ABSTRACT

Title of Document: NEW LIGAND MOTIFS FOR PLATINUM-BASED 'SHILOV CHEMISTRY' AND DETOURS INTO BASIC ORGANOMETALLIC RESEARCH

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The C-H activation reaction at cationic platinum centers utilizing chelating aromatic N-type ligands has been widely studied in TFE (trifluoroethanol): a weakly coordinating solvent. In our laboratory, recent studies involving a modified dipyridine methane ligand revealed that benzene C-H activation in water, methanol and the activation of alkane substrates in TFE is possible. Anionic Pt(II) centers created via an anionic dipyridyl borate ligand present a new and promising direction towards realizing selective oxidation of alkanes. Rapid CH activation of alkanes and arenes is possible in biphasic water/hydrocarbon solvent mixtutes. In the course of CH activation studies with $[dpbPt^{II}(Me)_2]^-$ (dpb = di-2pyridyl-dimethyl-borate), the complex was found to yield olefin hydrides upon alkane activation. The yield of olefin hydride complexes with the dpb ligand proved low (30-40%). A lipophilic ligand (d^tBupb = di-*t*-butylpyridyl-dimethyl-borate) activated various cyclic and

linear olefins with near quantitative yields. The resultant olefin hydride complexes proved to be catalysts for transfer dehydrogenation of cyclic alkanes (TONs up to 13).

We found that in the presence of a hydroxylic solvent, a very rapid oxidation of $[dpbPt^{II}(Me)_2]^-$ complex towards a Pt^{IV} species was observed. The proposed reaction mechanism includes rapid coordination of O_2 by the highly electron-rich metal complex with subsequent nucleophiilic substitution reaction at boron and a methyl group transfer from the boron atom to the Pt^{IV} center.

Oxidation with methyl iodide to give penta-coordinate $dpbPt^{IV}Me_3$ and its subsequent reaction with a hydroxylic solvent furnished the same product as under aerobic oxidation conditions. This proved that oxidation had to occur prior to methyl group transfer. Since in this case, our system can be considered as a mechanistic probe for Suzuki coupling, the insight into the nature of alkyl transfer provides a clear model of one the key steps of this widely-utilized transformation. Eventually, we were able to observe a *reversible* alkyl group transfer between Pt^{IV} and B in DMSO solutions.

To probe the transfer of an aryl group between Pt^{IV} and B, a $dpbPt^{IV}MePh_2$ complex and a $Pt^{IV}Me_3$ complex supported by (dpydphb = dipyridyl-diphenyl-borate) were synthesized. While phenyl transfer from Pt^{IV} to B was facile already in THF, the reverse, B-to-Pt^{IV} phenyl transfer was not observed due to the greater stabilization conferred to the complex by a B-Ph---Pt^{IV} moiety. The feasibility of a B-to-Pt^{IV} phenyl transfer was demonstrated when $[dpydphbPt^{II}Me_2]^-$ was oxidized by O_2 in isopropanol.

NEW LIGAND MOTIFS FOR PLATINUM-BASED 'SHILOV CHEMISTRY' AND DETOURS INTO BASIC ORGANOMETALLIC RESEARCH

By

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Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
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Doctor of Philosophy
2009

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Professor Andrei N. Vedernikov, Chair
Professor Michael P. Doyle
Professor Lawrence R. Sita
Professor Philip DeShong
Professor Nam Sun Wang

Dedication

To my grandparents

Israel Khaskin
Pessah Kivritskaya
Sofia Kaganov
Alexander Kaganov

"The Lord gave us farmers two strong hands so that we could take as much as we could grab with both of them," he preached with ardor on the courthouse steps or in front of the A & P as he waited for the bad-tempered gum-chewing young cashier he was after to step outside and give him a nasty look. "If the Lord didn't want us to take as much as we could get," he preached, "He wouldn't have given us two good hands to take it with." And the others murmured, "Amen."

-“Catch 22” (Joseph Heller)

"Why don't you use some sense and try to be more like me? You might live to be a hundred and seven too."
"Because it's better to die on one's feet than live on one's knees. I guess you've heard that saying before."
"Yes I certainly have," mused the treacherous old man, smiling again. "But I'm afraid you have it backward. It is better to *live* on one's feet than die on one's knees. *That* is the way the saying goes.
"Are you sure?" Nately asked with sober confusion. "It seems to make more sense my way."
"No, it makes more sense my way..."

-“Catch 22” (Joseph Heller)

“Destiny is a good thing to accept when it's going your way. When it isn't, don't call it destiny; call it injustice, treachery, or simple bad luck.”

-Real life (Joseph Heller)

Acknowledgements

First of all, I'd like to acknowledge my advisor, Andrei Vedernikov, without whom I wouldn't be at this point. There are very many details that go into that statement, but I won't list them except to say that he is the best advisor, period. For me. And I'm sure for many others after me and before me as well. In retrospect, it's been great and I learned a lot. I'm absolutely positive I would have learned a lot less and enjoyed my time here less with anyone else. Working in an area of chemistry that I love with one of the best advisors in the field… well, I guess I was really lucky with that combination. Were there things I was unhappy with? Sure. But the positives outnumber the (perceived) negatives so much, it's no contest. If you don't have a great graduate school experience, based on your chemistry knowledge and a desire to learn, with Andrei as an advisor, there is probably something wrong with you and I probably wouldn't get along with you.

I'd also like to thank the Vedernikov group. The postdocs Fabian Mohr (with whom I got to practice German), Nani Harohally, and Jing Zhang (from whom I learned about the Milstein group where I'll be going for my postdoc, but I'm not thanking him for keeping our apartment clean when he was my roommate because he failed at that despite being a good chemist). With the graduate students, I'd like to thank Julia Khusnutdinova for being my best friend over the last four years (chemistry discussions, proof reading, vacation trips, and watching movies included). Good luck to Greg Downs and Will Oloo as they try to publish papers and go through grad school. I'd like to thank my undergrads, since it was a pleasure to teach all of them chemistry. Even if it was frustrating, every time I finally got Daniel to repeat a

reaction, it was worth it. I was very happy to be working with them and I hope that they are successful in their endeavors. Ben Marguiles, Nicholas Anderson, Mike Talanov, Daniel Lew, and L. Murray Kraft, thanks to all of you guys for letting me experiment with teaching practical organic and organomeallic chemistry. All of you did a really good job in the lab. Well… except Mike who decided to join chemical engineering, but at least he had good hands before he betrayed us. But good luck to Nick in his grad studes with Scott Denmark, you'll certainly need it. And don't worry, despite all of us saying this every single April 1st on chemistry blogs, Denmark is not actually going to crash his Porsche into a tree before you graduate.

Outside of the group, I need to thank Dr. Doyle, to whose group meetings I often went to learn some outside chemistry. I presented three times at the Doyle group meetings and I'm grateful to his advice and feedback that I received. I won't lie though, it would have been a lot easier for me to make more Doyle group meetings if they were not at 8a.m. in the morning.

Learning about chemistry being done in the Doyle group enabled me to interact with many exceptional chemists who have come through the group. John Morgan, Emily, Richard, Ho-Jae, Wen-hua, and many other postdocs who have helped me out with my chemistry and were always a short walk away from my fumehood. Colin was even my teammate in intramural soccer. Graduate students in the Doyle group, Darren Bykowski, Arthur Catino, Jason Nichols, and Kousik Kundu became my friends. Since they were two years ahead of me, they gave me advice on how to write job applications, how to write grants and how to get through my candidacy. They could also be relied upon to go out to the bar to watch hockey

games. Thanks guys, it would have been much harder without you. I know I'm forgetting a lot of other Doyle group members from the past who I talked to on a daily basis three years ago, but Marcela, Christine, Tom, and everyone else, you've certainly made my experience in the connected Doyle/Vedernikov labs very memorable.

I want to acknowledge three members of the Isaacs group: Jason Lagona, Soumyadip Ghosh, and Regan Nally for also being great drinking partners who helped me navigate through graduate school.

On a technical support note… would my thesis be possible without our crystallographer Peter Zavalij, NMR staff Yiu-Fai Lam and Yinde Wang, ESI staff Noel Whittaker and Yu Li? Nope. Wouldn't have been possible. They made everything easy and were very happy to teach me (at least they looked sort of happy except for Noel – who was always suspicious of biochemists breaking the ESI) or to accommodate any special requests I had.

On a personal note, thanks to my other best friend, who I grew up with back in Kiev, Danya Moshinskiy. When I came to Washington, he let me stay on the couch and I spent almost every weekend at his house after I decided to stay in the city for good. In fact, if he hadn't gone to Maryland for his undergraduate degree in Psychology, I may not have ended up here for graduate school since this was one of the first departments I looked at when I decided to stay in the area. It's too bad that I can't visit as often since now he's married to Karen, but hey, if you end up with someone as great as Karen when you get married, than marriage is definitely not the bad thing I thought it was. I'll always be thinking of you guys, and I'm sure we'll see

each other many more times in the future even if our lives and plans have to take us to different continents and different cities yet again. As long as you are in Washington, I know I'll get to see BWI or Dulles in the future. You can come and visit me anytime and stay on my couch. But, as you know, if I end up with the same apartment that I had in Montreal – which Danya said reminded him of Raskolnikov's apartment from 'Crime and Punishment' – living arrangements might be tight.

I want to thank my family. My dad who taught me organic synthesis and who proof-read my thesis deserves special thanks. Two of my grandparents, Sofia and Alexander Kaganov passed away while I was in graduate school and I was very upset that I couldn't be there with them as much as I would have liked. My grandparents were very close to me, maybe more so than they can imagine and their deaths hurt my progress greatly. It was very hard to focus on my research at times as I kept thinking about them more than I let on to people around me, but I would be a fool not to try my best and make the most of the opportunity given to me by people who survived and fought World War 2, who survived Nazis, Stalin, and the hunger in the 1930s, then had to rebuild the Soviet Union and destroyed cities in Ukraine, who became doctors and chemists and made the most out of what life gave them so that I could actually be writing a thesis somewhere in America in the 21st century. This thesis is dedicated to them.

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List of Schemes

List of Abbreviations

Et_2O	diethylether
NADH	Nicotinamide adenine dinucleotide
σ	sigma
π	pi
TMEDA	tetramethylethylenediamine
dpm	dipyridylmethane
dmdpm	dimethyldipyridylmethane
THF	tetrahydroduran
dpms	dipyridylmethanesulfonate
DFT	Density Functional Theory
TFE	2,2,2-trifluoroethanol
^{1}HNMR	hydrogen-1 nuclear magnetic resonance
^{13}CNMR	carbon-13 nuclear magnetic resonance
^{19}FNMR	fluorine-19 nuclear magnetic resonance
POM	polyoxometalate
ESI/MS	electrospray ionization / mass spectrometry
MW	molecular weight
mL	milliliter
μL	microliter
g	gram
mg	milligram

min	minute
h	hour
CH	carbon-hydrogen
dpb	dipyridylborate
Tp/TPB	tris(pyrazolyl)borate
MeOH	methanol
EtOH	ethanol
DN	donor number
tBu	tert-butyl
nBu	n-butyl
dphdpb	diphenyldipyridylborate
DMSO	dimethylsulfoxide
Me	methyl
Ph	phenyl
TBE	tert-butyl-ethene
TBA	tert-butyl-ethane

Chapter 1: Introduction to Shilov Chemistry and CH activation in aqueous systems with a cationic Pt complex supported by the dimethyldipyridylmethane (dmdpm) ligand

1.1 Introduction

1.1.1 Importance of methanol and methane in the future economy

‘Simple’ may be a very good adjective to describe one of the smallest and most symmetric of organic molecules. Methane consists of five atoms: one central carbon surrounded by four hydrogen atoms in a tetrahedron arrangement; it is an odorless gas at room temperature. The effects of methane on modern society, and the tools that humans and certain bacteria utilize to effectively transform methane into energy or other types of molecules, are anything but simple.

Methane is by far the runaway main component of natural gas. Combustion of large amounts of this gas throughout the world is used for heating and for electricity production without much regard to the amounts of CO_2 produced. Natural gas is such an important part of the energy and geopolitical balance in the world today, that barring breakthroughs in renewable energy utilization, this main use for it will probably continue until peak production capacity is reached. However, just as with oil, methane is a valuable feedstock that can be converted to other commodity chemicals. It can be converted to Syngas, a mixture of CO and H_2, by heating with water vapor over a heterogeneous catalyst. Later, Syngas can be reformed into higher

alkanes by the high temperature Fischer-Tropsch process.[1,2] Research into conversion of Syngas into liquid fuel or commodity chemicals always generates interest during times of oil scarcity, such as before World War 2, the oil crisis of the 70s[3,4] and, indeed, today.[5]

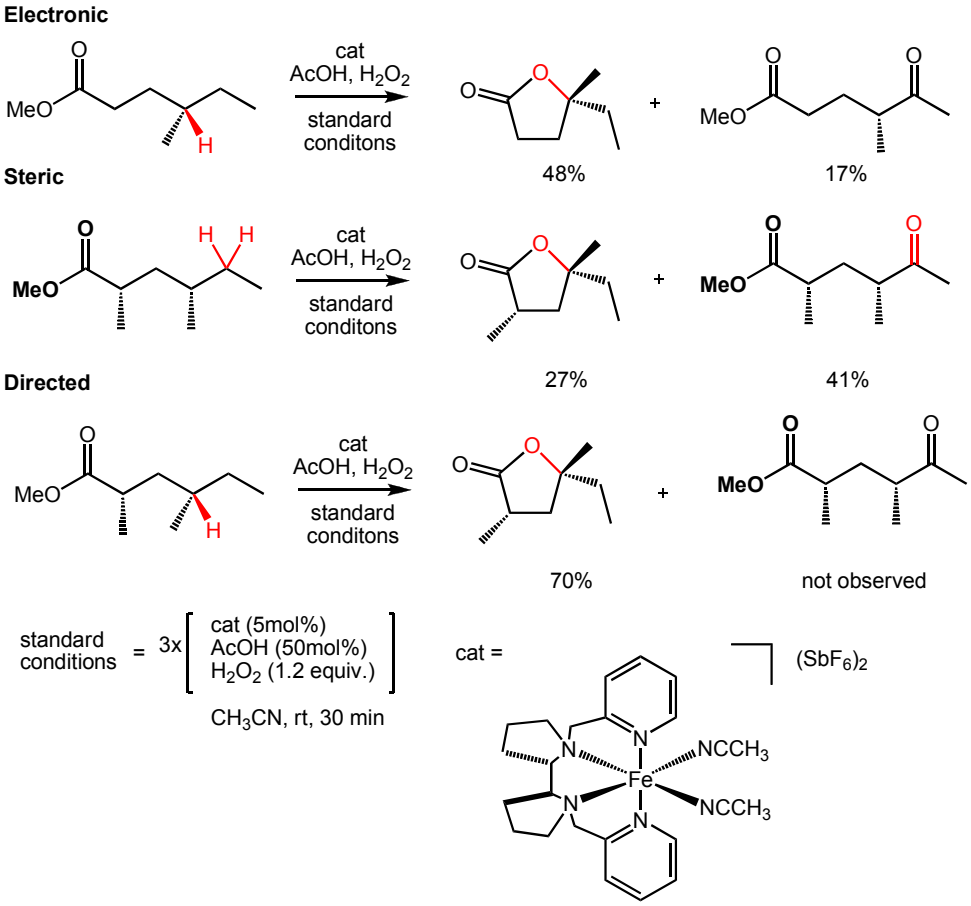
Barring carbon dioxide and Syngas, there is one other molecule into which methane is directly transformed daily directly on a colossal scale. That molecule is, of course, methanol. Most of this chemistry unfortunately, doesn't take place in an industrial facility – with an honorable exception of the aforementioned Fischer-Tropsch process on a rather small scale – it all happens in the world's lakes and oceans. Bacteria that live around extreme environments such as deep sea vents,[6] but also in swamps and lake-bottoms, have become masters at utilizing the methane-rich environment. They possess soluble methane-monooxygenase and particulate methane-monooxygenase (the latter is embedded inside the cell membranes) enzymes, that utilize either copper or iron catalytic sites in combination with NADH to activate dioxygen and the strong CH bond of methane to selectively produce methanol.[7-9] The enzyme does not over-oxidate the substrate beyond methanol and the solvent for this mild and homogeneous reaction is water from inside the cell. Methanol is then used by the bacterium to produce higher alkanes and to extract energy.[7-9,10] Much in the same way, humans could use methanol to produce higher oxygenated alkanes,[11,12] bypassing the need for Syngas. Or, since methanol is an easily transportable, clean-burning and efficient liquid fuel at room temperature, it could be used directly to power vehicles and to produce electricity. The only problem

with this proposal is that, as of today, we are unable to even come close to replicating this remarkable chemistry that takes place in a single-celled creature.[13,14]

1.1.2 Introduction to Shilov Chemistry

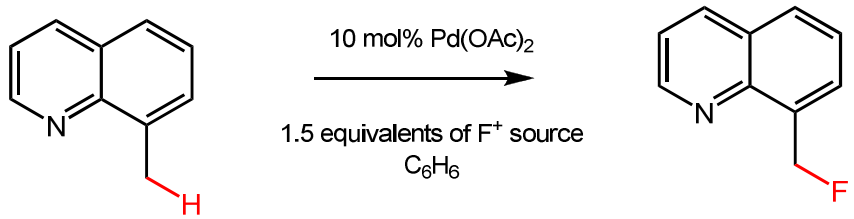
By studying homogenous catalytic systems that are able to replicate some aspect of the methane-to-methanol conversion process, it may become possible to answer important questions regarding which factors determine selectivity for the type of CH bond attacked and for the propensity by many systems towards over-oxidation. The field of CH functionalization has led to many important breakthroughs in organic synthesis.[15-17] A recent report by White discloses a very effective iron based catalyst that is able to selectively transform tertiary and secondary CH bonds (Scheme 1.1), and can be used with complex organic molecules containing varied functional groups.[18]

Scheme 1.1 CH oxidation under mild conditions with an iron catalyst



The Sanford group uses functional group directed CH activation to install various functionalities into pharmaceutically relevant heterocycles with a Pd based system (Scheme 1.2).[19]

Scheme 1.2 Directed CH bond functionalization with Pd catalyst

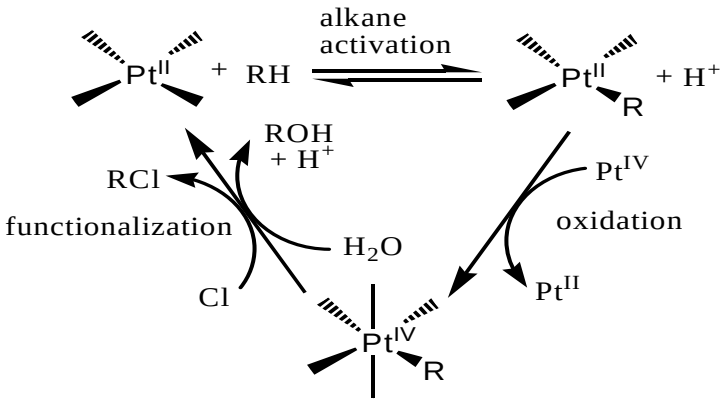


All these breakthroughs in CH functionalization, and many future ones, may be achieved without moving much closer to the goal of economic methanol

production, which was a main driving force for the establishment of the field of CH activation after the observation of one interesting reaction.

There are many other transition metals capable of inserting into a CH bond, and many excellent reviews summarizing these systems are available.[15-17] The focus of our and many other groups on platinum is based on a report from the early 1970s, where the 'initiator' of the field of CH activation, Alexander Shilov, noted that Pt salts dissolved in water, catalyzed the conversion of methane to methanol and methyl chloride (Scheme 1.3).[20,21] Shilov's decision to use Pt was based on earlier reports that the metal salts catalyzed H/D exchange in benzene and other aromatic substrates,[22] a sure sign that CH bond activation had occurred reversibly. The Shilov system is remarkable for being the first to produce functionalized products that result from the CH activation reaction. The relatively low temperature of 100^{o}C that enabled this transformation is promising for further industrial application. However, the slow reaction rate (~4 TONs in 4 hours), and the fact that oxygen could not be used as a terminal oxidant, have hampered the widespread use of this reaction. The only oxidant at the time that could be utilized in the original reaction was a molecule of Pt^{IV}, making the entire catalytic cycle prohibitively expensive. Progress towards catalytic methane functionalization has been made since the initial discover of the Shilov system and many excellent reviews are available,[23-27] but none of the reactions developed are yet commercially viable.

