-oxidation state is a good candidate for the coordination of carboranedithiols. The deprotonation of the thiols could be achieved using different ranges of bases like *n*-butyllithium, triethyl amine or even potassium carbonate. So square planar dithiolato-*o*-carboranyl complexes are expected to form with reaction of these dithiols with bis(benzonitrile)palladium(II) dichloride $[(\text{PhCN})_2\text{PdCl}_2]$ or with bis(triphenylphosphine)palladium chloride $[\text{PdCl}_2(\text{PPh}_3)_2]$. Similar reactivity can be expected with planar dichloridobis(triphenylphosphine)nickel(II) $[\text{NiCl}_2(\text{PPh}_3)_2]$. Other than above mentioned palladium compounds, reactions of these dithiols with different

coordination environment have been studied. For instance, other coordination compounds like rhodium trichloride hydrate, iridium trichloride hydrate and dichlorotris(triphenylphosphine)ruthenium(II) $[\text{RuCl}_2(\text{PPh}_3)_3]$ might form octahedral dithiolato-*o*-carboranyl metallic complexes.

1.5. Synthesis Attempts of 1,2,9,12-*ortho*-carboranetetrathiol

The 1, 2, 4, 5- benzenetetrathiol²² is an interesting compound which have been used to synthesize bimetallic complexes with dithiolene as a connecting moiety. For example, dimetallic complexes $[(\text{P-P})\text{M}(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)\text{M}(\text{P-P})]$, where M= Ni or Pd; P-P= Chelating bis(Phosphine) and trimetallic complexes $(\text{dcpe})\text{Ni}(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)\text{M}(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)\text{Ni}(\text{dcpe})$, where M= Ni or Pt; dcpe = 1,2-bis(dicyclohexylphosphino)ethane, consist of dithiolene-type connecting ligand.²⁰ With this inspiration of reactivity of benzetetrathiol with transition metals and some of the interesting reactivity observed in the carborane dithiols, we are interested to synthesize a *ortho*-carborane cage with four thiol groups in 1, 2, 9 and 12th positions and investigate the reactivity of such compound with the transition metals. Hence, setting the goal to synthesize carboranethiols having carbon and boron vertex linked thiol groups (-SH) in the carborane cage and explore their versatility to further synthesize their bimetallic complexes, would be a good direction for future. Several attempts and various synthetic routes to acquire the carboranetetrathiol, have been attempted. Taking 9,12-*o*-carboranedithiol as a starting compound and protecting the thiol groups followed by incorporation of thiol groups on C-H vertices could be the first choice. Then, deprotection of thiol groups

on 9 and 12 positions would produce the tetrathiol. Several protection protocols have been attempted, which turned out to be futile for what we anticipated. Having said that, endless efforts have been carried out to obtain the tetrathiol and switching to 1,2-*o*-carboranedithiol turns out to be somewhat working but isolation of the tetrathiol was never achieved. This might be decomposition or unwanted reaction of the tetrathiol with air or moisture because of the presence of electron rich sulfur atoms. While isolated and optimized yield along with the crystal structures have not been obtained, the protocol has opened up a hopeful avenue to synthesize the tetramercaptocarborane. Scheme 1.3 shows the synthetic route that has been employed to synthesize the tetrathiol.¹⁸



Scheme 1.3. Synthesis attempt of *o*-carboranetetrathiol

1.6. Transition Metal Assisted B-H Bond Activation of *ortho*-carborane

Icosahedral carboranes often are studied for activation of B-H vertices. An efficient synthetic route to activate the B-H bonds is desired and can be induced by several approaches. Our study focused on the activation of B-H vertices of *ortho*-carborane and its derivative- 1,2-(COOH)₂-*o*-carborane by using some transition

metal coordination compounds. Most importantly, transition metal assisted B-H functionalization has been emerging field of studies these days. The chemical functionalization of carboranes towards selective and straightforward B-H activation has been proved to be challenging in comparison with the facile derivatization at the C-H vertices because sometimes directing groups attached to C-H vertex like –COOH are required to activate the B-H and there is not any fixed and specific route reported so far for B-H activation. Whereas deprotonation using base is the most widely used C-H functionalization route. Transition metal catalyzed or promoted B-H activation has been observed in various cases. Different carboranyl ligands having sulfur, phosphorous and nitrogen as donor atoms have played important role to activate the B-H bond. Formation of B-S bond has already been discussed earlier in this chapter, which is itself a versatile B-H activation mode. Similarly, B-N, B-P and B-C activation modes have already been successful in carboranes.²³

Metal atoms π -bonded to carborane ligand are common and widely studied.²⁴ Meanwhile, less well known complexes in which the metal atom is σ -bonded to boron or carbon have also been prepared at ambient temperature is a good and facile example of B-H activation.²⁵ The facile intramolecular *ortho*-metalation observed in $(PPh_3)_3IrCl$ opened up the plausibility of activation of B-H via intramolecular oxidative addition.²⁵ This stimulated the drive for the intermolecular oxidative addition of Iridium at B (3) position when *ortho*-carborane was reacted with $(PPh_3)_3IrCl$ in refluxing toluene (figure 3). Additionally, carboranyl ligands with N and S as donor atoms could also be good choice to stabilize the

metal centers and activating the B-H bonds of carborane cage. Carboranyl-amidinate sulfides [1-S-2-C(NR)(NHR)(closo-1,2-C₂B₁₀H₁₀)]-R = iPr, Cy) (Figure 1.3) in THF at ambient temperature, generated a series of B(3) position activated products.^{23,26} (Scheme 1.4) Half sandwich iridium complexes are efficient reagents to induce B-H bond activation resulting metal boryl complexes.²⁷ Regioselective B-H bond activation occurred when 1,2-(COOH)₂-*o*-carborane is reacted with dicationic Cp*Ir fragment activating B(4,7) positions (figure 1.3).²⁸

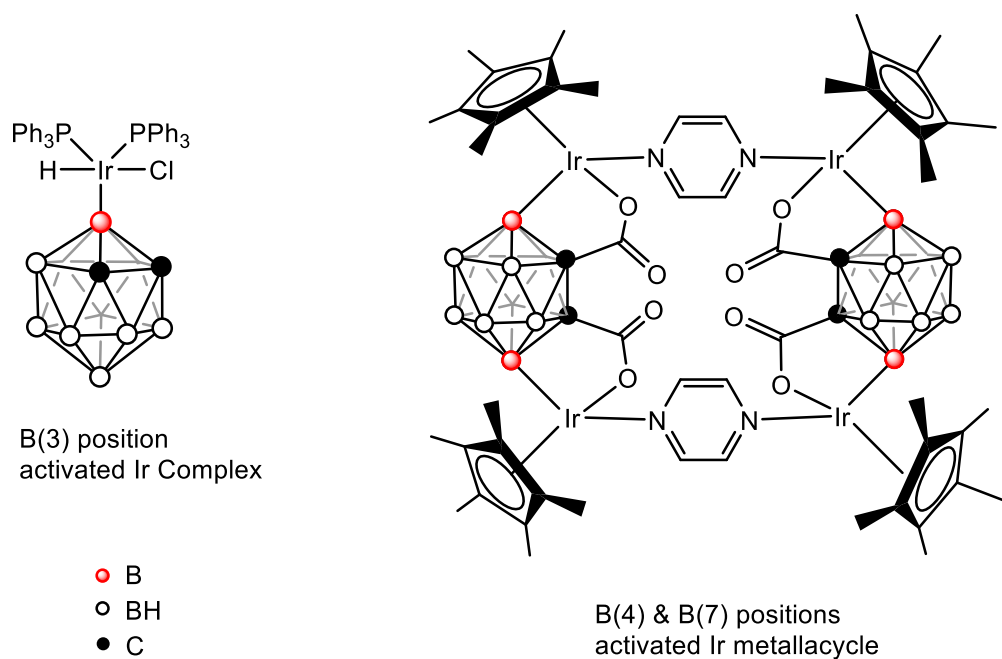
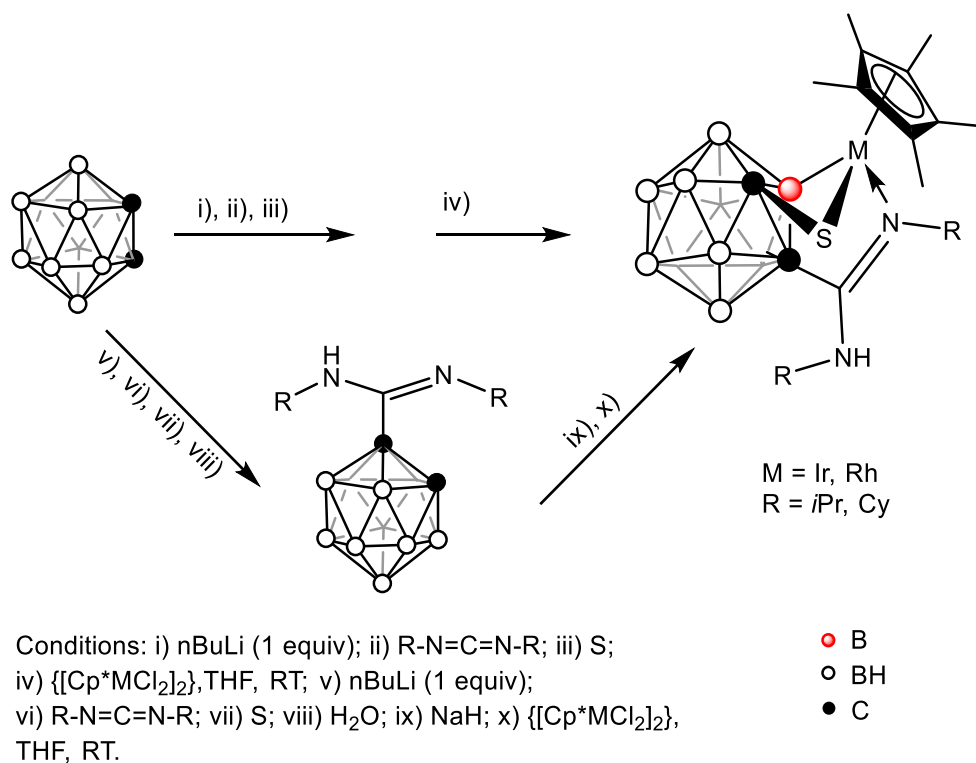


