

Synthesis of Early-Late Heterobimetallic Complexes and the Effect of their Metal-Metal
Interactions

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

Dr. Connie Lu

December 2009

Acknowledgements

I wish to acknowledge and thank those people who contributed to this thesis:

Dr. Connie Lu, and the other members of my committee, whose guidance and flexibility were the key to the successful completion of my masters degree. Dr. John Ellis, whose love of chemistry inspired me.

The founding members of my lab, Deanna Miller and Kit Zall, who started this journey with me and on whom I depended on in and outside of the laboratory. All other current members, including Keying Ding, Alex Rudd, and Steve Tereniak, whose support never wavered.

Richard F. Toussaint and Scott Greenwood, from whom I first learned to love science.

Bobby Arenivas and Cheryl Sperier, without whose understanding and encouragement I could not be where I am today.

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List of Abbreviations

NMR: nuclear magnetic resonance

IR: infrared

EPR: electron paramagnetic resonance

CV: cyclic voltammetry

EXAFS: extended X-ray absorption fine structure

FSR: formal shortness ratio

C: celcius

ESI-MS: electrospray mass spectrometry

d: doublet

dd: doublet of doublets

bs: broad singlet

td: triplet of doublets

DMSO: dimethylsulfoxide

THF: tetrahydrofuran

I. Specific Objectives and Significance

There is little understood about the effect that one transition metal center has on another. While the effects of main-group elements bonding to metals have been studied extensively, the comparable effects of metals on one another remain to be systematically explored. Heterobimetallic complexes, with two different transition metals, provide the opportunity to investigate this effect. One approach to understanding the metal-metal interactions in heterobimetallic complexes is to synthesize complexes and study their structural and electronic behavior for a wide range of transition metals. We propose specifically focusing on synthesizing novel “double-decker” ligands to yield early and late transition metal-metal stabilized bonds with one active metal site available to react. There are three aims proposed by this work. The first is to successfully synthesize double-decker ligands that have the potential to stabilize two transition metals from the opposite end of the d-block. The second is to insert early and late transition metals to bind to these double-decker ligands. The final goal is to understand the nature of the metal-metal interaction in these complexes through spectroscopic characterization methods. The strategy is to use a composite ligand of hard and soft donors to bind an early and late transition metal, respectively, within bonding range of each other. The ligand incorporates the early transition metal deep in its binding pocket, so that only the late transition metal is exposed. Thus, the effect of each metal on reactivity can be isolated and studied systematically.

Figure 1: Target Complex of a Heterobimetallic Complex with a Mixed Phosphine-Amide Double-Decker Ligand
M = Ti or Zr, R = ⁱPr or Ph

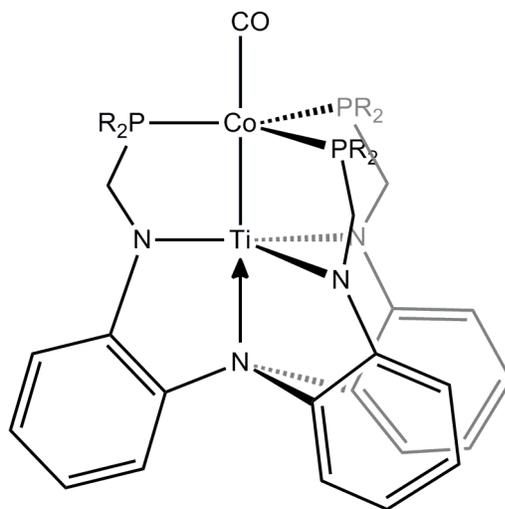


Figure 1 depicts the target heterobimetallic complex to be synthesized. The target complex will be characterized by techniques such as: NMR, to study solution behavior; EPR, to study the electronic structure; cyclic voltammetry, to study the redox behavior; and X-ray crystallography, to study the solid state structure.

II. Introduction and Background

In order to design catalysts involving transition metals, their electronic properties must be extensively characterized and well understood. Catalytic systems, such as the Fischer-Tropsch system and the hydroformylation reaction, are systems that can use heterobimetallic catalysts, but the role of each metal is not well understood. Heterobimetallic complexes with an early and late transition metal give the opportunity to more fully understand the bonding between two disparate metals, as well as evaluate their potential for catalysis. The synthesis of heterobimetallic complexes has been greatly advanced by the judicious design of the surrounding ligand. However, examples of complexes with a bond between an early and late transition metal are still quite limited as seen in Table 1 below.²

Table 1: Number of Early-Late Metal Complexes that are Crystallographically Characterized³⁻⁵¹

Group:	VIII			IX			X			
	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt	
IV	Ti	8	7	0	5	8	2	4	1	4
	Zr	3	5	1	2	9	7	1	2	0
	Hf	0	0	0	1	1	0	1	2	0
V	V	0	0	0	0	0	0	1	0	0
	Nb	4	0	0	1	1	0	1	0	0
	Ta	3	0	0	3	0	4	0	6	2

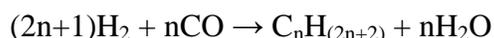
*Multi-metallic clusters are not included in this overview

In general, first-row transition metal pairs of Group IV with Group VIII and Group IV with Group IX have had the most complexes synthesized and studied, but even with these complexes, the picture is still very incomplete. While they have been synthesized and characterized structurally, there is not much known about the reactivity and electronic properties of the metal-metal bond. There are only a few examples of

Group V paired with any late metal belonging to Group IX or Group X metal. There are almost no examples of Group V paired with Group VII. Any combinations of these and other metal pairs where there are no examples would make for new and interesting targets to synthesize and characterize.

There is an obvious need to more extensively study the behavior of heterobimetallic complexes. The benefit of two metal centers in catalysis has recently revealed that, especially within small-molecule catalysis, two metal centers can act cooperatively together to accept or donate electron density to lower the redox barrier that would otherwise buildup on one metal center. Therefore, the question of the nature of the metal-metal bond is intriguing. Where the heterobimetallic metal-metal bond lies on the scale of polarity, from ionic to a covalent interaction, and what role that plays in reactivity is a question that has started to be answered but requires more systematic exploration across the periodic table.²

For example, the Fischer-Tropsch process is a catalytic process used for converting CO into a useable fuel as displayed in the equation below:



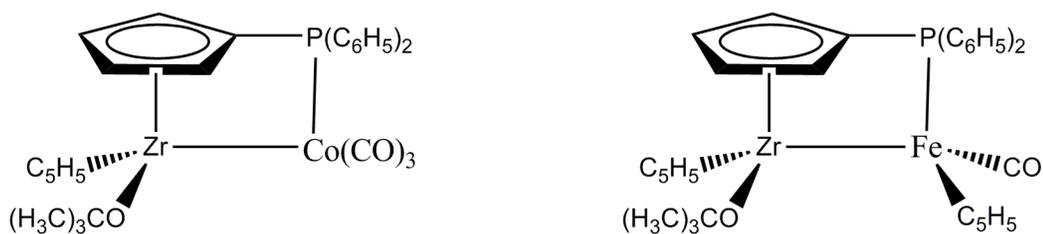
The most common transition metal catalysts include cobalt, iron, and ruthenium, where cobalt is the most active catalyst. When this reaction is initiated on the surface of an early transition metal support material, such as TiO₂, the early transition metal directly interacts with group 8-10 metals, shown spectroscopically by EXAFS.⁷³ The rate of methane formation at low temperature is increased by an order of magnitude or more by introducing the early transition metal support material. The reason for this change is not

clear, but it is thought that the metal-metal bond provides active sites for the dissociation of CO. Looking only at the surface interaction of these metals, it is very difficult to isolate the effect of the metal-metal bond. Therefore, it is important to characterize discrete complexes to fully understand this effect.⁷³

Synthesis

Bullock and Casey synthesized the first examples of heterobimetallic compounds in which an early group 4 metal and a late group 8 and 9 metal have a heterobimetallic bond supported by a ligand that can bind both metals as seen in Figure 2. For the Zr-Co complex on the left side of Figure 2, photolysis had to be used in addition to adding $\text{Na}^+\text{Co}(\text{CO})_4^-$ in order to drive off a CO and create the Zr-Co bond. For the Zr-Fe complex on the right side of Figure 2, $\text{K}^+(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ was used to displace a chloride from zirconium and make a Zr-Fe bond. The complex was then photolyzed to release CO and make the Fe-P bond.⁵²

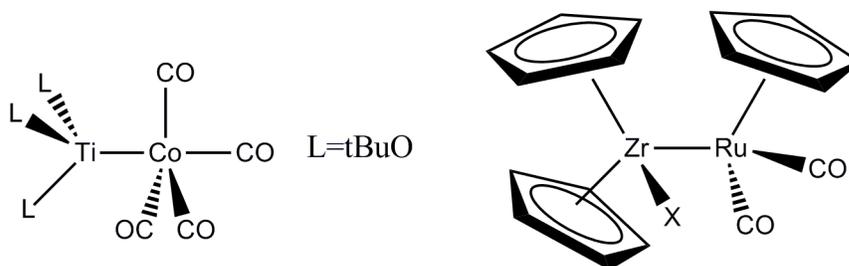
Figure 2: Early-Late Heterobimetallic Complexes of Bullock and Casey



Typical early-late heterobimetallic complexes include both bridged and unbridged metal-metal bonds. Most commonly, the early metal has alkoxy, imido, amido, or oxo “hard” ligands attached to it to stabilize the high oxidation state. The late transition metal usually is stabilized by “soft” ligands such as phosphines, sulfides, and heavier halogens.

Gade wrote a review to summarize polar early-late heterobimetallic complexes up to 2000.⁵³ In Figure 3, a few chosen representative examples of unsupported heterobimetallic complexes from the original references are shown.

