

Zirconocene Derivatives for Dehydrocoupling of Acetylenes
and Carbene-Phosphinidene Adducts and their Metal Complexes

By

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Abstract

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Anionic Group 4 metallocenes have seen a significant amount of attention over the last 20 years with particular interest in titanocene and zirconocene derivatives.¹⁻⁵ The synthesis and characterization of dichlorobis(η^5 -cyclopentadienyl)zirconium (zirconocene dichloride or Cp_2ZrCl_2 where $Cp = \eta^5\text{-C}_5\text{H}_5$) first described in 1954 by Wilkinson and Birmingham spurred extensive research in this field.⁶ A particularly interesting area of these zirconocene derivatives comes from the work by Negishi *et al.* where an anionic zirconocene compound can be oxidized resulting in the coupling of two phenylacetylene molecules.² Similar to the Negishi zirconocene chemistry, Stephan *et al.* published a synthetic route for an anionic zirconocene trihydride.⁷ Using both areas of research as a starting block, a catalytic process was investigated to dehydrocouple phenylacetylene using similar zirconocene derivatives. Although it was confirmed via Nuclear Magnetic Resonance (NMR) spectroscopy that a possible catalytic precursor was formed, no catalysis was successfully completed in this research.

A second aspect of fundamental main group chemistry involves the synthesis of carbene-phosphinidene adducts first described by Arduengo in 1997.⁸ The bonding scenario of the P-C bond of the carbene-phosphinidene adduct was confirmed to have both single and double bond character.⁹ With this unique property in mind, novel carbene-phosphinidene adducts were synthesized and characterized via single crystal X-ray diffraction techniques. Due to the interesting bonding nature of the carbene-phosphinidene adduct, the newly synthesized carbene-phosphinidene adducts were used in attempts to form metal complexes. Preliminary results indicate the formation of the first stable carbene-phosphinidene metal complex. Other preliminary results indicate the possibility of insertion reactions occurring with weaker P-C bonds in the carbene-phosphinidene adducts.

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List of Abbreviations Used

Å	Angstrom
Br	Broad
Cp	cyclopentadiene
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
°	Degrees
°C	Degrees Celsius
C ₆ D ₆	Deuterated benzene
δ	Chemical Shift
DFT	Density functional theory
Dipp	2,6-diisopropylphenyl
dipp diimine	N,N'-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene
dipp diamine	N,N'-bis(2,6-diisopropylphenylamine)ethane
d	Doublet
dppf	1,1'-Bis(diphenylphosphino)ferrocene
EtOH	Ethanol
Et ₂ O	Diethylether
g	Gram
hr	Hour
i-Pr	Isopropyl
IPr	1,3-bis(2,6-diisopropyl) imidizol-2-ylidene
J	Coupling constant
m	Medium, multiplet
MHz	Mega Hertz

mg	Milligram
mL	Milliliters
mmol	Millimole
NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance
ORTEP	Oakridge thermal ellipsoid plot
rt	Room temperature
s	Singlet, seconds, strong
SIPr	1,3-bis(2,6-diisopropylphenyl) imidazolidin-2-ylidene
sept	Septet
THF	Tetrahydrofuran
THF- <i>d</i> ₈	Deuterated tetrahydrofuran
t	Triplet

Introduction

Chapter 1: Zirconocene Derivatives to Couple Acetylene Molecules

Section 1.1 – Introduction to Metallocene Chemistry

Metallocene chemistry has seen much development since the discovery of ferrocene by Pauson and Kealy in 1951¹⁰. Bis(cyclopentadienyl)iron compound has two cyclopentadienyl (Cp) ligands in the η^5 -type coordination mode and since its discovery, has generated a significant amount of research into related metallocene compounds due to the remarkable sandwich structure and thermal stability.¹¹⁻¹⁴

The chemistry of group 4 metallocenes developed quickly with the extension of the Ziegler-Natta polymerization process where titanocene dichloride is used as a cocatalyst in conjunction with an aluminum alkyl based compound to polymerize ethylene cyclopentadiene derivatives, styrene and butadiene to give synthetic rubbers.^{11,15,16} Further research into the catalytic capabilities of the group IV metallocenes developed and zirconocene derivatives gained popularity in the general field of organometallic chemistry.¹⁶⁻¹⁹

Section 1.2 – Structure and Bonding of Zirconocene Derivatives

Zirconocenes have two cyclopentadiene (Cp) rings. The coordination mode of these complexes commonly form in a η^5 - bonding pattern but are also known to have a η^1 -bonding pattern with the metal center. The η^5 -Cp rings are common in literature due to the aromatic character of the anionic Cp ring and intrinsic stability that leads to the sandwich complex formation¹¹. The most common bonding structure of this type of zirconocene derivative follows the formula, $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrX}_2$. As the Cp rings attached are considered to be anionic with a -1

charge, the zirconium atom is likely to have oxidation states of +2, or +4, however, the +3 oxidation state is also possible; general examples of all three oxidation states are shown below in Figure 1.2.A.

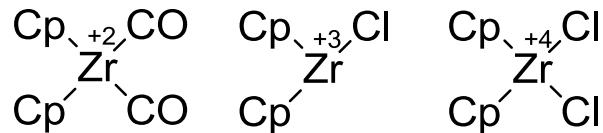


Figure 1.2.A: Oxidation states of zirconocene derivatives.

Analogues of zirconocene are known; neutral, anionic and cationic zirconocene derivatives are all successfully characterized and shown below in Figure 1.2.B.^{5,7,20,21} The versatile nature of the zirconocene derivative suggests it is applicable in various fields of chemistry including catalysis, dehydrocoupling for industrial purposes.^{18,22,23}

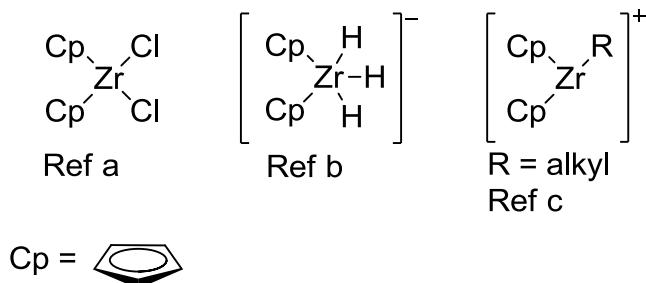
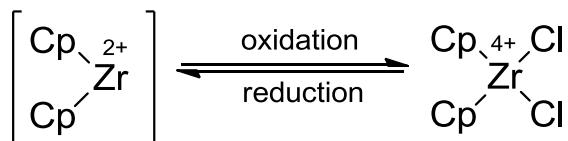


Figure 1.2.B: Zirconium (IV) derivatives;^{5,7,20,21} a) Negishi *et al.* *J. Am. Chem. Soc.* 1997, **113**, 1440; b) Stephen *et al.* *J. Am. Chem. Soc.* 1997, **119**, 11422; c) Marks *et al.* *J. Am. Chem. Soc.* 1994, **116**, 10016.

The various oxidation states enable zirconocene derivatives to be useful in many applications. An obvious example is the ability of the zirconium atom to undergo oxidative or reductive processes. A zirconocene complex in the +2 oxidation state can undergo an oxidation

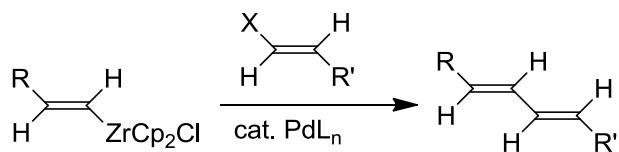
to lose two electrons and end in the +4 oxidation state. The reverse reaction can also occur where reduction occurs at the zirconium atom.



Scheme 1.2.A: Redox chemistry of zirconocene derivatives.

Section 1.3 – Development and Use of Zirconocene Derivatives

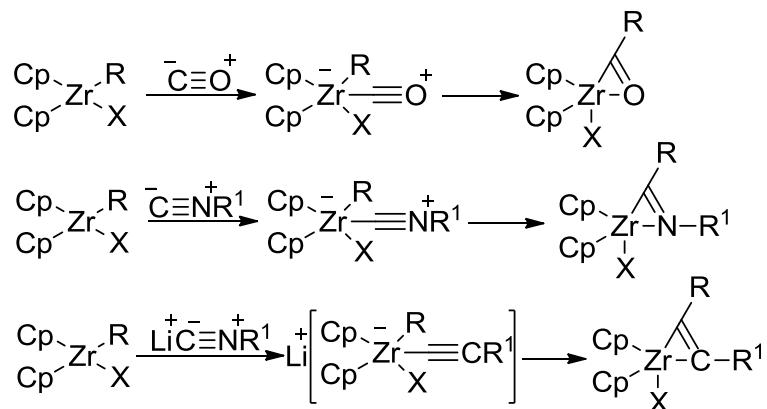
Zirconocene chemistry became increasingly popular in the 1960's and 1970's with new reports of carbon-carbon bond-forming reactions *via* hydrometallation.⁶ Originally, organoaluminum derivatives were considered for this process but proved to be difficult to work with due to the high Lewis acidity of the aluminum atom. In an attempt to improve the process, hydrozirconation *via* zirconocene hydrides was utilized in cross-coupling catalysis. Organozirconium reagents still limited carbon-carbon bond-formation to a few successful reactions; however, with the discovery of Ni and Pd-catalyzed cross-coupling reactions of organozirconocenes, the chemistry of zirconocene developed significantly.⁶



Scheme 1.3.A: Example of palladium catalyzed cross-coupling of an organylzirconocene derivative.⁶

Organozirconium chemistry continued to develop further and prove its synthetic capabilities with several applications including zirconium-catalyzed carboalumination of alkynes to migratory insertion reactions of zirconocene complexes.^{6,22} The reaction of alkylzirconocene

chloride with an equivalent of either alkyllithium or isonitrile proved to successfully insert at cold temperatures and further rearrange to form a stable anionic metallocycle.



Scheme 1.3.B: Example anionic zirconocene migratory insertion reactions.⁶

Section 1.4 – Anionic Zirconocene Derivatives and their Chemistry

The first zirconocene trihydride anion was synthesized and characterized in 1997 by Stephen *et al.* using the Cp* ligand *versus* Cp ligands.⁷ The difference between these ligands is shown below in Figure 1.4.A. Cp ligand species are known to commonly produce dimeric or polymeric metal hydride species due to the lack of steric bulk and the increased Lewis acidity of the electron deficient metal center thereby forming [Cp₂MH₂]_n.⁷ Cp* was chosen for this research due to the increased steric bulk from the methyl groups attached to the cyclopentadienyl ligand and the added electron density incorporated into the metal center which increases the likelihood of forming a monomeric species.⁷

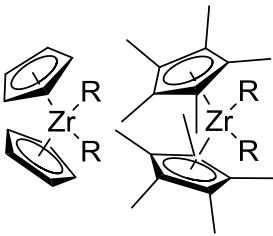
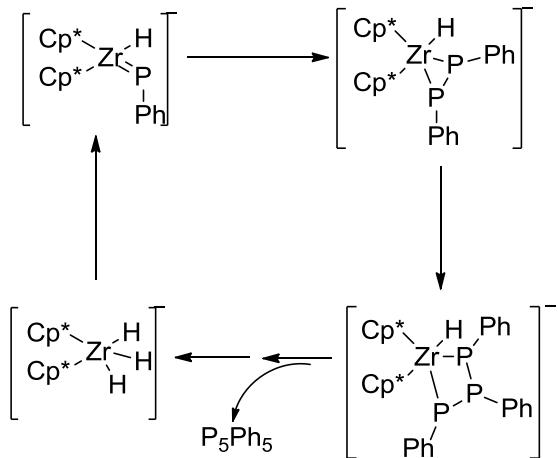


Figure 1.4.A: Examples of Cp_2ZrR_2 and $\text{Cp}^*_2\text{ZrR}_2$ respectively.

