Cyclopentadienyl Compounds of the First Row Transition Metals and Early Actinides: Novel Main-Group Bond Forming Catalysis and New Metallacycles

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CYCLOPENTADIENYL COMPOUNDS OF THE FIRST ROW TRANSITION METALS AND EARLY ACTINIDES: NOVEL MAIN-GROUP BOND FORMING CATALYSIS AND NEW METALLACYCLES

A Dissertation Presented

by

Justin Kane Pagano

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfilment of the Requirements
For the Degree of Doctor of Philosophy
Specializing in Chemistry

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ABSTRACT

Cyclopentadienyl first row transition-metal compounds have been well studied since the 1950’s, with the nearly ubiquitous \( \text{CpFe(CO)}_2\text{Me} \) (FpMe) \( (\text{Cp} = \eta^5\text{-C}_5\text{H}_5) \) being one of the first organometallics to be fully characterized. Despite the decades of study that have been poured into this complex, reactions between FpMe and primary phosphines have not been reported. Catalytic reactions with primary phosphines are generally understudied, including dehydrocoupling and P–C bond forming reactions such as hydrophosphination. A novel mechanism of dehydrocoupling and P–C bond formation that has received even more limited attention is \( \alpha \)-elimination. This dissertation describes efforts in proving that FpMe is a competent catalyst for \( \alpha \)-phosphinidene elimination through detailed trapping, labelling, and mechanistic studies. Additionally, the potential of \( \alpha \)-elimination for the catalytic synthesis of phospholes from commercially available starting materials is shown, which is currently unknown.

In the course of \( \alpha \)-elimination studies, it was found that \([\text{CpFe(CO)}_2]_2\) (Fp₂) is a visible-light activated photocatalyst for a variety of main-group bond forming reactions, including amine borane dehydrocoupling, siloxane formation, silyl cyanation, and the double hydrophosphination of terminal alkynes with secondary phosphines. By utilizing commercially available and inexpensive LED bulbs Fp₂ was an active catalyst for these reactions, which avoided the use of expensive, hazardous, and energy inefficient mercury arclamps.

During studies to determine whether other cyclopentadienyl first row transition-metal compounds could catalyze \( \alpha \)-elimination, it was found that \( \text{CpCo(CO)}_2\) and \( \text{Cp*Co(CO)}_2 \) (Cp* = \( \eta^5\text{-C}_5\text{Me}_5 \)) are active catalysts for ammonia borane dehydrocoupling and transfer hydrogenation. These compounds are rare examples of cobalt compounds able to catalytically dehydrocouple amine boranes as well as catalyze a rare example of transfer hydrogenation that utilizes ammonia borane as a hydrogen source.

I will also describe my year of research at Los Alamos National Laboratory (LANL) working under Dr. Jaqueline Kiplinger. Two primary projects are described herein: the first of which is the use of phenylsilane as a safe, versatile method for the synthesis of the bis(cyclopentadienyl) actinide hydrides \([\text{Cp*}_2\text{An(H)}(\mu-\text{H})]_2\) from the bis-alkyl complexes \( \text{Cp*}_2\text{AnMe}_2 \). It is shown that these hydrides are excellent precursors for the synthesis of a variety of actinide metallocenes. Additionally, in the case of uranium, by adjusting the equivalents of phenylsilane added, the oxidation state and nuclearity of the hydrides synthesized can be altered. Second, efforts in synthesizing a variety of novel actinacycles including actinacyclopentadienes, actinacyclocumulenes, a novel uranacyclop propane, and actinacyclopentadienicyclobutabenzenes that display alternating aromatic and antiaromatic character.
CITATIONS

Material from this dissertation has been published in the following form:


DEDICATION

To my family, friends, and colleagues who said “you can” when everyone else said “you never will”
ACKNOWLEDGEMENTS

First, I’d like to thank the NSF for funding throughout my graduate education, the DOE SCGSR program for a fellowship to conduct research at LANL, and the Glenn T. Seaborg Institute and LANL LDRD program for funding down south.

I’ve had the extraordinary opportunity to have two research groups and institutions I can identify with throughout my graduate career. It almost feels unreal. To everyone that I’ve worked with at UVM and LANL who doesn’t see their name here, thank you for all the help you have provided. You’ve made my graduate career perfect, as far as I can tell.

Thank you to coffee. I think that one is self-explanatory.

Thank you to my graduate committee members Dr. Matthew Liptak and Dr. Matthias Brewer for your support and excellent advice, even when grilling me during closed question sessions. Thank you to my chairperson, Dr. John Hughes. I’ve had the absolute pleasure of working with John these past few years keeping the trusty single crystal XRD up and running, and working with you has been fantastically rewarding.

Big shout out to Team Vortex. You guys are the coolest classmates I could have hoped for. I may be the first one out of here, but I hope to see you all again when we’re all making some sweet cash later in life. Extra big thanks go out to my labmates, past and present, in VT and in NM. You’ve made this experience of working my butt off for these past few years a real blast. Keep having fun and maintaining the spirit of the group while doing some awesome chemistry! I can’t wait to see your pubs and how your careers develop.
A major thank you must be extended to Dr. Karla A. Erickson for being my mentor in the lab getting started, but more importantly, my best friend throughout this experience. I can’t say enough good things about you, so I won’t even try, but I am just so pumped to be your labmate again.

I have to thank Dr. Jackie Kiplinger for being an awesome advisor and going out on a limb to write a proposal with me for the SCGSR fellowship. I can’t believe how well that worked out – really, in my wildest dreams, I didn’t expect that to be such a fun year, and I can’t wait to get back down there to continue that fun. I have to give a huge thank you to Dr. David Morris for being such a knowledgeable and patient person when helping me out with the finer points of spectroscopy.

Rory has really been the best possible advisor I could have imagined. I knew it from the second I visited UVM all those years ago that I wanted to work with Rory, and through all these years I’ve not once doubted that choice. Rory, you’re the man, and I can’t thank you enough for your mentorship, advice, and friendship. It’s been an absolute pleasure and honor these years, and I can’t wait to meet up with you at meetings and such in the future. I’ll be sure to stop back in sometime for a chat over professor juice!

I’ve left the most important thank you for the end. Thank you to my family: mom, dad, Jake, and Kathryn. You’ve all been so supportive through my life, and there aren’t words that can describe what you all mean to me. I love you all.
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LIST OF ABBREVIATIONS

AB = ammonia borane

An = actinide

Ar = aryl

BES = Basic Energy Sciences

bipy = 2,2′-bipyridine

Bu = butyl

Cp’ = Cp or Cp*

Cp = η₅-C₅H₅

Cp* = η₅-C₅Me₅

d = days

DFT = density functional theory

dmp = 2,6-dimesitylphenyl

dmpe = 1,2-(dimethylphosphino)ethane

DOE = Department of Energy

dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine

EPR = electron paramagnetic resonance

Et = ethyl
Et₂O = diethyl ether

Fp = [CpFe(CO)₂]⁻

GC = gas chromatography

h = hours

HSQC = heteronuclear single quantum coherence

hν = irradiation

IMe₄ = 1,3-dihydro-1,3,4,5-tetramethyl-2H-imidazol-2-ylidene

IMes = 1,3-dihydro-1,3-bis(2,4,6-trimethylphenyl)-2H-imidazol-2-ylidene

IR = infrared

LANL = Los Alamos National Laboratory

LED = light emitting diode

M = metal

Me = methyl

Mes = 2,4,6-trimethylphenyl

Mes* = 2,4,6-tri-tert-butylphenyl

MS = mass spectrometry

NHC = N-heterocyclic carbene

NICS = nucleus independent chemical shift

xv
NIR = near-infrared
NMR = nuclear magnetic resonance
OTf = triflate
PB = polyborazylene
Ph = phenyl
PTFE = polytetrafluoroethylene
R = generic substituent
SCGSR = Science and Graduate Student Research
SQUID = superconducting quantum interference device
’sBu = tert-butyl
TD-DFT = time dependent-density functional theory
terpy = 2,2’:2’,6’’-terpyridine
THF = tetrahydrofuran
TOF = turnover frequency
TON = turnover number
UV = ultraviolet
UVM = University of Vermont
vis = visible
VT = variable temperature

X = anionic ligand
Chapter 1: Introduction

1.1 Goals of this dissertation

The goal of this dissertation is to describe novel uses of fundamental E–H bond activation for bond-forming catalysis and energy applications. This is exemplified by the use of cyclopentadienyl ligated, earth abundant transition metal compounds for novel catalytic α-phosphinidene elimination from an iron complex, and further supported by the use of a homogeneous cobalt compounds for a rare example of ammonia borane dehydrocoupling and transfer hydrogenation. Low-energy, nonhazardous activation methods such as the use of LED bulbs for high-photon density visible light are shown to activate a commercially available cyclopentadienyl iron complex, which can catalyze a variety of E–H bond activating reactions, which avoids the use of hazardous and high-energy cost mercury arclamps. Additionally, it is shown that the Si–H bonds of a nonhazardous primary silane can be easily activated by actinide alkyl complexes to form actinide hydrides that avoids the use of hydrogen gas; this is of great importance in energy applications for understanding the complex interactions of nuclear fuels and waste cycles. Finally, pentamethylcyclopentadienyl metallocenes of the actinides are shown to support a variety of all carbon metallacycles, most of which are complementary to group 4 congeners, some of which display unique bonding motifs and stability that can be attributed to 5f-orbital and electron involvement. These fundamental bonding differences play crucial roles into understanding E–H activation processes at the actinides, which is poorly developed and understood when compared to the transition metals. All of the above studies focus on the use of cyclopentadienyl ligated compounds, which show that despite decades of study of these ubiquitous compounds, fundamental studies of E–H bond activation
processes can lead to novel catalysis and further energy applications for both hydrogen storage and nuclear fuel and waste applications.

1.2 The chemistry of CpFe(CO)₂X (FpX)

The family of compounds CpFe(CO)₂X (FpX) (X = alkyl, aryl, halide, pseudohalide) are some of the most classically studied and well understood in transition-metal chemistry. The original syntheses of the first compounds were reported by Wilkinson in 1956,¹ and in the sixty years since there have been thousands of papers published devoted to understanding the chemical properties and reactivity of these complexes.² Thus, a particular focus in this section will be on the most studied of all of the FpX family, FpMe.² FpMe is still synthesized by Wilkson’s original synthesis: reduction of [CpFe(CO)₂]₂ (Fp₂) with 2 equivalents of Na/Hg followed by quenching with 2 equivalents of MeI gives pure FpMe upon workup (Scheme 1.1).

![Scheme 1.1: Wilkinson’s 1956 synthesis of FpMe,¹ still used in modern preparations of the compound.](image)

FpMe is an Fe(II), 18-electron, air and moisture stable compound, which makes it operationally easy to handle and greatly contributed to the early study of its chemistry. Ligand substitution reactions of the carbonyl ligands were some of the earliest studied reactions of FpMe: irradiation with UV light or refluxing in THF in the presence of tertiary phosphines allows for the facile substitution of one carbonyl ligand with a phosphine.
Carbonyl insertion can be induced by heating FpMe in a polar solvent such as THF or MeCN with a neutral donor such as a tertiary phosphine or amine. The 16-electron intermediate in the carbonyl insertion reaction CpFe(CO)(COMe) is a species proposed to be involved in catalyst activation and catalytic cycles that utilize FpMe as a catalyst.

There are no known reactions that FpMe can catalyze at ambient temperature and pressure, which is unsurprising given the overall stability of the compound. There are three major ways to activate FpMe for catalytic reactivity: heating to at least 65 °C to induce carbonyl migration,\textsuperscript{3,4} irradiation with UV light (\( \lambda < 350 \text{ nm} \)),\textsuperscript{5-11} or protonolysis of the methyl ligand with strong acids to liberate methane gas (Scheme 1.2).\textsuperscript{12}

![Scheme 1.2: Three activation pathways of FpMe: heating to induce carbonyl insertion (top), UV light irradiation (middle), and protonolysis (bottom).](image)

With respect to FpMe catalyzed reactions, there are three particularly salient examples related to this dissertation. The first reaction is the dehydrocoupling of amine boranes \( R_2HNBH_3 \) (\( R = \text{H, Me} \)) as demonstrated by Manners and coworkers, who showed...
that irradiation of FpMe with UV light in the presence of amine borane gave dehydrocoupling products in excellent yields (Scheme 1.3).

**Scheme 1.3**: Dehydrocoupling of amine boranes by Manners and coworkers using FpMe activated by UV irradiation.

It is worthy to note that in this study, a variety of FpX compounds were used, most of which gave very little conversion to dehydrocoupling products with the exception of Fp2.

A second important catalytic study involving FpMe was performed by Nakazawa and coworkers, who showed that the double hydrophosphination of terminal aryl acetylenes with secondary aryl phosphines was effectively catalyzed by FpMe (Equation 1).³

![Equation 1](image)

Although high yields of the double hydrophosphination product were obtained with most substrates tested, the reactions required high temperature in neat solution for several days to be completed.

A final, noncatalytic reaction that is important to the contents of this dissertation is the deinsertion of silylene fragments from the closely related Fp(SiMe₂SiMe₃) as designed
by Pannell and coworkers in 1994, who showed that upon UV irradiation loss of dimethylsilylene (\(\text{:SiMe}_2\)) was achieved with formation of \(\text{FpSiMe}_3\) (Equation 2).\(^\text{13}\) This, importantly, displayed the ability for the Fp-platform to support main group low-valent fragment deinsertion reactions, which are closely related to catalytic \(\alpha\)-elimination (see section 1.7).

\[
\begin{array}{c}
\text{OC} \text{Fe} \text{SiMe}_3 \text{SiMe}_2 \text{OC} \\
\text{hv (\(\lambda < 350\) nm)} \\
\text{OC} \text{Fe} \text{SiMe}_3 \to \text{OC} \text{Fe} \text{SiMe}_3 + \text{:SiMe}_2
\end{array}
\]  \(\text{(2)}\)

Ruiz and coworkers have expanded the low-valent main group fragment expulsion chemistry highlighted by Pannell with related dimeric iron species containing phosphinidene ligands. They were able to synthesize \(\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu-\text{CO})(\mu-\text{PMes}^*)\) (\(\text{PMes}^* = 2,4,6\)-tri-\(\text{tert}\)-butylphenyl) and show that adding 1 atm CO resulted in the extrusion of \(\text{:PMes}^*\), which occurred and coupled to a second phosphinidene to form the diphosphene \(\text{Mes}^*\text{P=PMes}^*\) (Scheme 1.4).\(^\text{14}\) In this study the authors also synthesized the monometallic \(\text{CpFe(CO)}_2(\text{PHMes}^*)\) and showed that it was stable at ambient temperature for less than 1 day. The thermal degradation of this compound was found to form \(\text{FpH}\) and \(\text{:PMes}^*\), which also eventually formed the diphosphene \(\text{Mes}^*\text{P=PMes}^*\) (Scheme 1.4). It was further suggested by the authors that all \(\text{Fp(PHR)}\) complexes degrade in this fashion, with attempts at synthesizing \(\text{Fp(PHPh)}\) even at \(-196\) °C unsuccessful.
Scheme 1.4: Mes*P: release from bridging (top) and monomeric (bottom) Fp-species under mild conditions.

In Chapter 3, I show that the dimeric Fp$_2$ is a complementary catalyst to FpMe as displayed by Manners and coworkers with respect to ammonia borane dehydrocoupling. Also importantly, in Chapter 4 I discuss my work using FpMe as a catalyst for $\alpha$-phosphinidene elimination from primary phosphines. The previous work by Pannell showing that Fp(SiMe$_2$SiMe$_3$) can eliminate a silylene fragment and Ruiz who showed that Fp(PHR) complexes are thermally unstable and degrade to release :PR fragments support the assertion that FpMe is a promising preacatalyst for catalytic $\alpha$-phosphinidene elimination.

1.3 Visible light photocatalysis

Photocatalytic reactions are well known with ultraviolet light as a photon source. Ultraviolet light sources typically come from mercury arclamps, which are costly, hazardous, and produce enough heat such that reaction temperatures need to be regulated. The high energy photons from ultraviolet light sources are often needed for catalyst activation by ligand displacement or photoexcitation. Visible light is an attractive
alternative source of photons for catalysis, as sunlight or commercially available incandescent/LED bulbs are inexpensive and easy to handle.\textsuperscript{15-20} Indeed, visible light photocatalysis is a burgeoning field with promise to affect synthetic processes even on industrial scales.\textsuperscript{20} Many visible light photocatalysts rely on strong chromophores to absorb these lower energy electrons to provide a photoexcited species that can act as a redox-neutral oxidant or reductant, with the most ubiquitous photosensitizer \([\text{Ru(bipy)}_3]^{3+}\) operating on this principle.\textsuperscript{21}

Visible light photocatalysis is not desired simply for cost and environmental considerations. A myriad of powerful catalytic reactions have been discovered that use visible light as a photon source. For example, the sp\(^3\)–sp\(^3\) cross coupling of carboxylic acids with alkyl halides can be achieved using \([\text{NiCl}_2\cdot\text{glyme}]\) along with \([\text{Ir}[\text{dF(CF}_3\text{ppy)}_2(\text{dtbbpy})\text{PF}_6}\) (dF(CF\(_3\))ppy = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine, dtbbpy = 4,4’-di-\textit{tert}-butyl-2,2’-bipyridine) as a photocatalyst, which is a difficult reaction to achieve for any catalytic system.\textsuperscript{22}

There are a variety of methods to activate a compound for catalysis. Although some photocatalysts are activated by excitation of a transition-metal species to form a redox neutral photoredox agent, iron photocatalysts are often activated by ligand displacement: \([\text{CpFe(CO)}_2\text{Me}]\) (FpMe) and related compounds can be irradiated with UV light from a mercury arclamp to dissociate a carbonyl ligand, forming a 16-electron Fe(II) species that can then act as a catalyst or precatalyst for a myriad of reactions.

In Chapter 3, I describe my work in using \([\text{CpFe(CO)}_2\text{Me}])\) as a photoactivated catalyst as opposed to a photoredox catalyst for a variety of chemical reactions, including
ammonia borane dehydrocoupling, the double hydrophosphination of terminal aryl alkynes with secondary phosphines, siloxane formation, and silylcyanation. These reactions display comparative reactivity to related iron catalyzed processes that utilize thermal conditions or Hg arclamps for UV light irradiation.

1.4 Amine borane dehydrocoupling and transfer hydrogenation

Amine boranes, in particular the parent ammonia borane NH$_3$BH$_3$, have been of interest for hydrogen storage applications due to their high weight percent of H$_2$ as well as precursors for a variety of B–N bonded polymers and materials.$^{23,24}$ Although the thermal decomposition of ammonia borane in both the solid and solution state has been known for decades,$^{25}$ the catalytic dehydrocoupling of ammonia borane is, by contrast, a fairly recent development. In 2001, Manners and coworkers used Rh(I)/Rh(III) precatalysts to successfully dehydrogenate NH$_3$BH$_3$ at ambient temperature to afford borazine and an insoluble, oligomeric material.$^{26}$ Since this effort, there has been considerable attention devoted to developing a variety of catalysts for this transformation as well as understanding the catalytic mechanisms by which this process occurs. Indeed, a variety of heterogeneous and homogeneous transition-metal compounds, group 1 and 2 compounds, main group compounds, and even Bronsted acids have been shown to catalyze amine borane dehydrocoupling.$^{23,24,27}$ So far, the most active catalyst for NH$_3$BH$_3$ dehydrocoupling is Brookhart’s POCOP-Ir complex [POCOP = $\kappa^3$-P,C,P-1,3-(OPtBu$_2$)$_2$C$_6$H$_3$] as demonstrated by Goldberg and coworkers in 2006, who reported the dehydrocoupling of one equivalent of NH$_3$BH$_3$ in 14 min. at ambient temperature at 0.5 mol% loading (Equation 3).$^{28}$
The products of NH$_3$BH$_3$ dehydrocoupling are now well-characterized, with significant efforts from the groups of Manners, Weller, and Baker in identifying both reaction products and mechanistic pathways. Ideally, during catalytic dehydrocoupling reactions a maximum of two equivalents of H$_2$ is released from NH$_3$BH$_3$, as this results in the formation of fully soluble byproducts; if all three equivalents of H$_2$ are released, the result is the formation of boron nitride, a highly insoluble and stable ceramic ($\Delta H^\circ_{f,298K} = -59.97 \pm 0.37$ kcal/mol$^{29}$) that can only be removed by filtration. This would limit the potential for NH$_3$BH$_3$ to be a fuel source in practical applications.$^{30}$ Thus, while ammonia borane is technically 19.6% w/w hydrogen, only a maximum of ~13% of that hydrogen is practical for use, as any fuel cell that utilized NH$_3$BH$_3$ could not physically tolerate the production of boron nitride.

\[ \text{NH}_3\text{BH}_3 \xrightarrow{0.5 \text{ mol}\%} \text{THF, RT, 14 min.} \quad \text{H}_2 + (\text{NH}_2\text{BH}_2)_5 \]  

Efforts have been made towards regenerating the spent AB dehydrocoupling products back to NH$_3$BH$_3$ to create a recyclable fuel system. Methods to regenerate ammonia borane have been successful: Mertens and coworkers showed that spent BNH$_x$ materials could be recycled back to NH$_3$BH$_3$ by treatment with BCl$_3$ followed by H$_2$ and an auxiliary base, which proved to be problematic for practical applications as the bases required formed impure NH$_3$BH$_3$ that was not easily purified.$^{31}$ In 2009 Gordon and coworkers showed that spent polyaminoborane (PB) could be regenerated to form ammonia borane by reaction with 1,2-dithiolbenzene and Bu$_3$SnH as a reductant, however,
this created an excess of tin waste that made the regeneration process unsustainable.\textsuperscript{32} A complementary study in 2009 by Lentz and coworkers showed that hydrazine borane (N$_2$H$_4$BH$_3$) could also be used as a H$_2$ fuel source, but the 14.8\% w/w H$_2$ content could only be released at 150 °C, making it untenable as a practical fuel source (\textit{vide infra}).\textsuperscript{33} A major breakthrough occurred in 2011, when Sutton and Gordon extended the work of Lentz by demonstrating that PB could be converted to NH$_3$BH$_3$ cleanly by reaction with hydrazine in liquid ammonia at 60 °C, which is only limited in practical use by the challenges in efficient NH$_2$NH$_2$ formation (Scheme 1.5).\textsuperscript{34} Thus, the ability to regenerate NH$_3$BH$_3$ shows that practical use in fuel cells is indeed a possibility.

Scheme 1.5: Spent polyborazylene (``BNH'') recycling as shown by Sutton and Gordon in 2011.\textsuperscript{34}

Other considerations for practical applications of NH$_3$BH$_3$ as a fuel source include reaction temperature: the US Department of Energy (DOE) has stated that the maximum safe working temperature for a hydrogen fuel cell is 60 °C,\textsuperscript{30} which is coincidentally the maximum temperature that concentrated (> 1M) solutions of NH$_3$BH$_3$ can be stored at before uncontrolled thermal decomposition occurs.\textsuperscript{35,36} Additionally, the ability to recycle
spent NH$_3$BH$_3$ fuels is important, as the elimination of waste products from the overall cycle is desired. This, as described above, limits practical usage to harvesting only 2 equivalents of H$_2$ from each equivalent of NH$_3$BH$_3$ to avoid the generation of boron nitride.

Although the study of ammonia borane dehydrocoupling solely for H$_2$ production is a well-studied phenomenon,\textsuperscript{23,27} it is less common to see NH$_3$BH$_3$ utilized as a sacrificial hydrogen source for transfer hydrogenation. Some notable examples of this reactivity include Radosevich and coworkers utilized a $\kappa^3$-O,N,O-P(III) complex to successfully transfer hydrogenate azobenzene to 1,2-diphenylazine,$^{37}$ Waterman and coworkers who used triamidoamine-supported Zr(IV) to hydrogenate a variety of unsaturated organic substrates,$^{38}$ and Peters and coworkers who used a $\kappa^3$-P,B,P-Co(II) complex to transfer hydrogen from Me$_2$NHBH$_3$ to 1-octene or styrene to form octane or ethylbenzene.$^{39}$ Ammonia borane is a particularly useful hydrogen source as it contains three equivalents of H$_2$ that can be utilized for this reactivity (\textit{vida supra}).

In this dissertation, my efforts towards using half-sandwich cyclopentadienyl compounds for ammonia borane dehydrocoupling and transfer hydrogenation are discussed in chapter 2.
1.5 Fagan-Nugent coupling

The primary method of synthesizing phospholes and other main-group heterocycles is through the Fagan-Nugent coupling reaction, which was first disclosed in 1988.40 The Fagan-Nugent coupling reaction is the reaction of either an isolated or in situ prepared bis(cyclopentadienyl)zirconacyclopentadiene with a main-group element dichloride to generate a main-group, five membered heterocycle and Cp₂ZrCl₂ which can be reused in further reactions (Scheme 1.6).40-44

![Scheme 1.6: Fagan-Nugent coupling by 1) using Negishi’s protocol to form a zirconacyclopentadiene then 2) reaction with a dichlorophosphine to liberate a phosphole and regenerate Cp₂ZrCl₂. Note that step 2 can be performed with any main-group element dichloride.](image)

This seminal reaction is, to date, the most versatile method for the synthesis of phospholes and other heterocycles, but it still has downfalls.43-45 Although the Fagan-Nugent coupling appears to be general, there are still selectivity issues when considering potential main-group element dichlorides and zirconacyclopentadienes; in the case of the latter, selectivity effects of substituent position on the zirconacyclopentadiene ring are very limiting.46-52 Additionally, though Cp₂ZrCl₂ can be recovered from solution after the reaction in theory, this is often difficult if not impossible in practice. Finally, even with
recovery of \( \text{Cp}_2\text{ZrCl}_2 \) two equivalents of salt waste are created throughout the reaction, which limits large scale and industrial applications.

Improvements to the traditional Fagan-Nugent coupling have been discovered. A notable example related to this dissertation was found by Clegg and coworkers in 2001, who used CuCl to transmetalate \( \text{Cp}_2\text{Zr}(\eta^4-\text{C}_4\text{Ph}_4) \) and form a 1,4-dicuprate which could react with 2 equiv. \( \text{Ph}_2\text{PCl} \) to form 1,4-bis(diphenylphosphino)-1,2,3,4-tetraphenyl-1,3-butadiene (NUPHOS), a commercially useful diphosphine ligand (Scheme 1.7).\(^{53}\)

Scheme 1.7: Modification of classic Fagan-Nugent coupling to form NUPHOS by first transmetallating with CuCl followed by reaction with two equivalents of \( \text{Ph}_2\text{PCl} \).

### 1.6 Phosphinidene transfer

For more than 30 years, phosphinidene (:PR) transfer remains a mainstay reaction in the synthesis of value-added organophosphines. The first example of utilizing phosphinidene transfer for this was reported by Schmidt in 1966, where it was shown that heating \((\text{PPh})_5\) and 2,3-dimethylbutadiene in the melt for 18 h or by photoirradtion with a mercury arclamp would nonselectively release :PPh which was trapped by the butadiene to form 2,5-dihydro-3,4-dimethyl-1-phenylphosphole in low yields (Equation 4).\(^{54}\)

\[
\text{PhP} \quad \text{PhP} \quad \text{PPh} + \quad \begin{array}{c} \text{PhP} \quad \text{PPh} \\ \text{PhP} \quad \text{PPh} \end{array} \quad \xrightarrow{\text{Neat} \ \Delta \ or \ UV \ h_v} \quad \text{P} \\
\text{Ph} \quad \text{P} \quad \text{Ph} \]

Later, it was shown that other traps such as diorganodisulfides, biphenylene, and diketones were compatible with transfer of :PPh from \((\text{PPh})_5\) under either thermal or
photolytic conditions. Despite successful trapping, low yields of new organophosphines were obtained in all cases. A more successful method of generating phosphinidenes was discovered by Satgé and coworkers in 1986, who found that heating germylated phosphine chlorides released phosphinidene fragments, which were generally recombined to form diphosphetes, but with less sterically demanding substrates on phosphorus such as phenyl were able to be transferred to 2,3-dimethylbutadiene to form 1,2-diphenyl-3,6-dihydro-4,5-dimethylphosphorin.55

A major breakthrough in phosphinidene transfer was made by Mathey and coworkers in 1982 when they synthesized the first metal-stabilized 7-phosphanorbornadiene, which was able to transfer a W(CO)₅-protected phosphinidene fragment to an unsaturated organic substrate by rearomatization of the benzene fragment of the phosphanorbornadiene (Figure 1.1).56

![Figure 1.1: Landmark examples of organophosphinidene transfer reagents.](image)

The rearomatization of the non-phosphinidene fragment of the phosphanorbornadiene is the driving force for this reaction, and in fact these rearomatizations are the driving forces for the organophosphinidene transfer reagents developed thereafter. The syntheses of a variety of phosphorus heterocycles such as phosphirenes and phospholes were obtained by similar strategies by the Mathey and
Lammertsma groups.\textsuperscript{57-61} Though these 7-phospanorbornadienes were able to transfer phosphinidenes to other substrates, these reagents were often not general in their ability to transfer a variety of :PR to different organics, and many needed forcing conditions to transfer in poor yields. In 2005, Lammertsma and coworkers made another major advance when they discovered that M(CO)\textsubscript{5}-ligated (M = Mo, W) benzophosphinenes were much more versatile phosphinidene transfer reagents.\textsuperscript{62} By tuning the identity of the metal carbonyl bonded to phosphorus, they were able selectively transfer phosphinidene fragments to various unsaturated organics such as internal and terminal alkynes and alkenes, diynes, and ketones.\textsuperscript{63} The increased control of :PR transfer was exemplified by the ability to transfer one equivalent, then another to diynes to form tethered diphosphirennes. More recently, in 2012 Cummins and coworkers synthesized a phosphinidene bridged anthracene that was able to transfer :PR to 1,3-cyclohexadiene that did not require the use of a stabilizing metal carbonyl.\textsuperscript{64}

While these reagents allow for stoichiometric phosphinidene transfer, catalytic methods of :PR formation and transfer are desirable for large scale syntheses of organophosphines. To date, only one catalytic phosphinidene transfer reaction has been described. Layfield and coworkers showed that M(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} (M = Fe, Co) were able to catalyze formal :PR transfer from primary phosphines to N-heterocyclic carbenes (NHC) to form N-heterocyclic phosphinidenes (Equation 5).\textsuperscript{65}

\[
\begin{align*}
\text{Equation 5:} \\
\text{M(N(SiMe}_3\text{)}_2}_2 + 10 \text{ArPH}_2 + 10 & \rightarrow \text{C}_6\text{D}_6, 60^\circ\text{C} \\
0.25 - 7 \text{d} & \rightarrow \text{PAr} \\
\text{Ar} = \text{Ph, Mes} & \quad \text{R} = \text{Mes, R} = \text{H (IMes)} \\
\text{R} = \text{R} = \text{Me (IMes}_4) & 
\end{align*}
\]
Both catalysts were able to transfer primary aryl phosphines ArPH₂ (Ar = Ph, Mes) to IMes and IMe₄ over the course of 1 week. The importance of this study to my own work will be discussed in Chapter 4.