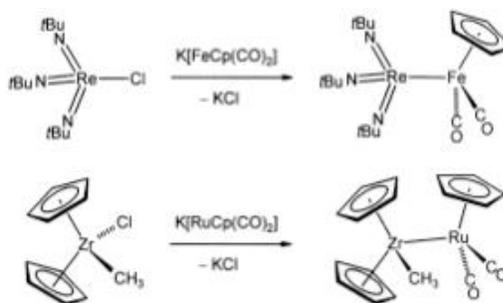
Figure 3: Representative Examples of Unsupported Heterobimetallic Complexes⁵³⁻⁵⁵



Almost all heterobimetallic complexes feature single metal-metal bonds, but there are rare exceptions of metal-metal multiple bonds in heterobimetallic complexes akin to homobimetallic complexes. Typically, the exceptions involve metal-metal clusters, but one discrete dinuclear example from Slaughter *et al.* is a triply bonded Ti-Rh complex described later in the bonding section.⁴²

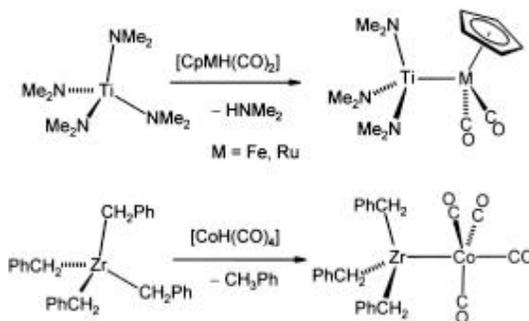
Synthetic methods for preparing these complexes include salt metathesis by using an early transition metal halide with an alkali metal salt of a late transition metal.^{25, 53}

Figure 4: Synthetic Methods for Heterobimetallic Complexes: Salt Elimintaion



In the first examples of a group 4 metal and a late transition metal forming a direct metal-metal bond, salt formation and photolysis to drive off CO were used as the driving forces for the reaction.¹³ In general, linking an early and late metal together is most often achieved by generating a salt as a byproduct, such as KCl. Commonly, an early transition metal halide is reacted with an alkali metal salt of an anionic late transition metal complex. This method is seen in Figure 4.

Figure 5: Synthetic Methods for Heterobimetallic Complexes: Amine and Alkane Elimination⁵³



Another synthetic strategy is reacting neutral complexes to form a less polar byproduct such as an amine or alkane and a metal-metal bond. Similar to a condensation reaction, these products result from a reaction with a hydrido-late transition metal complex with an amido or alkyl-early transition complex. The schemes shown in Figure 5 show examples of this.⁵³

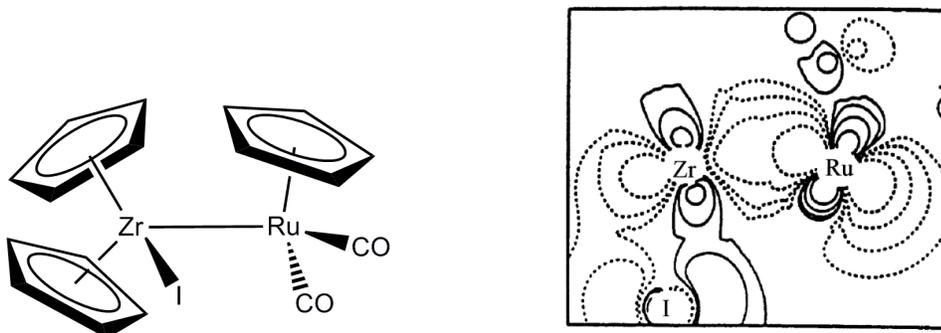
Yet another frequently used method employs reduction to get a metal-metal bond when the complex already has two metals within bonding range in a single complex and a halide ligand coming off of each metal. For example, a Ti-Rh bond has been formed by Na/Hg reduction and eliminating NaCl.⁴² It is important to note that single-electron

transfer from the late metal to the early metal can compete with the formation of the metal-metal bond because the early metal complex fragment can potentially be an oxidizing agent due to its electron deficiency. In addition, the late transition metal is reducing because it is electron-rich.⁵³

Bonding Theory

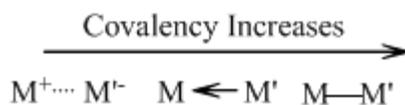
Heterobimetallic bonding interactions were first studied in intermetallic solids. Stability was found to be due to a Lewis acid and Lewis base interaction where the early transition metal center is thought to act as an electron acceptor towards the late metal. However, since these are not discrete complexes, the effects of the metal-metal bonds are not easily isolated. Calculated frontier orbitals for the heterobimetallic complex below showed that zirconium center contributed 15% and that ruthenium contributed 72% of the electron density towards creating this highly polar bond. Figure 6 shows a contour diagram of the bonding orbitals in this complex. A contour plot displays values of relative electron density around a specific area in a two-dimensional plot as seen for the Zr-Ru complex below.¹⁶

Figure 6: Contour diagram of Zr-Ru Complex^{48, 57}



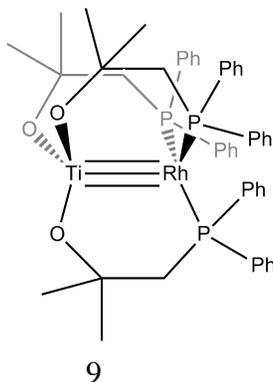
In an early-late heterobimetallic complex, the bond is highly polar due to the nature of the metals and large difference in their formal charges. The increased strength of the bond makes it shorter than the normal purely covalent, homometallic single bond. A partial negative density would reside at the late, low-valent transition metal while the positive on the early transition metal. This type of bond can also be thought of as almost ionic because it is so polar.⁵³

Figure 7: The Continuum of Heterobimetallic Bonds



As mentioned earlier, these complexes usually form single metal-metal bonds, but an example of a multiply bonded heterobimetallic complex is shown in Figure 8. Indeed, this Ti-Rh bond is short enough to be a multiply bonded metal complex at 2.2412(11) Å., considering that this length is 0.362 Å shorter than the sum of the covalent radii. In addition, the reduction in the bond length is a large deviation from a single bond with an FSR, formal shortness ratio, of 0.860.⁴²

Figure 8: Multiply Bonded Complex of Ti and Rh



Even with the energy differences of the d-orbitals between an early and late transition metal, the polarity of the resulting bond gives thermodynamic stability. Reported thermodynamic data for a series of heterobimetallic solids support this reasoning. Table 2 shows calculated dissociation energies of metal dimers in the gas phase, where the iron-iron dimer is the least stable of all combinations studied.⁵³

Table 2: Heterobimetallic Dissociation Energies

Table 2. Dissociation energies of the diatomic M-Fe molecules.

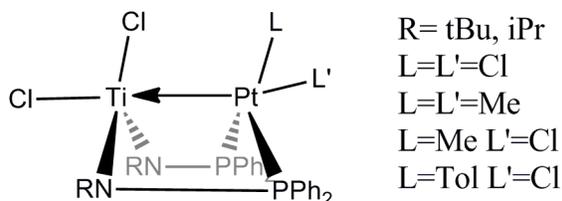
M-Fe	$D^\circ(\text{M-Fe})$ [kcal mol ⁻¹]	M-Fe	$D^\circ(\text{M-Fe})$ [kcal mol ⁻¹]
Sc-Fe	55	Fe ₂	18
Ti-Fe	42	Co-Fe	30
V-Fe	44	Ni-Fe	39
Cr-Fe	32	Cu-Fe	30

As seen in Table 2, the early-late metal bond is more stable than the comparable homobimetallic bond. With iron functioning as the more electron-rich transition metal, the electron-poor, or the earlier the metal is, the more stable the resulting bond will be. Even with two late metals (as seen in the second column of Table 2), they are still different enough that allow for some polarity of the bond. Even a small amount of polarity makes these bonds more stable than that of the iron dimer.

However, this type of bond does allow for intramolecular single electron-transfer that can lead to degradation of the complex. This means that the acidic early metal must be protected by appropriately designed ligands to protect it from degradation. In unsaturated heterobimetallic complexes, attenuating the metal-metal bonding by π -acceptor-ligand-metal interactions on late metals can play an important role. The hard ligands attached to the early transition metal help to stabilize the high oxidation state and

inhibit single-electron transfer.^{29,53,66} Specifically, phosphinoamides make for good ligands for stabilizing an early and late metal, and this is a precedent shown in the literature as seen in Figure 9.^{52, 62, 64}

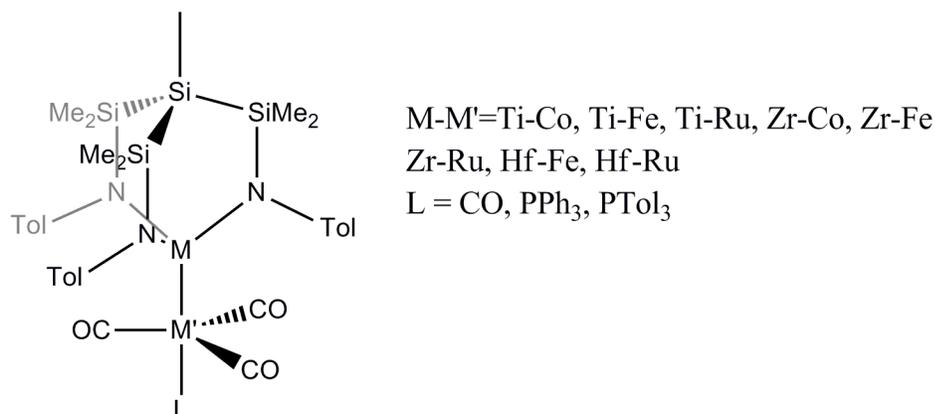
Figure 9: Nagashima's Phosphinoamide Ligands for Titanium and Platinum Dative Bonds



Incorporating the afore-mentioned hard ligands for the early metal along with a tripodal frame has been an effective combination for creating stable heterobimetallic metal-metal bonds. Theoretical calculations have shown that the tripod ligand design thermodynamically stabilizes a metal-metal complex with respect to a similar non-tripodal design.⁵³ In order to understand why this is the case, molecular orbital theory can be employed. Most of the complexes in Table 1 are d^{10} , and a total of ten d electrons results in a bond order of one. Only using MO theory is too simple an explanation for the complexes because the exception shown in Figure 8 is d^{10} but does not have a bond order of one. Therefore, a more complex understanding of the thermodynamic stability of incorporating a tripodal ligand frame in heterobimetallic complexes needs further investigation.