The trihydride, $[\text{Cp}^*_2\text{ZrH}_3]^-$, is an 18-electron species and is isoelectronic with known group V metal hydrides such as Cp_2TaH_3 .^{23,24} The difference between the group IV and group V isoelectronic species is that the group V hydrogen atoms of the metal-hydrogen bonds are acidic in nature compared to the group IV hydrogen atoms that exhibit strong hydridic character.²⁵

The ability of these anions to catalytically dehydrocouple phosphines was first speculated by Stephan *et al.* in 1995.³ It was later expanded upon by the same research group in 2006, where the catalytic dehydrocoupling of phosphines was reported using the same anionic zirconocene trihydride anion.¹⁹ This work extended to the dehydrocoupling of primary and secondary phosphines as well as bisphosphines.^{19,26} The catalytic dehydrocoupling is shown below.

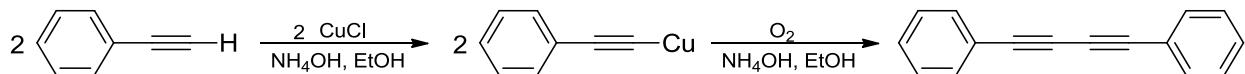


Scheme 1.4.A: Proposed catalytic cycle for the dehydrocoupling of primary phosphines.

The catalytic abilities of the anionic zirconocene trihydride give valuable insight into possible catalytic acetylene coupling. This is supported by the effectiveness of the zirconium trihydride in phosphine dehydrocoupling reactions due to the electron rich zirconium anion species and the redox stability of the metal center which is vital to the success of this reaction type.²⁷

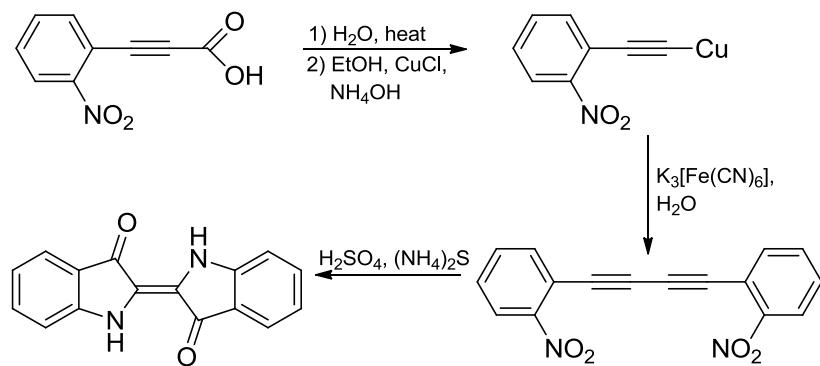
Section 1.5: - Acetylenic Coupling

The first acetylenic coupling was observed by Carl Glaser in 1869 when he successfully observed the oxidation of two copper(I) phenylacetylide molecules producing 1,4-diphenylbuta-1,3-diyne.²⁸



Scheme 1.5.A: The first example of acetylenic coupling.²⁸

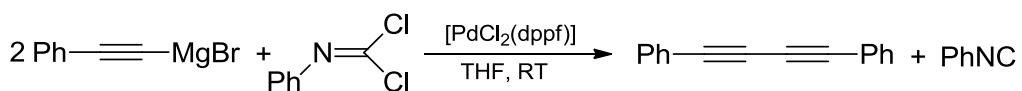
The research involving coupling acetylenic molecules expanded and grew through the late 1800's with Baeyer's work on the synthesis of indigo using potassium ferricyanide as an oxidizing agent.²⁹



Scheme 1.5.B: Indigo synthesis incorporating acetylenic coupling by Baeyer.²⁹

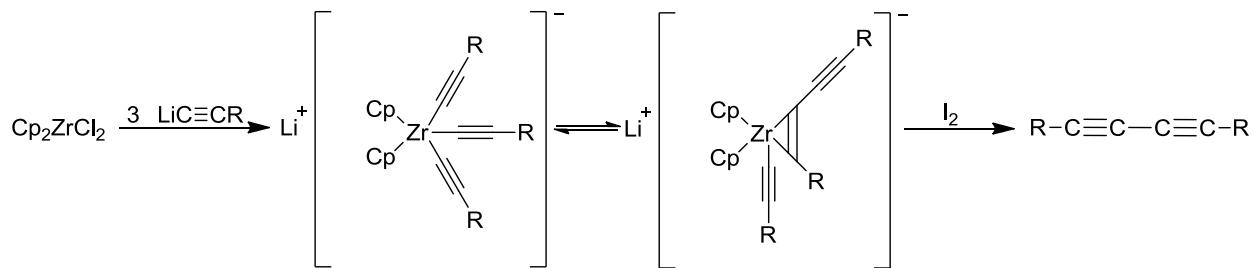
The work continued to expand with researchers in the early 1900's showing that many different oxidizing agents could be used in the process of coupling acetylenes.²⁸

Several organometallic acetylides were used successfully in coupling reactions and reported throughout the second half of the 20th century.²⁸ Some metalated alkynes include lithium, tin, zirconium and titanium.^{18,28,30,31} One of the most widely used examples is the magnesium alkynes. An example of this reaction is the homocoupling of alkynyl derivatives using a palladium catalyst which gives high yields²⁸.



Scheme 1.5.C: Palladium-catalyzed acetylenic coupling using a Grignard derivative.

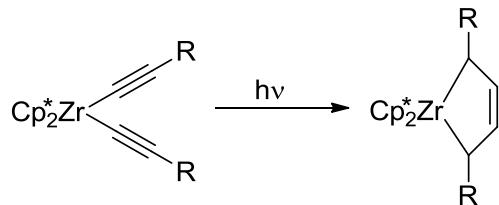
A reaction of particular interest involves the coupling of two phenylacetylene molecules *via* an anionic zirconocene derivative that undergoes a 1,2-migration and when treated with iodine produces coupled acetylenes in a moderate yield.²⁰



Scheme 1.5.D: Acetylenic coupling via an anionic zirconocene derivative and 1,2-migration by Negishi *et al.*²⁰

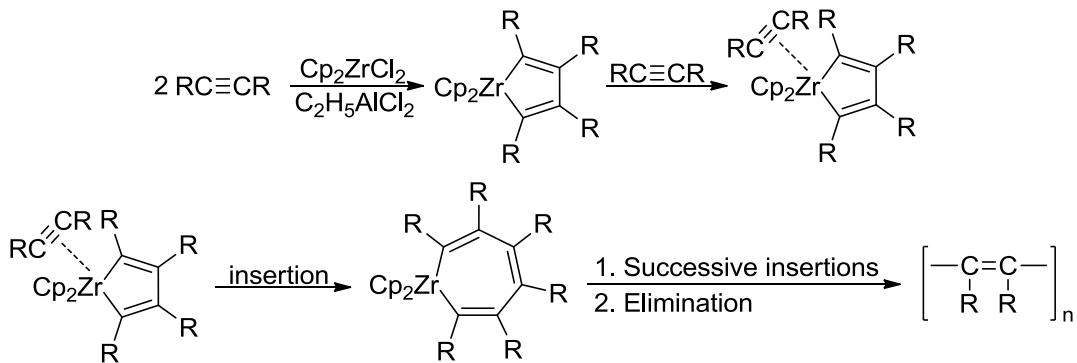
The formation of this zirconocene metallocycle has been studied at length and varying bonding scenarios have been presented.³² It has been indicated that metallocycles are likely intermediates in catalytic reactions of transition metal complexes with acetylenes. Bonding

scenarios presented by Rosenthal *et al.* in 1999 showed the rearrangement of $\text{Cp}_2^*\text{Zr}(\text{C}\equiv\text{CR})_2$ to a five-membered metallocycle as shown below.⁴



Scheme 1.5.E: An observed rearrangement of zirconocene diacetylide to form a metallocycle.⁴

Other research has shown the insertion of acetylides in a mechanistic way that grows the metallocycle and after which, elimination renders a polymeric unit.^{32,33} This polymerization required an alkylaluminum complex in the first reaction.



Scheme 1.5.F: Insertion reaction forming zirconocene metallocycle.³²

Section 1.6 – Computational Studies

Computational studies have examined the stability of zirconocene derivatives, which are closely related to this work. A study published in 2002 by Jemmis *et al.* compared the stability of zirconocene and titanocene derivatives using Density Functional Theory (DFT) Calculations.³¹

The molecules examined in the research paper, as shown below in Figure 1.6.A, are similar in structure to the proposed reaction intermediates and other possible side products that may be formed due to steric bulk and other factors.

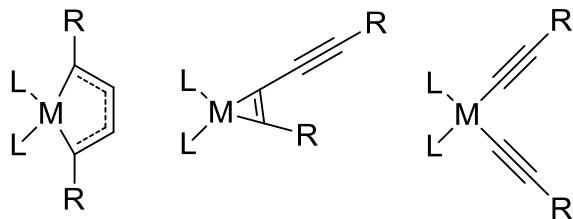


Figure 1.6.A: Bonding scenarios studied using DFT calculations.

The reaction intermediates examined in the Jemmis *et al.* paper are neutral in nature and cause some dissimilarity as the reaction intermediates in this work are anionic in nature. Preliminary computational studies using B3LYP/LANLDZ level of theory were performed by Dr. Jason Masuda to understand and examine the relative stability of the anionic reaction intermediates of the zirconocene derivatives. Not only was the computational data for the anionic zirconocene derivatives different than the neutral data, it also favoured the proposed reaction intermediate of this work compared to a neutral reaction intermediate which is not the primary goal of this thesis research.

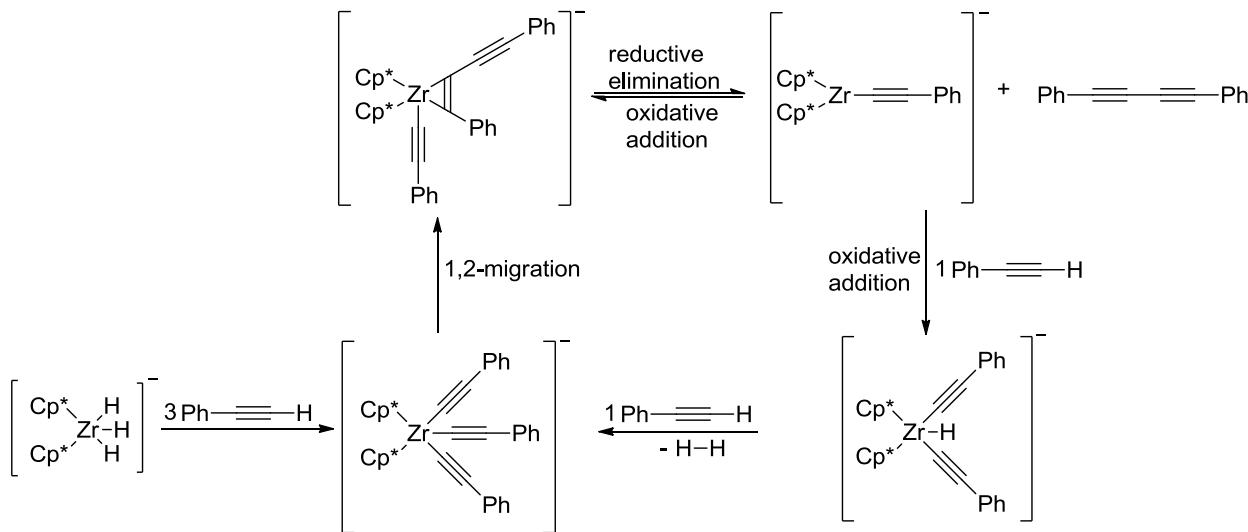
First looking at the work by Jemmis, it is postulated that zirconocene and titanocene derivatives favour a metallocyclocumulene intermediate before undergoing catalytic cleavage to form coupled acetylene molecules. While setting the reference energy to 0.0 kcal/mol for the diacetylide compound, it was determined that the metallocyclocumulene derivative was more stable than the cyclopropylene derivative in the neutral state. The calculations performed by Dr. Jason Masuda in the anionic state indicate that the energy associated with the

metallocyclocumulene compound is higher than the energy associated with the metallocyclopropylene; making the cyclopropylene derivative more stable in the anionic state.