1.7 α-Elimination

Dehydrocoupling reactions are known to or have been proposed to occur through either σ-bond metathesis⁶⁶ or oxidative addition–reductive elimination⁶⁷ steps for d⁰/d⁰fn metals or late transition metals, respectively. While these are the most well-studied mechanisms of dehydrocoupling, these are not the exclusive pathways by which this reactivity occurs. In 2002, Tilley and Neale discovered that the dehydropolymerization of stannanes occurs through a new mechanism of dehydrocoupling: α-elimination (Scheme 1.8).⁶⁸

![Scheme 1.8: Key transition state and deinsertion of the low-valent main group fragment in α-elimination.](image)
α-Elimination is the catalytic deinsertion of a low-valent main-group element fragment, which can go on to react in a variety of ways (Scheme 1.9).

Scheme 1.9: Generic catalytic cycle for alpha-elimination and possible end points for the liberated low-valent fragment.

The low-valent fragment can couple with a second fragment to form an E=E double bonded product, insert into a E–H bond of the starting main-group hydride and form a E–E single bond, continue to insert in E–H and E–E bonds to form polymeric materials, and importantly, be trapped by an unsaturated organic substrate such as 2,3-dimethylbutadiene to form a 5 membered main-group heterocycle. The final reaction is highly attractive for synthetic main group chemistry, but is unknown for reported examples of α-stannylene, α-stibinidene, and -arsinidene elimination. The wealth of reactivity that can be realized from α-elimination makes it a rife field for study.
Factors that induce α-elimination over other dehydrocoupling mechanisms are still not fully understood, but it is clear that high steric bulk around the main-group element–hydride allows for kinetic stabilization of the low-valent fragment, promoting elimination: Waterman and coworkers observed that in the case of triamidoamine-supported zirconium \([\kappa^5-N, N, N, N, C-\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2]\text{Zr}\) dehydrocoupling of arsines, the secondary arsine \(\text{Ph}_2\text{AsH}\) was found to dehydrocouple through σ-bond metathesis, while the sterically encumbered primary arsines \(\text{MesAsH}_2\) and \(\text{dmpAsH}_2\) were dehydrocoupled through α-arsinidene elimination to give \((\text{AsMes})_4\) and \(\text{dmpAs}=\text{Asdmp}\), respectively (Scheme 1.10).\(^73\)

![Scheme 1.10](image)

**Scheme 1.10**: Mechanistic variety in dehydrocoupling reactions of secondary and primary arsines catalyzed by a triamidoamine-supported zirconium complex.

Trapping during α-elimination using unsaturated organics failed with all reported systems due to the propensity for the organic to insert into a Zr–X bond,\(^73-76\) which allows
for facile hydroarsination or the related hydrophosphination. Thus, if catalytic $\alpha$-elimination for the formation of main-group heterocycles is the desired reaction, a system where these insertion reactions cannot occur is ideal.

In related work, Waterman and coworkers have shown that $\alpha$-silylene elimination using PhSiH$_3$ can be catalyzed triamidoamine-supported zirconium. This reaction appears to be promoted by the formation of strong Si–N bonds in the form of PhSiH$_2$NMMe$_2$, however, this particular catalytic reaction appears to only complete 4 turnovers. It was hypothesized that this is due to the 4 Zr–N bonds in the catalyst which are being degraded by the liberated phenylsilylene fragment. Importantly, however, it was shown that in some instances the phenylsilylene fragment was able to be trapped by diphenylacetylene to form 1,2,3,4,5-pentaphenylsilole, which again highlights the potential for $\alpha$-elimination as a route to value added molecules.$^{77}$

In chapter 4, I describe my work in using a simple iron compound CpFe(CO)$_2$Me (FpMe) as a catalyst for $\alpha$-phosphinidene elimination. I show that unusual phosphine dehydrocoupling products as well as the catalytic formation of phospholes is indeed occurring by $\alpha$-elimination, and I also show the limits of this current landmark display of this reactivity.

1.8 Proposed research at Los Alamos National Lab

In the fall of 2014, I was awarded a DOE SCGSR fellowship to spend a year working at Los Alamos National Laboratory with Dr. Jaqueline Kiplinger. As part of the application process for the fellowship, a research proposal was required. The original research proposal can be found in Appendix 1, I summarize it here because it bridges the
gap between the research I performed at UVM and at LANL in the context of this dissertation.

The goal of the proposed project was to synthesize a series of triamidoamine-supported thorium and uranium complexes to test 1) the potential catalytic synthesis of phosphaalkenes and 2) explore $\alpha$-phosphinidene elimination from these compounds. Both reactions formally involve the generation of low-valent phosphorus, a major goal of this dissertation. This would allow for facile comparison between zirconium(IV) and thorium(IV), $6d^05f^0$ compounds with energetically accessible $f$-orbitals in the case of thorium, and uranium(IV), which has a $6d^05f^2$ ground electronic state that would allow for studying the effect of $f$-electrons on reactivity. The starting molecules for this reaction were $[\kappa^5-N,N,N,N,C-Me_3SiNCH_2CH_2CH_2)_{2}NCH_2CH_2NSiMe_2CH_2]An$ (An = Th, U). The Waterman group has previously studied attempted phosphaalkene synthesis and $\alpha$-phosphinidene elimination from the zirconium(IV) congener of these molecules, both of which were unsuccessful. Although we found that phosphaalkenes were easily formed at zirconium by isocyanide insertion into Zr–PHR compounds, electrophilicities were found to add at phosphorus to afford phosphaformamide products was formed. We hypothesized that steric crowding at nitrogen prevented electrophilic attack at that position, which in turn favors addition at phosphorus. Thus, we proposed that using metals with larger atomic radii such as thorium or uranium would alleviate some steric crowding at nitrogen and even
allow for \( \eta^3 \)-coordination of the phosphaalkene, which would further avail nitrogen for electrophilic attack (Scheme 1.11).

Scheme 1.11: Proposed liberation of phosphaalkenes from triamidoamine-supported actinide complexes, with two potential coordination modes of the phosphaalkene moiety at the actinide shown.

In related work, we proposed that \( \alpha \)-phosphinidene elimination could be induced from these triamidoamine-supported actinide phosphido complexes. Scott and coworkers have shown that these actinide compounds are much more difficult to cyclometalate than related transition-metal congeners.\(^78,79\) Waterman and coworkers found that heating the related zirconium phosphido complexes led to cyclometalation to release \( \text{RPH}_2 \) instead of eliminating the phosphinidene fragment, thus, difficult cyclometalation could promote this reactivity (Scheme 1.12). Therefore, tren complexes that are less likely to cyclometalate may allow for \( \alpha \)-phosphinidene elimination.
As discussed in sections 1.6 and 1.7, phosphinidene transfer has been an important strategy to form phospholes and other phosphorus heterocycles, and my efforts towards utilizing catalytic α-phosphinidene elimination in this regard are discussed in Chapter 4. Additionally, the Fagan-Nugent coupling, discussed in section 1.5, has been perhaps the most versatile method for forming phospholes, a class of value added organophosphines that could be obtained from catalytic α-phosphinidene elimination. Inspired by my efforts to develop a catalytic phosphole synthesis, we decided to change course from the proposed research and I investigated the synthesis of a variety of Cp*₂An-based metallascycles which have potential use in actinide Fagan-Nugent coupling. In this dissertation, I will discuss preliminary efforts in expanding Fagan-Nugent coupling to the actinides. I primarily focused on the synthesis and characterization of a variety of novel all-carbon actinacycles, as well as finding methods to synthesize low-valent actinide sources for easy and safe syntheses of these and other metallascope-based actinide compounds. As a final disclaimer, during the course of our studies of these compounds, Walter and coworkers have published the synthesis and structure of some of the molecules I had made myself, which can be found in the references here. Despite this, I have written Chapter 5 to describe the work as conducted, which was prior to Walter’s publications.
1.9 The role of 5f-orbitals and 5f-electrons on reactivity

Although the role of d-orbitals and d-electrons on transition-metal chemistry is well understood, the role of 5f-orbitals and electrons is less so. Contributing factors to this deficit include the difficulty of obtaining and handling actinides, the added complexity of the greater number of electronic transitions possible with the seven 5f-orbitals versus five d-orbitals, and the increased computational power needed for theoretical studies on these compounds as a result of that complexity. Thus, one of the best ways to understand the direct effect of 5f-orbitals and electrons on reactivity is to compare the chemistry of transition-metal compounds, in particular group 4 and 6 compounds, to that of the two most easily handled and readily available actinides: thorium and uranium. Both natural thorium (²³²Th) and depleted uranium (²³⁸U) are weak α-emitters. Through careful manipulation and diligent laboratory practice they can be handled safely and without spread of radiological contamination and thus are the most commonly studied actinides.

There have been some systematic studies completed that compared the chemistry of actinides versus transition-metals that highlighted meaningful reactivity differences. Particularly salient examples include the reductive cleavage of azobenzene by various groups using Cp*₂UCl₂/(Na/Hg),[Cp*₃U], [Cp*₂UH]₂, [Cp*₂U][(µ-Ph)₂BPh₂], and [Cp*₂U]₂(µ-η⁶:η⁶-C₆H₆) to give Cp*₂U(=NPh)₂, a stable 20-electron, uranium(VI) species whose group 6 congeners would be unstable; the insertion of 2 equivalents of N₂CPh₂ into Cp*₂AnR₂ (An = Th, U; R = Me, Ph, -CH₂Ph) to form the 20-electron (Th) or 22-electron (U) bis-hydrazanato complexes Cp*₂An[η²-(N,N')-R–N–N=CPh₂] which were unattainable reactions with Zr/Hf congeners; and the role of highly stabilizing δ-
bonding interactions in uranium inverse sandwich complexes, studied prominently by Cummins and coworkers, that are greatly reduced or nonexistent in transition-metal and lanthanide congeners (Scheme 1.13).90,98
Scheme 1.13: Examples where 5f-orbitals and 5 electrons are directly involved in reactivity as exemplified by (1) Evans (2) Kiplinger and (3) Cummins. See text for details.
In all, the role of 5f-orbitals and electrons in actinide reactivity is still poorly understood, and thus a rife field for further study.

As was previously mentioned, DFT calculations on 5f-element complexes are more difficult than those of transition-metals due to the increased nodality and electron counts of the actinides. A result of this complexity is disagreement in the literature as to the actual contribution of 5f-orbitals in metal–ligand bonding in actinide complexes. Bursten describes 5f/6d-orbital and electron contributions in actinide chemistry by the “f’s essentially unaffected, d’s accommodate ligands,” or “FEUDAL” description, which accounts for many observed differences in transition-metal versus actinide bonding and behavior.88 For example, when comparing Cp2WCl2 versus Cp2UCl2, both of which contain two metal-localized electrons, the tungsten complex is diamagnetic with the 5d2 electrons being paired while the 5f2 electrons of the uranium complex residing in the nearly purely metal-based 5f orbitals in a spin-parallel arrangement, which accounts for the paramagnetism of the uranium species. In the case of Cp2UCl2, which contains “strong” anionic ligands, the metal–ligand interactions are dominated by uranium 6d orbitals, in line with the FEUDAL description of actinide complexes.88 Even with actinide metallocenes that feature unique bonding and reactivity from transition-metal metallocenes such as the bis(hydrazonato) complexes (vide supra) have relatively small 5f–non-Cp*-ligand bonding contributions, ranging from 8–13%; these small contributions are enough to lead to dramatically different reactivity patterns.86 Non-metallocene actinide compounds can feature much higher 5f-orbital contribution to metal–ligand bonding: uranyl ([UO2]2+) complexes have been shown to contain molecular orbitals that are nearly 100% 5f in
character, and the related, seminal linear-bis(imido) compounds U(NR)$_2$I$_2$(thf)$_n$ (R = 'Bu, n = 2; R = Ph, n = 3) discovered by Boncella and coworkers in 2005 were predicted to have 5f molecular orbital contributions between 23–43% (Figure 1.2). This displays the clear impact of compound symmetry and ligand sets on f-orbital contributions to molecular orbital manifolds.

![Figure 1.2: Linear-bis(imido) species synthesized by Boncella and coworkers in 2005 (left) and an example of the most common and important functional unit in U(VI) chemistry (right).](image)

Interestingly, calculations performed by Walter and coworkers on bis(cyclopentadienyl) actinacycles showed that these compounds contained metal–ligand molecular orbitals with 5f-contributions in the range of 20–40%, which is more consistent with the overlap observed in Boncella’s linear-bis(imido) species than other previously characterized actinide metallocenes.

Ultraviolet–visible–near-infrared (UV–vis–NIR) spectroscopy is incredibly important in 5f-element chemistry, in particular when studying organometallic uranium species. Uranium organometallics can have a metal oxidation state between 2–6, although uranium(IV) and uranium(VI) species are the most commonly synthesized. Unambiguous determination of uranium oxidation state through traditional techniques such as EPR or Evans Method is often challenging, and without the use of UV–vis–NIR spectroscopy...
requires the use of SQUID magnetometry to make an accurate measurement. UV–vis–NIR spectroscopy is much simpler and inexpensive to perform when compared to SQUID, and can provide the same information about uranium oxidation state. Indeed, the low energy (NIR; 6000 < ν < 15000 cm⁻¹) region of these spectra are dominated by Laporte-forbidden intraconfigurational f–f transitions that are often distinct between the different oxidation states of uranium. Although the intensity of the transitions in this region are orders of magnitude smaller (10 < ε < 500 cm⁻¹M⁻¹) than those that are formally allowed in the UV–vis region of these complexes (1000 < ε < 50000 cm⁻¹M⁻¹), they provide important clues not only to the oxidation state of uranium but also to the degree of covalency of metal–ligand bonding in these species.

1.10 Actinide hydrides

Transition-metal hydrides are an extremely important class of compounds that are studied due to their interesting bonding and structural properties, reactivity, and as intermediates in reactions and catalysis. These hydrides are often very reactive, and can participate in rich and diverse chemistry. Transition-metal hydrides are prominent as the necessary byproduct after α-elimination reactions, and also importantly are involved in the heterolytic cleavage of E–H bonds by the Fp-radical. Despite the years of study of transition-metal hydrides, the field of well characterized actinide hydrides is relatively young and not well understood. The first isolated actinide hydrides were discovered by Marks and coworkers in 1982, where hydrogenolysis of the actinide alkyls Cp*₂AnMe₂ (An = Th, U) yielded the actinide(IV) hydrides [Cp*₂An(H)(μ-H)]₂ and methane gas (Scheme 1.14).
Scheme 1.14: Mark’s pioneering synthesis of $[\text{Cp}^* \text{An(H)}(\mu \text{-H})]_2$ ($\text{An} = \text{Th, U}$) in 1981 by hydrogenolysis of $\text{Cp}^* \text{AnMe}_2$ in toluene solution.

Although the thorium complex was stable with respect to thermal degradation, it was found that the uranium complex would slowly equilibrate with $[\text{Cp}^* \text{U(H)}]_x$ and concomitant loss of $\text{H}_2$ even at ambient temperature. Regardless, since this discovery these hydrides have been shown to participate in coupling reactions, hydrogenation of unsaturated organics, the catalytic dimerization of propylene, and importantly, multi-electron reductions following loss of $\text{H}_2$ (vide infra).

Evans and coworkers have performed extensive research into the reductive chemistry of $[\text{Cp}^* \text{An(H)}(\mu \text{-H})]_2$ and $[\text{Cp}^* \text{U(H)}]_2$ towards a variety of organic substrates. They showed that these hydrides were able to reduce diorganodichalcogenides, cyclooctatetraene, and in the case of $[\text{Cp}^* \text{U(H)}]_2$ reduce azobenzene. These hydrides have been known to react intramolecularly as well: heating of the tetravalent hydride $[\text{Cp}^* \text{U(H)}]_2$ to 110 °C for one day affords the “tuck-in, tuck-over” complex $\text{Cp}^*[\mu-\eta^5: \eta^1: \eta^1-C_5\text{Me}_3(\text{CH}_2)_2](\mu \text{-H})_2\text{UCp}^*_2$ with concomitant loss of $\text{H}_2$ (Figure 1.3).
Figure 1.3: Evans’ “tuck-in, tuck-over” uranium complex (left), tetranuclear thorium octahydride (center), and thorium(III) hydride dimer (right) formed by heating actinide hydrides or by hydrogenolysis, highlighting the reactivity differences caused by simple cyclopentadienyl ligand substitutions.

The ability of this hydride to activate relatively inert C–H bonds of Cp*-methyls shows the power of these complexes as synthetic precursors. The identity of the cyclopentadienyl ligands has a profound effect on the reaction chemistry of these compounds: hydrogenolysis of (C₅Me₄H)₂ThMe₂ with 80 psi H₂ for three days at ambient temperature does not give a dimer analogous to Cp* systems, rather yielding the tuck-over, tetranuclear (C₅Me₄H)₄[µ-η⁵-C₅Me₃H(CH₂)-κC]₂Th₄(µ-H)₄(µ₃-H)₄ along with the ligand redistribution product (C₅Me₄H)₃ThMe, while hydrogenolysis of the thorium silyl-ansa-metalloocene [Me₂Si(C₅Me₄)₂]ThMe₂ gives the trivalent thorium hydride dimer [[Me₂Si(C₅Me₄)₂]Th(µ-H)₂]₂ with loss of methane gas (Figure 1.3).¹¹⁷ Evans and coworkers were also able to improve on the selectivity of forming the tetravalent Cp* hydride dimer by performing hydrogenolysis in the solid state, which exclusively gives the tetravalent compound without equilibration to the trivalent species, as is observed with
solution-state techniques. Overall, it is clear that these actinide hydrides are sensitive to changes in cyclopentadienyl ligand and hydride source.

In Chapter 6, I will describe my work in using phenylsilane as a safe, versatile hydride source for the synthesis of actinide hydrides. This work allows for avoiding the use of hydrogen gas, which is limiting in many radiological labs due to inherent increased hazard of radioactive fires, and provides an environmentally benign solution for the synthesis of these important and understudied compounds. I will also discuss the ability to selectively synthesize the trivalent uranium hydride \([\text{Cp}^* U(H)]_x\) over the tetravalent compound \([\text{Cp}^* U(H)(\mu-H)]_2\) by altering the equivalents of PhSiH₃ added to reaction mixtures, and clarify the solution identity of \([\text{Cp}^* U(H)]_2\) as described by Evans as an equilibrium between two species.

1.11 References


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Chapter 2: Cobalt catalyzed ammonia borane dehydrocoupling and transfer hydrogenation

2.1 Introduction

The dehydrocoupling of amine boranes by a large variety of homogeneous and heterogeneous catalysts has been studied in great detail.\textsuperscript{1-5} Amine boranes have great potential as hydrogen storage materials as well as precursors for polyamineboranes, which may have materials applications. Manners was the first to discover this reaction by utilizing rhodium precatalysts,\textsuperscript{6} which launched the extensive study in the field.\textsuperscript{2,7-12} Indeed, while the dehydrocoupling of amine boranes has been extensively studied, often times primary or secondary amine boranes such as \textsuperscript{t}BuNH\textsubscript{2}BH\textsubscript{3} or Me\textsubscript{2}NHBH\textsubscript{3} are the target substrates for these investigations.\textsuperscript{3,12-14} The parent amine borane, NH\textsubscript{3}BH\textsubscript{3} has been the subject of far fewer studies, presumably due to the difficulty of removing all water from NH\textsubscript{3}BH\textsubscript{3} and its poor solubility in most organic solvents.\textsuperscript{2,3} Despite this, NH\textsubscript{3}BH\textsubscript{3} has the greatest potential as a hydrogen storage material of all amine boranes, as it contains the most H\textsubscript{2} by weight (19\% w/w H\textsubscript{2}).

If NH\textsubscript{3}BH\textsubscript{3} is going to have real applications as a H\textsubscript{2} storage medium, there exists a need for air-stable, earth abundant compounds that can catalyze dehydrocoupling reactions.\textsuperscript{5} Certainly, there is merit for studying air-sensitive, platinum group metal compounds: perhaps the most efficient NH\textsubscript{3}BH\textsubscript{3} dehydrocoupling catalyst is (POCOP)-\textsuperscript{15} Ir(H)\textsubscript{2} (POCOP = \eta\textsuperscript{3}-1,3-(OP\textsuperscript{t}Bu\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{3}), which is known to be air-sensitive\textsuperscript{16} and contains iridium, an extremely rare metal. Although this compound displays impressive reactivity towards NH\textsubscript{3}BH\textsubscript{3} dehydrocoupling, it shows little promise for real world applications due to the air-sensitivity and cost of this compound. In addition to the already
high cost, platinum group metals are quickly dwindling in supply due to already limited reserves and the political volatility seen in the regions where many of these metals are found.\textsuperscript{17}

There certainly has been work done utilizing earth-abundant compounds that can catalyze this reactivity. Compounds of tin,\textsuperscript{18} iron,\textsuperscript{11,12} nickel,\textsuperscript{10,19} group IV metals,\textsuperscript{13} and even acid-catalyzed\textsuperscript{20} and metal free systems\textsuperscript{8} have been used to dehydrocouple NH$_3$BH$_3$. Despite the abundance of catalysts for this reaction, only one example of a cobalt compound has been reported to catalyze the dehydrocoupling of any amine borane: Peters reported that a bis-phosphinoboryl-supported cobalt compound was able to catalyze the dehydrocoupling of Me$_2$NHBH$_3$.\textsuperscript{14} Although these systems may not rival the reactivity of (POCOP)-Ir(H)$_2$,\textsuperscript{15} they can be sustainably synthesized and some even display air-stability.\textsuperscript{12}

Transfer hydrogenation is a valuable organic transformation that has received significant literature attention.\textsuperscript{21-23} Despite this importance, only limited effort has been brought to using amine boranes as sacrificial H$_2$ sources for this reactivity.\textsuperscript{22,24} Even fewer examples exist where NH$_3$BH$_3$ is the H$_2$ source, which is surprising given the ability for NH$_3$BH$_3$ to deliver up to three full equivalents of H$_2$ as opposed to Me$_2$NHBH$_3$ and tBuNH$_2$BH$_3$, which are more often used and can deliver only one or two full equivalents of H$_2$ respectively. Again, this is most likely due to the difficulty in removing all water from NH$_3$BH$_3$ and the limited solubility of NH$_3$BH$_3$ in most organic solvents. These issues can be circumvented by utilizing a benchtop stable catalyst that is soluble in solvents such as THF or diglyme.
Half-sandwich cobalt compounds Cp*Co(CO)I₂ (1) and CpCo(CO)I₂ (2) (Cp = η⁵-C₅H₅, Cp* = η⁵-C₅Me₅) are readily prepared from commercially available starting materials and are air-stable solids.²⁵ Although 1 and 2 have previously been utilized as precursors for further cobalt compounds²⁶-²⁸ as well as precatalysts for C–H functionalization,²⁹-³¹ we found that they are competent catalysts for the dehydrocoupling of ammonia borane. Herein, the ability of 1 and 2 to dehydrocouple NH₃BH₃ to a variety of B–N containing products under both anaerobic and aerobic conditions will be discussed. Furthermore, the ability for 1 to act as a hydrogenation catalyst for alkenes and alkynes using NH₃BH₃ as the hydrogen source, also under anaerobic or aerobic conditions will be discussed.

2.2 Ammonia borane dehydrocoupling

Treatment of NH₃BH₃ in a THF solution with 1 mol% 1 resulted in rapid gas evolution which was immediately followed by a color change from dark red to light green. Small conversion to dehydrocoupling products was observed after ca. 15 min. at ambient temperature by ¹¹B{¹H} NMR spectroscopy. After two freeze-pump-thaw cycles and heating the reaction mixture to 65 °C, gas evolution greatly increased and dehydrocoupling products were formed as evidenced by ¹¹B{¹H} NMR spectroscopy (Table 1). It should be noted that under these conditions, even after three days there was no observed reactivity when 'BuNH₂BH₃ or Me₂NHBH₃ were used instead of NH₃BH₃, thus, only NH₃BH₃ was included in this study.
Table 2.1: Initial optimization of reaction conditions for ammonia borane dehydrocoupling by 1

<table>
<thead>
<tr>
<th>Loading (mol %)</th>
<th>1.0</th>
<th>1.0</th>
<th>0.5</th>
<th>0.5</th>
<th>0.1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
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<td>65</td>
<td>23</td>
<td>65</td>
<td>23</td>
<td>65</td>
</tr>
<tr>
<td>Time (h)</td>
<td>72a</td>
<td>24</td>
<td>72a</td>
<td>24</td>
<td>72a</td>
<td>24</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>12</td>
<td>98</td>
<td>11</td>
<td>98</td>
<td>8</td>
<td>97</td>
</tr>
</tbody>
</table>

Reaction conditions: 5.0 mg 1, 32.4 mg, 64.9 mg, or 324.0 mg NH₃BH₃ for 1.0, 0.5, and 0.1 mol % loading respectively, 65 °C, 2 freeze-pump-thaw cycles were performed prior to heating and every 2 h thereafter. a Reactions did not reach completion after 72 h.

Catalyst loading did not seem to impact the consumption of NH₃BH₃ in any significant manner (Table 1). Furthermore, there was virtually no difference in the activities of 1 and 2 towards dehydrocoupling; thus, all further discussed reactivity was achieved using 1 as a catalyst (Tables 2 and 3).

Table 2.2: Concentration controlled amine borane dehydrocoupling by 1

<table>
<thead>
<tr>
<th>Catalyst Concentration (mM)</th>
<th>1.0</th>
<th>1.0</th>
<th>1.0</th>
<th>2.0</th>
<th>2.0</th>
<th>2.0</th>
<th>4.0</th>
<th>4.0</th>
<th>4.0</th>
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<tbody>
<tr>
<td>NH₃BH₃ Concentration (M)</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>98</td>
<td>97</td>
<td>97</td>
<td>99</td>
<td>98</td>
<td>96</td>
<td>99</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.20 mL 1 in THF, 0.20 mL NH₃BH₃ in THF, 65 °C, 2 freeze-pump-thaw cycles performed before heating and every 2 h thereafter, 24 h.
Table 2.3: Concentration controlled amine borane dehydrocoupling by 2

<table>
<thead>
<tr>
<th>Catalyst Concentration (mM)</th>
<th>1.0</th>
<th>1.0</th>
<th>1.0</th>
<th>2.0</th>
<th>2.0</th>
<th>2.0</th>
<th>4.0</th>
<th>4.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃BH₃ Concentration (M)</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
<td>1.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>99</td>
<td>96</td>
<td>98</td>
<td>99</td>
<td>97</td>
<td>97</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.20 mL 2 in THF, 0.20 mL NH₃BH₃ in THF, 65 °C, 2 freeze-pump-thaw cycles performed before heating and every 2 h thereafter, 24 h

Even at the lowest catalyst loading, the dehydrocoupling of NH₃BH₃ to a variety of products was nearly complete (> 97%) after 24 h at 65 °C in all cases. At ambient temperature reactivity was significantly slower, with no greater than 12% conversion to dehydrocoupling products observed after 72 h even with repeated freeze-pump-thaw cycles. Above 65 °C, thermal dehydrocoupling of NH₃BH₃ was competitive with the cobalt-catalyzed process as evidenced by control reactions, thus, this was the maximum temperature used in this study. The primary products formed were borazine (¹¹B¹H NMR = s, δ 31.1), borazane (¹¹B¹H NMR = s, δ -10.8), and small quantities of polyborazylene (¹¹B¹H NMR = s, δ 27.2) (eq. 1).²,³²

\[
\text{NH}_3\text{BH}_3 \xrightarrow{1 \text{ or } 2} \text{HB} \quad \text{BH} \quad \text{H}_2\text{B} \quad \text{polyborazylene}
\]

(1)
To assess homogeneity, a filtration test was performed. A standard reaction mixture (2.0 mM catalyst, 2.0 M NH$_3$BH$_3$) was allowed to react for one hour at 65 °C, after which the reaction was filtered through a 0.22 µm syringe filter and heated for an additional two hours. Monitoring the reaction by $^{11}$B{$^1$H} NMR spectroscopy before and after the filtration showed no significant change in reactivity. Although it is known that cobalt does not form an amalgam with mercury$^{33}$ and thus a mercury poisoning test would not prove homogeneity, a standard reaction was also run with an excess of mercury and no adverse effects were seen on reactivity. These two results are consistent with a homogeneous process, however, there is still a possibility that this is a heterogeneous process: in theory, there could be nanoparticles smaller than 0.22 µm that could pass through the syringe filter. Investigations into further tests to ensure homogeneity for not only this catalysis, but others in our lab are ongoing.

Because 1, 2, and NH$_3$BH$_3$ are air-stable compounds, the potential for dehydrocoupling under aerobic conditions was a distinct possibility. Due to the inherent value of benchtop stable catalysis,$^{34}$ this was an inviting target. Indeed, when dehydrocoupling reactions were run under aerobic conditions, successful reactions were observed (Table 3). Product distributions changed under these conditions, with polyborazylene becoming favored over borazine based on $^{11}$B{$^1$H} NMR spectroscopy integrations. Notably, when reactions were run in open reaction vessels (either to N$_2$ or air), they were significantly faster than those in PTFE-sealed NMR tubes that had been freeze-pump-thawed repeatedly. This trend is consistent with reported rhodium catalysts$^{7,35,36}$ and shows that these reactions are inhibited by hydrogen.
Although aerobic conditions were tolerated, adding excess water to the reaction resulted in no reactivity (Table 4). The volume of H₂ evolved during catalysis was 1.91 equiv. H₂ per equivalent of NH₃BH₃, giving an average turnover number (TON) of 1924 and a turnover frequency (TOF) of 496 h⁻¹ as an average of 3 trials (see experimental section for details). These values are modest when compared to platinum group catalysts, although 1 and 2 use cobalt, a much more abundant and less expensive transition metal than heavier group 9 metals such as iridium. In addition, 1 and 2 are supported by simple, commercially available cyclopentadienyl ligands as opposed to expensive POCOP ligands. Again, 1 and 2 are air-stable compounds that can catalyze NH₃BH₃ dehydrocoupling, although many platinum group compounds such as (POCOP)-Ir(H)₂ are known to be extremely air sensitive.

Investigation of the fate of the cobalt compound after catalysis gave evidence that 1 was retained. After completion of the reactions, only a single resonance for the pentamethylcyclopentadienyl methyl was observed by ¹H NMR (either C₆D₆ or THF-d₈), which was unchanged as compared to authentic samples of 1. Infrared spectroscopy was uninformative regarding the fate of the catalyst as broad and intense νBH bands centered around 2500 cm⁻¹ obstructed possible carbonyl stretches. In both cases, there was no evidence for the loss of cyclopentadienyl ligands, however, further studies are required to determine the true identity of the active catalyst.