Figure 1.3. B-H activated Ir metal *ortho*-carborane derivatives

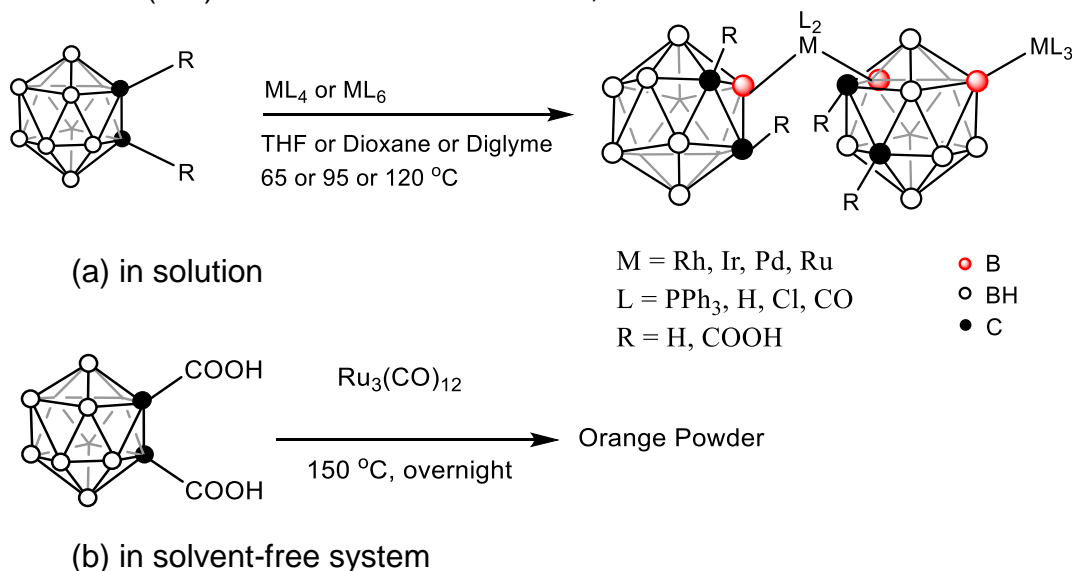


Scheme 1.4. Synthesis of carboranylaminidate sulfide complexes

With the drive from the above discussed B-H activation modes, several approaches for B-H functionalization of *ortho*-carborane and 1,2-(COOH)₂-*ortho*-carborane have been tried. -COOH groups attached to C-H vertices of *o*-carborane could serve as directing group for B-H vertices. For examples iridium mediated metallacycles have been synthesized which shows -COOH group directing to activate B(4) and B(7) positions of the cage. Anticipation of such activation can also be expected when these clusters are subjected to high temperatures using polar solvents like diglyme. B(3) position activated metal complexes can be expected upon heating up to 65 – 160 °C these clusters with rhodium or iridium compounds. It is quite rational to obtain some polymer crystals of carboranyl

rhodium or iridium containing complexes. Solid state reactions of *ortho*-carborane and ruthenium carbonyl at high temperature could activate B-H vertices.

Reaction of different molar ratios of *ortho*-carborane or 1,2-(COOH)₂-*ortho*-carborane with Wilkinson's catalyst (Rh(PPh₃)₃Cl), Rhodium chloride hydrate in different solvents like THF, dioxane, toluene and diglyme have been attempted to synthesize polymeric metal complexes (Scheme 1.5) where transition metal might activate B(3) or B(8) positions. While the anticipated products were not obtained, the idea directed us to investigate the reactivity without using any solvents. Therefore, reaction of *ortho*-carborane with ruthenium carbonyl in a sealed tube at 150 °C produced an unidentified orange product. IR studies were carried in order to compare the IR stretching frequencies of ruthenium carbonyl. The observed IR data for Ru₃(CO)₁₂ in hexane are 2060 cm⁻¹, 2030 cm⁻¹ and 2011 cm⁻¹.

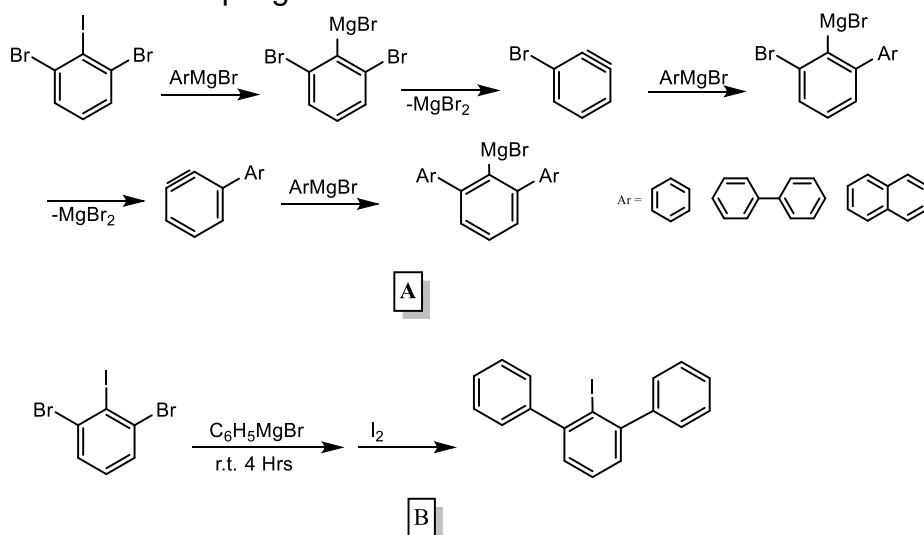


Scheme 1.5. B-H activation by transition metals

CHAPTER 2

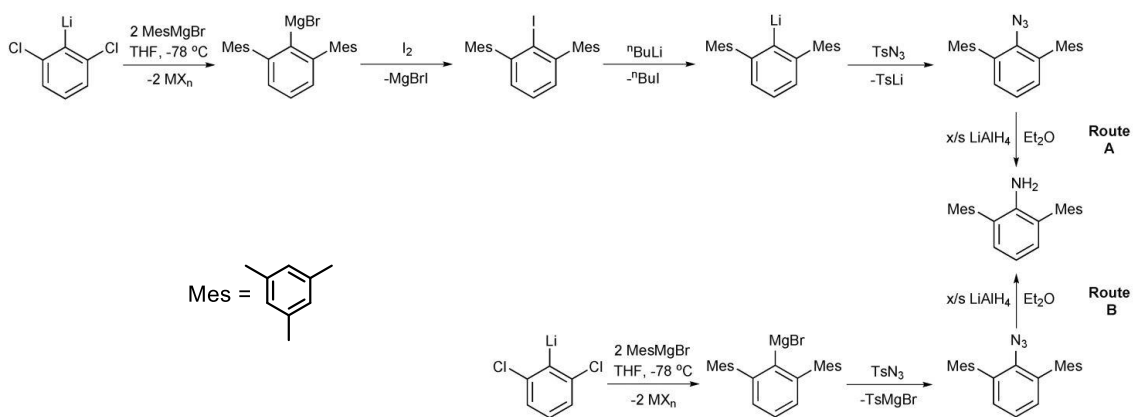
SYNTHESIS OF *m*-TERPHENYL ANILINE FOR CYCLIZATION

m-Terephenyls are important class of organic compounds because of the use of their steric pocket that can be important to study the reactivity with main group elements and transition metals. They have been synthesized from various methods. Phenyl rings with three halogen atoms can undergo selective halogen-metal exchange reaction to give Grignard reagent followed by nucleophilic addition on meta positions due to steric and electronic reasons to produce the terphenyls.²⁹ However, this is not only the synthetic route available in literature. The following scheme, 2.1A, shows the mechanistic route for the synthesis of *m*-terphenyls and scheme 2.1B shows an improved and superior literature route involving an Ullmann cross-coupling.²⁹



Scheme 2.1. Synthetic routes of *m*-terphenyls

Sterically bulkier amines have been obtained much more importance because they are excellent for tuning with respect to the steric pocket they provide. These sterically crowded compounds can be versatile ligands from main group elements to transition metals like Tantalum and Thallium.^{30,31} For instance, tantalum alkyl and silyl complexes of terphenyl imido ligand suggests switching of functionality of amino group for bonding modes with transition metal.³⁰ More sterically hindering amides that are based upon the terphenyl substituent, has been used to stabilize a variety of low coordinate main group element species.^{32,33} Additionally, it is necessary to note that tuning the central atom of the framework ring is to provide altered ligation properties. Accordingly, m-terphenyl attached with aryloxides³⁴, thiolates³⁵, amidos³⁰, imidos²⁹ and carboxylates³⁶ have been reported in literature. These compounds have been used as ancillary ligands for both transition and main group elements. However, terphenyl ligand with a donor atom in the central ring and an acceptor heteroatom on the branched phenyl ring or vice-versa, could be quite interesting. Figure 2.1 shown below are some reported terphenyl ligands with amino group on the central phenyl ring. The scheme 2.2 below shows the two most important routes (A and B) for the synthesis of terphenyl ligands.^{33,37,38}



Scheme 2.2. Synthesis of 2, 6-Mes₂-C₆H₃NH₂ via multistep process (route A) and by a modified two-pot process (route B).

