Title
Photoreactivity of Bis(pentamethylcyclopentadienyl) Rare Earth Allyl Complexes

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Photoreactivity of Bis(pentamethylcyclopentadienyl) Rare Earth Allyl Complexes

THESIS

submitted in partial satisfaction of the requirements
for the degree of

MASTER OF SCIENCE

in Chemistry

by

Casey William Johnson

Thesis Committee:
Professor William J. Evans, Chair
Professor Alan F. Heyduk
Professor A. S. Borovik

2015

Dedication

To

my parents, close and casual friends and family, Music, and Science

in recognition of their worth

an apology

I am nothing more than a little boy inside
That cries out for attention, yet I always try to hide
‘Cause I talk to you like children
Though I don’t know how I feel
But I know I’ll do the right thing
If the right thing is revealed

Aaron Lewis
“Epiphany”

and redemption

Now that I know what it’s like to fall freely
I can taste blood for the ones who I envy
Trying to make it right, they won’t catch me
Now that I know, just watch what I’ll do

Nicholas Lofton Hexum
“Seal The Deal”

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Acknowledgements

I would like to express my thanks, appreciation, and gratitude to my committee chair and advisor, Bill Evans, who has the work ethic, mindset, and substance of a genius: a man who does more in a week than I hope to do in several months, he has shown me that true preparation and hard work is more than showing up early and moving things from place to place. It is having a near-obsessive understanding of topics at hand with a thought process devoid of excuses. He has tolerated my mistakes more than was necessary and given me much more than I believe I have given him, but how else is one supposed to feel in the face of excellence? If I am to have half the dedication and passion in any career or pastime that Bill has had in all of his, then I shall become an accomplished man indeed. Thanks Bill.

I want to thank my committee members, Andy Borovik and Alan Heyduk, who were both there when I needed valuable perspective in my career. Andy told me that I would do well at UCI when I was visiting the spring before my first year, and he did not disappoint. Alan gave me the motivational discussion that drove me to do what I should have been doing for months. Both showed me different approaches to learning and different ways of understanding. I enjoyed Alan's way of 'cutting out the crap' to get at what was really happening and determining its relevance, even it if was cutting out and cutting at organic chemists. And though I had used the word to describe a paper he had given me illustrating the progression of an entire scientific field, I cannot be certain that Andy found all the papers that I gave to him as 'tasty'.

I give my thanks and appreciation to all the teachers I've had throughout the years that helped me get to this point. In addition to Bill, Andy, and Alan, my graduate teachers Liz Jarvo, Jenny Yang, and Matt Law were incredible and ever-patient when helping me learn their subjects. I thank the University of California, Irvine for the opportunity to attend your school. I still remember and reminisce about my undergraduate chemistry professors: Dr. Pak, I still draw much of my love and drive for the field of materials from your classes and our discussions, and I didn't go to the In-n-Out as much as you would have guessed over the past two years; Dr. Holland, your organic chemistry class, as well as your research laboratory and glovebox, had major effects on my career choices, and as soon as this thesis is finished, I am going to find and beat you at whatever RTS you are currently playing; Dr. Holman, you taught me all I know on how to write and present on science, and considering how shy and lazy as I used to be, that's quite impressive; Dr. Rodriguez, I always enjoyed talking with you in the hallway, and I thank you for attending my show at the First Nash once, as I still feel honored; Dr. De Jesus, I will never understand why you always committed the crime of wearing socks with sandals, but I still remember your Advanced Organic class, as it was like you were the hip DJ playing all the classic reactions of chemistry. Thank you Idaho State University for your funding and the life-changing experience I had attending your school.

Though many will go unnamed because of the sheer number, I would like to thank my friends from over the years and the incredible times we had, as they've made lasting impressions on my life and influenced who I've become. Chad, Zach, Jeff, Steve, and Miles; without you guys, the last two years may have easily been the worst of my life. We went through a lot of tough and enjoyable times together: late night and last minute studying, finding amazing food to eat, going to the Pub for lunch so we could go to lab the rest of the day with a 'bit of a buzz', actually getting off campus to do anything, talking about chemistry, talking way more about women, talking about how we were going to make it through this. I know that some of us have left and gone on different paths, but that doesn't mean we have made it. I would thank all the colleagues of chemistry and graduate students I've met at/through AGS; we always had a blast and made the best of graduate school with the odds stacked against us! Thanks for the countless memories. Thanks to the people of Pocatello, who were some authentic and down to earth people that can't be found anywhere else: My Brothers in Phi Delta Chi, thank you for letting me share the experiences with you. Through the incredibly good times, to the exceptionally awful ones, we always tried to stick together, which is a lesson I learned best from witnessing it; To all the fools and homies who came and went to house parties across the town and throughout the years, I wouldn't trade the nights we shared for anything. I met some real characters and heard some great stories, so thank you; Kourtney Wright, my sister from another mother, I know you've got success ahead of you, wherever you point yourself to, so go get it!

To all the musicians I've ever shared the stage with: it has been my great pleasure and dearest honor to have made incredible moments with music alongside you. I would especially like to thank Shawn Barnby and my Marauders! Shawn showed me how a musician battles everyday with the spectrum of life and comes out on top and ready for more. I miss you everyday brother. I miss Dorian Hitchcock, ol' Dr. D, who is probably at home making mustache wax, smoking salmon, or whatever it is the original hipster does. And yes, I miss Jeff May the Third. Or second. Either way, you're going to be a great father, but don't forget the guitar.

Of course, I have to thank my one and only Rommy Andrea Coutelin. Since meeting her, she has made an incredible impact on my life. Through seeling her kindness, helpful attitude, selflessness, and will to go on day by day, I continuously try to better myself every day. She is patient and understanding (she hangs out and puts up with me, of course she has to be) with her school and her kids, all of which she loves dearly. She cares for her friends and family in a way I wish I can emulate one day. Her support of my career and hobbies makes me wonder if she keeps any for herself, which I always find confirmed by her grades and conversation. Making her smile is worth the entire day for me. I am sure I tire her out, which is probably why she takes so many naps, and I wouldn't have it any other way. Te amo mi amor, my Coutelin.

Most importantly, I want to thank Mom and Dad. Two incredible people who have always wanted a family, and I could not be more fortunate to be in theirs. They taught me all of what I know and give me the reasons and values I have for what I do today. Considering how dramatically my life has been since I moved out from under their loving roof, the main reason I still consider myself a good person is because of them and how they care for me and want the best for me. I feel like I broke their hearts a few too many times and tried to help them out harder than I could really manage (but once again, how else is one supposed to feel in the face of such excellence?). They always wanted me to be a doctor. I don't know whether I'll end up a surgeon, a Ph.D. candidate, or something like Dr. Dre, but I know I am going to make you proud, as it is the least I can do. I also thank my sisters Amanda, Megan, Mackenzie, and Lindsey: You guys are why I can even talk to other people or appreciate things outside of my own scope. We've had a tough road and will continue to travel on one, but knowing I have you guys around makes it possible. So to my family: thank you, and I love you.

Abstract of the Thesis

Photoreactivity of Bis(pentamethylcyclopentadienyl) Rare Earth Allyl Complexes

By

Casey William Johnson

Master of Science in Chemistry

University of California, Irvine, 2015

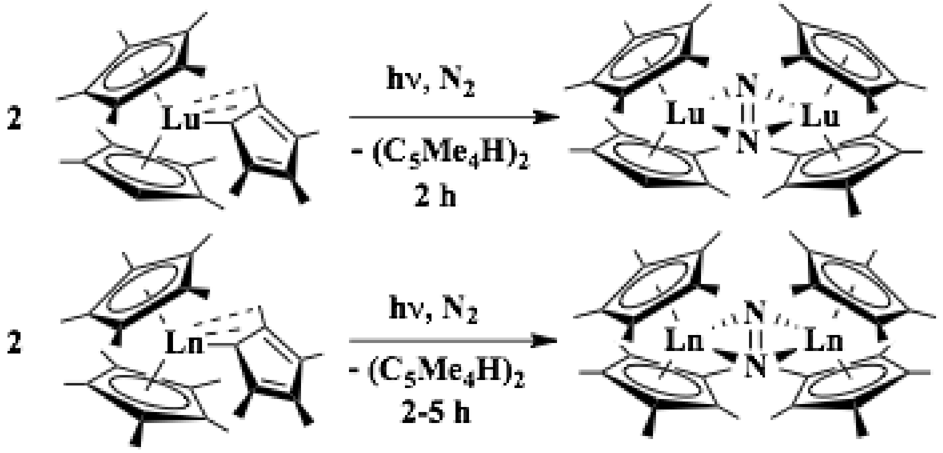
Professor William J. Evans, Chair

Dinitrogen can be reduced by photochemical activation of the trivalent rare earth bis(pentamethylcyclopentadienyl) allyl complexes $(\eta^5\text{-}C_5Me_5)_2Ln(\eta^3\text{-}C_3H_4R)$ (Ln = Y, Lu; R = H, Me) to form the $(N{=}N)^{2-}$ complexes, $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$. This demonstrates that productive organolanthanide photochemistry is not limited to complexes of the unusual $(\eta^3\text{-}C_5Me_4H)^{1-}$ ligand found in the heterometallic complexes $(C_5Me_5)_2(C_5Me_4H)Ln$ and $(C_5Me_5)(C_5Me_4H)_2Ln$ (Ln = Y, Lu, Dy). Photolytic activation of $(C_5Me_5)_2Ln(C_3H_5)$ (Ln = Y, La) in the presence of isoprene provides a rare photopolymerization route to polyisoprene. Irradiation of $(C_5Me_5)_2Y(C_3H_4Me)$ in the absence of other substrates results in the isolation of the corresponding 'tuckover' complex, $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$.