2.3 Transfer hydrogenation

Given the established air stability of dehydrocoupling reactions using 1 and 2, this system had promise for benchtop organic transformations. Transfer hydrogenation was an
attractive target, because NH$_3$BH$_3$ could potentially deliver 3 equiv. of H$_2$ to unsaturated organics. Thus, the transfer hydrogenation of a variety of unsaturated organics using NH$_3$BH$_3$ as a hydrogen source was attempted. Gratifyingly, all substrates were reduced to give hydrogenation products (Figure 2.1).

\[ \text{Figure 2.1: Unsaturated organics and their reduced products} \]
Nearly complete conversion of the unsaturated substrates to other products was observed in all cases as observed by $^{13}$C{\textsuperscript{1}H} NMR spectroscopy and GC. It should be noted that competitive hydroboration is a known process in reactions where NH$_3$BH$_3$ is used as a sacrificial hydrogen source.$^{21,37}$ For most substrates, some boron-containing side products were observed in the region of the $^{11}$B{\textsuperscript{1}H} NMR spectrum associated with hydroboration ($\delta$ 45–55 ppm). Most boron-containing products were similar to those seen in the dehydrocoupling catalysis (vide supra). Hydroboration products were not detected by $^{13}$C{\textsuperscript{1}H} NMR spectroscopy or by GC/MS, which suggests that these are minor products. 2-vinylpyridine appeared to be the best substrate in this proof-of-concept study, where only dehydrocoupling products were seen by $^{11}$B{\textsuperscript{1}H} NMR spectroscopy and complete conversion to 2-ethylpyridine was observed by $^{13}$C{\textsuperscript{1}H} NMR spectroscopy and GC. All transfer hydrogenation reactions gave similar results whether they were performed in a PTFE-sealed NMR tube or in an open Schlenk flask fitted with a condenser. A control reaction of 2 mM of 1 in THF with 50 equiv. of styrene was heated to 65 °C under one atm. of H$_2$. No reaction occurred even after seven days, which is consistent with transfer hydrogenation rather than hydrogenation from ambient H$_2$ generated by dehydrocoupling of NH$_3$BH$_3$. Peters’ PBP-supported cobalt compound is also able to catalyze transfer hydrogenation, although it uses Me$_2$NHBH$_3$ as the hydrogen source.$^{14}$ It should be noted that Peters’ compound was much more selective than 1 and was able to give nearly quantitative yields of hydrogenated products, however, that compound and reaction were not reported to be air-stable.
In conclusion, half-sandwich cobalt compounds 1 and 2 were able to catalyze ammonia borane dehydrocoupling. These represent rare examples of homogeneous cobalt compounds that can catalyze this reactivity. In addition, these compounds are able to catalyze transfer hydrogenation from NH$_3$BH$_3$ to unsaturated organics. Finally, these compounds display excellent robustness with respect to operating under aerobic conditions for both dehydrocoupling and transfer hydrogenation reactions.

2.4 Experimental
2.4.1 General Considerations
All manipulations were performed under an inert atmosphere of N$_2$ using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents unless otherwise specified. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer, using an external reference of 10 % BF$_3$•Et$_2$O in CDCl$_3$ for $^{11}$B NMR experiments and residual solvent resonances for $^1$H and $^{13}$C{$^1$H} experiments (δ 3.58 and δ 67.31, respectively). GC spectra were collected using a Varian Saturn 2100T gas chromatograph. Ammonia borane was purchased from Sigma Aldrich and opened August 2014, after which it was stored at –35 °C under an inert atmosphere of N$_2$. THF-$d_8$ was purchased from Cambridge Isotopes and was stored over Na at –35 °C in the dark under an inert atmosphere of N$_2$. All other reagents were obtained from commercial suppliers and dried by conventional means as necessary. Stock solutions of CpCo(CO)$_2$ (1.0 mM, 2.0 mM, 4.0 mM), Cp*Co(CO)$_2$ (1.0 mM, 2.0 mM, 4.0 mM), and NH$_3$BH$_3$ (1.0 M, 2.0 M, 4.0 M) were prepared in a glovebox using anhydrous THF, volumetric glassware, and were stored at –30 °C in the dark prior to use. CpCo(CO)$_2$, Cp*Co(CO)$_2$, and [Cp*Co(CO)]$[PF_6]$ were prepared according to literature procedures. Borazine, borazane, cyclodiborazane, B-
(cyclodiborazanyl)aminoborohydride,\textsuperscript{39} polyborazylene,\textsuperscript{2} and polyaminoborane\textsuperscript{3} were identified by their reported $^{11}$B NMR chemical shifts as compared to the unreacted ammonia borane as an internal reference.

Safety note: Handling amine boranes represents a series of potential hazards. A resource to help identify potential safety issues is [http://h2bestpractices.org/docs/nbh_h2_storage_survey.pdf](http://h2bestpractices.org/docs/nbh_h2_storage_survey.pdf)

2.4.2 Typical procedure for dehydrocoupling reactions
Stock solutions of Cp*Co(CO)$_2$ (0.20 mL, 2.0 mM) in THF and NH$_3$BH$_3$ (0.20 mL, 2.0 M) in THF were added to a PTFE-sealed NMR tube (quartz or borosilicate) in an N$_2$-filled glovebox, whereupon immediate gas evolution and a color change from dark red to light green occurred. After two freeze-pump-thaw cycles, an initial $^{11}$B{$^1$H} NMR spectrum was collected. The solution was then heated to 65 °C, and $^{11}$B{$^1$H} NMR spectra were collected at 2 h, 4 h, 6 h, 8 h, and 24 h intervals. After each NMR experiment, an additional freeze-pump-thaw cycle was performed to remove H$_2$.

2.4.3 Typical procedure for aerobic dehydrocoupling reactions
A mixture of solutions of Cp*Co(CO)$_2$ (0.40 mL, 2.0 mM) in THF and NH$_3$BH$_3$ (0.40 mL, 2.0 M) in THF were measured in an N$_2$ filled glovebox, then transferred in air and thoroughly mixed before being added to a Schlenk flask fitted with a condenser, septum, and venting needle. An initial aliquot of the reaction mixture was analyzed by $^{11}$B{$^1$H} NMR, and the reaction mixture was heated to 65 °C. Additional $^{11}$B{$^1$H} NMR spectra were collected using a quartz NMR tube at 1 h, 1.5 h, 2 h, and 3 h intervals.

2.4.4 Typical procedure for transfer hydrogenation reactions
A stock solution of Cp*Co(CO)I₂ (0.20 mL, 2.0 mM) in THF was added to the unsaturated organic (0.0690 mmol) followed by addition of a stock solution of NH₃BH₃ (0.20 mL, 2.0 M). This solution was quickly transferred to a PTFE-sealed NMR tube (quartz or borosilicate) in an N₂-filled glovebox, whereupon immediate gas evolution and a color change from dark red to light green occurred. Initial ¹¹B{¹H} and ¹³C{¹H} NMR spectra were collected, then the solution was heated to 65 °C. Additional NMR spectra were collected after 3 h, 6 h, and 24 h intervals.

2.4.5 Typical procedure for aerobic transfer hydrogenation reactions
A stock solution of Cp*Co(CO)I₂ (0.40 mL, 2.0 mM) in THF was added to the unsaturated organic (0.138 mmol) which was then added to a stock solution of NH₃BH₃ (0.40 mL, 2.0 M) in air before being thoroughly mixed and transferred to a Schlenk flask fitted with a condenser, septum, and venting needle. Initial ¹¹B{¹H} and ¹³C{¹H} NMR spectra were collected, then the solution was heated to 65 °C. Additional NMR spectra were collected using a quartz NMR tube after 3 h, 6 h, and 24 h intervals.

2.4.6 Determination of H₂ volume produced
A mixture of solutions of Cp*Co(CO)I₂ (0.40 mL, 2.0 mM) in THF and NH₃BH₃ (0.40 mL, 2.0 M) in THF were measured in an N₂ filled glovebox, then transferred in air and thoroughly mixed before being added to a Schlenk flask fitted with a condenser that was connected to a gas burette (Figure S.1). The reaction was then heated to 65 °C and allowed to run for 4 h, whereupon there was no further visible gas evolution. The actual pressure of H₂ gas evolved was determined as follows:

\[ P_{H_2} = P_{atm} - P_{THF} - P_{column} - P_{H_2O} \]
Where $P_{H_2}$ is the actual pressure of $H_2$ gas, $P_{atm}$ is the atmospheric pressure, $P_{THF}$ is the vapor pressure of THF at the measured ambient temperature (20–22 °C), $P_{column}$ is the pressure caused by the weight of water in the gas burette, and $P_{H_2O}$ is the vapor pressure of H$_2$O measured at ambient temperature. The moles of H$_2$ produced were calculated using the ideal gas law. Turnover number (TON) was determined by the following equation.$^{40,41}$

$$TON = \frac{n_{H_2}}{n_{cat}}$$

Turnover frequency (TOF) is defined as the TON for the first hour of the reaction.
Figure 2.2: Experimental setup for determination of moles of H₂ gas produced
2.5 References


(2) Staubitz, A.; Robertson, A. P. M.; Manners, I. Chem. Rev. 2010, 110, 4079-4124.

(3) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. Chem. Rev. 2010, 110, 4023-4078.


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Chapter 3: Visible light photocatalysis using a commercially available iron complex

3.1 Introduction

Photocatalyzed reactions using visible light have grown in importance because they are considered “green” due to their safety profile and the abundance of visible photons from solar irradiation.\textsuperscript{1-6} However, high energy light sources such as mercury arc lamps which emit photons in the UV ($\lambda < 300$ nm) region, remain commonplace for many photochemical/photocatalytic reactions. In addition to the high energy consumption of mercury lamps, the lamps themselves are costly, have disposal complications, and require proper shielding to prevent injury to users. Reactions that use either ambient sunlight or visible light emitted from modern CFC or LED bulbs obviate the need for these hazardous and expensive light sources.\textsuperscript{1-3,5,6} Additionally, earth-abundant transition-metal catalysts are desirable when compared to noble metal compounds due to high costs, dwindling supplies, and toxicity of these elements. For these reasons, identifying green, visible light driven, earth abundant transition-metal photocatalysts is an emerging area of study.

Iron is one of the most abundant transition-metals, thus, iron catalyzed reactions are often characterized as green chemistry. One of the most well photochemically characterized transition-metal compounds is \(\text{[CpFe(CO)\textsubscript{2}]\textsubscript{2}}\) (1) (Cp = $\eta^5$-C\textsubscript{5}H\textsubscript{5}), with initial studies dating back almost 40 years.\textsuperscript{7} Photoactivation of 1 and related CpFeX(CO)\textsubscript{2} (X = halogen, pseudohalogen, alkyl) derivatives occurs by several routes, though common photoproducts arise (Scheme 3.1). For CpFeX(CO)\textsubscript{2} dissociation of either the X or carbonyl ligand depends on the identity of X: when X is a halogen or pseudohalogen, UV irradiation results in X dissociation, and when X is an alkyl ligand carbonyl loss is observed (Scheme 3.1, A).\textsuperscript{7-13} In the case of 1, UV irradiation results in carbonyl ligand loss followed
by dissociation to form CpFe\(^{\bullet}\)(CO)\(_2\) either directly or through recombination with dissociated carbon monoxide. Interestingly, it has also been known for some time that irradiation of 1 with visible light (\(\lambda > 500\) nm), results first in conversion of the bridging carbonyls to terminal carbonyls followed by rapid dissociation to form CpFe\(^{\bullet}\)(CO)\(_2\) (Scheme 3.1, B).\(^{14-16}\) This is notable as the same iron radical is generated by both photoactivation pathways.\(^{17}\) Iron catalysis by visible light activation is known, with a seminal report by Nicholas in 2002 that used the related [Cp*Fe(CO)\(_2\)]\(_2\) (Cp* = \(\eta^5\)-C\(_5\)Me\(_5\)) and near-IR irradiation to catalyze the allylic amination of olefins with nitroarenes.\(^{18}\) Reports by Sotais and Darcel that hydrosilylation of various C=O and C=N containing molecules have followed that utilized more complex iron precatalysts, limiting the green applications of this process.\(^{19-23}\)
Scheme 3.1: A) Photoactivation of CpFe(CO)$_2$X derivatives for catalysis. B) Low energy photoactivation of 1 utilized in this work.

With this all in mind, it was hypothesized that \textit{in situ} generated CpFe•(CO)$_2$ could engage in the rich catalytic chemistry already demonstrated for UV-irradiated CpFe(CO)$_2$X (X = Me, I, OTf) compounds.\textsuperscript{8-10,24,25} In this chapter, I describe my work utilizing visible light activated 1 for a variety of catalytic reactions. The visible light source utilized in this study is simple, commercially available LED light bulbs. The catalytic reactions tested were previously promoted by heat or UV irradiation, including the formation of siloxanes from tertiary silanes, silylcyanation, amine borane dehydrocoupling, and the double hydrophosphination of terminal acetylenes with secondary aryl phosphines. These reactions were comparable or in some cases improved reactivity over their UV or thermal processes involving 1 or derivatives.

3.2 Results and discussion

Pannell reported that UV irradiation of a DMF solution of 20 equivalents of PhMe$_2$SiH in the presence of 5 mol % CpFe(CO)$_2$Me for four hours at ambient temperature resulted in the quantitative formation of (PhMe$_2$Si)$_2$O.\textsuperscript{12} In contrast, Nakazawa proposed that the above reaction conditions give exclusive formation of the disilane (PhMe$_2$Si)$_2$, although this report was later retracted.\textsuperscript{26} Under LED irradiation ($\lambda_{\text{irr}} > 500$ nm, 6–15 W, 450–800 lumens) at ambient temperature for one hour, PhMe$_2$SiH was quantitatively converted to (PhMe$_2$Si)$_2$O by 4 mol % 1 in DMF, as evidenced by mass spectrometry and

$$\text{PhMe}_2\text{SiH} \xrightarrow{4 \text{ mol}\% \ 1, \ \text{LED}} \text{DMF, 4 h} \quad \text{(PhMe}_2\text{Si)}_2\text{O} + \text{H}_2 \quad 100\%$$


$^{29}\text{Si NMR spectroscopy (δ = –22)}$ (Equation 1). On one occasion over four trials, however, some disilane $(\text{PhMe}_2\text{Si})_2$ was observed by mass spectrometry. All further attempts to repeat this reactivity resulted only in formation of the siloxane. Nevertheless, these results again demonstrate the ability of 1 to engage in the same catalytic reactivity under LED irradiation as that of FpMe under UV irradiation.

Nakazawa and coworkers reported that UV irradiation of a THF solution of 50 equivalents of Et$_3$SiH and 500 equivalents of MeCN with 2 mol % of FpMe quantitatively afforded Et$_3$SiCN over 48 h as determined by GC/MS.$^9$ The silylcyanation of Et$_3$SiH was also carried out using 1 and LED light. The reaction of 50 equivalents of Et$_3$SiH and 500 equivalents of MeCN in the presence of 1 in THF at ambient temperature with visible light irradiation for 48 h gave Et$_3$SiCN in 12% conversion as an average over three trials as determined by GC (Equation 2).

Unlike the other reactions described, substantially poorer performance was observed under visible light conditions versus that of the UV conditions. This shows that despite the facile activation of 1 to catalyze a variety of reactions, clear improvements in catalyst design are possible.

Manners reported that the UV irradiation from a medium pressure Hg lamp of a THF solution of R$_2$NHBH$_3$ (R = H, Me) with 5 mol % of 1 at ambient temperature resulted in the dehydrocoupling of these substrates.$^{24,25,27}$ Similarly, when a THF solution of R$_2$NHBH$_3$ with 5 mol % of 1 at ambient temperature was irradiated with visible light open
to a N₂ atmosphere for four hours, a color change from dark red to green was observed with gas evolution. Analysis of the solutions by ¹¹B NMR spectroscopy revealed conversions to products akin to what was observed under UV conditions as studied by Manners and coworkers (Scheme 3.2).²⁴,²⁵ The catalytic dehydrocoupling of Me₂NHBH₃ gave the cyclic dimer (Me₂NBH₂)₂ in 94% conversion as evidenced by ¹¹B NMR spectroscopy (δ = 5.7) as well as (Me₂N)BH (δ = 29).²⁵ The equivalents of evolved hydrogen were measured using a gas burette, and showed that 0.89±0.02 equivalents of hydrogen were produced over an average of three trials. Similar to Manners’s system, irradiation throughout the course of the reaction is not required despite the potentially different routes by which 1 is activated in these reactions.²⁴,²⁵ When a reaction mixture as described above was only irradiated for one hour and the reaction was then allowed to stir at ambient temperature for an additional three hours, similar conversions to

Scheme 3.2: The LED light catalyzed dehydrocoupling of Me₂NHBH₃ (top) and NH₃BH₃ (bottom). Percent conversions for the products are listed below, with literature values obtained by irradiation from an Hg lamp in parentheses.²⁴,²⁵
dehydrocoupled products were observed. Both 1 and visible light irradiation are necessary for dehydrocoupling to occur; a control reaction of Me₂NHBH₃ with 5 mol % of 1 at ambient temperature both without direct visible light irradiation and in the rigorous exclusion of light for three days failed to afford any dehydrocoupling products. Additionally, visible light irradiation of a THF solution of Me₂NHBH₃ or NH₃BH₃ at ambient temperature for seven days failed to give any dehydrocoupling products. These observations confirm the need for both 1 and irradiation to achieve dehydrocoupling in this system.

Similarly, reaction of a THF solution of NH₃BH₃ with 5 mol % of 1 under visible light irradiation gave a mixture of known products, though the ratio of products differed from what was observed under UV irradiation. Indeed, the product distribution under visible light conditions are consistent with greater hydrogen loss (i.e., activity) than under UV irradiation. Nevertheless, the products observed are consistent with Manners’s proposal of β-hydride elimination to afford H₂N=BH₂ for the UV-activation system. In contrast to Me₂NHBH₃, when a mixture of 5 mol % of 1 and NH₃BH₃ in THF solution was irradiated with LED light for one hour at ambient temperature, and the reaction was then allowed to stir without irradiation for an additional three hours at ambient temperature, no conversion to dehydrocoupling products was observed by ¹¹B NMR spectroscopy. This is in contrast to a similar experiment using UV light, which suggests that the different photoactivation pathways of 1 can cause substantial changes in reactivity in specific cases.
Visible light activation of 1 also provided an active catalyst for reactions that employed FpMe at elevated temperature. Nakazawa reported that FpMe is an effective catalyst for the double hydrophosphination of terminal aryl alkynes with secondary aryl phosphines.\textsuperscript{28} These reactions, however, require forcing conditions (110 °C for 3 days). Interestingly, reaction of aryl acetylenes with Ph\textsubscript{2}PH in the presence of 5 mol % of 1 at ambient temperature proceeded smoothly to give the corresponding double hydrophosphination products as identified by \textsuperscript{31}P NMR spectroscopy, with only minimal dehydrocoupling to (PPh\textsubscript{2})\textsubscript{2} detected (Table 3.1).

| R =  
<table>
<thead>
<tr>
<th>% double hydrophosphination\textsuperscript{c}</th>
<th>% dehydrocoupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsuperscript{a}</td>
<td>88 (71)</td>
</tr>
<tr>
<td>Me\textsuperscript{a}</td>
<td>92 (74)</td>
</tr>
<tr>
<td>\textsuperscript{t}Bu\textsuperscript{b}</td>
<td>89 (85)</td>
</tr>
<tr>
<td>F\textsuperscript{b}</td>
<td>85 (78)</td>
</tr>
<tr>
<td>\textsuperscript{t}OMe\textsuperscript{b}</td>
<td>82 (72)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: 0.056 mmol 1, 1.12 mmol Ph\textsubscript{2}PH, 0.56 mmol acetylene, neat, ambient temperature, LED irradiation, 20 h.  
\textsuperscript{b} Reaction conditions: 1) 0.056 mmol 1, 1.12 mmol Ph\textsubscript{2}PH, 0.56 mmol acetylene, neat, ambient temperature, 20 h.  
\textsuperscript{c} Reaction conditions: 2) 1 mL THF, LED irradiation, 12–36 h.  
\textsuperscript{c} Percent conversions are listed along with isolated yields in parentheses.
Similar to the other reactions studied, all components were necessary to achieve desired reactivity. The reaction of two equivalents of Ph₂PH and phenylacetylene without I and the reaction of two equivalents of Ph₂PH, phenylacetylene, and 5 mol % I in the strict absence of light gave only the Z-vinylphosphine²⁹ and unidentifiable products as evidenced by ³¹P NMR spectroscopy even after five days of photoirradiation. Notably, no double hydrophosphination was observed in either control, which highlights the need for all components to be present to achieve double hydrophosphination. Upon extended reaction times (> 30 h), significant formation of the solid double hydrophosphination products was observed in all cases except for reactions containing phenylacetylene or para-tolylacetylene, where complete reactions were observed in solution. In all other cases, dissolution of the solid in minimal THF followed by further 12 h of visible light irradiation led to complete reactions. With all double hydrophosphination reactions, isolation of the pure phosphine products was simple: removal of volatiles followed by washing with hexanes to remove the iron catalyst, excess Ph₂PH, and acetylene gave the diphosphinoethanes as off-white solids.

Other unsaturated substrates were not hydrophosphinated under these conditions. Internal alkynes, styrene derivatives, and internal alkenes were unreactive under these conditions, even with additional heating to 55 °C. In all cases no conversion of the diphenylphosphine to any new phosphorus containing products was observed by ³¹P NMR spectroscopy.

Interestingly, when reactions were performed in C₆D₆ and were monitored by ¹H NMR spectroscopy CpFe(CO)₂H was observed (δ_Fe-H = −11.74)¹⁴ throughout the course of
the reaction. This iron compound was not proposed to be involved in the thermal double hydrophosphination of terminal aryl alkynes using FpMe,\textsuperscript{28} and its existence may be an artifact of a bimetallic activation of diphenylphosphine. It is already known that CpFe(CO)\textsubscript{2}H thermally decomposes to \textsuperscript{1}\textsubscript{30} which indicates that it is likely an off-cycle intermediate. Importantly, Nakazawa and coworkers proposed an active species of CpFe(CO)(PPh\textsubscript{2}) in their work using \textsuperscript{2} and a thermal process,\textsuperscript{28} which is not a likely compound in the visible light driven reaction. The potentially different active species and methods of activation of Ph\textsubscript{2}PH doubtlessly contribute to the differences observed in reactivity.

### 3.3 Conclusions

In conclusion, a simple, commercially available iron compound \textsuperscript{1} has been shown to be an effective photocatalyst using low wattage LED lights as the photon source. When \textsuperscript{1} is photoactivated in this manner, it can engage in a variety of reactions including siloxane formation, silylcyanation reactions, amine borane dehydrocoupling, and the double hydrophosphination of terminal aryl acetylenes with Ph\textsubscript{2}PH. Although in most cases the reactivity of \textsuperscript{1} was comparable to previously described iron catalyzed reactions that utilized UV irradiation or high temperatures, improved reactivity was observed in the double hydrophosphination reactions with milder conditions, suggesting that this kind of activation may demonstrate broader utility than the examples presented in this chapter. Ongoing studies into the mechanism of these reactions, in particular double hydrophosphination, as well as broadening the substrate scope of these reactions is ongoing.
3.4 Experimental

3.4.1 General considerations

All manipulations were performed under an inert atmosphere of N₂ using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer, using external references of 10% BF₃•Et₂O in CDCl₃ for ¹¹B NMR experiments, SiMe₄ in CDCl₃ for ²⁹Si experiments, and 85% H₃PO₄ in H₂O for ³¹P NMR experiments (all references correspond to δ = 0). ¹H NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer and were referenced to residual solvent impurities (δ = 7.16 for benzene-d₆). ³¹GC spectra were collected using a Varian Saturn 2100T gas chromatograph and mass spectra were collected on an Applied Biosystems 4000QTrap Pro. Ammonia borane was purchased from Sigma Aldrich and opened August 2014, after which it was stored at –35 °C under an inert atmosphere of N₂. Ph₂PH³² and CpFe(CO)₂Me³³ were prepared by modified literature procedures and were stored under an inert atmosphere of N₂ prior to use. All other reagents were obtained from commercial suppliers and dried by conventional means as necessary. Three different commercially available LED light bulbs were used over the course of trials; their UV/vis–NIR spectra were measured using a Princeton Instruments Acton 2300 spectrometer and are displayed in Appendix 2. The temperature in the experimental setup was measured to be slightly above room temperature (25–28 °C) and was checked routinely to ensure minimal fluctuations in temperature.

3.4.2 Generation of (PhMe₂Si)₂O from PhMe₂SiH: A PTFE-sealed reaction vessel was charged with 1 (70.8 mg, 0.20 mmol), PhMe₂SiH (0.77 mL, 5.0 mmol), N,N-
dimethylformamide (4.6 mL), and a stir bar. The reaction was irradiated using an LED light source for 1 h, after which an aliquot was taken for $^{29}\text{Si}[^1\text{H}]$ and MS analyses, which revealed a complete reaction.

### 3.4.3 Silylcyanation of Et$_3$SiH with MeCN

A PTFE-sealed reaction vessel was charged with 1 (100.1 mg, 0.52 mmol), Et$_3$SiH (4.2 mL, 26 mmol), MeCN (13.6 mL, 260 mmol), THF (2 mL), and a stir bar. The reaction was irradiated using an LED light source for 96 h, during which time slow gas evolution was observed. Aliquots were taken every 24 h, and reactivity ceased after 48 h as evidenced by GC/MS analysis.

### 3.4.3 Dehydrocoupling of Me$_2$NHBH$_3$

A 50 mL Schlenk flask was charged with a stir bar, Me$_2$NHBH$_3$ (30.0 mg, 0.51 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N$_2$ and was photoirradiated using an LED light source for 4 h at ambient temperature, after which an aliquot was taken and was analyzed by $^{11}\text{B}[^1\text{H}]$ NMR spectroscopy.

#### Table 3.2 Product distribution of dehydrocoupling reactions described in 3.4.3

<table>
<thead>
<tr>
<th>product</th>
<th>(Me$_2$N)$_2$BH$^{24,34}$</th>
<th>(Me$_2$NBH$_2$)$_2$$^{24}$</th>
<th>Me$_2$NHBH$_3$$^{24}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$ (ppm)</td>
<td>29.0</td>
<td>5.8</td>
<td>–13.0</td>
</tr>
<tr>
<td>% conversion</td>
<td>8</td>
<td>86</td>
<td>6</td>
</tr>
</tbody>
</table>

### 3.4.4 Determination of hydrogen produced from dehydrocoupling of Me$_2$NHBH$_3$

A 50 mL Schlenk flask was charged with a stir bar, Me$_2$NHBH$_3$ (30.0 mg, 0.51 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was attached to a gas burette and was irradiated using an LED light source for 4 h. After this time, the volume of H$_2$O displaced
was measured and the equivalents of H₂ produced were determined by previously described methodology.³⁵

3.4.5 Limited LED irradiation dehydrocoupling of Me₂NHBH₃: A 50 mL Schlenk flask was charged with a stir bar, Me₂NHBH₃ (30.0 mg, 0.51 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N₂ and was irradiated with using an LED light source for 1 h at ambient temperature, then was covered in aluminum foil in the dark to exclude light for 3 h. An aliquot was then taken for ¹¹B[¹H] NMR spectroscopic analysis.

Table 3.3 Product distribution of dehydrocoupling reactions described in 3.4.5

<table>
<thead>
<tr>
<th>product</th>
<th>(Me₂NBH₂)₂</th>
<th>Me₂NHBH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (ppm)</td>
<td>5.6</td>
<td>−13.1</td>
</tr>
<tr>
<td>% conversion</td>
<td>91%</td>
<td>9%</td>
</tr>
</tbody>
</table>

3.4.6 Dehydrocoupling of NH₃BH₃: A 50 mL Schlenk flask was charged with a stir bar, NH₃BH₃ (15.7 mg, 0.50 mmol), 1 (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N₂ and was photoirradiated with using an LED light source for 4 h at ambient temperature, after which an aliquot was taken and was analyzed by ¹¹B[¹H] NMR spectroscopy.
Table 3.4 Product distribution of dehydrocoupling reactions described in 3.4.6

<table>
<thead>
<tr>
<th>product</th>
<th>Borazine$_6^3$</th>
<th>Polyborazylene$_6^3$</th>
<th>B-(cyclodiborazanylidaminoborohydride$^{24}$</th>
<th>NH$_3$BH$_3^{36}$</th>
<th>Unknown</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (ppm)</td>
<td>30.9</td>
<td>27.4</td>
<td>–5.2, –10.9, –26.8</td>
<td>–21.8</td>
<td>–0.1</td>
</tr>
<tr>
<td>% conversion</td>
<td>54</td>
<td>21</td>
<td>20</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

3.4.7 Limited LED irradiation dehydrocoupling of NH$_3$BH$_3$: A 50 mL Schlenk flask was charged with a stir bar, NH$_3$BH$_3$ (15.7 mg, 0.50 mmol), I (9.0 mg, 0.025 mmol), and THF (5 mL). The reaction was placed under a slight positive pressure of N$_2$ and was irradiated with using an LED light source for 1 h at ambient temperature, then was covered with aluminum foil in the dark for 3 h to exclude light. At this time an aliquot was taken for $^{11}$B NMR spectroscopic analysis.

Table 3.5 Product distribution of dehydrocoupling reactions described in 3.4.7

<table>
<thead>
<tr>
<th>product</th>
<th>NH$_3$BH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ (ppm)</td>
<td>–22.3</td>
</tr>
<tr>
<td>% conversion</td>
<td>100%</td>
</tr>
</tbody>
</table>

3.4.8 Double hydrophosphination of terminal acetylenes with Ph$_2$PH: A PTFE-sealed NMR tube was charged with I (5.4 mg, 0.015 mmol), Ph$_2$PH (0.05 mL, 0.30 mmol), and R–C≡C–H (0.15 mmol). The reaction was placed in an oil bath and ambient temperature and was photoirradiated using a LED light source for 20 h, after which $^{31}$P{$^1$H} NMR
showed optimal conversion. The NMR tube was then brought into a N₂ filled glovebox and poured into a 20 mL scintillation vial, after which volatiles were removed under reduced pressure. The residual sticky residue was washed with hexanes (2 x 1 mL), and volatiles were again removed under reduced pressure to give pure bisphosphinoethanes (R = Ph (71%), p-Tol (74%)) as off-white solids. NMR data matched previously described literature values.²⁸

### 3.4.9 Double hydrophosphination of other terminal acetylenes with Ph₂PH

A PTFE-sealed NMR tube was charged with 1 (5.4 mg, 0.015 mmol), Ph₂PH (0.05 mL, 0.30 mmol), and R–C≡C–H (0.15 mmol). The reaction was placed in an oil bath and ambient temperature and was photoirradiated using a LED light source for 20 h, after which the reaction mixture had turned solid. The reaction was brought into a N₂ filled glovebox, after which THF (1 mL) was added to the solid which was vigorously shaken until all of the solid had dissolved. The residual dark red reaction mixture was photoirradiated using a LED light source for a further 12–36 h, after which $^{31}$P[$^1$H] NMR spectroscopy showed optimal conversion. The NMR tube was then brought into a N₂ filled glovebox and poured into a 20 mL scintillation vial, after which volatiles were removed under reduced pressure. The residual stick residue was washed with hexanes (2 x 1 mL), and volatiles were again removed under reduced pressure to give pure bisphosphinoethanes (R = 4-’BuPh (85%), 4-FPh (78%), 4-MeOPh (72%)) as off-white solids. NMR data matched previously described literature values.²⁸

### 3.5 References


Chapter 4: Iron catalyzed α phosphinidene elimination from primary phosphines

4.1 Introduction

Compared to the number of methods for C–C, C–O, and C–N bond forming reactions, there exist fewer main-group bond forming reactions, despite these elements making up the majority of the p-block.\textsuperscript{1-4} Main-group E–E bonded species are desirable for the study of their intrinsic properties, potential applications as materials precursors and materials with interesting optical and electronic properties, and as new ligands for transition-metal compounds. Thus, exploring new methods for E–E and E–C bond forming reactions is desirable. Würtz coupling, the classic E–E bond forming reaction, requires harsh conditions and creates both stoichiometric salt waste and product (Equation 1).

\[
\text{E–Cl} + \text{E'–Cl} \xrightarrow{\text{Na, } \Delta} 2 \text{NaCl} + \text{E–E'} \quad (1)
\]

On an industrial scale, these considerations make Würtz coupling unusable. An attractive alternative to Würtz coupling is dehydrocoupling.\textsuperscript{3,5-7} Dehydrocoupling is the catalytic formation of an E–E bond from two main-group element–hydrides with the concomitant release of hydrogen (Equation 2).

\[
\text{E–H} + \text{E'–H} \xrightarrow{\text{cat.}} \text{H}_2 + \text{E–E'} \quad (2)
\]

This reaction is particularly attractive for a variety of reasons. First, the only byproduct of the reaction is hydrogen, which is easily removed and can be utilized for further chemistry or for hydrogen fuel applications.\textsuperscript{5,6} The loss of hydrogen also provides an entropic driving force for this reactivity. Additionally, this reaction is catalytic, which is a great improvement over classic methods. Dehydrocoupling catalysts are essential to this reactivity, as dehydrocoupling is formally a symmetry forbidden process. There are a
variety of mechanisms of dehydrocoupling, but perhaps the most well studied is \( \sigma \)-bond metathesis (Scheme 4.1).³

Scheme 4.1: Generic catalytic cycle of dehydrocoupling by sigma bond metathesis.