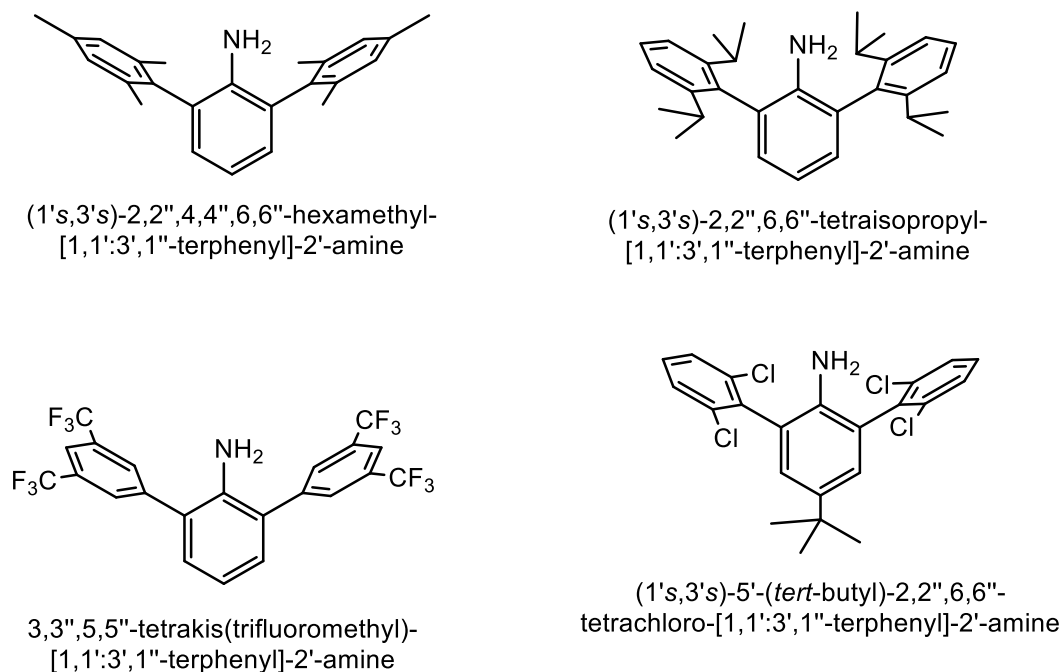
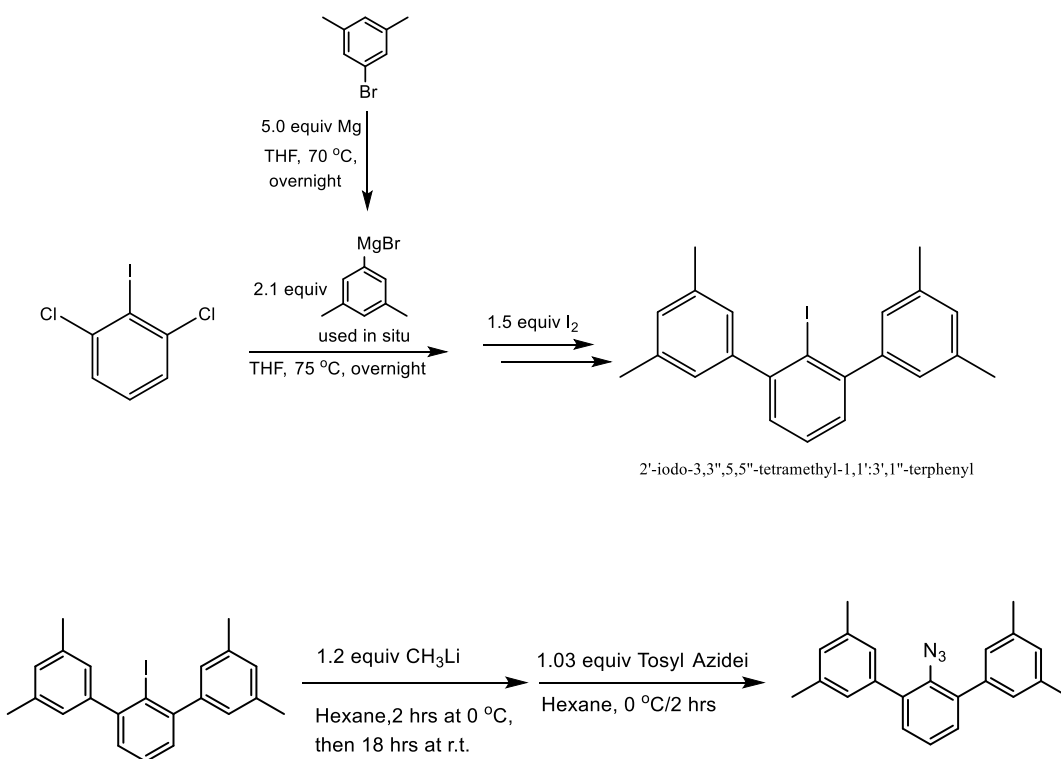


Figure 2.1. Some of the reported terphenyl amines

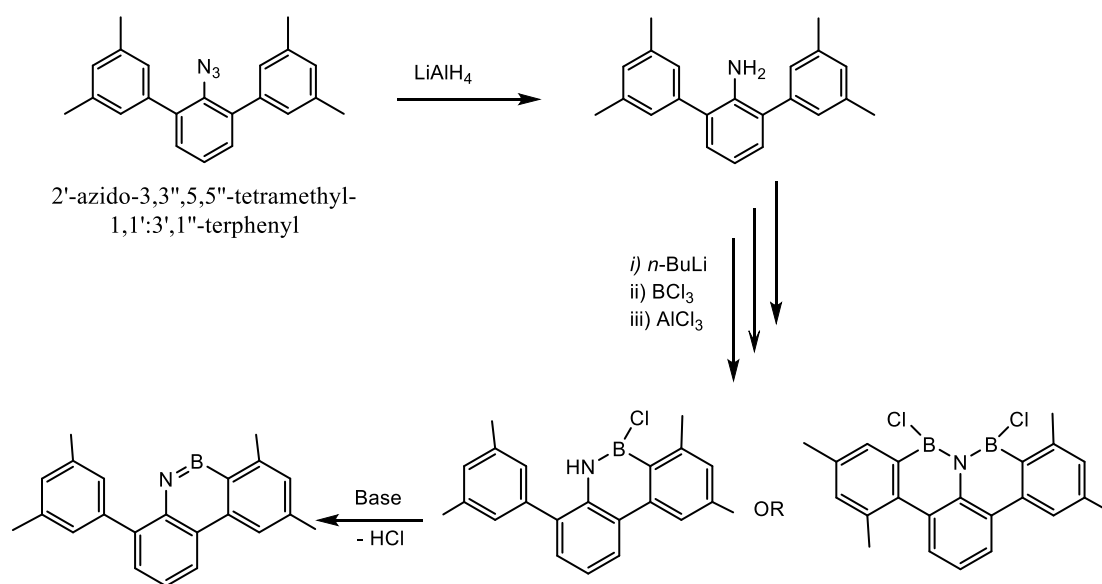
The synthesis of novel terphenyl ligand is discussed here. The synthesis of 2'-iodo-3,3'',5,5''-tetramethyl-1,1',3',1''-terphenyl (Scheme 2.3) in a good yield, has set up foundation to synthesize the amino version. The coupling aryl Grignard

reagent is prepared in situ from 1-bromo-3,5-dimethylbenzene and magnesium metal.



Scheme 2.3. Synthesis of terphenyl iodide and azide

However, the synthesis of iodide into amine employing the route in scheme 2.4 ended up with a mixture of products and was confirmed by ¹H NMR experiment and mass spectroscopy. Isolation of the amine from the mixture would direct to the attempted cyclization of the amino terphenyl (scheme 2.4).



Scheme 2.4. Conversion of terphenyl azide into amine followed by cyclization via borylation

The *m*-terphenyl aniline we wish to synthesize is aimed to employ for the cyclization using boron trichloride (scheme 2.4). This compound would be interesting in the sense that it has nitrogen as a donor atom on the central phenyl ring and electron deficient boron atom attached on the substituted phenyl ring, forming a 6 membered C₄BN ring. Substitution of both amino protons might form two C₄BN rings. Such cyclic incorporation of hetero atom containing ring could change the planarity of phenyl rings and could also tune interesting electronic and optical properties. Several synthetic routes to synthesize the terphenyl aniline has been employed but separation and purification to the optimized yield has not been satisfactory to move on further.

CHAPTER 3

EXPERIMENTAL SECTION

Materials and general considerations

1,2-*o*-carboranedithiol, 9,12-*o*-carboranedithiol and 1,2-(COOH)₂-*ortho*-carborane were prepared according to literature procedures.^{11,18} (C₆H₅CN)₂PdCl₂, Ru₃(CO)₁₂, RuCl₂(PPh₃)₃, NiCl₂(PPh₃)₂, PdCl₂(PPh₃)₂, S₂Cl₂, NaBH₄, AlCl₃, K₂CO₃, 1-bromo-3,5-dimethylbenzene and 1,3-dichloro-2-iodobenzene were purchased from various chemical companies and used as received. Only dry solvents were used in the experiment. Most of the reactions were performed in standard schlenk line technique unless otherwise noted. ¹H, ³¹P and ¹¹B NMR spectra were obtained from Bruker Advance III-HD 300 and 400 MHz Spectrometer.