Using basic computational calculations, the anionic metallocyclopropene derivative was found to be more energetically stable by 10 kcal/mol than the diacetylide derivative.

Section 1.7 - Objectives

The focus of this research will be to investigate and test the ability of an anionic zirconocene derivative to catalytically couple phenylacetylene molecules. The use of the anionic zirconocene trihydride is chosen for several reasons including its stability, simplicity in preparation and its electron richness coming from both the Cp^* ligands *versus* the Cp ligands and the fact that the zirconium atom is electron rich due to its anionic nature. The zirconocene trihydride has also demonstrated the ability to catalytically activate P-H bonds.¹⁹ Negishi *et al.* have successfully shown a synthetic route to coupling phenylacetylene using a zirconocene derivative; however it is a non-catalytic route.²⁰ Based on the previous successful research, the goal in this work is to use an anionic zirconocene hydride to catalytically dehydrocouple phenylacetylene in a similar fashion as Negishi. In addition to this, the nature of the intermediate zirconocene complex will be studied to determine the structure.



Scheme 1.7.A: Proposed catalytic cycle.

A successful catalytic zirconocene derivative would improve the synthesis presented by Negishi and provide further insight into the chemistry of the anionic zirconium trihydride complex developed by Stephan *et al.*^{7,20} The proposed synthesis follows some of the general rules and guidelines for green chemistry described by Anastas.³⁴ This includes the removal of an intermediate step where the addition of free iodine (I_2), would not be required to release coupled phenylacetylene. Making reactions catalytic follows another principle outlined by Anastas where it is indicated that catalytic reagents are superior to stoichiometric reagents.³⁴ The goal will be to offer a clean and sustainable alternative to this traditional chemical synthesis.

Chapter 2: Reactivity of Carbene-Phosphinidene Adducts

Section 2.1 – Electron Rich Phosphine Ligands

Important research regarding N-heterocyclic carbenes involves the creation of stable carbon-chalcogen double bonds (chalcogen being a group 16 element) that have shown

widespread industrial applications especially in catalysis.⁸ Catalytic capabilities have been demonstrated with imidazole-2-thiones and further research has shown the analogous synthesis in forming carbon-selenium and carbon-tellurium double bonds.³⁵ This success was further developed in an attempt to create stable carbon-pnictogen bonds (pnictogen being a group 15 element) where the first carbene-phosphinidene adduct was synthesized.⁸ The new carbene-phosphinidene adduct was postulated as being a possible nucleophilic catalyst.⁸ It was not until January 2013, during our investigations into these systems, that Bertrand *et al.* published more carbene-phosphinidene structures using several different carbenes.³⁶ The simplistic method of synthesis and ease of characterization was a further indication of possible unexplored importance of this type of molecule.

Section 2.2 – Carbenes as Ligands

Carbenes are regularly used as ligands in organometallic chemistry³⁷⁻³⁹. Carbenes are neutral compounds where the carbon atom has 6 valence electrons including a lone pair of electrons. The location of these electrons depends on the electronic configuration of the carbene molecule. The carbon of the carbene can be in either a singlet or triplet state and from this assignment are considered either a Fischer or Schrock carbene when coordinated to a metal centre, respectively^{40,41}. The development of the carbene classifications are named after Ernst Otto Fischer and Richard R. Schrock who have both won Nobel Prizes in Chemistry for their work in sandwich complexes and olefin metathesis respectively.

Fischer carbenes are electrophilic in nature while Schrock carbenes are nucleophilic. The bonding scenario of both Fischer and Schrock carbenes is shown in Figure 2.2.A. As shown with the Fischer carbene, a pair of electrons is donated to the metal center forming a σ -bond. The

metal center that the carbene is associated with is usually an electron rich, late transition metal that donates electron density into the empty π -orbitals of the carbon. The opposite describes Schrock carbenes as they are π -donors and generally form stable carbon-metal bonds with electron deficient, early transition metals.

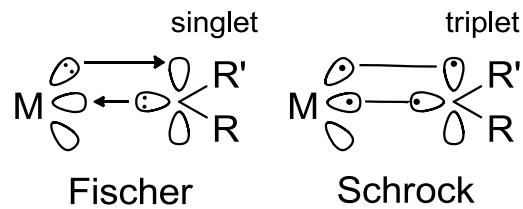
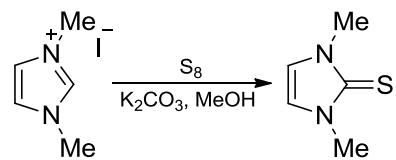


Figure 2.2.A: Singlet and triplet carbene states.

The electronic configuration of Schrock carbenes is considered to be similar to bi-radicals where two degenerate p -orbitals containing spin-aligned electrons are in the triplet state causing the Schrock carbene to have an sp hybridization with a linear geometry. The Fischer carbene electronic configuration contains no degeneracy in the same p -orbitals and the two electrons are spin-paired causing the carbene to be in the singlet state with an sp^2 hybridization and a bent geometry.

The first isolable reported N-heterocyclic Carbene was originally reported by Arduengo *et al.* in 1986 as the formation of 1,3-dimethylimidazole-2-thione. This carbene-thione was developed just before the first synthesis of carbene by Bertrand in 1988 and full characterization by Arduengo in 1991.^{35,42}



Scheme 2.2.A: Synthesis of 1,3-dimethylimidazole-2-thione by Arduengo *et al.*³⁵

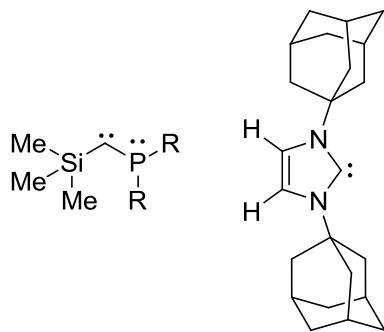


Figure 2.2.B: Left – first reported stable carbene; Right – first carbene characterized by single crystal x-ray diffraction.⁴²

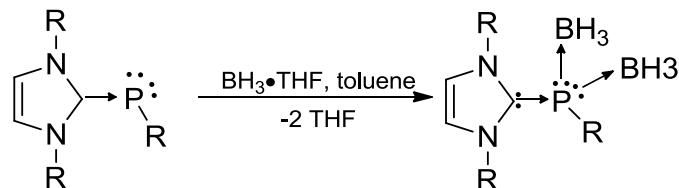
Section 2.3 – Bonding Scenario of Carbene-Phosphinidene Adducts

The stability of singlet carbenes can be described using different scenarios as shown below. The scenario relating to the carbon-pnictogen double bonding scenario involves a push-push mesomeric mechanism. The substituents attached to the singlet carbene are electronegative in nature helping to form the inductive σ -donation of the carbon valence electrons while the substituents introduce mesomeric effects by donating π -electron density towards the p -orbitals of the carbon atom.

N-heterocyclic carbenes fall under this type of inductive/mesomeric configuration. Amino substituents act to stabilize the carbene making this type of carbene common in organometallics. The π -electron donation by the amino substituents can compete with the π -electron donation of the pnictogen towards the carbon. This competition is what gives the carbon-pnictogen double bond character variability. If the amino substituents were to completely

fill the empty *p*-orbital on the carbon, a pnictogen such as phosphorus would be incapable of donating its lone pair of electrons into the carbon orbitals. This would cause a single bond between the carbon and phosphorus with a σ -bond formed from a lone pair of electrons donated from the carbon to the phosphorus. If however, the phosphorus were to favourably donate its lone pair of electrons to the *p*-orbital preventing the amino groups to donate electron density, the carbon-phosphorus bond would contain double bond characteristics. This competition for bond character is in constant equilibrium with some intermediate bond distance between a single and double bond.

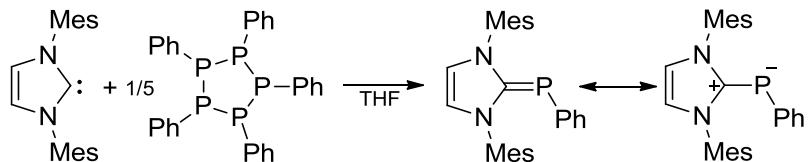
The bonding of phosphinidene was examined by Arduengo and Clyburne in 1997 where the carbene-phosphinidene adduct was reacted with two equivalents of borane. The outcome resulted in the formation of a 2:1 borane:phosphinidene product and no evidence of a 1:1 formation.⁹



Scheme 2.3.A: Single bond character of a carbene-phosphinidene.⁹

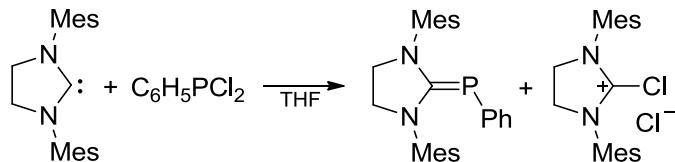
Section 2.4 – Synthesis of Carbene-Phosphinidene Adducts

The synthesis of the carbene-phosphinidene compound was originally reported as a reaction of carbene with a cyclic oligomer of pnictinidenes which forms a stable carbene-pnictinidene adduct.



Scheme 2.4.A: Carbene-pnictinidene adduct formation *via* cyclic pnictinidene oligomers.

A separate reduction step was done in order to produce the cyclic oligomer and was simplified in the original research requiring no separate reduction step by simply reacting the carbene with a pnictogen dichloride compound. This simplified synthesis with dichlorophenylphosphine was successful in yielding both the desired carbene-phosphine adduct and the Cl₂ salt of the carbene⁸. Although the reaction was successful, it seemed to be counterproductive as there was a significant loss of valuable starting material from the oxidation of the carbene to form the corresponding chloride salt.



Scheme 2.4.B: Simplified synthesis of carbene-phosphinidene adducts.

Section 2.5 - Objectives

The goal of the research surrounding the formation of electron rich phosphine ligands includes the development of novel carbene-pnictinidene adducts. In this research, the synthesis of the carbene-phosphinidene adducts will be considered and improvement will be explored. The character of the carbon-phosphorus bond is of particular interest and will be investigated. The electrophilic donation and π -accepting abilities of the carbenes will be examined based on the characteristic NMR shifts and the C-P bond lengths from X-ray crystallographic data. The ability of these adducts to form metal complexes has not been previously reported and due to the lone

electron pair(s) on the phosphorus atom, this metal complex formation will also be studied. It is believed that small metals that cannot undergo oxidation-reduction reactions would likely form stable complexes. Sterically unhindered metals are also expected to form complexes more easily than sterically hindered analogs.