Chapter 1

Introduction and Background

Recently, the traditional view that rare earth complexes have minimal photochemistry was overturned by the observation that dinitrogen can be reduced to $(N{=}N)^{2-}$ by photolysis of the Ln^{3+} mixed ligand tris(cyclopentadienyl) rare earth complexes $(C_5Me_5)_2(C_5Me_4H)Ln$, **1-Ln** (Ln = Y, Lu, Dy), and $(C_5Me_5)(C_5Me_4H)_2Lu$.[1] The products of the two electron reductions of N_2, namely $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **2-Ln**, and $[(C_5Me_5)(C_5Me_4H)Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, respectively, are formed in reactions in which $(C_5Me_4H)^{1-}$ is oxidized to $(C_5Me_4H)_2$, Figure 1.[1]



1-Ln; Ln = Y, Lu, Dy **2-Ln**

$$2\,(C_5Me_4H)^{1-} \longrightarrow (C_5Me_4H)_2 + 2\,e^{1-}$$
$$N_2 + 2\,e^{1-} \longrightarrow (N{=}N)^{2-}$$

Figure 1. Reduction of dinitrogen with $(C_5Me_5)(C_5Me_4H)_2Lu$ (top reaction) and $(C_5Me_5)_2(C_5Me_4H)Ln$, **1-Ln** (Ln = Y, Lu, Dy), under photolytic conditions and formal half-reactions.

Observing a photochemical activation of a lanthanide-containing compound that could lead to the potent reduction of dinitrogen was unexpected considering Ln^{3+} ions are poor absorbers.[2-6] This low absorption is due to the Laporte forbidden nature of $4f \rightarrow 4f$ transitions which cannot relax via vibronic coupling, a consequence of the contracted nature of the 4*f* orbitals. Although lanthanide complexes can display intense emission properties, particularly with Eu^{3+} and Tb^{3+} in the red and green regions, respectively, this emission requires sensitizers to absorb the light. Laporte allowed ligand-to-metal charge transfer (LMCT) and ligand-to-ligand charge transfer (LLCT) transitions are known for the lanthanides,[4] but photoactivation does not generally lead to productive lanthanide-based transformations.[2-9] The other rare earth ions, Sc^{3+} and Y^{3+}, also have limited metal based photochemistry since they are d^0 species.[2-6] Although the 5*f* valence orbitals have a better radial extension than the 4*f* orbitals, there are still relatively few examples of photochemically activated reactions with actinide complexes.[10-13]

Density functional theory analysis of the unexpected rare earth photochemistry in Figure 1 suggests that absorptions involving the unusual $(\eta^3\text{-}C_5Me_4H)^{1-}$ ligand were responsible.[1] Specifically, two absorptions at 412 and 437 nm that are present in the heteroleptic $(C_5Me_5)_2(C_5Me_4H)Ln$ and $(C_5Me_5)(C_5Me_4H)_2Ln$ complexes, but not in the homoleptic analogs, $(C_5Me_5)_3Ln$ or $(C_5Me_4H)_3Ln$, appear to be involved. Due to the unprecedented nature of this photochemical activation, it was desirable to test the generality of this photoactivity beyond the two classes of mixed ligand tris(cyclopentadienyl) complexes shown in Figure 1.1. It was of particular interest to determine if this photoactivity depended on the unusual trihapto binding mode displayed by the $(C_5Me_4H)^{1-}$ ligand found in each of these complexes. Extending the reactions of Y, Dy, and Lu ions to the larger metal ions in the lanthanide series is problematic because synthesis of pure $(C_5Me_5)_2(C_5Me_4H)Ln$ and $(C_5Me_5)(C_5Me_4H)_2Ln$ complexes for the larger lanthanides (La, Ce, Pr, Nd, Sm) is complicated by ligand rearrangement.[14]

Given the trihapto nature of the suspected photoactive $(\eta^3\text{-}C_5Me_4H)^{1-}$ ligand, it was of interest to determine if the structurally related allyl complexes, $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$,[15-17] **3-Ln**, could be similarly photoactivated. If so, this could provide a more facile synthetic route to the reduced dinitrogen complexes, $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **2-Ln**, since the allyl complexes are precursors to the heteroleptic $(C_5Me_5)_{3-x}(C_5Me_4H)_xLn$ complexes.[18,19] They are also precursors to the loosely-ligated tetraphenylborate cationic metallocene complexes, $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$,[17,20-22] which can be used to synthesize the $(N{=}N)^{2-}$ complexes.[23]

In this thesis, evidence will be provided to show that the allyl complexes **3-Y**, **3-La**, and **3-Lu**, as well as the newly synthesized methylallyl derivatives of these complexes, $(C_5Me_5)_2Y(C_3H_4Me)$, **4-Ln**, are photoactive, and that this reactivity can be used not only to reduce dinitrogen, but also to polymerize isoprene. Photopolymerization of isoprene has only been observed in a few instances in the literature and generally involves radical initiators.[24-26] Investigations of the photoactivity for these complexes with various solvents under an argon atmosphere will also be discussed. Density functional theory (DFT) was used to explain the photochemistry of this allyl metallocene system.

Chapter 2

Synthesis and Structure of $(C_5Me_5)_2Ln(C_3H_4Me)$

Introduction

While investigating the photochemical activation of the rare earth allyl complexes $(C_5Me_5)_2Ln(C_3H_5)$, **3-Ln**, it became of interest to determine the fate of the ligand that was suspected to undergo photolysis. To aid in identifying possible organic byproducts of the allyl complexes, the methylallyl analog of **3-Ln**, namely $(C_5Me_5)_2Ln[\eta^3\text{-}CH_2C(Me)CH_2](THF)_x$ (Ln = Y, La, Lu; x = 0, 1), **4-Ln,** was synthesized from a methylallyl Grignard reagent and $(C_5Me_5)_2LnCl_2K(THF)$[16] and fully characterized.

Experimental Details

The syntheses and manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using glovebox, vacuum line, and Schlenk techniques. Solvents were dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium potassium alloy, degassed, and vacuum transferred prior to use. KC_5Me_5,[27] $(C_5Me_5)_2Ln(C_3H_5)$,[16] **2-Ln**, and $(C_5Me_5)_2LnCl_2K(THF)$[16] were prepared according to the literature. 2-Methylallylmagnesium chloride (0.5 M, in THF) and 1,4-dioxane were purchased from Sigma-Aldrich and were used as received. ^1H NMR spectra and were obtained on a Bruker DRX500 MHz spectrometer with a BBO probe at 25 °C, and ^{13}C NMR spectra were obtained the same spectrometer operating at 126 MHz with a TCI cryoprobe at 25 °C unless otherwise specified. IR samples were prepared as KBr pellets and the spectra were obtained on a Varian 1000 FT-IR system or a Jasco FT/IR-4700 - ATR-PRO ONE. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS analyzer.

$(C_5Me_5)_2Y[\eta^3-CH_2C(Me)CH_2]$, 4-Y. In a dinitrogen-filled glovebox , a 0.5 M solution of 2-methylallylmagnesium chloride in THF (7.20 mL, 3.60 mmol) was added dropwise to a stirred suspension of $(C_5Me_5)_2YCl_2K(THF)$ (1.937 g, 3.577 mmol) in toluene (125 mL). After stirring overnight, the solvent was removed under vacuum, producing a pale yellow tacky solid that was then suspended in 125 mL of hexanes. Dropwise addition of 1,4-dioxane (5 mL) to the stirred slurry gave in an immediate color change to neon yellow. After stirring for 12 h, the yellow slurry was centrifuged and filtered. The solvent was removed under vacuum to yield **4-Y** as a yellow microcrystalline solid. To ensure the complete removal of coordinating solvents, the yellow solid was ground to a fine powder and placed into a sublimation tube equipped with a greaseless Teflon stopcock and attached to a vacuum line. The yellow powder was dried under high vacuum (1×10^{-5} torr) at 45 °C for 8 h. The temperature was raised by 5 °C every 12 h until reaching 55 °C. After an additional 12 h, the yellow powder was brought into a glovebox free of coordinating solvents and stirred in hexanes for 30 min. The yellow solution was centrifuged and filtered. Solvent was removed under vacuum to yield a yellow microcrystalline solid (1.052 g, 70%). Yellow crystals suitable for X-ray crystallography were grown from a saturated hexane solution at −35 °C. ^{1}H NMR (C_6D_6): δ 2.19 (d, 4H, $CH_2C(Me)CH_2$), 1.96 (s, 33H, $(C_5Me_5)_2$, $CH_2C(Me)CH_2$). ^{13}C NMR (C_6D_6): δ 169.8, 117.1, 64.6, 29.4, 11.6. IR: 3054m, 2966s, 2908s, 2859s, 2725s, 2391vw, 2287vw, 1509m, 1437w, 1379w, 1316m, 1247m, 1161w, 1025s, 951w, 849m, 767s, 677m cm^{-1}. Anal. Calcd for $C_{24}H_{37}Y$: C, 69.55; H, 9.00. Found: C, 69.49; H, 9.24.