3.1. Reactions of bis(benzonitrile)dichloridepalladium(II) [(C₆H₅CN)₂PdCl₂]

With 1, 2-(COOH)₂-*ortho*-carborane and *ortho*-carborane

In four teflon screw cap tubes with magnetic stir bars, 15 mg 1,2-(COOH)₂-*ortho*-carborane dissolved in 1.5 ml toluene and labeled A through D. The other reagents were added as follows. Tube A - 1.0 equiv. (C₆H₅CN)₂PdCl₂, Tube B - 1.0 equiv. (C₆H₅CN)₂PdCl₂ and 2.5 equiv. triethylamine, Tube C - 2.0 equiv. (C₆H₅CN)₂PdCl₂ and Tube D - 2.0 equiv. (C₆H₅CN)₂PdCl₂ and 2.5 equiv.

triethylamine. Nothing changed (color of mixtures and NMR experiment results) when the tubes with reaction mixtures were stirred at room temperature for 24 hours. Then the reaction mixtures were submerged in a pre-heated oil bath at 90 °C and stirred for 18 hours. The reaction did not happen and same experimental set up was employed to repeat the reaction using diglyme as solvent at 120 °C. In both of cases, brownish black precipitate was observed and ¹¹B NMR experiments revealed decarboxylation of the carboranyl dicarboxylate. Same experiments were performed where *ortho*-carborane and (C₆H₅CN)₂PdCl₂ were heated at 120 °C. Unfortunately, reactions did not take place rather (C₆H₅CN)₂PdCl₂ decomposed into free palladium.

With 1,2-*o*-carboranedithiol and 9,12-*o*-carboranedithiol

20 mg of 1,2-*o*-carboranedithiol or 9,12-*o*-carboranedithiol was dissolved in 2 ml of dry THF in an overnight dried 20 ml vial. 2.5 equiv. of trimethylamine was added and stirred for 15 minutes. Then 1.0 equiv. of (C₆H₅CN)₂PdCl₂ was added. The reddish colored reaction mixture stirred at room temperature, where no reaction was observed. Then the reaction was heated for 15 hours at 55 °C. Formation of brownish or blackish precipitate and NMR monitoring confirmed the decomposition of (C₆H₅CN)₂PdCl₂. Same reaction conditions were repeated taking 2.0 equiv. of (C₆H₅CN)₂PdCl₂, but the desired product was not obtained.

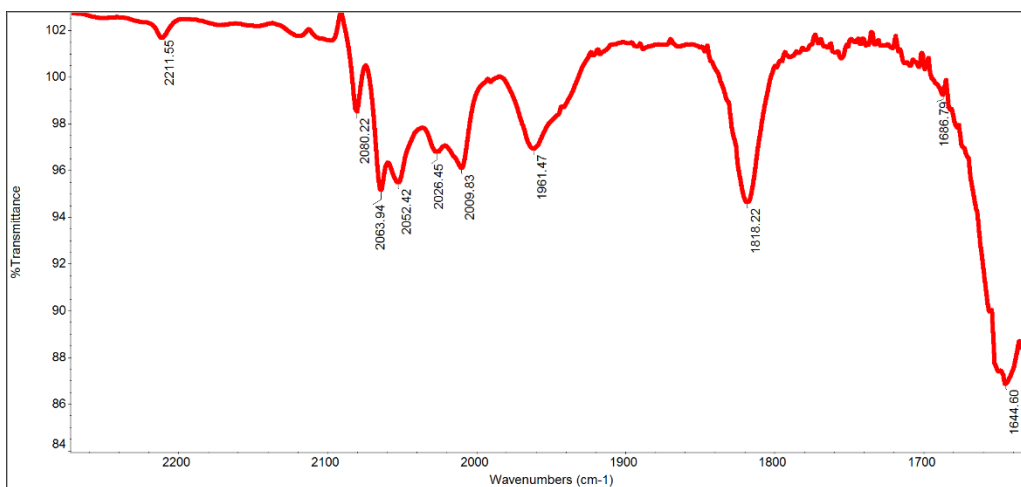
3.2. Reactions of Ruthenium Carbonyl [Ru₃(CO)₁₂]

With 1,2-*o*-carboranedithiol and 9,12-*o*-carboranedithiol

The following reaction was performed inside the glovebox and work up was done under the fume hood after the completion of reaction. 10 mg of each of the 1,2-*o*-carboranedithiol and 9,12-*o*-carboranedithiol were dissolved in 2 ml of toluene separately in two 20 ml vials. Then 23 mg (1.0 equiv.) of Ru₃(CO)₁₂ and heated for 15 hours at 60 °C and checked NMR. While no reactivity observed, the reaction mixtures were further heated to 80 °C for another 15 hours. The rough yellowish reaction mixtures were NMR monitored but no reactivity observed in any of the cases.

With *ortho*-carborane

While no reactivity was observed by heating *ortho*-carborane and Ru₃(CO)₁₂ in toluene at 90 °C, the following reaction was carried out without using solvents. 4 mg of *ortho*-carborane and 27.5 mg (1.0 equiv) Ru₃(CO)₁₂ were sealed in pyrex glass tube and heated overnight at 150 °C. While the crystals formed diffracted poorly, the orange colored reaction solids were extracted with THF and IR was taken suggesting some reactivity as shown in the spectra 3.1.



* Reported IR data for $\text{Ru}_3(\text{CO})_{12}$ in hexane: 2060, 2030 and 2011 cm^{-1}

Spectra 3.1. IR spectra from the reaction between *o*-carborane and $\text{Ru}_3(\text{CO})_{12}$ in THF

3.3. Reactions of Dichlorotris(triphenylphosphine)ruthenium(II) [$\text{RuCl}_2(\text{PPh}_3)_3$]

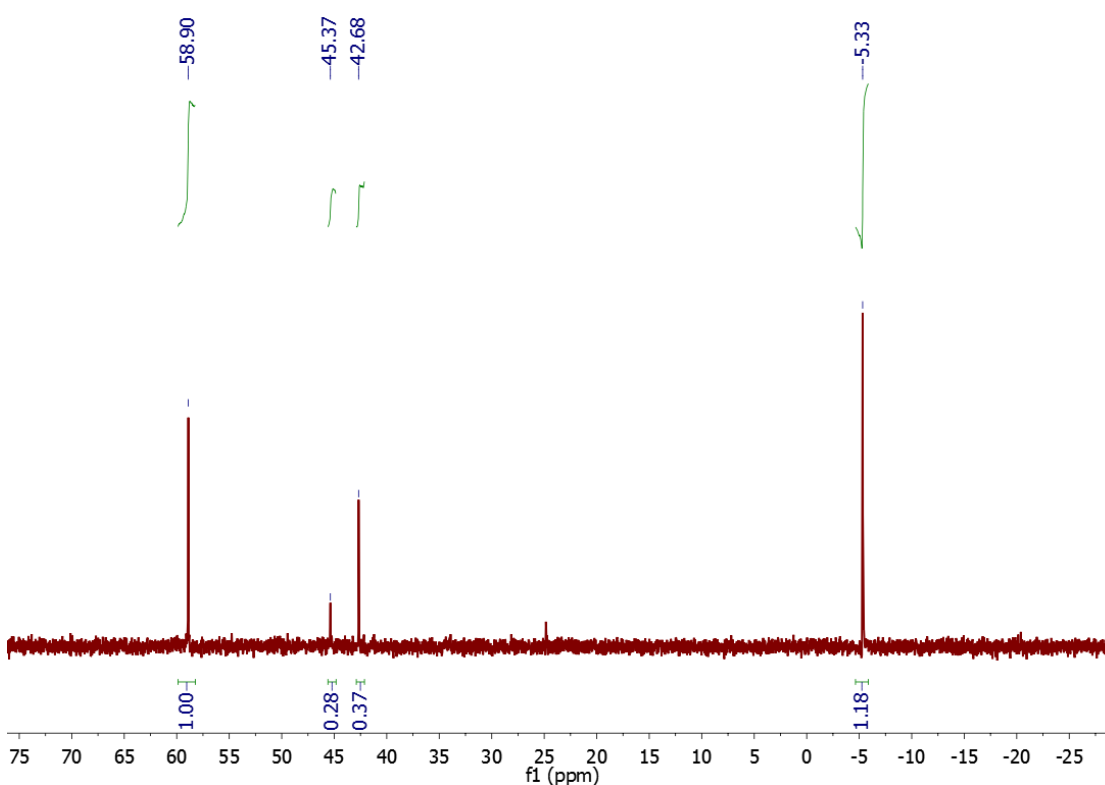
With 9,12-*o*-carboranedithiol

The following reaction was performed inside glovebox. 4 mg 9,12-*o*-carboranedithiol was dissolved in 2 ml of C_6D_6 and 2.5 equiv. of triethylamine was added. After stirring for 15 minutes, 1.0 equiv. of $\text{RuCl}_2(\text{PPh}_3)_3$ was added. The reaction mixture was stirred at room temperature overnight. Then the reaction mixture was filtered and solvent allowed to evaporate overnight. Suitable crystals were grown using acetonitrile, which turned out to be triphenylphosphonium oxide.