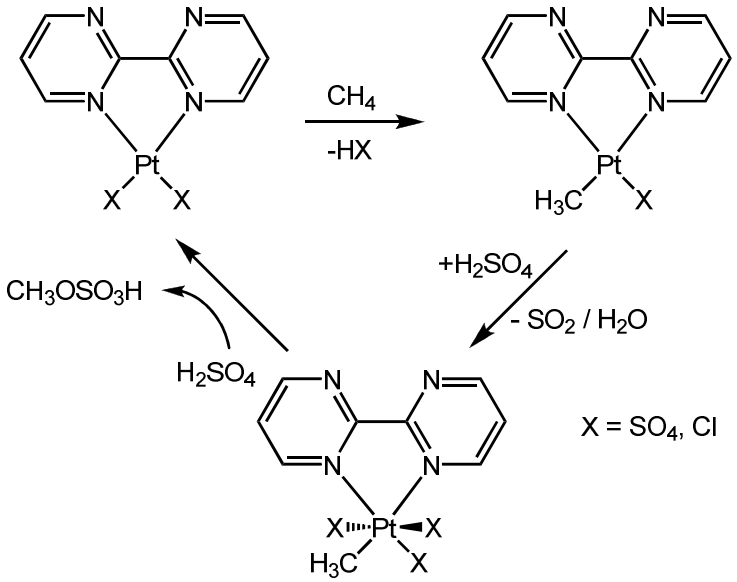
Scheme 1.3 The Shilov Catalytic Cycle



1.1.3 Variations on the original Shilov system; Mechanistic considerations

One reaction of note was developed by Periana and the Catalytica group; it utilizes bypyrimidine as ligand for Pt in fuming sulfuric acid, which also acts as an oxidant for the overall process (Scheme 1.4).[28] Although the conversion rate for methane to methanesulfonic acid was impressive (70% one pass yield – reaction is thereafter inhibited), the water produced in the reaction eventually shut down the catalysis and the methanesulfonic acid product proved to be difficult to isolate and economically convert to methanol. It is remarkable that methane bisulfate is produced in 90% selectivity and that the complex remains stable under the reaction conditions. The ligand is not oxidized and even if dissociation of the metal does occur, precipitation of Pt black is precluded by the harsh reaction conditions that serve to effectively 'dissolve' the metal.[24]

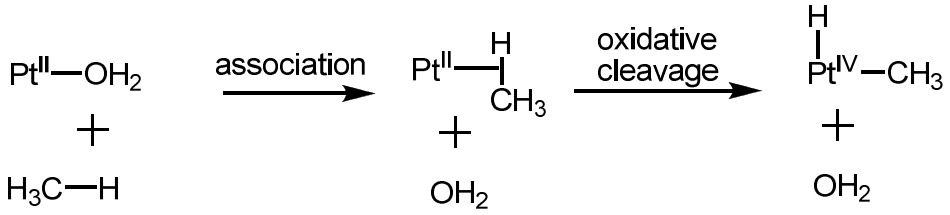
Scheme 1.4. The Catalytica system for methane bisulfate formation



In order for 'Shilov Chemistry' or similar approaches to become economical, oxygen is the only oxidant that can be seriously considered. Even hydrogen peroxide may become too expensive on an industrial scale depending on the ultimate fate of the methanol produced. Still, the initial observation eventually engendered a lot of excitement and mechanistic studies of the Shilov cycle were undertaken.[25] It was found that certain copper salts could act as an oxidant instead of a molecule of Pt^{IV};[29] in this case, the coupling of the CH activation reaction to Wacker-like oxidation chemistry could prove fruitful in realizing the use of oxygen as a terminal oxidant. Other oxidation strategies include the use of tandem Pt complexes / polyoxometalates (POM) that can be regenerated by molecular oxygen,[30] or perhaps POMs can be utilized in the future.[31] Often however, the use of other metals for tandem oxidations results in lower selectivity for methanol.[32(and references therein)]

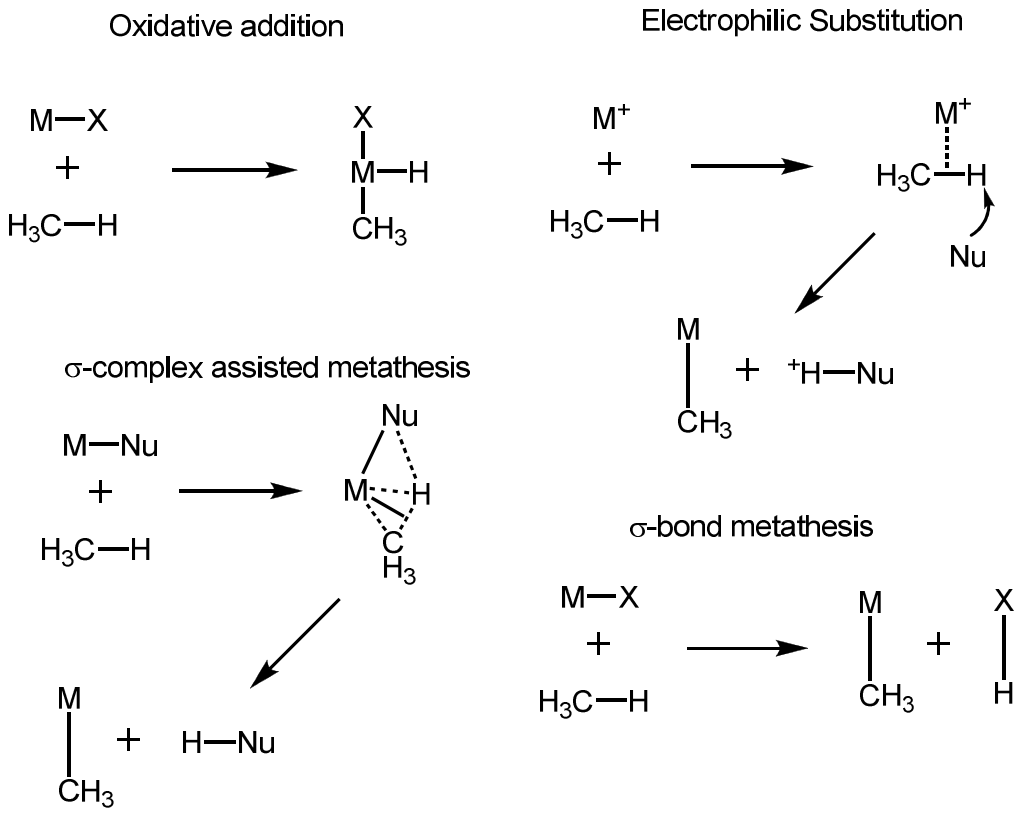
Water, far from being the green solvent of choice only due to its cost and environmental considerations, proved indispensible to the reaction since it was found that a molecule of water was necessary during the final functionalization step of the Shilov cycle.[33] The oxidized Pt^{II} species undergoes nucleophilic attack by an OH^- or Cl^- ion to generate methanol and methyl chloride respectively, and to reform the original catalyst. This nucleophilic attack proposal for the mechanism of reductive elimination of functionalized organic products was originally suggested by Shilov. The chloride ion that leads to methyl chloride originates from the Pt salts; in a large scale industrial setting where Pt^{IV} oxidizing salts would be ideally replaced by a cheaper oxidant such as dioxygen, the amount of methyl chloride generated would be ideally minimized. The first step of CH activation, the coordination of a strong σ–CH bond, is the slowest step for the entire cycle. It is at this step that the water molecule proves to be duplicitous. Despite being necessary for facile nucleophilic attack during the last stage of the cycle, the aqua or hydroxo ligands bind tightly to Pt^{II}. It is the replacement of an aqua ligand by the σ–CH bond of a molecule of methane that proves to be the most difficult of all. The subsequent splitting of a very strong CH bond by the Pt center, is relatively rapid and can happen in a reversible fashion.[34-38] The enthalpy of the CH bond of methane is ~109 kcal/mol and there is a small entropy penalty that is offset by the loss of the aqua ligand (Scheme 1.5). However, the two new bonds that are formed if oxidative addition is the operating mechanism would have energies of 73-74 kcal/mol (Pt^{II}-H bonds)[39] and ~30-37 kcal/mol for a new Pt^{IV}-CH_3 bond.[40,41] From simple energy considerations, it is then not too surprising that CH activation can occur so easily in certain Pt^{II} systems.

Scheme 1.5. Coordination and oxidative cleavage of CH bonds with Pt^{II} complexes



There are other mechanistic pathways other than the oxidative cleavage of a CH bond, that may be operative in creation of a metal carbon bond in the Shilov system (Scheme 1.6).

Scheme 1.6. Possible CH activation mechanisms with metal centers



The electrophilic substitution pathway depicted in Scheme 4 was suggested as the pathway operative in the Catalytica system due to harsh conditions and the absence of strong nucleophiles. This mechanism may be operable in Pd catalyzed CH bond functionalization reactions as well.[42] The σ-bond metathesis pathway is often

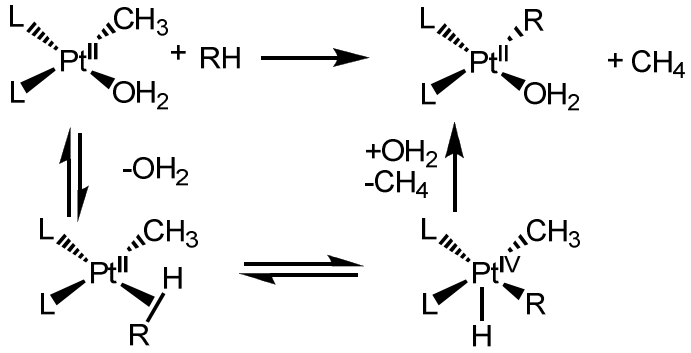
operative in high valent and early transition metals where a change of oxidation state is difficult or impossible (in the case of d_0 transition metals). The sigma bond metathesis reaction is not likely to occur at a late transition metal such as Pt, but considerable care must be taken in ruling it out. The recently reported mechanism of σ-complex assisted metathesis[43] is very similar to the σ-bond metathesis pathway and it requires for a nucleophile to be co-ordinated to the metal in order to assist with the CH cleavage step by attacking the hydrogen in the transition state. This last mechanism has also been shown to be operative in some low valent, later transition metal systems.[43] The conditions of the Shilov cycle are favorable for this mechanism, but multiple H/D exchange events after CH activation (Scheme 1.7) and isolation of Pt^{IV} hydrides has lent sufficient weight to the oxidative coupling mechanism.

Scheme 1.7 Example of aromatic CH activation

Research in the area of methane functionalization with platinum often focuses on modifying the ligand environment around the Pt center in order to enable faster CH activation and/or fast oxidation by oxygen of the resulting Pt-CH_3 species[44] and by using a model probe in order to gauge the effectiveness of a particular ligand system in CH activation. The monoalkyl complex represented in Scheme 1.8 is actually the complex that would be obtained by CH activation with a disolvento complex. However, it is much more difficult to activate methane with the less electron rich Pt^{II} center in a disolvento complex, which often exists as a dimer in solution.[45] Disolvento Pt^{II} centers are not amenable to facile CH activation and until

recently,[46] successful examples have been rare. Thus, the monoalkyl complex, which has more electron density on the metal center and can subsequently split a coordinated σ–CH bond more easily, is utilized to judge whether a particular ligand scaffold improves the rate of CH activation.

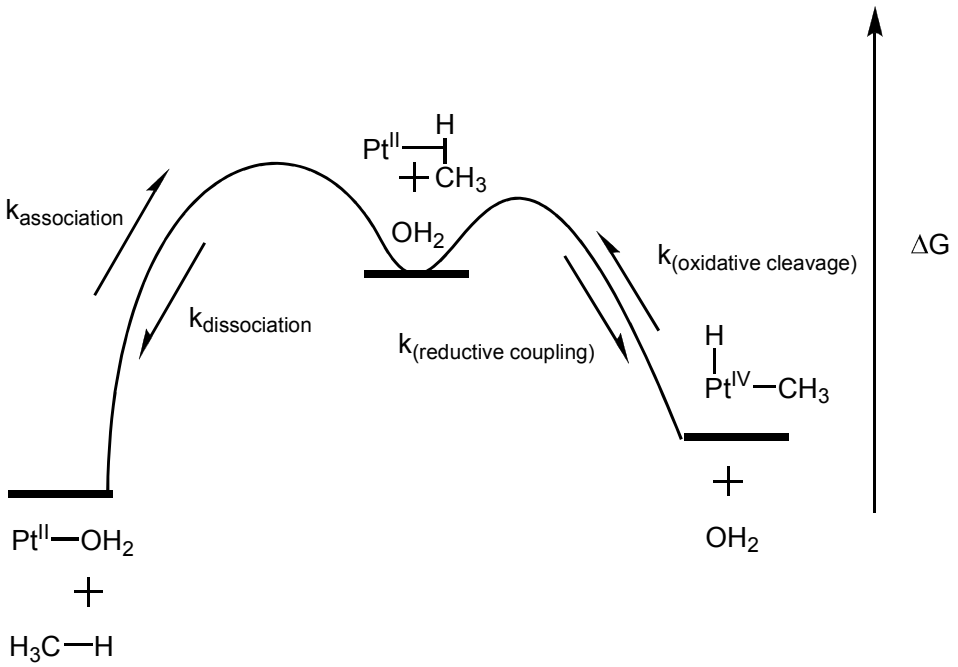
Scheme 1.8 A monoalkyl Pt^{II} probe of CH activation



Another good argument for using the monoalkyl probe is that in the entire transformation as presented by Scheme 6 is energetically degenerate in the case of methane activation by a monomethyl complex. A ^{13}C labeled methane that became incorporated into the complex would be proof of CH activation and equilibrium would drive the activation of aryl species in an open system as well as formation of stronger Pt-Csp^2 bonds. In the case of CH activation with a disolvento complex, the product monomethyl complex is often thermodynamically uphill and it will not be observed in solution; in this case the observation of H/D exchange is a telling sign that activation has occurred. By the principle of microscopic reversibility, it is also possible to gain insight into the alkane activation pathway taken by a solvent complex, since a similar mechanism would be operative in a reverse reaction, the

protonation and reductive cleavage of a monomethyl complex to generate a Pt solvento species (Scheme 1.9).

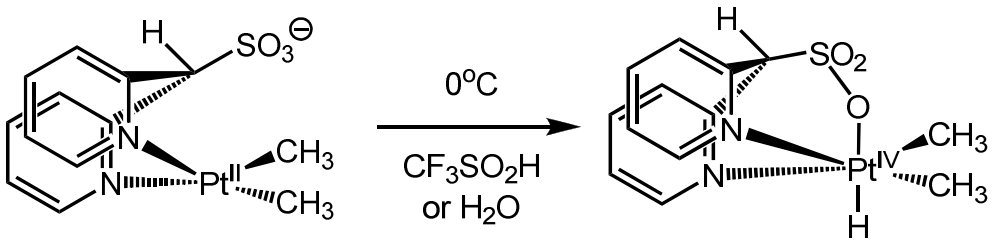
Scheme 1.9. Energy landscape of CH activation, or M-C bond protonolysis



The strategy of using a monomethyl Pt^{II} complex to probe CH activation provides valuable insight into the overall mechanism. If RH is deuterated methane (CD_4), it is observed that the lower reaction in Scheme 1.8 if very facile and highly reversible. Multiple CH bond breaking (oxidative cleavage) and reforming (reductive coupling) events occur such that various isotopomers (CH_3D, CH_2D_2, CHD_3) become visible in solution. From this result, it is possible to determine that the rate limiting step in the reaction is solvent displacement ($k_{association}$, Scheme 1.9) by the alkane and not CH bond cleavage ($k_{oxidative\ cleavage}$, Scheme 1.9). It can be concluded that the transition state mostly involves either concerted or associative ligand exchange from measurements of reaction entropy,[47] a result which has recently been contested.[48-51]

Finally, solid evidence for the intermediacy of a Pt^{IV} hydride complex in these numerous CH bond breaking and reforming events has been obtained by stabilizing the Pt^{IV} octahedral geometry with a specially designed scorpionate ligand dipyridylmethylsulfonate (dpms) (Scheme 1.10).[52] Although alkyl hyride Pt^{IV} complexes have been observed before,[53-55] this was the first report of these species being generated in aqueous solution. The dimethyl hydride Pt^{IV} complex was generated by protonation of a Pt^{II} dimethyl species via triflic acid or dissolution in water, and it decomposes by the reductive elimination of methane. By the principle of microscopic reversibility, it can be concluded that the reverse thermodynamically unfavorable reaction (the CH bond activation of methane by a monomethyl monosolvent Pt^{II} species) proceeds through the very same dimethyl hydride intermediate obtained by protonation in Scheme 1.10. An interesting result was the incorporation of ^{13}C label into the methyl groups of the Pt^{IV} species under an atmosphere of $^{13}CH_4$. This mechanism may, with some caution, be extended towards most Shilov-like systems (where a monomethyl hydride Pt^{IV} is believed to be involved) that operate in hydroxylic environments under mild conditions. If nothing else, this result offers solid evidence for one of the mechanisms in Scheme 4; it has so far proven difficult to isolate reaction intermediates of other proposed mechanisms.

Scheme 1.10. Generation of a long-lived dimethylPt^{IV}hydride



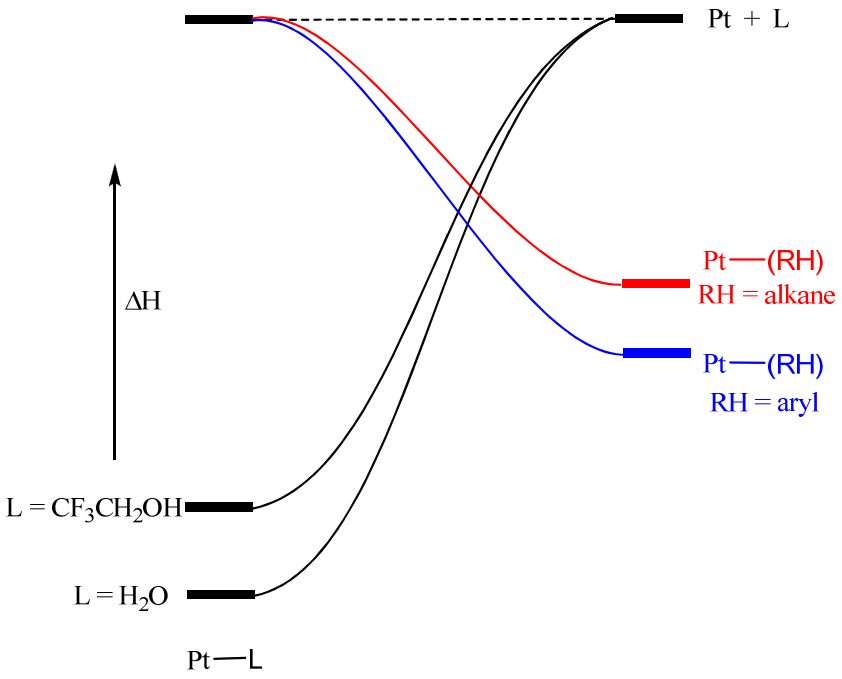
It is hoped that these results will be applicable to an eventual working system based on a disolvento complex. Even if the CH activation step to generate an M-CH_3 species is thermodynamically unfavorable, as it is in this case of the dpms supported disolvento complex, the product could be trapped in the oxidation step of the catalytic cycle right after formation.

To probe the CH activation reaction, model systems are often tested in trifluoroethanol (TFE) solvent, with the resultant correspondingly higher energy $LPt^{II}(Me)(TFE)$ (L = bidentate ligand) species as the starting material instead of $LPt^{II}(Me)(OH_2)$ (Scheme 1.11).[25,35] TFE is a weaker donor to Pt than the aqua ligand, and thus more easily replaced by the CH bond of an alkyl or aryl. It is still, however, a hydroxylic solvent and a mimic of the conditions that are operative in the Shilov cycle where both water and methanol are present. While the use of this solvent does hint at apparent selectivity of all the Pt complexes tested – the CH bonds of alkanes and arenes are activated preferentially to the CH bonds of TFE – it is too expensive and it cannot replace water for the task of carrying out nucleophilic attack on the intermediate Pt^{IV}-Me species in the functionalization step of the Shilov Cycle (Scheme 1.3). Despite these shortcomings, TFE based systems allow for observation of CH activation reactions that would not take place in water (due to decomposition at high temperatures) by lowering the overall reaction energy and to a smaller extent, by improving the solubility of metallic species and/or the substrate (Scheme 1.11).

The intersection points on the energy diagram in Scheme 1.11 represent hypothetical energy levels for the resultant transition states. The main benefit of utilizing TFE comes from destabilization of the ground state of the complex as a M-

TFE bond vs. free M and TFE is less thermodynamically favorable than M-OH_2 vs. free M and OH_2. The oxygen atom in TFE is less electron rich than in water and the lone pair experiences weaker interactions with Pt d-orbitals.

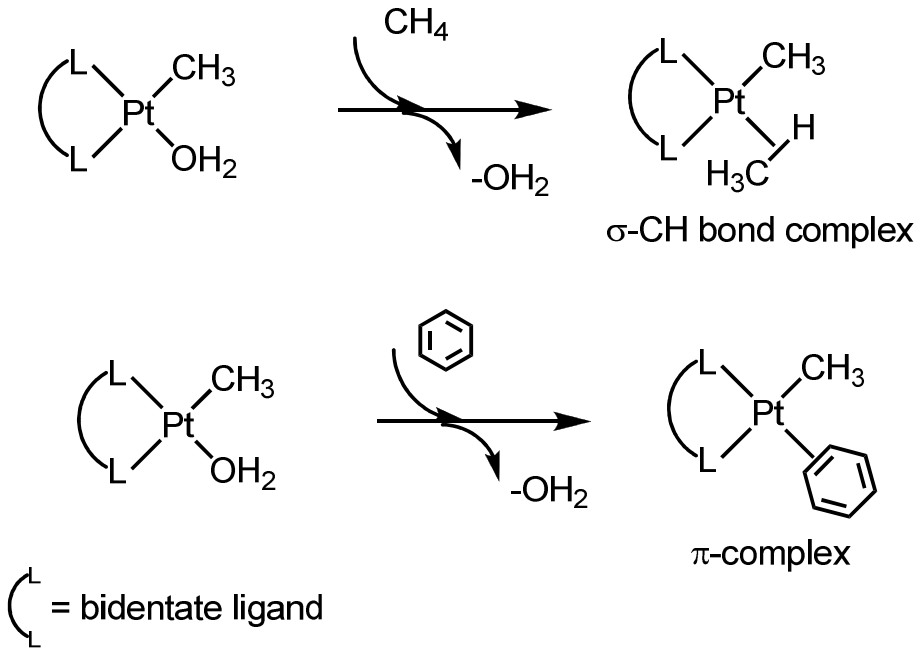
Scheme 1.11. Factors Affecting Kinetics of Associative Ligand Substitution at Pt^{II}



TFE also has a much lower effective molar concentration than water, once again decreasing the overall Gibbs free energy (ΔG) required for the reaction since there are less molecules of solvent to compete with the alkane substrate for the metal center. It's also possible to lower the energy of the transition state by activating aryl CH bonds as opposed to those of the alkane. It is therefore not surprising that the first test for the robustness of a new Pt complex in CH activation is often carried out in TFE, with the molecule of interest being benzene. Benzene can be activated more readily probably due to the fact that it is able to form a coordinated π-complex before

slipping to a σ-CH bond coordination mode and the subsequent CH bond breaking event (Scheme 1.12).[56] This Pt-π–bond is stronger and creates a longer lived intermediate than the corresponding σ–CH bond of coordinated methane or other alkanes. Thus, the transition energy is lowered by finding a substrate that can bind more favorably with the metal center.