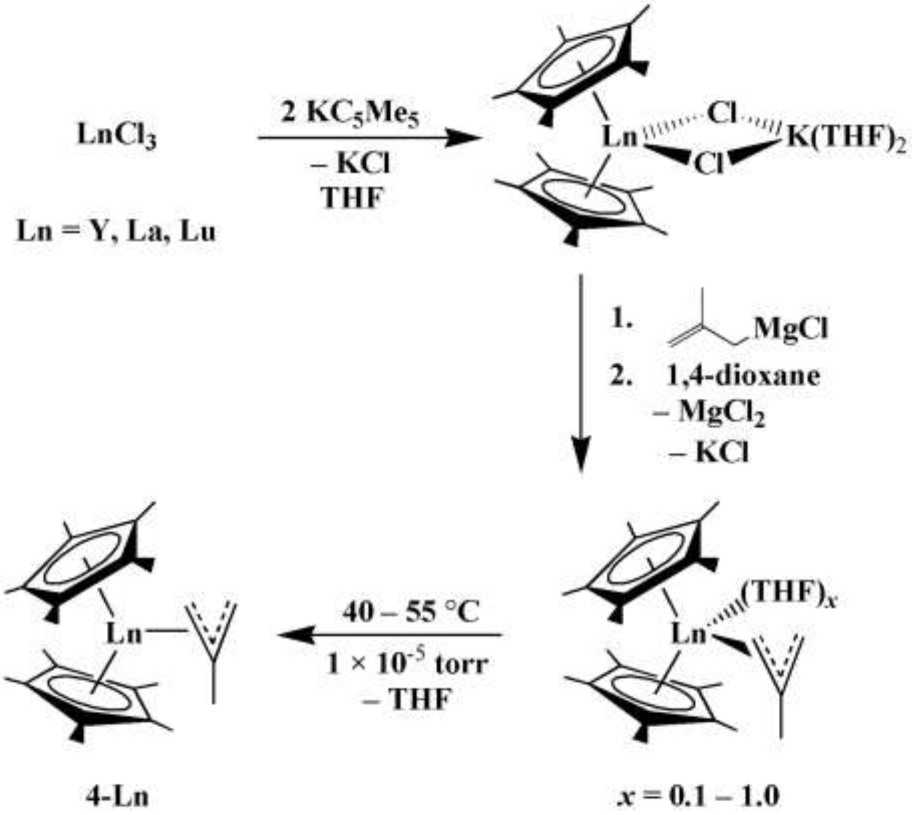
$(C_5Me_5)_2La[\eta^3-CH_2C(Me)CH_2](THF)$, 4-La. As described above for **4-Y**, 2-methylallylmagnesium chloride (3.69 mL, 1.84 mmol) was reacted with $(C_5Me_5)_2La(\mu-Cl)_2K(THF)$ (1.142 g, 1.843 mmol) in toluene (125 mL), making a slightly yellow solution.

1,4-dioxane (2 mL) was added to isolate **4-La**, a neon yellow microcrystalline powder (0.412 g, 42 %). Pale yellow crystals suitable for X-ray crystallography were grown from a saturated toluene solution at −35 °C. ^{1}H NMR (C_6D_6): δ 3.51 (s, 4H, THF), 2.63 (s, 4H, THF), 2.08 (s, 3H, $CH_2C(\mathit{Me})CH_2$), 2.00 (s, 30H, $(C_5\mathit{Me}_5)_2$), 1.33 (s, 4H, $C\mathit{H}_2C(Me)C\mathit{H}_2$). ^{13}C NMR: ($C_6D_6$) δ 72.6, 71.2, 27.6, 26.2, 12.0. Anal. Calcd for $C_{28}H_{45}LaO$: C, 62.68; H, 8.45. Found: C, 62.63; H, 8.50.

$(C_5Me_5)_2Lu[\eta^3\text{-}CH_2C(Me)CH_2]$, 4-Lu. As described above for **4-Y** and **4-La**, 2-methylallylmagnesium chloride (3.62 mL, 1.81 mmol) was reacted with $(C_5Me_5)_2Lu(\mu\text{-}Cl)_2K(THF)$ (1.136 g, 1.810 mmol) in toluene (125 mL), making a slightly yellow solution. 1,4-dioxane (2 mL) was added to isolate **4-Lu**, a neon yellow microcrystalline powder (0.456 g, 52 %). Yellow crystals suitable for X-ray crystallography were grown from a saturated toluene solution at −30 °C. Any coordinating solvent was removed in a manner similar for **4-Y** as described above. ^{1}H NMR (C_6D_6): δ 2.87 (s, 4H, $C\mathit{H}_2C(Me)C\mathit{H}_2$), 2.30 (s, 3H, $CH_2C(\mathit{Me})CH_2$), 1.96 (s, 30H, $(C_5\mathit{Me}_5)_2$). ^{13}C NMR (C_6D_6): δ 117.1, 63.8, 29.9, 11.6. Anal. Calcd for $C_{24}H_{37}Lu$: C, 57.59; H, 7.45. Found: C, 57.26; H, 7.57.

Results and Discussion

The new complexes **4-Y**, **4-La**, and **4-Lu** were synthesized by first reacting two equivalents of KC_5Me_5 with $LnCl_3$ to yield the “ate” salt, $(C_5Me_5)_2YCl_2K(THF)$, followed by the addition of 2-methylallylmagnesium chloride, yielding a bright yellow solvated product, eq 1. The solvated species were then held under low pressures and mild heating for 48-72 hr. Single crystals of **4-Y** suitable for analysis by X-ray diffraction methods were grown at −35 °C from a saturated hexane solution, whereas X-ray quality crystals of **4-Lu** were grown at −30 °C from a saturated toluene solution. The structural data showed no coordinating solvents bound to either metal center. Crystals of THF solvated **3-La** were grown from saturated toluene solutions at −35 °C.



(1)

X-ray Crystallographic Data. Crystallographic information was obtained for complexes **4-Y**, **4-La**, and **4-Lu** shown in Figures 2, 3, and 4, respectively, as thermal ellipsoid plots. Select bond lengths angles for complexes **3-Ln** and **4-Ln** where Ln = Y, La, and Lu are given in Table 1.

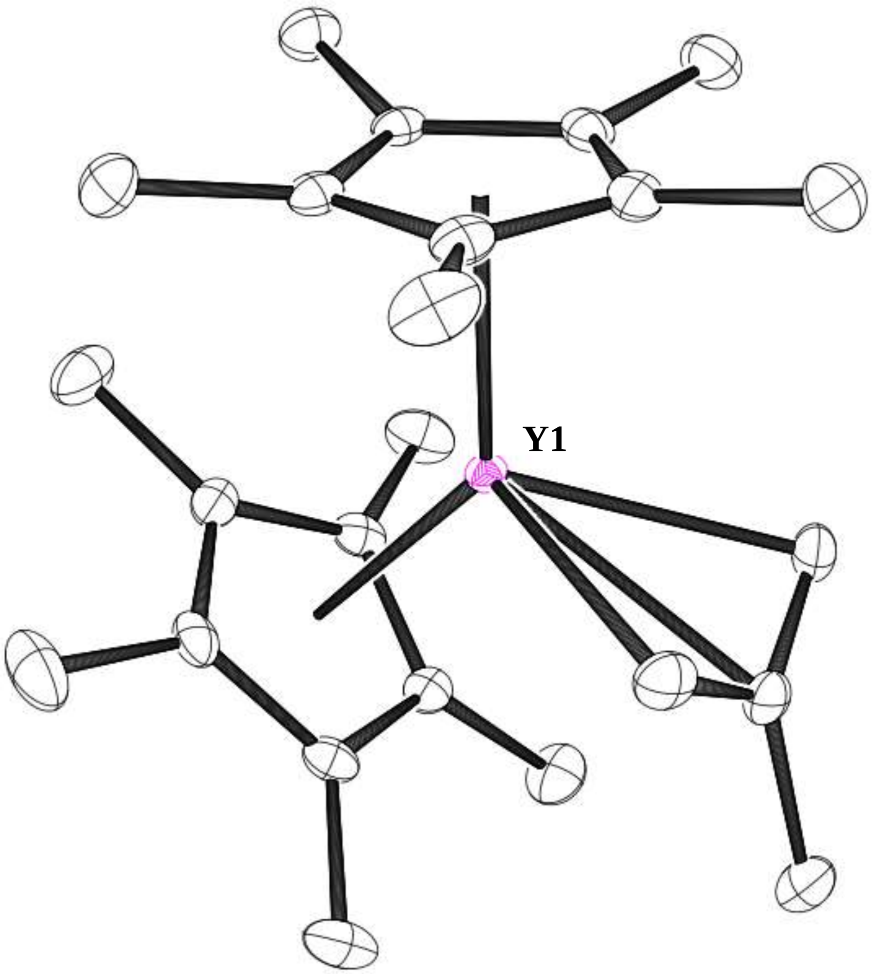


Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2Y(C_3H_4Me)$, **4-Y**, drawn at the 50% probability level. The second independent molecule of **4-Y** in the unit cell and hydrogen atoms are omitted for clarity.