With 1,2-*o*-carboranedithiol

The following reaction was performed inside glovebox. 19 mg 1,2-*o*-carboranedithiol was dissolved in 2 ml of C_6D_6 and excess of triethylamine was

added. After stirring for 15 minutes, 1.0 equiv. of $\text{RuCl}_2(\text{PPh}_3)_3$ was added and the reaction mixture was stirred at room temperature. Then the reaction mixture was filtered. The solvent was allowed to evaporate overnight and washed several times with minimal amount of hexane. Then suitable crystals were grown using acetonitrile. Unfortunately, new peaks at 58.8 ppm and 45.3 ppm in ^{31}P NMR were not confirmed if the desired product was obtained because of poor crystals.



Spectra 3.2. ^{31}P NMR of crude product after the reaction between 1,2-*o*-carboranedithiol and $\text{RuCl}_2(\text{PPh}_3)_3$

3.4. Reactions of Bis(triphenylphosphine)nickel(II) dichloride $[\text{NiCl}_2(\text{PPh}_3)_2]$

With 9,12-*o*-carboranedithiol

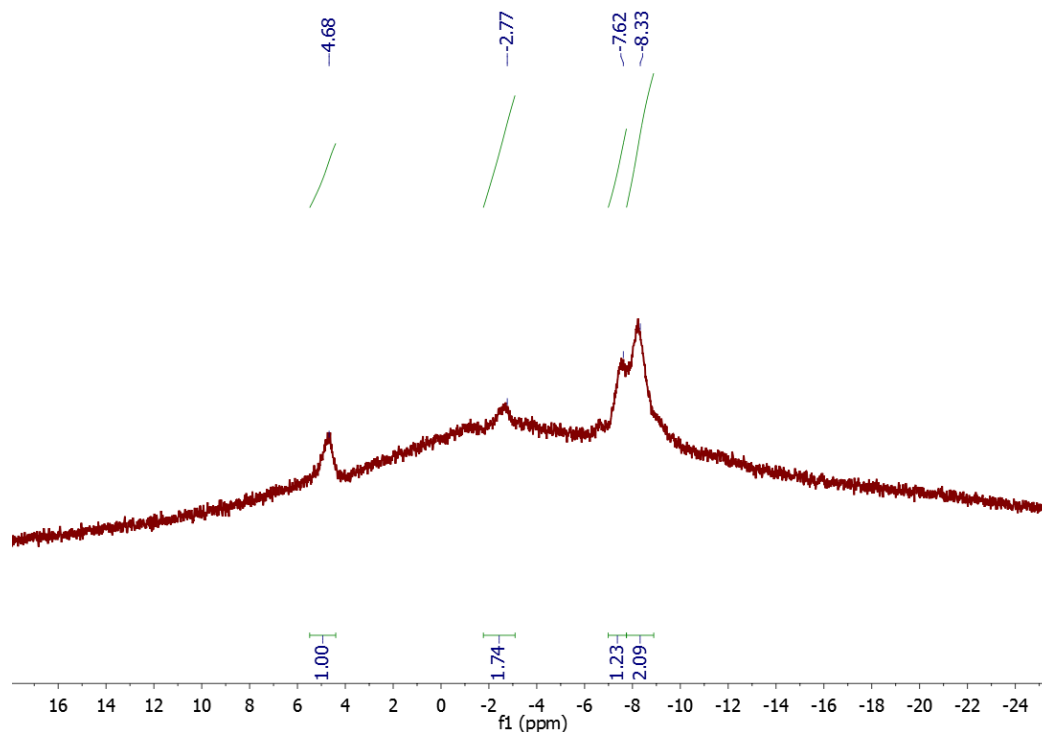
10.1 mg of 9,12-*o*-carboranedithiol was dissolved in 2 ml of dry THF and 2.5 equiv. of triethylamine was added and stirred for 15 minutes. 1.0 equiv. of

$\text{NiCl}_2(\text{PPh}_3)_2$ was added and stirred for 15 hours at room temperature. Solvent was removed in rotovap from slightly greenish yellow reaction mixture. Then solids were washed with several times with hexane and crystals were grown from ether/hexane, which turned out to be starting dithiol. Similar experiment was performed using 1,2-*o*-carboranedithiol, where our anticipated products were not formed.

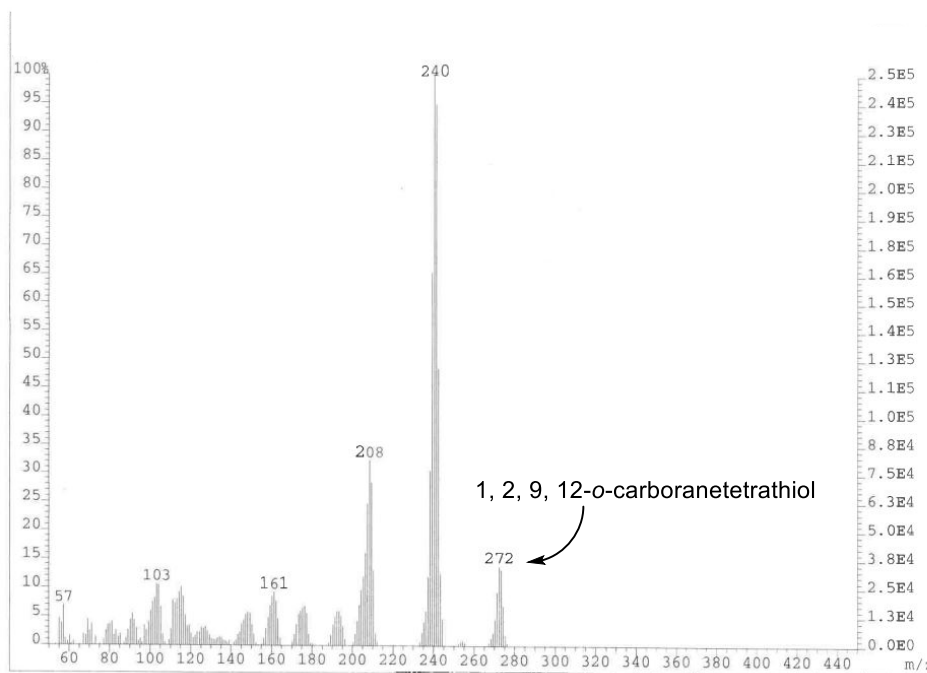
3.5. Synthesis attempt of 1,2,9,12-*o*-carboranetetrathiol

In a 50 ml schlenk flask, 0.58 g (4.4 mmol, 3.03 equiv) of anhydrous AlCl_3 was added to a solution of 0.3 g (1.4 mmol) of 1,2-*o*-carboranedithiol in 20 ml of dichloromethane at 0 °C in an inert atmosphere of N_2 . Then 2.02 equiv. of S_2Cl_2 was added slowly and dropwise during 10 minutes. The reaction allowed to reach room temperature and boiled at 40 °C in a preheated oil bath for 5-6 hours. The yellow color solution turned red during the course of reaction indicating the formation of polysulfide. The reaction was monitored by TLC. After cooling the reaction mixture, the red solution was poured into 50 ml of DI water. The yellowish white precipitate obtained was washed several times with water and dried. Then the precipitate was dissolved in 20 ml of 2% NaOH alcohol solution. 1.0 equivalence of NaBH_4 was added slowly and stirred for 15 hours at room temperature. The solution was poured into 30 ml of water and filtered solution was saturated by adding pieces of dry ice. The precipitate obtained was extracted with diethyl ether. Solvents were removed after drying organic layers with MgSO_4 . While no suitable crystals were not obtained, mass spectroscopy and ^{11}B NMR showed the possibility of the formation of the tetrathiol. The chemical shifts

(Spectra 3.3) in ^{11}B NMR experiments revealed the intact carborane cage but isolation and crystallization of the expected product was not achieved.



Spectra 3.3. ^{11}B NMR spectra of 1,2,9,12-*o*-carboranetetrathiol (confirmation not yet by crystal structure)



Spectra 3.4. Mass spectrum of 1,2,9,12-*o*-carboranetetrathiol

3.6. Reaction of 9,12-*o*-carboranedithiol with bis(triphenylphosphine)palladium chloride [PdCl₂(PPh₃)₂]

10 mg of 9,12-*o*-carboranedithiol was dissolved in 2 ml of dry THF in a 20 ml vial and 2.5 equiv. triethylamine was added and stirred for 15 minutes. 1.0 equiv. of PdCl₂(PPh₃)₂ was added and reaction mixture was stirred for 24 hours at room temperature. During the course of reaction, the yellowish solution changed dark orange. THF was then removed and obtained solids washed several times with hexane. This reaction can also be performed using dichloromethane as solvent and excess of anhydrous K₂CO₃ for deprotonation of thiol protons. Recrystallization of solid from ether/hexane afforded orange crystals. However, those crystals diffracted poorly and the exact product obtained was not concluded.