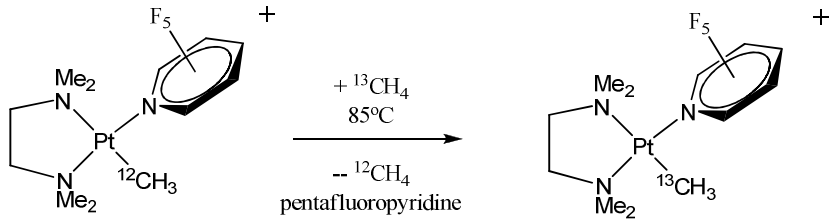
Scheme 1.12. π and σ–CH Pt complexes



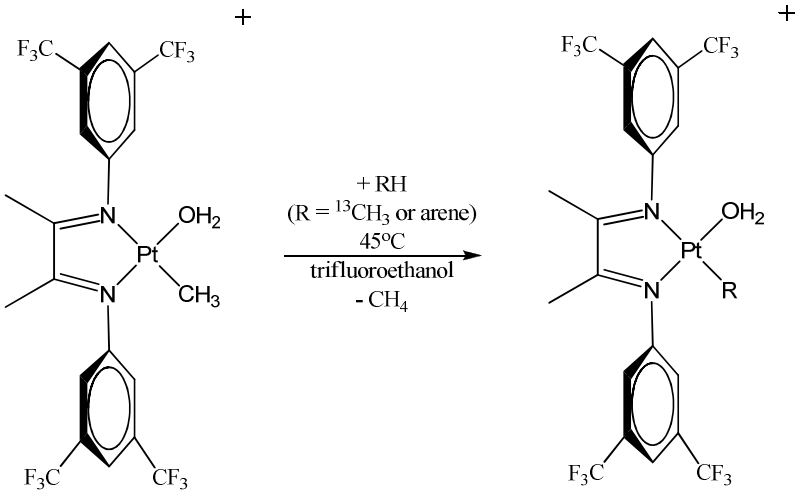
Ultimately, testing a candidate ligand platform's potential in CH activation involves moving to stronger coordinating solvents that would reflect catalytic conditions, and shifting to the use of alkanes as opposed to arenes. As early as 1997, Bercaw and Labinger used TMEDA supported Pt complexes in pentafluoropyridine (C_5F_5N) solvent to activate methane (Scheme 11).[57] Irreversible substrate activation was observed with arenes: benzene was activated to quantitatively produce the phenyl complex and release methane after several days at 85°C. In the case of deuterated benzene, multiple deuterated isotopomers were observed. More recently, Tilset has

observed activation in TFE in the presence of at least one equivalent of water (Scheme 1.13).[58-59] It is believed that the reaction occurs by the reversible displacement of the aqua ligand by TFE, followed by irreversible displacement of the TFE with benzene. A mechanism whereby the aqua ligand is lost and a three-coordinate intermediate is generated was discounted on the basis of the small, negative entropy of the reaction. The inverse reaction order in added water also means that direct substitution of the aqua ligand by benzene is not likely in this system.

Scheme 1.13 Examples of selected CH activation systems



Holtcamp, M.W.; Labinger, J.A.; Bercaw, J.E. *J.Am.Chem.Soc.* **1997**, *119*, 848-9.



Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O.B.; Swang, O.; Tilset, M. *J.Am.Chem.Soc.* **2000**, *122*, 10831-45.

Our group's goal is to design ligand systems that would destabilize the ground state of the complex, without increasing the transition state energy by a similar amount so that CH activation chemistry can be observed in very strongly donating solvents such as water and methanol. The latter solvent is the product of the oxidation of methane and it's important to gauge whether the catalyst will be stable in the presence of methanol and whether it will be selective for the CH bonds of methane over the more polar and less electron rich CH bonds of methanol.

1.2 Design of Dimethyl-Dipyridylmethane (dmdpm) ligand

The ultimate success in activating CH bonds comes from a complex's ability to accomplish both dissociation of solvent and the oxidative cleavage of a CH bond. Shteinmann showed in the late 1970s,[60] that the rates of deuterium incorporation depend on the nature of the ligand L that is bound to platinum in $PtCl_2L_2$ and $PtCl_3L^-$. The stronger the trans effect of the ligand, the lower the rate of deuterium incorporation into cyclohexane that was observed. This result suggested that at least with strong trans effect ligands, the rate of ligand substitution does not reflect the ease of CH activation.[60] Rapid H/D exchange is observed in alkanes and arenes when ligands with weak trans effects are used.[61]

It is important to note that most of the successful Pt based CH activation ligand scaffolds in the literature are nitrogen donors; the examples provided in Scheme 1.13 are thus representative. Examples of phosphine donor ligands facilitating CH activation are rare.[62-64] This may be due to the strong trans effect (ability of a ligand to lower the energy of a M-L bond trans to it) of the phosphine ligand; the alkane cannot bind as well to the metal center and the splitting of the CH

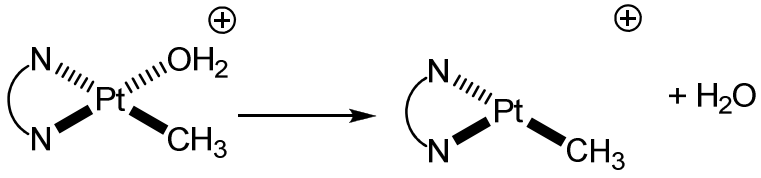
bond to form a Pt^{IV} now becomes more thermodynamically unfavorable, as the resulting complex would have two strong trans-influencing ligands (a phosphine trans to a methyl or hydride) trans to each other. The CH bond splitting step can become rate determining under these conditions and weak trans-influencing nitrogen donors are thus favored for CH activation. A ligand that is too electron poor however, will result in a more electrophilic metal center and lower CH activation rates. This last issue is not anticipated to be a problem with most nitrogen based scaffolds.

1.2.1 Our approach to ligand design for CH activation

Our approach towards designing a ligand system is ultimately an empirical one that is based on Density Functional Theory (DFT) calculations. In the late 90s, Vedernkov et al. used *ab initio* and DFT methods to evaluate a range of ligands and their effects on the success of the methane activation reaction.[65-70] It was confirmed that nitrogen based donors are in fact the preferred ligands for platinum in this transformation. When actively designing ligands six years later, we decided also to exploit steric effects. A sterically hindered square planar Pt^{II} metal center would not bind the aqua ligand as strongly as a non-hindered complex. A sterically hindered metal center would also mean an increased selectivity for the activation of primary CH bonds and in fact. Steric bulk may be a factor necessary for the subsequent selectivity in the activation of CH bonds of methane over those of the methanol molecule – the latter being twice as large. Since the loss of the aqua ligand is believed to be the rate determining step in the overall reaction when weak trans effect ligands

are used, our approach towards screening potential ligand scaffolds involves calculating the ΔG for this dissociation reaction (Figure 1.1).

Figure 1.1 Loss of aqua ligand from square planar Pt^{II} complex.

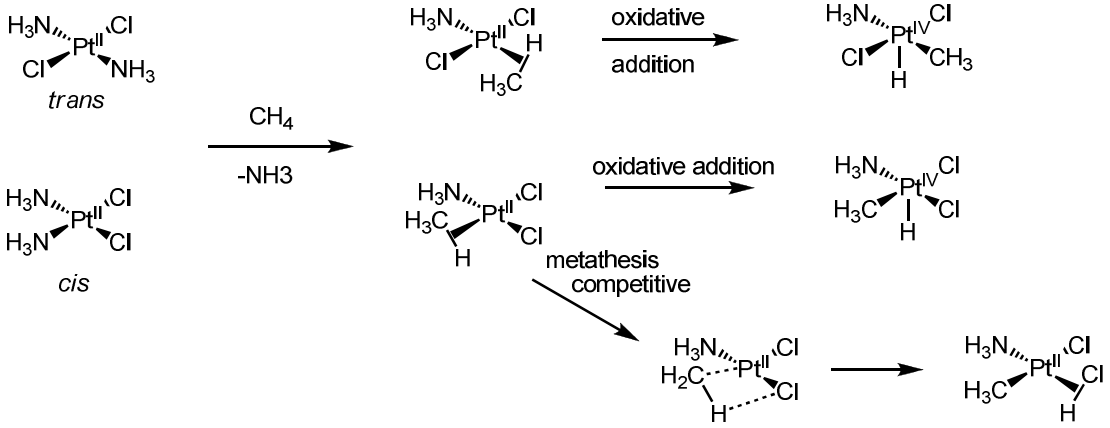


Steric effects may also have a negative influence on the rate of CH activation. Zhong, Bercaw and Labinger found that sterically hindered diketimine complexes had lower rates of benzene activation with respect to non-hindered ones.[71] The lower rates are assumed to be due to the difficulty experienced by benzene in approaching the hindered Pt center. However, a methane molecule is much smaller than coordinated benzene. The energy of the σ-CH bonded methane intermediate is expected to be destabilized to the same extent as that of the starting aqua ligated complex without significantly affecting the transition state energy of the CH bond splitting step, or that of the presumed Pt^{IV} hydride intermediate. As applied to the ligands used in this work, this hypothesis was confirmed by relevant DFT calculations and will be discussed below.

Even if the displacement of water is not the rate determining step, the appropriate ligand would lower the overall energy profile of the reaction. Evaluating the entire CH bond co-ordination and breaking pathway would involve modeling the oxidative cleavage, σ-bond metathesis, and the electrophilic substitution pathways involved in CH bond splitting. Often, the energetic differences between these

pathways are slight and may depend on the steric arrangement of ligands, the type of ligand that dissociates, and on the reaction medium. For example, Hush and coworkers found that $(NH_3)_2PtCl_2$ has displacement of ammonia by methane as the rate limiting step in both the trans and the cis complex.[72] In the trans complex, oxidative addition to form a Pt^{IV} hydride was favored over other pathways, but in the cis complex, oxidative addition and σ-bond metathesis became competitive (Scheme 1.14).

Scheme 1.14. Computational results for the $(NH_3)_2PtCl_2$ system



Later, when investigating the possibility of chloride displacement from the same cis complex, Goddard and coworkers concluded that the oxidative addition pathway becomes favored by ~10 kcal/mol.[73] As mentioned earlier, calculations on the Catalytica system that modeled the reaction medium concluded that the CH activation event occured by electrophilic substitution[74] or a (the way it is recently termed) σ-CAM mechanism.[75] Thus, caution has to be used when deciding which mechanism is operative as the lowest energy pathway appears to depend very much on a particular ligand and reaction conditions. It would be time prohibitive for us to

model all the possible CH activation mechanisms in each of our proposed ligand systems. What is clear is that solvento ligand substitution does play a large role in the overall reaction and the modeling of this relatively easy transformation offers a quick and reliable diagnostic for the suitability of a particular ligand platform.

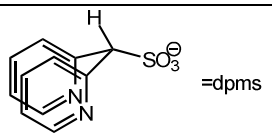
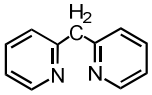
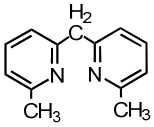
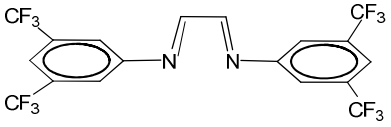
1.2.2 Development of the dmdpm motif

With the recent advent of fast computer processors, an entire ligand on a Pt center can be modeled in a reasonable time frame and the full normal mode analysis and the Gibbs energy calculations could be carried out. As mentioned earlier, our analysis invoving calculations of the Gibbs energy for the reaction depicted in Figure 1.1 does not take into account the "actual" mechanism of the replacement of the aqua ligand by methane in our systems (dissociative or associative) but the data produced will reflect a trend among a group of similar metal complexes. The Gibbs energy associated with the actual (gas-phase) reaction could be smaller if an associative or concerted transition state is involved as compared to purely dissociative mechanism of aqua-for-methane ligand substitution. That means the numbers we obtain can be an upper energy boundary for the reaction if the mechanism is truly a dissociative one.

As applied to real systems, the solvent effect and especially the effect of higher solvent concentration relative to the substrate would affect the position of equilibrium in Fig. 1.1 and the corresponding Gibbs energy, ΔG. Taking all the factors into account, the $\Delta G^{\neq}$ for the dissociation of the aqua ligand will have a small (few kcal) error against measured experimental kinetic rates, and it will reflect a very accurate trend across a group of similar ligands such as bidentate nitrogen donor

ligands and nitrogen based scorpionates. The ligands presented in Table 1 are a representation of the many different scaffolds that were checked via DFT.

Table 1.1 ΔG^{o} for loss of aqua ligand from associated $LPt^{II}(Me)(OH_2)$ complexes (reaction in Fig. 1.1)

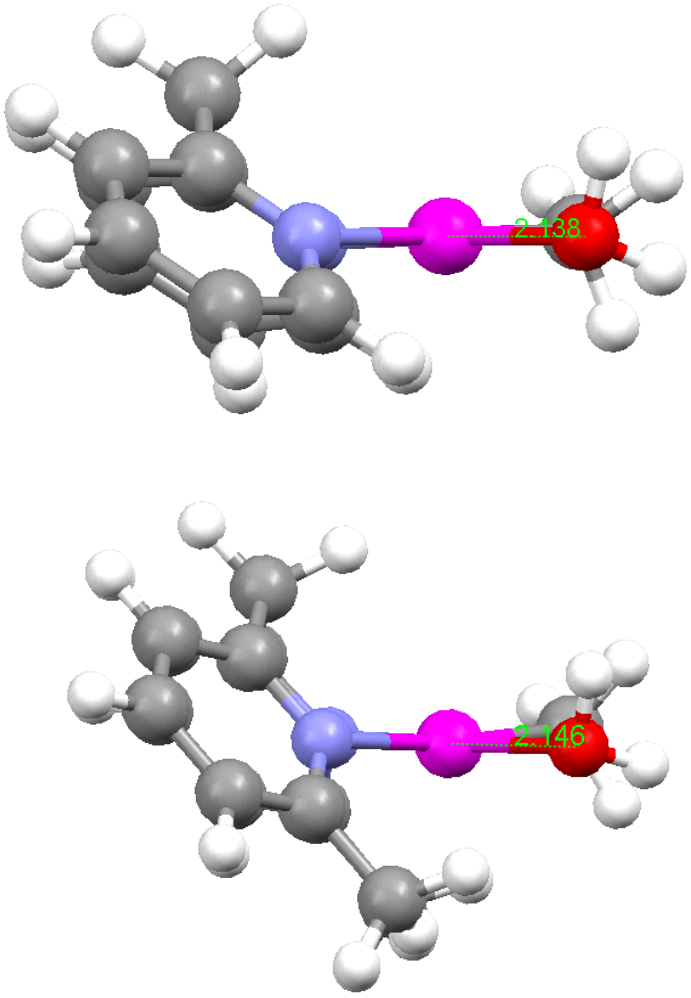
Ligand	ΔG^{o}_{298}, kcal/mol
 =dpms	24.2
 =dpm	21.6
 =dmdpm	18.5
	16.9

The low ΔG^{o} for the diketimine ligand that is very similar to the one used by the Tilset and Bercaw groups (two methyl groups in the diketimine backbone are missing – Scheme 1.13) is immediately apparent. This ligand is similar to the one used by Zhong et al. in order to measure steric and electronic effects of diketimines on CH activation. It was found that this scaffold is less active than one with two methyl groups in the diketimine backbone.[71] The latter ligand holds the current record for fastest measured rate of CH activation by a cationic complex in TFE as well;[36] the diketimine scaffold genereally has proven very valuable as a mechanistic CH activation probe. The reason for the robustness of the system may not only be

electronic in nature. The large phenyl groups may provide steric bulk that can favor aqua ligand dissociation, although this has been disputed by the results of Zhong et al. Chen and Gerdes believe that the Ph groups coordinate to the Pt center in the three coordinate intermediate (formed in a dissociative process) that they observe in the gas phase.[49] However, this pathway may not play a large role in solution chemistry.[50] Platinum complexes supported with diketimines also suffer from low water solubility and this very important factor may make them undesirable in further exploration of practical variants of Shilov chemistry.

We decided to explore the dipyridylmethane ligand system due to earlier reports where complexes supported by similar pyridine based motifs showed interesting CH activation activity.[55,76-80] The dipyridylmethanesulfonate (dpms) ligand used by Vedernikov to isolate a dimethylhydride Pt^{IV} complex,[52] is a surprisingly poor candidate for CH activation according to Table 1.1. Interestingly, this could be due to the pendant sulfonate's propensity to form strong intramolecular hydrogen bonds to the aqua ligand. This effect would only become more pronounced in non-hydroxylic solvents, but it would also make this ligand a poor choice for an aqueous environment. Once the sulfonate is removed, a 3 kcal/mol reduction in overall reaction energy is achieved. By introducing two ortho methyl groups and thereby adding steric bulk to the relatively simple dpm ligand, energy is once again lowered by another 3 kcal/mol. The ortho methyl groups would be too far away from the Pt center to undergo intramolecular CH activation (Figure 1.2), but they are close enough to sufficiently destabilize the ground state by distorting the ideal square planar geometry around a d^8 metal center.

Figure 1.2 Side on views of the DFT optimized structures of dpmPt(Me)$(OH_2)^+$ (top) and dmdpmPt(Me)$(OH_2)^+$ (bottom) with Pt-O bond lengths indicated. Bond lengths in Angstroms (Å) 1Å=100pm

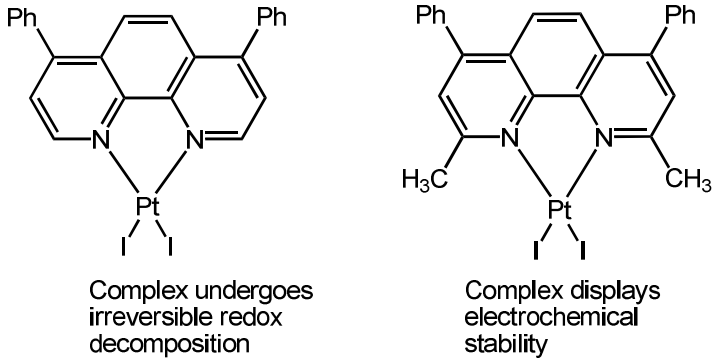


This relatively simple ligand is also expected to generate a more water soluble cationic complex than in the case of the diketimine. Even if the Gibbs energy of reaction in Fig. 1.1 is underestimated, if it is assumed that the data from Table 1.1 form a trend, then dmdpm is separated from the successful diketimine motif by only 1.6 kcal/mol. If Pt complexes supported by the latter can display rapid CH activation in TFE, then complexes supported by dmdpm should display CH activation in water at, or close to, room temperature. This result would be significant since, except for the

Shilov system, no Pt complex has proven to be effective for CH activation in purely aqueous systems.

Interestingly, the DFT calculated structure of the dmdpm complex shows a longer Pt-O bond than the corresponding structure for the dpm complex (Figure 1.2). The deviation of Pt from the mean plane created by the four ligands bonded to platinum is 6.6 pm in the dmdpm ligand versus 0.6 pm for the dpm case. Steric effects significantly effecting reactivity are not unknown in Pt(II) chemistry. A phenanthroline system that contains a five membered Pt cycle allows for reversible access to a Pt(IV) species when methyl groups are present in ortho positions to the two nitrogen donors. The complex without the ortho substituents undergoes irreversible reduction as determined by cyclic voltametry (Figure 1.3).

Figure 1.3 Effect of ortho substituents on reactivity

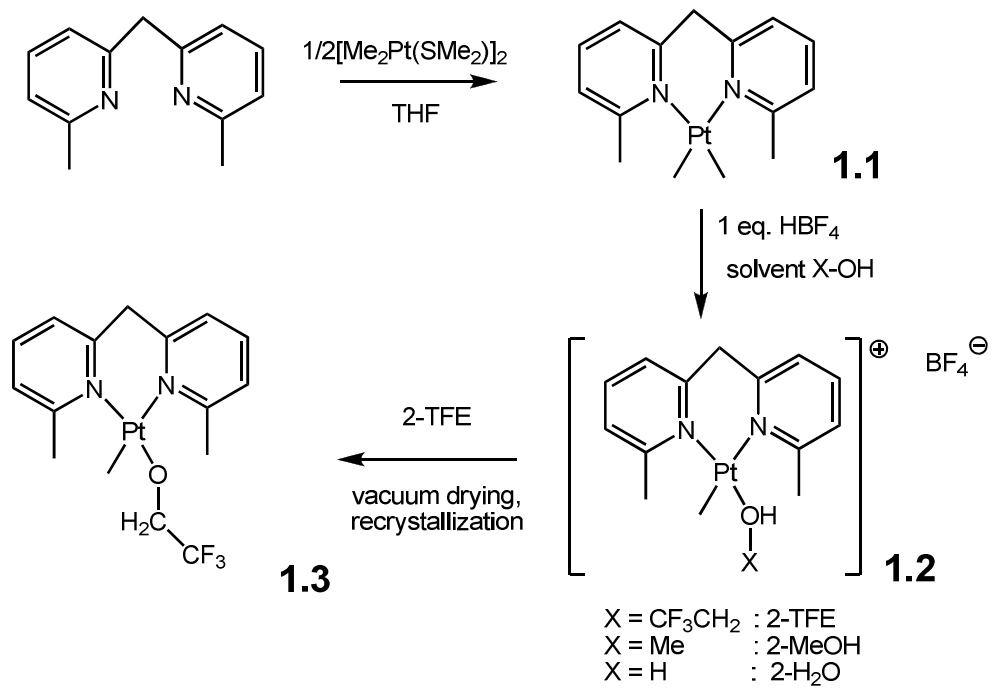


Of note in this report is the large displacement of Pt(II) from the mean plane defined by the four ligands (0.222 Å) in the sterically crowded complex, while no such displacement is observed for the complex that does not contain ortho methyl groups.[81] Therefore, based on our DFT observation and prior literature results, we were expecting interesting CH activation results with the actual complex in hand.

1.3 Synthesis of the dmdpm supported Pt complexes and associated activity in CH activation: Results and Discussion

The dmdpm ligand was synthesized by coupling of lutidine and picoline. The monomethyl contaminant that inevitably formed was removed by flash column chromatography to obtain the pure ligand. Reaction with a dimethylsulfide Pt precursor $[Pt(Me)_2(SMe_2)]_2$[82] gave the corresponding dimethyl complex **1.1**. Treatment of complex **1.1** with 1 equivalent of HBF_4 in methanol or trifluoroethanol, provided pure solutions of cationic **1.2**(methanol) and **1.2**(TFE) respectively. Since **1.1** is insoluble in water, the corresponding aqueous solution of **1.2** can be obtained by treating a solution of **1.1** with HBF_4 in a 3:1 mixture of methanol to water. The resulting solution is reduced to ~20% of the original volume under high vacuum and refilled with water 3 times to obtain a pure aqueous solution of **1.2**; this avoids the chance possibility of double protonolysis**.** Reducing the volume to dryness results in a product that shows varying activity in CH activation when it is dissolved in the corresponding solvent. Tellingly, an attempt to crystallize **1.2**(aqua) by re-dissolving a dry sample obtained in TFE in water gave crystals of neutral compound **1.3** (Scheme 1.1.5; Figure 1.4).