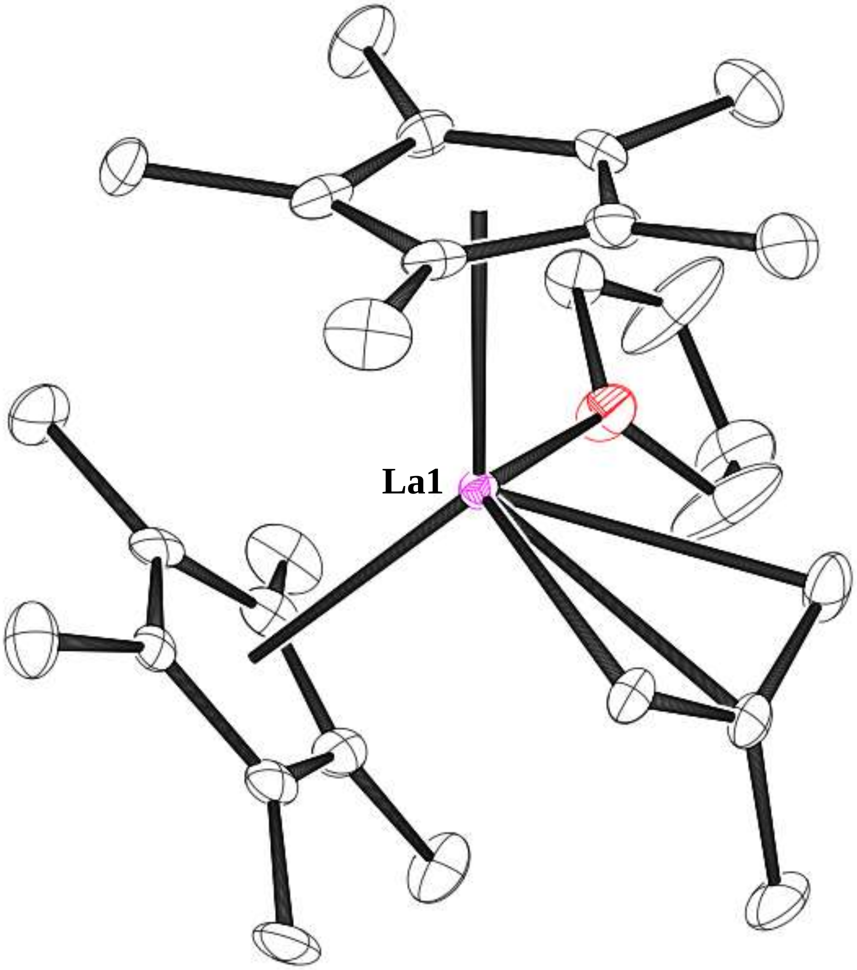


Figure 3. Preliminary thermal ellipsoid plot of $(C_5Me_5)_2La(C_3H_4Me)(THF)$, **4-La**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

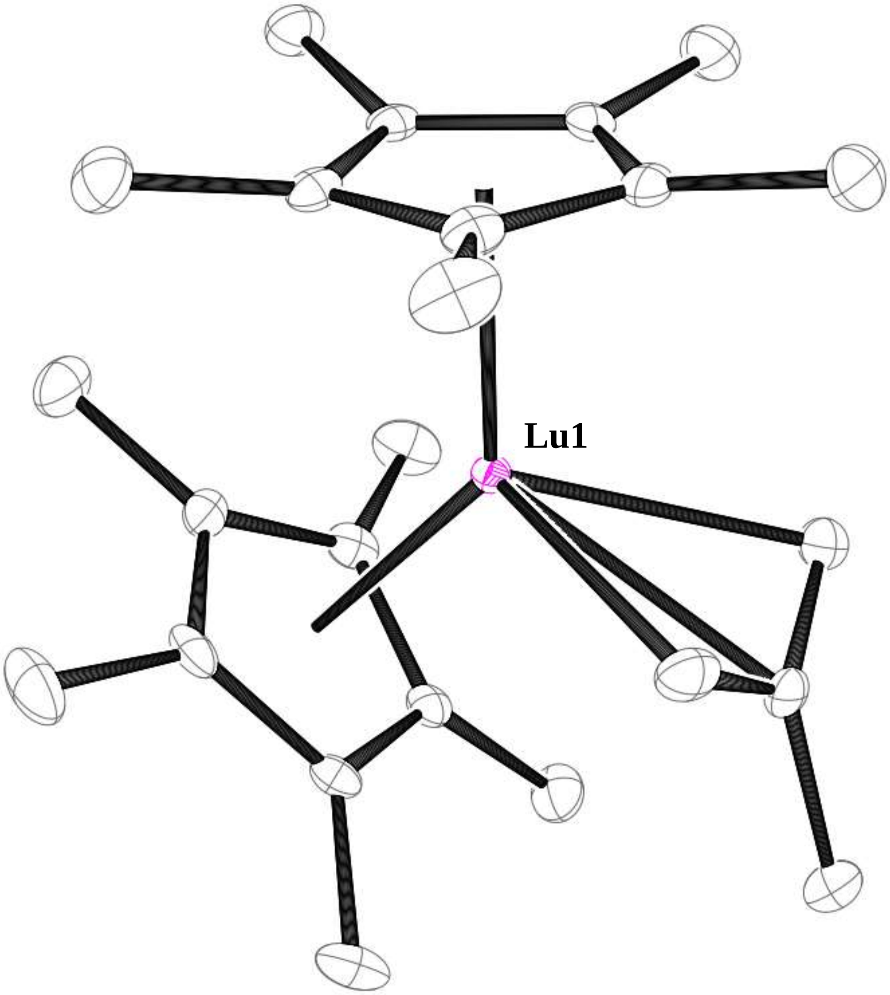


Figure 4. Thermal ellipsoid plot of $(C_5Me_5)_2Lu(C_3H_4Me)$, **4-Lu**, drawn at the 50% probability level. The second independent molecule of **4-Lu** in the unit cell and hydrogen atoms are omitted for clarity.

Table 1. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) for $(C_5Me_5)_2Y(C_3H_5)$,[16] **3-Y**, $(C_5Me_5)_2Lu(C_3H_5)$,[16] **3-Lu**, $(C_5Me_5)_2Y(C_3H_4Me)$, **4-Y**, and $(C_5Me_5)_2Lu(C_3H_4Me)$, **4-Lu**.

Cmpd	Ln−C(centroid)		C(centroid)−Ln −C(centroid)	Ln−C(allyl)			C(allyl)−C(allyl)		C(allyl) −C(allyl) −C(allyl)
3-Y	2.381	2.362	138.8	2.582(2)	2.601(2)	2.582(2)	1.392(3)	1.391(3)	125.9(2)
3-Lu	2.318	2.301	138.5	2.549(5)	2.545(5)	2.548(4)	1.383(9)	1.382(8)	127.7(5)
4-Y	2.403	2.365	135.7	2.570(2)	2.702(2)	2.562(2)	1.403(3)	1.401(3)	123.24(2)
4-Lu	2.349	2.309	135.7	2.523(2)	2.654(2)	2.523(2)	1.403(3)	1.396(3)	123.4(2)

As shown in Table 2, notable similarities exist between the coordination environments for complexes of **3-Ln** and **4-Ln**. C(allyl)−C(allyl) distances for the **3-Ln** and **4-Ln** complexes range from 1.382(8) Å to 1.403(3) Å. These bond distances are intermediate between the typical values for $C(sp^3)$–$C(sp^2)$ single bonds and $C(sp^2){=}C(sp^2)$ double bonds of 1.51 Å and 1.32 Å, respectively,[29] indicating a delocalized π system across the allyl ligand.

The allyl complexes **4-Y**, **4-La**, and **4-Lu** are similar to the photochemically active compounds, $(C_5Me_5)_2Ln(\eta^3–C_5Me_4H)$, **1-Ln**, and $(C_5Me_5)(C_5Me_4H)_2Lu$ in Figure 1 in terms of their yellow color, two $(\eta^5\text{-}C_5Me_5)^{1-}$ rings, and one η^3-ligand. They are also similar to their corresponding allyl complexes, $(C_5Me_5)_2Ln(C_3H_5)$, **3-Ln**, in color and ligand environment, and comparisons in bond lengths and angles show the coordination environments of the **4-Ln** complexes are comparable to those of the **3-Ln** complexes. As such, they were good candidates to investigate for the photochemistry observed in Figure 1, excluding **4-La**. Aliquots of **4-La** were found to be partially solvated after rigorous desolvation attempts, and irradiation of the resulting samples yielded an ^{1}H NMR spectrum consistent with the presence of a THF ring opened product. Therefore, the complex will not be considered further in this thesis.

Chapter 3

Photoreactivity of Rare Earth Allyl Complexes with Dinitrogen

Introduction

To determine if complexes beyond $(C_5Me_5)_2(\eta^3\text{-}C_5Me_4H)Ln$, **1-Ln**, and $(C_5Me_5)(C_5Me_4H)_2Ln$ could be photoactivated to reduce N_2 to $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **2-Ln**, irradiation of the rare earth allyl complexes $(C_5Me_5)_2Ln(C_3H_4R)$, **3-Ln** (Ln = Y, Lu; R = H) and **4-Ln** (Ln = Y, R = Me), in the presence of dinitrogen was explored. Samples of **3-Lu**, **3-Y**, and **4-Y** were irradiated and analyzed by ^{1}H NMR spectroscopy and gas chromatography/mass spectrometry (GC/MS). Complex **3-Y**, **3-Lu**, and **4-Y** were further characterized by UV-visible absorption spectroscopy and studied by density functional theory (DFT) calculations.