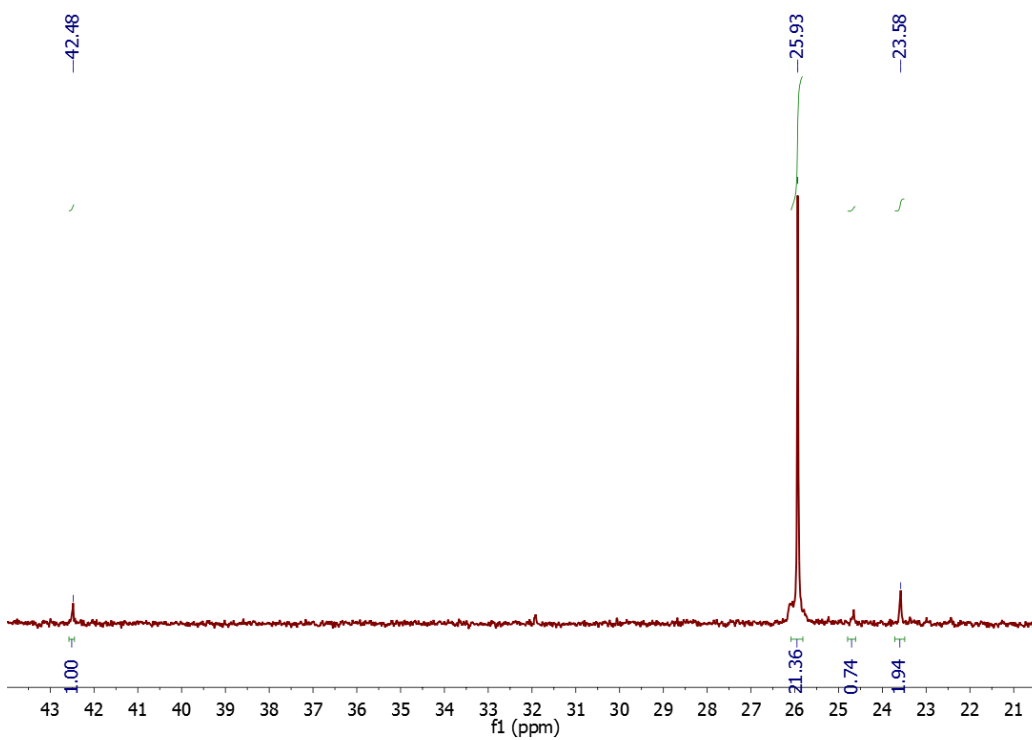
3.7. Synthesis of Bis(triphenylphosphine)palladium carboranyl dithiolate (PdC₂B₁₀S₂(PPh₃)₂) complex

Method A

10 mg of 1,2-*o*-carboranedithiol was dissolved in 15 ml dry THF in a schlenk flask. 2.02 equiv. of *n*BuLi (1.6 M in hexane) was added at 0 °C and stirred overnight at room temperature. Then 1.0 equiv. of PdCl₂(PPh₃)₂ was added. The reaction mixture was stirred for 3 hours at room temperature and THF was removed using rotovap. Then the product was extracted with minimal amount of wet ether (3x) and dried with MgSO₄. After filtration, solvent was removed and the solid was recrystallized using diethyl ether/hexane (~1.5 ml/ 3 drops from disposable pipete), which afforded yellow crystals.

Method B

In a 20 ml vial with a magnetic stir bar, 10 mg of 1, 2-*o*-carboranedithiol was dissolved in 2 ml of dry dichloromethane and 4.5 equiv. of anhydrous K_2CO_3 was added and stirred for 15 minutes. Then 1.0 equiv. of $PdCl_2(PPh_3)_2$ was added and the reaction mixture was stirred for 21 hours at room temperature during which yellow solution turned dark orange. Then ^{31}P NMR experiment was performed to monitor the reaction. The reaction was further stirred for 9 hours at room temperature and filtered. The solvent was then removed and washed with hexane several times. Recrystallization of the products from ether/hexane (~1.5 ml/ 3 drops from disposable pipete) produced yellow crystals. The product was confirmed by ^{31}P NMR experiment and crystal structure. ^{31}P NMR (C_6D_6) 25.92 ppm

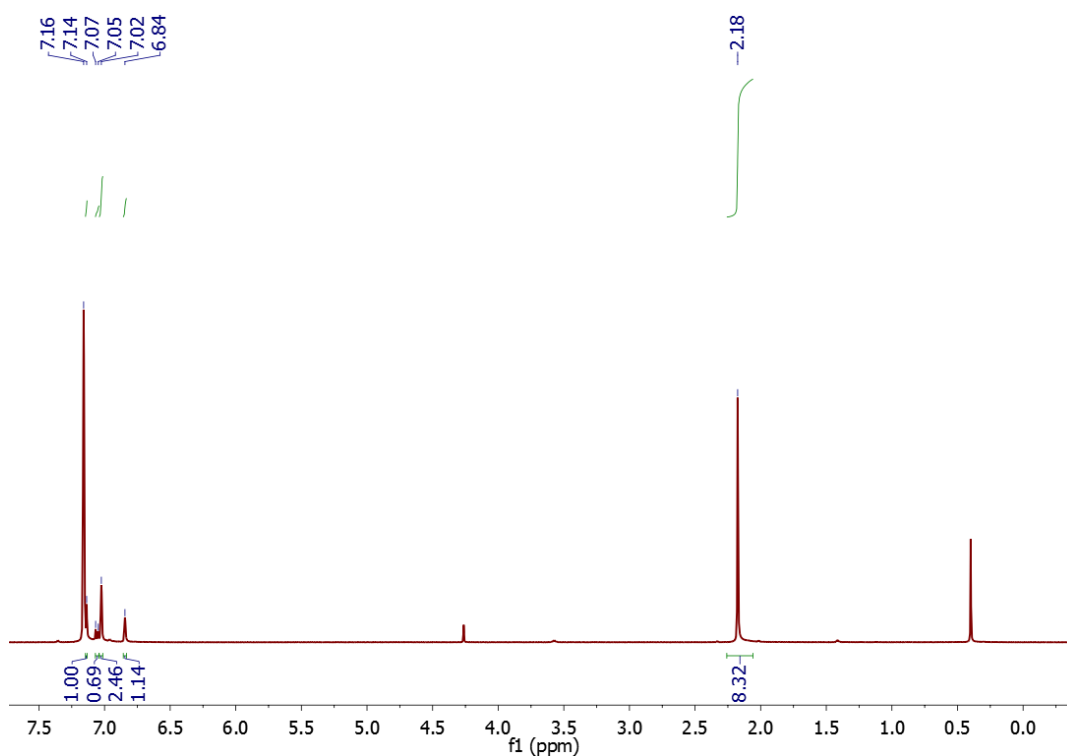


Spectra 3.5. ^{31}P spectra of $PdC_2B_{10}S_2(PPh_3)_2$ complex

3.8. Synthesis of terephenyl iodide (2'-iodo-3,3',5,5''-tetramethyl-1,1',3',1''-terphenyl) [Ar*I]

A 500 ml three neck RB flask was charged with a magnetic stir bar and 6.701 g (5.0 equiv.) of Mg metal. The middle neck was connected to a reflux condenser, septa on one side arm and an addition funnel on the other neck. After flushing the flask with N₂ from the schlenk line, the system was made airtight. Then about 300 ml of dry THF from a storage flask was transferred to the three-neck flask via cannula. About 75 ml of the THF was also transferred to addition funnel to dilute 1-bromo-3,5-dimethylbenzene before addition. The system was kept refluxing at 70 °C in an oil bath. 21.365 g (115.5 mmols, 2.1 equiv.) of 1-bromo-3,5-dimethylbenzene was dissolved in 50 ml THF in a separate one neck RB flask and transferred to the addition funnel using a syringe. After adding 1-2 ml of 1, 2-dibromoethane to activate Mg metal, 1-bromo-3,5-dimethylbenzene solution was slowly added to the main flask and refluxed for 15 hours at 70 °C. The following day, 15 g (1.0 equiv.) of 1,3-dichloro-2-iodobenzene solution (prepared by dissolving in 50 ml THF in a flask and flushing with nitrogen), was added slowly in portions (10 minutes interval) via long needle and syringe. After addition was complete, the reaction mixture is kept refluxing for 15 hours at 75 °C. Then the reaction was allowed to cool to room temperature. The reaction mixture is now transferred via cannula to a 2L one-neck RB flask kept at ice bath containing 21 g (1.5 equiv.) of I₂ dissolved in 50 ml THF. Then 200 ml of DI water was added. After removal of ice bath, calculated amount of sodium sulfite (1 to 1 moles with I₂) was added and the reaction mixture stirred until the red color turned light yellow.

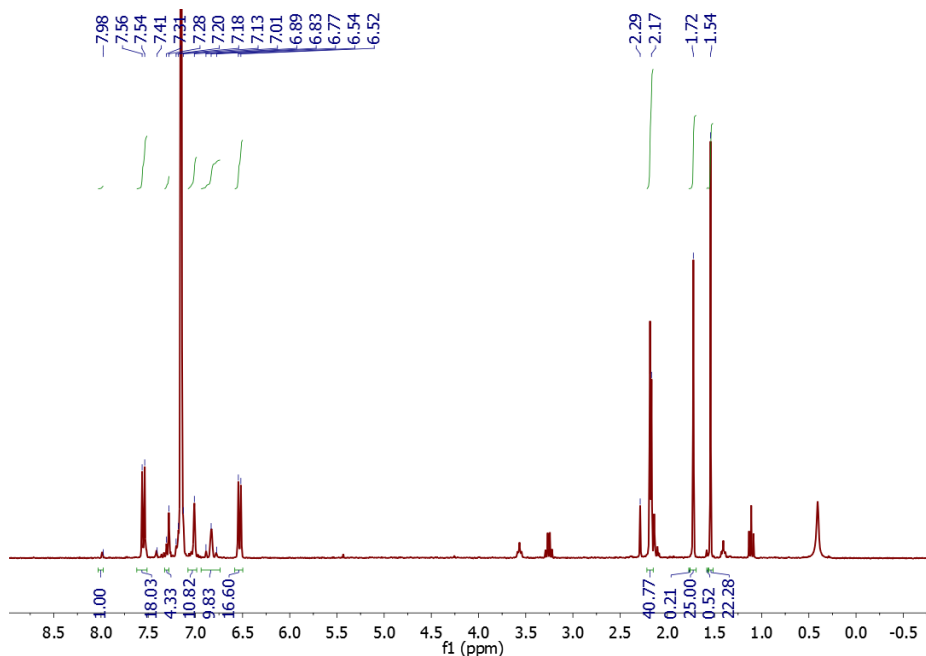
Sodium sulfite was filtered and organic layers separated from aqueous layer using diethyl ether. Aqueous layers washed with ether three times. The combined organic layers dried with $MgSO_4$ and solvents were removed using rotovap. The thick oily liquid obtained was recrystallized with ether/methanol/hexane (5:5:1 by volume). The yellowish white crystals of Ar*I was washed several times with cold methanol. The product was confirmed by mass spectroscopy and 1H NMR. The remaining mother liquor also afforded crystals of the product after repeated recrystallization. Total Yield ~ 60 %