The key transition state in \( \sigma \)-bond metathesis is the four-centered kite-like transition state that is part of a \([2\sigma+2\sigma]\) cycloaddition reaction. This allows for the formation of new E–E bonds without a change of oxidation state of the metal. Many \( d^0/d^0fn \) metal compounds catalyze dehydrocoupling through this mechanism as a result. Although dehydrocoupling through \( \sigma \)-bond metathesis has been shown to catalyze the formation of a variety of E–E bonds, limitations arise when considering the formation of high molecular weight polymers⁸⁻¹² and more complicated E–C bonds.²

A second mechanism of dehydrocoupling is oxidative addition–reductive elimination, which is common for late metal compounds (Scheme 3.2).
Scheme 4.2: Generic mechanism of dehydrocoupling by oxidative addition–reductive elimination.

Key to this mechanism is the change in oxidation state as the reaction proceeds, which is why this reactivity is common to late transition metals with redox flexibility. Although oxidative addition and reductive elimination are more classically understood reaction steps than σ-bond metathesis, late metal compounds have been less studied than \( d^0/d^{10} \) compounds for dehydrocoupling catalysis and thus this reactivity has been more poorly studied.

An alternative mechanism of dehydrocoupling is α elimination, which was first discovered by Tilley and Neale in 2002 in their study of \( \text{CpCp}^*\text{HfHCl} \) (\( \text{Cp} = \eta^5\text{-C}_5\text{H}_5 \), \( \text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5 \)) catalyzed stannane dehydrocoupling (Scheme 4.3).⁸
The key step operant in this mechanism is the formal deinsertion of the Mes$_2$Sn: fragment from the stannyl complex, which also regenerates the catalyst.$^{8,10}$ Importantly, a trapping experiment under stoichiometric conditions that utilized 2,3-dimethylbutadiene resulted in formation of 1-mesityl-2,5-dihydro-3,4-dimethylstannole. Although deinsertions of low-valent main group fragments have been known for decades, this was the first example of catalytic deinsertion of such a fragment and thus was deemed $\alpha$-elimination to differentiate the two processes.$^{8,10,12}$ Further study of this and related systems allowed for Tilley and coworkers to also identify $\alpha$-stibinidene elimination using CpCp*Hf(SbHR)Cl (R = Mes, dmp) complexes.$^{13}$ It was found that when CpCp*Hf(SbHMes)Cl was allowed to thermally decompose, the cyclotetraastibine (SbMes)$_4$ was found along with regeneration of the hafnium hydride CpCp*HfHCl in solution; in the case of CpCp*Hf(SbHdmp)Cl, decomposition led to the isolation of the

\[ \text{Scheme 4.3: Neale and Tilley’s seminal discovery of Mes}_2\text{SnH}_2 \text{ dehydrocoupling by } \alpha- \text{stannylene elimination.} \]
distibene dmpSb=Sbdmp along with the hydride. Isotope effect studies along with kinetic studies of the thermal degradation showed signs in both systems that α-stibinidene elimination was occurring as opposed to a σ-bond metathesis mechanism. Waterman and coworkers have shown mechanistic variety when examining the dehydrocoupling of arsines by a triamidoamine-supported zirconium complex: the secondary arsine Ph₂AsH was found to dehydrocouple to (AsPh₂)₂ by SBM, although the primary arsines MesAsH₂ and dmpAsH₂ were found to form (AsMes)₄ and (dmp)As=As(dmp) by α-arsinidene elimination, respectively.¹ In all, these results show that catalytic α-elimination from group 15 hydrides is a viable mechanism of dehydrocoupling, however, catalytic trapping experiments in all cases were unsuccessful which limited the application of this reaction type to organoelement synthesis, and notably phosphines have not currently been shown to dehydrocouple through α-elimination.

While Tilley has shown trapping of ‘Mes₂Sn’ (vide supra), stoichiometric phosphinidene transfer has long been a strategy towards phospholes and other related phosphorus heterocycles.¹⁴⁻²⁶ These compounds are desirable due to interesting electronic and optical properties for their use as materials precursors.²⁷,²⁸ The seminal synthesis of phospholes was achieved by Schmidt in 1966,²⁹ by reaction of the cyclic phosphine (PPh)₅ in the melt with 2,3-dimethylbutadiene or photolyzed the reagents with UV light to give the phosphole product in poor yields. More generally, stoichiometric reactions have allowed for controlled syntheses of phospholes, with perhaps the most ubiquitous method being Fagan-Nugent coupling (Scheme 4.4).³⁰⁻³⁴
A Fagan-Nugent coupling first involves the generation of a zirconacyclopentadiene by the reaction of Cp₂ZrCl₂ with 2 n-BuLi, followed by the addition of 2 equivalents of an alkyne. The resultant zirconacyclopentadiene can be used *in situ* or isolated, and then reacted with an equivalent of RPCl₂ (R = alkyl, aryl, halogen) to give the desired phosphole and regenerate Cp₂ZrCl₂.¹⁴ Although this method is the most general, it is certainly not ubiquitous, and while Cp₂ZrCl₂ can be recovered at the end of the process, an equivalent of salt is produced in the reaction. Thus, Fagan-Nugent coupling is not a viable method for the synthesis of phospholes on an industrial or practical scale.

In related work in phosphole synthesis, there has been significant work done by Mathey, Lammertsma, and Cummins in designing phosphinidene bridged organics that can transfer the phosphinidene to other unsaturated substrates (Figure 4.1).

---

**Scheme 4.4:** The Fagan-Nugent coupling reaction to form phospholes by transmetallation from a zirconacyclopentadiene to a dichlorophosphine.

**Figure 4.1:** Important advances in organophosphinidene transfer reagents.
Indeed, the original discovery by Mathey and coworkers that synthesized 7-phosphanorbornadienes that were able to transfer phosphinidenes launched an ongoing effort into phosphinidene transfer reactions. In 2005, Lammertsma and coworkers developed a series of protected 3H-benzophosphepines that represented a more facile precursor synthesis and transfer the protected phosphinidene under much more mild conditions. Finally, in 2012, Cummins and coworkers were able to synthesize a phosphinidene-bridged anthracene that was able to transfer the unprotected phosphinidene to a variety of dienes under mild conditions. These three reagents are successful because they produce aromatized byproducts upon the transfer of the phosphinidene fragment. Although these reagents are necessarily limited to stoichiometric phosphinidene transfer, they do demonstrate the potential of this reaction to provide value added molecules that are difficult to synthesize by other means.

There have been few catalytic syntheses of phospholes reported. These reports were initiated with the intramolecular hydrophosphination of phosphinoalkenes and alkynes. More recently, palladium-catalyzed routes to phospholes and phosphole oxides have been reported. These methods represent substantial advances but engage in P–C bond formation at a late stage and rely on largely prefabricated frameworks. Catalytic methods that employ simple precursors, produce phospholes that could be further elaborated, and utilize earth-abundant metal catalysts are therefore desirable.

Cyclopentadienyl iron compounds have been known to engage in deinsertion reactions of low-valent fragments. Pannell has shown that CpFe(CO)\(_2\)(SiMe\(_2\)SiMe\(_3\)) will deinsert Me\(_2\)Si: under photolysis. Angel and coworkers have shown that a variety of
mononuclear and binuclear cyclopentadienyl iron compounds with bulky phosphido or phosphinidene ligands appear to release a phosphinidene fragment with gentle heating or UV photolysis, and importantly, showed that similar compounds with less sterically encumbered backbones are thermally unstable, apparently releasing phosphinidene fragments even at $-196^\circ$C.$^{40,41}$

A report by Layfield and coworkers in 2016 showed that $\text{M(N(SiMe}_3)_2}$ ($\text{M} = \text{Fe, Co}$) were able to catalyze the synthesis of N-heterocyclic carbene phosphinidenes from primary phosphines and N-heterocyclic carbenes (NHCs).$^{42}$ It was suggested that various mechanisms were potentially operant: phosphinidene transfer from the metal to a coordinated NHC or vise-versa, formation of cyclic phosphines that could transfer a :PR fragment to the free NHC (a known reaction), or a concerted C–P bond forming process. In this report, the unusual observation that in these reactions formation of secondary phosphines $\text{R}_2\text{PH}$ ($\text{R} = \text{Ph, Mes}$) as well as the cyclic phosphine ($\text{PPh}_3$) were observed.$^{42}$ This “aryl addition” is unknown in reported dehydrocoupling or P–C bond forming reactions. Regardless, this report and those related to phosphinidene deinsertion from cyclopentadienyl iron compounds or organic phosphinidene transfer reagents highlight 1) phosphinidene fragments can be used for P–C bond forming reactions to access difficult to synthesize, value added molecules 2) although stoichiometric reactions are well understood, catalytic $\alpha$ phosphinidene elimination is greatly understudied and 3) iron compounds appear to be excellent candidates to catalyze this reactivity.

In this chapter, efforts to successfully catalyze $\alpha$-phosphinidene elimination and trapping reactions using the ubiquitous iron compound $\text{CpFe(CO)}_2\text{Me}$ (1) are described.
Dehydrocoupling reactions of PhPH₂ and Ph₂PH suggested that “typical” dehydrocoupling mechanisms are not operant. Furthermore, the successful trapping of phosphinidenes using alkynes, dienes, and disulfides strongly suggest an α-phosphinidene elimination mechanism and eliminate alternative processes. These reactions represent the first catalytic trapping of phosphinidenes for the synthesis of phospholes and suggest that this reactivity is a potentially valid method for the synthesis of complex organophosphines. Detailed deuterium labelling and reactivity studies were also performed, which lend evidence that α phosphinidene elimination is indeed the active mechanism.

4.2 Dehydrocoupling reactions

Treatment of primary or secondary phosphines with 10 mol % of 1 at 65 °C in a 1:9 C₆H₆:Et₂O solution resulted in gas evolution along with, primarily, the expected products of dehydrocoupling (Table 4.1).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>PhPH₂</th>
<th>Ph₂PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major products, %</td>
<td>(PhPH)₂, 6%</td>
<td>(PPh)₂, 42%</td>
</tr>
<tr>
<td>(PhPH)₂PPh, 45%</td>
<td>PPh₃, 2%</td>
<td></td>
</tr>
<tr>
<td>Ph₂PH, &lt; 1%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: 0.42 mmol phosphine, 0.021 mmol 1, 0.50 mL 1:9 C₆H₆:Et₂O, 65 °C, 12–48 h. a Substrate only 40% consumed after 48 h. b Substrate only 58% consumed after 48 h. c Conversion measured by ³¹P NMR spectroscopy.

However, these reactions also yielded several unusual observed products. The triphosphine (PhPH)₂PPh was reliably observed in the dehydrocoupling of PhPH₂, which is rare for this reaction. ⁷ Additionally, during the course of this dehydrocoupling, low
conversion (< 1%) to Ph$_2$PH was observed as evidenced by $^{31}$P NMR spectroscopy. Similarly, the formation of PPh$_3$ in 2% conversion was observed in the dehydrocoupling of the secondary phosphine Ph$_2$PH. Formation of Ph$_2$PH was also observed in the catalytic phosphinidene transfer from primary phosphines to N-heterocyclic carbenes to form N-heterocyclic phosphinidenes as observed by Layfield and coworkers, who used M(N(SiMe$_3$)$_2$)$_2$ (M = Fe, Co) to catalyze this transformation.$^{42}$ Interestingly, reaction of Mes*PH$_2$ (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) with 10 mol% 1 at 65 °C for six hours resulted in formation of the diphosphine (Mes*PH)$_2$ ($^{31}$P NMR $\delta = -61.9$), as well as the unexpected intramolecular C–H activation product 5,7-bis(1,1-dimethylethyl)-2,3-dihydro-3,3-dimethyl-1H-phosphindole. The dehydrocoupling of sterically encumbered primary phosphines RPH$_2$ (R = tBu, Mes, dmp) (Mes = 2,4,6-Me$_3$C$_6$H$_2$; dmp = 2,6-Mes$_2$C$_6$H$_3$) with 10 mol% 1 at 65 °C for 48 h resulted in no reactivity. Increasing the temperature to 100 °C, as well as extended reaction times up to seven days did not result in any conversion to dehydrocoupling products or other phosphorus containing products. Exposure to ambient light did not appear to affect reaction conditions, as all dehydrocoupling reactions were performed both with and in the strict absence of ambient light. All dehydrocoupling reactions were performed in PTFE-sealed NMR tubes that were freeze-pump-thawed twice before heating to ensure rapid removal of hydrogen, and when dehydrocoupling was observed through $^{31}$P NMR spectroscopy, every four hours thereafter.

Dehydrocoupling of Ph$_2$PH under similar conditions gave primarily the diphosphine (PPh$_2$)$_2$ in 42% conversion. In similar fashion to the dehydrocoupling of PhPH$_2$, the “pseudoredistribution” product PPh$_3$ was also observed in these reactions in
~2% conversion as evidenced by $^{31}$P NMR spectroscopy. While tetraphenyldiphenysilane is the expected product of dehydrocoupling of Ph$_2$PH, the observation of PPh$_3$ in this reaction is highly unusual and points to unique reactivity as compared to previously studied dehydrocoupling reactions. In all, observations made in the discussed dehydrocoupling reactions led to the intriguing hypothesis that α-phosphinidene elimination was the operative mechanism of dehydrocoupling and thus trapping experiments were carried out to help confirm this hypothesis.

4.3 Successful trapping reactions

Treatment of phenylphosphine with ten equivalents of diphenylacetylene and 5 mol % 1 at 65 °C in a 9:1 Et$_2$O:C$_6$H$_6$ solution for three hours resulted in reliable, low conversion to 1,2,3,4,5-pentaphenylphosphole (2) (2%). Although this is a noncatalytic conversion, this provides initial proof of :PPh fragment trapping. The major identifiable byproduct of this reaction is the correspondoing 1,2-bis(phosphino)ethane (3) arising from double hydrophosphination of diphenylacetylene with phenylphosphine. This is unsurprising as a byproduct, as 1 is a known hydrophosphination catalyst under thermal conditions.$^{43}$ Competitive hydrophosphination can be controlled under these conditions by adding one atmosphere of H$_2$ to the above described reaction mixture. This allows for improved
conversion (12%) to the desired phosphole product as identified by $^{31}$P NMR spectroscopy ($\delta = 15$ ppm) (Scheme 4.6).

Scheme 4.6: Catalytic synthesis of 1,2,3,4,5-pentaphenylphosphole (2) and the bis(phosphino)ethane (3) with and without an atmosphere of H$_2$.

More successful trapping was achieved using 2-butyne. Treatment of phenylphosphine with ten equivalents of 2-butyne with 5 mol% 1 at 65 °C for three hours in a 9:1 Et$_2$O:C$_6$H$_6$ solution gives 2,3,4,5-tetramethyl-1-phenylphosphole (4) in 53% conversion as evidenced by $^{31}$P NMR spectroscopy ($\delta = 16$ ppm, Equation 3). The other products of this reaction were unknown in the literature; however, no competitive hydrophosphinination occurred. In contrast to diphenylacetylene, introducing an atmosphere of H$_2$ did not seem to improve the conversion of this reaction.
Trapping experiments with 2,3-dimethyl-1,3-butadiene were strongly suggestive of α-phosphinidene elimination. Treatment of five equivalents of 2,3-dimethyl-1,3-butadiene and phenylphosphine with 5 mol % of 1 in a 9:1 Et₂O:C₆H₆ solution gave the secondary phosphine (5), phosphole (6), and tetrahydrodiphosphorin (7) products as a mixture in 18%, 53%, and 29% conversions, respectively, as evidenced by $^{31}$P NMR spectroscopy (Equation 4). There was a pronounced solvent effect on reactivity, with only mixtures of Et₂O:C₆H₆ in ratios between 9:1 and 3:1 producing trapping results in all reactions (Tables 4.2–4.3). Indeed, this strong solvent effect proved to be crucial to observing any reactivity, α-phosphinidene elimination or otherwise. The products 6 and 7 are suggestive of phosphinidene trapping, but the formation of the hydrophosphination product 5$^{43}$ avails the possibility that 6 arises from the ring closure of 5.$^{36,37}$ Monitoring the formation of these products by $^{31}$P NMR spectroscopy does not reveal any obvious dependence on the concentration of 5 in the formation of 6. The potential ring-closure pathway was disproven by two additional experiments. First, isolated samples of 5 are not converted to 6 under catalytic conditions with or without an added atmosphere of H₂. Second, when PhPD₂ is used as a substrate only D₂ and 5-d₂ are observed by $^{2}$H NMR spectroscopy, where a ring closure would require formation of HD as well as deuteration of 6 and 7.

\[
\text{PhPH}_2 + 5 \xrightarrow{5 \text{ mol}\% \text{ 1 \text{ in 9:1 Et}_2\text{O:C}_6\text{H}_6 \text{ 3 h}}} \text{PhHP} + \text{PhP} + \text{PhP—PPh} \tag{4}
\]

Greater selectivity for trapping products is observed at higher temperatures. For example, heating the reaction of phenylphosphine with equimolar 2,3-dimethyl-1,3-butadiene at 100 °C as opposed to 65 °C gave exclusive formation of 6 and 7 in an
approximately 3:1 ratio. Increasing the equivalents of 2,3-dimethyl-1,3-butadiene to ten with respect to PhPH₂ did not improve selectivity with respect to 6 or 7. On one occasion at 100 °C, quantitative conversion to 6 was observed; however, attempts to reproduce this level of selectivity have been unsuccessful. Two pathways to form 7 are plausible (Scheme 4.7). In pathway A, 7 is formed by the sequential trapping of two ‘PPh’ equivalents to first form 6, and the second transfer event affords 7. Pathway B involves condensation of two phosphinidene fragments to form 1,2-diphenyldiposphene, which could undergo a [4+2] cycloaddition with 2,3-dimethyl-1,3-butadiene to form 7. Two observations support pathway A over B. First, monitoring reactions by 31P NMR spectroscopy reveals a decrease in concentration of 6 with a concomitant increase in the concentration of 7. Second, addition of PhPH₂ to a completed catalytic reaction (i.e., phosphine and diene substrates have been consumed) results in decreased concentration of 6 with an increase in the concentration of 7.

Scheme 4.7: Potential routes to form 7, with route A being the proposed route in this study.
An additional reaction that supports an α-phosphinidene elimination mechanism is a trapping experiment with EtSSEt. The reaction of PhPH₂ with equimolar EtSSEt and 5 mol % of 1 at 65 °C for one hour in a 9:1 Et₂O:C₆H₆ solution gives PhP(SEt)₂ in quantitative conversion as evidenced by ³¹P NMR spectroscopy (Scheme 4.8). The insertion of phenylphosphinidene into the S–S bond of diethyl disulfide is a known reaction. Formation of PhP(SEt)₂ by successive oxidative addition–reductive elimination steps may be possible. However, 1 does not react with EtSSEt under catalytic conditions in the absence of PhPH₂, which suggests a pathway involving S–S bond activation at iron is unlikely.

$$\text{PhPH}_2 + \text{EtSSEt} \xrightarrow{5 \text{ mol% 1 \quad 9:1} \text{Et}_2\text{O}:\text{C}_6\text{H}_6 \quad 1 \text{ h}} \xrightarrow{\text{S-S Insertion}} \text{EtSSEt} \quad \text{100 %}$$

Scheme 4.8: Insertion of phenylphosphinidene into the S–S bond of diethyl disulfide.

4.4 Mechanistic studies and proposed catalytic cycle for α-phosphinidene elimination

In order to disprove other potential mechanisms to afford the trapping products discussed in section 4.3, a variety of reactions were performed. Schmidt has shown that (PPh)₅ can transfer :PPh in the melt or under photolysis conditions (vida supra). Trapping products in our studies do not appear to result from reaction of (PPh)₅ with 2,3-dimethyl-1,3-butadiene, which is known, as (PPh)₅ is not observed in either dehydrocoupling or trapping reactions. Additional experiments utilizing (PPh)₅ as a ‘PPh’ source in all trapping reactions in place of PhPH₂ gave only minor conversion to 6 and 7, with various unidentifiable products also being observed by ³¹P NMR spectroscopy. The internal alkynes diphenylacetylene and 2-butyne as well as EtSSEt did not trap
Phosphinidene when (PPh)$_5$ was used in place of PhPH$_2$ under catalytic conditions. Given these results, (PPh)$_5$ was shown to not be the source of ‘PPh’ in this catalysis.

Phosphenium (PPhH$^+$) cations were also a potential reactive species in this catalysis. These species have previously been shown to be highly reactive in cycloadditions, 45,46 insertion reactions, 47-51 and polymerization reactions, 52 but importantly could react to afford all the trapping products observed in this chemistry. An important negative result that supports an α-phosphinidene elimination mechanism is the failure of $N$-methylimidazole to trap a phosphorus containing substrate. Reaction of PhPH$_2$ with 20 equivalents of $N$-methylimidazole under standard catalytic conditions did not result in any reaction. This observation rules out the formation of a phosphenium ion, which would be readily trapped by this substrate. 49
Scheme 4.9: Proposed catalytic cycle for α-phosphinidene elimination from primary phosphines catalyzed by 1.

A proposed catalytic cycle is shown in Scheme 4.9. Activation of 1 would occur by migratory insertion of the methyl ligand rather than carbonyl loss or protonation based on the relatively low acidity of primary phosphines\textsuperscript{53} and prior study of migratory insertion reactions of 1.\textsuperscript{54,55} Additional studies show that relatively strong acids are required to induce methane loss.\textsuperscript{56} This activation method is supported by the persistence of 1 at the end of catalysis. Reaction of 1-d\textsubscript{3} under standard catalytic conditions reveals quantitative restoration of the precatalyst by \textsuperscript{2}H NMR spectroscopy upon complete conversion of substrates. Activation of the phosphine would follow by oxidative addition of a P–H bond to give an iron(IV) intermediate that could engage in α-phosphinidene elimination.\textsuperscript{40,41} The observed dehydrocoupling products of P–H and P–P insertion as well as condensation are
consistent with other α elimination reactions, and furthermore primary phosphide complexes supported by the Fp-platform are known to eliminate phosphinidenes. After α-phosphinidene elimination, reductive elimination of H₂ would close the catalytic cycle and is also consistent with the observation of H₂ and R–H products in the dehydrocoupling reactions of primary and secondary phosphines, respectively.

4.5 Unsuccessful trapping reactions

Despite the success of trapping with the reagents discussed in section 4.3, the majority of reagents that were used to attempt trapping reactions were unsuccessful (Table 4.2). For example, all internal alkynes other than 2-butyne and diphenylacetylene were unable to trap transient phosphinidenes. This list includes 3-hexyne, bis(trimethylsilyl)acetylene, 2-ethynylpyridine, 1-phenyl-2-trimethylsilylacetylene, and 1-methyl-2-phenylacetylene. The inability of 1-methyl-2-phenylacetylene to trap phosphinidenes is particularly surprising, as both the symmetric methyl and phenyl substituted alkynes were able to trap. Terminal alkynes were also unsuccessful at trapping phosphinidenes: phenylacetylene, 1-hexyne, tert-butylacetylene, and trimethylsilylacetylene were not fruitful for this reactivity. The diynes 1,4-diphenylbutadiyne and 1,4-bis(trimethylsilyl)butadiyne were also unable to trap phosphinidenes. Alkenes outside of 2,3-dimethyl-1,3-butadiene did not trap phosphinidenes as well, with styrene, 1-octene, 1-hexene, 1,1,2,2-tetramethylethene, 2-vinylpyridine, and acrylamide. Perhaps the most surprising unsuccessful trap was 1,3-cyclohexadiene, which was shown to accept a phosphinidene by Cummins and coworkers,²⁵ and is suggestive that an unusual mechanism of actual phosphinidene release
is evident (vida infra). Diketones were also unsuccessful trapping agents, as 2,3-butanedione, 2,4-pentanedione, and benzil (a previously studied phosphinidene trap)\textsuperscript{44} did not trap phosphinidenes as well. The diimines $N,N$-dimesityl-dimethylimine and $N,N$-(2,6-diisopropylphenyl)-dimethylimine were also unsuccessful traps for phosphinidene fragments, although these have not previously been used as traps in this reaction type. Tris(trimethylsilyl)silane, a trap for silylene fragments that insert into the Si–H bond of the compound, was not an effective trap for phosphinidenes under these catalytic conditions. The addition of W(CO)$_5$(thf) to trapping reactions did not improve or affect any successful or unsuccessful trapping reactions, which is suggestive that the phosphinidene formed in these reactions is too short-lived to coordinate to the tungsten fragment. Attempted trapping reactions with azobenzene provided the cyclic pentamer (PPh)$_5$ in high conversion almost immediately upon mixing reagents, which currently is beyond our understanding of this system. Another previously studied trap for phosphinidene fragments is biphenylene, which allows for insertion into a C–C bond of the cyclobutadiene unit of the molecule to give the phosphole product, although this was not observed in trapping reactions using $\mathbf{1}$ and primary phosphines. Finally, although Layfield showed that NHCs were viable traps in phosphinidene transfer reactions catalyzed by $\mathbf{M}(\text{N(SiMe}_3)_2)_2$ (M = Fe, Co), they were not successful in this system presumably due to ligand exchange between the carbonyl ligands of $\mathbf{1}$ and the NHCs to form unreactive iron species.
<table>
<thead>
<tr>
<th>General trap type</th>
<th>Traps tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal alkynes&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3-hexyne, bis(trimethylsilyl)acetylene, 2-ethynylpyridine, 1-phenyl-2-trimethylsilylacetylene, 1-methyl-2-phenylacetylene</td>
</tr>
<tr>
<td>Terminal alkynes&lt;sup&gt;a&lt;/sup&gt;</td>
<td>phenylacetylene, 1-hexyne, trimethylsilylacetylene, tert-butylacetylene</td>
</tr>
<tr>
<td>Internal diynes&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1,4-diphenylbutadiyne, 1,4-bis(trimethylsilyl)butadiyne</td>
</tr>
<tr>
<td>Alkenes&lt;sup&gt;a&lt;/sup&gt;</td>
<td>styrene, 1-hexene, 1-octene, 1,1,2,2-tetramethylethene, acrylamide, 2-vinylpyridine</td>
</tr>
<tr>
<td>Diketones&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2,3-butanedione, 2,4-pentanedione, benzil</td>
</tr>
<tr>
<td>Diimines&lt;sup&gt;b&lt;/sup&gt;</td>
<td>N,N-dimesityl-dimethylimine, N,N-(2,6-diisopropylphenyl)-dimethylimine</td>
</tr>
<tr>
<td>Others&lt;sup&gt;b&lt;/sup&gt;</td>
<td>tris(trimethylsilyl)silane, W(CO)_3(thf), BH₃•THF, IMes, IDipp, azobenzene, biphenylene, N-methylimidazolere</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 0.021 mmol 1, 0.42 mmol phosphine, 4.2 mmol trapping reagent, 65–100 °C, 9:1 Et₂O:C₆H₆, 5 d.  
<sup>b</sup> Reaction conditions: 0.021 mmol 1, 0.42 mmol phosphine, 2.1 mmol trapping reagent, 65–100 °C, 9:1 Et₂O:C₆H₆, 5 d.

Given the limited success of the successful and unsuccessful trapping reactions described in this section and section 4.3, we hypothesize that we are eliminating a triplet phosphinidene as opposed to a singlet phosphinidene. The latter species are known to be
electrophilic and more importantly, highly and selectively reactive to perform facile insertions.\textsuperscript{57-61} Triplet phosphinidenes are more commonly proposed as reactive intermediates in transfer reactions,\textsuperscript{29,44} and in the case of $\alpha$-phosphinidene elimination catalyzed by 1 is likely due to the propensity for iron to perform single electron chemistry. Additionally, Mathey has shown that $N$-methylimidazole is able to stabilize and facilitate transfer of singlet phosphinidenes, while triplet phosphinidenes are noted to not be assisted by this reagent,\textsuperscript{62} which is consistent with the reactivity in this study (\textit{vida supra}). The likely formation of triplet phosphinidenes is further complicated by the relatively sterically congested inner-sphere ligand set around iron in the proposed catalytic cycle, which would prevent potential precoordination events by unsaturated substrates to aid in clean phosphinidene transfer. This, along with the high reactivity of phenylphosphinidene would allow for a myriad of nonproductive, competitive processes that account for the small substrate scope and sometimes unselective reactivity of trapping and dehydrocoupling reactions catalyzed by 1.

4.6 Future directions

Although $\alpha$-phosphinidene elimination catalyzed by 1 is an important study in the field of low valent main-group chemistry, the reaction is clearly limited in scope and synthetic practicality. As 1 is preserved throughout catalysis (\textit{vida supra}), it must be removed from any reaction mixtures to give an isolated, value-added phosphine product; 1, however, is an extremely robust compound and thus is difficult to remove from reaction mixtures. All attempts to isolate phosphine products were met with failure, which included column chromatography, chemical modification of the phosphorus containing products to
impart some solubility difference by oxidation or coordination of Lewis acids, fractional crystallization, and sublimation. Additionally, the release of singlet phosphinidene fragments is ideal for organophosphine synthesis, so promotion of that over triplet phosphinidenes is important. Thus, for practical synthetic usage of $\alpha$-phosphinidene elimination, a new catalyst is desirable.

Because catalytic phosphinidene transfer is known for iron and cobalt complexes, group 8 and 9 metal compounds are reasonable candidates for new catalysts. In the work described in this chapter, cyclopentadienyl compounds are also known to promote this reactivity, and it is clear that removing steric bulk from the transition-metal center will help to promote this reactivity as this may allow for a precoordination event to facilitate clean phosphinidene transfer and more sterically encumbered phosphines could be tolerated which is known to promote $\alpha$-elimination reactions.