Experimental Details

General procedures were as described in Chapter 2. Propene and isobutylene were purchased from Sigma-Aldrich and were used as received. Accurate mass spectra were recorded on a Thermo Scientific Trace GC Ultra. All photolysis experiments were conducted in a hood with aluminum foil covered windows and a Hanovia medium pressure, 450-watt, mercury vapor lamp (PC451050/610741). The 5.5 inch long lamp was clamped to hang inside a 13 inch x 1.5 inch diameter cavity of a double-walled quartz water cooling jacket. Tap water at 24 °C flowed through the jacket at a rate of 6.4 L per minute and kept the temperature in the hood between 25 °C and 27 °C. Samples were placed adjacent to the outer wall of the cooling jacket in the middle of the hood. Absorption spectra were collected using a Cary 50 Scan UV-Vis spectrometer at 25 °C in toluene or hexanes. Density functional theory (DFT) calculations performed by Megan E. Fieser and the Filipp Furche group were carried out on **3-Lu**, **3-Y**, and **4-Y**, using the hybrid meta-generalized gradient approximation functional TPSSh.[30] Small-core

ECPs[31] and def-TZVP basis sets[32] were used for Y and Lu. All calculations were performed using the Turbomole quantum chemistry software.[33] Time-dependent DFT (TDDFT) calculations[35] were also performed to simulate the UV−vis spectrum for **3-Lu**, **3-Y** and **4-Y**. A full description of the computational methods is reported in Megan E. Fieser's dissertation.[14]

Photolysis of $(C_5Me_5)_2Lu(C_3H_5)$, 3-Lu, to Form $[(C_5Me_5)_2Lu]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 2-Lu. In a nitrogen-filled glovebox free of coordinating solvents, **3-Lu** (12 mg, 0.025 mmol) was dissolved in C_6D_6 (1 mL) and transferred to a sealable J-Young NMR tube equipped with a greaseless stopcock. Under irradiation for 24 h, the yellow solution became deep red, and ^1H NMR analysis revealed full conversion to **2-Lu**.[23]

Photolysis of $(C_5Me_5)_2Y(C_3H_5)$, 3-Y, to Form $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 2-Y. As described for **3-Lu** above, irradiation of a yellow solution of **2-Y** (10 mg, 0.025 mmol) for 12 h gave a 1.5:1 mixture of **3-Y** and **2-Y** by ^1H NMR spectroscopy.[23]

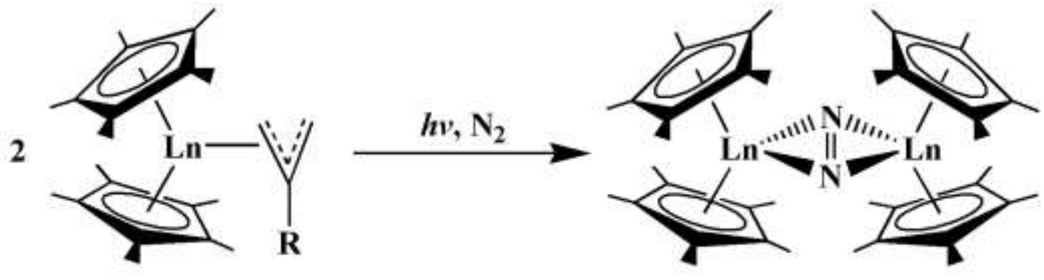
Photolysis of $(C_5Me_5)_2Y(C_3H_4Me)$, 4-Y, to Form $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, 2-Y. As described above for **3-Lu** and **3-Y**, photolysis of a yellow solution of **4-Y** (10 mg, 0.025 mmol) for 14 h gave a 1:2 mixture of **4-Y** and **2-Y**.[23]

Large Scale Yttrium Photolyses. Large scale reactions were run in 250 mL round bottom vessels containing **3-Y** (500 mg, 1.25 mmol) and **4-Y** (518 mg, 1.25 mmol) dissolved in toluene (~50 mL). After the magnetically stirred solutions had been irradiated for 24 h, the yellow solutions became red-orange. The solutions were centrifuged and filtered before the solvent was removed under vacuum. The resulting red-orange powders were shown by ^1H NMR spectroscopy to contain the starting material and the **2-Y** product in ratios of 1.2:1 for **3-Y** and 1:1.1 for **4-Y**.[23]

GC/MS Studies. Photolysis experiments were run in methylcyclohexane to analyze the gas present in the head-space above the solution. GC/MS analysis of the gas formed after irradiation of **3-Y** (50 mg, 0.1 mmol) and **4-Y** (61 mg, 0.12 mmol) in methylcyclohexane (7 mL) under N_2 revealed significant molecular ion peaks at m/z = 41.16 and 56.03 at retention times (RT) of 1.72 and 2.32 min, respectively. Analogous reactions run with ~50 mg of **3-Y** or **4-Y** in 4 mL of toluene-d_8 revealed peaks at m/z = 42.14 and 57.18 at RT = 1.72 and 2.32 min. The same analyses were performed on pure gas samples of propene and isobutylene, wherein significant molecular ion peaks were found at m/z = 41.16 and 56.03 at retention times (RT) of 1.72 and 2.32.

Results and Discussion

Photolysis of solutions of **3-Y**, **3-Lu**, and **4-Y** in benzene under dinitrogen produced the $(N{=}N)^{2-}$ complexes, $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (Ln = Y, **2-Y**; Lu, **2-Lu**), which were identified by ^{1}H NMR spectroscopy,[23] eq 2. Only in the case of **2-Lu** was the reaction quantitative in 24 h. For **3-Y** and **4-Y**, conversions of only 40-45% were observed in 24 h with the N_2 reduction product, **2-Y**, being the only metallocene product as determined by ^{1}H NMR spectroscopy. Using cyclooctane as an internal standard, it appeared that **4-Y** generated about 50% more **2-Y** than **3-Y** in the same time period.



(2)

R = H; Ln = Y, 3-Y; Lu, 3-Lu
R = Me; Ln = Y, 4-Y

2-Ln; Ln = Y, Lu

GC/MS analysis of the gas present in the head-space above large-scale irradiation of **3-Y** under N_2 in methylcyclohexane gave a molecular ion peak that matched the m/z and retention time of a standard sample of propene. The analogous experiment in toluene-d_8, gave a peak with an m/z one mass unit higher appropriate for propene-d_1. Analogous photolysis of **4-Y** in methylcyclohexane gave a peak with the correct m/z of isobutene and the corresponding reaction in toluene-d_8 gave a peak one mass unit higher. These results are consistent with formation of allyl and methylallyl radicals upon photolysis that hydrogen abstract from solvent to form propene and isobutene.[35,36] No evidence was obtained for dimers of allyl and methylallyl radicals. Hydrogen abstraction from solvent would be expected to be prevalent based on the much higher concentration of solvent compared to the radical concentration.

UV-visible absorption spectra were taken of **3-Y**, **3-Lu**, and **4-Y** (Figure 5), to determine how they compared with photoactive **1-Ln** (Figure 1). The spectra of the allyl complexes are similar to those of **1-Y** and **1-Lu**[1] in that they contain two broad absorptions with the lowest energy absorption being near the 405 nm emission of the medium pressure mercury vapor lamp used for irradiation.

A DFT study on $(C_5Me_5)_2Ln(\eta^3\text{–}C_3H_5)$, **3-Ln** (Ln = Lu, Y), revealed that the HOMO has electron density located on the allyl ligand while the LUMO is a d_{z^2} orbital on the metal center, Figure 4. Time-dependent DFT (TDDFT) studies were done to calculate an excitation spectrum of **3-Ln**, from which excitation wavelengths around λ_{max} = 360 and 390 nm were predicted for **3-Lu** and excitation wavelengths around λ_{max} = 370 and 390 nm were predicted for **3-Y**. These excitation energies match the experimental spectra, but the oscillator strength for the low energy excitation (λ_{max} = 389 nm) for **3-Lu** is not as high as would be expected from theory. Upon closer analysis of the absorptions, the lowest energy absorption for both **3-Y** and **3-Lu** is the

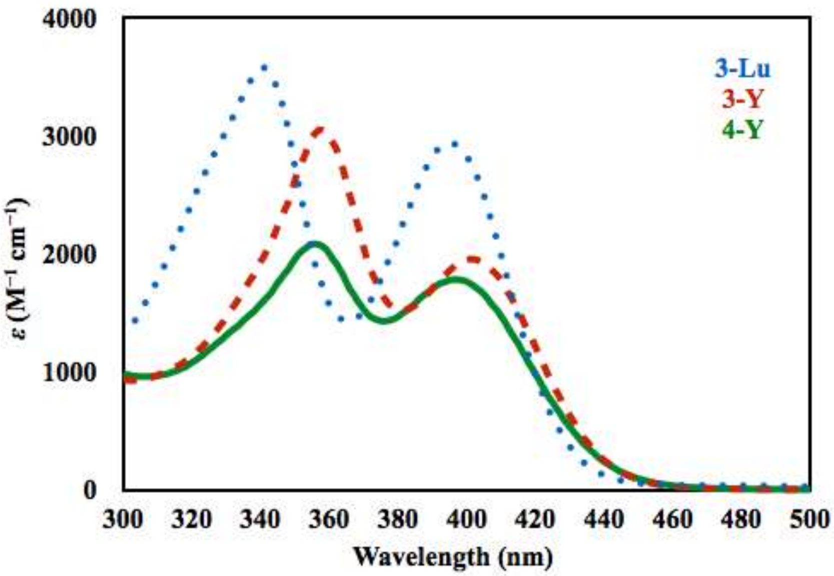


Figure 5. UV-vis spectra of $(C_5Me_5)_2Y(C_3H_5)$, **3-Lu** (dotted blue line), $(C_5Me_5)_2Y(C_3H_5)$, **3-Y** (dashed red line), and $(C_5Me_5)_2Y(C_3H_4Me)$, **4-Y** (solid green line) obtained from 0.46 mM hexane solutions at room temperature.

HOMO-LUMO ligand-to-metal charge transfer (LMCT) from the trihapto allyl ligand to a d_{z^2} orbital. This is analogous to the first two excitations of **1-Y** and **1-Lu**, which were also predicted from DFT to be LMCT transitions from the trihapto ligand to a d_{z^2} orbital that led to the observed photoreduction chemistry. The next excitations for **3-Y** and **3-Lu** less than λ_{max} = 300 nm are all predicted to be LMCT from the $(\eta^5\text{-}C_5Me_5)^{1-}$ ligands to d_{z^2} orbital which is also analogous to the calculations of **1-Ln**.