Spectra 3.6. 1H NMR (C_6D_6) spectra of terphenyl iodide

3.9. Synthesis attempts of 2'-azido-3,3'',5,5''-tetramethyl-1,1':3',1''-terphenyl [Ar*N₃]

In a 50 ml schlenk flask, 121 mg (0.3 mmol) of Ar*I in 15 ml of dry hexane was added slowly and dropwise of MeLi (1.6 M in hexane, 1.2 equiv.) at 0 °C. After addition was completed in 15 minutes, the reaction mixture was stirred for 18 hours at room temperature. Then 1.02 equiv. of tosyl azide was added dropwise over 5 minute at 0 °C. After stirring for 2 hours at room temperature, the reaction mixture was quenched by wet diethyl ether and further stirred for 1 hour. The yellow solution obtained was filtered from insoluble solids and dried with MgSO₄. Removal of solvents afforded dark orange crystalline solids. Recrystallization from minimal amount of diethyl ether/hexane (2 ml/0.5 ml) afforded unidentified orange crystals at bottom of vial and needle shaped colorless crystals mixed with orange crystals.



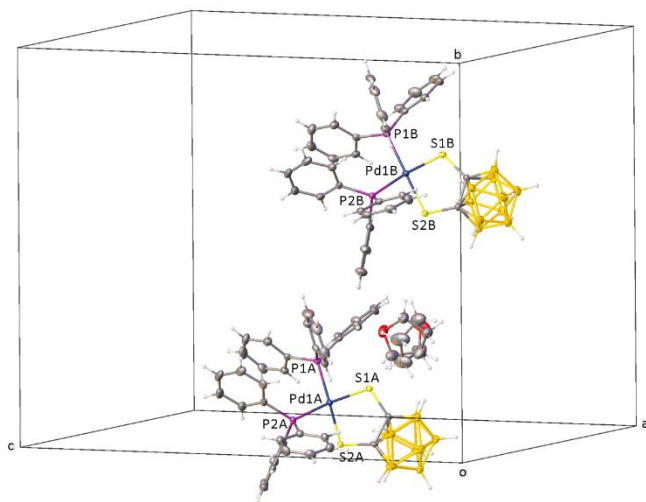
Spectra 3.7. ¹H NMR (C₆D₆) spectra of mixture of products

CHAPTER 4

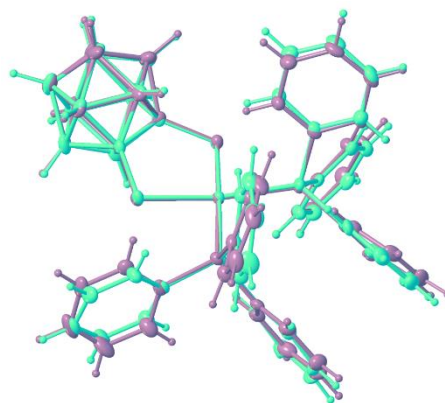
RESULTS AND DISCUSSION

4.1. Synthesis and reactivity of $\text{PdCl}_2(\text{PPh}_3)_2$ with *ortho*-carboranedithiols

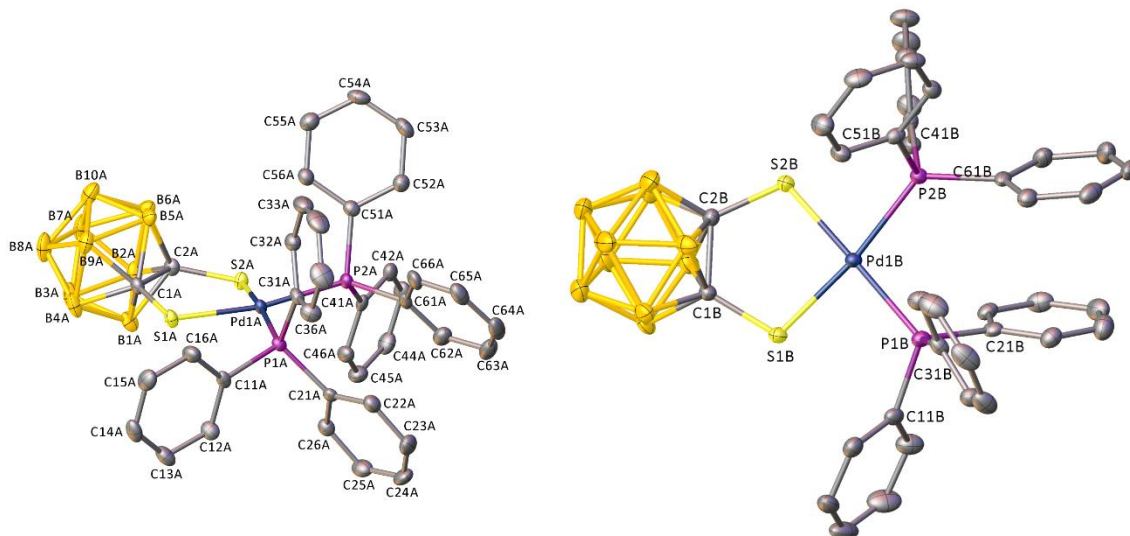
Square planar $\text{PdCl}_2(\text{PPh}_3)_2$ is a good candidate for the construction of palladium metal coordination to sulfur atoms of carboranedithiols. The electron donating carboranyl group increases electron density at the sulfur atoms of 1, 2-*o*-carboranedithiol. Therefore, deprotonating the thiol protons by using the bases like *n*Buli or K_2CO_3 replaced chlorine atoms forming Pd-S bond and most likely prevents the B-H activation of the carborane cage. So square planar Bis(triphenylphosphine)palladium carboranyl dithiolate ($\text{PdC}_2\text{B}_{10}\text{S}_2(\text{PPh}_3)_2$) complex is formed as expected (scheme 1. 2) in a good yield (~45% yield). The compound crystallizes in the monoclinic system and is consistent with the space group P21/c. The asymmetric unit consists of two crystallographically independent but chemically identical $\text{Pd}(\text{C}_2\text{H}_{10}\text{B}_{10}\text{S}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ complexes and one THF molecule. The two palladium complexes were numbered identically except for atom label suffixes A or B. Formation of this compound is confirmed by ^{31}P NMR and crystallography (Figure 4.1 & Spectra 1). However, reaction of $\text{PdCl}_2(\text{PPh}_3)_2$ with 9,12-*ortho*-carborane formed a broad signal around 26 ppm in ^{31}P NMR but is not confirmed yet either it formed such Pd-Complex at B-H vertices.



Asymmetric unit of the crystal. Displacement ellipsoids drawn at the 60% probability level. Two crystallographically independent, chemically identical Pd complexes, disordered THF.



Overlay of the two independent complexes.



Displacement ellipsoid plot of the molecular structure of complex A and B. Displacement ellipsoids drawn at the 60% probability level.

Figure 4.1. Crystal structures of $\text{Pd}(\text{C}_2\text{H}_{10}\text{B}_{10}\text{S}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ complexes

Table 4.1. Bond lengths of some selected atoms in Pd(C₂H₁₀B₁₀S₂)(P(C₆H₅)₃)₂ complex

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1A	S1A	2.3148(7)	Pd1B	S1B	2.3138(7)
Pd1A	S2A	2.3268(6)	Pd1B	S2B	2.3401(7)
Pd1A	P1A	2.2906(7)	Pd1B	P1B	2.3136(7)
Pd1A	P2A	2.3160(7)	Pd1B	P2B	2.3257(7)
S1A	C1A	1.785(3)	S2A	C2A	1.778(3)
S2A	C2A	1.778(3)	S2B	C2B	1.779(3)

Table 4.2. Bond angles of some selected atoms in Pd(C₂H₁₀B₁₀S₂)(P(C₆H₅)₃)₂ complex

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1A	Pd1A	S2A	91.75(2)	S1B	Pd1B	S2B	91.08(2)
S1A	Pd1A	P2A	171.07(2)	S1B	Pd1B	P2B	172.25(2)
P1A	Pd1A	S1A	87.44(2)	P1B	Pd1B	S1B	87.36(2)
P1A	Pd1A	S2A	171.98(2)	P1B	Pd1B	S2B	175.06(2)
P1A	Pd1A	P2A	97.55(2)	P1B	Pd1B	P2B	99.11(2)
P2A	Pd1A	S2A	84.32(2)	P2B	Pd1B	S2B	82.82(2)
C1A	S1A	Pd1A	104.28(8)	C1B	S1B	Pd1B	104.57(8)
C2A	S2A	Pd1A	104.35(8)	C2B	S2B	Pd1B	104.45(8)

4.2. Synthesis of terphenyl iodide [Ar*I] and challenges for synthesis of Ar*NH₂

The synthesis of the terphenyl iodide was achieved following synthetic shown in scheme 16A. The chlorides coupled with the in situ prepared grignard reagent (3, 5-dimethylmagnesium bromide) at 75 °C with a good yield. For the synthesis of terphenyl aniline Ar*N₃, a similar synthetic route was followed as shown in scheme 7A but several challenges were faced and did not proceed as we expect. Initially, n-BuLi was chosen to synthesize the lithium salt of the terphenyl as described in the literature, which always formed Ar*H in our case. However, switching to MeLi as deprotonating base was the best choice where formation of azide and amine were observed according to mass spectroscopy. The main problem was the formation of mixture of Ar*H, ArN₃ and ArNH₂. The literature synthetic routes have reported isolated yield of the azide followed by reduction into amines. However, it was observed that quenching the reaction with water killed our desired product into Ar*H as one of the major impurities. Several approaches to separate the azide from its impurities were tried but doing so transformed the suspected azide into some unidentified products. One of approach followed was trituration of azide using cold methanol followed by recrystallization in diethyl/hexane formed crystals, which were not completely resolved by crystallography.