Discussion

Chapter 3 – Zirconocene Derivatives

Section 3.1 – Synthesis of Starting Materials

The synthesis of starting materials presented some difficulties that persisted for two months until the discovery of the problem. The solvents used to synthesize all starting materials contained a significant amount of water that interfered with the reactions leading to decomposition. The reason for this issue is not fully understood and completely unexpected as the columns in the solvent purification system are packed with anhydrous alumina and are expected to remove contaminants including water for approximately 400L of solvent. Approximately 100L of solvent had been passed through the columns in the solvent system so it is believed that the solvent company may have accidentally provided non-anhydrous solvents. A simple method was used to dry the solvents sufficiently enough to allow for good reaction yields and termination of decomposition as described below.

The solvents were dried with a small amount of potassium hydride (KH). After allowing the solvent to stir overnight, it was passed through a packed alumina/Celite filter frit to remove all traces of KH and other contaminants. Pentane, diethylether and THF were all dried using this method. Subsequently, all reaction yields improved to literature values.

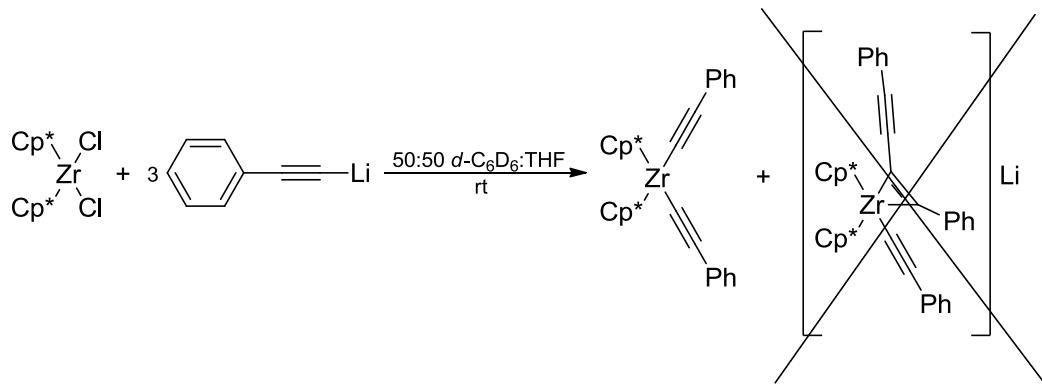
The synthesis of both $\text{Cp}^*_2\text{ZrH}(\mu^2\text{-H}_2\text{AlH}_2)$ and $[\text{Cp}^*_2\text{ZrH}_3]\text{Li}$ used in this research followed routine literature work-ups and provided desired yields.^{7,20} Both zirconocene derivatives were confirmed *via* NMR spectroscopy to ensure the products were pure. In addition, the anionic trihydride species seems to be stable, for months at a time, when kept at room temperature in an inert (O_2 -free) atmosphere. The μ^2 -aluminum intermediate species is not stable for longer than 1 week and must be kept in screw-cap vials in an inert atmosphere freezer to slow the process of decomposition.

The decomposition of the aluminum intermediate is likely attributed to small amounts of lithium aluminum hydride (LiAlH_4) present in the final product. The rate of decomposition might be diminished if the solution in THF and extraction with pentane was filtered a second time through a fine frit with Celite instead of a simple Celite pipette technique. The subsequent formation of the anionic trihydride is not interfered or reduced from the small presence of LiAlH_4 indicating the second filtration may not be necessary.

Section 3.2 – Synthetic Method A

Several studies involving the bonding structure of zirconocene metallocycles including the σ - and π - bonding scenarios involving a zirconium metal center indicate a plethora of possible products that likely exist in some equilibrium.^{2,4,31,32,43-45} The goal to synthesize a zirconocene derivative with a cyclopropylene addition was unsuccessful. It was believed that this derivative would be capable of releasing coupled acetylene molecules with the addition of more equivalents of acetylene. This was supported by the catalytic capabilities of the anionic zirconocene trihydride to dehydrocouple phosphines.¹⁹

The anionic zirconocene trihydride and lithium phenylacetylide were prepared according to literature sources.^{7,46} In an attempt to successfully synthesize the zirconocene cyclopropylene intermediate derivative, two synthetic routes were undertaken.



Scheme 3.2.A: Method A to achieve desired catalyst.

The method A shown above in Scheme 3.2.A is similar to the Negishi work. The original synthesis uses Cp_2ZrCl_2 instead of the bulkier Cp^* ligands. Several attempts to produce the anionic reaction intermediate were deemed unsuccessful. This cyclopropylene derivative was not observed with the addition of 3 equivalents of phenylacetylene nor upon gentle heating and allowing the reaction to slowly heat over several days. NMR spectroscopy confirmed two products; zirconocene diacetylides and lithium phenylacetylide.

Initial observations suggested that steric bulk may play a factor in the lack of formation and also the bonding of the 3rd lithium phenylacetylide. It is believed that the lithium cation prefers the phenylacetylide molecule over the anionic zirconocene derivative. Further testing was performed with the goal of using a less favourable cation that would be initially associated with phenylacetylide. Attempts to use tetraphenylphosphonium chloride to create a phenylacetylene anion with a tetraphenylphosphonium cation were unsuccessful in multiple attempts. It is

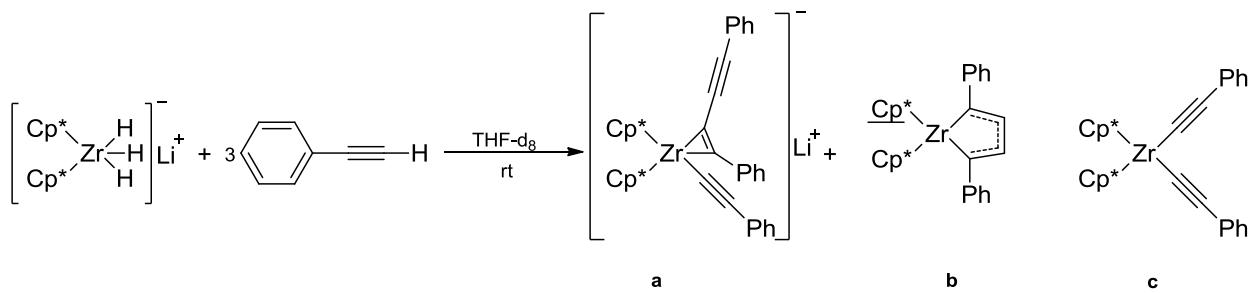
believed that this ionic interaction is too unfavourable to form a stable compound both in the solid phase and in solution.

The steric bulk of the Cp* rings were thought to be a possible factor as the original synthesis was performed with Cp ligands. An NMR study that will be discussed later in this chapter has determined that steric hindrance does not play a factor in the formation of the zirconocene cyclopropylene intermediate even while using the bulkier Cp* ligands.

The method following Negishi's work proved to be unsuccessful in forming the bulkier zirconocene intermediate and is ultimately attributed to the synthetic route being unfavourable due to the ionic interactions. It is possible the intermediate species may be present and capable of forming however in amounts too low for detection.

Section 3.3 – Synthetic Method B

A second synthetic method was performed using the anionic zirconocene trihydride. This zirconocene derivative was hypothesized to be favourable as it is an anionic compound making the transition from a neutral compound to an anionic compound as required in the first method of synthesis not necessary. The exchange of the lithium cation from the phenylacetylene to the zirconocene derivative is removed. The promising nature of the anionic trihydride was also believed to help promote the catalysis step, making this synthetic route of particular importance and a main focus in this research.



Scheme 3.3.A: Synthesis of zirconocene cyclopropylene intermediate *via* synthetic method B.

Interesting observations and results were recorded during several attempts of this reaction. Initially, the reaction of the anionic zirconocene trihydride with three equivalents of phenylacetylene was done on an NMR scale. The first reactions were done in a 50:50 mixture of C_6D_6 and THF to cut down on cost as deuterated-THF is expensive; ca. \$25 per 1 mL ampule of deuterated solvent. The results from the NMR spectroscopic data showed no formation of the zirconocene cyclopropylene derivative and a mixture of many products that were undistinguishable. Research by Choukroun also support this finding where it is indicated that the reaction of the zirconocene diacetylidyde ($\text{Cp}_2\text{Zr}(\text{C}\equiv\text{CPh})_2$) with 1 equivalent of lithium phenylacetylidyde in C_6D_6 does not produce any zirconocene cyclopropylene intermediate.⁴³

The reaction shown in Scheme 3.3.A was also tested in both sunlight and darkness. This was completed on the basis of the research completed by Choukroun⁴³. Their results indicated that in darkness, with addition of 2 or 3 equivalents of lithium phenylacetylidyde only the diacetylidyde zirconocene derivate is formed. This reaction remains at this stage if kept in the darkness for several days. When this reaction was repeated using Cp^* ligands, the same outcome was observed. The colours observed during the progression of the reaction in both light and dark varied as well. In darkness, the colour appeared green to the naked eye and upon standing for approximately 1 hour, the colour changed to vibrant red. This change in colour is likely due to a

widening in the HOMO/LUMO energy gap. A red colour observed also indicates a transition to a longer wavelength and should likely involve more conjugation within the system.⁴⁷ This can be confirmed by the presence of the zirconocene cyclocumulene derivative observed in the NMR spectra for 2 and 3 equivalents of phenylacetylene. The Figure **b** compared to Figure **c** in Scheme 3.3.A shows more conjugation with the formation of the cyclocumulene ring.

A thorough investigation into the addition process of the phenylacetylene molecule onto the zirconium atom centre was performed. The sequential addition of 1 equivalent of phenylacetylene was monitored *via* $^{13}\text{C}\{\text{H}\}$ NMR spectroscopy. This reaction was performed to determine if the Cp^* rings were too sterically hindered for the addition of three equivalents. If by the third addition of phenylacetylene, no cyclopropylene derivative would be observed or if free phenylacetylene was floating in solution, it would be observed spectroscopically.

The addition of two and three equivalents of the acetylene to the anionic zirconocene trihydride produced a mixture of products. Three distinguishable products were determined from the mixture. The first, zirconocene diacetylidyde, which was confirmed with the characterization data from both Rosenthal and Choukroun.^{4,43} The next product observed in the NMR spectra was that of the cyclocumulene derivative. The α and β carbons observed at 181.7 and 118.4 ppm respectively matched that of the literature data stating that α and β carbons should appear at 179.4 and 118.4 ppm respectively. Finally, the desired zirconocene cyclopropylene derivative was observed with the main carbon peaks observed at 108.8/126.5 ($\text{C-}\beta/\text{C}_d$), 99.9 (C_c), 130.3, 134.9 ($\text{C}_a/\text{C-}\alpha$) and 193.4 (C_b) ppm. These values correspond similarly to the literature values given by Choukroun in 2000 as 107.4/126.4 ($\text{C-}\beta/\text{C}_d$), 97.6 (C_c), 130.4, 134.9 ($\text{C}_a/\text{C-}\alpha$) and 205.9 (C_b) ppm.⁴³ The slight differences in the chemical shifts are attributed to the use of Cp^* ligands versus Cp ligands.