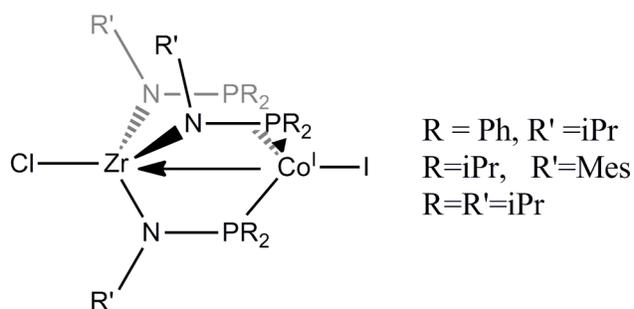
The tripodal frame has been successfully used for a wide range of heterobimetallic complexes.^{1, 29, 53, 66}

Figure 10: Tripodal Ligand Frame for Heterobimetallic Complexes^{23, 45, 53}



Not only is a tripodal ligand design of interest, but it has been shown that for an interaction between cobalt(I) and zirconium(IV), a more electron rich substituent on this type of ligand such as a diisopropylphosphine, gives more electron density to the cobalt center and hence, strengthens the dative bond from cobalt to zirconium.⁶⁸

Figure 11: Greenwood's Phosphinoamide Ligands for Zr and Co Dative Bonds



A shortening of 0.1Å is seen for the Co-Zr bond by simply switching from a diphenylphosphine to diisopropylphosphine as the soft ligand attached to cobalt. This shows what a large role the ligand plays in the synthesis of heterobimetallic complexes. In addition, the dative interaction of the Co-Zr bond encouraged by an electron-donating ligand was seen to perturb multielectron redox activity to lower potentials at the cobalt(I) center. Corresponding compounds lacking the electron-withdrawing zirconium center

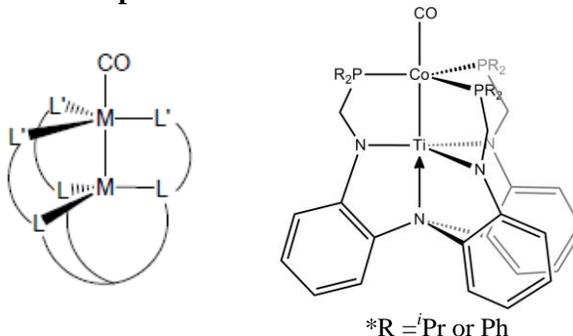
showed nearly 1 V more negative reduction potentials than the Co/Zr complex.

Exploiting this feature may be promising for small molecule activation.⁶⁸

An advantage to using the tripodal frame with the proposed “double-decker” design is to shield the distal metal and to isolate the effects of reactivity to only the single, exposed metal. The buried metal can be varied to give more insight into the mechanism of already useful bimetallic processes.¹

The Fischer-Tropsch reaction is a good example of this, in which the surface chemistry where the metal-metal bond is formed is not well understood. Combining an early and late transition metal within a supporting scaffold is a simple model of the active metals in this catalysis from which the nature of the metal-metal bond could be isolated. The known TiO₂-supported Fischer-Tropsch process can be modeled for titanium bonded to cobalt, for example, using this type of “double-decker,” tripodal ligand frame as shown in Figure 12. In this way, the reason for the increased hydrocarbon production with the introduction of the early transition metal oxide could be tackled from a fundamental understanding.^{1, 73}

Figure 12: General Tripodal “Double-Decker” Heterobimetallic Complex

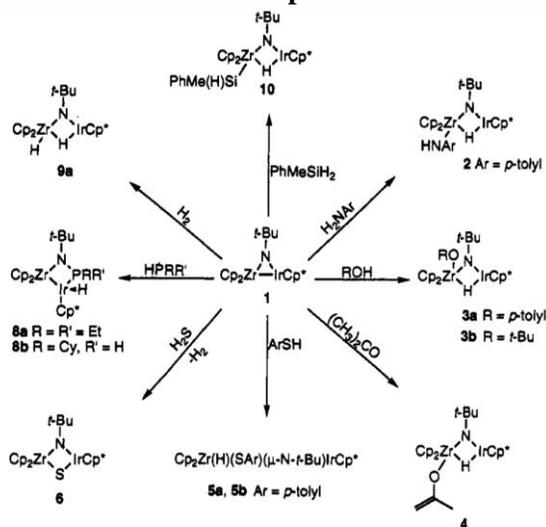


Reactivity

Heterobimetallic bonds typically react with polar bonds within substrates in an asymmetric fashion. For example, the early transition metal center can react with the

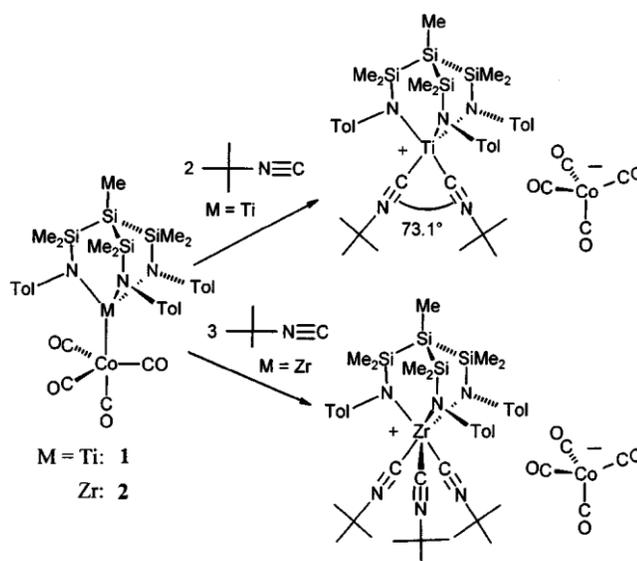
more basic part of the substrate, and the late transition metal center reacts with the more acidic part, cleaving the metal-metal bond in the process. In this way, the metal-metal bond between an early and late transition metal is ideal for heterolytic cleavage of polar substrates. This reactivity can also be extended to nonpolar substrates such as H_2 which can be cleaved heterolytically as H^+ and H^- . Bergman and coworkers show this effect in their Zr-Ir complexes for both polar and nonpolar substrates as seen in Figure 12. In their system, the imido bridge is important for keeping the heterobimetallic complex together when the metal-metal bond is broken. In addition, this particular complex is more reactive than those before it because both metals are unsaturated and are linked by an imido ligand, which is relatively less reactive. For example, with amines, the “hard” nitrogen added across the Zr-Ir bond so that the nitrogen bonded to the zirconium. Similar examples are shown in Figure 13. There is one exception in Figure 13 where a phosphine inserts across the iridium-imido bond instead of the iridium-zirconium bond to give an iridium hydride.⁴⁵

Figure 13: Wide Range of Cooperative Reactivity of Bergman and Coworkers' Zr-Ir Complex



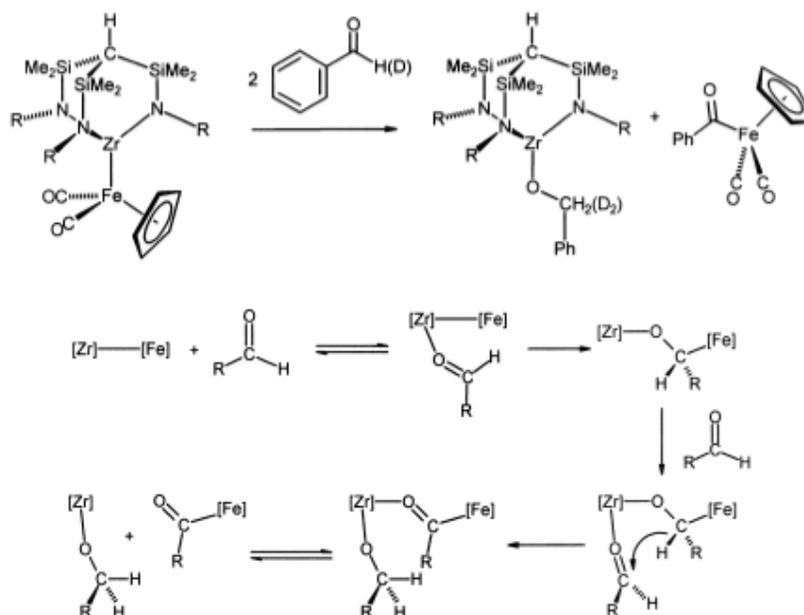
The first interaction of a polar substrate with a heterobimetallic bond is thought to be the formation of the Lewis acid-base adduct occurring at the early transition metal. This adduct is seen as the initial step in the ionic dissociation of the metal-metal bond if the late transition metal fragment is poorly Lewis basic.⁵³ An example of this is seen in Figure 14 where a reaction with tBuNC results in the dissociation of the metal-metal bond.⁵⁷

Figure 14: Ionic Cleavage of Ti-Co and Zr-Co Bonds^{23,57}



Aryl aldehydes are known to react with a zirconium-early metal complex in a Cannizzaro-like disproportionation to give the aryl-M complex and benzoxy-zirconium complex. The Cannizzaro reaction involves the base-induced disproportionation of an aldehyde that does not have a hydrogen in the alpha position. Figure 15 is a proposed mechanism of this transformation.⁵⁸

Figure 15: Zr-M Cannizzaro-like Reaction with Aryl Aldehydes

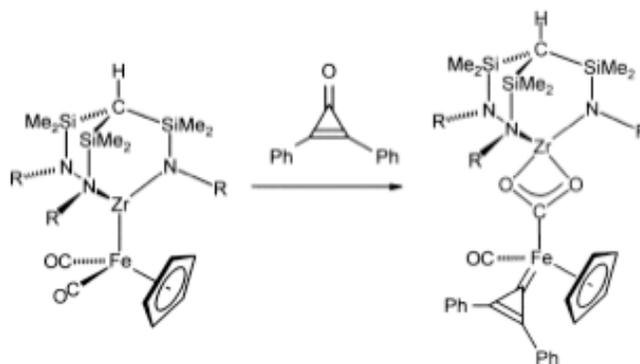


After the aldehyde binds to the early transition metal center, it inserts into the metal-metal bond, opening a coordination site on the zirconium center to add a second aldehyde molecule. The hydride transfer step is important, as it is similar to the analogous intermediate for the Cannizzaro disproportionation. This was verified isotope-labeling experiment by using deuteriated benzaldehyde to show that the hydrogen transfer only happened between the benzylic positions without involving other hydrogen atoms.⁵⁸

Carbonyl bond cleavage with oxygen atom and carbene transfer reactions have occurred with Zr-M complexes. The metal-metal bond breaks with the late metal complex bound to the reduced carbene ligand. Both metals must participate; when the discrete metal complex fragments react, they are unable to produce the reduced carbene product. This is a good example of cooperative reactivity of the two metal fragments.