DFT studies on the methylallyl complex, **4-Y**, reveal a similar HOMO and LUMO as seen for both **3-Y** and **3-Lu**, Figure 6. The TDDFT predicted similar excitations near λ_{max} = 360 and 390 nm as was found for **3-Y**. The oscillator strength of the excitation for **4-Y** near λ_{max} = 390 nm is slightly higher than that for **3-Y**, while the oscillator strength of the excitation for **4-Y**

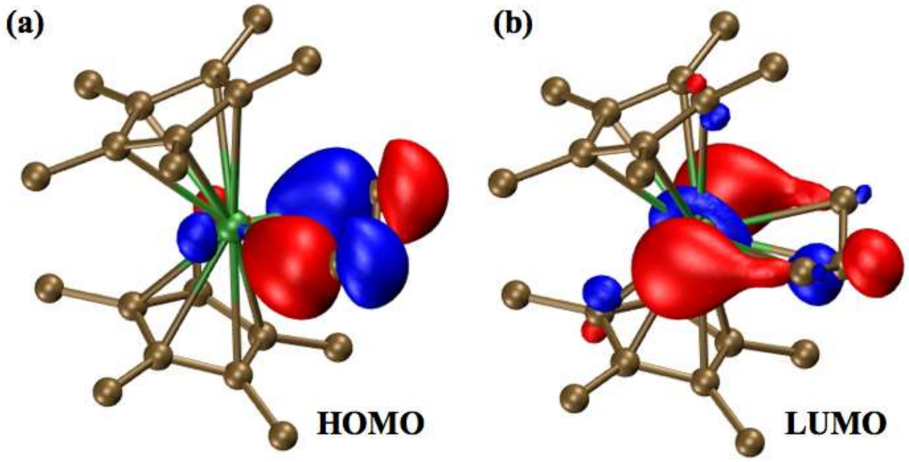


Figure 6. Molecular orbital plots of (a) the HOMO and (b) the LUMO for **3-Lu**, using a contour value of 0.06.

near λ_{max} = 360 nm is almost half that for **3-Y**. This matches the observed differences in the experimental UV-vis spectra.

As shown in eq 2, the allyl complexes **3-Lu**, **3-Y**, and **4-Y** can be photoactivated to reduce N_2 to $(N{=}N)^{2-}$. They are similar to the photochemically active compounds, $(C_5Me_5)_2Ln(\eta^3\text{-}C_5Me_4H)$, **1-Ln**, and $(C_5Me_5)(C_5Me_4H)_2Ln$ in terms of their UV-vis spectra. DFT calculations suggest that the source of the photoactivity is a LMCT band near λ_{max} = 390 nm arising from a transition between the HOMO of the allyl complexes, which is localized on the allyl ligand, and the LUMO, which is mainly d_{z^2}. The calculations indicate that this would generate an allyl radical and an excited state Y^{2+} species "$(C_5Me_5)_2Y$" which should be capable of reducing dinitrogen based on reactivity and EPR spectroscopic studies on the recently discovered Y^{2+} complexes.[37,38] Identification of propene and isobutene by GC/MS in the head-space over the photolysis solution is consistent with formation of the allyl radicals followed by hydrogen abstraction.[35,36] Reactions done in toluene-d_8 show propene-d_1 and isobutene-d_1 are produced, which is consistent with radical abstraction from solvent. This result is parallel to postulated pathway of photolysis of the $(C_5Me_5)_{3-x}(C_5Me_4H)_xLn$ complexes which have $(C_5Me_4H)_2$ byproducts from formation of C_5Me_4H radicals.[1]

Chapter 4

Photopolymerization of Isoprene

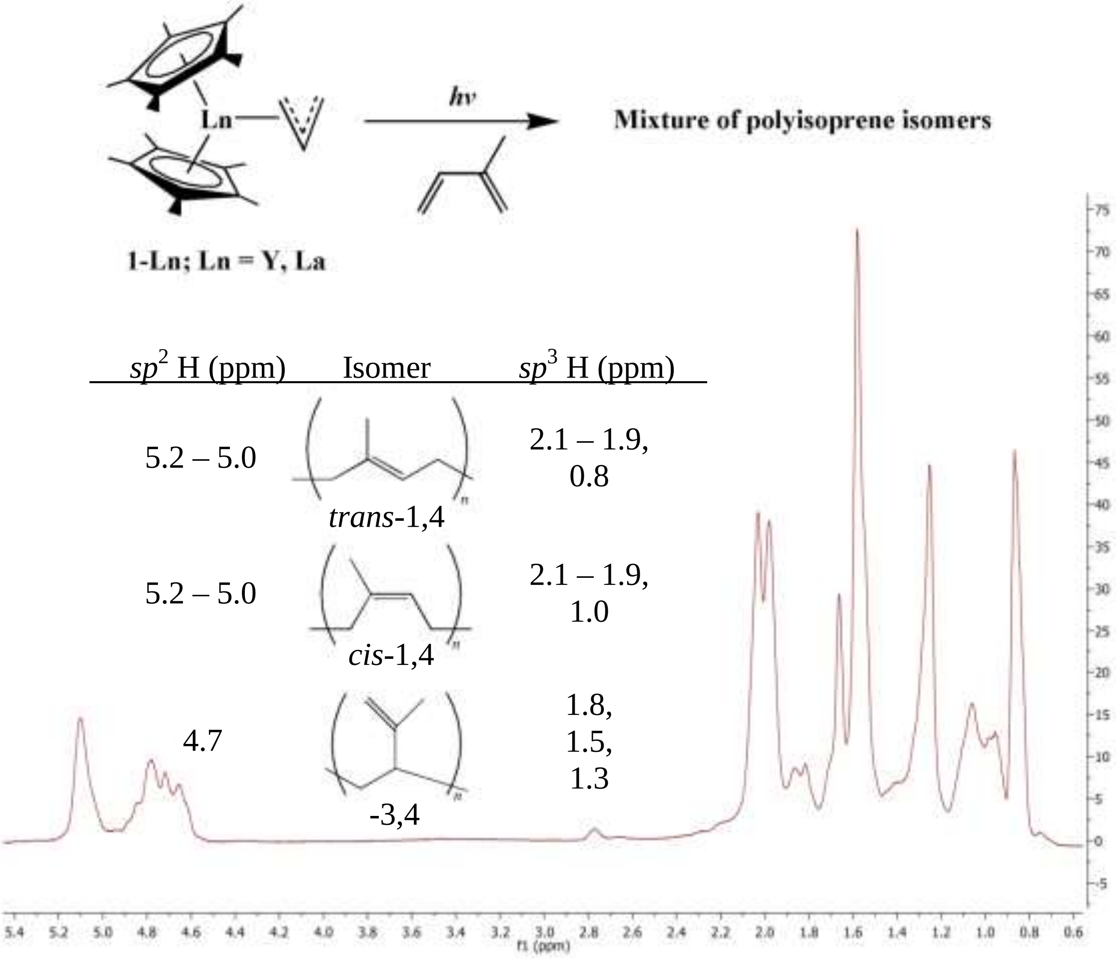
Introduction

As mentioned in Chapter 1, the rare earth allyl complex $(C_5Me_5)_2Lu(C_3H_5)$, **3-Lu**, was shown by Dr. Megan Fieser to form a polymer when irradiated in neat isoprene,[14] though the polymer formed was not fully characterized. The cis-1,4-isomer of polyisoprene is applied commercially as an synthetic analog for natural rubber[39] and has had few instances of being formed via photoactivation.[24-26] To further explore this example of photopolymerization, **3-Y** and **3-La** were irradiated in neat isoprene, and the polymers generated were analyzed via NMR spectroscopy and gel permeation chromatography (GPC).

Experimental Details

General procedures were as described in Chapter 2. Isoprene (Acros) was dried over molecular sieves and degassed by three freeze-pump-thaw cycles.

Isoprene Reactivity. In an argon-filled glovebox, ~50 mg of **3-Ln** (Ln = Y, La) and a magnetic stir bar were added to a sealable 50 mL sidearm Schlenk flask equipped with a greaseless stopcock. The flask was added to the high vacuum line and argon was removed under vacuum. Isoprene (approximately 10 mL) was vacuum transferred into the flask. After irradiation for 12 h, gel had formed on the side of the flask near the light source. The amount of gel continued to increase over the course of 8 days of irradiation. Excess isoprene was removed under vacuum to leave a thick gel that was analyzed by GPC at the Goodyear Tire Company to be low molecular weight with a number average molar mass (M_n) and mass average molar mass (M_w) < 6000. ^1H NMR and ^{13}C NMR spectra in $CDCl_3$ of the polymer that had been washed with MeOH and treated with HCl contained resonances for cis-1,4-, trans-1,4-, and 3,4-polyisoprene with the largest peaks for 3,4- polyisoprene shown in Figure 7.[40-42]



sp^2 H (ppm)	Isomer	sp^3 H (ppm)
5.2 – 5.0	*trans*-1,4	2.1 – 1.9, 0.8
5.2 – 5.0	*cis*-1,4	2.1 – 1.9, 1.0
4.7	-3,4	1.8, 1.5, 1.3

Figure 7. ^{1}H NMR spectrum of the gel isolated after irradiation of $(C_5Me_5)_2Y(C_3H_5)$, **3-Y**, in neat isoprene with a table of assigned chemical shifts for the isomers of polyisoprene based on literature values.[40-42] While it can be seen that peaks describing both *sp*^{2} and *sp*^{3} bonding environments can indicate the presence of an isomer, significant overlap hinders any viable degree of quantification.