The observation of these compounds, especially the zirconocene cyclopropylene, confirmed that sterics are not an issue as was originally believed in this research. The addition of further equivalents of phenylacetylene did not indicate the release of coupled phenylacetylene. Free acetylene was observed with the addition of the further equivalents phenylacetylene. The lack of catalytic formation of coupled phenylacetylene indicates an unfavourable exchange towards the addition of new phenylacetylene releasing the coupled molecules.

Attempts to recrystallize the contents from the NMR tube with three equivalents of phenylacetylene and zirconocene trihydride have been unsuccessful to date. Recrystallization from cold THF and also layering solvent (THF then pentane) techniques were attempted separately with no success.

Future work for this research project includes the continued attempt to fully crystallize zirconocene cyclopropylene from the reaction mixture. Also, changing the Cp* ligands to a mixture of Cp/Cp* or simply Cp may provide a more favourable exchange of coupled phenylacetylene with new acetylene.

Chapter 4 – Carbene-Phosphinidene Adducts

Section 4.1 – Synthesis of Starting Materials

The synthesis of the starting materials was met with some minor challenges as noted in Chapter 3, Section 3.1. The synthesis of the diamines, diimines, carbene salts and finally the carbene itself followed routine literature syntheses and work-up.^{40,42} The diamines, diimines and carbene salts are all air stable products that can be kept for extended periods of time after their original synthesis in plastic Nalgene screw top containers.

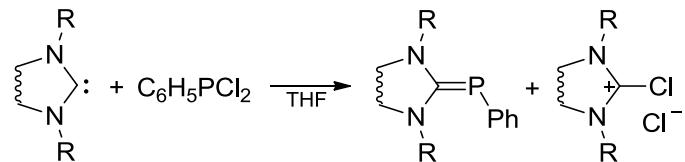
The conversion of the carbene salt to the carbene itself was completed in an O₂-free glove box and the product can be stored for years at a time as well. The syntheses of the SIPr and IPr carbenes were very straightforward and required a simple work-up. The benzimidazol-2-ylidene carbene has a very low melting point and at room temperature is a moist solid making it difficult to work with. To avoid these difficulties, the benzimidazol carbene is kept in the freezer until use for facile weighing purposes. The carbene salts are all off-white to yellow in colour with the SIPr carbene being the lightest and the benzimidazol carbene having a yellow colour.

The use of dry solvents in this research again is of the utmost importance for the production of desired yields during the conversion of the carbene salt to the stable carbene. With the synthesis of the SIPr and IPr carbene, THF was used and with the benzimidazol carbene, diethylether was used in the synthesis. These solvents were discovered to contain H₂O which was not expected causing low yields of the desired carbene product. This problem was remediated by drying the solvents with potassium hydride and then filtering the solvents through an alumina/Celite packed filter. After the drying process was complete, the repeat synthesis of these carbene produced significantly higher yields matching those of the literature data.

Section 4.2 – Synthesis of Carbene-Phosphinidene Adducts

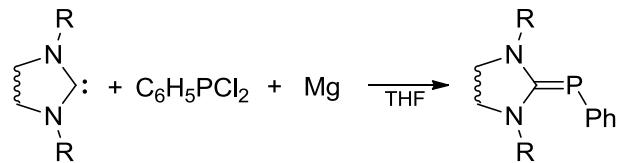
As with the synthesis of the starting materials, the carbene-phosphinidene adduct yield was significantly hindered with the use of wet solvents and was immediately improved upon their drying. The relative ease of synthesis of the carbene-phosphinidene adducts was demonstrated by Arduengo in 1997 with the reaction of P₅Ph₅ with carbene to form the desired adduct⁸. The P₅Ph₅ oligophosphine must be synthesized first in a separate reaction and then used in the following reaction with a carbene to form the desired phosphinidene adduct. The proposed

improved synthesis that was reported in the same research paper indicated that the reaction of dichlorophenylphosphine *in situ* with the carbene produced both the carbene-phosphinidene adduct and the carbene salt.



Scheme 4.2.A: Reaction of carbene with dichlorophenylphosphine.

Improvement of these synthetic pathways was successful where a non-interfering reducing agent was used to reduce the dichlorophenylphosphine to P₅Ph₅ *in situ* with the carbene to produce only the carbene-phosphinidene adduct. The reducing agent chosen to improve this synthesis was magnesium metal dust. This new synthesis was successful in cutting down on the overall reaction time and produced good yields (78-83%) by eliminating the formation of the carbene salt.



Scheme 4.2.B: Carbene with dichlorophenylphosphine and magnesium metal to produce carbene-phosphinidene adduct.

Three different carbene-phosphinidene adducts were synthesized in this manner and were also synthesized as shown in Scheme 4.2.A as pentaphenylcyclopentaphosphane was already synthesized from previous research and available for use.

The first carbene-phosphinidene synthesized in this research was 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene phenylphosphinidene (SIPr phosphinidene). The resulting product is off-white to pale in colour and was produced in a good yield (83%). The $^{31}\text{P}\{\text{H}\}$ NMR peak was visible at δ -8.90 ppm as a singlet which is comparable to the literature value reported by Bertrand as δ -10.2 ppm.³⁶ The crystal structure is reported below with relevant bond lengths.

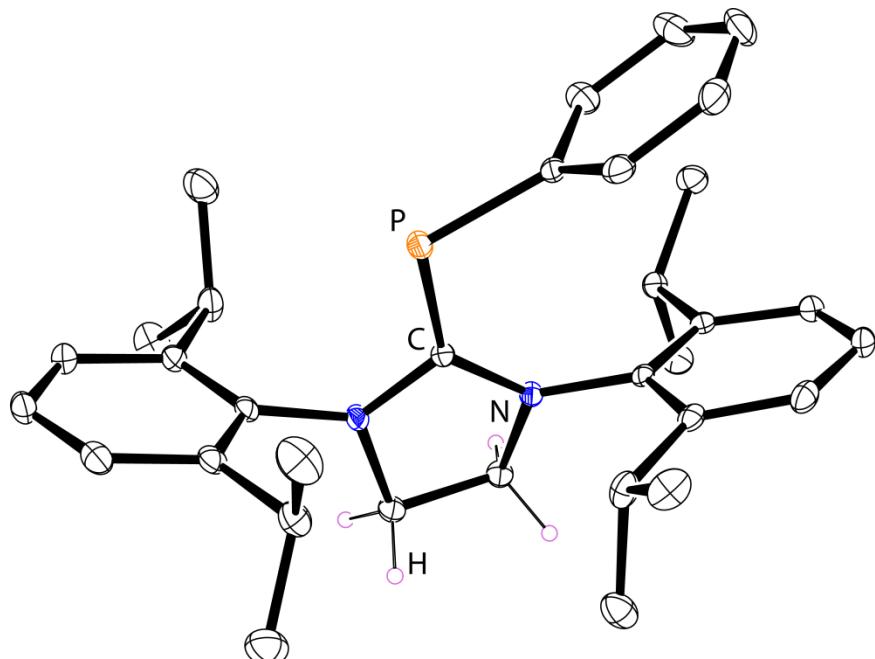


Figure 4.2.A: Crystal structure of 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene phenylphosphinidene. Most hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. Selected bond distances (\AA) and angles ($^\circ$): P(1)-C(1) 1.7460(19), P(1)-C(28) 1.8447(19), C(1)-N(1) 1.366(2), C(1)-N(2) 1.379(2), N(1)-C(1)-N(2) 107.56(15), C(1)-P(1)-C(28) 101.87(8).

The bond length of the P(1)-C(1) bond is shorter than those reported for similar carbene-phosphinidene reactions. This indicates a bond that is closer to a double bond. This is consistent with the reported literature.^{9,48} The report from Robinson indicates the bond length of a carbene-phosphinidene with hydrogen as the substituent on phosphorus has a P-C bond length of 1.763(2)

\AA but when the carbene is coordinated to PCl_3 , the P-C bond length grows to $1.871(11)$ \AA .⁴⁸ This lengthening of the P-C bond is not due to the orbital filling of the carbon from the backbone of the carbene but rather the electron withdrawing effects of the chlorine atoms causing a lengthening of the bond. The bond angle for the C(1)-P(1)-C(28) recorded at $101.87(8)^\circ$ is very similar to that of the C(1)-P(1)-H(1) bond angle reported by Robinson as $102(2)^\circ$.⁴⁸

A second carbene-phosphinidene adduct was synthesized with ease and very similar to the SIPr phosphinidene molecule. The unsaturated carbene backbone, or IPr carbene, was reacted with dichlorophenylphosphine and magnesium metal to generate the carbene-phosphinidene adduct as a yellow solid in good yields (79%). The $^{31}\text{P}\{^1\text{H}\}$ NMR phosphorus peak for the IPr phosphinidene is shifted upfield to δ -19.73 ppm which is comparable to Bertrand's result for the same carbene-phosphinidene adduct corresponding to δ -18.9 ppm.³⁶ This shift from the saturated to unsaturated carbene is indicative of the increased electron density being donated from the amine groups of the carbene to the carbon which prevents the back donation of electron density from the phosphorus towards the carbon *p*-orbitals. This causes the P-C bond to lengthen and shift further away from the typical non-polarized phosphaalkenes that have a ^{31}P NMR peak anywhere between δ 230-420 ppm.³⁶ The higher field NMR peak indicates the growing electron richness of the phosphorus atom.

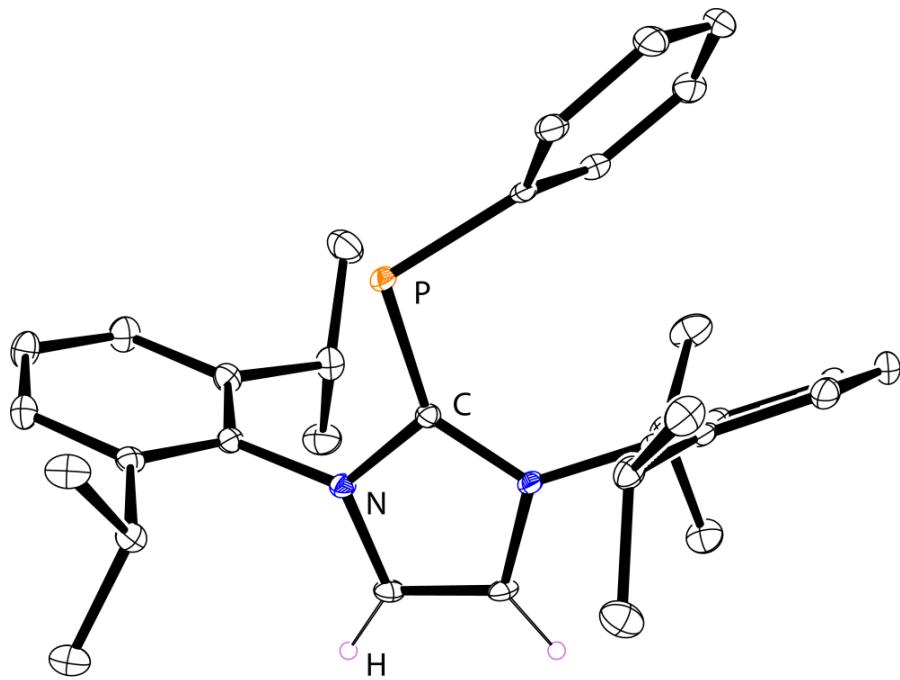


Figure 4.2.B: Crystal structure of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene phenylphosphinidene. Most hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. Selected bond distances (\AA) and angles ($^\circ$): P(1)-C(1) 1.7640(13), P(1)-C(28) 1.8241(14), C(1)-N(1) 1.3783(17), C(1)-N(2) 1.3792(17), N(1)-C(1)-N(2) 104.30(10), C(1)-P(1)-C(28) 104.73(6).