When two metals are used, the benefit of having the early transition metal is to activate the complex for nucleophilic attack by the late transition metal. Once the zirconium-oxygen bond is formed, it can then react further with an iron-bound carbonyl to give the final product. Instead, when an analogous monometallic chlorozirconium complex was added, the oxygen-transfer product was not seen, and a mixture of products was obtained where the desired zirconium-oxo product shown in Figure 16 was not even identified as a minor component. In both previous examples, the polar metal-metal bond is the easily cleaved, reactive “interface”.⁵⁸

Figure 16: Deoxygenation using a Heterobimetallic Complex

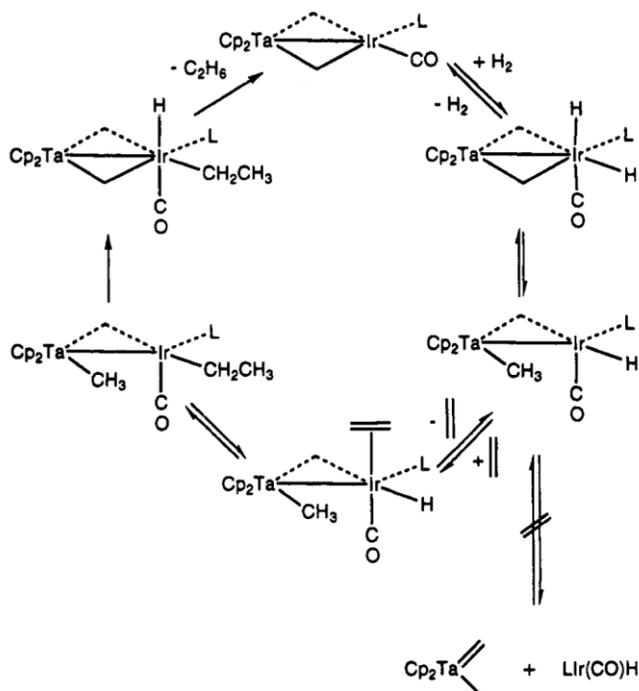


Key Examples of Catalytic Applications

Bergman and coworkers also showed how a heterobimetallic complex, in this case tantalum and rhodium, can be used to catalyze the hydrogenation of alkenes. Figure 16 shows the catalytic scheme for their proposed mechanism. The key step in the hydrogenation is reductive elimination of one of the bridging methylenes. They show that it is important to have the early metal attached to the late metal by substituting the early metal with a ligand that is similar in nucleophilicity or Lewis acidity. By substituting in a phosphine for Cp₂Ta, the bridge elimination is less energetically

favorable and therefore, the hydrogenation is much slower. For example, using $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{Ir}(\text{CO})(\text{PPh}_3)$ resulted in rates that were 150 times slower than the bimetallic tantalum-iridium complex.⁵⁹

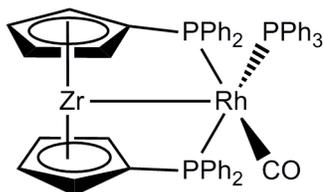
Figure 17: Proposed Mechanism of the Hydrogenation of Alkenes



Hydroformylation reactions can be performed using a heterobimetallic complex. Hydroformylation is important industrially for converting alkenes to aldehydes. The particular complex shown in Figure 18 can catalytically produce heptanals from 1-hexene. Above 50 °C, this catalyst has a maximum initial turnover frequency of >600 mol aldehyde/(mol catalyst*hour). The activation step of CO in the hydroformylation of olefins was proposed to be catalyzed by the same Zr-Rh heterobimetallic complex shown in Figure 18. This heterobimetallic complex showed a higher or as high an activity range than some of the best phosphine/chelate catalytic systems. The metal-metal bond alters

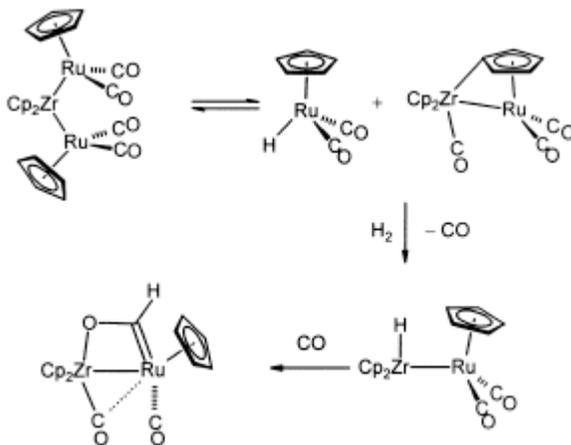
the rhodium center by determining the coordinative and electronic features compared to the metal alone.⁶⁰⁻⁶³

Figure 18: A Heterobimetallic Catalyst of the Hydroformylation Reaction



The work of Bullock and Casey was important to lay the foundation for heterobimetallic complexes and their potential use for catalysis in the Fischer-Tropsch process. The goal in the Casey group was to split dihydrogen asymmetrically into H^- and H^+ to reduce CO. There was no evidence of Fischer-Tropsch catalysis, however. The stoichiometric reduction of CO to a metalloxy carbene is effected as shown in Figure 19.^{48, 50, 52, 65}

Figure 19: Conversion of CO using a Heterobimetallic Complex⁵⁰



Spectroscopy

Spectroscopy can play a special role in elucidating information about heterobimetallic complexes. For example, EPR can help elucidate the electronics of the metal-metal bond, and CV can be used to study how reduction potentials are affected by this bond.

IR

Infrared spectroscopy (IR) can be used to track any metal complex that contains a carbon monoxide like the compounds made by Bullock and Casey as seen in Figure 2.⁵² For the complexes seen in Figure 10, IR plays a key role in characterizing early-late pairs of metals. As they changed the early transition metal from titanium to zirconium to hafnium, increased ionic character was seen in the shift of the carbonyl IR bands from 1978 to 1932 cm^{-1} . With these results, their group theorized that the titanium fragment is the best as a π -acceptor to allow for more charge redistribution from the late to the early metal.²⁹ A similar experiment can be done for our proposed complex (Figure 1) where the early metal is shielded from all reactivity by the tripodal ligand, while the late metal can be varied and tracked with IR by capping it with a carbonyl group. In addition, we can vary the early transition metal and keep the metal-CO bond the same to see how the second metal affects the late transition metal.

Gade compares the stretching frequencies of early and late complexes involving Fe-M to those of only $[\text{CpFe}(\text{CO})_2]^-$. He discusses that the CO vibration shows that the negative charge of the late metal is somewhere in between the two metals.⁵³

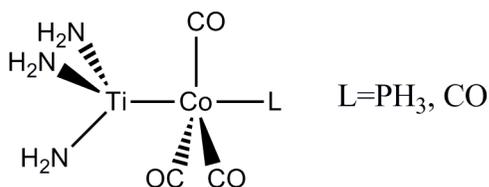
Table 3: IR CO stretching frequencies for Ti-Fe, Zr-Fe, and Hf-Fe all with a [CpFe(CO)₂] fragment.^{25, 28, 29, 53, 54, 69}

Complex	$\bar{\nu}_{\text{sym}}(\text{CO}), \bar{\nu}_{\text{asym}}(\text{CO})$ [cm ⁻¹]
<i>Ti-Fe</i>	
[(MeSi[SiMe ₂ N(<i>p</i> -Tol)] ₃)Ti-FeCp(CO) ₂]	1978, 1931
[[HC[SiMe ₂ N(<i>p</i> -Tol)] ₃]Ti-FeCp(CO) ₂]	1975, 1928
[[MeC(CH ₂ NSiMe ₃) ₃]Ti-FeCp(CO) ₂]	1968, 1916
[(Me ₂ N) ₃ Ti-FeCp(CO) ₂]	1948, 1898
<i>Zr-Fe</i>	
[(MeSi[SiMe ₂ N(<i>p</i> -Tol)] ₃)Zr-FeCp(CO) ₂]	1961, 1910
[[CH ₂ (CH ₂ NSiMe ₃) ₂](Cp)Zr-FeCp(CO) ₂]	1947, 1895
[Cp ₂ (Me)Zr-FeCp(CO) ₂]	1937, 1872
<i>Hf-Fe</i>	
[(MeSi[SiMe ₂ N(<i>p</i> -Tol)] ₃)Hf-FeCp(CO) ₂]	1969, 1915
K[FeCp(CO) ₂]	1866, 1772

X-Ray

X-ray crystallography is useful for determining not only the structure of a complex but if two metals might be within bonding range for a dative bond. For example, Jasen *et al* show that transaxial ligands replaced by better donors, like phosphines, show a contraction in the metal-metal bond as seen in Figure 20 (the structures have been simplified down to what was studied computationally). One of original structures is shown in Figure 14. Both X-ray crystallography and computations show that the π -accepting ability of CO to backbond weakens the metal-metal bond and lengthens the bond as compared to stronger donors.²³