![Figure 4.2: Potential compounds that could catalyze formal ‘PR’ transfer to form phospholes (left) or $\alpha$-phosphinidene elimination (right).](image)

With this in mind, one intriguing potential set of compounds for this catalysis is the family of Vollhardt’s compounds $\text{Cp}'\text{Co}(\eta^2\text{-C}_2\text{HR})_2$ ($\text{Cp}' = \text{Cp}, \text{Cp}^*; R = \text{H}, -\text{SiMe}_3$) which were primarily used for [2+2] and [2+2+2] cycloadditions of alkynes to form cyclobutenes and benzenes, respectively (Figure 4.2). These compounds readily lose ethylene ligands to provide “$\text{Cp}'\text{Co}$” in solution, which clearly contains an unencumbered steric
pocket that could accommodate both phosphine and acetylene ligands. This may allow for formal \([2+2+1]\) cycloadditions of two alkynes and a phosphine to form phospholes. Although this would probably not operate through \(\alpha\)-phosphinidene elimination, it would involve formal ‘PR’ transfer to catalytically synthesize phospholes, which would be important to expanding the reaction type. A compound more likely to catalyze true \(\alpha\)-phosphinidene elimination would be the ruthenium congener to \(1\) \(\text{CpRu(CO)}_2\text{Me (RpMe)}\) (Figure 4.2).\(^{54,71,72}\) RpMe is able to undergo similar activation steps to \(1\),\(^{54}\) which could catalyze the same reactivity, with the advantage of ruthenium over iron being the propensity for ruthenium to do two-electron chemistry.\(^{73}\) This may facilitate singlet phosphinidene elimination versus triplet phosphinidene elimination and provide much cleaner transfer than observed for \(1\).

4.7 Conclusions

In conclusion, the ubiquitous iron complex \(\text{FpMe (1)}\) was shown to catalyze \(\alpha\)-phosphinidene elimination from primary phosphines. This rare reaction type was observed first in unusual dehydrocoupling products, and was consistent with trapping experiments using internal alkynes, 2,3-dimethyl-1,3-butadiene, and EtSSEt. The phosphole products obtained from the trapping reactions of the alkynes are otherwise difficult to obtain, and demonstrate the potential of this reaction type for value-added organophosphine synthesis. Although some conversions of the trapping reactions were poor, in particular those of internal acetylenes, modification of reaction conditions provided some degree of control to improve product yields of the phospholes. Deuterium labelling studies, monitoring the concentration of reaction products, and the failure of certain compounds to stop reactivity
provided key evidence for the proposed α-phosphinidene elimination mechanism. Further studies in catalyst modification to better control this reactivity are currently underway.

4.8 Experimental

4.8.1 General Considerations
All manipulations were performed under an inert atmosphere of N₂ using Schlenk line or glovebox techniques using oxygen-free, anhydrous solvents. Benzene-\(d_6\) was degassed and dried over NaK alloy. NMR spectra were recorded using a Bruker AXR 500 MHz spectrometer, using an external reference of 85% H₃PO₄ for \(^{31}\)P NMR experiments and residual solvent resonances for \(^1\)H NMR experiments (\(\delta = 7.16\)). Reagents were obtained from commercial suppliers and dried by conventional means as necessary. FpMe\(^{74}\) (1) and PhPD\(^{2,75}\) were prepared by literature methods. (PhPH)\(^2\),\(^{75}\) (PhPH)\(^2\)PPh,\(^7\) and (PPh\(^2\))\(^2\) were identified by their literature \(^{31}\)P chemical shift values.

4.8.2 Typical procedure for dehydrocoupling reactions
A solution of phosphine (0.42 mmol) in 0.50 mL of a 10% benzene in Et₂O mixture was added to solid FpMe (1, 4.0 mg, 0.021 mmol) and the resultant solution was quickly transferred to a PTFE-valved NMR tube. The solution was subjected to two freeze-pump-thaw cycles before being heated to 65 °C. A freeze-pump-thaw cycle was performed at least every 24 h to remove evolved hydrogen.

4.8.3 Typical procedure for trapping experiments
A solution of phosphine (0.42 mmol) and 2,3-dimethylbutadiene (0.84 mmol) or internal acetylene (4.2 mmol) in 0.50 mL of a 10% benzene in Et₂O was added to solid FpMe (1, 4.0 mg, 0.021 mmol), then quickly transferred to a PTFE-sealed NMR tube. The solution was subjected to two freeze-pump-thaw cycles before being heated to 65 °C. A freeze-
pump-thaw cycle was performed approximately every 30 min. to remove evolved hydrogen.

4.8.4 Typical procedure for trapping experiments under hydrogen pressure
A solution of phosphine (0.42 mmol) and 2,3-dimethylbutadiene (0.84 mmol) or internal acetylene (4.2 mmol) in 0.50 mL of a 10% benzene in Et₂O was added to solid FpMe (I, 4.0 mg, 0.021 mmol), then quickly transferred to a PTFE-sealed NMR tube. The solution was subjected to four freeze-pump-thaw cycles, then approximately 1 atm of hydrogen was introduced. The tube was then heated to 65 °C and no further freeze-pump-thaw cycles were performed.

4.8.5 Supplementary information

Table 4.3 Solvent effects on trapping reactions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>% consumption PhPH₂ᵃᵇ</th>
<th>Timeᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran</td>
<td>4</td>
<td>4 d</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>4 d</td>
</tr>
<tr>
<td>Toluene</td>
<td>0</td>
<td>4 d</td>
</tr>
<tr>
<td>Hexanes</td>
<td>0</td>
<td>4 d</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2</td>
<td>4 d</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>4</td>
<td>4 d</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>11</td>
<td>12 h</td>
</tr>
</tbody>
</table>
Table 4.4 Effects of various Et₂O:C₆H₆ ratios on reactivity of trapping reactions

<table>
<thead>
<tr>
<th>Ratio of Et₂O:C₆H₆</th>
<th>% consumption PhPH₂ᵃᵇ</th>
<th>Timeᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>11</td>
<td>12 h</td>
</tr>
<tr>
<td>20:1</td>
<td>19</td>
<td>24 h</td>
</tr>
<tr>
<td>9:1</td>
<td>100</td>
<td>4 h</td>
</tr>
<tr>
<td>5:1</td>
<td>100</td>
<td>4 h</td>
</tr>
<tr>
<td>4:1</td>
<td>100</td>
<td>4 h</td>
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<tr>
<td>3:1</td>
<td>100</td>
<td>4 h</td>
</tr>
<tr>
<td>2:1</td>
<td>12</td>
<td>4 d</td>
</tr>
<tr>
<td>1:1</td>
<td>0</td>
<td>4 d</td>
</tr>
<tr>
<td>0:1</td>
<td>0</td>
<td>4 d</td>
</tr>
</tbody>
</table>

ᵃ Reaction conditions: 0.021 mmol FpMe, 0.42 mmol PhPH₂, 0.84 mmol 2,3-dimethyl-1,3-butadiene, 0.50 mL solvent.ᵇ% consumption PhPH₂ measured by ³¹P NMR spectroscopy.ᶜ Maximum % consumption PhPH₂ was seen after this time or reactions were stopped after 4 days.

4.9 References


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(6) Staubitz, A.; Robertson, A. P. M.; Sloan, M. E.; Manners, I. *Chem. Rev.* **2010**, *110*, *4023-4078*.


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Chapter 5: The synthesis and reactivity of uranium and thorium actinacycles

5.1 Introduction

Metallcyclic compounds have been known for transition-metal compounds for decades in the literature. These compounds have great importance as intermediates in catalysis, their unique geometries to study bonding, and as precursors for main-group heterocycles.¹⁻³ Given the ubiquity of group 4 metallacycles and the parallels drawn between these transition-metals and the early actinides Th and U, it is surprising that there is a distinct lack of actinacycles known in the literature. All carbon metallacycles of the actinides are even more rare; the first bis(pentamethycyclopentadienyl)-actinide complex \( \text{Cp}^*\text{2U}(\eta^2\text{-C}_4\text{Ph}_4) \) (1) was synthesized by Marks and coworkers by salt metathesis between dilithiotetraphenylbutadiene and \( \text{Cp}^*\text{2UCl}_2 \) (2) in 1981,⁴ and it was not until 2015 that Walter and coworkers synthesized \( \text{Cp}^*\text{2Th}(\eta^2\text{-C}_4\text{Ph}_4) \) (3) by reduction of \( \text{Cp}^*\text{2ThCl}_2 \) (4) with excess KC₈ in the presence of diphenylacetylene.⁵ Outside of metallocene based, all carbon actinacycles, Meyer and coworkers have described the syntheses of \([\{(\text{AdArO})_3\text{N})\text{U}_2(\mu–\eta^2:\eta^1\text{-1,2-(CH)}_2\text{-cyclohexane})\}]\) and \([\{(\text{AdArO})_3\text{N})\text{U}_2(\mu–\eta^2:\eta^2\text{-1,2-(CH)}_2\text{-cyclopentane})\}]\) (Ad = adamantyl, Ar = (1,4,7-tris(3-Ad-5-tert-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane)) by intra- or intermolecular C–C coupling reactions between alkynes and \([\{(\text{AdArO})_3\text{N})\text{U}(\text{dme})\}]\) (dme = 1,2-dimethoxyethane).⁶ There are limited other examples of bis(cyclopentadienyl)-actinacycles in the literature, notably synthesized by Walter and coworkers. The thoracycloprenene \( \text{C}_5\text{Bu}_3\text{H}_2\text{Th}(\eta^2\text{-C}_2\text{Ph}_2) \) (5)⁷ and thoracyclocumulene \( \text{Cp}^*\text{2Th}(\eta^4\text{-C}_4\text{Ph}_2) \) (6) were accessed by similar methods to 3.⁸ Interestingly, both compounds displayed reactivity more closely resembling actinide bis(alkyl) complexes such as \( \text{Cp}^*\text{2AnMe}_2 \) (An = U (7), Th (8)) as opposed to group 4
congeners, with insertion reactions being exclusively favored over ligand displacements.9-11 This was particularly surprising as the titanium complexes (C₅R₅)Ti(η²-C₂(SiMe₃)₂) (R = H (9), Me (10)) known as “Rosenthal reagents” are incredibly powerful “(C₅R₅)Ti(II)” synthons which allow facile access to a variety of bis(cyclopentadienyl)-titanium(IV) compounds.12-17 An actinide congener to Rosenthal reagents is highly desirable, as there is a distinct lack of easily accessible actinide starting materials and certainly not any known “Cp*₂An(II)” equivalents. If such a reactive species were to exist, it would provide access to new and exciting areas of actinide chemistry.

Since the first synthesis of biphenylene in 1893 by Hosaeus,18 antiaromatic molecules have been desired due to their interesting properties, notably, their inherent instability. Vollhardt and coworkers have extensively studied the use of cobalt catalyzed cyclizations to form a family of paraphenylenes, which contain this cyclobutene unit that repeats throughout the molecule.19-27 Metal-containing antiaromatic molecules are known, all of which are ligated with porphyrinoids. These metal-containing antiaromatics are known for iron,28 nickel,29-32 zinc,29,33 gold,34 and uranium.35 In these systems, the metal participates in the antiaromaticity, and the prophyrinoid fragments are prefabricated to be Hückel antiaromatic before the metal is added.36-39 Osmium and ruthenium fragments have been shown to be able to stabilize normally unstable organics such as cyclobutadiene and pentalene by forming aromatic metallacycles.40-48 Despite this body of work, there have been no reports of a metal-supported antiaromatic system, where the metal does not directly participate in the antiaromaticity.
Although the reductive coupling at group 4 metallocenes, in particular those of zirconocenes, are well known and nearly ubiquitous reactions,\textsuperscript{15,16,49-57} we noted an interesting exception from Buchwald and coworkers in 1994, where the reductive coupling of 1,2-bis((trimethylsilyl)ethynyl)benzene with Negishi’s reagent \((\text{C}_5\text{H}_5)_2\text{ZrCl}_2\) treated with two equivalents of \(n\)-BuLi) failed to couple the alkynes, but instead gave a bis-alkyne complex.\textsuperscript{58}

![Figure 5.1: Attempted reductive coupling of 1,2-bis((trimethylsilyl)ethynyl)benzene by Negishi’s protocol, which instead gave a zirconocene-based bis-alkyne.](image)

With the previously observed differences in reactivity between transition-metal compounds and \(f\)-elements,\textsuperscript{10} we hypothesized that actinide systems may be more amenable to allow for the desired C–C coupling reaction.

Indeed, the observed paucity of bis(cyclopentadienyl)-actinacycles was intriguing and seemed to be a ripe area of study. Comparisons between group 4 (no \(f\)-electrons/accessible \(f\)-orbitals), Th(IV) (no \(f\)-electrons, accessible \(f\)-orbitals), and U(IV) (2 \(f\)-electrons, accessible \(f\)-orbitals) compounds is broadly important to further understand the effects of \(f\)-electrons and \(f\)-orbitals on well-known reactions for transition metals,\textsuperscript{10,59} as the study of actinide complexes is far less advanced than that of the d-block. A fundamental
understanding of the unique structures and reactivity imparted by f-orbitals/electrons is important for not only basic knowledge, but better understanding applications in nuclear fuels and waste remediation. With all of this in mind, a careful study of the synthesis, structure, and reactivity of uranium and thorium metallacycles was carried out. In this chapter, the successful syntheses of the first examples of uranacyclocumulenes \( \text{Cp}^*\text{U}(\text{C}_4\text{R}_2) \) (R = SiMe\(_3\) (11), Ph (12)), compounds 6 and a new thoracyclocumulene \( \text{Cp}^*\text{Th}(\text{C}_4(\text{SiMe}_3)_2) \) (13), a direct uranium congener to Rosenthal’s reagents \( \text{Cp}^*\text{U}(\text{C}_2(\text{SiMe}_3)_2) \) (14) which possesses reactivity consistent with a “\( \text{Cp}^*\text{U}(\text{II}) \)” synthon, and the unique \( \text{Cp}^*\text{An}(2,5-\text{Ph}_2\text{-cyclopenta}[3,4]\text{cyclobuta}[1,2]\text{benzene}) \) (An = U (15), Th (16) which possess an antiaromatic cyclobutane ring at their center. Finally, preliminary attempts made with Fagan-Nugent coupling reactions using a variety of the synthesized actinacycles are described.

5.2 Unreactive actinacyclocumulenes: synthesis, structure, and origins of stability

When 2 or 4 is treated with 2.1 equivalents of KC\(_8\) in the presence of 1,4-bis(trimethylsilyl)butadiyne in toluene solution for 3 h, the actinacyclocumulenes 11 or 13 can be isolated in 87% and 72% yields, respectively (Equation 1).

\[
\text{An = U (2), Th (4)} \quad + \quad 2.1 \text{ KC}_8 \quad \xrightarrow{\text{Me}_3\text{Si} \quad \equiv \quad \equiv \text{SiMe}_3 \quad 50 ^\circ \text{C}, \text{Toluene, 3 h}} \quad \text{An = U (11), 87\%}
\]

\[
\text{An = Th (13), 72\%}
\]

Compound 11 is isolated as a yellow-brown powder, with behavior consistent with U(IV) as evidenced by \( ^1\text{H} \) NMR spectroscopy (δ = 2.22 and −2.50 for −SiMe\(_3\) and C\(_5\)Me\(_3\)
resonances in C\textsubscript{6}D\textsubscript{6}, respectively) and a silent \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectrum. The UV/vis–NIR spectrum of 1 is also consistent with a U(IV) species with low intensity Laporte forbidden f–f transitions (\(\varepsilon < 20 \text{ cm}^{-1}\text{M}^{-1}\)) in the NIR region.\textsuperscript{60} In a similar fashion to 11, 13 can be isolated as a dark red powder with diagnostic \textsuperscript{1}H NMR features (\(\delta = 1.79\) and 0.56 for C\textsubscript{5}Me\textsubscript{5} and –SiMe\textsubscript{3} resonances in C\textsubscript{6}D\textsubscript{6}, respectively). The dark red coloration of 13 is highly unusual for organometallic Th(IV) species, with most compounds ranging in color from yellow to white. Compound 13 also displays UV/vis–NIR spectral features consistent with most characterized Th(IV) compounds, with no features in the NIR region. When comparing the UV/vis regions between compounds 11 and 13, clear similarities can be seen with intense but narrow features (\(\nu_{1/2} < 2500 \text{ cm}^{-1}\)) corresponding to cumulene bonding–antibonding transitions at 33175 cm\textsuperscript{1} and 34025 cm\textsuperscript{1} respectively and broader features centered at 29370 cm\textsuperscript{1} (11) and 29970 cm\textsuperscript{1} (13). The UV/vis region for 11 also contains 3 additional features below 25000 cm\textsuperscript{1}, which are due to the cumulene \(\pi–f\) transitions (\textit{vide infra}).
Figure 5.2: Deconvoluted UV/Vis spectra of compounds 11 and 13.

Single crystals suitable for X-ray diffractometry of 11 and 13 were grown from concentrated hexane and pentane solutions, respectively, at –30 °C overnight and their solid state structures are presented below.
Figure 5.3: The molecular structures of 11 (left) and 13 (right) with thermal ellipsoids displayed at the 50% probability level.

Both 11 and 13 crystallized in the monoclinic space group P2(1)/c. Experimental and predicted metrical parameters of compounds 11 and 13 as well as the zirconium congener Cp*₂Zr(C₄(SiMe₃)₂) (20) have been tabulated below.
Table 5.1: Experimental and predicted bond lengths and angles of 11, 13, and 20.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \text{Cp}^*\text{U(C}_4\text{SiMe}_3)_2 )</th>
<th>( \text{Cp}^*\text{Th(C}_4\text{SiMe}_3)_2 )</th>
<th>( \text{Cp}^*\text{Zr(C}_4\text{SiMe}_3)_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M–C}_\alpha ) Experiment</td>
<td>2.495(2), 2.510(2)</td>
<td>2.575(4), 2.560(4)</td>
<td>2.422(4), 2.426(5)</td>
</tr>
<tr>
<td>Theory</td>
<td>2.481, 2.479</td>
<td>2.588, 2.584</td>
<td>2.440, 2.447</td>
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<tr>
<td>( \text{M–C}_\beta ) Experiment</td>
<td>2.439(2), 2.439(2)</td>
<td>2.498(4), 2.499(4)</td>
<td>2.305(4), 2.307(4)</td>
</tr>
<tr>
<td>Theory</td>
<td>2.437, 2.437</td>
<td>2.520, 2.519</td>
<td>2.322, 2.324</td>
</tr>
<tr>
<td>( \text{C}<em>\alpha–\text{C}</em>\beta ) Experiment</td>
<td>1.300(3), 1.302(3)</td>
<td>1.300(5), 1.299(6)</td>
<td>1.291(6), 1.293(6)</td>
</tr>
<tr>
<td>Theory</td>
<td>1.317, 1.317</td>
<td>1.317, 1.317</td>
<td>1.305, 1.305</td>
</tr>
<tr>
<td>( \text{C}<em>\beta–\text{C}</em>\beta’ ) Experiment</td>
<td>1.316(3)</td>
<td>1.317(6)</td>
<td>1.337(6)</td>
</tr>
<tr>
<td>Theory</td>
<td>1.318</td>
<td>1.320</td>
<td>1.321</td>
</tr>
<tr>
<td>( \text{C}_\alpha– )</td>
<td>151.5(2), 152.1(2)</td>
<td>153.2(4), 152.4(4)</td>
<td>152.5(4), 152.3(4)</td>
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<tr>
<td>Theory</td>
<td>150.5, 150.7</td>
<td>152.6, 152.8</td>
<td>152.7, 152.8</td>
</tr>
</tbody>
</table>

The An–C bond lengths and angles for 11 and 13 are consistent with previously characterized U(IV) and Th(IV) species. Notably, the \( \text{C}_\alpha–\text{C}_\beta \) and \( \text{C}_\beta–\text{C}_\beta’ \) bond distances are consistent with \( \text{C}=\text{C} \) double bond lengths and with a butatriene-type cumulene structure, and are also in good agreement with predicted data.

The syntheses of 6 and 12 were carried out in analogous fashion to those of 11 and 13. When 2 or 4 was reacted with 2.1 equivalents of KC8 in the presence of 1,4-diphenylbutadiyne in a toluene solution at 50 °C for 3 h, compounds 6 and 12 can be isolated in 74% and 84% yields, respectively. Unlike compounds 11 and 13, both 6 and 12 display unusual spectroscopic behavior. In particular, compound 12 displays pseudodiamagnetic behavior when examined by NMR spectroscopy, with \( ^1\text{H} \) NMR resonances...
entirely in the normal paramagnetic region (between 0 and 10 ppm) and an easily attainable $^{13}$C{$^1$H} NMR. $^1$H–$^{13}$C HSQC (Heteronuclear Single Quantum Coherence) spectroscopy shows that the $^1$H NMR resonance corresponding to the C$_5$Me$_5$ ($\delta = -0.90$) is coupled to a $^{13}$C resonance at $\delta = -52.1$, showing that 12 is still a paramagnetic complex. This hypothesis is confirmed by UV/vis–NIR spectroscopy, with features in the NIR region consistent with previously characterized U(IV) species. In the high energy region, an unusually detailed spectrum was observed with multiple, distinct features between 32500 cm$^{-1}$ and 25000 cm$^{-1}$ that are not commonly seen for bent-metallocene uranium compounds.

Figure 5.4: Deconvoluted UV/vis spectrum of 12. Note the unusual abundance of features between 32500 cm$^{-1}$ and 25000 cm$^{-1}$. 

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Compound 6, like the –SiMe₃ derivative 13, can be isolated as a dark red solid, which again is an unusual color for Th(IV) compounds. Additionally, like compound 12 the UV/vis–NIR spectrum of 6 displays an unusually detailed high energy region.

![Figure 5.5: Deconvoluted UV/vis spectrum of 6. Note the unusually detailed high energy region between 34000 cm⁻¹ and 21000 cm⁻¹.](image)

The origin of the unusually detailed high energy regions at ambient temperature of the electronic spectra of 6 and 12 is currently underway. We hypothesize that this may be due to an extended pi-system from the phenyl groups on the cumulene ligand creating vibronic coupling of electronically excited states, however, without TD-DFT to support this conclusion this cannot be stated outright. Regardless, though ambient temperature vibronic coupling of electronically excited states is common for UO₂²⁺ anions, these spectra are rare for U(IV) metallocenes.
Single crystals of 6 and 12 suitable for X-ray diffractometry were grown from saturated pentane solutions at –30 °C for 48 h, and their molecular structures are shown below.

![Molecular structures of 6 and 12](image)

**Figure 5.6:** The molecular structures of 6 (left) and 12 (right) with thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms in both figures are omitted for clarity; for 12, only one component of the Cp* and phenyl disorders are displayed for clarity.

Compound 6 crystallized in the monoclinic space group P2(1)/c and contains similar Th–Cα and Th–Cβ bond distances to 13 (Th–Cα = 2.522(2) and 2.545(2) Å (6), 2.575(4) and 2.570(4) Å (13); Th–Cβ = 2.523(2) and 2.531(2) Å (6), 2.498(4) and 2.499(4) Å (13)), and also contains Cα–Cβ and Cβ–Cβ' bond distances of 1.318(3) Å, 1.318(3) Å, and 1.310(3) Å, which are again consistent with the proposed butatriene structure. Compound 12 crystallized in the orthorhombic space group Cmca and contained two mirror planes, resulting in a 1:1 split of the Cp* and phenyl ligands. Only the uranium atom and cumulene carbons were not split over two positions. Like compound 6, compound 12 contains comparable U–Cα and U–Cβ bond distances to 11 (U–Cα = 2.439(2) Å (12), 2.495(2) and
2.510(2) Å (11); U–Cβ = 2.462(2) Å (12), 2.439(2) and 2.439(2) Å (11) and Cα–Cβ and Cβ–Cβ' bond distances of 1.308(3) Å, and 1.314(3) Å, respectively, again consistent with a butatriene ligand.

The reactivity of compounds 6 and 11–13 with a variety of substrates was explored, as the zirconium congener 20 is known to be a highly reactive species with ligand displacements, ligand rearrangements, and the formation of bimetallic species all being facile transformations. The closely related Cp*₂Ti(η⁴-C₄Ph₂) (21), in fact, will easily form bimetallic complexes like 22 upon irradiation or gentle heating. Thus, it was surprising to us that all 4 actinacyclocumulenes were unreactive with all tested substrates. Oxidants and reductants were unreactive with 6 and 11–13, which was expected due to their lack of electrochemical behavior when studied by cyclic voltammetry. Interestingly, efforts to form bimetallic species were all met with failure. Heating the compounds at 50 °C even for up to seven days failed to result in dimerization, and extended heating above 100 °C only resulted in the complete degradation of the compounds. Photoirradiation also failed to degrade any of the compounds even after seven days. Attempts to form heterobimetallic species were also unsuccessful: reaction of 11 with Negishi’s reagent, (Ph₃P)₂Pt(η²-C₂H₄), and (C₅Bu₃H₂)₂Th(N₃)₂ failed to yield any new products even upon heating at moderate (50–65 °C) temperatures for up to two days. Ligand displacement reactions also did not appear to be viable with these compounds, as reaction of 6 and 11–13 with 5 equiv. PhC≡CPh failed to give the known actinacyclopentadienes 1 or 3, even with heating or photoirradiation. Walter and coworkers showed that 6 was amenable to some insertion reactions: iPrN=C=NPr, PhNCS, and benzophenone were all able to insert into the Th–C
bond upon extended heating at 110 °C, though PhCN was able to insert at ambient temperature. I did not attempt any similar reactions with 11–13, and there are currently no future plans to do so.

Clearly, there were major differences in reactivity between group 4 metalloocene based cumulenes and their actinide counterparts. X-ray crystallography provided no clues to the origin of the observed stability, nor did NMR or UV/vis–NIR spectroscopies (vida supra). IR spectroscopy provided an initial clue as to why these compounds were so stable: the frequencies of the cumulene ligand stretches were vastly different between the actinacyclocumulenes and 20. Although 11 and 13 had Cα–Cβ stretches at 1582 cm–1 and 1572 cm–1, compound 20 had a Cα–Cβ stretching frequency of 1608 cm–1, which is significantly stronger and points to a potential π-backbonding interaction.

5.3 Cp*2U(C2(SiMe3)2), a true U(II) synthon

When 2 is treated with 2.1 equivalents of KC8 in the presence of 4 equivalents of Me3Si–C≡C–SiMe3 in toluene first at ambient temperature for 15 h, then at 50 °C for 3 h, the uranacyclop propane 14 can be obtained as a dark brown powder in 74% yield upon workup. Compound 14 displays typical 1H NMR behavior for a paramagnetic U species (δSiMe3 =8.24, δC2Me5 =–6.32), as well as a silent 13C{1H} NMR spectrum. UV/vis–NIR spectroscopy contains low energy features related to Laporte forbidden f–f transitions, consistent with previously characterized U(IV) compounds. The high energy region is dominated by broad, intense bands centered at 29900 cm–1 and 22700 cm–1, with smaller features at 33330 cm–1 and 32500 cm–1. Due to the lack of a thorium congener to compare electronic spectrum, it is difficult to assign which transitions may involve f-electrons.
Cyclic voltammetry (CV) of 14 in a THF solution using [NPr₄][BARF] as a supporting electrolyte displayed two reversible reductive events ($E^{1/2} = -1.892$ V and $-2.128$ V vs. Fe⁰/Fe⁺), likely due to a U(IV)/U(III) couple and a reductive event at the (Me₃Si–C=C–SiMe₃)²⁻ ligand, respectively. Single crystals of 14 suitable for X-ray diffractometry were grown from a saturated pentane solution at –30 °C for 96 h and its solid state structure is shown below.

![Molecular structure of 14](image)

**Figure 5.7:** The molecular structure of 14 with thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Compound 14 crystallizes in the triclinic space group Pı and has a bent-metalloocene framework with the propene ligand in the metallocene wedge. The C₁–C₂ bond distance of 1.352(4) Å is typical for a C=C double bond and is consistent with the proposed (C₂(SiMe₃)₂)²⁻ ligand, as opposed to a η²–Me₃SiC≡CSiMe₃, neutral ligand. The U–C₁ and U–C₂ bond distances of 2.313(3) Å and 2.319(3) Å are considerably shorter than a typical
U–C alkyl bond (Cp*₂UMe₂; U–C = 2.424(7) Å and 2.414(7) Å) as well of those of compounds 11 and 12 (11: U–Cₜ = 2.462(2) Å; 12: U–Cₜ = 2.439(2) Å).

Given the drastic decrease in steric bulk around the uranium metal in 14 as compared to 5 (Cp* vs (C₅'Bu₃H₂) ligands), we wanted to test the viability of 14 as a “Cp*₂U(II)” synthon. Gratifyingly, 14 proved to be an incredibly reactive species with a large variety of substrates.

Alkynes proved to be excellent precursors to numerous uranocyclopentadienes. The reaction of 14 with 2 equivalents of diphenylacetylene, 2-butyne, or 1-phenyl-2-trimethylsilylacetylene in Et₂O at ambient temperature for 10 minutes gave the uranocycles 2, 17, and 18 in quantitative yields upon removal of Et₂O and free bis-trimethylsilylacetylene under reduced pressure at 50 °C. Given the difficulty in previous syntheses of these compounds (vida supra), the ease of using 14 was incredibly striking.

We then set our sights on other unsaturated substrates. The reaction of 14 with 1 equivalent of 1,4-bis(trimethylsilyl)butadiyne or 1,4-diphenylbutadiyne under similar conditions gave 11 and 12 in quantitative yields. We noted that despite the incredible stability of 11 under harsh and forcing conditions, 14 was incredibly reactive even given the similar substitution pattern. Compound 14 was also able to instantaneously reduce PhN=NPPh, Ph₂C=N–N=CPh₂, PhSSPh, PhN=C(Ph)(H), and 2,2’-bipyridine (bipy) to form Cp*₂U(=NPh)₂ (23),
Cp*₂U(⁻N=CPh₂)₂ (24), Cp*₂U(SPh)₂ (25), Cp*₂U(κ²⁻N,N-(NPh)₂(CPhH)₂) (26), and Cp*₂U(bipy) (27) in quantitative yields.

Scheme 5.1: Reagents and conditions (i) 2 equiv RC≡CR', toluene, RT, 15 min. (ii) 1 equiv. RC≡C–C≡CR, toluene, RT, 15 min. (iii) 1 equiv. PhN=NPh, toluene, RT, 15 min. (iv) 1 equiv. Ph₂C=N–N=CPh₂, toluene, 15 min. (v) 1 equiv. PhSSPh, toluene, RT, 15 min. (vi) 2 equiv. PhN=C(H)(Ph), toluene, 15 min. (vii) 1 equiv. 2,2'-bipyridine, toluene, 15 min.