The bond distance corresponding to P(1)-C(1) was shown to be longer than the SiPr phosphinidene adduct shown in Figure 4.2.A. The lengthening of this bond in the IPr derivative is consistent with the NMR data. The increased electron density in the carbene backbone pushes the density towards the amines and therefore towards the carbon *p*-orbitals. This additional electron density can then compete to occupy the empty carbon orbitals that prevent electrons from back donating from the phosphorus. The C(1)-P(1)-C(28) bond angle for the IPr phosphinidene adduct is 104.73(6) $^\circ$ which is only two degrees off from reported literature as stated above by Robinson as 102(2) $^\circ$.⁴⁸

The final carbene-phosphinidene adduct synthesized in this research involved the reaction of a small carbene with dichlorophenylphosphine and magnesium metal to generate 1,3-

bis(diisopropyl)benzimidazol-2-ylidene phenylphosphinidene in good yields (78%) as a bright orange-red powder. The $^{31}\text{P}\{\text{H}\}$ NMR peak was visible as a singlet at δ -35.2 ppm which corresponds to the literature value by Bertrand at δ -34.6 ppm.³⁶ The high-field NMR peak further indicates the increasing single bond character and the likelihood that the additional conjugation and electron density in the carbene backbone is stabilizing the empty *p*-orbitals of the carbon and therefore preventing the back-donation of the lone electron pairs of the phosphorus atom.

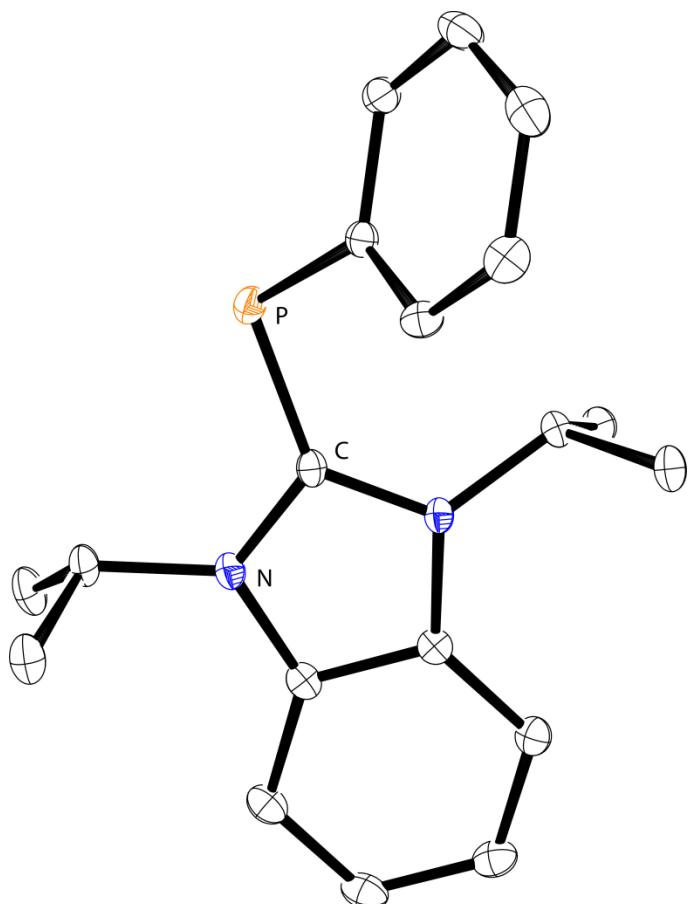


Figure 4.2.C: Crystal structure of 1,3-bis(diisopropyl)benzimidazol-2-ylidene phenylphosphinidene. Most hydrogen atoms are emitted for clarity; ellipsoids are set at 50% probability. Selected bond distances (\AA) and angles ($^\circ$): P(1)-C(1) 1.7787(16), P(1)-C(14) 1.8240(14), C(1)-N(1) 1.3794(18), C(1)-N(2) 1.3949(19), N(1)-C(1)-N(2) 106.45(12), C(1)-P(1)-C(28) 102.91(7).

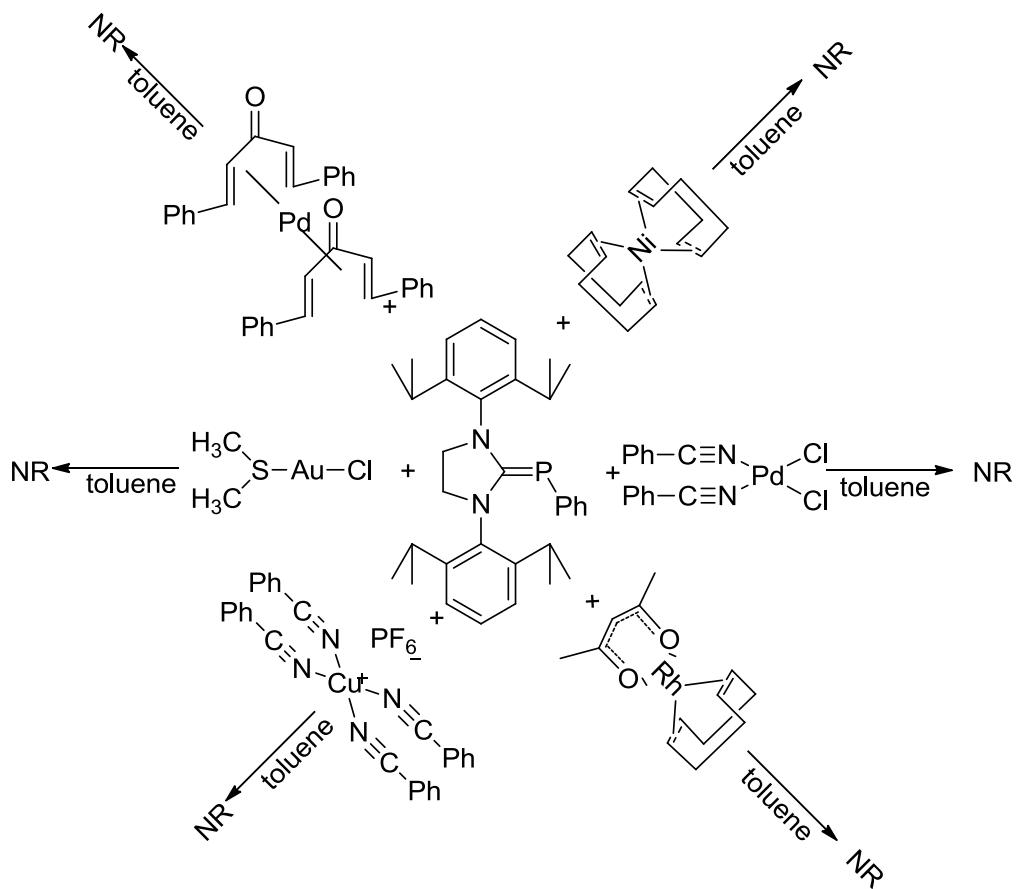
Crystallographic data for the benzimidazol phosphinidene show an increasing C(1)-P(1) bond length. This increasing bond length is now longer than the reported carbene-phosphinidene hydride with the small carbene phenylphosphinidene bond length of 1.7787(16) Å and the reported carbene phosphinidene hydride by Robinson reported as 1.763(2) Å.

Crystallographic and NMR data support each other mutually and can be described in a simple relationship. As the P-C bond lengthens, the NMR peak shifts high-field and therefore more electron density is present in the carbene creating a more stabilized carbene and less stable P-C bond.

Section 4.3 – Carbene-Phosphinidene Adducts and their Metal Complexes

The ability for this type of carbene-phosphinidene to react with metal centers at the phosphorus atom has not yet been reported in the literature. The properties of the carbene-phosphinidene adduct as a ligand to bond to metals was of particular interest in this research. Late transition metals were chosen as they would participate in favourable soft-soft acid base interactions.

Several metals were chosen as possible chelating metals but were not successful in attaching to the phosphorus. Attempted reactions are shown below.



Scheme 4.3.A: Reaction of SPr phosphinidene with Nickel(COD)₂, chloro(dimethylsulfide)gold (I), bis(benzonitrile)dichloropalladium (II), (Acetylacetone)(1,5-cyclooctadiene)rhodium(I), Bis(dibenzylideneacetone)palladium(0) and Tetrakis(acetonitrile)copper(I) hexafluorophosphate.

As seen in reaction Schemes 4.3.A, no reactions were visible by $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy. The lack of metal complexation is likely due to the steric hinderence of the ligands attached to the metal centres. Steric factors were reduced by reacting the SPr phosphinidene adduct with a copper iodide. The single peak in the $^{31}\text{P}\{\text{H}\}$ NMR spectra was found to be shifted far up-field to -31.4 ppm. This shift has given primary evidence that the first carbene-phosphinidene metal complex. The shift in the NMR spectra would indicate the formation of a metal coordination. At this time, crystals from this complex have grown in solution however; they lost crystallinity due to desolvation before they are able to be run. Further attempts to grow

crystals are considered as future work and will confirm the first stable carbene-phosphinidene metal complex.

In addition to this hypothesized metal complex, the smallest carbene-phosphinidene adduct, benzimidazol phosphinidene, was reacted with copper iodide. The resulting $^{31}\text{P}\{\text{H}\}$ NMR spectra did not give a clear indication that a metal complex had formed. Instead, it is hypothesized that the copper iodide performed some sort of insertion reaction as there are two broad peaks in the spectra at -16.7 and -36.9 ppm. These peaks were not identifiable.

This result may have been unexpected but led the research in a new direction and gave a better general understanding of the bonding and strength of the P-C bond and the affect the carbene has on the stability of the overall adduct. The longer P-C bond was too weak to form a metal complex and instead broke to insert the copper complex. The more stable P-C bond in the SiPr phosphinidene was able to chelate the copper iodide and create the metal complex.

As future work, it would be interesting to test the threshold at which the P-C bond becomes too weak to chelate metals to the phosphorus atom and instead inserts them thereby breaking the P-C bond. Other metal complexations and insertion reactions could be attempted with more success with the increasing understanding of the bonding capabilities of the carbene-phosphinidene adduct.

Chapter 5 – Conclusions

Section 5.1 – Zirconocene Derivative Chemistry

The ability for an anionic zirconocene derivative to participate in catalytic methods for the dehydrocoupling of acetylene molecules was shown to be unfavourable. This lack of catalysis has been attributed to unfavourable exchange of coupled acetylene molecules for new acetylene molecules. The zirconocene cyclopropylene molecule was visible in NMR spectroscopy and is considered to be a possible catalytic precursor.

Further investigation indicated that using a different cation for the formation of the acetylide molecule was unsuccessful. A thorough investigation into the process in which the phenylacetylene molecule adds to the zirconocene derivative was studied. The results indicate that it is possible to sterically fit three equivalents of phenylacetylene which undergoes immediate rearrangement to form the cyclopropylene.² No release of coupled phenylacetylene was observed.