Scheme 1.15 Synthesis of complexes **1.2** and **1.3**

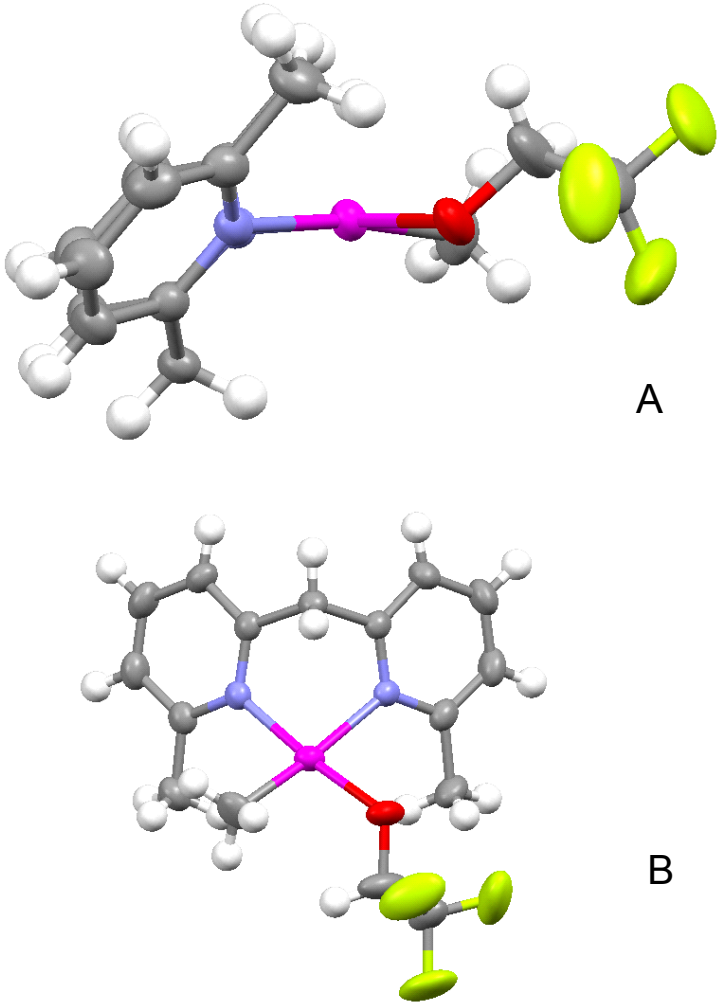


The crystal structure of **1.3**, although expected to deviate from **1.2** (TFE) in the length of the Pt-O bond, shows that the Pt(II) center is pushed out of the mean plane defined by the plane of the N,N,C,O ligands by 0.103 Å. Although compound **1.3** could serve as a model for how the steric bulk distorts the square planar coordination sphere of Pt^{II} just as predicted, CH activations studies had to be carried out with the cationic complexes **1.2**.

Neither compound **1.3** nor **1.2** could be isolated in analytically pure form. Samples of **1.3** had an appreciable ^{19}F NMR signal due to BF_4^-(-150.6 ppm); 1,4-difluorobenzene standard showed that the amount of BF_4^- anion present was about 15%. Hence, the samples of **1.3** mentioned above contained about 15 % mol. of **1.2**. Prologed exposure of mixtures of **1.3** and **1.2** to high vacuum never reduced the amount of the BF_4^- anion below 10%.

When **1.2** was prepared in situ by the method outlined above, samples of cationic complex **1.2** pure by NMR spectroscopy (~100% BF_4^- anion by 1,4-difluorobenzene or TFE ^{19}F NMR standard) could be repeatedly obtained. The solutions and the subsequent activation products were very amenable to analysis by low voltage ESI-MS methods.

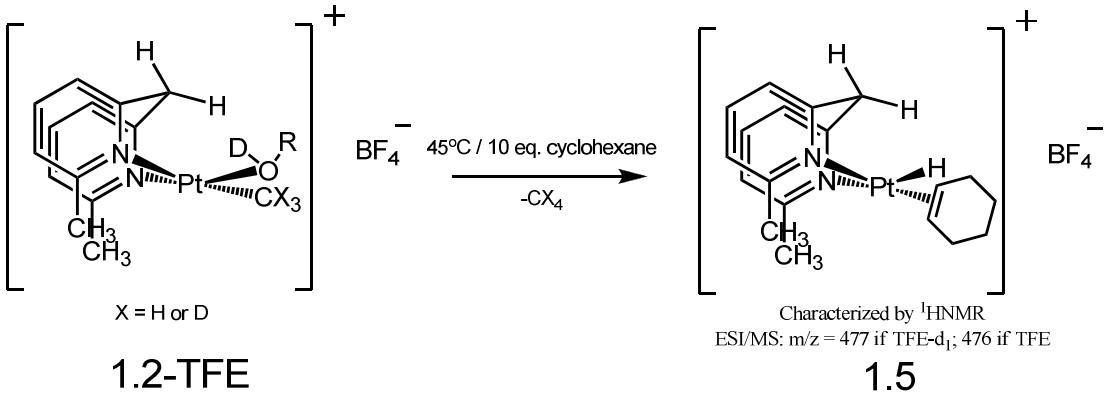
Figure 1.14. Compex **1.3** crystal structure (Mercury drawing) side-on (A) and top (B) views at 50% probability ellipsoid level



1.3.1 CH activation studies with complex **1.2**

After obtaining **1.2**(TFE), the CH activation of this complex was tested with benzene and cyclohexane in TFE solution. Both of these substrates are activated at room temperature to give phenyl complex **1.4**(TFE) and cyclohexene hydride **1.5**, respectively (Scheme 1.16). However, since solutions of the complex are stable at 45°C under the reaction conditions, the activation was monitored at a controlled temperature of 45°C; the results are summarized in Table 1.2. The rates of reaction were followed by ^{1}H NMR spectroscopy and determined under pseudo first order (at least 10 eq. substrate) reaction conditions.

Scheme 1.16 Activation of cyclohexane with 2-TFE



1.2-TFE 1.5

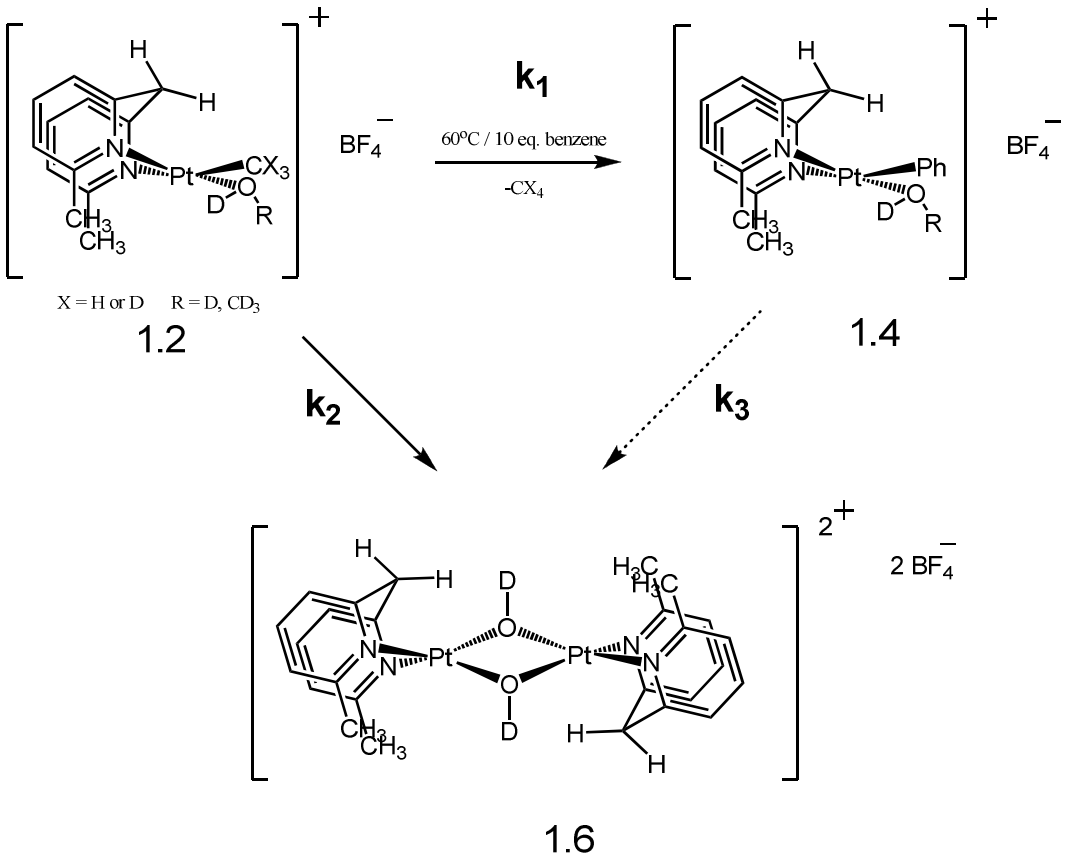
Table 1.2. Kinetic parameters of activation of benzene and cyclohexane by **1.2**-TFE in TFE at 45°C.

	Benzene	Cyclohexane
k_{obs}	(4.05 +/- 0.07)e-5 s^{-1}	(1.11 +/- 0.03)e-5 s^{-1}
Half-life, h	4.76+/-0.08	17.3 +/- 0.5
$\Delta G_1^{\neq}$	22.7 kcal/mol	23.5 kcal/mol

Both reactions can also be observed at room temperature. The identity of the phenyl complex was confirmed by an independent synthesis of **1.4**(TFE) from the diphenyl analogue of **1.1**, and by ESI-MS. The identity of **1.5** was confirmed via ^{1}H NMR spectroscopy of the product that produced a hydride signal at -21.6 ppm integrating as 1H and two inequivalent Pt bound olefin signals integrating as 2H, as well as by ESI-MS.

In methanol or water solutions, **1.2** was reasonably reactive towards the CH bonds of benzene, but not those of cyclohexane, at 60°C. However, a considerable side reaction that led to dinuclear complex **1.6**, was also observed in water (Scheme 1.17); complex **1.6** was identified by ESI-MS. In methanol, another side reaction (activation of the CH bonds of methanol or methanolysis) was accompanied by decomposition of Pt containing species towards Pt black.

Scheme 1.17 Activation of benzene in water and methanol



It is conceivable that alkane substrates can also be activated in water and methanol, but that the rate of activation is much slower than that of side reactions and decomposition, making it difficult to observe the reaction. The rate of CH activation (k_1) can be estimated by determining the observed pseudo-first order rate constant for disappearance of starting material with substrate present, and performing a linear subtraction of the decomposition rate without substrate obtained in a control reaction (Equations 1 and 2).

$$k_{obs} = k_1 + k_2 \qquad (1)$$

$$k_{obs} - k_2 = k_1 \qquad (2)$$

The results of our kinetic studies are summarized in Table 1.3. Although the k_{obs} is comparable to that of k_2, the latter value reflects the large excess of solvent (especially in low MW H_2O or D_2O) compared to the amount of substrate that was present in reaction solutions. Taking concentrations of a solvent and a substrate into account would, in the case of methanol solvent for example, lead to a greater second-order rate constant for activation of benzene $k_{cor}=k_1/[PhH]$ than for the methanolysis reaction ($k_2/[MeOH]$ and $k_3/[MeOH]$) since the MeOH is present in a greater concentration (~3 orders of magnitude greater than benzene). However, the decomposition reactions preclude this system from being used in practice.

The $\Delta G^{\neq}$ values of 25.5 and 26.3 kcal/mol for activation of benzene in methanol and water respectively, are greater that the DFT calculated values (see Table 1.1) since an allowance should be made for the CH bond breaking step after the σ-bond bound intermediate has been obtained.

Table 1.3 Kinetic parameters of activation of benzene with complex **1.2** in methanol, water, and TFE; [PhH] = 0.0236M (TFE and MeOH) or 0.0118M for D_2O

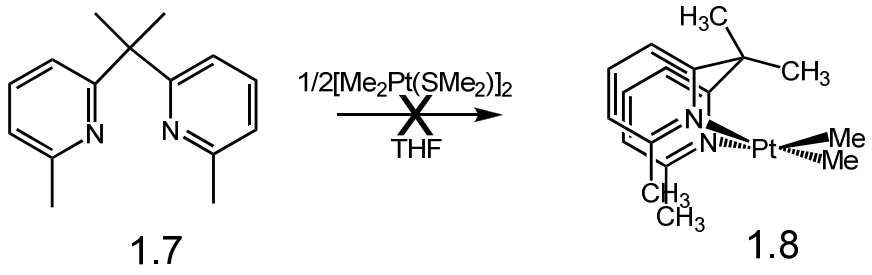
	CF_3CH2OD (45°C)	CD_3OD (60°C)	D_2O (60°C)
k_{obs}	(4.05 ± 0.07)e-5 s^{-1}	(1.51± 0.04)e-5 s^{-1}	(3.1± 0.1)e-6 s^{-1}
k_2	<1e-7 s^{-1}	(1.22 ± 0.08)e-5 s^{-1}	(2.2 ± 0.1)e-6 s^{-1}
$\Delta G_1^{\neq}$	22.7 ± 0.1 kcal/mol	25.5 ± 0.3 kcal/mol	26.3 ± 0.1 kcal/mol

1.3.2 Conclusion and future plans

We can conclude that DFT modeling can be a valuable tool in desigining a system that will activate CH bonds at room temperature in aqueous solutions. The key parameter of such a system is low DFT-calculated dissociation energy of the aqua ligand. Stability and side reactions might not be as much of a problem as they were in the case of **1.2** at 60°C. **1.2** is stable indefinitely in a water solution, and undergoes slow decomposition in methanol ($t_{1/2}$ = ~1 month) at room temperature.

Encouraged by our initial success, we decided to slightly modify the dmdpm motif to decrease dissociation energy of the aqua ligand and obtain additional 3 kcal/mol reduction in energy. The even more sterically hindered ligand **1.7** provided the necessary energy change, but it did not form the Pt complex **1.8** when mixed with the Pt precursor (Scheme 1.18). We are currently exploring modifications to the dmdpm motif to achieve desired reactivity.

Scheme 1.18. Attempted synthesis of complex **1.8**.



1.7 1.8

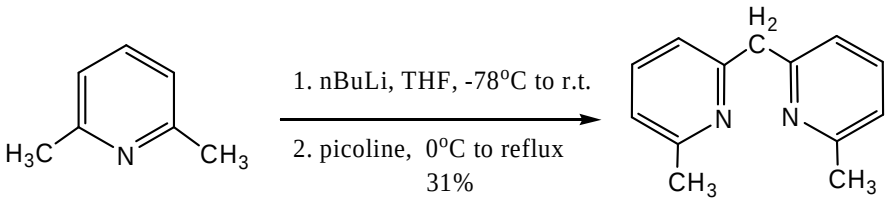
In conclusion, we have synthesized the first Pt(II)(solvento)(alkyl) complex capable of undergoing CH activation reactions in pure water and methanol. Interestingly, unlike the diketimine systems utilized by Bercaw, Labinger and Tilset, these complexes are very sensitive towards extra equivalents of acid. We obtained an

interesting alkoxide complex **1.3**, a neutral derivative of the protonated cationic complex **1.2**(TFE), which confirmed that through careful ligand modification, it may be possible to influence the steric and electronic environment around the Pt metal center and promote facile CH activation in coordinating solvents. Although side reactions in water preclude further study of this system for practical application, ligand optimization currently underway should furnish a more reactive and more stable species.

1.4 Experimental

1.4.1 Synthesis and Reactivity of Ligands and Complexes

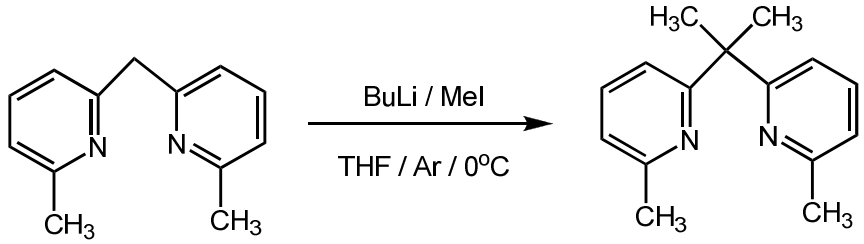
Bis(6-methylpyridin-2-yl)methane, dmdpm



This ligand has been previously reported.[83,84] To achieve a large scale synthesis, a modified procedure (reported in reference 84) was adopted. 53.6 g of 2,6-lutidine (500 mmol) were cooled to -78°C in dry THF under argon. 53.0 mL of 10M BuLi solution (530 mmol) in hexanes was added while maintaining vigorous stirring. The mixture was allowed to react for half an hour, after which the reaction was allowed to reach room temperature on its own. Subsequently, the temperature was lowered to 0°C and 9.90 mL (100 mmol) of 2-picoline were added dropwise to the solution. The solution was refluxed for one day, the temperature was lowered and the reaction was quenched with water over an ice bath. The products were extracted with diethyl ether, washed with water, conc. $NaHCO_3$ solution, and brine, then dried over anhydrous $MgSO_4$, filtered and concentrated. The resulting products were purified by vacuum distillation to give a mixture of the product and a monomethyl-pyridine methane admixture in a 2:1 ratio was obtained pure, concentrating after column chromatography (ether/hexane; 27/73) as a yellow, crystalline solid* (6.20 g, 31% yield on picoline). The spectral data matched literature reports.[83,84] mp 35-37°C.

*Reported as an oily residue in reference 83; only NMR data reported in reference 84. Oily residues of dmdpm for us meant at least a 3% admixture of monomethyl-pyridine methane admixture that were unacceptable for kinetic studies. Very pure dmdpm is a dry solid.

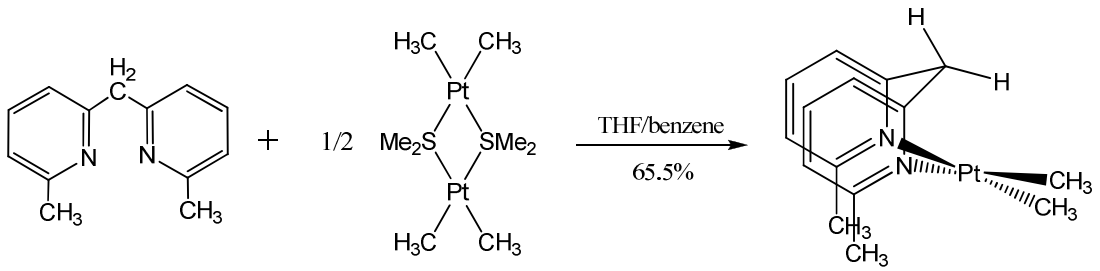
Bis(6-methylpyridin-2-yl)propane, 1.7



To a dry flask flushed with argon and 50 mL. of dry THF at 0°C, 0.4 grams of (2mmol) of dmdpm were added. To this mixture was added 0.80 ml of 2.5M Butyl Lithium solution (2 mmol) and the reaction was vigorously stirred for five minutes after which 26 μL. of MeI (2 mmol) were added. The mixute was allowed to stir at 0°C for half an hour, after which time a second portion of BuLi was added (0.80 mL of 2.5M soln.) and after five minutes 50 μL of MeI were added as well. The reaction was allowed to slowly reach room temperature, after which time it was quenched with water. The product was extracted in ether and washed with water, conc. NH_4Cl solution and brine. After drying over $MgSO_4$, the product was dried under vacuum to obtain a wet, reddish oil. The product was purified by column chromatography (1/10 : Et_2O/hexanes) to obtain **1.7** as a pale red solid in ~75% yield (0.30 grams).

^{1}H NMR (22°C, $CDCl_3$), δ : 7.29 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 1H), 1.67 (s, 1H).
^{13}CNMR (22°C, $CDCl_3$), δ : 167.1, 156.8, 135.9, 120.0, 118.4, 48.0, 28.5, 24.7.

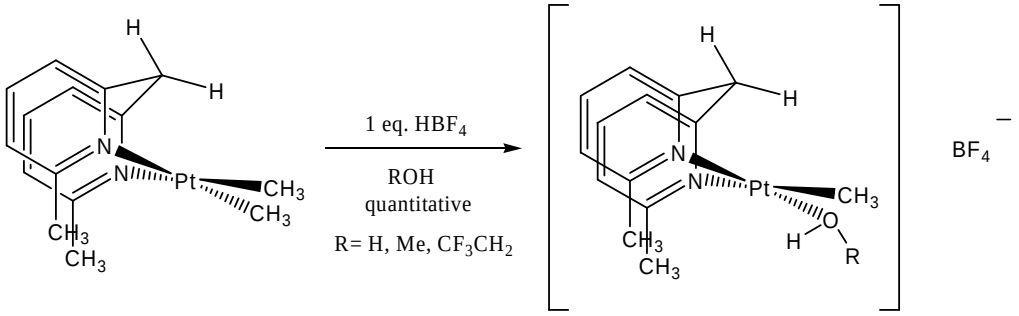
Bis(6-methylpyridin-2-yl)methane-dimethyl-platinum(II), dmdpmPt(Me)$_2$, 1.1



63 mg of dmdpm (0.32 mmol) were dissolved in 3 mL of THF in a vial equipped with a stirring bar. 100 mg (0.16 mmol) of $[Pt(CH_3)_2(SMe_2)]_2$ platinum precursor were added to the vial. The mixture was capped and allowed to stir for 3 hours until significant amounts of a white precipitate had formed. The THF solvent was then evaporated to dryness under high vacuum to give a light yellow solid. The solid was washed with three 1 mL portions of benzene that were carefully decanted with a Pasteur pipette to give **1.1** as a white solid, (88 mg, 65.5%) that is sparingly soluble in benzene. mp 205-210°C (dec.).

^{1}H NMR (22°C, C_6D_6), δ : 6.70 (t, 2H, *J*=7.5Hz), 6.41 (d, 2H, *J*=7.5 Hz), 7.34 (d, 2H,
J=7.5 Hz), 5.65 (d, 1H, *J*=13.2 Hz), 3.26 (d, 1H, *J*=13.2 Hz), 2.82 (s, 6H), 1.56 (s, 6H, J_{Pt-H}=89.7 Hz).