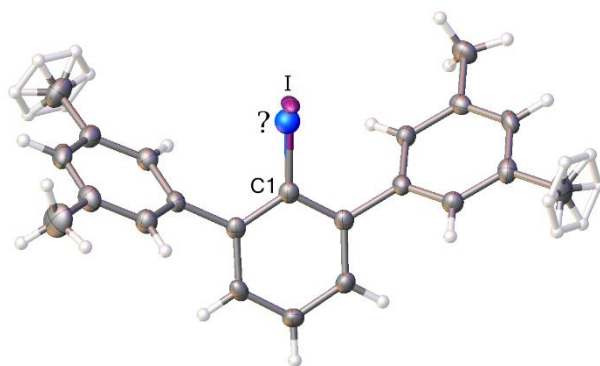


Figure 4.2. Crystal structure from crystals of reaction between Ar*I and tosyl azide (not confirmed whether there is -NH_2 or -N_3 or -I group in the central phenyl ring)

4.3. Conclusion and future perspectives

In summary, a facile route involving the use of either *n*-BuLi or anhydrous potassium carbonate as deprotonating base to synthesize a square planar bis(triphenylphosphine)palladium carboranyl dithiolate ($\text{PdC}_2\text{B}_{10}\text{S}_2(\text{PPh}_3)_2$) complex has been developed. This compound suggests that the 1,2-*o*-carboranedithiol can be a good starting electron donating carboranyl nucleophile to stabilize other transition metals with same geometry. The investigation of the reaction between this dithiol with dichlorotris(triphenylphosphine)ruthenium(II) has opened up a scope to find the plausibility of forming carboranyl dithiolato complexes with geometry other than square planar. Similarly, with the reactivity as suggested by ^{31}P NMR, the 9,12-*o*-carboranedithiol can form such analogue complex given more detail studies and suitable method to grow crystals.

The tetrathiolated carborane would be expected to serve as a versatile ligand for the synthesis of various bimetallic complexes. Those complexes could

be further explored for the possible applications for studying the oxidation-reduction environment in the same complex.

As per the inspiration from the literature, the synthesis of the novel terephenyl iodide (2'-iodo-3,3",5,5"-tetramethyl-1,1',3',1"-terphenyl) has therefore provided strong evidence of versatility of exploiting and tuning the sterically hindered pocket. This synthesis has led to explore a better approach for its conversion into the amino version. These amines could be incorporated with heteroatoms like boron, sulfur, phosphorous, which would again be interesting to study optical, electronic and even the lone pair of electrons of these heteroatoms coordination to transition metals.

REFERENCES

- (1) Plesek, J. *Chemical Reviews* **1992**, *92*, 269.
- (2) Bohn, R. K.; Bohn, M. D. *Inorganic Chemistry* **1971**, *10*, 350.
- (3) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorganic Chemistry* **1963**, *2*, 1089.
- (4) Fein, M. M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorganic Chemistry* **1963**, *2*, 1111.
- (5) Johnson, B. F. G.; Roberts, Y. V.; Parisini, E. *Inorganica Chimica Acta* **1993**, *211*, 17(6) Bregadze, V. I. *Chemical Reviews* **1992**, *92*, 209.
- (7) Davidson, M. G.; Hibbert, T. G.; Howard, J. A. K.; Mackinnon, A.; Wade, K. *Chemical Communications* **1996**, 2285.
- (8) Oliva, J. M.; Schleyer, P. v. R.; Aullon, G.; Burgos, J. I.; Fernandez-Barbero, A.; Alkorta, I. *Physical Chemistry Chemical Physics* **2010**, *12*, 5101.
- (9) Scholz, M.; Hey-Hawkins, E. *Chemical Reviews* **2011**, *111*, 7035.
- (10) Oliva, J. M.; Serrano-Andrés, L.; Klein, D. J.; Schleyer, P. v. R.; Michl, J. *International Journal of Photoenergy* **2009**, *2009*, 9.
- (11) Plesek, J.; Hermanek, S. *Collection of Czechoslovak Chemical Communications* **1979**, *44*, 24.
- (12) Hermansson, K.; Wójcik, M.; Sjöberg, S. *Inorganic Chemistry* **1999**, *38*, 6039.
- (13) Teixidor, F.; Barberà, G.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Inorganic Chemistry* **2006**, *45*, 3496.
- (14) Zakharkin, L. I.; Ogorodnikova, N. A. *Journal of Organometallic Chemistry* **1968**, *12*, 13.
- (15) Smith, H. D.; Obenland, C. O.; Papetti, S. *Inorganic Chemistry* **1966**, *5*, 1013.
- (16) Plesek, J.; Janousek, Z.; Hermanek, S. *Collection of Czechoslovak Chemical Communications* **1980**, *45*, 1775.
- (17) Zhang, X.; Tang, X.; Yang, J.; Li, Y.; Yan, H.; Bregadze, V. I. *Organometallics* **2013**, *32*, 2014.
- (18) Zakharkin, L. I.; Pisareva, I. V. *Journal of Organometallic Chemistry* **1984**, *267*, 73.
- (19) Baše, T.; Bastl, Z.; Šlouf, M.; Klementová, M.; Šubrt, J.; Vetushka, A.; Ledinský, M.; Fejfar, A.; Macháček, J.; Carr, M. J.; Londesborough, M. G. S. *The Journal of Physical Chemistry C* **2008**, *112*, 14446.
- (20) Arumugam, K.; Shaw, M. C.; Chandrasekaran, P.; Villagrán, D.; Gray, T. G.; Mague, J. T.; Donahue, J. P. *Inorganic Chemistry* **2009**, *48*, 10591.
- (21) Won, J.-H.; Kim, D.-H.; Kim, B. Y.; Kim, S.-J.; Lee, C.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 1443.

- (22) Dirk, C. W.; Cox, S. D.; Wellman, D. E.; Wudl, F. *The Journal of Organic Chemistry* **1985**, *50*, 2395.
- (23) Yao, Z.-J.; Jin, G.-X. *Coordination Chemistry Reviews* **2013**, *257*, 2522.
- (24) Miller, V. R.; Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *Journal of the American Chemical Society* **1974**, *96*, 3090.
- (25) Hoel, E. L.; Hawthorne, M. F. *Journal of the American Chemical Society* **1975**, *97*, 6388.
- (26) Yao, Z.-J.; Su, G.; Jin, G.-X. *Chemistry – A European Journal* **2011**, *17*, 13298.
- (27) Yao, Z.-J.; Jin, G.-X. *Organometallics* **2011**, *30*, 5365.
- (28) Yao, Z.-J.; Yu, W.-B.; Lin, Y.-J.; Huang, S.-L.; Li, Z.-H.; Jin, G.-X. *Journal of the American Chemical Society* **2014**, *136*, 2825.
- (29) Du, C. J. F.; Hart, H.; Ng, K. K. D. *The Journal of Organic Chemistry* **1986**, *51*, 3162.
- (30) Gavenonis, J.; Tilley, T. D. *Organometallics* **2002**, *21*, 5549.
- (31) Ditre, T. B.; Carpenter, A. E.; Ripatti, D. S.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorganic Chemistry* **2013**, *52*, 13216.
- (32) Clyburne, J. A. C.; McMullen, N. *Coordination Chemistry Reviews* **2000**, *210*, 73.
- (33) Twamley, B.; Haubrich, S. T.; Power, P. P. In *Adv. Organomet. Chem.*; Robert, W., Anthony, F. H., Eds.; Academic Press: 1999; Vol. Volume 44, p 1.
- (34) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 3428.
- (35) Rekken, B. D.; Brown, T. M.; Fettinger, J. C.; Lips, F.; Tuononen, H. M.; Herber, R. H.; Power, P. P. *Journal of the American Chemical Society* **2013**, *135*, 10134.
- (36) Hagadorn, J. R.; Que, L.; Tolman, W. B.; Prisecaru, I.; Münck, E. *Journal of the American Chemical Society* **1999**, *121*, 9760.
- (37) Kays, D. L. *Chemical Society Reviews* **2016**, *45*, 1004.
- (38) Wright, R. J.; Steiner, J.; Beaini, S.; Power, P. P. *Inorganica Chimica Acta* **2006**, *359*, 1939.