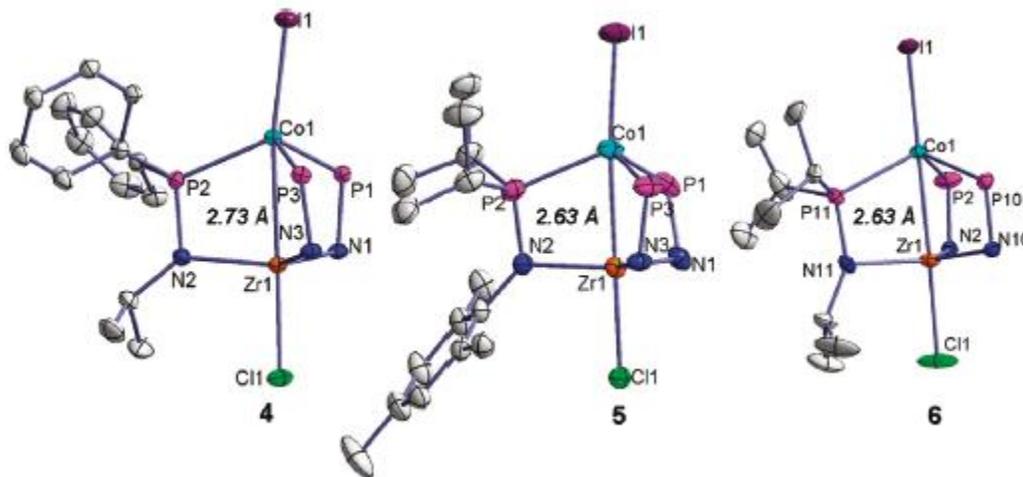
Figure 20: Complex Studied by X-ray Crystallography



X-ray crystallography also played a key role in the characterization of Greenwood's complexes. Shown in Figure 21, X-ray crystallography definitively shows

the Zr-Co interatomic distance. In these particular complexes, the Zr and Co are within bonding distance. The difference in the zirconium-cobalt bond length is a function of the electron-richness of the phosphine substituents. The more electron density is imparted on the cobalt center, the more its donation to zirconium is strengthened. Similar studies could be conducted with our double-decker complexes. Many other referenced sources use X-ray crystallography to elucidate key structural properties of heterobimetallic complexes.

Figure 21: X-Ray Structures of the Zr-Co complexes of Greenwood, *et al.*⁶⁸ Hydrogen atoms and all except for one phosphoamide have been omitted for clarity.



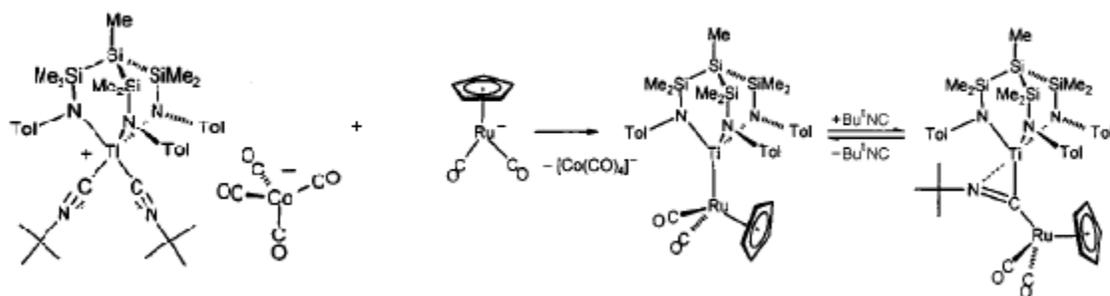
NMR Spectroscopy

NMR spectroscopy is used as a basic spectroscopy as one way to characterize any complex. Specific coupling or lack of coupling between NMR-active metals such as ^{103}Rh and ^{13}C can show how appreciably the metal interacts with a ligand. Bullock and Casey show a demonstration of this in their complexes. In their Mo-Rh complex, a terminal CO was attached to the Mo center. Interestingly, the IR band at 1801 cm^{-1} was lower in energy than what was expected for a terminal carbonyl, and they speculated

whether it might bridge the metals. The NMR spectra, however, showed no appreciable interaction between the ^{103}Rh and the ^{13}CO .⁵²

NMR spectroscopy can also be key to elucidating a mechanism of reaction as seen in Figure 22.

Figure 22: Insertion of *t*BuNC into a Heterobimetallic Complex⁵⁷



The mechanism for this cationic early transition metal complex reacting with a nucleophilic metal complex was unclear. Through using NMR, it was found that fast nucleophilic substitution of the ligand (isocyanide in this case), initially leads to a Ti-Ru complex that over a period of time inserts the ligand. This supports the predissociation of the heterobimetallic Ti-Co complex before reacting with the Ru. The isocyanide substrate coordinates to the early transition metal and causes the metal-metal bond to be cleaved to give the insertion product.⁵⁷

Cyclic Voltammetry

Greenwood *et al.* also performed electrochemical experiments on their complexes and found out that the Zr-Co bond is dative with the electrons from Co^{I} donating onto the Zr^{IV} center. The more electron-rich the phosphine substituents are, the more electron density is donated onto the acidic zirconium center. This effect was described earlier in

the bonding section on page 12. Comparing reduction potentials of their complexes, they found that the amount of dative donation of cobalt to zirconium makes a large difference so that the Co^{I} center can be reduced at milder potentials.⁶⁸ In general, electrochemistry has not been extensively used to characterize heterobimetallic complexes, and it will be interesting to see if similar results are found.

EPR

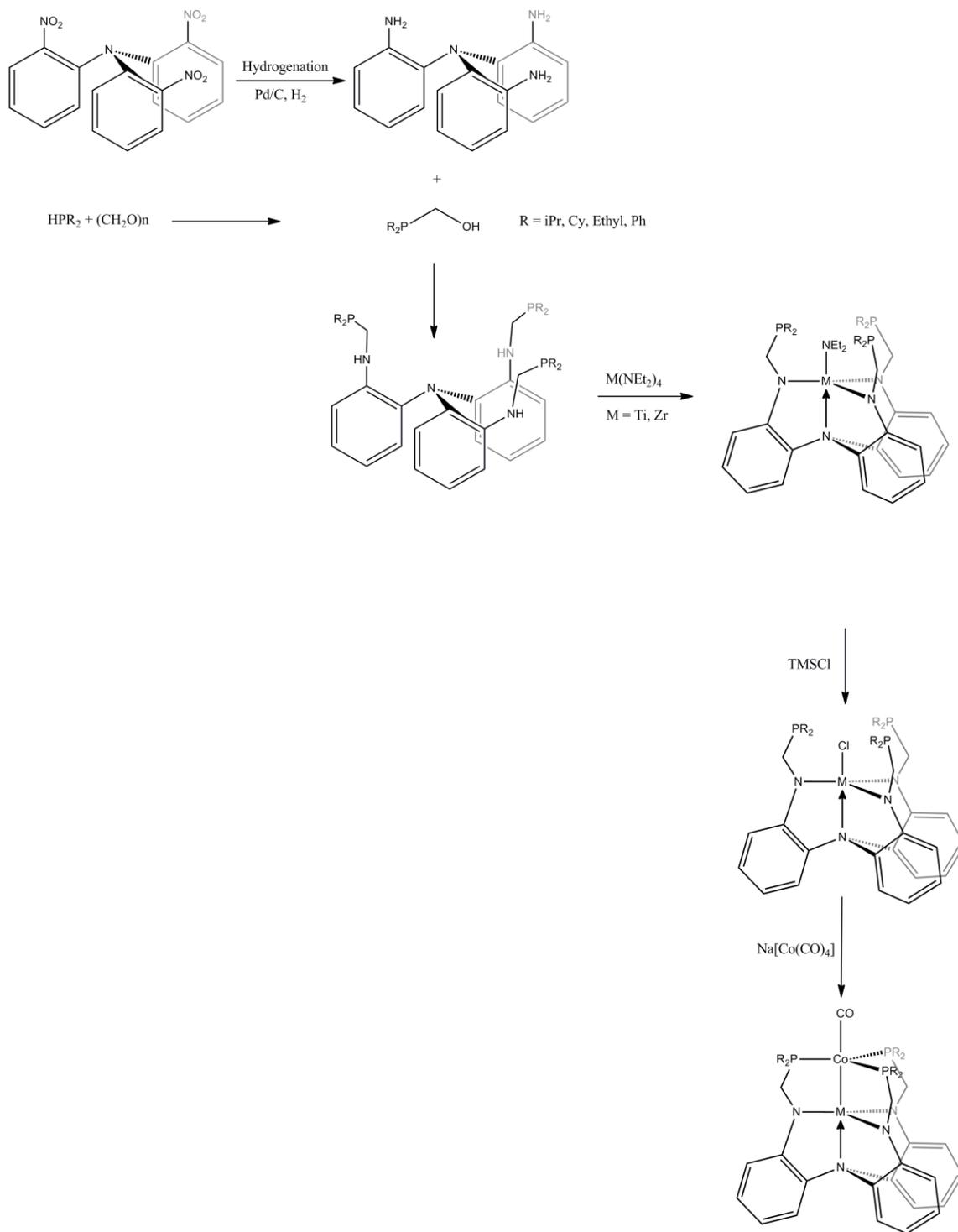
To our knowledge, there are no examples of EPR used to characterize a heterobimetallic complex. However, this technique would be useful to locate an unpaired electron in a paramagnetic species.