Bis(6-methylpyridin-2-yl)methane-methyl-solvento-platinum(II)-tetrafluoroborate, dmdpmPt(Ph)(solvento)$^+BF_4^-$, dmdpmPt(Me)(solvento)$^+BF_4^-$, 1.2



10mg of neutral complex **1.1** (0.024 mmol) were added to a vial with ~2 mL of CD_3OD or CF_3CH_2OD under air to form a suspension. 2.7 μL of HBF_4/H_2O solution (50% by weight, 0.021 mmol) were added via microsyringe to the suspended complex all at once with rapid stirring. After one minute, the suspension had mostly dissolved and the solution became clear. The reaction was allowed to proceed for a further

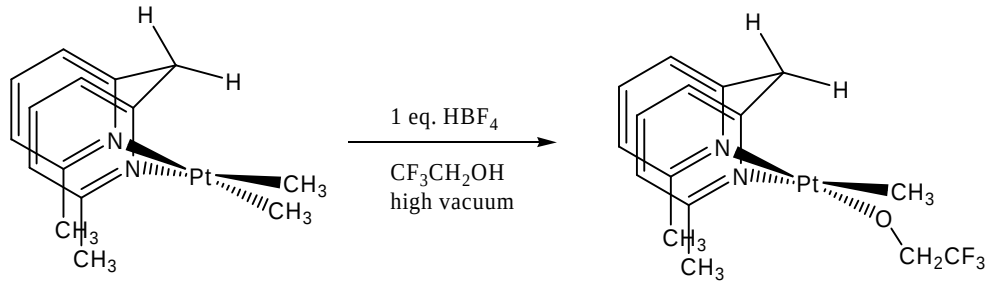
hour, after which the solution was filtered through a cotton plug and used as is for kinetic studies. The methanol complex exists as a mixture of methanolic and aqua complexes with the methanolic being the major isomer (~95%). The complex is very sensitive to extra amounts of acid and will over-protonate readily. Over-protonation will occur in pure D_2O with any amount of strong acid. To obtain D_2O stock solutions, a vial was charged with a 3 mL 3:1 mixture of CD_3OD/D_2O and 10 mg of **1.1** were added, followed by 2.7 μL of HBF_4/H_2O solution. After the suspension had dissolved, the solution was concentrated to 0.5 ml under high vacuum (just before a precipitate developed), then diluted to 4 mL with D_2O* and subsequently concentrated under vacuum to a 0.5 mL volume again. The concentration/dilution procedure was repeated two more times until a stock solution of **1.2** in pure D_2O was obtained.

^{1}H NMR (22^{o}C, CD_3OD), δ : 7.86 (t, 1H, *J*=7.9 Hz), 7.80 (t, 1H, *J*=7.9 Hz), 7.56 (d, 1H, *J*=7.9 Hz), 7.50 (d, 1H, *J*=7.9 Hz), 7.42 (d, 1H, *J*=7.9 Hz), 7.36 (d, 1H, *J*=7.9 Hz), 5.51(d, 1H, *J*=14.2 Hz), 4.55 (d, 1H, *J*=14.2 Hz), 2.91 (s, 6H), 0.88 (s, 3H, J_{Pt-H}=75.4 Hz)**

ESI/MS: $C_{15}H_{21}N_2OPt^+$ 440.1365; calc. 440.1302**

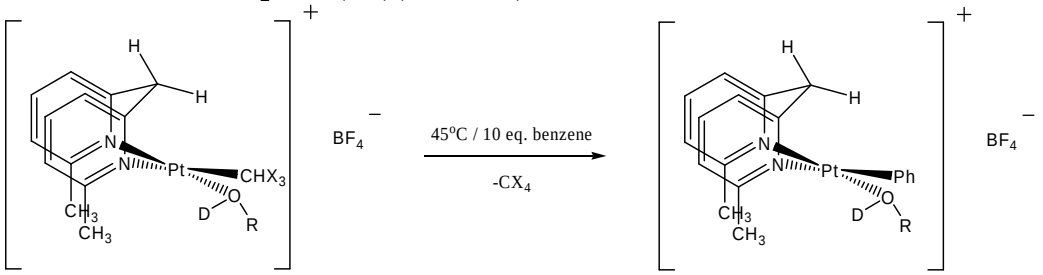
*It is critical not to evaporate to dryness to avoid formation of the neutral analogue of complex **1.3**.
When formed in a deuterated solvent, the methyl group attached to the platinum center is always mostly deuterated and integrates to <<3H. All three isotopomers are seen. The assignment is confirmed by a parallel synthesis in a non-dueterated solvent and ESI-MS. The product is dried under vacuum and redissolved in a deuterated solvent. No H/D exchange occurs after loss of the first methyl group during synthesis, or upon heating in any solvent at 45^{o}C without hydrocarbon substrate. The byproduct of this synthesis is neutral complex **1.3.

Bis(6-methylpyridin-2-yl)methane-methyl-trifluoethano-platinum(II), dmdpmPt(Me)(CF3CH2O), 1.3



The same general procedure is followed as that for the synthesis of cationic **1.2**. Complex **1.1** is protonated in TFE solvent with 1 equivalent of HBF_4/H_2O solution. The solution is concentrated and then dried under high vacuum overnight. ^1H NMR and ESI/MS spectral data for complex **1.3** is exactly the same as that for **1.2** except for an apparently coordianted TFE peak that is found in the same region as trace TFE solvent. ^{19}F NMR shows that upon addition of 1,4-difluorobenzene standard (1eq), the BF_4 peak integrates as <<4 and 3 fluorines from TFE are present. Crystals of complex **1.3** are obtained by redissolving it in methanol and slowly layering the solution with water. It is impossible to obtain this complex in a completely pure form via this method, since some cationic impurity (at least 10%) **1.2** is always present.

Bis(6-methylpyridin-2-yl)methane-phenyl-solvento-platinum(II)-tetrafluoroborate, dmdpmPt(Ph)(solvento)$^+$BF4$^-$, 1.4



X = H or D R = CF_3CH_2, CD_3

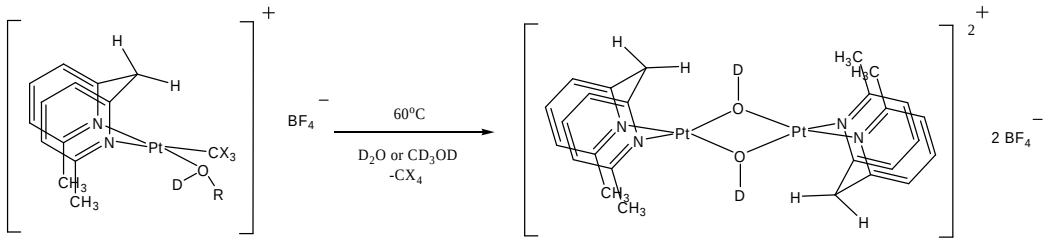
Stock solutions of **1.2** in a deuterated solvent, are placed into an NMR Young tube and 10 eq. of benzene are added. The Young tube is then subjected to temperatures of 60°C for water and methanol solvents, and 45 °C for TFE. A kinetic plot was obtained by taking an NMR spectrum for the former solvents periodically by cooling

the solution quickly to room temperature. For TFE, the NMR was obtained automatically at one hour intervals. In all cases, the disappearance of the starting material can be conveniently followed by integrating the ortho methyl peaks of the ligand (no deuterium incorporation occurs). Methane gas in produced along with two new multiplets of the coordinated phenyl group during the course of the reaction. A pure product could be obtained from TFE solutions (>95% as established by ^{19}F NMR and ^{1}H NMR). However, two of the ligand peaks are overlapping with the phenyl peaks and the ortho-H phenyl signal is obscured by the benzene. ESI/MS was obtained for the associated aqua complex reaction with benzene in pure H_2O.

^{1}HNMR (22^{o}C, CF_3CH_2OD), δ : 7.49 (t, 1H, *J*=7.2 Hz), 7.40 (t, 1H, *J*=7.2 Hz), 7.18 (d, 1H, *J*=7.2 Hz), 7.50 (d, 1H, *J*=7.2 Hz), 7.42 (d, 1H, *J*=7.2 Hz), 6.77-6.82 (m, 4H), 6.69-6.73 (m, 2H) 5.47 (d, 1H, *J*=14.9 Hz), 4.16 (d, 1H, *J*=14.9 Hz), 2.74 (s, 3H), 2.17 (s, 3H).

ESI/MS $C_{19}H_{21}N_2OPt^+$ 488.1282; calc. 488.1302

Bis-(Bis(6-methylpyridin-2-yl)methane-hydroxo-platinum(II) Bistetrafluoroborate, [dmdpmPt(OH)$^{+}$]2[BF4^{-}]2, 1.6

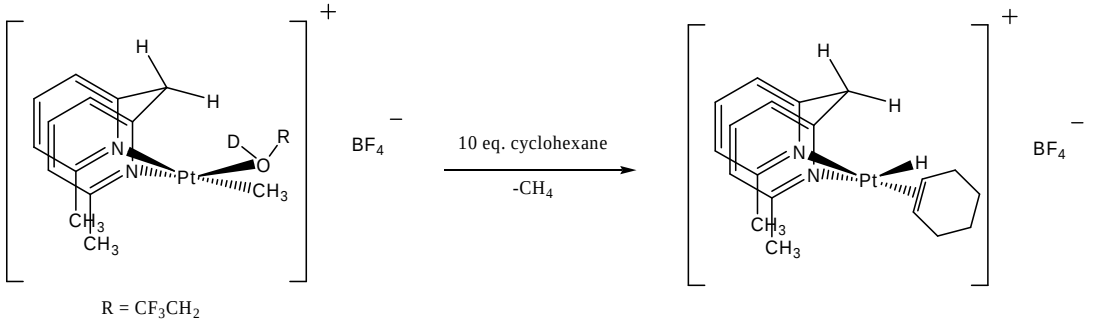


During the benzene activation reaction to form **1.4** in water, dinuclear species **1.6** is formed as a byproduct. The ^{1}H NMR shows a mixture of two very closely overlapping isomers (cis/trans) and the ESI/MS shows one mass envelope in the expected region. Data for the major isomer, believed to be trans, is reported.

^{1}H NMR (22^{o}C, D_2O), δ : 8.23 (t, 4H, *J*=7.8 Hz), 7.95 (d, 4H, *J*=7.8 Hz), 7.74 (d, 4H, *J*=7.8 Hz), 5.94 (d, 2H, *J*=15.3 Hz), 4.98 (d, 2H, *J*=15.3 Hz), 3.46 (s, 12H).

ESI/MS: $C_{26}H_{32}N_4O_2Pt_2^{++}$ 410.0896; calc 410.0832

Bis(6-methylpyridin-2-yl)methane-hydrido-cyclohexene-platinum(II) Tetrafluoroborate, dmdpmPt(H)(C_6H_{10})$^+$BF4$^-$, 1.5



R = CF_3CH_2

Complex **1.2**, prepared by the method described above, was dissolved in 1 mL of CF_3CH_2OD solvent in an NMR Young tube and 10eq of cyclohexane were added. The reaction was followed via ^{1}H NMR. A good linear correlation is obtained for a first order rate law for the formation of the hydrido olefin complex.

^{1}H NMR (22^{o}C, CF_3CH_2OD)*, δ : 7.85 (t, 1H, *J*=8.2Hz), 7.80 (t, 1H, *J*=8.2Hz), 7.52 (bd, 2H, *J*=8.2Hz), 7.42 (d, 1H, *J*=8.2Hz), 7.33 (d, 1H, *J*=8.2Hz), 5.74 (bm, 1H, J_{Pt-H}=81.5 Hz), 5.23 (d, 1H, *J*=14.8Hz, J_{Pt-H}=72.8 Hz), 5.18 (bt, 1H, *J*=6.4Hz), 4.38 (d, 1H, *J*=14.8Hz), 2.85 (bs, 3H), 2.74 (s, 3H), -21.6 (s, 1H, J_{Pt-H}=599.4 Hz).
ESI/MS: $C_{19}H_{25}N_2Pt^+$ 476.1560; calc 476.1665

*8 protons (CH_2 groups) on the cyclohexene ligand are not observed due to overlap with the TFE solvent (that was suppressed) and the large excess of free cyclohexane present in solution.

1.4.2 Plots of kinetic reaction data

Kinetics were obtained from ^{1}H NMR spectra taken in controlled atmosphere NMR tubes at 60 ^{o}C for D_2O and CD_3OD and at 45 ^{o}C for TFE. Pseudo first order conditions were achieved by adding 10 equivalents of substrate (cyclohexane or benzene) to 10mg of complex 1.2 dissolved in 1mL of solvent. Plots of control runs

measuring decomposition of starting material in D_2O or CD_3OD at 60 ^oC are not reported here but they were performed to determine k_2 and had very reproducible, clean first order kinetics. Energy of Activation values can be obtained from applying the Eyring equation to the slope. Energies for activation in D_2O or CD_3OD are obtained by applying the Eyring equation to a linear subtraction of slope of reaction minus the slope of the control. The correction for benzene concentration, 0.0236M in CD_3OD and TFE and 0.0118M for D_2O (the solubility of ~20 uL benzene in 1mL of water at 60 ^oC)[85] was applied. The rate law of bimolecular reaction is given by (1). However, since benzene is present in a large excess, the rate dependence can be simplified to (2). A correction for the concentration of substrate must still be made when calculating energy via the Eyring equation (3) where T is the temperature at which reaction was performed, R is the gas constant, h is Plank's constant and k_B is Boltzmann's constant. The pseudo-first order rate constant k_{obs} obtained from the slope of the plots of natural log of starting material over material at time T. vs. time, was thus divided by the concentration of benzene given above (to give k_{cor}) when used to determine the energy of activation. In the case of water and methanol reactions, the observed pseudo-first order rate constant obtained for the control reaction was subtracted from the rate constant obtained in NMR tubes charged with benzene, then the molar benzene correction was applied (4). In the case of TFE, no significant decomposition had occurred.

(1) $$d[P]/dt = k[complex][substrate]$$

(2) $$d[P]/dt = k[complex]$$

(3) $$\Delta G^{\neq} = -RT*\ln(k_{cor}h/k_BT)$$

(4) $$k_{cor} = (k - k_{control})/[M_{benzene}]$$

Although the R^2 values are within acceptable limits for all graphs, the best R^2 values were obtained for the TFE solvent where no decomposition had occurred and where the reaction was allowed to take place inside the NMR spectrometer at an elevated temperature. It is believed that temperature variability inside the lab/heating oil bath, caused small deviations in the other case of the other two solvents. Eyring plot analysis was attempted, however reproducible data was not obtained perhaps due to uncontrollable temperature changes in the oil bath during the reaction.

Figure E1.1 First order plot of the reaction between **1.2** and benzene in D_2O

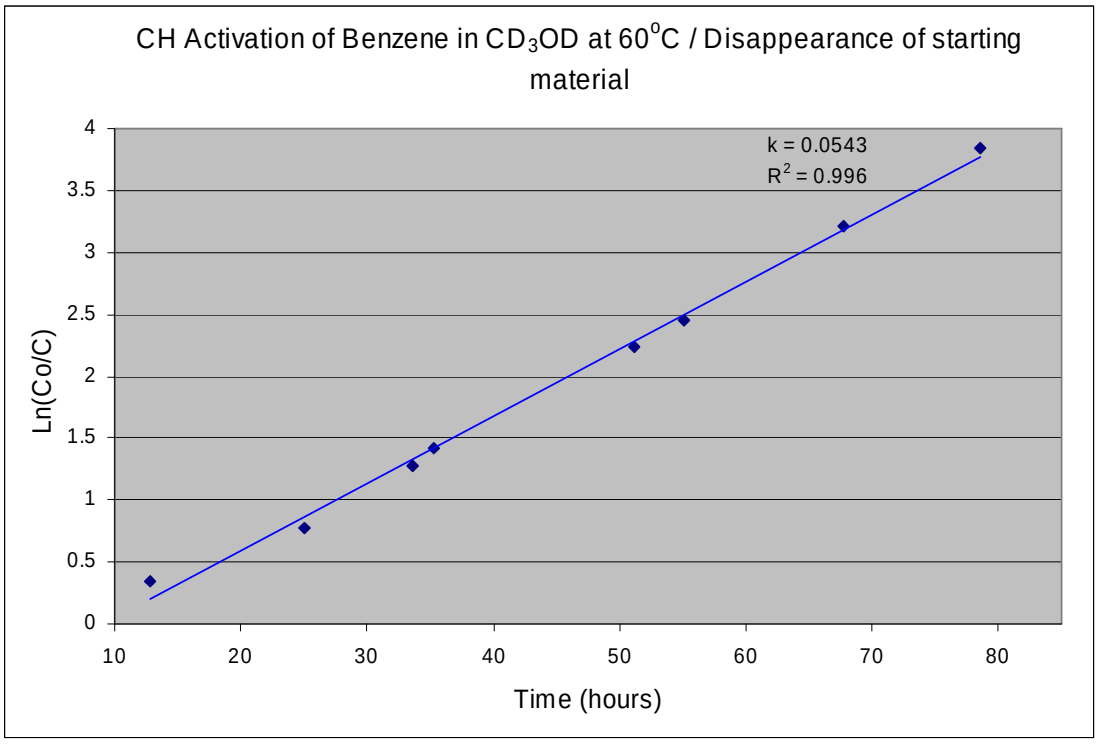


Figure E1.2 First order plot of the reaction between **1.2** and benzene in CD_3OD

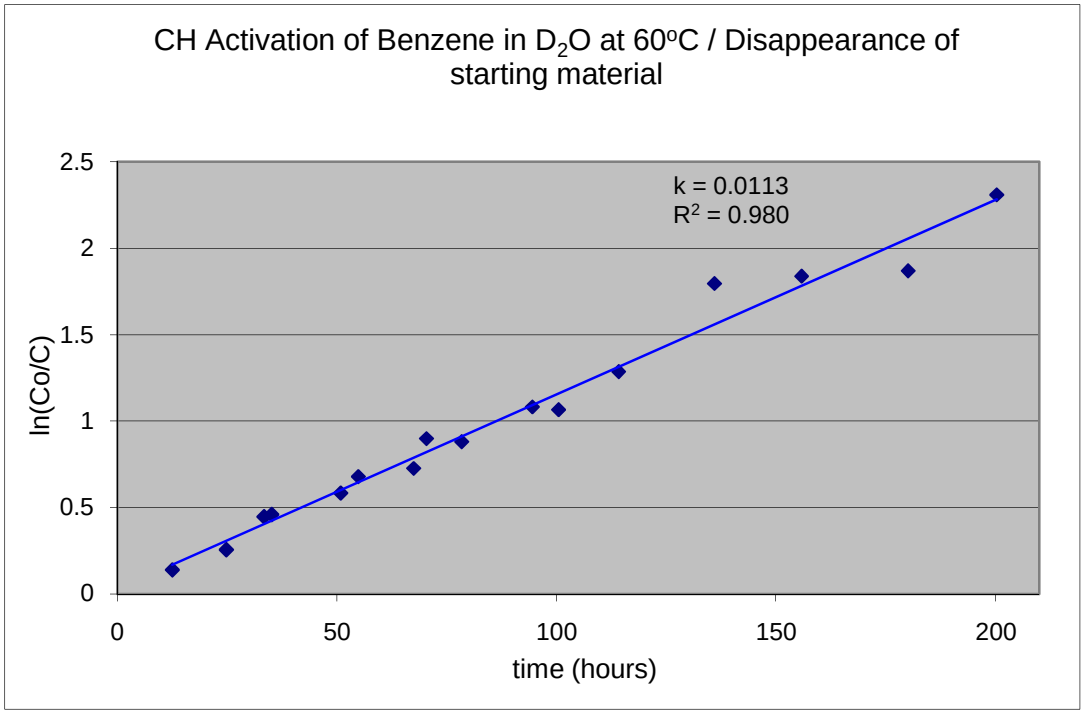


Figure E1.3 First order plot of the reaction between **1.2** and benzene in TFE

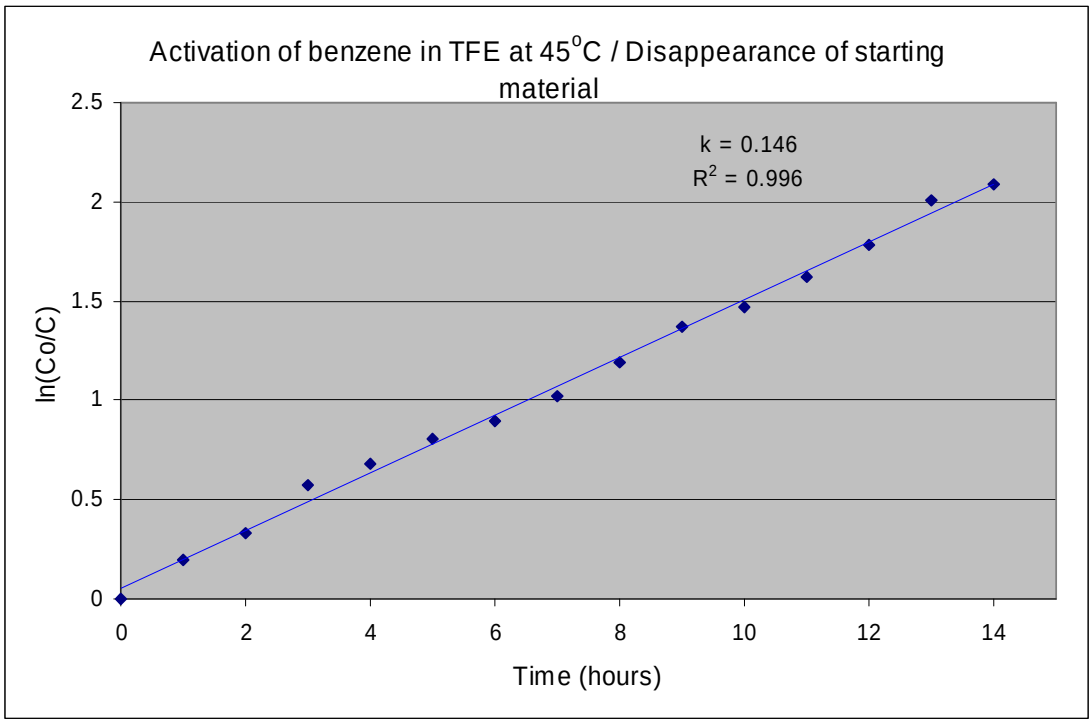
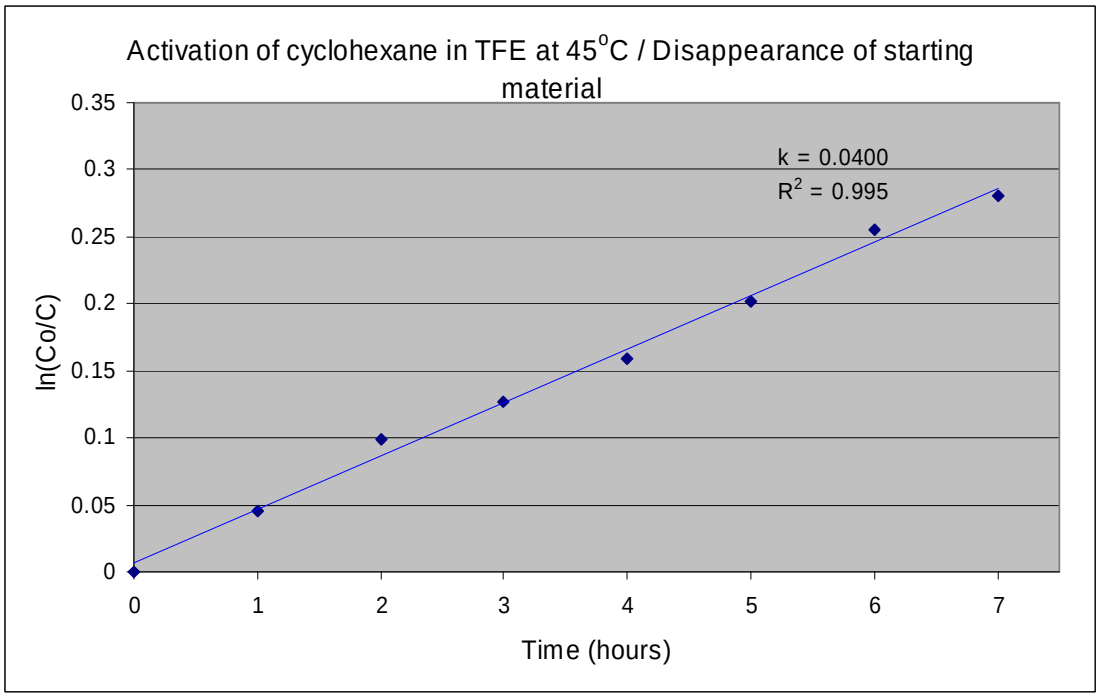