Previous syntheses of all compounds in scheme 5.1 are more involved or hazardous than those of the reductive coupling using 14. For example, previous syntheses of the
metallacyclopentadienes involved either a) KC₈ reduction of 2 in the presence of 2 equivalents of alkyne at 50 °C b) formation of [Cp*₂U(H)]₂ or [Cp*₂U(H)(µ-H)]₂, followed by reaction with 2 equivalents of alkyne at 50 °C. Both of these synthetic routes require elevated temperatures, which can cause thermal rearrangements of the metallacyclopentadiene unit and ruin the integrity of the compounds. The uranacyclocumulenes have only been previously synthesized by KC₈ reductions, similar to the metallacyclopentadienes, and though there is no thermal rearrangement observed upon heating the compounds (see section 5.2), workup is still complicated compared to removing bis(trimethylsilyl)acetylene under reduced pressure. The uranium(VI) bis(imido) 23 shows the ability of 14 to access uranium compounds outside of the starting tetravalent state, and avoids the preparation of sterically encumbered, reducing uranium species such as Cp*₃U that can be difficult to access or the use of RCRA-regulated materials such as Na/Hg amalgam. The use of 14 as a two-electron reductant is displayed by reaction with equimolar PhSSPh to form the uranium disulfide 25, displaying again the ability of this compound to obviate the need for strong reductants or the use of uranium hydrides to access these complexes.⁶²-⁶⁵ Compound 14 is also an effective reagent for coupling imines at uranium: reaction of 14 with two equivalents of PhN=C(Ph)(H) gives 26 in quantitative yield, again with the operationally simple workup of removing volatiles. This represents the first reported synthesis of this compound. Finally, compound 14 can reduce 2,2′-bipyridine to form the formally uranium(III) adduct 27, eliminating the need for KC₈,⁶⁶ Na/Hg,⁶⁷ or uranium hydrides⁶²,⁶³ while also displaying the ability of 14 to act as a viable precursor for all known uranium oxidation states except for 2 and 5.
5.4 An unprecedented coupling to form antiaromatic cyclobutene rings

The reaction of toluene solutions of 2 or 4 with 2.1 equiv. of KC₈ in the presence of 1,2-bis(phenylethynyl)benzene at 50 °C for 18 h gives 15 or 16 in 58% and 62% yields, respectively (Equation 2).

\[
\begin{align*}
\text{An} = U (2), \text{Th} (4) & \quad + \quad \begin{array}{c}
\text{Ph} \\
\text{Cl}
\end{array} \\
\text{An} & \quad \xrightarrow{\text{Toluene, 50 °C, 18 h}} \\
\text{An} & \quad \begin{array}{c}
\text{An} \\
\text{Ph}
\end{array}
\end{align*}
\]

An = Th (15, 58%), U (16, 62%)
Compound 15 can be isolated upon filtration through Celite to remove graphite. Subsequent crystallization from n-hexane at –30 °C for 24 h affords the desired compound in 58% yield. There are six resonances for the inequivalent aryl protons and C₅Me₅ ligand in the ¹H NMR spectrum of 15 consistent with the proposed structure, with a diagnostic resonance for the metallocene fragment (δC₅Me₅ = 1.95 in THF-d₈). Notably, 15 is isolated as a bright yellow, crystalline solid, an unusual color for organometallic Th(IV) compounds.

Figure 5.8: Deconvoluted UV/vis spectra of 15 (bottom) and 16 (top).
Compound 16 can be isolated in 62% yield as a brown-red solid after filtration through Celite to remove graphite and removal of volatiles under reduced pressure. Compound 16 displays NMR spectroscopic data consistent with previously characterized paramagnetic uranium(IV) compounds; the $^1$H resonances are broadly spaced and the $^{13}$C NMR spectrum is silent. Alternatively, 16 can be synthesized in quantitative yield by the reaction of a toluene solution of metallacyclopropene 2 with equimolar 1,2-bis(phenylethynyl)benzene at ambient temperature for 15 minutes. Upon scaling up the reaction, there appeared to be no quantifiable decrease in yield. This route is particularly convenient, as workup only requires removal of the volatile byproduct Me₃Si–C≡C–SiMe₃ under reduced pressure, obviating the need for filtration.

The UV/vis spectrum of 15 displays a broad feature between 15000–34000 cm⁻¹, which is typical of Cp*₂An-based compounds. Compound 16 displays a broad feature as well as low energy, low intensity bands due to charge transfer transitions. The presence of charge transfer transitions for 16 is interesting given the apparent similarity of 16 near the metal to a uranium dialkyl species such as Cp*₂UMe₂, where no charge transfer bands are observed.⁶⁰ The observation that 16 does not behave like a simple dialkyl compound is further borne out in the NIR region of the spectrum, where the numerous, low intensity, f–f Laporte forbidden transitions typical of a U(IV) species are observed; however, these transitions are still much greater in intensity (50 cm⁻¹M⁻¹ < $\varepsilon$ < 200 cm⁻¹M⁻¹) than those observed for Cp*₂UMe₂ and other $\sigma$-donor, uranium(IV) metallocene compounds ($\varepsilon$ < 70 cm⁻¹M⁻¹).⁶⁰ Indeed, in both the UV/vis and NIR regions of 16, extremely high molar absorptivities are observed, which is suggestive of a more covalent U–(ligand) interaction.
than is typical for uranium(IV) metallocenes, further highlighting the uniqueness of the cyclobutabenzenzene ligand.

Compounds 15 and 16 crystallize in the monoclinic space group P2(1)/n from saturated n-hexane and n-pentane solutions at ~30 °C, respectively, and their molecular structures are shown in Figure 5.9.

![Molecular structures of 15 (left) and 16 (right) with thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms have been omitted for clarity.](image)

**Figure 5.9:** Molecular structures of 15 (left) and 16 (right) with thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Important bond lengths and angles of 15 and 16 are summarized in Figure X.

![Important bond angles (left) and lengths (right) of the cyclobutene units of 15 and 16.](image)

**Figure 5.10:** Important bond angles (left) and lengths (right) of the cyclobutene units of 15 and 16. The pentamethycyclopentadienyl rings are omitted for clarity.
Notably, the C$_2$–C$_3$ bond length of 15 and 16 are 1.620(3) Å and 1.620(6) Å, respectively, which are much longer than a typical C–C σ-bond but is consistent with a C–C σ-bond in strained systems (e.g., 2,2,3,3,5,6,6-octamethylheptane, C$_3$–C$_4$ = 1.63 Å; 2,3-diadamantyl-2,3-dimethylbutane, C$_3$–C$_4$ = 1.64 Å; 3,8-dichloro-1,1,2,2-tetraphenyl-1,2-dihydrocyclobuta[b]naphthalene, C$_{butane}$–C$_{butane'}$ = 1.724(5) Å; diadamantane–triadamantane, C$_{diad}$–C$_{triad}$ = 1.704(4) Å). The C$_2$–C$_3$ bond lengths of 15 and 16 are considerably shorter than that observed in Buchwald’s zirconium bis(alkyne) (C$_2$–C$_3$ = 2.319(7) Å). This bond length in 15 and 16 is emphasized to highlight the C–C coupling observed with the actinide metallocenes, which was unattainable with zirconocene systems. In contrast to biphenylene which has symmetrical C–C bridging bonds (1.514(3) Å), symmetrical aryl C–C bonds (1.426(3) Å), and perfectly 90° angles, 15 and 16 have distorted cyclobutene units. The C$_2$–C$_5$ and C$_3$–C$_6$ bond lengths of 15 and 16 (15, C$_2$–C$_5$ = 1.425(2) Å, C$_3$–C$_6$ = 1.502(3) Å; 16, C$_2$–C$_5$ = 1.491(7) Å, C$_3$–C$_6$ = 1.493(7) Å) are consistent with C–C single bonds and the C$_5$–C$_6$ bond lengths (15, C$_5$–C$_6$ = 1.400(3) Å; 16, C$_5$–C$_6$ = 1.410(7) Å) are typical for an aryl C–C bond. For compounds 15 and 16, the C$_5$–C$_2$–C$_3$ and C$_6$–C$_3$–C$_2$ bond angles (15 = 85.9(1)° and 85.7(1)°; 16 = 85.9(4)° and 86.1(4)°) and the C$_2$–C$_5$–C$_6$ and C$_3$–C$_6$–C$_5$ (15 = 94.1(2)° and 94.4(2)°; 16 = 94.2(4)° and 93.9(4)°) are consistent with the relative lengths of the C$_2$–C$_3$ > C$_5$–C$_6$ bonds. Despite the unusual cyclobutene portion of the ligand, the uranacylcopentadiene unit remains otherwise relatively undistorted when compared to previously characterized actinacylcopentadienes. All together, these data support the proposed bond connectivity of 15 and 16.
To assess the level of aromaticity and antiaromaticity displayed in the non-Cp* ligands of 15 and 16, Nucleus Independent Chemical Shift (NICS) calculations were performed by collaborators at the University of Minnesota (Dr. Jing Xie and Dr. Laura Gagliardi). NICS is a computational technique in which the ring current of a cyclic moiety is measured directly in the plane of the ring, and often times several increments of 0.5 Å above and below the plane of the ring. In this technique, negative values correspond to an aromatic ring, while positive values correspond to an antiaromatic ring. Calculations were performed at the PBE0/6-31G(d,p)&SDD level of theory, and the results of those calculations are displayed below in Figure 5.11.

Figure 5.11: a) NICS profiles computed in the axis perpendicular to the four-, five-, and six membered rings, with the shielding tensors where the NICS values were calculated displayed with blue spheres. b) NICS and B\textsuperscript{ind} for compound 16. c) NICS and B\textsuperscript{ind} for compound 15. Calculations displayed were performed at the PBE0/6-31(d,p)&SDD level of theory.

Compound 15 gives NICS(0) values of –7 ppm, 10 ppm, and –9 ppm for the 5, 4, and 6 membered rings respectively, which suggest low aromatic character for the thoracyclopentadiene, antiaromatic character for the cyclobutene, and aromatic character
for the terminal benzene ring. Compound 16 gives NICS(0) values of –35 ppm, 12 ppm, and –10 ppm for the 5, 4, and 6 membered rings respectively. While the antiaromaticity of the cyclobutene fragment and the aromaticity of the benzene fragment remain relatively unchanged, the uranacyclopentadiene, in contrast to the thoracyclopentadiene in 15, has highly aromatic character. This suggests that the remaining two valence electrons from the U(IV) ion are able to participate in the bonding of 16 and contribute to the Hückel aromaticity ([4n+2] \(\pi\)-electrons) of this ring. This points to a rare example where there is direct evidence for \(f\)-electron involvement in an actinide complex. Indeed, upon examination of the actinacyclopentadienes 3 and 2 by NICS, similar results were found: the thoracyclopentadiene 3 was found to have a NICS(0) value of 3 ppm, while the uranacyclopentadiene 2 had a NICS(0) value of –33 ppm. These results are consistent with what were found for 15 and 16, and again support the hypothesis that the uranium atom can donate its remaining 5\(f^2\) electrons into the \(\pi\)-system to satisfy Hückel’s rule.

5.5 Attempts at Fagan-Nugent coupling with actinacycles and chlorophosphines
Initial probes to the reactivity of some of the above mentioned actinacycles with chlorophosphines were attempted. First, the reaction of 1 and 3 with dichlorophenylphosphine was carried out using C₆D₆ or THF-đ₈ as solvents (Scheme 5.2).

Scheme 5.2: Reactions of 1 and 3 with PhPCl₂ in both C₆D₆ and THF-đ₈. Quantitative conversion to the phosphorus and actinide products were observed by ¹H and ³¹P NMR spectroscopy.

Interesting, a strong solvent dependence on reactivity was observed. When using nonpolar, aprotic solvent C₆D₆ no Fagan-Nugent coupling or any other reactivity was observed even upon heating at 80 °C for up to 72 h. Switching to the polar, aprotic solvent THF-đ₈ resulted in quantitative conversions to the phosphorus containing heterocycles: while the thorium complex 3 gave 1,2,3,4,5-pentaphenylphosphole in 100% conversion after 24 h as evidenced by ³¹P NMR spectroscopy,⁶⁸ the uranium complex 1 required two equivalents of PhPCl₂ to complete the reaction and provided the unexpected product
1,2,3,4,5,6-hexaphenylphosphorin in 100% conversion after 4 h at 50 °C as observed by 31P NMR spectroscopy. Clearly, the mass balance in the latter reaction is nonsensical and is currently under further investigation.

A similar trend in reactivity is observed when the reaction between 1 and 3 with two equivalents of Ph2PCl2 was performed in C6D6 or THF-d8 (Scheme 5.3).

Scheme 5.3: Reactions of 1 and 3 with two equivalents of Ph2PCl in C6D6 or THF-d8. Quantitative yields for the phosphorus containing products were observed by 31P NMR; the percent conversion to 1,2,3,4-tetraphenyl-(Z,Z)-1,3-butadiene was not calculated.

The reaction of 1 with two equivalents of Ph2PCl did not yield the expected product of 1,4-bis(diphenylphosphino)-1,2,3,4-tetraphenyl-(Z,Z)-1,3-butadiene (NUPHOS); rather, it gave the protonated ligand 1,2,3,4-tetraphenyl-(Z,Z)-1,3-butadiene and quantitative conversion to the diphosphine (Ph2P)2 in 100% conversion by 31P{1H} NMR
spectroscopy. The source of protons on the liberated organic fragment is currently unknown, but under investigation. The reaction of 3 with two equivalents of Ph₂PCl in THF-₅₀ at 50 °C for 24 h gave NUPHOS in 100% conversion as evidenced by ³¹P NMR spectroscopy. This is particularly gratifying as the equivalent reaction with (C₅H₅)₂Zr(η²-C₄Ph₄) was studied by Clegg and coworkers; the liberation of NUPHOS in that study required 1) the use of two equivalents of CuCl to transmetalate and 2) only gave the ligand in 44% yield upon workup. These results, along with those shown in Scheme 5.2, clearly demonstrate differences in reactivity between zirconium(IV), thorium(IV), and uranium(IV), which must be a direct result of the influence of 5f-orbitals and -electrons on reactivity.

The uranium compounds 11, 12, and 15 were also reacted with PhPCl₂ and Ph₂PCl₂ under conditions similar to described above, however, in all cases an intractable mixture of unidentifiable products was observed by ³¹P NMR spectroscopy. Similar results were observed when the thorium compounds 6, 13, and 16 were subjected to the same conditions. Clearly, not all actinacycles are suitable Fagan-Nugent coupling partners for chlorophosphines; at this point, it is premature to say whether this is due to the involvement of the actinide ion or inherent instability in the would-be liberated phosphine, as these compounds are not known in the literature.

5.6 Conclusions

In conclusion, a variety of actinacycles were synthesized, primarily by KC₈ reduction of Cp*₂AnCl₂ (An = Th, U) in the presence of unsaturated organics. The metallacyclocumulenes Cp*₂An(η⁴-RC₄R) (An = Th, U; R = –SiMe₃, Ph) were fully
characterized and in contrast to group 4 cumulenes, were found to be surprisingly unreactive towards ligand displacement and modification reactions with a large variety of reagents. In contrast to the unreactive metallacyclocumulenes, the novel uranacyclopropene \( \text{Cp}^* \text{U}(\eta^2-\text{Me}_3\text{SiC} \text{CSiMe}_3) \) was synthesized through the KC\(_8\) route and was shown to be highly reactive with unsaturated organics, dichalcogenides, azides, and chlorophosphines. The new actinacyclopentadienecyclobutabenzene \( \text{Cp}^* \text{An}(2,5-\text{Ph}_2\text{cyclopenta}[3,4]\text{cyclobuta}[1,2]\text{benzene} \ (\text{An} = \text{Th, U}) \) were synthesized and fully characterized by both experimental and theoretical techniques. These compounds display a unique bonding motif that is highlighted by the central cyclobutene ring, which is formally Hückel antiaromatic and represents the first example of a metal supported antiaromatic ring. Finally, preliminary reactions between actinacycles and chlorophosphines show that these tetravalent 5f-element compounds have unique reactivity from transition-metal congeners, a rare example where 5f-orbitals and -electrons are directly involved in reactivity.

5.7 Experimental

5.7.1 General Considerations

Unless otherwise noted, all reactions and manipulations were performed at ambient temperature in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (N\(_2\)) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Chemical shifts for \(^1\text{H}\) NMR spectra are reported in parts per million (ppm) were referenced to proteo solvent impurities (\(\delta = 7.16\) for \(\text{C}_6\text{D}_6\), 3.58 for THF-\(d_8\)).
5.7.2 Materials
Unless otherwise noted, reagents were purchased from commercial suppliers and were used without further purification. C$_6$D$_6$ and THF-d$_8$ (Cambridge Isotope Laboratories) were purified by storage over activated 3 Å molecular sieves for at least 48 h prior to use. Celite and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h before use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for at least 24 h, passed through a column of activated alumina, and were stored over activated 3 Å molecular sieves prior to use. Compounds 2–4, 6, 12, and 14 were prepared according to literature procedures.

Caution: Depleted uranium (primary isotope $^{238}$U) is a weak α-emitter (4.197 MeV) with a half life of $4.47 \times 10^9$ years and natural thorium (primary isotope $^{232}$Th) is a weak α-emitter (4.012 MeV) with a half life of $1.41 \times 10^{10}$ years; manipulations should be carried out in a monitored fume hood or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β- counting equipment.

5.7.3.1 Preparation of Cp*$_2$U(η$^2$-C$_4$Ph$_4$) (1), method A: A 20-mL scintillation vial equipped with a stir bar was charged with KC$_8$ (0.0453 g, 0.173 mmol), Cp*$_2$UCl$_2$ (2, 0.100 g, 0.171 mmol), diphenylacetylene (0.0615 g, 0.35 mmol), and toluene (3 mL). The reaction was heated to 50 °C for 12 h, after which it was filtered through a Celite-padded coarse-porosity fritted funnel that was extracted with toluene (2 x 3 mL) until the washings ran clear. Volatiles were removed under reduced pressure to give a gummy brown solid, which was extracted with pentane (5 mL), filtered through a Celite-padded coarse-porosity fritted funnel that was extracted with pentane (2 x 5 mL) until the washings ran clear.
Volatiles were again removed under reduced pressure to give a brown solid identified as pure \( \text{Cp}^*\text{U}(\eta^2-\text{C}_4\text{Ph}_4) \) (1) by \(^1\text{H} \) NMR spectroscopy. \(^1\text{H} \) NMR data were consistent with literature values.\(^4\)

### 5.7.3 Method B:

A PTFE-lined NMR tube was charged with a \( \text{C}_6\text{D}_6 \) (0.2 mL) solution of 14 (0.0199 g, 0.029 mmol) and a \( \text{C}_6\text{D}_6 \) (0.2 mL) solution of diphenylacetylene (0.0104 g, 0.059 mmol) at ambient temperature. After standing for 15 min., \(^1\text{H} \) NMR spectroscopy reveals quantitative conversion to 1.

### 5.7.4 Preparation of \( \text{Cp}^*\text{U}(\eta^4-\text{C}_4(\text{SiMe}_3)_2) \) (11), method A:

A 20 mL scintillation vial equipped with a stir bar was charged with \( \text{KC}_8 \) (101.0 mg, 0.747 mmol, 2.1 eq) and was heated to 50 °C. \( \text{Cp}^*\text{UCl}_2 \) (2, 206.1 mg, 0.356 mmol) and 1,4-bis(trimethylsilyl)butadiyne (69.2 mg, 0.356 mmol) were added to the \( \text{KC}_8 \) as a 5 mL toluene solution and the reaction was allowed to heat for 3 h. The reaction mixture was then filtered through Celite, extracted with 3 mL of toluene, and volatiles were removed under reduced pressure to give a brown residue. This residue was extracted with 10 mL of hexane, which was then filtered and volatiles were removed under reduced pressure to give a yellow-brown solid identified as 11 (217.9 mg, 0.310 mmol, 87%). Single crystals suitable for X-ray diffractometry were grown from a saturated hexane solution at –30 °C over 24 h. \(^1\text{H} \) NMR (296 K, \( \text{C}_6\text{D}_6 \), 400 MHz): \( \delta \) 2.22 (s, 18H, –SiMe3), –2.50 (s, 30H, C\(_5\)Me\(_5\)). ATR-IR (Neat, 296 K, cm\(^{-1}\)): 2955, 2929, 2895, 1582, 1434, 1376, 1243, 1107, 1085, 1067, 1020, 833, 751. UV/Vis (Toluene, 296 K, 0.25 mM, cm\(^{-1}\) (M\(^{-1}\)cm\(^{-1}\)): 33000 (1680), 22000 (300). NIR (Toluene, 296 K, 15 mM, cm\(^{-1}\) (M\(^{-1}\)cm\(^{-1}\)): 14500 (17), 13500 (13), 12000 (3), 11000 (4), 9500 (15), 8000 (10),

5.7.4.2 Method B: A PTFE-lined NMR tube was charged with a C_{6}D_{6} (0.2 mL) solution of 14 (0.0223 g, 0.033 mmol) and a C_{6}D_{6} (0.2 mL) solution of 1,4-bis(trimethylsilyl)butadiyne (0.0065 g, 0.033 mmol) at ambient temperature. After standing for 15 min., ^1H NMR spectroscopy reveals quantitative conversion to 1.

5.7.5 Preparation of Cp^{*}2Th(η^{4}-C_{4}(SiMe_{3})_{2}) (13): A 20 mL scintillation vial equipped with a stir bar was charged with KC_8 (129.0 mg, 0.954 mmol, 2.1 eq) and was heated to 50 °C. Cp^{*}2ThCl_{2} (4, 260.5 mg, 0.454 mmol) and 1,4-bis(trimethylsilyl)butadiyne (88.3 mg, 0.454 mmol) were added to the KC_8 as a 5 mL toluene solution and the reaction was allowed to heat for 3 h. The reaction mixture was then filtered through Celite, extracted with 5 mL of toluene, and volatiles were removed under reduced pressure to give a brown-red residue. This residue was extracted with 10 mL of hexane, which was then filtered and volatiles were removed under reduced pressure to give an oily brown-red solid, which was dissolved in minimal pentane and was cooled to −30 °C overnight to give a red crystalline solid suitable for X-ray diffractometry identified as 2 (227.9 mg, 0.327 mmol, 72%). ^1H NMR (296 K, C_{6}D_{6}, 400 MHz): δ 1.79 (s, 30H, C_5Me_5), 0.56 (s, 18H, −SiMe_3). ^13C{^1H} NMR (296 K, C_{6}D_{6}, 125 MHz): δ 153.9 (s, Me_3SiC_4SiMe_3), 122.1 (s, C_5Me_5), 11.4 (s, C_5Me_5), 2.4 (s, −SiMe_3). One cumulene resonance is assumed to be under the C_{6}D_{6} peak. ATR-IR: (Neat, 296 K, cm⁻¹): 2969, 2955, 2934, 2893, 1571, 1431, 1377, 1242, 1087, 1021, 834, 752. UV/Vis (Toluene, 296 K, 0.5 mM, cm⁻¹ (M⁻¹cm⁻¹): 33500 (1520). mp:
213–216 °C. Anal. Calcd. for C\textsubscript{30}H\textsubscript{48}Si\textsubscript{2}Th (mol. wt. 696.91): C, 51.70; H, 6.94. Found: C, 51.41, H, 6.82.

5.7.6 Preparation of Cp\textsuperscript{2}U(2,5-Ph\textsubscript{2}-cyclopenta[3,4]cyclobuta[1,2]benzene) (15): A 20 mL scintillation vial was charged with KC\textsubscript{8} (0.1441 g, 1.07 mmol, 2.1 equiv.) and a stir bar, followed by addition of Cp\textsuperscript{2}UCl\textsubscript{2} (2, 0.2940 g, 0.507 mmol) and 1,2-bis(phenylethynyl)benzene (0.1412 g, 0.507 mmol) as a 5 mL toluene solution. The reaction was heated to 50 °C (18 h) then was filtered through a Celite-padded coarse-porosity fritted funnel which was extracted with toluene (5 mL) until the washings ran clear. Volatiles were removed from the filtrate under reduced pressure at 50 °C and the brown-red residue was extracted with pentane (2 x 10 mL), filtered through a coarse-porosity fritted funnel, and volatiles were again removed under reduced pressure to give a brown-red solid identified as pure Cp\textsuperscript{2}U(2,5-Ph\textsubscript{2}-cyclopenta[3,4]cyclobuta[1,2]benzene) (15) (0.2475 g, 0.314 mmol, 62%). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 296 K, 400 MHz): δ 5.09 (s, 2H, Ar), 4.36 (s, 2H, Ar), 3.97 (s, 30H, C\textsubscript{5}Me\textsubscript{5}), 1.37 (m, 4H, Ar), 0.73 (s, 2H, Ar), –16.04 (s, 4H, Ar). ATR-IR (Neat, 296 K, cm\textsuperscript{-1}): 3505, 2903, 2853, 2724, 2636, 1589, 1483, 1434, 1376, 1159, 1106, 1067, 1027, 952, 910, 742, 699. UV/vis (Toluene, 296 K, 0.25 mM, cm\textsuperscript{-1}(cm\textsuperscript{-1}M\textsuperscript{-1})): 35700 (25250), 34700 (27200), 33000 (31000). NIR (Toluene, 296 K, 5 mM, cm\textsuperscript{-1}(cm\textsuperscript{-1}M\textsuperscript{-1})): 13000 (125), 11800 (50), 10500 (60), 10200 (45), 9200 (200), 8750 (100), 7900 (80), 6700 (35), 6000 (150). mp: 273 °C (decomposition). Anal. Calcd. for C\textsubscript{42}H\textsubscript{44}U (mol. wt. 786.84): C, 64.11; H, 5.64. Found: C, 64.02; H, 5.68.

5.7.7 Preparation of Cp\textsuperscript{2}Th(2,5-Ph\textsubscript{2}-cyclopenta[3,4]cyclobuta[1,2]benzene) (16): A 20 mL scintillation vial was charged with KC\textsubscript{8} (0.0938 g, 0.694 mmol, 2.1 equiv.) and a
stir bar, followed by addition of Cp*₂ThCl₂ (4) (0.1895 g, 0.330 mmol) and 1,2-
bi(phenylethynyl)benzene (0.0920 g, 0.330 mmol) as a 5 mL toluene solution. The
reaction was heated to 50 °C (18 h) then was filtered through a Celite-padded coarse-
porosity fritted funnel which was extracted with toluene (5 mL) until the washings ran
clear. Volatiles were removed from the filtrate under reduced pressure at 50 °C to give a
dark brown oil, which was layered with 10 mL of n-hexane and cooled to –30 °C for 24 h,
giving a bright yellow solid identified as Cp*₂Th(2,5-Ph₂-
cyclopenta[3,4]cyclobuta[1,2]benzene) (16) (0.1496 g, 0.192 mmol, 58%). ¹H NMR (THF-
d₈, 296 K, 400 MHz): δ 7.79 (d, J = 7.7 Hz, 4H, o-Ar), 7.40 (t, J = 7.2 Hz, 4H, m-Ar), 7.44
(t, J = 7.6 Hz, 2H, m-Ar), 7.55 (m, 2H, Ar), 7.04 (m, 2H, Ar), 1.97 (s, 30H, C₅Me₅). ¹³C{¹H}NMR (THF-d₈, 296 K, 125 MHz): δ 205.8 (s, Ar), 152.5 (s, Ar), 145.3 (s, Ar), 131.8 (s, Ar), 128.8 (s, Ar), 128.5 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 125.9 (s, Ar), 124.2 (s, Ar), 121.6 (s, C₅Me₅), 11.6 (s, C₅Me₅). ATR-IR (Neat, 296 K, cm⁻¹): 2966, 2879, 2631, 1588,
1437, 1377, 1084, 913, 745, 700. UV/vis (Toluene, 296 K, 0.5 mM, cm⁻¹·cm⁻¹·M⁻¹): 33550
64.60; H, 5.68. Found: C, 64.22; H, 5.77.

5.7.8 Preparation of Cp*₂U(η²-C₄Ph₂(SiMe₃)₂) (18): A 20 mL scintillation vial was
charged with 14 (0.0199 g, 0.0293 mmol) and a stir bar, followed by addition of 1-phenyl-
2-trimethylsilylacetylene (0.0104 g, 0.0586 mmol) and Et₂O (1 mL), which resulted in an
immediate color change from brown to bright red. The reaction was allowed to stir at
ambient temperature for 30 minutes, after which volatiles were removed under reduced
pressure first at ambient temperature for 10 minutes, then at 50 °C for 20 minutes to ensure
removal of all bis(trimethylsilyl)acetylene. This gave Cp*₂U(η²-C₄Me₂(SiMe₃)₂) as a red powder (0.0251 g, 0.0293 mmol, 100%). UV/Vis–NIR (Toluene, 296 K, cm⁻¹ (M⁻¹cm⁻¹)): 32680 (8265), 25575 (4015), 22175 (1980), 18350 (800), 14500 (75), 14085 (80), 13800 (90), 12400 (40), 10600 (30), 9500 (40), 9000 (55), 8650 (60), 8250 (70), 7850 (40), 7220 (40), 6220 (30), 5950 (35). ¹H NMR (C₆D₆, 296 K, 400 MHz): δ 7.37 (d, J = 8.6 Hz, 4H, o-Ar-H), 6.85 (t, J = 7.2 Hz, 4H, m-Ar-H), 5.88 (t, J = 7.2 Hz, 2H, p-Ar-H), 4.16 (bs, ν₁/₂ = 17 Hz, 18 H, -SiMe₃), 3.81 (s, 30H, C₅Me₅). mp: 213–214 °C. Anal. Calcd. for C₄₂H₅₈Si₂U (mol. wt. 857.11): C, 58.85; H, 6.82. Found: C, 58.74; H, 6.88.

5.7.9 Preparation of Cp*₂U(=NPh)₂ (23): A 20 mL scintillation vial was charged with 2 (0.0175 g, 0.0258 mmol) and a stir bar, followed by addition of PhN=NPh (0.0047 g, 0.0258 mmol) and Et₂O (1 mL). The reaction was allowed to stir at ambient temperature for 30 minutes, after which volatiles were removed under reduced pressure first at ambient temperature for 10 minutes, then at 50 °C for 20 minutes to ensure removal of all bis(trimethylsilyl)acetylene. This gave Cp*₂U(=NPh)₂ as a dark brown solid (0.0178 g, 0.0258 mmol, 100%). ¹H NMR data are consistent with literature values. ¹H NMR (C₆D₆, 296 K, 400 MHz): δ 9.31 (s, 4H, Ar-H), 4.11 (s, 30H, C₅Me₅), 2.94 (s, 4H, Ar-H), 0.80 (s, 4H, Ar-H).

5.7.10 Preparation of Cp*₂U(–N=CPh₂)₂ (24): A 20 mL scintillation vial was charged with 2 (0.0145 g, 0.0214 mmol) and a stir bar, followed by addition of Ph₂C=N–N=CPh₂ (0.0077 g, 0.0214 mmol) and Et₂O (1 mL). The reaction was allowed to stir at ambient temperature for 10 minutes, after which volatiles were removed under reduced pressure first at ambient temperature for 10 minutes, then at 50 °C for 20 minutes to ensure removal
of all bis(trimethylsilyl)acetylene. This gave \( \text{Cp}^* \text{U}(\text{N}=\text{CPh}_2)_2 \) (8) as a brown solid (0.0186 g, 0.0214 mmol, 100%). \(^1\)H NMR data are consistent with literature values. \(^1\)H NMR (C\(_6\)D\(_6\), 296 K, 400 MHz): \( \delta \) -1.92 (s, 30H, \( C_5 \)Me\(_5\)).

5.7.11 Preparation of \( \text{Cp}^* \text{U}(\kappa^2-\text{N},\text{N}-(\text{NPh})_2(\text{CPhH})_2) \) (26): A 20 mL scintillation vial was charged with 2 (0.0270 g, 0.0398 mmol) and a stir bar, followed by PhN=\( \text{C} \)(Ph)(H) (0.0146 g, 0.0806 mmol) and Et\(_2\)O (1 mL). The reaction was allowed to stir at ambient temperature for 10 minutes, after which volatiles were removed under reduced pressure first at ambient temperature for 10 minutes, then at 50 °C for 20 minutes to ensure removal of all bis(trimethylsilyl)acetylene. This gave \( \text{Cp}^* \text{U}(\kappa^2-\text{N},\text{N}-(\text{NPh})_2(\text{CPhH})_2) \) (11) as a dark-red solid (0.0347 g, 0.0398 mmol, 100%). \(^1\)H NMR data are consistent with literature values. \(^1\)H NMR (C\(_6\)D\(_6\), 296 K, 400 MHz): \( \delta \) 10.77 (s, 30H, \( C_5 \)Me\(_5\)), 8.32 (d, 2H, \( J = 8.3 \) Hz, Ar), 8.11 (s, 1H, Ar), 7.81 (t, 2H, \( J = 8.0 \) Hz, Ar), 6.35 (t, 2H, \( J = 7.8 \) Hz, Ar), -0.80 (s, 1H, Ar), -9.92 (t, 2H, \( J = 8.0 \) Hz, Ar), -33.62 (s, 2H, Ar).