Results and Discussion

Irradiation of **3-Y** and **3-La** in neat isoprene led to formation of low molecular weight polyisoprene. NMR evidence showed that a mixture of cis-1,4-, trans-1,4- and 3,4-polyisoprene had formed with a predominance of the 3,4-isomer shown in Figure 7. This is consistent with radical polymerization of isoprene as opposed to rare-earth metal based coordination polymerization that can give specific isomers.[43-50] Although selective polymerization was not observed in this case, the photopolymerization of isoprene is not often observed[24-26] and may provide new methods of control in polymerization reactivity.

Chapter 5

Photoreactivity of $(C_5Me_5)_2Ln(C_3H_4Me)$ in Inert Conditions

Introduction

During the course of this study, it became desirable to observe the irradiation of rare earth allyl complexes in the absence of dinitrogen, isoprene, or other added substrates for possible reactivity such as solvent activation. Activation of arenes by trivalent rare earth complexes has been observed in metallocene hydrides via hydrogen exchange[51,52] and H/F exchange,[53] the alkyl samarium metallocenes $(C_5Me_5)_2SmMe(THF)$[54] and $[(C_5Me_5)_2SmMe]_3$[55] via σ-bond metathesis to form methane, and ligand reduction through steric crowding.[21] This also presented the opportunity to access reactivity of the allyl complexes with other compounds that is unique to photoactivation. To probe the extent of this photoreactivity, irradiation of $(C_5Me_5)_2Ln(C_3H_4Me)$, **4-Ln** (Ln = Y, Lu), under argon atmospheres and in hydrocarbon solvents was explored. Reactivity found with the organic compound fluorene ($C_{13}H_{10}$) will also be described.

Experimental Details

General procedures were as described in Chapter 2. Fluorene was purchased from Sigma-Aldrich and sublimed prior to use.

$(C_5Me_5)_2Y(\mu\text{-H})(\mu\text{-}\eta^1\text{:}\eta^5\text{-CH}_2C_5Me_4)Y(C_5Me_5)$, 5-Y, through Photolysis of $(C_5Me_5)_2Y(C_3H_4Me)$, 4-Y In an argon-filled glovebox free of coordinating solvents, **4-Y** (103.8 mg, 0.2505 mmol) was dissolved in benzene (~30 mL) and transferred to a sealable 125 mL sidearm Schlenk flask equipped with a greaseless stopcock. While stirring, the yellow solution was open to reduced pressure and quickly closed three times in succession to achieve a headspace of reduced pressure. After 2.5 h of irradiation with stirring, the yellow solution had become red. The apparatus was brought back into an argon-filled glovebox free of coordinating solvents. After adding a small amount of toluene (~3 mL), volatiles were removed under reduced pressure to afford a red oil. X-ray quality crystals were grown from a concentrated pentane solution at −30 °C. X-ray crystallography of the red crystals were analyzed as the previously reported $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$, **5-Y**, in a new unit cell, and ^{1}H NMR spectroscopy correlated with what is found in the literature.[56]

$(C_5Me_5)_2Y(\eta^3\text{-}C_{13}H_9)$, 6. In an argon-filled glovebox free of coordinating solvents, **4-Y** (118.1 mg, 0.2850 mmol) and fluorene (196.8 mg, 1.184 mmol) were dissolved in benzene (~30 mL) and transferred to a sealable 125 mL sidearm Schlenk flask equipped with a greaseless stopcock. The solution was put under reduced pressure in the same manner as described above for **5-Y**. After 4 h of irradiation with stirring, the yellow solution remained yellow. This was brought back into an argon-filled glovebox free of coordinating solvents. After adding a small amount of toluene (~3 mL), the yellow solution was pumped down to a yellow oil that was extracted with pentane, filtered, and pumped back down to a yellow oil containing **6**. Crystals of **6** suitable for X-ray crystallography were formed by dissolving the crude oil in hot hexanes and slowly cooling the sample to room temperature, then placing the sample in a freezer at −30 °C for 2 days. ^{1}H NMR (C_6D_6): δ 8.26 (d, 2H), 7.28 (m, 4H), 7.20 (t, 2H), 5.95 (s, 1H), 5.95 (t, 2H), 2.00 (s, 15H, C_5Me_5), 1.19 (s, 15H, C_5Me_5).

Formation of $(C_5Me_5)_2Y(\eta^3\text{-}C_{13}H_9)$, 6, from $(C_5Me_5)_2Lu(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Lu(C_5Me_5)$, 5-Y. **5-Y** (10.4 mg, 0.014 mmol) was dissolved in C_6D_6 (0.5 mL), forming a red solution. Fluorene (2.5 mg, 0.014 mmol) was added and the red solution was transferred to a J-Young NMR tube equipped with a greaseless Teflon stopcock. This was placed under static vacuum using reduced pressure and heated at 70 °C for 4 h, leaving a yellow solution that showed the formation of **6** by ^{1}H NMR spectroscopy.

X-ray Crystallographic Data. Crystallographic information was obtained for complex **6** and is shown in Figures 7. Select bond lengths and angles for complex **6** are given in Table 2 with $(C_5Me_5)_2(C_5Me_4H)Y$, **1-Y**, as well as **3-Y** and **4-Y** for comparison.

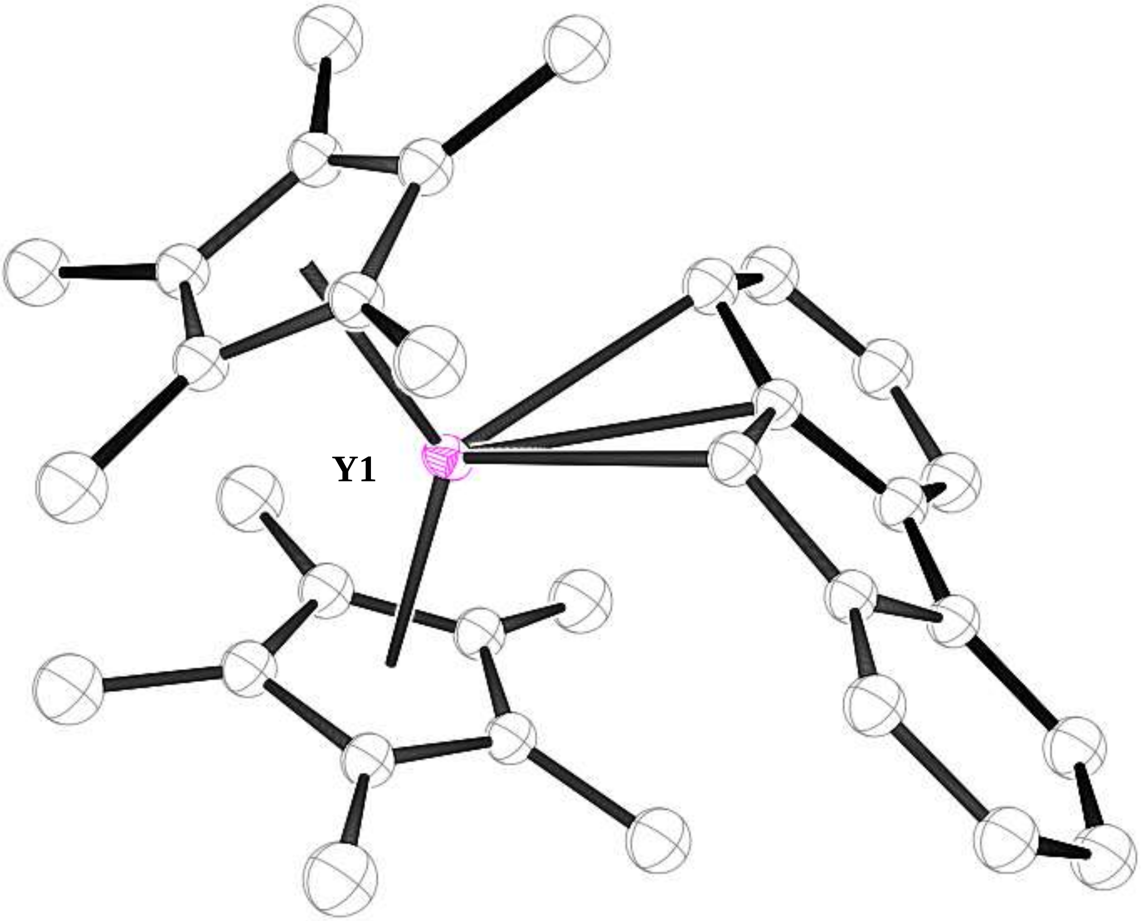


Figure 8. Preliminary thermal ellipsoid plot of $(C_5Me_5)_2Y(\eta^3\text{-}C_{13}H_9)$, **6**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) for $(C_5Me_5)_2Y(C_{13}H_9)$, **6**, $(C_5Me_5)_2Y(C_5Me_4H)$,[1] **1-Y**, $(C_5Me_5)_2Y(C_3H_5)$,[16] **3-Y**, and $(C_5Me_5)_2Y(C_3H_4Me)$, **4-Y**.