Figure E1.4 First order plot of the reaction between **1.2** and cyclohexane in TFE



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Chapter 2: Facile Arene C-H Bond Activation and Alkane Dehydrogenation with Anionic $LPt^{II}Me_2^-$ in Hydrocarbon-Water Systems (L = Dimethyldi(2-pyridyl)borate)

2.1 Introduction

2.1.1 Introduction : Activation of CH bonds with anionic Pt^{II} complexes

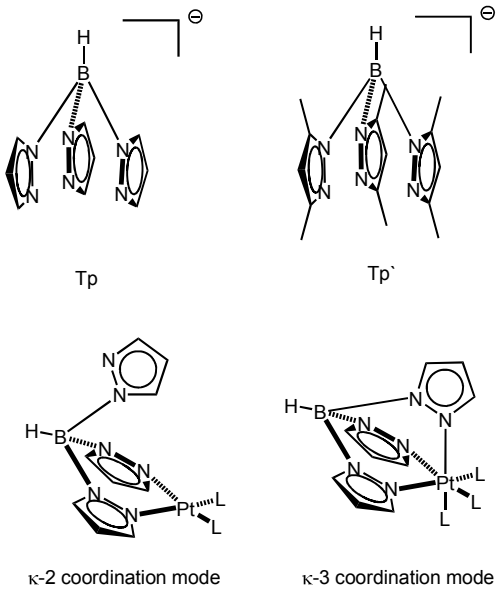
Although the results obtained in Chapter 1 were promising with regard to activation of alkane in water, the associated complex decomposed at the elevated temperature (60^oC) required to observe the reaction in an acceptable timeframe due to

unfavorable kinetics. Another ligand motif that lowered the energy required for aqua ligand dissociation (Table 1.1) even more than dmdpm by at least a further 3 kcal/mol, needed to be introduced. As well, it is experimentally established that Pt^{II} complexes supported by neutral N,N ligands are not easily oxidized.[1,(Chapter 1)] The same was true for the dmdpm motif. The monomethyl-aqua cationic complexes **1.2** that were investigated for CH activation in Chapter 1 proved to be stable towards air. Kinetics of benzene activation showed no deviation when measured under either an inert atmosphere of argon or under air. We decided to investigate anionic ligands for several reasons: i) related $LPt^{IV}R_2H$ and $LPt^{II}R(solv)$ complexes are neutral and may be more soluble in hydrocarbons than their ionic counterparts. That may be important for certain CH-activation and functionalization reactions that occur in hydrocarbon solvent such as alkane dehydrogenation; ii) a similar anionic dipyridine ligand, dpms, showed promise at both CH activation in weakly polar solvents and at aerobic oxidation of Pt^{II} monoalkyls in water; iii) there were other reports that oxidation of Pt^{II} center becomes more facile in anionic complexes which is a result of increasing electron density at either the ligand or the metal center.[2-7]

There are very promising reports in the literature regarding the use of anionic ligands at a Pt center in observing fundamental new types of reactivity.[8-10] One of the most widely used motifs is the trispyrazolylborate (Tp) or the methylated (Tp`) version (Figure 2.1) first developed by Trofimenko.[11-12] The negative charge is centered in on the boron atom, but can presumably be shifted to the Pt center[13] or directly though an empty d metal orbital if the boron is close enough. A big advantage of the ligand is its ability to coordinate in a κ^2 (two coordinate) or a κ^3 (three

coordinate) (see Scheme 2.1) fashion. The first coordination mode can be envisioned as stabilizing a square planar Pt^{II} center, while the second scorpionate motif will stabilize a Pt^{IV} octahedral geometry. Certainly, the ability of this ligand to stabilize two oxidation states effectively has resulted in its widespread use in other areas of Organometallic chemistry.[11]

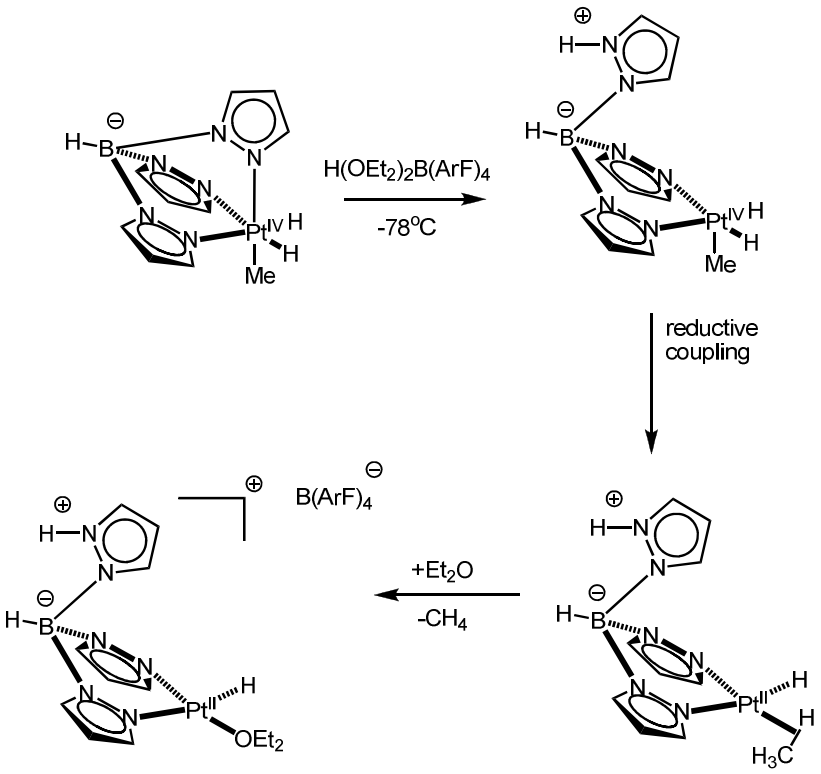
Scheme 2.1. Trispyrazolylborate ligands and coordination modes



The availability of the κ^3 coordination mode has allowed for the isolation of both the $Pt^{IV}Me(H)_2$ and $Pt^{IV}(Me)_2H$ complexes with the Tp and Tp` ligands.[14-18] The resultant complexes are stable towards air and moisture, but do incorporate deuterium at elevated temperatures in CD_3OD both into the hydride and the methyl ligands.[19] The stability of the Pt^{IV} coordination mode is a problem for catalysis, as reductive elimination must take place in order to produce a functionalized alkane. It is possible to eliminate one equivalent of methane to produce a $Pt^{II}Me$(solvent) complex with very strong acids at -78^{o}C (Scheme 2.2).[20] The protonation occurs at one of the

pyrazolyl arms, leading to a five-coordinate intermediate that is then more disposed towards reductive elimination.

Scheme 2.2 Acid assisted reductive elimination at $TpPtMe(H)_2$

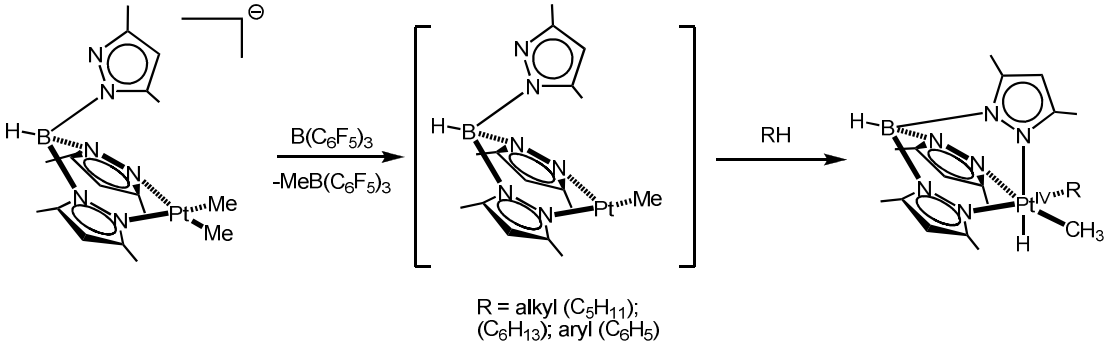


Aromatic CH activation can be observed with the dihydride complexes in the presence of catalytic $B(C_6F_5)_3$, although the exact mechanism by which the reactive intermediate necessary for activation is generated is unclear.[16]

Preparation of $TpPt(Me)_2H$ was first reported by Canty.[17] This complex was isolated by the protonation of anionic precursor κ^2 $TpPt(Me)_2^-$ with phenol. Later, HCl was used to make the Tp` analogue; $TpPt(Ph)_2H$ and $Tp`Pt(Ph)_2H$ are synthesized in a similar fashion.[18] These alkyl and aryl hydride Pt^{IV} complexes are stable at elevated temperatures, once again suggesting that the κ^3 coordination mode

of the ligand would play a negative, stabilizing role in a catalytic cycle. However, interesting chemistry towards CH activation was observed by Goldberg with the Tp`Pt(Me)$_2$ precursor when it was treated with the methide abstractor B(C_6F_5)$_3$ (which can abstract CH_3 from Pt^{II}-Me bonds) to generate a reactive three coordinate intermediate (Scheme 2.3).[21] The intermediate could bind n-pentane, cyclohexane and benzene. After oxidative cleavage of the coordinated CH bond had occurred, the Pt^{IV} oxidation state was trapped by the κ^3 mode of the Tp ligand.

Scheme 2.3. Activation of alkanes and arenes with TpPt(Me) intermediate

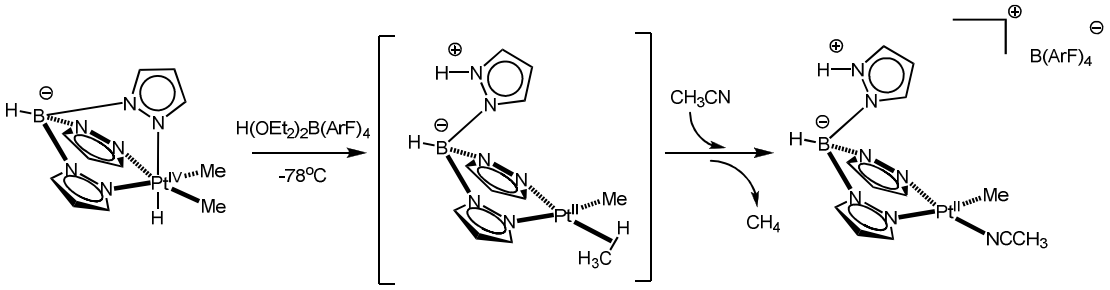


The proposed intermediate generated in Scheme 2.2 is the one that would form in a dissociative alkane activation mechanism from a starting LPt(Me)(OH_2) complex. The parallels of the Tp system towards the original Shilov system and similar systems are apparent from this CH activation reaction. Unlike the cationic complexes reviewed in Chapter 1, however, reductive coupling and subsequent elimination of methane does not occur to form LPt(Me)(OH_2) due to "overstabilization" afforded to Pt^{IV}. In the case of cycloalkane activation, presence of a vacant coordination site provided by dissociation of one of the pyrazolyl arms *cis* to the alkyl ligand site may lead to β-hydride elimination and produce an olefin hydride complex. That this

reaction is not observed speaks to the considerable stability of the κ^3 coordination mode.

The dimethylhydride complex Tp`Pt$(Me)_2$H can be activated in the same manner as the dihydrides in Scheme 2.2, by the introduction of a strong acid to decoordinate one of the pyrazolyl arms.[22] The five-coordinate intermediate undergoes reductive coupling to produce a σ-bonded CH_4 that can be displaced by solvent irreversibly (Scheme 2.4).

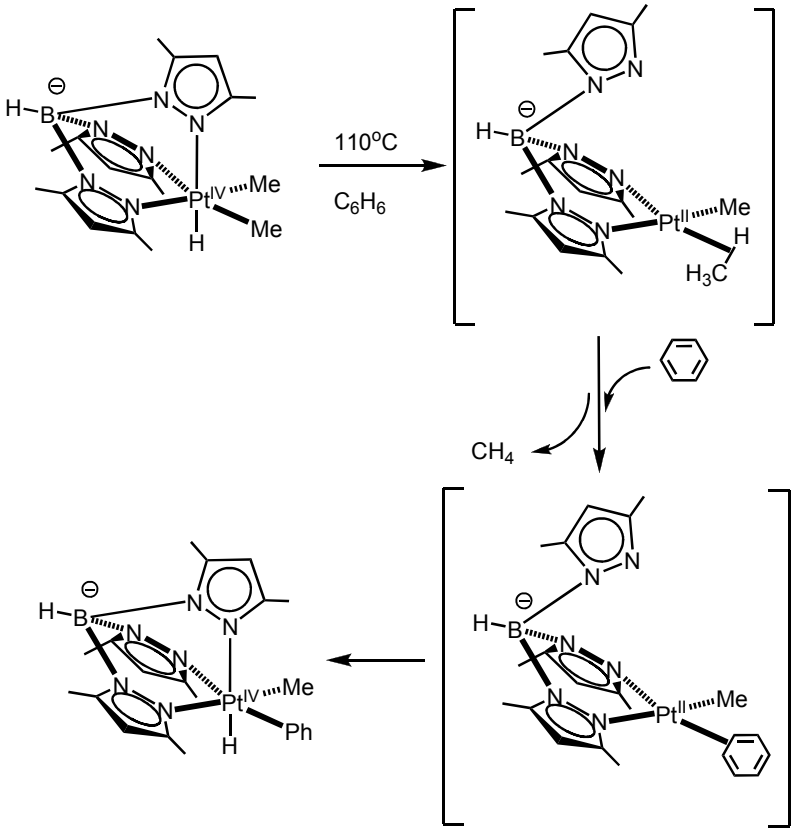
Scheme 2.4. Activation of Tp`Pt$(Me)_2$H by strong acid



Heating Tp`Pt$(Me)_2$H accomplishes decoordination of the pyrazolyl arm in a reversible fashion. When a suitable solvent such as benzene is present, evidence for the decoordination can be observed since it's a π bond of benzene that displaces a σ-bound methane before reversible oxidative cleavage can take place.[23] The benzene is oxidatively cleaved to give a Tp`$Pt^{IV}$(Me)(Ph)(H) complex and the pyrazolyl arm re-coordinates (Scheme 2.5). Eventually, both methyl groups are replaced by phenyl to give Tp`Pt$(Ph)_2$H. It was noted that the rate of product formation is not affected by the type of substrate (CH_3CN, C_6H_6, other aryls) present to displace the coordinated methane. The large measured entropy also led to the conclusion that the rate determining step of the reaction was dissociative loss of coordinated methane to

generate a three coordinate intermediate versus an associative pathway that is believed to be ubiquitous for complexes supported by neutral N,N ligands.

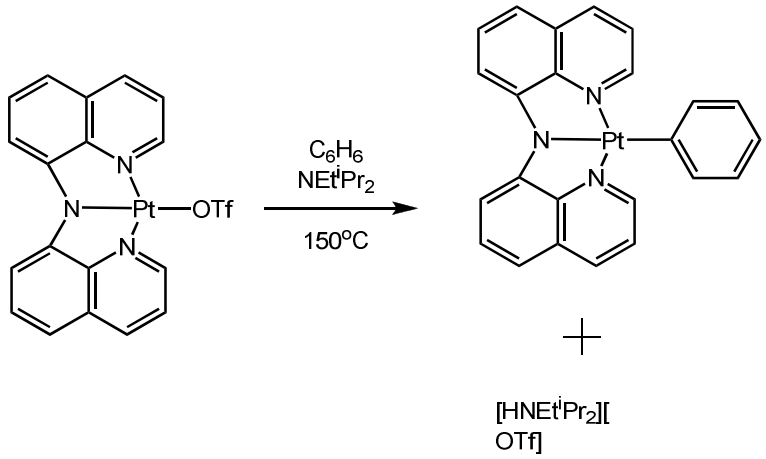
Scheme 2.5. Activation of benzene by Tp`Pt(Me)$_2$H



The anionic *mer*-coordinating ligand system depicted in Scheme 2.6 was used to activate benzene by Peters.[24] This result is very significant for Pt based Shilov chemistry since it represents CH activation by a complex that does not have a sacrificial alkyl ligand present. Recently, similar reactivity has been observed with the diketimine scaffold, but it is limited to activation of functionalized substrates such as olefins and not alkanes (allylic hydrogens) in the case of Pt.[25] Similar ligand

motifs to the Peters system, with a neutral bridging donor, have been used in CH activation studies as well, however an alkyl precursor was needed.[26,27]

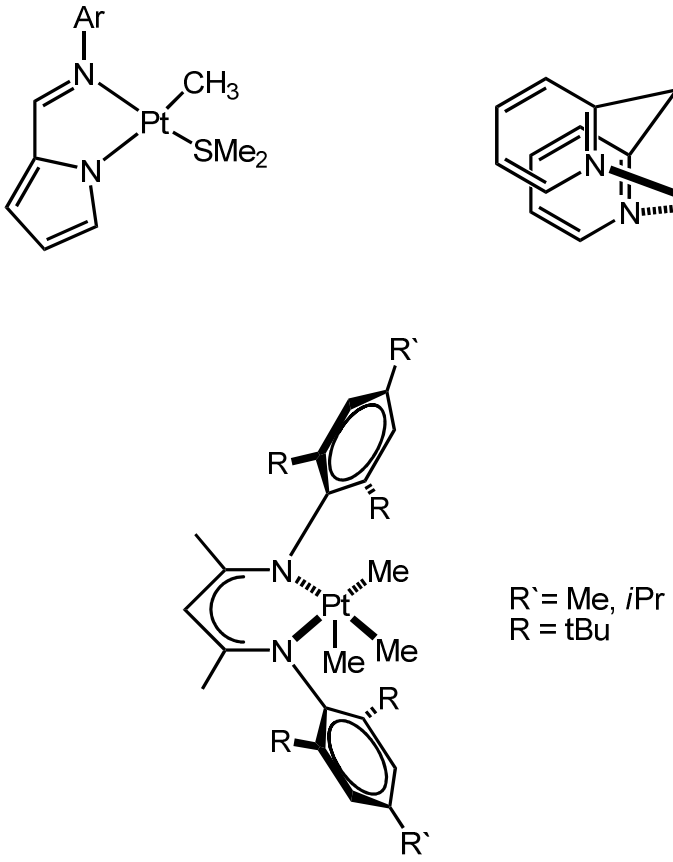
Scheme 2.6. CH activation without a sacrificial alkyl moiety



Other anionic ligands scaffolds used for CH activation or Shilov chemistry are depicted in Figure 2.1. The 2-(N-Arylimino)pyrrolide supported complexes can activate benzene at elevated temperatures,[28] and have recently been implicated in catalytic hydroacylation chemistry where one of the steps of the catalytic cycle involves benzene activation.[29] The diketiminate motif has been successfully used for CH activation of alkanes by the Goldberg group.[30-32] Some of the chemistry observed with the resultant hydrido olefin complexes has direct relevance to material that will be covered by Chapter 6 and is discussed in the introduction there. The sulfonate anionic ligand utilized by Vedernikov was first discussed in Chapter 1. Although it allows for the observation of important intermediates relevant to Shilov chemistry, the sulfonate introduces a sizable barrier for decoordination of the aqua ligand (Table 1). Thus, alkane CH activation has not been observed for associated Pt(Me)(solvento)

complexes (solvent = alcohol, water) to date, although oxidation of these complexes is very facile and can occur with oxygen from air.[33-35] Subsequent reductive elimination from these complexes furnishes methanol, the ultimate product of selective methane functionalization, in high yield.[33]

Figure 2.1. Anionic ligand scaffolds for CH activation



2.1.2 Consideration for the design of the dipyridylborate ligand scaffold

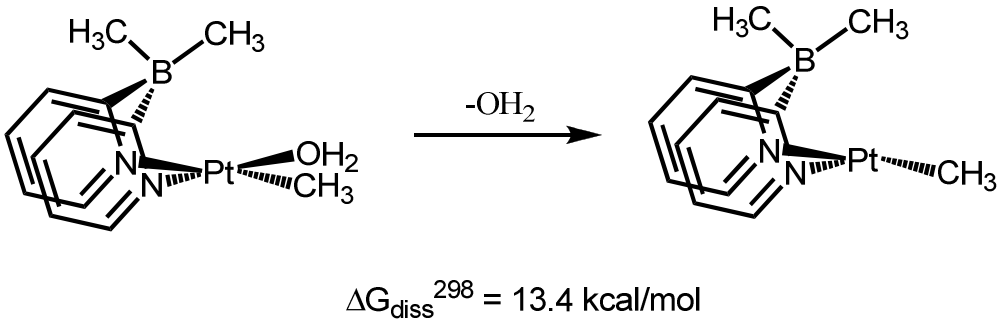
Based on examples outlined in the Introduction, we decided to explore anionic ligands. Not only have these ligands proved useful in the activation of CH bonds, but potentially, the greater electron density at the Pt center could lead to more facile oxidation after CH activation has occurred. An undesirable factor that had to be addressed was the stability of Pt^{IV} complexes supported by the Tp and Tp` ligands.