Section 5.2 – Carbene-Phosphinidene Adduct Chemistry

The synthesis and reactivity of carbene-phosphinidene adducts was reviewed and reported herein. The synthesis from the original Arduengo work was improved by using magnesium metal as a reduction agent *in situ* to avoid the loss of valuable starting material.⁸ Three novel carbene-phosphinidene adducts have been characterized *via* single crystal X-ray diffraction. The P-C bond lengths of the crystal structures were compared to their respective $^{31}\text{P}\{\text{H}\}$ NMR peaks and were determined to correlate as expected. As the carbene becomes nucleophilic in the *p*-orbital of the carbon atom, the phosphorus atom is less likely to donate electron density thereby making a longer P-C and an upfield shift in the NMR peak.

Metal complexation in its preliminary stages seems to be successful with carbene-phosphinidenes that exhibit stronger P-C bonds and metal insertion reactions seem to occur when the adducts contain a weaker P-C bond.

Chapter 6 – Experimental

Section 6.1 – Experimental Preface

All reactions were completed under an atmosphere of dry, O₂-free N₂ via Schlenk line techniques or using an MBraun UNIlab double station glove box. Pentane, diethylether, dichloromethane, toluene and tetrahydrofuran (THF) were purchased and dried using an Innovation Technology Grubbs'-type solvent purification system. Further purification of pentane, THF and diethylether were required. These solvents were treated with a minimal amount of potassium hydride (KH) and allowed to stir overnight. The solvents were then filtered through Celite and alumina and stored over activated molecular sieves (4Å) before use.

The compounds, bis(1,2,3,4,5-pentamethylcyclopentadienyl)zirconocene dichloride, bis(cyclopentadienyl)zirconocene dichloride, potassium *tert*-butoxide, *n*-butyl lithium, lithium aluminum hydride, phenylacetylene, potassium hydride, tetraphenylphosphonium chloride, nickel COD, magnesium metal, dichlorophenylphosphine, chloro(dimethylsulfide)gold(I), (acetylacetato)(1,5-cyclooctadiene)rhodium(I), palladium dichloride, benzonitrile, tetrakis(acetonitrile)copper(I) hexafluorophosphate, bis(dibenzylideneacetone)palladium(0), tris(pentafluorophenyl)borate, and copper iodide were purchased from commercial sources such as Sigma-Aldrich Co.

^1H , ^{31}P , $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^{11}B NMR spectroscopic experiments were completed on Bruker AV 300 MHz and Bruker AV 500 MHz spectrometers at Nuclear Magnetic Resonance Research Resource (NMR³) at 25°C. Internal references were used in deuterated solvents for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR while 85% H_3PO_4 was used as reference for $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR and Et_2OBF_3 was used for ^{11}B NMR. Reported coupling constants are absolute values.

Melting Points were performed on an Electrothermal MEL-Temp 3.0 using glass capillaries prepared under inert conditions. Infrared spectroscopy samples were prepared under inert conditions and spectra were produced on a Bruker Vertex 70 Infrared Spectrometer with characterization using OPUS 6.0 software for Windows.

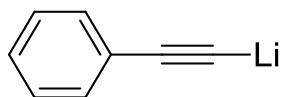
X-ray crystallographic data was completed by Dr. Jason Masuda. Data collection was accomplished using APEX2⁴⁹, cell refinement using SAINT⁴⁹, data reduction via SAINT, structure identification was possible using APEX2⁵⁰, and molecular graphics were created through ORTEP-3v2 for Windows⁵¹.

Section 6.2 – Experimental Procedures and Characterization

Section 6.2.1 – Zirconocene Starting Materials

Experiment 6.2.1.A

Synthesis of lithium phenylacetylide

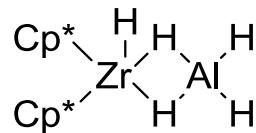


To a 20 mL scintillation vial containing 250 mg (2.45 mmol) of phenylacetylene in 10 mL of dry pentane was added 1.53 mL of 1.6M *n*-BuLi in hexane. The reaction was allowed to stir for 2

days. The solution was decanted, after which, the residual solid was washed with pentane and decanted again. The solid was dried under vacuum to yield a white powder. Yield: 253mg (95%).

Experiment 6.2.1.B

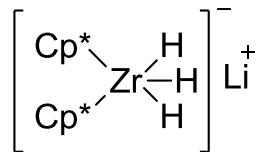
Synthesis of $\text{Cp}^*_2\text{ZrH}(\mu^2\text{-H}_2\text{AlH}_2)$



To a 20 mL scintillation vial containing a solution of 442 mg (1.55 mmol) of $\text{Cp}^*_2\text{ZrCl}_2$ in 6 mL of dry THF was added a solution of LiAlH_4 in 2 mL of dry THF. The reaction was left to stir for 1.5 h after which, the solution was filtered and the solvent was removed via vacuum evaporation. The remaining solid residue was extracted with pentane. The solution was filtered again and evaporation of the solvent produced a white powder. Yield: 395 mg (99%).

Experiment 6.2.1.C

Synthesis of anionic zirconocene trihydride



To a stirred solution of 208 mg (0.85 mmol) of $\text{Cp}^*_2\text{ZrH}(\mu^2\text{-H}_2\text{AlH}_2)$ in 10 mL of dry diethylether was added 1.06 mL of 1.6M *n*-BuLi in hexane. The solution was allowed to stir overnight after which, a precipitate was observed. The solvent solution was decanted, and the

residual solid was washed with more diethylether. The solid was decanted again and evaporated to yield an off-white powder. Yield: 149 mg (47%).

Section 6.2.2 – Reactions of Zirconocene Derivatives

Experiment 6.2.2.A

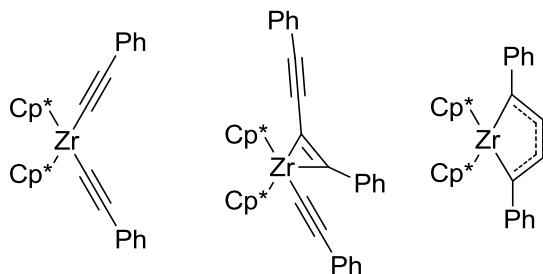
Synthesis of $\text{Li}[\text{Cp}^*_2\text{Zr}(\text{C}\equiv\text{CPh})(\eta^2:1,2\text{-PhC}_2\text{C}\equiv\text{CPh})]$ – NMR study

In a sealable J-Young type NMR tube containing 75mg (0.336 mmol) of $\text{Li}[\text{Cp}^*_2\text{ZrH}_3]$ was added 0.369 mL (0.336mml) phenylacetylene in 0.75mL of $d_8\text{-THF}$. A green coloured solution was observed and no single product was observed.

^1H NMR ($d_8\text{-THF}$, 298K) δ : 0.86 (br d, 2H, ZrH_2H), 7.13 (br m, 5H, $\text{C}\equiv\text{C}(\text{C}_6\text{H}_5)$)

$^{13}\text{C}\{\text{H}\}$ NMR ($d_8\text{-THF}$, 298K) δ : 12.57 (C_5Me_5), 109.78, 125.64, 126.24, 127.20, 127.28, 127.89, 128.14, 128.52, 129.85, 221.48.

A second equivalent of phenylacetylene is added to the J-Young NMR tube and mixed for several minutes. A deep green colour was observed and NMR data suggests the appearance of three products shown below.



NMR data supporting left structure – diacetilide

$^{13}\text{C}\{\text{H}\}$ NMR ($d_8\text{-THF}$, 298K) δ : 12.50 (C_5Me_5), 118.4 ($\text{C}-\beta$), 121.2 (C_5Me_5), 127.2 (*ipso*-C), 127.4 (*p*-Ph), 128.6 (*m*-Ph), 130.9 (*o*-Ph), 155.5 ($\text{C}-\alpha$).

NMR data supporting centre structure – cyclopropylene

$^{13}\text{C}\{\text{H}\}$ NMR (d_8 -THF, 298K) δ : 12.50 (C_5Me_5), 108.8 (C_5Me_5), 125.6, 126.0, 126.5, 128.2, 128.4, 128.6, 129.3, 129.8, 130.9 (Ph), 128.3, 127.9, 144.5 (*ipso*-C), 108.8, 126.5 (C- β / C_d), 99.9 (C_c), 130.3, 134.9 (C_a/C- α), 193.4 (C_b).

NMR data supporting right structure – cyclocumulene

$^{13}\text{C}\{\text{H}\}$ NMR (d_8 -THF, 298K) δ : 11.8 (C_5Me_5), 113.1 (C_5Me_5), 118.4 (C- β), 128.3 (*p*-Ph), 134.9 (*o*-Ph), 144.5 (*ipso*-C), 181.7 (C- α).

A third equivalent of phenylacetylene is added to the J-Young type NMR tube and allowed to mix for several hours. In the first hour, the solution was deep green and upon inspection under white light, the solution was bright red in colour. The exposure to light eventually caused the solution to turn red and remain that colour.

Experiment 6.2.2.B

Attempted synthesis of $\text{Li}[\text{Cp}^*_2\text{Zr}(\text{C}\equiv\text{CPh})(\eta^2\text{-1,2-PhC}_2\text{C}\equiv\text{CPh})]$ – Zirconocene dichloride + $\text{Li}[\text{C}\equiv\text{CPh}]$

In a 20 mL scintillation vial containing a solution of 239 mg (0.82 mmol) of $\text{Cp}^*_2\text{ZrCl}_2$ in 7 mL of dry THF was added a solution of 265 mg (2.45 mmol) of lithium phenylacetylidyne in 5 mL of 50:50 of THF:pentane. The reaction was allowed to stir overnight after which, the solution was filtered and the solvent was evaporated giving a dark red/brown solid. Yield: 412 mg (96%). NMR characterization indicates the formation of zirconocene diacetylidyne and free phenylacetylene.

NMR data corresponding to zirconocene diacetylidyne

$^{13}\text{C}\{\text{H}\}$ NMR (d_8 -THF, 298K) δ : 12.3 (C_5Me_5), 117.8 (C- β), 120.4 (C_5Me_5), 127.4 (*ipso*-C), 127.8 (*p*-Ph), 128.1 (*m*-Ph), 131.2 (*o*-Ph), 152.5 (C- α).

NMR data corresponding to phenylacetylene

$^{13}\text{C}\{\text{H}\}$ NMR (d_8 -THF, 298K) δ : 81.3 (C- α), 84.5 (C- β), 123.2 (*ipso*-C), 128.1 (*m*-Ph), 128.1 (*p*-Ph), 131.2 (*m*-Ph)

Experiment 6.2.2.C

Attempted synthesis of tetraphenylphosphonium phenylacetylido

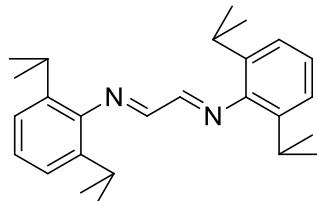
To a 20 mL scintillation vial containing a solution of 108 μL (0.979 mmol) of phenylacetylene in 12 mL of dry THF was added slowly 39 mg (0.979 mmol) of potassium hydride. The reaction mixture was left to stir for 2 hours until the evolution of gas had ceased. A light white flakey precipitate was observed. Next, 367 mg (0.979 mmol) of tetraphenylphosphoniumchloride was added to the solution with the precipitate. After stirring for a further 1 hour, a heavy/dense precipitate was observed. The solution was filtered and the resulting clear yellow/brown liquid was placed in the freezer. NMR data indicated the lack of formation of the desired ionic species.