5.7.12 Preparation of \( \text{Cp}^* \text{U}(\text{bipy}) \) (27): A 20 mL scintillation vial was charged with 2 (0.0260 g, 0.0383 mmol) and a stir bar, followed by addition of 2,2'-bipyridine (0.0060 g, 0.0383 mmol) and Et\(_2\)O (1 mL). The reaction was allowed to stir at ambient temperature for 10 minutes, after which volatiles were removed under reduced pressure first at ambient temperature for 10 minutes, then at 50 °C for 20 minutes to ensure removal of all bis(trimethylsilyl)acetylene. This gave \( \text{Cp}^* \text{U}(\text{bipy}) \) (9) as a brown solid (0.0255 g, 0.0383 mmol, 100%). \(^1\)H NMR data are consistent with literature values. \(^1\)H NMR (C\(_6\)D\(_6\), 296 K, 400 MHz): \( \delta \) 0.15 (s, 30H, \( C_5 \)Me\(_5\)), -19.98 (d, 2H, \( J = 10.5 \) Hz, bipy), -41.35 (t, 2H, \( J = 8.4 \) Hz, bipy), -81.27 (t, 2H, \( J = 6.7 \) Hz, bipy), -94.00 (s, 2H, bipy).
5.8 References


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Chapter 6: The synthesis, reactivity, and tuneability of actinide hydrides from phenylsilane

6.1 Introduction

Transition-metal hydrides are some of the most widely studied organometallic species in the literature.\textsuperscript{1-9} From the study of hydrides as ligands for organometallic species to the catalytic and industrial relevance of these species in large-scale processes, the metal–hydride bond remains one of the most important in chemistry even today. Although there have been thousands of examples of studied transition-metal hydrides, there has been much more limited attention focused on the study of f-element hydrides, in particular the study of actinide hydrides.\textsuperscript{10-18} The first isolable and studied actinide hydrides \([\text{Cp}^*\text{An(H)}(\mu-\text{H})]_2\) (An = Th (1), U (2)) were synthesized by Marks and coworkers in 1981 by hydrogenolysis of the dialkyl precursors \(\text{Cp}^*\text{AnMe}_2\) (An = Th (3), U (4)).\textsuperscript{19} These compounds were originally used as precursors to new organometallic species such as \(\text{Cp}^*\text{An(O=CM}e_2\text{)}_2\) (An = Th (5), U (6)) as well as competent hydrogenation catalysts.\textsuperscript{19-21} Since this pioneering report, 1, 2, and the related uranium (III) \([\text{Cp}^*\text{U(H)}]_x\) (7) have been used as multielectron reductants to synthesize a large variety of organoactinide species, mainly by Evans and coworkers.\textsuperscript{17,22-26} Indeed, these species proved to be versatile reductants, which were able to reduce organodichalcogenides, azobenzene, and cyclooctatetraene.
Figure 6.1: Isolable actinide hydrides 1, 2, and 7 discussed in this chapter. Note the a) An(IV) oxidation state of 1 and 2 and b) the unambiguous nuclearity of 7.

Intriguingly, while in Marks original reports he described the U(III) hydride as “\((2/x)[\text{Cp}^*\text{U(H)}]_x\)”, Evans had altered the formulation of this species to simply \([\text{Cp}^*\text{U(H)}]_2\), presumably on the strength of a solid-state X-ray structure of a dimer. This discrepancy between the classical and more modern reports raised interesting questions: notably, what is the *solution* identity of this important compound, and how does the solution behavior of this compound affect reactivity? To answer these questions, we had to find a new way to access 1, 2, and 7 as the only previous syntheses of these compounds involves the hydrogenolysis of compounds 3 and 4; due to the inherent hazards of hydrogen gas and the potential for a fire in a radiological laboratory, use of hydrogen was limited to extremely specific cases.

Phenylsilane appeared to be a good candidate for a hydride source for the syntheses of these compounds for a variety of reasons: it is a relatively innocuous, easy to handle liquid, it is commercially available and relatively inexpensive, and it is easily removed under reduced pressure. The safety aspect of phenylsilane is especially important when considering translating synthetic methodology from the early actinides to transuranics, where the use of pyrophoric reagents is extremely regulated if not banned outright.
Additionally, the use of phenylsilane to generate transition-metal hydrides \textit{in situ} which go on to react with other species has been known for decades. We noted a report by Harrod and coworkers where it was noted that 3 and 4 displayed little if any ability to dehydrocouple PhSiH₃, and instead generated what were described as “unknown species”\textsuperscript{28}. Intrigued by this report, and by preliminary experiments ran by Dr. Nicholas Travia (LANL) where the reaction of Cp*₂ThPh₂ (8) with 2 equivalents of PhSiH₃ seemed to generate 1 in low yields, we investigated the possibility of using PhSiH₃ as an efficient hydride source.

In this chapter, efforts in utilizing PhSiH₃ as an efficient and easy to use hydride source for compounds 1, 2, and 7 are described. The reactivity of these compounds with the classically reduced organodichalcogenides and azobenzene was attempted, as well as the reductions of a number of new substrates such as alkynes, bipy and terpy, elemental sulfur, and benzophenone azine. The ability to tune the oxidation state and nuclearity of the uranium hydrides 2 and 7 is demonstrated by simply changing the equivalents of PhSiH₃ added to the reaction mixture. Additionally, although compound 7 has been described in the literature as a dimer in the solid state, it is shown that the solution behavior of this compound displays behavior consistent with a monomer-dimer equilibrium. Finally, although 2 is a reasonable precursor for many organoactinide compounds, it is shown that 7 displays much richer and complex reactivity.

6.2 Phenylsilane as an alternative to hydrogen for the synthesis of [Cp*₂An(H)(µ-H)]₂

My study of actinide hydrides began by reaction of Cp*₂AnMe₂ (An = Th (3), U (4)) with 5 equiv. of PhSiH₃ at 50 °C in toluene. After addition of PhSiH₃ to solutions of 3
and 4, there was a rapid color change from pale yellow to dark red (3) or from dark orange-red to dark brown (4) along with slow gas evolution (Equation 1).

Upon removal of solvent at ambient temperature, $^1$H NMR (C$_6$D$_6$) showed diagnostic resonances for the hydrides of 1 ($\delta_{\text{Th-H}} = 19.43$ ppm) or 2 ($\delta_{\text{U-H}} = -343$ ppm), along with complete consumption of compounds 3 ($\delta_{\text{Th-Me}} = -0.19$ ppm, $\delta_{\text{C}_5\text{Me}_5} = 1.92$ ppm) or 4 ($\delta_{\text{U-Me}} = -124$ ppm, $\delta_{\text{C}_5\text{Me}_5} = 5.03$ ppm).$^{19}$ Additionally, the diagnostic $^1$H NMR resonance for PhSiH$_3$ ($\delta_{\text{Si-H}} = 4.23$ ppm) was completely consumed and the presence of PhMeSiH$_2$ ($\delta_{\text{Si-H}} = 4.46$, q) was easily confirmed.$^{29}$ In the case of 2, some of the trivalent uranium hydride 7 was observed ($\delta_{\text{C}_5\text{Me}_5} = -9.73$ ppm), although this is to be expected due to the observed equilibrium between 2 and 7 in the presence of H$_2$ (or an H$_2$ equivalent such as PhSiH$_3$). Thus, the ability to cleanly synthesize 1 and 2 by this methodology was
clear, and the chemical integrity of these compounds in solution was tested by reaction with a variety of substrates.

Scheme 6.1: Reactions of *in situ* generated 1 and 2 from 3 and 4 to generate actinide species. Reagents and conditions: (i) 1 equiv. REER, 5 equiv. PhSiH3, toluene, 50 °C, 0.25–5 h, 9 (100%), 10 (69%), 11 (81%), 12 (95%), 13 (77%). (ii) 2 equiv. PhC≡CPh, 5 equiv. PhSiH3, toluene, 50 °C, 3 h, 14 (68%), 15 (61%). (iii) 5/8 equiv. S8, 5 equiv. PhSiH3, toluene, 50 °C, 0.25 h, 80%. (iv) 1 equiv. 2,2ʹ-bipyridine, 5 equiv. PhSiH3, toluene, 50 °C, 15 h, 69%. 

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It appeared that compounds 1 and 2 displayed similar, if not improved, reactivity when compared to their isolated counterparts. The preparation of a number of Cp*₂An(ER₂) (An = Th, E = S, R = Ph (9); An = U, E = S, R = Ph (10); E = Se, R = Ph (11); E = Te, R = Ph (12); E = S, R = Me (13)) was easily achievable, with yields ranging between 69% and 100%. These reactions clearly show the ability of in situ generated hydrides 1 and 2 to behave as their isolated counterparts. With these results in mind, we chose to expand the library of compounds that could be prepared by this methodology. The first targets in mind were the actinide metallacyclopentadienes Cp*₂An(η⁴-C₄Ph₄) (An = Th (14), U (15)), as these molecules had only previously been synthesized by inconvenient methods such as the reaction of PhC≡CPh with sterically crowded reductants Cp*₃U, [Cp*₂U][(µ-Ph)₂BPh₂], or [Cp*₂U]₂(µ-η⁶:η⁶-C₆H₆), or reactions which required the use of pyrophoric reagents such as the reduction of Cp*₂AnCl₂ (16) with Na/Hg or KC₈ in the presence of PhC≡CPh. By simply generating the hydrides 1 and 2 in solution and adding two equivalents of diphenylacetylene, 14 and 15 are accessible in 68% and 61% yields, respectively. Although the yield of 14 is lower than that reported by reduction of 16 with excess KC₈ in the presence of two equivalents of diphenylacetylene (68% versus 75%), the yield of 15 is significantly improved over the literature values and only requires a one step synthesis to obtain the necessary starting materials. Overall, this methodology provides facile access to actinide metallacyclopentadienes in comparable, if not improved yields, over previously described methods that employ pyrophoric or difficult to obtain precursors.
Finally, the preparations of Cp*₂ThS₅ (17) and Cp*₂U(bipy) (18) were achieved by similar methodology: the dialkyl precursors 3 or 4 were treated with 5 equiv. of PhSiH₃ in toluene at 50 °C for 30 minutes, followed by addition of 5/8 equiv. of S₈ (for 17) or 1 equiv. of bipy (for 18). These compounds can be isolated in 80% and 69% yields, respectively, upon the simple workup of removal of volatiles at 50 °C for 30 minutes. Again, this methodology represents a marked improvement in ease of synthesis from previously described preparations. For example, 17 was originally prepared from salt metathesis between Cp*₂ThCl₂ (19) and Li₂S₅ by Ryan and coworkers in 1986 in 75% yield,³² which required both the preparation of Li₂S₅ and a lengthy workup involving multiple filtrations/extractions, while 18 has been previously prepared by reduction of Cp*₂UI(bipy) with Na/Hg or KC₈,³³,³⁴ again showing the advantage of this methodology to obviate the need for pyrophoric reagents.

Despite the power of this methodology, the generation of 1 and 2 in situ presents problems for the syntheses of certain organometallic complexes. For example, despite the report by Evans that 7 can reduce azobenzene to form the U(VI) bis-imido Cp*₂U(=NPh)₂ (20),²² our methodology was not suitable for this reduction. This may be because of two reasons: the increased reducing power of a U(III) species when compared to a U(IV), or the presence of reactive PhSiH₃ that may react with U–N bonds that are formed in these species. The latter hypothesis was supported by two important results: it has been reported by Burns and coworkers that An–N bonds are highly reactive with silanes,³⁵ which is
consistent with the observed degradation of 20 by $^1$H NMR, and the failure to be able to synthesize related An–N bonded species by this methodology.

![Figure 6.2: Phenylsilane mediated degradation of bis-imido 20 under these conditions.](image)

Indeed, when *in situ* generated 1 and 2 were reacted with benzophenone azine (Ph$_2$C=N–N=CPh$_2$), the expected Cp$_2$An(–N=CPh$_2$)$_2$ (An = Th (21), U (22))$^{36}$ were not observed by $^1$H NMR, but instead similar degradation as observed in the reduction of azobenzene was shown. At this point, the reasonable hypothesis that only two equivalents of PhSiH$_3$ were required to react with the actinide bis-alkyl precursors 3 and 4 to form the An(IV) hydrides 1 and 2. However, this was not the case: the Th(IV) hydride was not formed in quantitative yield even upon extended heating under these conditions, however, in the case of uranium $^1$H NMR showed formation of the U(III) hydride 7 as opposed to the U(IV) hydride 2.

### 6.3 Selective formation of the U(III) hydride [Cp$_2$U(H)]$_x$ by addition of phenylsilane

When Cp$_2$U$\text{Me}_2$ (4) was treated with 2 equiv. of phenylsilane in toluene at 50 °C for 15 minutes, a color change from orange-red to dark brown was observed along with the slow bubbling of gas. Although visually this reaction appeared to proceed similarly to the previous methodology which employed 5 equiv. of PhSiH$_3$, $^1$H NMR of the brown residue
revealed a new set of Cp*2U containing products: instead of a predominant peak at $\delta = -2.59$ (the C5Me5 resonance of 2), the major product was observed at $\delta = 3.03$ at ambient temperature as well a minor resonance at $\delta = -9.37$. These results led us to believe that we were able to selectively form a set of U(III) hydrides by simply altering the equivalents of PhSiH3 added to the reaction mixture.

Indeed, these reactions conditions provided facile access to the more reactive 7 as opposed to 2, which was borne out in the reaction chemistry. First, reaction of in situ generated 7 with dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) gave Cp*2U(dmpe)(H) (23) in 94% yield after only 15 minutes at ambient temperature. Additionally, reaction of 7 with terpy (terpy = 2,2ʹ:6ʹ,2ʺ'-terpyridine) at 50 °C for 24 h gave Cp*2U(terpy) (24) in 94% yield. These two reactions help to further establish the oxidation state of 7 in solution, as both are formally U(III) species, and also allows for the synthesises of 23 and 24 in improved yields over previous literature values. The reaction of 7 with PhN=NPh and Ph2C=N–N=CPh2 gratifyingly gave Cp*2U(=NPh)2 (20) and Cp*2U(–N=CPh2)2 (22) in 95% and 83% yields, respectively. This is a marked improvement over the previous methodology, as again, excess PhSiH3 in the reaction mixture did not allow for the
The synthesis of U–N bonded species and shows promise for the synthesis of other uranium species that may be reactive with PhSiH₃.

Scheme 6.2: Reactions of in situ generated 7 from 4. Reagents and conditions: (i) 1 equiv. PhN=NPh, 2 equiv. PhSiH₃, toluene, 50 °C, 1 h, 95%. (ii) 1 equiv. Ph₂C=N–N=CPh₂, 2 equiv. PhSiH₃, toluene, 50 °C, 24 h, 83%. (iii) 1 equiv. dmpe, 2 equiv. PhSiH₃, toluene, 50 °C, 0.25 h, 94%. (iv) 1 equiv. terpy, 2 equiv. PhSiH₃, toluene, 50 °C, 24 h, 94%. (v) 2 equiv. RC≡CRʹ, 2 equiv. PhSiH₃, toluene, 50 °C, 0.25–0.5 h, 100% (15), 100% (25), 84%.

The synthesis of a number of metallacyclopentadienes was also attempted using this methodology to great success. The reaction of 7 with 2 equivalents of 2-butyne,
diphenylacetylene, or 1-phenyl-2-trimethylsilylacetylene gave the uranacyclopentadienes 
Cp*₂U(C₄R₂R’₂) (R = R’ = Ph (15); R = R’ = Me (25); R = Ph, R’ = –SiMe₃ (26)) in 100%, 
100%, and 84% yields respectively. Although 15 had been previously synthesized by 
Marks in 1981, 25 and 26 were new compounds. Both compounds display ¹H NMR data 
consistent with a paramagnetic species (δC₅Me₅ = 1.52, δU–Me = –3.62 and –4.56 (25), δC₅Me₅ 
= 4.16. δSiMe₃ = 3.81 (26)), as well as silent ¹³C{¹H} spectra. The oxidation state of both 
25 and 26 can be confirmed by UV/vis–NIR spectroscopy, which have weak Laporte-
forbidden f–f transitions (ε < 150 M⁻¹cm⁻¹) in the low-energy region (15000 > ν > 5000 
cm⁻¹) consistent with previously characterized U(IV) species. Single crystals suitable for 
X-ray diffractometry of 25 and 26 were grown from saturated pentane solutions at –30 °C 
and their solid state structures are presented below.
Figure 6.3: Molecular structure of 25 with thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms have been omitted for clarity.
**Figure 6.4:** Molecular structure of 26 with thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms have been omitted for clarity.

![Molecular structure of 26](image1)

**Figure 6.5:** Select bond lengths of 15, 25, and 26. Black: 15, blue: 25, green: 26.

Both 25 and 26 crystallize in the monoclinic space group C2/c and display similar metrical parameters to the previously characterized 15, consistent with the proposed uranacyclopentadiene structure. These parameters are also consistent with typical U(IV) bent-metalloocene complexes.

The reaction of *in situ* generated 7 with 2 equiv. of PhN=C(H)(Ph) at 50 °C for 24 h was also carried out, which formed Cp*₂U(κ²-N,N-(NPh)₂(CPhH)₂) (27) in 74% yield upon trituration with pentane. ¹H NMR shows behavior typical of a paramagnetic species, and the UV/vis–NIR spectrum of 27 is consistent with previously characterized U(IV) species. Although spectral data and elemental analyses help to confirm the elemental makeup of 27, unfortunately crystals suitable for X-ray diffractometry were not obtained.
Although the synthetic potential of this methodology was clear to us given the suite of reactivity observed, the actual identity of 7 in solution was still uncertain. The inconsistencies between Marks’s and Evans’s descriptions of 7 (vide supra) led to further study to the solution behavior of this compound. I sought out to establish two important details about 7: the oxidation state of uranium and the nuclearity of the compound. The oxidation state of 7 was clearly established by UV/vis–NIR spectroscopy, with features in the low energy region similar to previously characterized U(III) species as well as features remarkably consistent with the U(III) hydride 23. Spectra of 7 were collected on two samples: one with isolated 7 and one with a crude reaction mixture of 7 generated using our PhSiH3 methodology. Gratifyingly, both spectra appeared nearly identical, showing that even with PhMeSiH2 in solution we maintained some of 7; however, this alone was not enough to establish that there was not a large amount of 2 as the low-energy features of U(III) compounds ($\varepsilon < 500 \text{ cm}^{-1}\text{M}^{-1}$)$^{37,38}$ are much more intense than those of U(IV) compounds ($\varepsilon < 150 \text{ cm}^{-1}\text{M}^{-1}$). As a second experiment, a crude reaction mixture of 7 was studied by VT-NMR. Notably, at 20 °C there appeared to be 3 Cp*-containing products: $\delta = 3.03$ (s, $\nu_{1/2} = 6$ Hz), $-2.59$ (s, $\nu_{1/2} = 20$ Hz), and $-9.37$ (s, $\nu_{1/2} = 8$ Hz) in a 10:1:1 ratio. The peak at $\delta = -2.59$ corresponds to the tetravalent hydride 2, which is expected due to the known equilibrium between 2 and 7 at this temperature, while the peak at $\delta = -9.37$
was previously hypothesized to be the U(III) hydride 7. At 50 °C, the resonances at δ = –2.59 and –9.37 had predominantly shifted to the resonance at δ = 3.03.

Figure 6.6: Variable temperature ¹H NMR of a mixture of 2, 7a, and 7b. Note the nearly complete loss of 2 and 7b at 50 °C.

With these results in mind, we proposed that there exists an equilibrium between two trivalent uranium hydride species, presumably the monomer and dimer, however, the existence of a dimer–trimer equilibrium cannot be definitively ruled out. We believe this is unlikely because the known [Cp₂U(µ-Cl)]₃ is an extremely insoluble compound,³⁹ thus a related hydride would most likely be insoluble; yet, no precipitate is observed in reaction mixtures. Diffusion ordered spectroscopy (DOSY) would help to ascertain the relative
molecular weights of the species observed by $^1$H NMR, however, a lack of reliable solid state data of 7 and low intensity resonances made this experiment unreliable.

In conclusion, the bent-metalloccene based actinide hydrides $[\text{Cp}^*\text{An(H)}(\mu-\text{H})]_2$ (An = Th, U) can be synthesized in quantitative yield by reaction of $\text{Cp}^*\text{AnMe}_2$ with 5 equiv. of PhSiH$_3$ at 50 °C in toluene. These hydrides prove to be versatile multielectron reductants for the synthesis of a variety of actinide complexes. The oxidation state of the uranium hydrides can be tuned by simply altering the equivalents of PhSiH$_3$ added to the bis-alkyl from 5 to 2, yielding the tetravalent and trivalent hydrides respectively. The trivalent hydride $[\text{Cp}^*\text{U(H)}]^x$ proved to be a more versatile precursor for a number of actinide complexes. Finally, the solution state identity of $[\text{Cp}^*\text{U(H)}]^x$ was examined, which shows an apparent equilibrium between a monomeric and dimeric species in solution. The use of PhSiH$_3$ as a hydrogen equivalent for lanthanide and transuranic compounds is currently underway, as well as searching for other nonhazardous, easy to handle reagents to use as hydrogen equivalents.

6.4 Experimental Considerations

6.4.1 General Considerations

Unless otherwise noted, all reactions and manipulations were performed at ambient temperature in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (N$_2$) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Chemical shifts for $^1$H NMR spectra are reported in parts per million (ppm) were referenced to proteo solvent impurities ($\delta = 7.16$ for C$_6$D$_6$, 3.58 for THF-$d_8$).
6.4.2 Materials

Unless otherwise noted, reagents were purchased from commercial suppliers and were used without further purification. C₆D₆ and THF-d₈ (Cambridge Isotope Laboratories) were purified by storage over activated 3 Å molecular sieves for at least 48 h prior to use. Celite and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h before use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for at least 24 h, passed through a column of activated alumina, and were stored over activated 3 Å molecular sieves prior to use.

Caution: Depleted uranium (primary isotope ²³⁸U) is a weak α-emitter (4.197 MeV) with a half life of 4.47 x 10⁹ years and natural thorium (primary isotope ²³²Th) is a weak α-emitter (4.012 MeV) with a half life of 1.41 x 10¹⁰ years; manipulations should be carried out in a monitored fume hood or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β- counting equipment.

6.4.3 Isolation of [Cp*₂ThH(µ-H)]₂ (1): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂ThMe₂ (3) (0.0249 g, 0.0468 mmol) and benzene (1 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.0253 g, 0.234 mmol) added, which resulted in an immediate color change from pale yellow to red along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). The volatiles were then removed under reduced pressure at 50 °C to give [Cp*₂ThH(µ-H)]₂ (1) as a red powder (0.0453 g, 0.0449 mmol, 96%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 1.¹⁹ ¹H NMR (C₆D₆): δ 19.43 (s, 4H, Th–H), 2.18 (s, 60H, C₅Me₅).
6.4.4 Isolation of [Cp*2UH(µ-H)]2 (2): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*2UMe2 (4) (0.0270 g, 0.0501 mmol) and benzene (1 mL). The reaction mixture was heated to 50 °C and PhSiH3 (0.0271 g, 0.250 mmol) added, which resulted in an immediate color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). The volatiles were then removed under reduced pressure at 50 °C to give [Cp*2UH(µ-H)]2 (1) as a dark brown powder (0.0496 g, 0.0486 mmol, 97%). The 1H NMR spectrum collected in C6D6 was consistent with the data previously reported for complex 2.19 1H NMR (C6D6): δ –2.43 (s, 60H, C5Me5), –324.42 (s, 4H, U–H).

6.4.5 Synthesis of Cp*2ThMe2 (3): A 50-mL round-bottom flask equipped with a stir bar was charged with Cp*2ThCl2 (1.03 g, 1.79 mmol) and Et2O (15 mL). To this stirring solution, MeMgBr (3.0 M in Et2O, 1.79 mL, 5.38 mmol, 3 equiv.) was added by syringe. After 5 minutes, 1,4-dioxane (0.790 g, 8.96 mmol, 5 equiv.) was added drop-wise to the solution over the course of another 5 minutes, resulting in an exothermic reaction and the precipitation of a white solid. After stirring at room temperature for 1 h, the volatiles were removed from the reaction mixture under reduced pressure; first at room temperature, then at 50 °C to ensure the removal of all excess 1,4-dioxane. The residual white solid was extracted with hexane (75 mL), and the hexane extract was filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles removed under reduced pressure to give Cp*2ThMe2 (3) as a white powder (0.844 g, 1.58 mmol, 88%). The 1H
NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 3.¹⁹ ¹H NMR (C₆D₆): δ 1.91 (s, 30H, C₅Me₅), –0.18 (s, 6H, Th–Me).

6.4.6 Synthesis of Cp*₂UMe₂ (4): A 100-mL round-bottom flask equipped with a stir bar was charged with Cp*₂UCl₂ (2.59g, 4.47 mmol) and Et₂O (25 mL). To this stirring solution, MeMgBr (3.0 M in Et₂O, 4.47 mL, 13.4 mmol, 3 equiv.) was added by syringe. After 5 minutes, 1,4-dioxane (1.97 g, 22.3 mmol, 5 equiv.) was added drop-wise to the solution over the course of another 5 minutes, resulting in an exothermic reaction and the precipitation of a white solid. After stirring at room temperature for 1 h, the volatiles were removed from the reaction mixture under reduced pressure; first at room temperature, then at 50 °C to ensure the removal of all excess 1,4-dioxane. The residual red-orange solid was extracted with hexane (150 mL), and the hexane extract was filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles removed under reduced pressure to give Cp*₂UMe₂ (4) as an orange powder (1.89 g, 3.52 mmol, 79%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 4.¹⁹ ¹H NMR (C₆D₆): δ 5.20 (s, 30H, C₅Me₅), –134.1 (s, 6H, U–Me).

6.4.7 Synthesis and isolation of [Cp*₂UH]ₓ (7): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.140 g, 0.260 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.064 mL, 0.520 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C for 10 minutes (until gas evolution had ceased), after which volatiles were removed under reduced pressure at 50 °C to give a dark brown powder identified as pure [Cp*₂UH]ₓ (0.132 g, 0.260 mmol, 100%). ¹H NMR (C₆D₆, 296 K, 400
MHz): δ 3.03 (s, C₅Me₅, ν₁/₂ = 10 Hz), −9.37 (s, C₅Me₅, ν₁/₂ = 20 Hz). Some [Cp*₂U(H)(μ-H)]₂ was also observed at ambient temperature: ¹H NMR (C₆D₆, 296 K, 400 MHz): δ = −2.59 (s, C₅Me₅, ν₁/₂ = 6 Hz). IR (ATR-IR, 296 K, Neat, cm⁻¹): 2965, 2880, 2360, 2342, 1426, 1378, 1099, 719, 695, 688.

6.4.8 Synthesis of Cp*₂Th(SPh)₂ (9): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂ThMe₂ (3) (0.0997 g, 0.187 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.0987 g, 0.912 mmol) added, which resulted in an immediate color change from pale yellow to red along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). PhSSPh (0.0411 mg, 0.188 mmol) was added to the reaction mixture, which resulted in an immediate color change from red to yellow and vigorous gas evolution. After stirring for 5 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give Cp*₂Th(SPh)₂ (6) as an off-white, semi-crystalline powder (0.126 g, 0.187 mmol, 100%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 9.²² ¹H NMR (C₆D₆, 298 K): δ 7.84 (d, J = 7.8 Hz, 4H, o-Ar-H), 7.04 (t, J = 7.8 Hz, 4H, m-Ar-H), 6.90 (t, J = 7.0 Hz, 2H, p-Ar-H), 2.02 (s, 30H, C₅Me₅).

6.4.9 Synthesis of Cp*₂U(SPh)₂ (10): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (4) (0.0260 g, 0.0483 mmol) and toluene (1 mL). The reaction was heated to 50 °C and PhSiH₃ (0.0261 g, 0.241 mmol) added, which resulted in a color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes).
PhSSPh (0.0105 g, 0.0483 mmol) was added to the reaction mixture, resulting in a color change to dark red and the evolution of gas. After stirring for 1 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give Cp*₂U(SPh)₂ (10) as a red solid (0.0421 g, 0.0646 mmol, 69%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 7.⁴⁰ ¹H NMR (C₆D₆, 298 K): δ 13.13 (s, 30H, C₅Me₅), 1.24 (t, J = 7.0 Hz, 2H, p-Ar-H), 0.34 (s, 4H, m-Ar-H), –33.43 (s, 4H, o-Ar-H).

### 6.4.10 Synthesis of Cp*₂U(SePh)₂ (11):

A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (4) (0.0325 g, 0.0603 mmol) and toluene (2 mL). The reaction was heated to 50 °C and PhSiH₃ (0.0327 g, 0.302 mmol) added, which resulted in an immediate color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). PhSeSePh (0.0188 g, 0.0603 mmol) was added to the reaction mixture at 50 °C, which resulted in an immediate color change to dark red and the evolution of gas. After stirring for 1 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give Cp*₂U(SePh)₂ (11) as a red solid (0.0399 g, 0.0486 mmol, 81%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 11.²² ¹H NMR (C₆D₆, 298 K): δ 14.08 (s, 30H, C₅Me₅), 2.58 (t, J = 6.9 Hz, 2H, p-Ar-H), 0.92 (d, 4H, J = 5.2 Hz, o-Ar-H), –31.67 (s, 4H, m-Ar-H).

### 6.4.11 Synthesis of Cp*₂U(TePh)₂ (12):

A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (4) (0.0300 g, 0.0557 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.0301 g, 0.279 mmol) added, which
resulted in an immediate color change from orange-red to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). PhTeTePh (0.0228 g, 0.0557 mmol) was added to the reaction mixture at 50 °C, which resulted in a color change to red and vigorous evolution of gas. After stirring for 3 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give Cp*₂U(PhTe)₂ (12) as a red solid (0.0485 g, 0.0528 mmol, 95%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 12.²³ ¹H NMR (C₆D₆): δ 15.28 (s, 30H, C₅Me₅), 3.88 (t, J = 7.1 Hz, 2H, p-Ar-H), 1.73 (d, J = 7.2 Hz, 4H, m-Ar-H), –27.22 (s, 4H, o-Ar-H).

6.4.12 Synthesis of Cp*₂U(SMe)₂ (13): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (4) (0.0355 g, 0.0659 mmol) and toluene (2 mL). The reaction was heated to 50 °C and PhSiH₃ (0.0357 g, 0.330 mmol) added, which resulted in an immediate color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). MeSSMe (0.0062 g, 0.0659 mmol) was added to the reaction mixture at 50 °C, which resulted in an immediate color change to dark red and the evolution of gas. After stirring for 1 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give Cp*₂U(SMe)₂ (13) as a red solid (0.0307 g, 0.0510 mmol, 77%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 13.⁴⁰ ¹H NMR (C₆D₆, 298 K): δ 10.86 (s, 30H, C₅Me₅), –20.88 (s, 6H, S–Me).