While a high oxidation state can be stabilized by electron rich ligands, Tp and Tp`, the possible κ^3 binding mode serves to stabilize Pt^{IV} to a much greater extent by generating these complexes' preferred octahedral geometry when required. Stabilization of Pt^{IV} may be important when oxidative cleavage of an alkane to generate an alkyl hydride or oxidation of a Pt(Me)(solvent) complex are rate limiting steps in the overall catalytic cycle. However, as outlined in the introduction, the $TpPt^{IV}$ oxidation state is too stabilized towards reductive elimination, and strong acids or very high temperatures are needed to accomplish transformations at these complexes. An anionic ligand such as the diketiminate that is unable to bind in a κ^3 fashion, served as a benchmark for our search. The example provided in Figure 2.1 (bottom) is a trimethyl Pt^{IV} complex supported by a diketiminate ligand. This was the first example of a five-coordinate Pt^{IV} complex[36] that was unusual not only for its geometry, but also for its stability. With Tp and Tp` Pt^{IV} complexes, generation of the five coordinate intermediate is believed to be the important initial first step before subsequent reductive coupling. It is only after decoordination of the third pyrazolyl arm at elevated temperatures, or after the addition of strong acids, that elimination is observed indirectly. In the diketiminate case a five-coordinate intermediate is already available. However, the stabilization provided by the electron rich ligand grants unusual stability to this complex. Nonetheless, at elevated temperatures, reductive elimination to give ethane and three coordinate Pt^{II} transients readily occurs. The fast reactivity of these transients with CH bonds that will be described in more detail in Chapter 6, moved us on the path of designing our own, exclusively κ^2 anionic ligand scaffold, based upon the principles of aqua ligand dissociation outlined in Chapter 1.

2.1.3 Design of the dipyridylborate ligand scaffold

After an initial DFT screening (by the method described in Chapter 1 pp. 19-26), we found that the dipyridylborate (dpb) ligand had a Gibbs free energy of dissociation of 13.4 kcal/mol (Scheme 2.7)! This result was even better than the one obtained for the record holder diketimine supported complexes that could tolerate a few equivalents of water and could activate methane under ambient conditions. Compared to the original Shilov system, this result is better than our calculated energy of aqua ligand dissociation from *cis*-$Pt(Cl)_2(OH_2)_2$ of 15.3 kcal/mol.

Scheme 2.7 The proposed dipyridylborate supported $Pt^{II}(Me)(OH_2)$ complex.



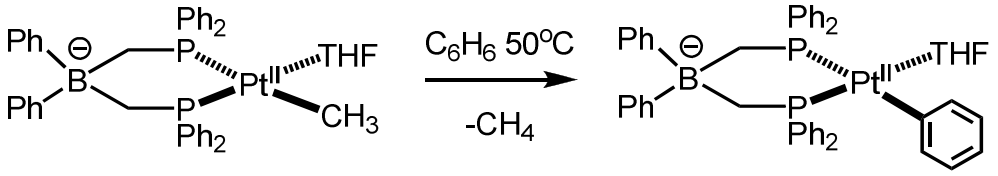
ΔG_{diss}^{298} = 13.4 kcal/mol

The complex $dpbPt^{II}(Me)(OH_2)$ and the putative three coordinate intermediate displayed in Scheme 2.7 are zwitterionic complexes. They are overall neutral and solubility in water may be an issue that needs to be addressed. The dmdpm supported Pt^{II} species discussed in Chapter 1 proved to be soluble in water in the required concentrations. However, we anticipated using biphasic water/hydrocarbon media if we ran into problems with lipophilic, water-insoluble organometallics in the future.

2.1.4 Previous Reports of CH activation with Pt^{II} supported by zwitterionic ligands

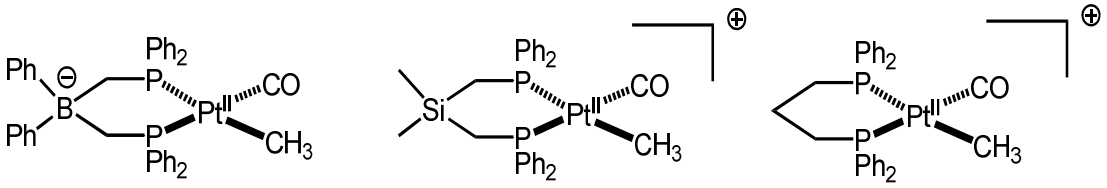
There were positive literature reports about the use of zwitterionic supported Pt^{II} complexes in CH activation as well. Peters and C.J. Thomas found that zwitterionic borate complexes with phosphine donors activated benzene at 50°C in THF solution (Scheme 2.8).[37] The rate of reaction was dependent upon THF concentration, but to a much lesser degree than in the case of analogous cationic complexes that had CH_2 or $SiMe_2$ in the backbone of the ligand in place of diphenylborate.[13]

Scheme 2.8 Activation of benzene by a zwitterionic complex at mild temperatures



The cationic analogues and the zwitterionic complex were treated with CO to substitute the THF ligand and to measure the electron density at the metal center as measured by the ν_{CO} IR stretching frequency (Figure 2.2).

Figure 2.2. Zwitterionic complex and cationic analogues



It was determined that the zwitterionic complex possessed much greater electron density at the Pt center.[13] In the 2003 article, it was reported that the rate of THF self-exchange at $[Ph_2B(CH_2PPh_2)_2Pt(Me)(THF)$ was independent of THF concentration while THF concentration played a role in the case of cationic complexes. The authors suggested that the negative charge on the borate is disseminated to the phenyl groups on the phosphines, which help to displace the THF molecule to form the reactive

intermediate. However, an alternative explanation may be that the THF ligand is weakly bound to electron-rich Pt^{II} centers and is easily displaced due to weaker binding between THF and higher energy *d*-orbitals of the electron rich Pt center. The higher rate of deuterium incorporation can be accounted by considering that an anionic ligand can stabilize the higher oxidation Pt^{IV} hydride intermediates and so lower the energy required for oxidative cleavage of a coordinated alkane. These intermediates would not be overly stabilized as in the case of the trispyrazolyl borate ligand as they would be forced to be five-coordinate or to have a weakly binding ligand in the free axial position that would presumably originate from the solvent. Thus, the electron-rich zwitterionic ligand scaffold could both lower the energy required for solvent dissociation and the energy required for oxidative cleavage of a CH bond at the same time. Replacing the phosphines by nitrogen donors that do not exert a strong *trans* effect (Scheme 2.7), it may be possible to observe very rapid CH activation in hydroxylic solvents.

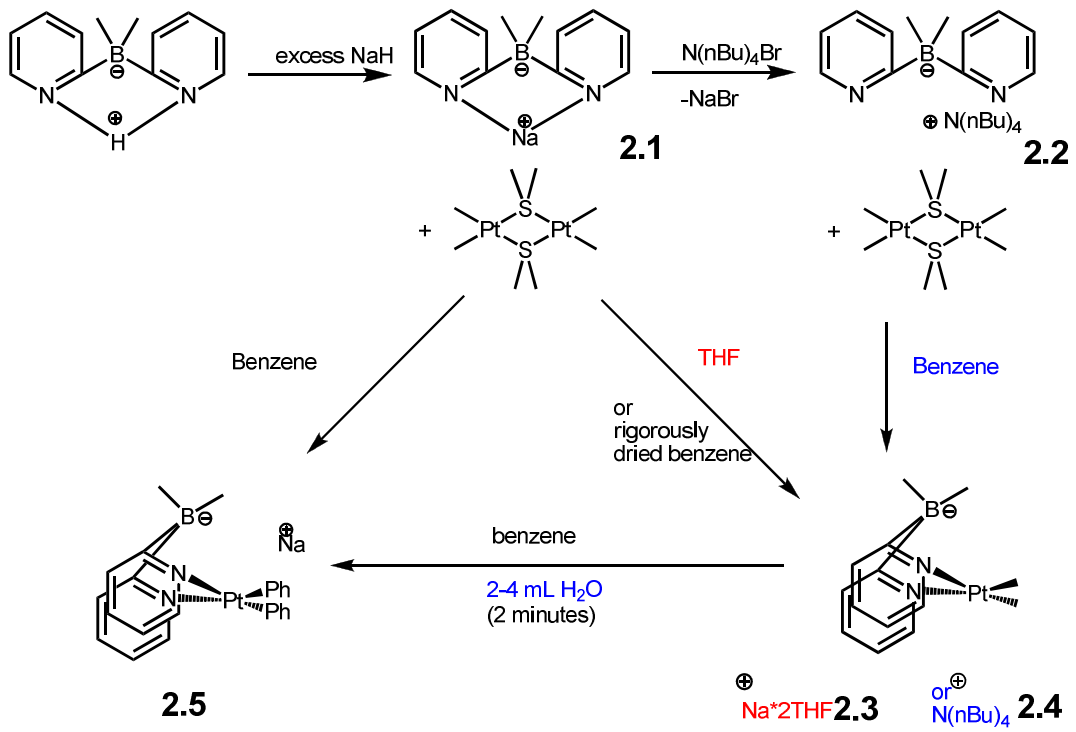
Greater electron density at platinum can come into play in oxidative cleavage. The energetically higher d-orbitals would be more disposed towards transferring electron density to the antibonding σ^* orbital. As well, electron density could more easily be transferred to another electrophile such as dioxygen. What the two reports from the Peters group showed, was that it was not necessary to make the Pt center increasingly electron poor and electrophilic in order to carry out CH activation, but that a variety of factors had to be considered.

2.2 Results and Discussion

2.2.1 Synthesis of Pt complexes and initial reactivity

Anionic dpb ligand, in a form of sodium salt NaL, **2.1**, was prepared by reacting hydrogen dimethyldi(2-pyridyl)borate with an excess of sodium hydride in dry THF. Subsequent metathesis of **2.1** with $(n\text{Bu})_4\text{NBr}$ afforded the tetra-*n*-butylammonium analogue $(n\text{Bu})_4\text{NL}$, **2.2** (Scheme 2.9). Corresponding dimethylplatinum(II) derivatives MLPtMe_2, **2.3** (M=Na) and **2.4** (M = $n\text{Bu}_4\text{N}$), were synthesized using a ligand exchange reaction between **2.1** or **2.2** and precursor $\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2$ in dry THF and were fully characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. When not carefully dried benzene was utilized instead of THF in the attempted synthesis of **2.3**, a reaction occurred which produced, besides free dimethyl sulfide, a white precipitate that was sparingly soluble in benzene. It was washed with a minimum amount of benzene to give pure diphenyl complex NaLPtPh_2, **2.5** (12 h, 88% isolated yield).

Scheme 2.9. Synthesis of dpbNa and dpbN(nBu)$_4$ and associated Pt complexes

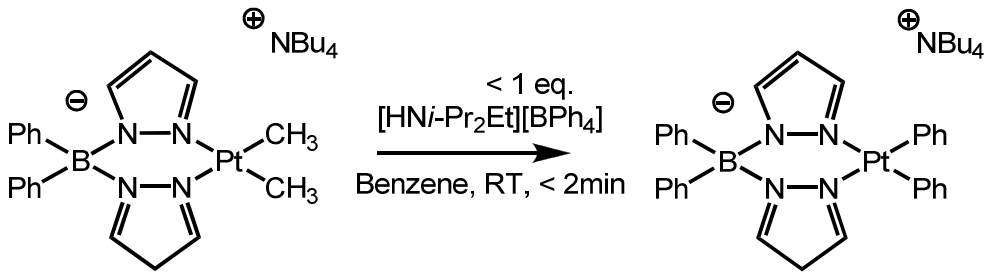


We were initially surprised by the results as they suggested that even trace amounts of water could serve the role of a catalyst and that a 'double' CH activation reaction could happen in the presence of coordinating dimethylsulfide at room temperature.

2.2.2 Relevant double CH activation results reported by Peters and Tilley groups

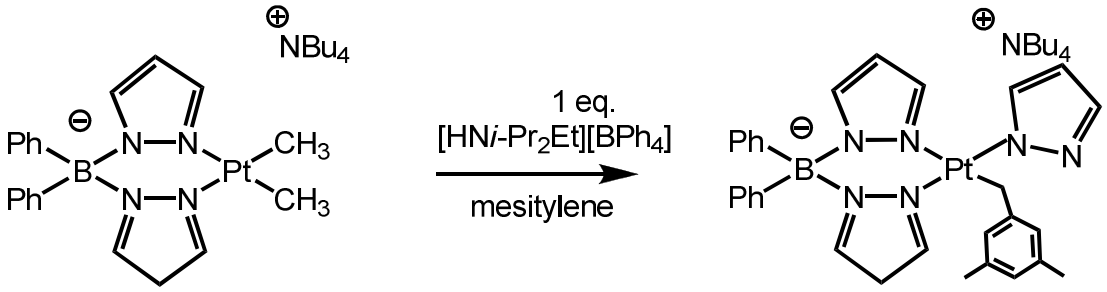
At this time however, a report in the literature from Peters and C.M. Thomas appeared where similar reactivity was observed with a dipyrazolylborate anionic ligand (Scheme 2.10).[38] Removing the third pyrazolyl arm meant that the protonated dimethyl hydride Pt^{IV} complex could easily reductively couple and eliminate methane, and then coordinate and activate benzene. The reaction was very rapid and was complete from the time acid was added and until an NMR spectrum was obtained.

Scheme 2.10. DiphenyldipyrazolylboratePt^{II}(Me)$_2$ complex in CH activation



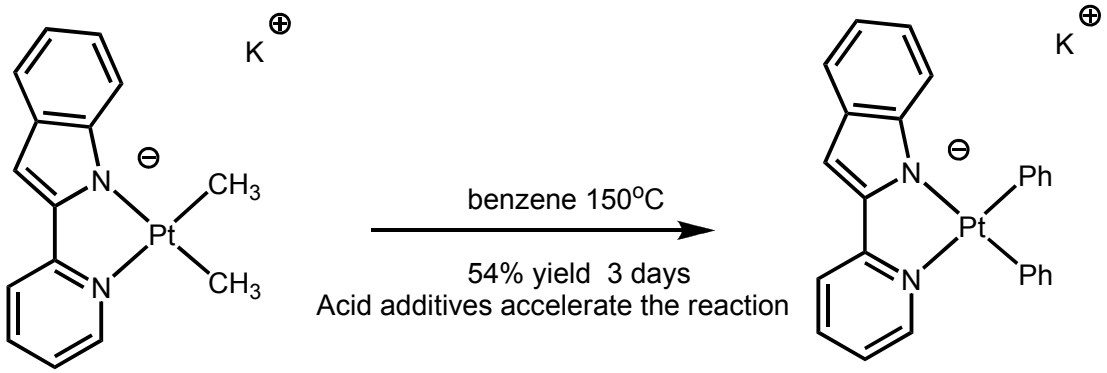
Most significantly, acid proved to be a *catalyst* in the original report. Thus, after both methyl groups were replaced by phenyls, the presumed Pt^{IV}(Ph)$_2$H intermediate could be deprotonated to give the product in Scheme 2.10. The acid could then go on to protonate another molecule of starting material. Significant but yet substoichiometric amounts of H^+ (0.7 equivalents) were needed for this transformation to take place. Other anionic borate ligands were investigated in the double CH activation reaction in that study, and a trend seemed to emerge correlating reactivity with distance between the Pt and anionic B centers. CH activation at sp^3 carbon atoms, benzylic CH bonds of mesitylene, was successful but disproportionation of one molecule of complex occurred concurrently (Scheme 2.10). The system in Scheme 2.10 and 2.11 was not successful at activation the CH bonds of alkanes even at elevated temperatures. However, the reaction was tolerant towards addition of coordinating ligands such as acetonitrile and THF, once again suggesting that the greater electron density at the Pt center favored dissociation of solvent.

Scheme 2.11. Activation of sp3 CH bonds with Diphenyldipyrazolylborate$Pt^{II}(Me)_2$.



Later, a report by Karshtedt and Tilley noted similar double CH bond activation with the monoanionic 2-(2`-pyridyl)indolide (PyInd) ligand (Scheme 2.12).[39]

Scheme 2.12. Double CH activation with $[PyIndPt^{II}(Me)_2]^-[K]^+$



The double CH activation reaction in Scheme 2.12 required very high temperatures and was accelerated by the addition of acids. However, the authors claimed that two different pathways could be operative and that in the absence of acid, direct oxidative addition at a 16 electron Pt^{II} center was operative. These results were backed up by using 10 mol % *N*,*N*,*N*',*N*'-tetramethyl-1,8-naphthalenediamine "proton sponge" in the reactions. The mixtures with the proton sponge did not show any differences in yield. A reviewer of the Tilley and Karstedt manuscript suggested that adventitious water may play a role in the reaction but the role of water was discounted since

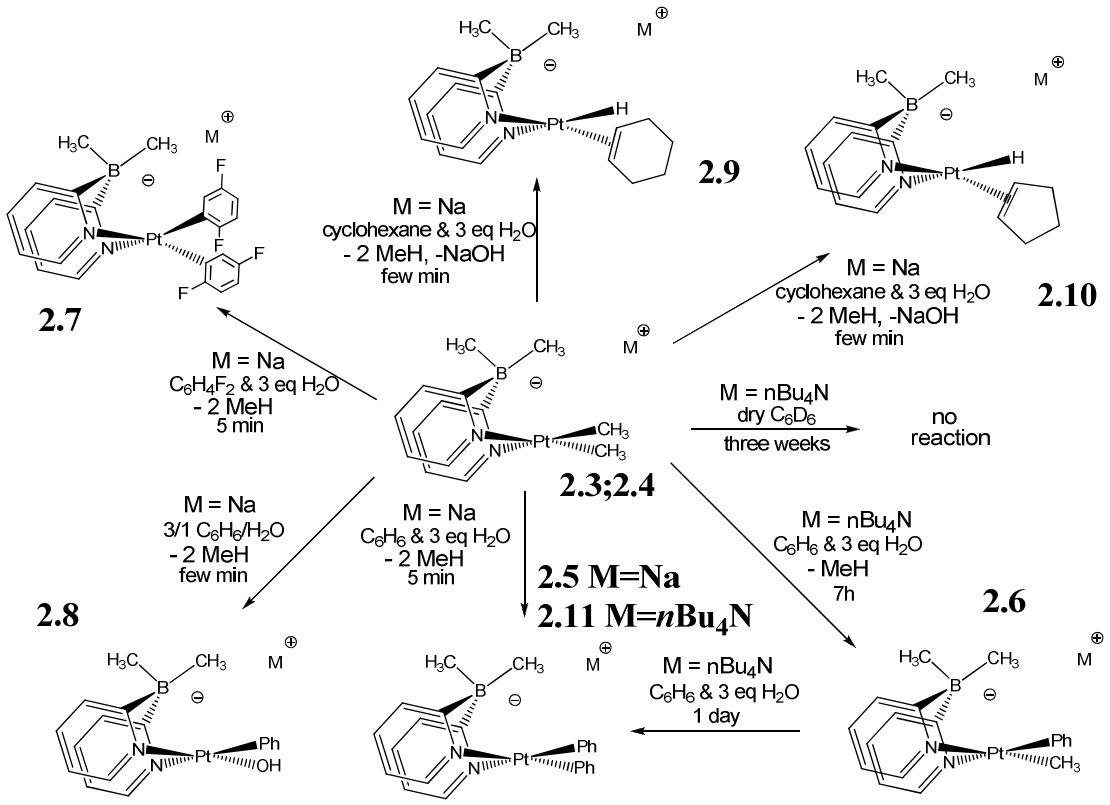
additions of significant amounts of water caused decomposition. We disagree with this conclusion and agree with the mechanism proposed by Peters. From our results, it was clear that both adventitious water and the nature of the cation played a large role in reactivity (Scheme 2.9) and substoichiometric amounts of water in the Karshtedt and Tilley system that the authors did not address, could have played a very large role at 150^{o}C. Peters' and C.M. Thomas' results support an initial protonation at the Pt^{II} center; it appears that the rate acceleration observed by Karshtedt and Tilley in the presence of acids supports this conclusion as well.

2.2.3 Experiments proving the mechanism and further reactivity

We proved trace amounts of water present in 'dry' benzene were responsible for catalyzing the remarkable activation of two benzene solvent molecules in our system. The role of water in the acid catalysis of benzene activation with the anticipated reaction product **2.3** was revealed in separate experiments. Interestingly, no phenyl complexes formed after 12 hours of reaction time with the same batch of 'dry' benzene if the $^{n}Bu_4N$ ligand analogue **2.2** mixed with the platinum precursor was used instead. The dimethyl complex was the only species present after the solvent was evacuated. The role of sodium cation in promoting CH activation catalysis by trace water was established in separate experiments as well. We found that complex **2.4** does not react with benzene that was rigorously dried over Na-benzophenone adduct, and mixed under a fresh atmosphere of dry argon, even after 3 weeks at room temperature (Figure 2.3; 2.3-1). In contrast, when anhydrous benzene was combined with **2.4** and three equivalents of water to produce a biphasic system, a

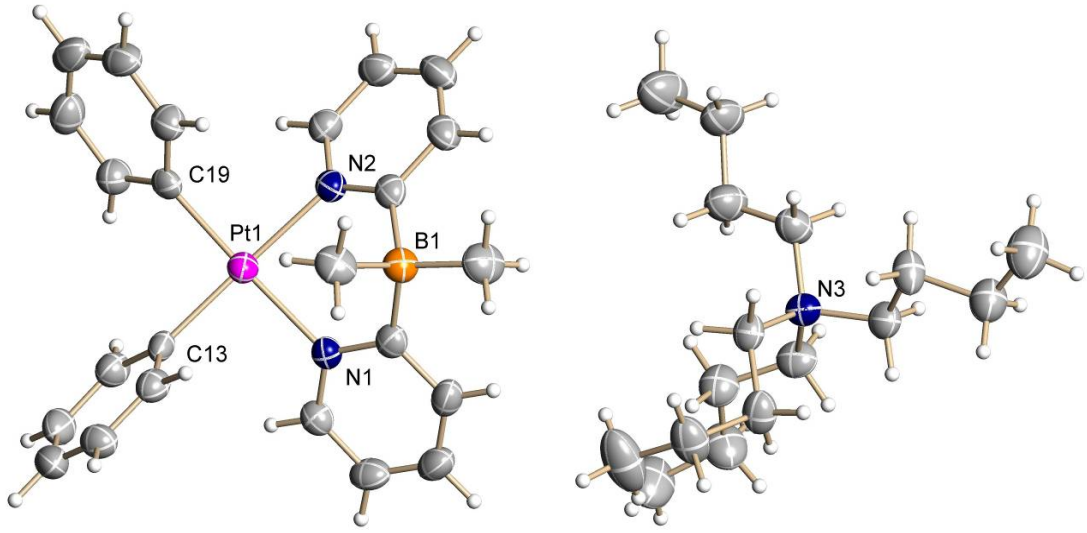
slow reaction occurred leading in one day to the diphenyl complex **2.6** in >90% isolated yield (Figure 2.3; 2.3-2).