Section 6.2.3 – Carbene and Phosphinidene Starting Materials

The basic preparation of the starting materials is outlined below. Characterization data has been omitted but all starting materials were confirmed by NMR analysis and compared to known literature values.^{35,40,42} 2,6-diisopropylaniline, glyoxal, formic acid, *n*-propanol, sodium borohydride, hydrochloric acid, triethylorthoformate, sodium hydride and formaldehyde were all purchased from Sigma-Aldrich Co. or similar.

Experiment 6.2.3.A

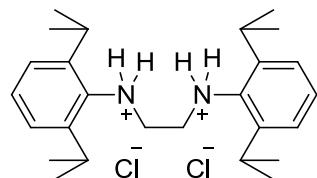
Synthesis of N,N'-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene



To a 500mL schlenk flask containing 23.1 mL (0.314 mol) of 40% aqueous glyoxal was added 32mL (0.662 mol) of n-propanol and 80mL (4.4 mol) of water. 84.5mL (0.507 mol) of 2,6-diisopropylaniline was added to the stirred solution. The mixture was heated to 70°C overnight. The reaction was quenched slowly with 160mL of water while ensuring continuous stirring. A yellow precipitate formed and was collected via filtration. The reaction produced 86.2 g of diimine corresponding to a 90% yield. Spectroscopic data matched those in the literature.⁵²

Experiment 6.2.3.B

Synthesis of N,N'-bis(2,6-diisopropylphenylamine)ethane

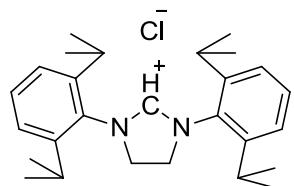


To a two neck 500 mL round bottom flask was added 35.27 g (93.7 mmol) of dipp diimine with 200 mL THF, after which, 14.3 g (378.0 mmol) of sodium borohydride was added slowly with stirring. A condenser and septum were added and the flask was heated to reflux (70°C) overnight. The following day, the reaction was quenched with a 5M HCl solution (50:50 H₂O:HCl). The quenching process was vigorous producing white foam. The addition of the

hydrochloric acid solution continued until while foam ceased to produce. The reaction was evaporated to near dryness at which point the solid was washed with ether and promptly evaporated again producing 35.6 g of dipp diamine; Yield 84%. Spectroscopic data matched that of the literature.⁵²

Experiment 6.2.3.C

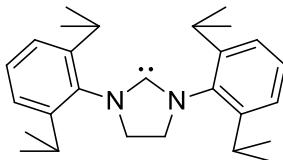
Synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazolidium chloride (SIPr carbene salt)



To a 1 L round bottom flask was added 500 mL of thiethylorthoformate followed by 25 g (55.1 mmol) of 2,6-diisopropylphenyl diamine. To the stirred solution was added 5 pipette drops of formic acid and the reaction was heated to reflux (125°C) in a silicon oil bath for two days. The remaining triethylorthoformate was filtered off and the residual solvent was evaporated to yield 20.4 g the SIPr carbene hydrochloride salt; yield 87%.

Experiment 6.2.3.D

Synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr carbene)

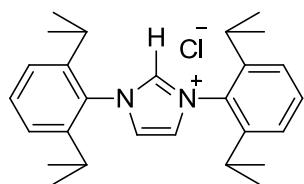


To a dry 500 mL schlenk flask containing 200mL THF was added 23.18 g (54.5 mmol) of SIPrHCl salt, 5.21 g (217.1 mmol) of NaH (4 equiv.) and 0.609 g (5.4 mmol) of 5 mol%

potassium t-butoxide. The reaction was allowed to stir under a nitrogen atmosphere for one day. The reaction was then filtered through Celite and the filter cake was washed with additional THF. The filtrate was evaporated to yield 19.96 g of the desired carbene as an off-white powder; yield 93%. Recrystallization from pentanes grew needle-like crystals and confirmed a clean product.

Experiment 6.2.3.E

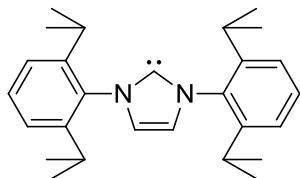
Synthesis of 1,3-bis(2,6-diisopropylphenyl)imidizolium chloride (IPr carbene salt)



To a 1 L round bottom containing a stirred solution of 25 g (55.4 mmol) of dipp diimine in 500mL of toluene was added 2.0g (66.6 mmol) of paraformaldehyde. The reaction was heated for 1 hour at 100°C until the majority of the paraformaldehyde was dissolved. The solution was cooled to 40°C after which 16.5mL 4M HCl in dioxane was added with a syringe. The reaction was heated again to 70°C for 5 hours after which the solution was brown with a white precipitate. The heat was turned off and the reaction was allowed to stir for three days. The now dark purple precipitate was filtered, washed with THF washing much of the purple colour through leaving a light purple product. The solid was evaporated to dryness to yield 18.67 g of the IPr hydrochloride salt; yield 79%.

Experiment 6.2.3.F

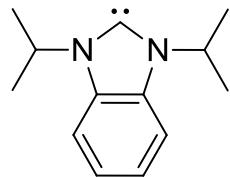
Synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr carbene)



To a 20 mL scintillation vial containing a solution of 500 mg (1.18 mmol) of IPr salt in 12mL of THF was added 131 mg (1.17 mmol) of potassium *tert*-butoxide. The reaction was allowed to stir for 4 hours after which the solvent was evaporated to yield 386 mg of the desired IPr carbene; yield 84%.

Experiment 6.2.3.G

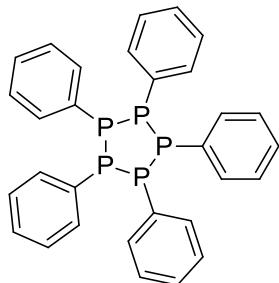
Synthesis of 1,3-bis(isopropyl)benzimidazol-2-ylidene



To a 100 mL round bottom flask was added 5.447 g (16.5 mmol) of benzimidizolium carbene salt and 1.851 g (16.5 mmol) potassium *tert*-butoxide in dry diethylether. The solution was allowed to stir overnight after which, it was evaporated. The resulting crude solid was re-dissolved in pentane and evaporated again to 3.14 g yield sticky yellow solid; yield 93%.

Experiment 6.2.3.H

Synthesis of (pentaphenyl)cyclopentaphosphine

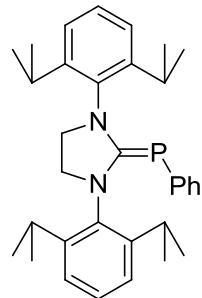


To a scintillation vial was added 276.2 μL (2.04 mmol) dichlorophenylphosphine and 74mg (3.05 mmol) of magnesium metal in dry THF. The reaction was allowed to stir overnight after which, the solution was filtered and then the resulting solution was evaporated to dryness to yield 0.786 mg of the desired P_5Ph_5 as an off-white powder; yield 71%.

Section 6.2.4 – Carbene-Phosphinidene Adducts

Experiment 6.2.4.A

Synthesis of SIPr Phosphinidene



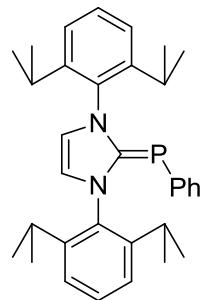
To a 20 mL scintillation vial containing a stirred solution of 1.00 g (2.55 mmol) of SIPr carbene in 7 mL of dry THF was added 346 μL (2.55 mmol) of dichlorophenylphosphine. In a separate

20 mL scintillation vial, was added 108 mg (4.46 mmol) of magnesium in 5 mL of dry THF. This mixture was allowed to stir for 5 minutes after which it was added to the first vial. The reaction was allowed to stir overnight and then filtered through Celite and evaporated. The crude solid was dissolved in pentane, filtered again through Celite and evaporated again to give SIPr phosphinidene. Yield: 911mg (72%).

¹H NMR (C₆D₆, 298K) δ: 1.19 (d, 12H, CH-CH₃, ³J_{HH} = 4.1), 1.30 (d, 12H, CH-CH₃, ³J_{HH} = 4.1), 3.45 (sept, 4H, CH-CH₃, ³J_{HH} = 4.1), 3.52 (s, 4H, CH₂-CH₂), 6.756 (m, 6H, C_{Ar}H), 6.72-7.33 (m, 5H, C₆H₅). ³¹P{¹H} NMR (C₆D₆, 298K) δ: -8.90 (s)³⁶

Experiment 6.2.4.B

Synthesis of IPr Phosphinidene

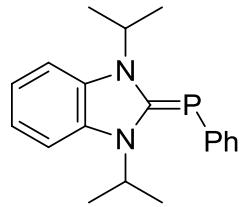


To a 20 mL scintillation vial containing a stirred solution of 300 mg (0.772 mmol) of IPr carbene in 7 mL of dry THF was added 105 μL (0.772 mmol) of dichlorophenylphosphine. In a separate 20 mL scintillation vial, was added 37.6 mg (1.54 mmol) of magnesium in 5 mL of dry THF. The mixture was allowed to stir for 5 minutes after which, it was added to the first vial. The reaction was allowed to stir overnight and then filtered through Celite and evaporated. The crude solid was dissolved in pentane, filtered again through Celite and evaporated again to give IPr phosphinidene. Yield: 303 mg (79%).

^1H NMR (C_6D_6 , 298K) δ : 1.13 (d, 12H, $\text{CH}-\text{CH}_3$, $^3J_{\text{HH}} = 6.9$), 1.44 (d, 12H, $\text{CH}-\text{CH}_3$, $^3J_{\text{HH}} = 6.8$), 3.45 (sept, 4H, $\text{CH}-\text{CH}_3$, $^3J_{\text{HH}} = 4.1$), 6.18 (s, 2H, $\text{CH}-\text{CH}$) 7.09-7.14 (m, 6H, $\text{C}_{\text{Ar}}\text{H}$), 6.95-7.35 (m, 5H, C_6H_5). $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 298K) δ : -19.73 (s)³⁶.

Experiment 6.2.4.A

Synthesis of benzamidizol-2-ylidene phenylphosphinidene

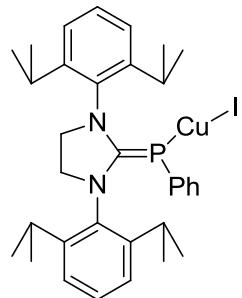


To a 50 mL round bottom flask containing a stirred solution of 0.400 g (1.96 mmol) of benzamidizol-2-ylidine carbene in 15 mL of dry THF was added 0.216 g (0.392 mmol) of pentaphenylcyclophosphine. The reaction was allowed to stir overnight and then filtered through Celite and evaporated. The crude solid was dissolved in pentane, filtered again through Celite and evaporated again to give a bright red solid. Yield: 441mg (73%).

C_6D_6 ^1H NMR (C_6D_6 , 298K) δ : 1.50 (d, 12H, $\text{CH}-\text{CH}_3$, $^3J_{\text{HH}} = 4.1$), 4.43 (sept, 4H, $\text{CH}-\text{CH}_3$, $^3J_{\text{HH}} = 4.1$), 7.05 (m, 9H, $\text{C}_{\text{Ar}}\text{H}$), $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 298K) δ : -35.2 (s)³⁶

Experiment 6.2.4.A

Synthesis of SIPr-phosphinidene copper iodide



To a NMR tube containing a solution of 0.050 g (0.001 mmol) of SIPr carbene in 0.75 mL of anhydrous chloroform was added 0.0191 g (0.001 mmol) of copper iodide.

$^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 298K) δ : -31.4 (s)

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