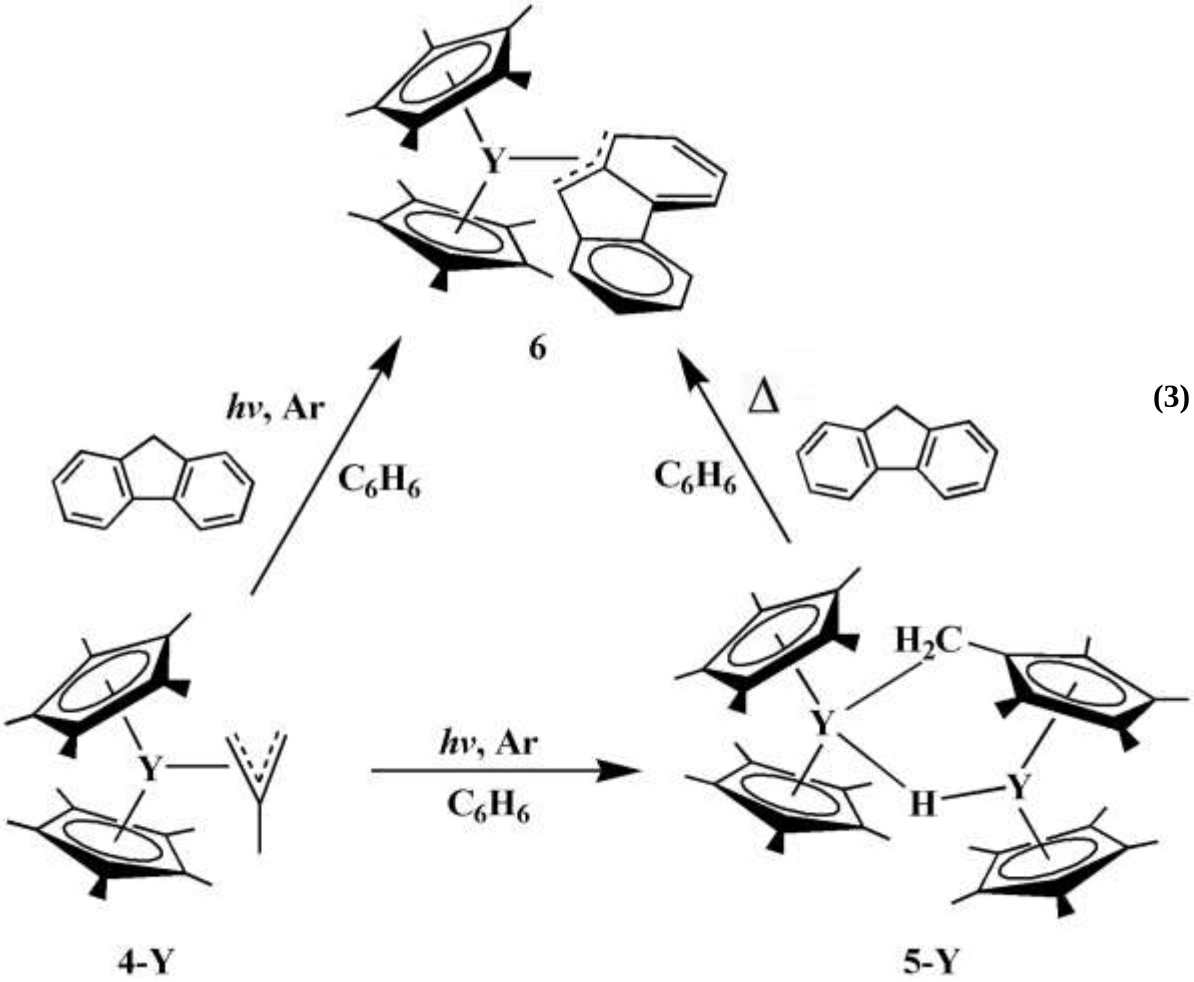
Cmpd	Y−C(centroid)		C(centroid)−Y −C(centroid)	Y−C(η^3 ligand)			C(η^3 ligand) −C(η^3 ligand)		C(η^3 ligand) −C(η^3 ligand) −C(η^3 ligand)
6	2.371	2.329	136.6	2.837	2.753	2.543	1.437	1.416	131.5
1-Y	2.378	2.344	134.5	2.879	2.738	2.534	1.504	1.447	127.0
3-Y	2.381	2.362	138.8	2.582(2)	2.601(2)	2.582(2)	1.392(3)	1.391(3)	125.9(2)
4-Y	2.403	2.365	135.7	2.570(2)	2.702(2)	2.562(2)	1.403(3)	1.401(3)	123.24(2)

Results and Discussion

Photolysis of solutions of **4-Y** in benzene under an argon atmosphere, eq 3, resulted in the conversion to and isolation of the 'tuckover' hydride complex, $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$, **5-Y**, previously reported in the literature.[56] The hydride peaks are visible for **5-Y** in the ^1H NMR spectra when the irradiation is performed in benzene-d_6, suggesting that the C_5Me_5 or C_3H_4R ligands are viable sources of hydrogen for the formation of the hydride. Heated solutions of complexes **3-Y** and **4-Y** kept in the absence of a light source did not show any formation of **5-Y**, suggesting that reaction proceeds in a photochemical manner.

Irradiation of **4-Y** with fluorene ($C_{13}H_{10}$) resulted in isolation of the complex $(C_5Me_5)_2Y(\eta^3\text{-}C_{13}H_9)$, **6**, eq 3. A heated solution of the 'tuckover' hydride, **5-Y**, with fluorene also showed the formation of complex **6** by ^1H NMR spectroscopy. This raises the possibility that complex **5-Y** is formed initially when **4-Y** is irradiated in the absence of dinitrogen, and it is the 'tuckover' hydride that reacts with fluorene.

Given the trihapto nature of the photoactive ligand, $(C_5Me_4H)^{1-}$, observed in the first photochemically active rare earth complexes $(C_5Me_5)_2(C_5Me_4H)Ln$, **1-Ln**, and $(C_5Me_5)(C_5Me_4H)_2Lu$[1], as well as the allyl and methylallyl ligands seen in **3-Ln** and **4-Ln**, it was



(3)

unexpected that **6** could be isolated in solution after irradiation. The fluorenide ligand, $(C_{13}H_9)^-$, found in **6** is also seen to adopt a trihapto coordination mode by X-ray crystallographic data. Y−C(η^3 ligand) distances given in Table 2 for complexes **6** and **1-Y** are comparable within 0.05 Å or less, suggesting a similar binding mode between the two complexes. A related compound, $(C_5Me_5)_2La(C_{13}H_9)$, was isolated as a yellow solid by Benjamin L. Davis when $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ was reacted with potassium fluorenide, $KC_{13}H_9$; the resulting product was argued not to exhibit an η^3 binding mode when the La−(η^3 ligand) distances of the fluorenide complex were compared to La−C(allyl) distances of other lanthanum allyl complexes.[57] Crystals of complex **6** are yellow, another similarity seen in the previously mentioned photoactive compounds. These characteristics may suggest complex **6** is a photochemically active compound that would be seen to react during irradiation, but as seen in irradiations of **3-Ln** and **4-Ln** with dinitrogen in Ch. 3, reactions are not often observed to go to completion.

In contrast to the reactivity observed for **4-Y**, irradiated samples of **4-Lu** in benzene under an argon atmosphere did not produce evidence for the formation of the corresponding 'tuckover' complex $(C_5Me_5)_2Lu(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Lu(C_5Me_5)$, **5-Lu**, observed in the literature, as no significant correlations can be seen by ^1H NMR spectroscopy.[58] Additionally, solutions of pure **5-Lu** are described as orange, while yellow solutions of **4-Lu** become green in color after significant irradiation. Two examples of mono(pentamethylcyclopentadienyl) lutetium-containing complexes that appear green in solution exist in the literature: a bipyridyl-stabilized complex containing both butatrienediyl and terminal acetylide ligands,[59] and a series of similar lutetium alkyls supported by functionalized terpyridine ligands.[60,61] To our knowledge, there has not been a recorded isolation of a green crystal containing a bis(pentamenthylcylcopentadienyl) lutetium moiety in its structure.

Chapter 6

Summary and Conclusions

The rare earth allyl complexes $(C_5Me_5)_2Ln(C_3H_5)$, **3-Ln** (Ln = Y, La, Lu), and $(C_5Me_5)_2Y(C_3H_4Me)$, **4-Y**, have been shown to exhibit reactivity similar to the photochemically active compounds, $(C_5Me_5)_2Ln(\eta^3–C_5Me_4H)$, **1-Ln** (Ln = Y, Dy, Lu), and $(C_5Me_5)(C_5Me_4H)_2Lu$ observed in Figure 1. The newly synthesized methylallyl complexes, **4-Ln** (Ln = Y, La, Lu), are comparable to their corresponding allyl complexes, **3-Ln**, in color and coordination environment. **3-Lu**, **3-Y**, and **4-Y** can be photoactivated to reduce N_2 to $(N=N)^{2-}$, forming $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$, **2-Ln** (Ln = Y, Lu). UV-vis spectral analysis and DFT calculations indicate that a LMCT between the η^3 allyl ligand and the metal center may be what generates an excited state species capable of reducing dinitrogen.[40,41] Propene and isobutene found in irradiations of **3-Y** and **4-Y**, respectively, suggests the formation of allyl radicals, similar to postulated pathway of photolysis seen in complex **1-Ln** and $(C_5Me_5)(C_5Me_4H)_2Lu$.[1] Photopolymerization of isoprene with **3-Y** and **3-La** was observed to form an isomeric mixture of polyisoprene. Irradiation of **4-Y** under argon and with fluorene show that the formation of the 'tuckover' hydride complex $(C_5Me_5)_2Y(\mu\text{-}H)(\mu\text{-}\eta^1:\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$, **5-Y**, may occur in the absence of other substrates. These photolytic studies with the allyl complexes have shown that this is a viable way to activate organolanthanide complexes, wherein the reduction of N_2, photopolymerization of isoprene, and activation of C-H bonds all become possible.

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