III. Research Progress

Results and Discussion

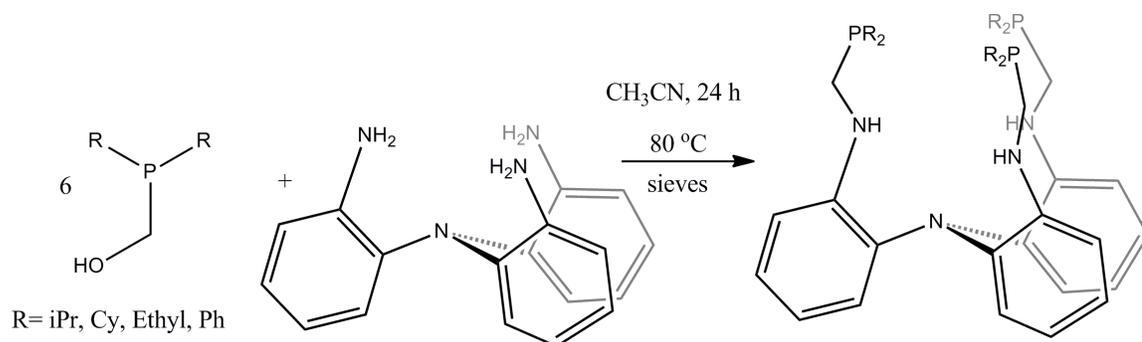
The overall scheme for the ligand bound to the early and late transition metal is depicted in Figure 23 below. My research efforts have focused on preparing tripodal ligand systems that are designed to support an early and late transition metal. The target ligand (seen in Figure 1) was prepared from precursors with slight variations of known preparations.

Figure 23: Overall Synthetic Roadmap of Research Project



The most progress was achieved in the laboratory for the synthesis of the ligand with R = ⁱPr depicted in Figure 24.

Figure 24: Ligand Synthesis



This ligand can be prepared from a condensation of a phosphine alcohol and a phenylated amine. After isolating the ligand from the sieves, the crude NMR showed that the product was not pure tris-substituted. Stored cold, the bis- and tris-substituted precipitated out as a white solid, and an additional 1.5 equivalents of the phosphine alcohol was added to drive the reaction to the trisubstituted ligand. Yields of the tris-substituted product were only 10%. However, the NMR spectra showed that there was only the tris-substituted product present. Attempts to optimize the reaction by using a plethora of solvents and temperatures, showed that the best solvent was acetonitrile, and this limited the maximum temperature at which the reaction would proceed (80° C). Sieves were also introduced because this particular reaction produces water, but that also made it quite difficult to make sure that all product was separated from the sieve dust. This ligand has been characterized by ¹H and ³¹P NMR and positive ESI-MS, although

larger scale reactions need to be conducted to verify that this ligand can be made reproducibly.

Tetrakis(diethylamide) titanium (IV) and tetrakis(diethylamide)zirconium(IV) have also been synthesized according to known preparations in anticipation of the subsequent metallation.

Experimental

General:

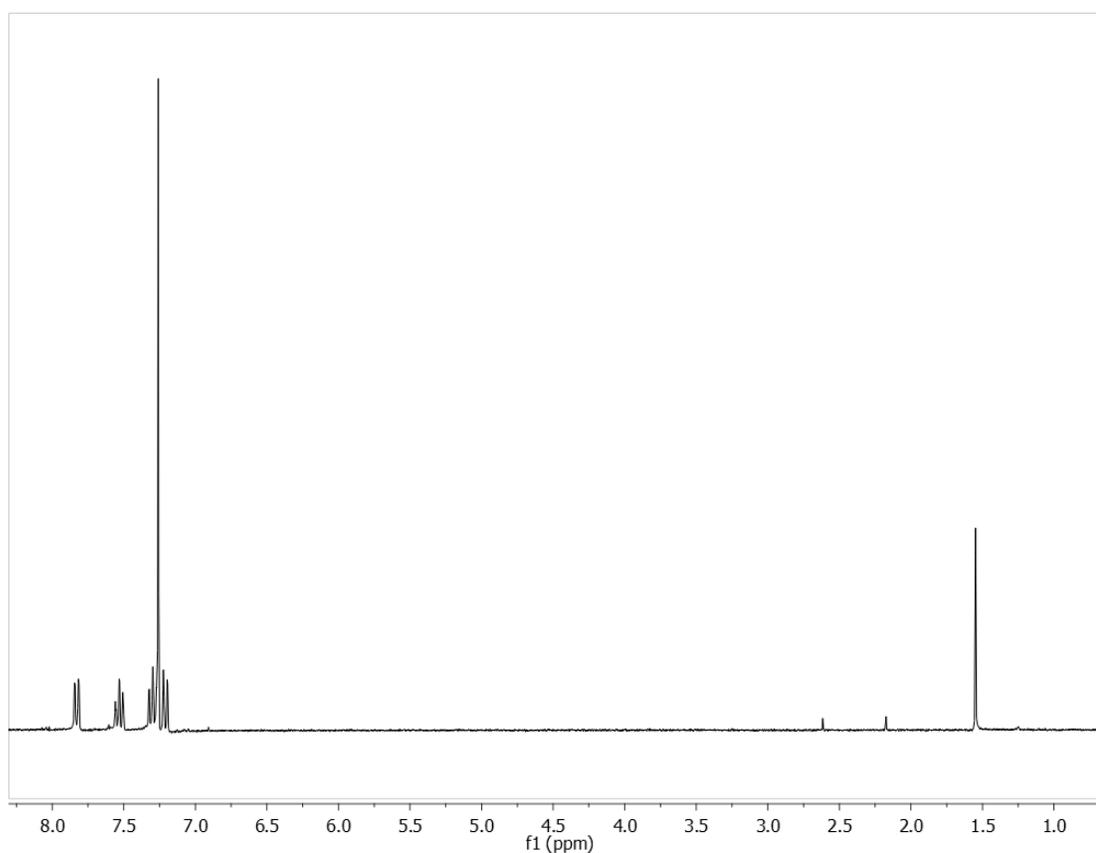
Experiments were conducted under a nitrogen atmosphere using standard Schlenk and glovebox techniques unless otherwise stated. 3Å molecular sieves used for these reactions were heated for 48 hours at 250 °C. Reagents and solvents were purchased commercially. NMR spectra were acquired on Varian Inova VMX-300MHz and VI-500MHz instruments. ESI-MS data were taken using a Bruker BioTOF II instrument.

Synthesis of Tris(2-nitrophenyl)amine⁷⁵:

In 60 mL of DMSO, 2-nitroaniline (10.0 g, 72.4 mmol), 1-fluoro-2-nitrobenzene (30.5 mL, 289.6 mmol), and K₂CO₃ (60.0g, 434.4 mmol) was stirred for 72 hours at 150°C under a flow of nitrogen. The reaction mixture was allowed to cool to room temperature and diluted with 1.0 L of water. This was filtered to give an orange-brown solid. The filtered product was stirred in boiling methanol (1.0 L) for 20 minutes and filtered through a medium porosity frit while still hot. The product was washed with cold methanol (3 x 100 mL) and dried under vacuum to give a dark yellow product.⁷⁵ Further purification was achieved by the modification of the preparation as follows. In order to further purify the product, crystallization in of a minimal amount of acetone for one to

two days was performed below 30 °C. If necessary, sublimation was used to further purify the product by subliming the bis-substituted product at 120°C. After the bis-substituted product was discarded, the tris-substituted product was sublimed at 180°C. (55%, 15.2 g) ^1H NMR (δ , CDCl_3 , 300 MHz) 7.83 (dd, 3H, $J = 1.5$ Hz, $J = 8.4$ Hz), 7.53 (td, 3H, $J = 1.5$ Hz, $J = 8.1$ Hz), 7.30 (td, 3H, $J = 1.2$ Hz, $J = 8.1$ Hz), 7.21 (dd, $J = 1.0$ Hz, $J = 8.1$ Hz).

Figure 25: ^1H NMR of Tris(2-nitrophenyl)amine

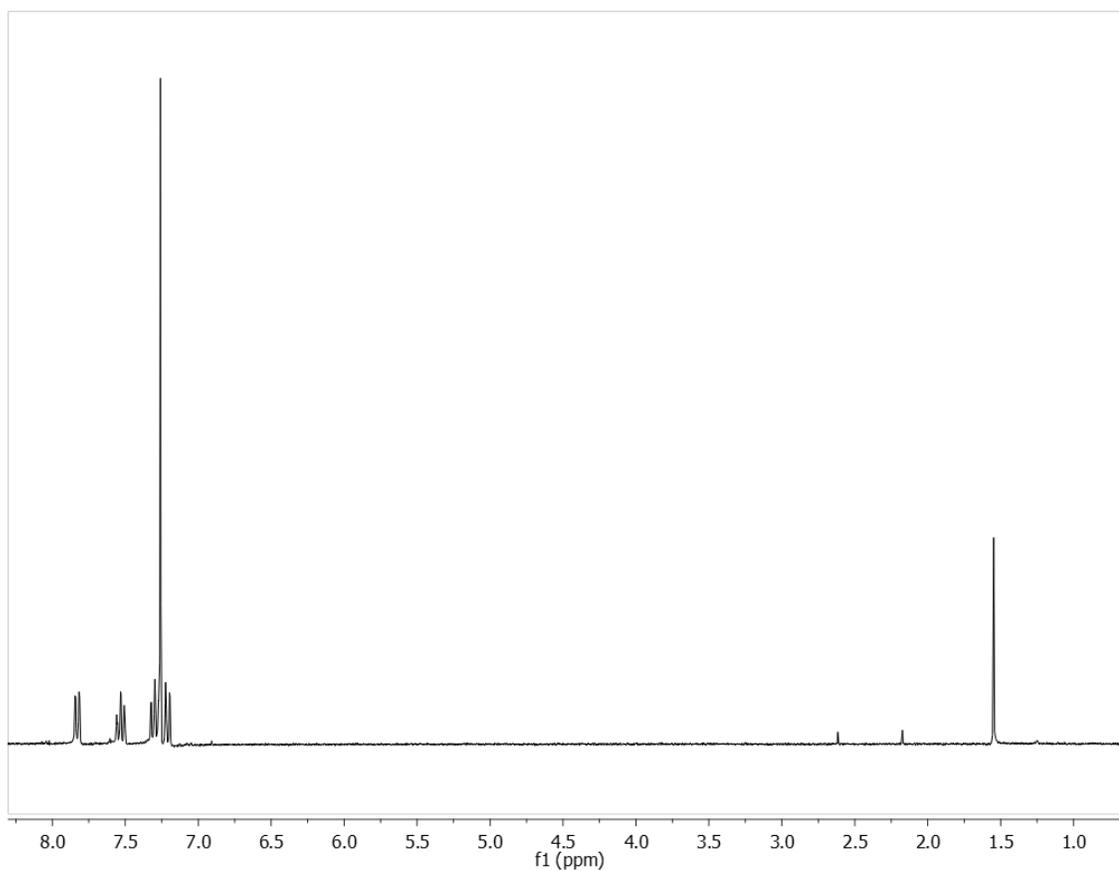


Synthesis of Tris(2-aminophenyl)amine:

In 50.0 mL of THF, tris(2-nitrophenyl)amine (10.0 g, 26.3 mmol) and 10% Pd/C (2.8 g, 2.6 mmol) were placed in a Parr reactor with 200 to 300 psi of H_2 gas (excess). The

reaction was allowed to react for 12 hours, and the reaction mixture was filtered over celite and washed with THF. The filtrate was concentrated by vacuum. The gray solid was washed with cold diethyl ether, and the off-white solid was isolated on a medium-porosity frit.⁷⁵ (73.4%, 5.61 g) ¹H NMR (δ, CDCl₃, 300 MHz): 6.99 (td, 3H, J = .9 Hz, J = 4.8 Hz), 6.91 (dd, 3H, J = 0.9 Hz, J = 4.5 Hz), 6.73 (dd, 3H, J = 0.9 Hz, J = 4.5 Hz), 6.70 (td, 3H, J = 0.6 Hz, J = 4.5 Hz), 3.70 (bs, 6H).

Figure 26: ¹H NMR of Tris(2-aminophenyl)amine

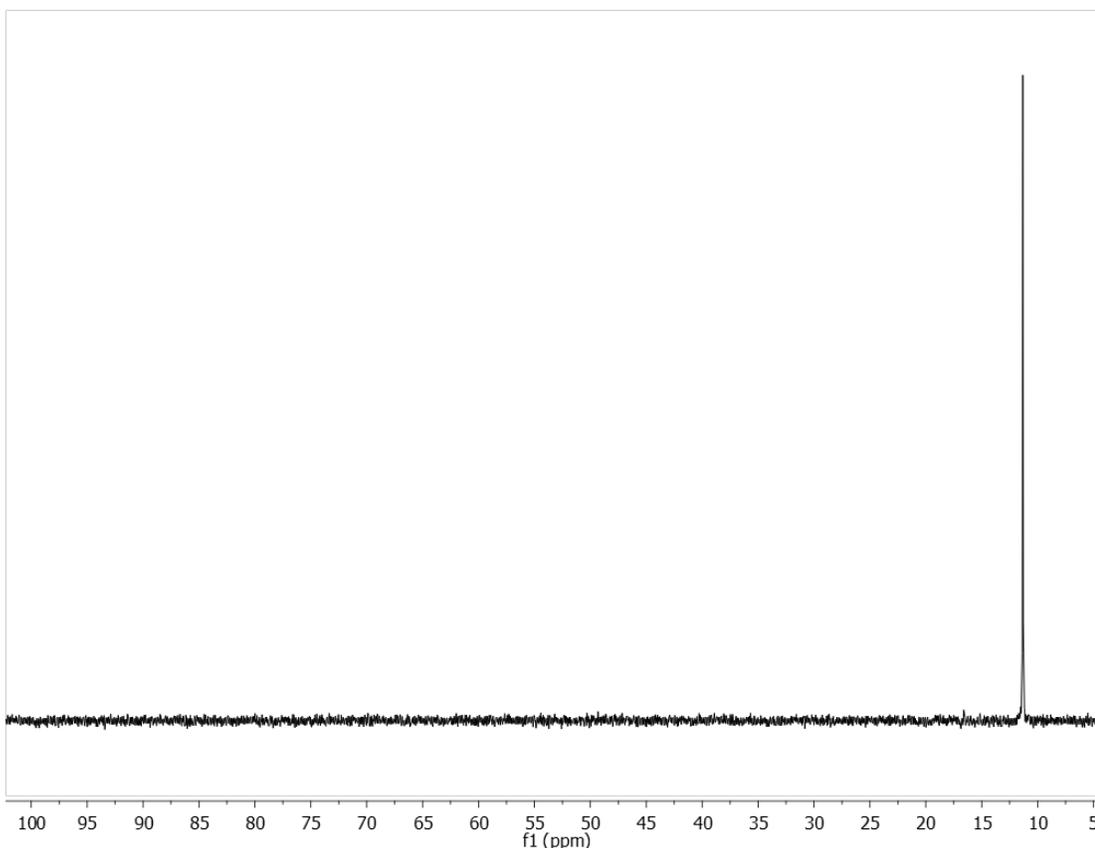


Synthesis of (Diisopropylphosphino)methanol:

A neat solution of diisopropylphosphine (2.44 g, 20.3 mmol) and paraformaldehyde (0.64 g, 20.3 mmol) was stirred for 12 hours at 60°C under a nitrogen atmosphere.⁷⁶ A similar

synthesis for diphenylphosphine can be employed. All phosphines were purchased from Strem. (85%, 2.55 g) ^1H NMR (δ , CDCl_3 , 300 MHz): 4.03 (d, 2H, $J = 4.2$ Hz), 1.90 (sept., 2 H, $J = 3.9\text{Hz}$), 1.14 (d, 12H, 7.2 Hz). ^{31}P NMR (δ , CDCl_3 , 300 MHz): 11.3.

Figure 27: ^{31}P NMR of (Diisopropylphosphino)methanol

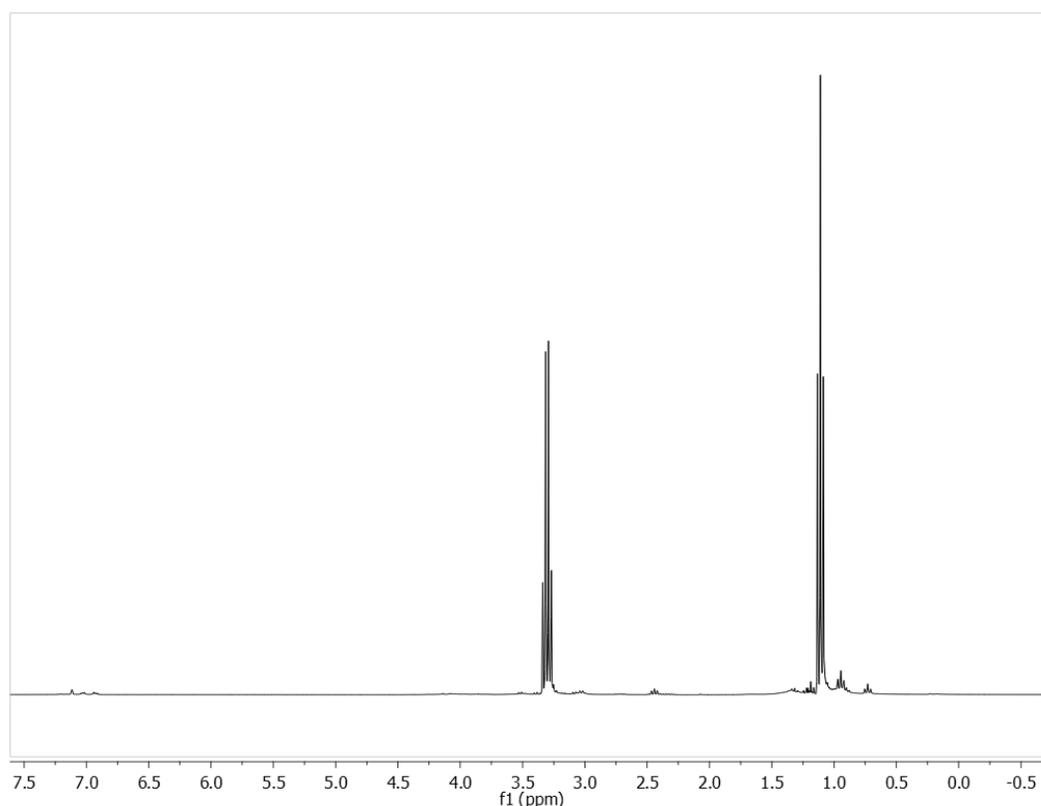


Synthesis of Tetrakis(diethylamino)titanium and Tetrakis(diethylamino)zirconium:

Lithium diethylamide (2.00 g, 25 mmol) was dissolved in toluene and brought to below 10°C under a nitrogen atmosphere. Zirconium tetrachloride (1.38 g, 5.92 mmol) was dissolved in toluene and added drop wise through an addition funnel. A brown intermediate product was precipitated initially, and after all zirconium tetrachloride was added over a time period of 30 minutes, the reaction was refluxed for 2 hours. A pale

yellow solution remained over a white precipitate of lithium salts. The solution was filtered, and the filtrate was evaporated to dryness. Distillation of the residue gave pure orange tetrakis(diethylamino)zirconium. A similar synthesis was employed for tetrakis(diethylamino)titanium.⁷⁷ (7.16%, 0.144g) ¹H NMR (δ , C₆D₆, 300 MHz): 3.33 (q, 16H, J = 6.9 Hz), 1.14 (t, 24H, J = 6.9 Hz).