6.4.13 Synthesis of Cp*₂Th(η⁴-C₄Ph₄) (14): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂ThMe₂ (3) (0.0635 g, 0.119 mmol) and toluene (3 mL). The
reaction mixture was heated to 50 °C and PhSiH₃ (0.0645 g, 0.597 mmol) added, which resulted in a color change from beige to dark orange-red along with the vigorous evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). Diphenylacetylene (0.0425 g, 0.239 mmol) was added to the reaction, which resulted in more vigorous gas evolution. The reaction was allowed to stir while open an additional 5 minutes, after which it was closed and allowed to react at 50 °C for 3 hours. The volatiles were removed from the reaction mixture under reduced pressure to afford a brown oil. The oil was layered with hexane (5 mL), which resulted in the immediate precipitation of a yellow solid. The solid was collected by filtration (medium porosity fritted funnel), washed with hexane (3 mL), and dried under reduced pressure to give Cp*₂Th(C₄Ph₄) (14) as a bright yellow crystalline solid (0.0695 g, 0.0812 mmol, 68%). The ¹H NMR spectrum collected in THF-d₈ was consistent with the data previously reported for complex 14.³¹ ¹H NMR (THF-d₈, 298 K): δ 7.50 (d, J = 5.1 Hz, 2H, p-Ar-H), 7.32 (m, 2H, p-Ar-H), 7.01 (t, J = 7.0 Hz, 4H, m-Ar-H), 6.81 (t, J = 7.0 Hz, 4H, m-Ar-H), 6.70 (d, J = 7.0 Hz, 4H, o-Ar-H), 6.43 (d, J = 7.0 Hz, 4H, o-Ar-H), 1.99 (s, 30H, C₅Me₅).

6.4.14 Synthesis of Cp*U(η⁴-C₄Ph₄) (15): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (4) (0.0460 g, 0.0854 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.0462 g, 0.427) added, which resulted in a color change from dark orange to dark brown along with the vigorous evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). Diphenylacetylene (0.0304 g, 0.171 mmol) was added to the reaction, which resulted in more vigorous gas evolution. The reaction was allowed to stir while open an
additional 5 minutes, after which it was closed and allowed to react at 50 °C for 3 hours. The volatiles were removed from the reaction mixture under reduced pressure to give a brown oily residue, which was redissolved in minimal hexane (1 mL), and cooled to –30 °C to give Cp*2U(C4Ph4) (15) as a brown crystalline solid (0.0451 g, 0.0524 mmol, 61%). The 1H NMR spectrum collected in C6D6 was consistent with the data previously reported for complex 15.19 1H NMR (C6D6, 298 K): δ 6.15 (s, 30H, C5Me5), 5.68 (m, 4H, m-Ar-H), 4.47 (m, 4H, o-Ar-H), –0.66 (t, J = 6.8 Hz, 2H, p-Ar-H), –1.42 (t, J = 6.8 Hz, m-Ar-H), –37.32 (t, J = 6.9 Hz, o-Ar-H). One p-Ar-H resonance is located under the C5Me5 resonance.

6.4.15 Synthesis of Cp*2ThS5 (17): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*ThMe2 (3) (0.0260 g, 0.0488 mmol) and toluene (1 mL). The reaction mixture was heated to 50 °C and PhSiH3 (0.0264 g, 0.244 mmol) added, which resulted in a color change from beige to dark orange-red along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). The reaction was cooled to ambient temperature and S8 (0.0078 g, 0.0305 mmol) was added, which immediately resulted in more vigorous gas evolution and a color change to bright yellow. The volatiles were removed from the reaction mixture under reduced pressure to give Cp*2ThS5 (17) as a yellow powder (0.0259 g, 0.0388 mmol, 80%). The 1H NMR spectrum collected in C6D6 was consistent with the data previously reported for complex 17.32 1H NMR (C6D6, 298 K): δ 2.04 (s, 30H, C5Me5).

6.4.16 Synthesis of Cp*2U(bipy) (18): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*2UMe2 (4) (0.0785 g, 0.146 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and PhSiH3 (0.0789 g, 0.729 mmol) added, which resulted in
the vigorous evolution of gas and a color change from dark orange to dark brown. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). 2,2′-Bipyridine (0.0225 g, 0.146 mmol) was added to the reaction mixture, which resulted in more (slow) gas evolution. The scintillation vial was sealed and the reaction was heated at 50 °C for 15 h. The volatiles were removed from the reaction mixture under reduced pressure, yielding an oily brown residue. This residue was taken up in hexane (7 mL) and filtered (medium porosity fritted funnel). The filtrate was collected and placed under reduced pressure until the volume of the solution reached ~ 1 mL. The solution was cooled to –30 °C overnight, which resulted in the precipitation of a green solid. The solid was collected on a medium-porosity frit, washed with hexane (1 mL), and dried under reduced pressure to give Cp*₂U(bipy) (18) as a green solid (0.0668 g, 0.101 mmol, 69%). The ¹H NMR spectrum collected in C₆D₆ was consistent with the data previously reported for complex 18.³³ ¹H NMR (C₆D₆, 298 K): δ 0.13 (s, 30H, CsMe₅), –19.93 (d, J = 6.0 Hz, 2H, bipy), –41.38 (t, J = 6.0 Hz, 2H, bipy), –81.30 (t, J = 6.0 Hz, 2H, bipy), –93.77 (t, J = 6.1 Hz, 2H, bipy).

6.4.17 Synthesis of Cp*₂U(–N=CPh₂)₂ (22): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.048 g, 0.090 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.023 mL, 0.186 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution had ceased (10 minutes). Benzophenoneazine (0.033 g, 0.091 mmol) was added to the reaction mixture at 50 °C, which resulted in vigorous gas evolution, and the reaction was stirred at 50 °C for 24 h. The volatiles were
removed under reduced pressure to give Cp*₂U(–N=CPh₂) (8) as a brown, waxy solid (0.064 g, 0.074 mmol, 83%). The ¹H NMR spectrum collected in C₆D₆ was consistent with data previously reported for complex 8. ³⁶ ¹H NMR (C₆D₆, 296 K, 400 MHz): δ = –1.87 (s, 30H, C₅Me₅).

6.4.18 Synthesis of Cp*₂U(=NPh)₂ (20): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.050 g, 0.093 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.023 mL, 0.186 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution had ceased (10 minutes). Azobenzene (0.016 g, 0.088 mmol) was added to the reaction mixture at 50 °C, which resulted in vigorous gas evolution, and the reaction was stirred at 50 °C for 1 hour. The volatiles were removed under reduced pressure to give Cp*₂U(=NPh)₂ (9) as a waxy, dark brown solid (0.061 g, 0.089 mmol, 95%). The ¹H NMR spectrum collected in C₆D₆ was consistent with data previously reported for complex 9. ⁴¹ ¹H NMR (C₆D₆, 296 K, 400 MHz): δ = 9.27 (t, 4H, J = 7.8 Hz, m-Ar-H), 4.14 (s, 30H, C₅Me₅), 2.92 (d, 4H, J = 7.4 Hz, o-Ar-H), 0.87 (t, 2H, J = 8.0 Hz, p-Ar-H).

6.4.19 Synthesis of Cp*₂U(dmpe)(H) (23): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.102 g, 0.190 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.047 mL, 0.380 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C for 10 minutes (until gas evolution had ceased). The reaction mixture was cooled to ambient temperature and dmpe (0.032 mL, 0.190 mmol) was added.
by microsyringe. After stirring at 50 °C for 15 minutes, volatiles were removed under reduced pressure to give an oily brown residue. This residue was quickly washed with pentane (2 mL), and the volatiles were removed under reduced pressure to give Cp*₂U(dmpe)(H) (23) as a dark brown powder (0.118 g, 0.179 mmol, 94%). The ¹H NMR spectrum collected in C₆D₆ was consistent with data previously reported for complex 23.²¹

¹H NMR (C₆D₆, 296 K, 400 MHz): δ = –6.08 (s, 30H, C₅Me₅).

6.4.20 Synthesis of Cp*₂U(terpy) (24): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.051 g, 0.095 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.023 mL, 0.186 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution had ceased (10 minutes). Then 2,2′:6′,2″-terpyridine (0.022 g, 0.094 mmol) was added and the reaction stirred at 50 °C for 24 h, resulting in a gradual color change from dark brown to dark teal. Volatiles were removed under reduced pressure to give Cp*₂U(terpy) (23) as a dark teal waxy solid (0.066 g, 0.089 mmol, 94%). The ¹H NMR spectrum collected in C₆D₆ was consistent with data previously reported for complex 23.³³ ¹H NMR (C₆D₆, 296 K, 400 MHz): δ = 15.56 (s, 30H, C₅Me₅), –8.14 (s, 2H, terpy), –19.64 (s, 2H, terpy), –28.48 (s, 2H, terpy), –40.51 (s, 2H, terpy), –46.83 ppm (s, 1H, terpy).

6.4.21 Synthesis of Cp*₂U(η²-C₄Ph₄) (15) (from 7): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.058 g, 0.107 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.026 mL, 0.214 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The
reaction was stirred at 50 °C until gas evolution ceased (10 minutes). Diphenylacetylene (0.038 g, 0.214 mmol) was added to the reaction mixture, which resulted in vigorous gas evolution, and the reaction stirred at 50 °C for 30 minutes. The volatiles were removed under reduced pressure to give Cp*₂U(C₄Ph₄) (10) as a dark brown powder (0.092 g, 0.107 mmol, 100%). The ¹H NMR spectrum collected in C₆D₆ was consistent with data previously reported for complex 10.¹⁹ ¹H NMR (C₆D₆, 296 K, 400 MHz): δ 6.15 (s, 30H, C₅Me₅), 5.68 (m, 4H, m-Ar-H), 4.47 (m, 4H, o-Ar-H), −0.66 (t, J = 6.8 Hz, 2H, p-Ar-H), −1.42 (t, J = 6.8 Hz, m-Ar-H), −37.32 (t, J = 6.9 Hz, o-Ar-H). One p-Ar-H resonance is located under the C₅Me₅ resonance.

6.4.22 Synthesis of Cp*₂U(η²-C₄Me₄) (25): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*₂UMe₂ (0.028 g, 0.052 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH₃ (0.013 mL, 0.104 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution ceased (10 minutes). 2-Butyne (0.006 g, 0.104 mmol) was added to the reaction mixture, which resulted in vigorous gas evolution, and the reaction stirred at 50 °C for 30 minutes. The volatiles were removed under reduced pressure to give Cp*₂U(C₄Me₄) (25) as a bright red powder (0.032 g, 0.052 mmol, 100%).

¹H NMR (C₆D₆, 296 K, 400 MHz): δ 0.45 (s, 30H, C₅Me₅), −3.61 (s, 6H, C₄Me₄), −4.55 (s, 6H, C₄Me₄). IR (ATR-IR, Neat, 296 K, cm⁻¹): 3569, 2967, 2888, 2822, 2722, 1488, 1436, 1375, 1219, 1063, 1019, 735. UV/Vis (Toluene, 296 K, 0.2 mM, cm⁻¹ (cm⁻¹M⁻¹)): 32895 (12525), 22300 (3200). NIR (Toluene, 296 K, 20 mM, cm⁻¹ (cm⁻¹M⁻¹)): 13700 (87), 12950 (40), 10700 (35), 10275 (25), 8800 (90), 8500 (75), 8150 (125), 7800 (70), 6600 (20), 6300
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6.4.23 Synthesis of Cp*_{2}U(\eta^{2}-C_{4}Ph_{2}(SiMe_{3})_{2}) (26): A 20-mL scintillation vial equipped with a stir bar was charged with Cp*_{2}UMe_{2} (0.037 g, 0.064 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and PhSiH_{3} (0.016 mL, 0.128 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution ceased (10 minutes). 1-phenyl-2-trimethylsilylacetylene (0.022 g, 0.128 mmol) was then added to the reaction mixture, which resulted in vigorous gas evolution, and the reaction mixture stirred at 50 °C for 1 hour. The volatiles were removed under reduced pressure to give Cp*_{2}U(C_{4}Ph_{2}(SiMe_{3})_{2}) (26) as a bright red powder (0.046 g, 0.054 mmol, 84%). ^{1}H NMR (C_{6}D_{6}, 296 K, 400 MHz): δ 7.37 (d, J = 8.6 Hz, 4H, o-Ar–H), 6.85 (t, J = 7.2 Hz, 4H, m-Ar–H), 5.88 (t, J = 7.2 Hz, 2H, p-Ar–H), 4.16 (bs, ν_{1/2} = 17 Hz, 18 H, –SiMe_{3}), 3.81 (s, 30H, C_{5}Me_{5}). UV/Vis–NIR (Toluene, 296 K, cm^{-1} (M^{-1}cm^{-1})): 32680 (8265), 25575 (4015), 22175 (1980), 18350 (800), 14500 (75), 14085 (80), 13800 (90), 12400 (40), 10600 (30), 9500 (40), 9000 (55), 8650 (60), 8250 (70), 7850 (40), 7220 (40), 6220 (30), 5950 (35). mp: 213–214 °C. Anal. Calcd. for C_{42}H_{58}Si_{2}U (mol. wt. 857.11): C, 58.85; H, 6.82. Found: C, 58.74; H, 6.88.

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Figure 6.7: $^1$H NMR of [Cp$_2$UH]$_x$ (7) at 20 °C.
Figure 6.8: $^1$H NMR spectrum of [Cp*$_2$UH]$_x$ (7) at 50 °C.
Figure 6.9: $^{1}$H NMR spectrum of Cp*/2U(C₄Me₄) in C₆D₆ (25).
Figure 6.10: IR spectrum of Cp*₂U(C₄Me₄) (25).
Figure 6.11: NIR (top) and UV/vis (bottom) spectra of Cp*₂U(C₄Me₄) (25)
6.5 References


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(27) At the time of writing, 25 g of phenylsilane costs $260 from Sigma Aldrich. The only major hazard associated with phenylsilane according to its SDS is flammability; it is not inherently pyrophoric.


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Chapter 7: Conclusions

7.1 Transition-metal conclusions

In conclusion, FpMe is shown to be a competent catalyst for \( \alpha \)-phosphinidene elimination from primary phosphines. The development of catalytic \( \alpha \)-phosphinidene elimination has been a particularly interesting field of study described in this dissertation. Clearly, identifying new catalysts for this reaction is warranted. The well-studied family of half-sandwich group 8 transition-metal compounds is an attractive target for further development of this reactivity. A clear challenge to be solved in this field is the development of a complex that will catalyze singlet \( \alpha \)-phosphinidene elimination as opposed to triplet \( \alpha \)-phosphinidene elimination, as singlet phosphinidenes are known to react in ways that are beneficial to synthesizing value added, complex organophosphines such as phospholes and phosphirenes. Yet, given the success of FpMe to catalyze this desirable reactivity, catalysts that are able to release triplet phosphinidenes are also needed to study. In all, it would be beneficial to understanding catalyst design principles that preferentially eliminate singlet or triplet phosphinidenes.

Additionally, it was shown that Fp2 is a competent photoactivated catalyst for a variety of main-group bond forming reactions. Visible light photocatalysis, generally, is another intriguing field that is prominently emerging for organic chemistry, but has been ignored for main-group E–E or E–C bond forming reactions. Indeed, the study presented in this dissertation utilizing Fp2 as a photoactivated catalyst appears to be the first example of main-group bond forming reactions utilizing visible light. Given the success of these reactions, in particular that of the double hydrophosphination of terminal aryl acetylynes with Ph₂PH, it appears that visible light photocatalyzed reactions have great potential for
main-group bond forming reactions. Using compounds with well-characterized photochemistry for these reactions is therefore a field rife for study. In particular, the photosensitizers of the Ru(bipy)$_3^{2+}$ family have been prominently used in organic bond-forming reactions, yet have not been utilized in main-group bond forming catalysis.

7.2 Actinide conclusions

In conclusion, phenylsilane was shown to be an effective alternative to hydrogen for the synthesis of thorium and uranium hydrides, and in the case of uranium, the oxidation state and nuclearity of the complexes was controlled by altering the amount of phenylsilane added. The expansion of this chemistry to transuranic elements is the clear next step in the field. Chemists who work with transuranic elements must be even more cautious than those working with the early actinides due to the inherent radiological hazard of working with these elements, which can limit synthetic protocols utilized in these laboratories. Thus, nonhazardous synthetic protocols are especially valued in transuranic element compound syntheses. The establishment of methods for the syntheses of transuranic hydrides would allow for the further studies of these compounds for nuclear fuels and radiological waste interactions, two important areas of study.

Finally, the synthesis of all-carbon actinide metallacycles is an emerging field of study with clear implications in understanding the role of 5$f$-orbitals and electrons on reactivity. The actinide–metallacycle bonding interactions have been shown to be fundamentally different than those of both transition-metal compounds as well as previously studied actinide metallocenes, which are borne out in the electronic spectra of these compounds. Clearly, TD-DFT calculations are required to understand the origin of
the transitions observed in the UV/visible spectra of these compounds to better understand why these compounds are fundamentally different than both transition-metal and other actinide metallocenes. Additionally, the aromaticity of actinide metallacycles appears to be greatly influenced by the presence of unpaired 5f-electrons as observed by comparison of thorium(IV) and uranium(IV) compounds, another example where 5f-electrons are directly influencing chemical properties. The synthesis of uranium metallacycles of varying oxidation states will allow for a better understanding of how 5f-electrons influence the aromaticity of these systems.
Comprehensive Bibliography


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Appendix 1: Original SCGSR research proposal for work at LANL

The goal of the proposed project is to synthesize a series of triamidoamine-supported thorium and uranium complexes to test a potentially catalytic synthesis of phosphaalkenes and to explore α-elimination reactions. These transformations are highly related in that they generate a low-valent phosphorus fragment. Formally d⁰ Th(IV) and Zr(IV) compounds can easily be compared. Th(IV) complexes may be able to afford reactivity unseen by related Zr(IV) complexes due to the relative size of the metals and accessible 5f-orbitals that may be available to accept electron density from bonding ligands in the Th(IV) systems. Additionally, parallel studies with isostructural U(IV) complexes provide the opportunity to probe the potential influence of f-electrons on the reaction chemistry. Unique reactivity with the ancillary ligand is anticipated in each case.

Initially, we would like to synthesize two known triamidoamine-supported actinide complexes \([\kappa^5-N,N,N,C-Me_3SiNCH_2CH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]An\) (An = Th, U) to attempt to synthesize phosphaalkenes in stoichiometric and catalytic fashions. We have demonstrated that the zirconium analog of this complex is able to afford a phosphaalkene on zirconium by the following route (eq 1).¹

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \text{Me}_3\text{Si} \\
\text{Si} & \quad \text{Si} \\
\text{N} & \quad \text{N} \\
\text{Si} & \quad \text{Si} \\
\text{Zr} & \quad \text{Zr} \\
\text{RPH}_2 & \quad \text{PH}_2 \text{SiMe}_3 \\
\text{1} & \quad \text{2}
\end{align*}
\]

Unfortunately, attempts to liberate the phosphaalkene from the metal center by reaction with an electrophile gave only the phosphaformamide product. We proposed that
steric crowding at nitrogen prevents attack there, instead favoring addition at phosphorus (eq 2).\textsuperscript{1}

\[
\begin{align*}
&\text{Me}_3\text{Si} \quad \text{N} \quad \text{Zr} \quad \text{N} \quad \text{SiMe}_3 \\
&\quad \text{Me}_3\text{Si} \quad \text{N} \quad \text{Zr} \quad \text{N} \quad \text{SiMe}_3
\end{align*}
\]

We hypothesize that a larger metal, such as thorium, may allow for electrophilic attack to occur at nitrogen instead of phosphorus, thus preserving the phosphaalkene moiety. In addition, it may be possible for the phosphaalkene at thorium to wrap around and coordinate in an $\eta^3$ fashion. This coordination would allow for even more facile access to phosphorus, thus increasing the success of liberating a phosphaalkene upon electrophilic attack. If this scheme is successful, transfer of H may be possible and by adding an excess of isocyanide and primary phosphine phosphaalkenes may be generated catalytically, which would represent the first catalytic synthesis of these molecules. This would prove to be an exciting result, as phosphaalkenes have been used as precursors for highly interesting $\pi$-conjugated, P–C backbone polymers.\textsuperscript{2}

At the same time, we would also like to study the thermal degradation pathways of triamidoamine supported thorium complexes with phosphide and arsenide ligands. We have shown in the past that zirconium complexes bearing arsenide ligands can engage in $\alpha$-arsinidene elimination, providing access to unusual As–As bonded products.\textsuperscript{3} However, such reactivity has not been seen for phosphorus, which undergoes cyclometalation for loss of RPH\textsubscript{2}. Scott and coworkers showed that triamidoamine-supported thorium complexes

\[\text{Me}_3\text{Si} \quad \text{N} \quad \text{Zr} \quad \text{N} \quad \text{SiMe}_3 \]

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are much more difficult to metalate than related transition-metal congeners,\textsuperscript{4} which leads us to believe that these complexes would be excellent candidates to induce $\alpha$-elimination and expand on this unique reactivity (eq 3).

\[
\begin{array}{c}
\text{Me}_3\text{Si} \quad \text{EHR} \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{SiMe}_3
\end{array} \xrightarrow{\Delta} \quad \begin{array}{c}
\text{Me}_3\text{Si} \quad \text{H} \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} \quad \text{N} \quad \text{N} \quad \text{N}
\end{array} + \text{[ER]} \xrightarrow{-\text{H}_2} \begin{array}{c}
\text{Me}_3\text{Si} \quad \text{An} \quad \text{N} \quad \text{N} \quad \text{SiMe}_3 \\
\text{Me}_3\text{Si} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{SiMe}_3
\end{array}
\]

(3)

Recently, Liddle and coworkers demonstrated that the cyclometallation reaction is easier for uranium than thorium due to greater $f$-orbital (and $f$-electron) participation of the bonding for uranium relative to thorium.\textsuperscript{5} Therefore, studies with the isostructural uranium system will be necessary to see if the $f$-electrons in the U(IV) system will facilitate or hinder the catalytic synthesis of phosphaalkenes. All aspects of this project have excellent precedence on experimental design previously used in our research group at UVM. As the syntheses of $[\kappa^5\text{N},\text{N},\text{N},\text{N},\text{C-Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NSiMe}_2\text{CH}_2]\text{An}$ (An = Th, U) have been previously described, we will follow established syntheses and protocols to obtain these complexes.\textsuperscript{6,7} The triamidoamine ligand will be synthesized at UVM. Kiplinger’s group at the Los Alamos National Laboratory (LANL) are established leaders in the field of actinide chemistry and have developed easy and safe routes to the thorium and uranium starting materials needed to synthesize the actinide (An = Th, U) complexes.\textsuperscript{8} Furthermore, many primary phosphines and isocyanides are commercially available compounds, which would allow for quick access to these reactions. More complex phosphines will be synthesized at UVM and shipped to LANL as needed.

The production of phosphaalkenes and low valent phosphinidene fragments are easily monitored by $^{31}\text{P}\{^{1}\text{H}\}$ and $^{1}\text{H}$ NMR spectroscopy, as these reactions are ideal to
scale down to NMR tube size. LANL has several multinuclear NMR spectrometers that will be available to monitor the reactions described above and new single-crystal X-ray diffractometers to obtain structural characterization as needed. Reactions will be scaled up at LANL, where large-scale chemistry with actinides is possible. Isolation of phosphaalkenes from the catalyst should also be straightforward, with triamidoamine-supported thorium and uranium complexes easily being removed from a reaction mixture by column chromatography.

This proposed project not only expands upon rare or previously unseen reactivity, but also allows for further comparison between Zr(IV) and Th(IV), both d⁰ metal centers, and with U(IV), an f² metal center.⁹ We believe that understanding more ways to induce α-elimination will allow for further generalization of this rare reactivity type and allow for further use of main-group elements in everyday, industrial processes. Furthermore, despite the large number of molecules that include a P=C moiety, there is still no catalytic process to synthesize these molecules despite their emergent importance in materials. This project allows for a unique opportunity to merge academic and practical interests in a concise and efficient fashion. In addition to these benefits, this project fits well within the mission of the BES Heavy Element Radiochemistry priority research interest, allowing for the direct comparison of two d⁰ metals (Th(IV) has f-orbitals available for bonding and Zr(IV) does not) one f² metal center (U(IV) has f-electrons available for bonding and Zr(IV) and Th(IV) do not). This should help to further elaborate upon the role of f-orbitals and f-electrons in reactivity of actinide complexes.
We believe that this collaboration will be essential to the success of this proposal. The Kiplinger group has access to actinide chemistry facilities at LANL where large amounts of radioactive natural thorium and depleted uranium materials can be handled safely. LANL also has a number of experts in actinide electrochemistry, spectroscopy and theory. Working with these experts will be critical to understanding the importance of f-orbitals/electrons in the catalytic synthesis of phosphaalkenes and/or α-elimination reactions. In addition, our group at UVM already has extensive experience in synthesizing and working with triamidoamine ligands.\textsuperscript{1,3,10}

Importantly, the work outlined in this proposal would also help to advance my doctoral dissertation project which contains themes of P–C bond formation both by classic hydrophosphinination reactions and by the extrusion and trapping of low valent phosphinidene fragments. My initial dissertation project involved the attempted synthesis of phosphaalkenes using half-sandwich iron complexes of the type CpFe(CNR)\textsubscript{2}(PHR'), which was unsuccessful due to the unstable Fe–PHR' linkage. This proposed work would allow me to realize this initial goal in a way that would merge our research interests with those of the Kiplinger group.

In conclusion, we propose to use the well-defined actinide complexes $[\kappa^5-$N,N,N,N,C-Me\textsubscript{3}SiNCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}]\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}NSiMe\textsubscript{2}CH\textsubscript{2}]\textsubscript{An}$ (An = Th, U) to generate phosphaalkenes at the metal center followed by catalytic or stoichiometric liberation. In addition, we propose to use related primary phosphido- and arsenido–Th(IV) and U(IV) complexes to promote α-phosphinidene and arsinidene elimination. These reactions would proceed through formally low-valent main-group element fragments, which would greatly
assist my doctoral dissertation and provide access to interesting molecules. We believe that
the relative size of Th(IV) and U(IV) versus that of Zr(IV), as well as the availability of
low-lying f-orbitals in Th(IV) and U(IV) and the f-electrons in U(IV) will allow for this
interesting reactivity to occur despite these same reactions being unsuccessful when
attempted with the zirconium congener 1.

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(10) Roering, A. J.; Leshinsky, S. E.; Chan, S. M.; Shalumova, T.; MacMillan, S. N.;
Appendix 2: Setup for LED photolysis and UV/visible spectra of lamps

Figure A2.1: Experimental setup. A commercially available LED bulb (foreground) is aimed at the sample (back, PTFE-sealed NMR tube) which rests in a silicone oil bath partially covered in aluminum foil to shield from ambient irradiation as well as focus the
photons from the LED bulb. The entire setup excluding the bulb rests on a lab jack in a fume hood.
Figure A2.2: UV/vis spectrum of an OSRAM Sylvania Ultra LED A19 Lamp – generation 5, operating power of 6 W and output of 450 lumens.
Figure A2.3: UV/vis spectrum of a Green Energy Lighting Corp. LED A19 lamp, operating power of 6.8 W and output of 500 lumens.
Figure A2.4: UV/vis spectrum of a GE LED Lamp A19, operating power of 13 W and output of 800 lumens.
Appendix 3: X-ray Crystallography

All data were collected on either a Bruker D8 APEX II diffractometer, with CCD detector, and was cooled with a KRYO-FLEX liquid nitrogen vapor-cooling device or collected on a Bruker D8 Quest diffractometer, with CMOS detector in shutterless mode, and crystals were cooled to using an Oxford Cryostream liquid nitrogen cryostat. Both data collections employed graphite monochromatized MoKα (λ = 0.71073 Å) radiation. Hemispheres of data were collected with ω scans. Data collection, initial indexing, and cell refinement were handled with APEX II software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out with SAINT+ software. The data were corrected for absorption with the SADABS program. The structure was solved with direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Structure solution and refinement were performed with SHELXTL. Additional details of data collection and structure refinement are shown below.
Table A3.1 Crystallographic refinement parameters

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<th>U CBB</th>
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<th>U TMS cumulene</th>
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<tr>
<td>CCDC #</td>
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<td>1501132</td>
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<tr>
<td></td>
<td>Th TMS cumulene</td>
<td>Th Ph cumulene</td>
<td>C$_4$Me$_4$ U</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C$<em>{30}$H$</em>{48}$Si$_2$Th</td>
<td>C$<em>{36}$H$</em>{40}$Th</td>
<td>C$<em>{28}$H$</em>{42}$U</td>
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</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>696.91</td>
<td>704.72</td>
<td>616.66</td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Monoclinic</td>
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</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>10.664(1)</td>
<td>9.476(2)</td>
<td>12.024(2)</td>
<td></td>
</tr>
<tr>
<td><strong>b [Å]</strong></td>
<td>18.047(2)</td>
<td>34.252(8)</td>
<td>14.635(2)</td>
<td></td>
</tr>
<tr>
<td><strong>c [Å]</strong></td>
<td>15.569(2)</td>
<td>10.347(3)</td>
<td>13.996(2)</td>
<td></td>
</tr>
<tr>
<td><strong>β [°]</strong></td>
<td>97.40(2)</td>
<td>116.15(2)</td>
<td>95.19(2)</td>
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<tr>
<td><strong>V [Å$^3$]</strong></td>
<td>3162.4(6)</td>
<td>3014.4(3)</td>
<td>2456.6(6)</td>
<td></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2(1)/c</td>
<td>P2(1)/c</td>
<td>C2/c</td>
<td></td>
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<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
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<td><strong>ρ [g/cm$^3$]</strong></td>
<td>1.464</td>
<td>1.553</td>
<td>1.667</td>
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<tr>
<td><strong>μ(MoKα)</strong></td>
<td>4.806</td>
<td>4.968</td>
<td>6.619</td>
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<tr>
<td><strong>T [K]</strong></td>
<td>139</td>
<td>100</td>
<td>100</td>
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<tr>
<td><strong>2θ$_{max}$ [°]</strong></td>
<td>64.12</td>
<td>57.40</td>
<td>57.24</td>
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<tr>
<td><strong>min/max trans.</strong></td>
<td>0.2604/0.5445</td>
<td>0.2484/0.4021</td>
<td>0.2874/0.6263</td>
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<tr>
<td><strong>Total reflns</strong></td>
<td>64929</td>
<td>7313</td>
<td>14162</td>
<td></td>
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<tr>
<td><strong>Unique reflns</strong></td>
<td>10990</td>
<td>6920</td>
<td>2990</td>
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<td><strong>Parameters</strong></td>
<td>298</td>
<td>344</td>
<td>139</td>
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<tr>
<td><strong>R$_1$(wR$_2$) (all data)</strong></td>
<td>0.0321 (0.0765)</td>
<td>0.0230(0.0381)</td>
<td>0.0171 (0.0411)</td>
<td></td>
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<tr>
<td><strong>Instrument</strong></td>
<td>D8 QUEST</td>
<td>APEX II</td>
<td>APEX II</td>
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<td><strong>CCDC #</strong></td>
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