Figure 28: ¹H NMR of Tetrakis(diethylamino)zirconium

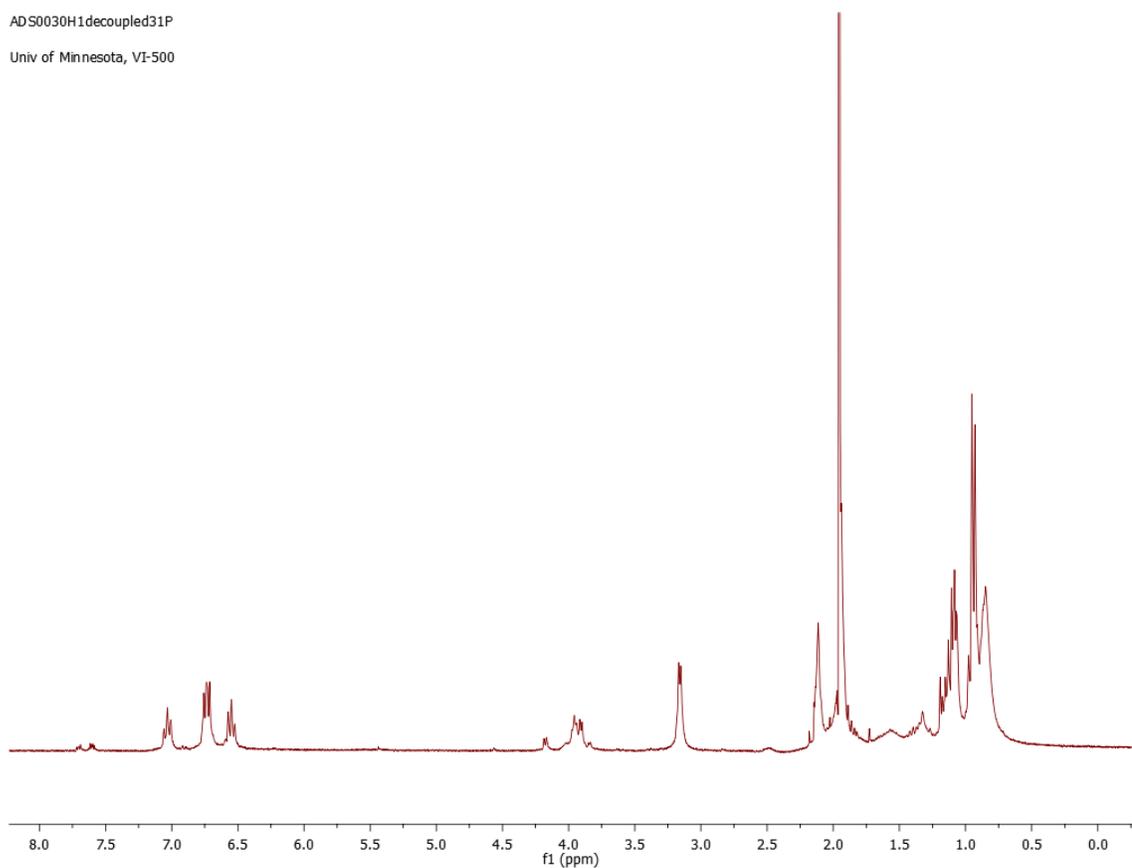


Synthesis of Tris(2-diisopropylphosphinomethylaminophenyl)amine:

In acetonitrile, (diisopropylphosphino)methanol (0.203 g, 1.03 mmol) and sieves were added to tris(2-aminophenyl)amine (.100 g, 0.343 mmol) in a nitrogen atmosphere. After two days at 80 °C, the product according to NMR looked like a mixture of bis- and tris-substituted. After an extra addition of (diisopropylphosphino) methanol (.0064 g, .0435

mmol) overnight at 80 °C, the crude NMR spectra showed a tris-substituted product. (10%, 10 mg) ^1H NMR (δ , CD_3CN , 300 MHz): 7.03 (dt, 3H, $J = 1$ Hz $J = 7.5$ Hz), 6.74 (dd, two sets of 3H overlapping, $J = 10$ Hz), 6.55 (dt, 3H, $J = 1$ Hz, $J = 7$ Hz), 3.93 (bs, 3H), 3.14 (s, 6H), 1.00 (m, 36H)

Figure 29: Decoupled Phosphorous Crude ^1H NMR of Ligand



^{31}P NMR (δ , CD_3CN , 300 MHz): 3.58 ppm.

Figure 30: ^{31}P NMR of Ligand

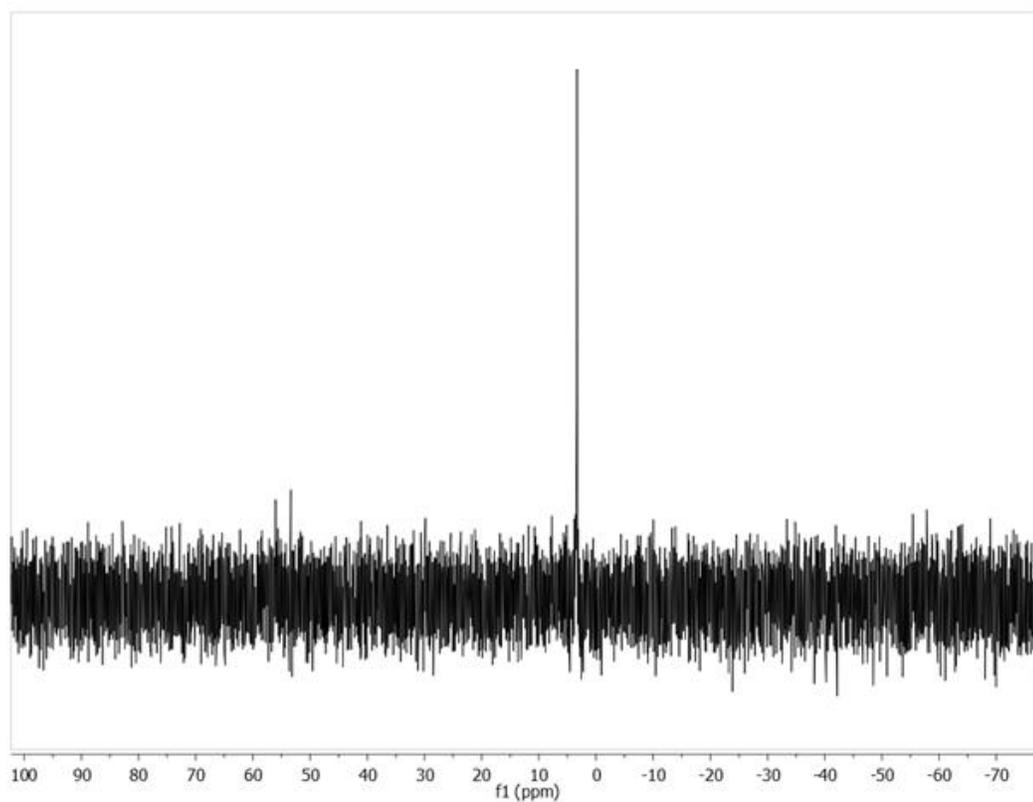
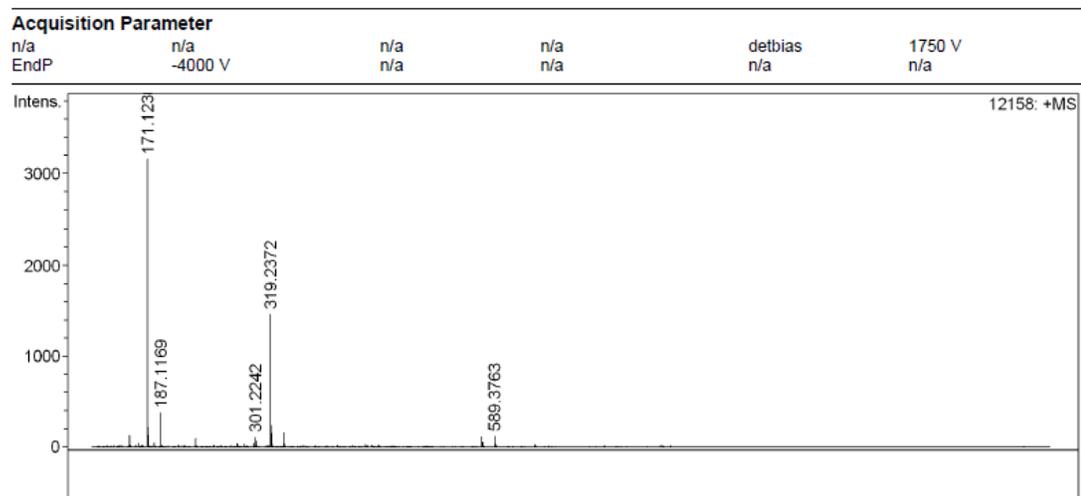


Figure 31: Positive ESI-MS of Ligand



The ESI-MS does not show evidence of the full ligand intact, but it is thought that the peak at 319 m/z is the ligand without the phosphine.

IV. Future Work

After completion of the synthetic roadmap, full characterization of these complexes must be done, including X-ray crystallography if possible. The bonding of these complexes should be studied. For example, the incorporation of a broad range of substituents is crucial for fully understanding how the metal-metal interaction affects different types of groups. Using sterically bulky groups, various heteroatom donors, or electron-donating or withdrawing groups are just a few of the many types of substituents that should be characterized in relation to the metal-metal interaction. Reactivities of the complexes should be compared by kinetic studies or other methods. For example, is there possible stereo-selectivity of the products if chiral groups are introduced to the heterobimetallic complex? Factors, such as spin-state and polarity of the metal-metal bond, should be explored in relation to the reactivities of the heterobimetallic complexes.

After elucidating a pattern of the metal binding to the ligand system, the “buried,” distal metal will be varied to see how this changes the exposed metal’s reactivity towards capping ligands. For example, using IR to monitor the change in CO frequencies when CO is used for the capping ligand would be a good place to start with these studies. At this point, it is also crucial to compare how a ligand binds to a certain metal alone and how it binds to that same metal when it is supported by a metal-metal interaction.⁵³ Using known complexes and synthesizing any unknown complexes of interest, we can compare

how and to what degree the metal-metal interaction affects the binding of specific capping ligands.

Once this is established, the next goal is to systematically stabilize metal pairs across and down the periodic table and to fully characterize these complexes. It is important to establish if there are any trends as the metals are varied.

In conclusion, these studies would only start to uncover the nature of metal-metal interactions, but every step brings us closer to a fundamental understanding and an ability to apply this understanding in catalysis.

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