Figure 2.3. CH bond activation at dipyridylborato supported Pt(II) Complexes.



The identity of **2.11** was confirmed by X-ray diffraction (Figure 2.4). The platinum-boron distance, at 3.306 Å, is the shortest distance found in all Pt^{II} complexes supported by an anionic borate ligand. The large basicity of the complex and the ease of double CH activation compares well with trends of reactivity and Pt-B distances between Pt^{II} and B established by Peters and C.M. Thomas. The Pt-B distance in the [Diphenyldipyrazolylborate$Pt^{II}(Me)_2$][N(nBu)$_4$] is reported to be 3.460 Å.[38]

Figure 2.4. Crystal structure of complex **2.11.**



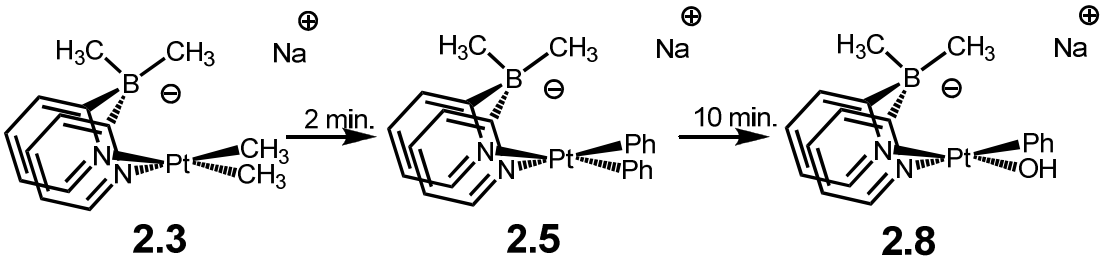
Four methane isotopologues CH_nD_{4-n} (n = 4÷1) were observed in the case of C_6D_6. Formation of an intermediate product *n*Bu_4NLPtPh(Me), **2.6**, in high yield, was evident after first 7h of the reaction (Figure 2.3; 2.3-3). Most remarkably, the sodium analogue, $NaLPtMe_2$, reacted with benzene and two equivalents of H_2O in the time of mixing to produce **2.4** (90% isolated yield, Scheme 2.5), thus establishing that the activity of Na^+ is necessary to dramatically enhance the catalytic effect. The effect of the Na^+ cation on the reactivity of $LPtMe_2^-$ was confirmed in experiments with *n*Bu_4NLPtMe_2, wet benzene, and an additive of $NaBAr^F{}_4$, sodium tetrakis(3,5-bis(trifluoromethyl) phenyl)borate, a good source of "naked" electrophilic Na^+.[40]

An initially slow reaction could be brought to completion virtually immediately upon addition of 0.5 equivalents of $NaBAr^F{}_4$. An acid source such as 0.5 equivalents of the protonated form of the dpbH ligand (hydrogen dimethyldi(2-pyridyl)borate) also produced an immediate reaction upon addition, proving the role of acid catalysis in the reaction. 0.5 equivalents of the sodium form of the ligand

compound **2.1**, also reacted to form the diphenyl complex after 1.5 hours, during which the progress of the reaction could be followed by NMR. The slower reaction time, as opposed to the $NaBAr^F{}_4$ additive, was attributed to the coordinated nature of sodium in **2.1**. Benzene saturated with water reacted instantaneously with a solution of **2.3** to produce diphenyl complex **2.5** cleanly. Our conclusion is that the homogenous reaction between $[dpbPtMe_2]^-$ and benzene occurs in the organic phase and could be catalyzed with even trace amounts of water, whereas Na^+ ions dramatically enhance the catalytic effect. Similar to benzene, clean CH bond activation with $NaLPtMe_2$ could be achieved with *para*-difluorobenzene and 3 equiv. of water to form **2.7** ($NaLPt(2,5\text{-}F_2C_6H_3)_2$ in 92% isolated yield).

Importantly, $NaLPtMe_2$ was also shown to carry out CH bond activation in the presence of larger amounts of water, in biphasic 3/1 benzene water systems. The reaction was complete in less than 2 minutes, but upon removal of all volatiles under vacuum, the solid residue was found by NMR to be a mixture of diphenyl complex **2.5** (80%) and a hydroxo phenyl complex NaLPtPh(OH) **2.8** (15% Figure 2.3; 2.3-5). Longer reaction times, 10-12 minutes, led to the disappearance of the kinetic product **2.5** and the exclusive formation of **2.8** (Scheme 2.13).

Scheme 2.13. Biphasic reactions of $NaLPtMe_2$ in benzene/water mixtures



The intermediacy of **2.5** was proven by reacting a pure sample of this complex with a 3/1 benzene water mixture, which produced **2.8** in >90% yield after 10 minutes (Scheme 2.13). Interestingly, the diphenyl product **2.5** is much less reactive than **2.3**; it was stable in wet (containing dissolved D_2O) C_6D_6 or in pure D_2O for at least a few days, though showing H/D exchange between PtPh fragments and D_2O in both cases (in the latter case complete deuteration of the coordinated phenyl ligands was complete after <15 hours).

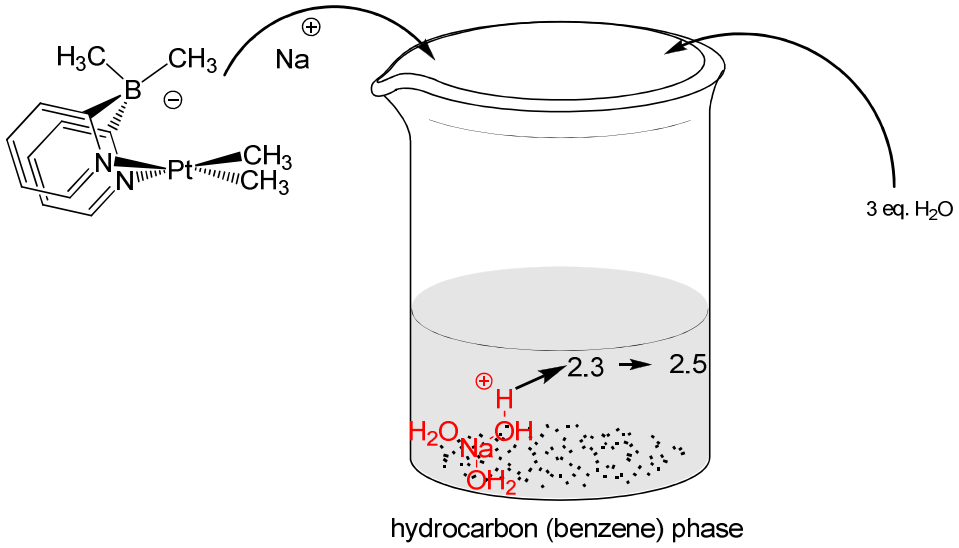
High reactivity of **2.3** towards arenes prompted us to test it in alkane CH bond cleavage. When 3 equiv. of water were added to a stirred suspension of **2.3** in cyclohexane, a vigorous gas evolution occurred at the water/cyclohexane interface. After removal of the solvent under vacuum and the extraction of the strongly alkaline residue with cyclohexane, hydrido cyclohexene complex LPtH(cyclo-C_6H_{10}), **2.9** was isolated in 42% yield (Figure 2.3). Under the same conditions, cyclopentane was dehydrogenated to produce **2.10** (Figure 2.3) in 33% isolated yield. We suggest that poor solubility of **2.3** in alkanes might be responsible for the low yields that was proven subsequently correct (see Chapter 6). In 2:1 alkane water mixtures, both substrates reacted with **2.3** to produce the LPtH(olefin) complexes in essentially the same yields as with 3 equiv of water.

2.2.4 Mechanistic Considerations for the biphasic reaction

The mechanism of the reaction between complex **2.3** and hydrocarbons might involve protonation of anionic $LPt^{II}Me_2^-$ with H_2O to form a very reactive lipophilic $LPt^{IV}Me_2H$ which could be efficiently extracted into the organic phase.[41] In water-

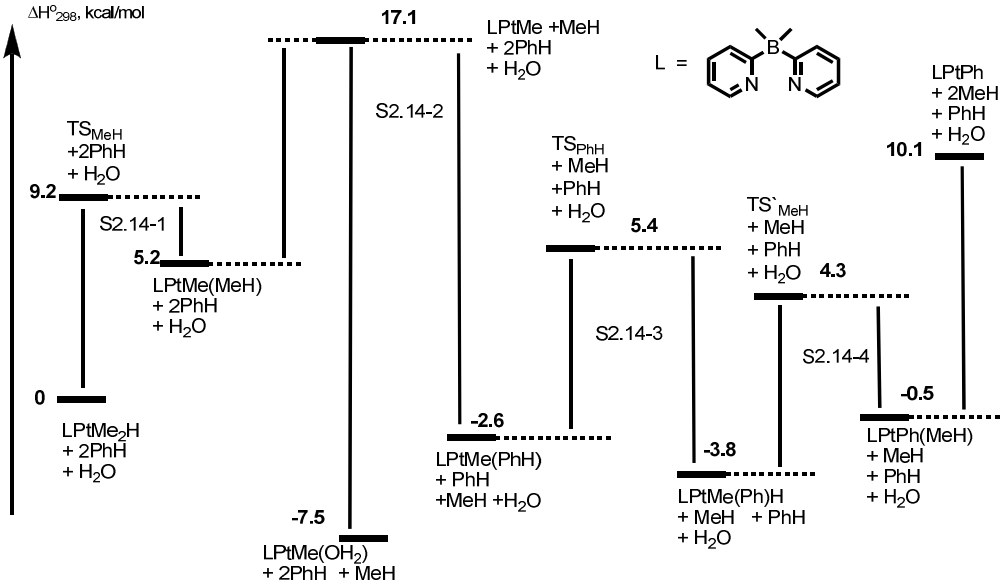
poor systems, the Na^+ ion could coordinate few equivalents of H_2O, so enhancing acidity of H_2O in the organic phase, and thus accelerating formation of $LPt^{IV}Me_2H$ (Figure 2.5).

Figure 2.5 Reactivity of complex **2.3** in benzene with a few eq. of H_2O



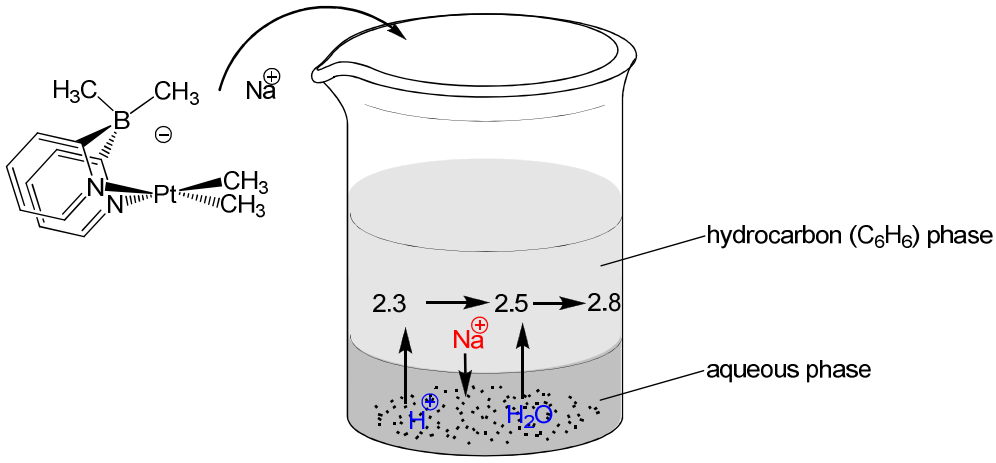
According to our DFT calculations, the CH reductive coupling of $LPt^{IV}Me_2H$ is facile (Scheme 2.14(S2.14-1)).

Scheme 2.14. DFT calculations of intermediates in CH activation reactions



Considering the MeH ligand in the LPtMe(MeH) intermediate as a good leaving group, we suggest that MeH for PhH (Scheme 2.14(S2.14-2)) and MeH for H_2O substitution has similar activation barriers, so that benzene can win a kinetic competition with H_2O for Pt^{II} in the organic phase, where the [PhH]/[H_2O] ratio is high. Subsequent benzene CH bond oxidative cleavage might lead to $LPt^{IV}Ph(Me)H$, (Scheme 2.14-(S2.14-3)), which could lose H^+ in a reaction with OH^-, producing $LPtPh(Me)^-$, eliminate methane (Scheme 2.14-(S2.14-4)), or react with the second PhH and form $LPtPh_2^-$ in a similar reaction sequence. The fact that energies of TS_{PhH} and TS_{MeH} are very close to each other is consistent with the observed multiple deuterium incorporation in the methane liberated in reaction between **2.3** and C_6D_6 and involving $LPt^{IV}Ph(Me)H$. Finally, the Na^+ ion could enhance acidity of water in the organic phase and accelerate formation of $LPtR_2H$ in it, since both **2.3** and **2.5** are benzene-soluble (Figure 2.6).

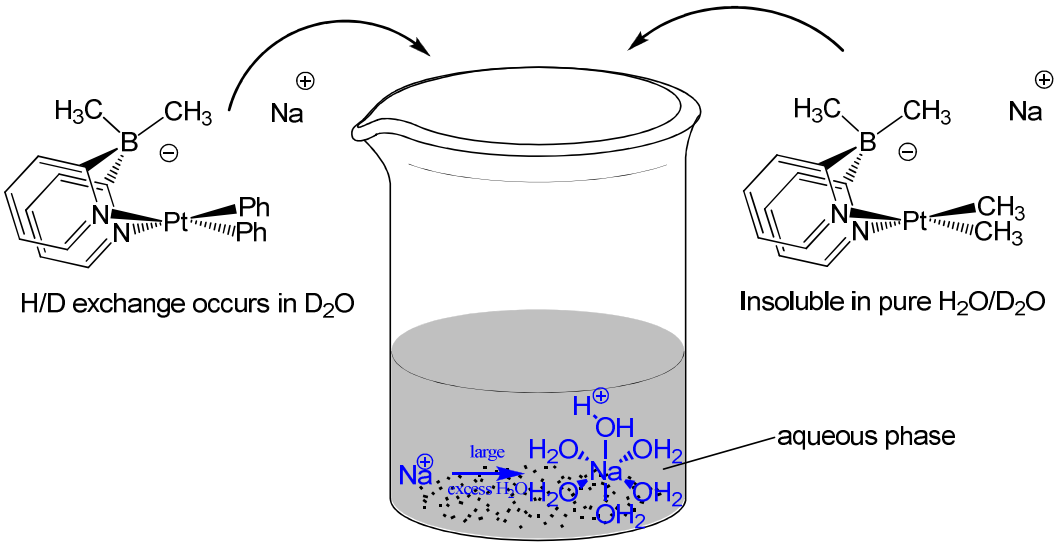
Figure 2.6 Reactivity of complex **2.3** in a biphasic environment



The more thermodynamically favorable product **2.8** is eventually formed in highly basic biphasic systems.

In a purely aqueous solution, the effect of Na^+ on the rate of reaction between PhH and $[LPtMe_2]^-$ is expected to be nonexistent. Each sodium ion would theoretically bind a maximum of six water molecules and the acidity of the bulk solvent would not be increased to any significant extent (Figure 2.7). It is possible to observe H/D exchange with complex **2.5** in pure D_2O without forming the more thermodynamically stable complex **2.8**. The mechanism of H/D exchange may be due to reversible protonation and the formation of the Pt^{IV} intermediate, but this exchange is slow (12h.-1day) on the timescale of the double CH activation reaction. The reason why **2.8** does not form in purely aqueous systems may be much higher basicity of **2.3** as compared to **2.5** and therefore much lower concentration of nucleophilic hydroxide anions responsible for hydrocarbon substitution in Pt^{II}(RH) transients in aqueous solutions of **2.5**.

Figure 2.7 Reactivity of complexes **2.3** and **2.5** in an aqueous environment



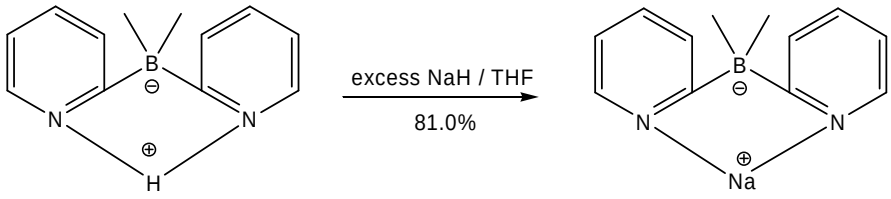
2.2.5 Conclusion

To the best of our knowledge, a combination of high basicity of the $Pt^{II}Me_2$ fragment, high reactivity of the related Pt^{II} transients toward CH bonds, and tolerance of water, are currently the unique features of the dpb system presented here. Although we were unable to generate the desired LPt(Me)(OH_2) complexes in this study, the rapid CH activation reaction, even with sp^3 CH bonds of alkanes, leads us to believe that the desired monosolvento complexes will lead to fast CH activation results as well. The most surprising result was that water acted as a mild acid catalyst to initiate the double CH activation reaction in hydrocarbon media; the role of the appropriate cation proved crucial and depended upon the nature of the solvent that surrounded the reactive system. In summary, we determined that it was possible to use a biphasic hydrocarbon-water system to obtain products of CH activation. We found that Pt^{II} dipyridine complexes can be electronically tuned for facile alkane and arene CH bond activation in hydrocarbon-water systems.

2.3Experimental

2.3.1 Synthesis and Reactivity of Ligands and Complexes

Sodium dimethyldi(2-pyridyl)borate, Na(dp-BMe_2), 2.1

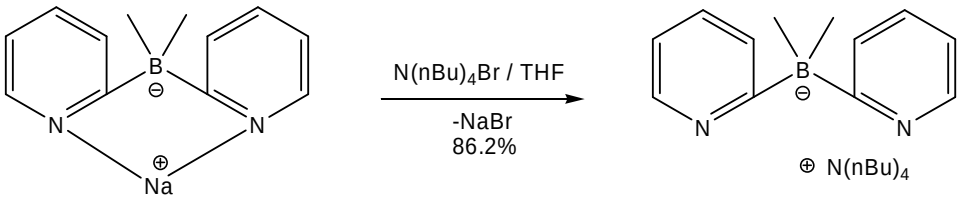


Solid H(dp-BMe_2) (200 mg, 1.01 mmol) was dissolved in 3 mL of THF and NaH was added (98 mg, 4.04 mmol) slowly with rapid evolution of hydrogen gas being

observed. The solution with excess sodium hydride was stirred overnight and filtered on the next day. The filtrate was concentrated under high vacuum and dried for a further 2 hours under high vacuum to give an off white solid. This solid was washed three times with benzene, and the benzene was decanted. The remaining residue was dried under high vacuum for a further hour to give a flaky, white solid (180 mg, 81.0% yield). Compound **2.1** is very hygroscopic and should be stored under an inert atmosphere.

^{1}H NMR (22^{o}C, THF-d8), δ: 8.27 (dd, 2H, *J*=4.9Hz, 3.0 Hz), 7.47 (d, 2H, *J*=6.2 Hz), 7.18 (td, 2H,*J*=7.9 Hz, 3.0 Hz), 6.62-6.67 (m, 2H), 0.03 (bm, 6H).
^{13}C NMR (22^{o}C, THF-d8), δ: 194.6 (q, $J_{C\text{-}B}$=48.8 Hz), 147.9, 133.3, 127.3 (m), 117.6, 13.1 (q, $J_{C\text{-}B}$=41.0 Hz).
Anal. Calcd. for $C_{12}H_{14}BN_2Na$: C, 65.49; H, 6.43; N, 12.74. Found: C, 65.77; H, 6.90; N, 12.32.

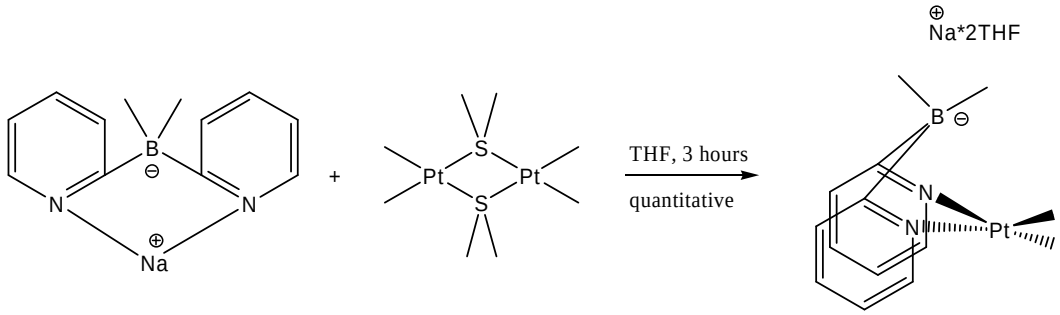
Tetra(*n*-butyl)ammonium dimethyldi(2-pyridyl)borate, *n*Bu$_4$N(dp-BMe$_2$), 2.2



Solid Na(dp-BMe$_2$) (18.7 mg, 0.0850 mmol) was dissolved in 1.5 mL of THF and (*n*Bu)$_4$NBr (27.4 mg, 0.0850 mmol) was added to the solution. The solution was stirred for 1 hour and was then filtered. The reaction flask and filter were washed with two portions of 0.75 mL of THF. The filtrate was dried under high vacuum for one hour to obtain a light yellow gel that crystallized on standing (32.2 mg, 86.2% yield). As with **2.1**, this compound is also hygroscopic and should be stored under an inert atmosphere.

^{1}H NMR (22^{o}C, THF-d8), δ: 8.24 (d, 2H, *J*=3.2 Hz), 7.44 (d, 2H, *J*=8.0 Hz), 7.13 (td, 2H, *J*=8.0 Hz, 1.6 Hz), 6.50-6.55 (m, 2H), 3.38-3.42 (m, 8H), 1.64-1.72 (m, 8H), 1.35 (sextet, 8H, *J*=7.5 Hz), 0.95 (t, 12H, *J*=7.5 Hz), 0.14 (bm, 6H).
^{13}C NMR (22^{o}C, THF-d8), δ: 148.7, 133.0, 126.9 (m), 117.4, 59.7, 25.2, 20.8, 14.3, 13.7 (q, *J*C-B= 42 Hz). Signal of the *ipso*-carbon at 195 ppm was not always observed due to boron splitting.
Anal. Calcd for $C_{26}H_{50}BN_3$: C, 76.51; H, 11.49; N, 9.56. Found: C, 76.56; H, 11.15; N, 9.21.

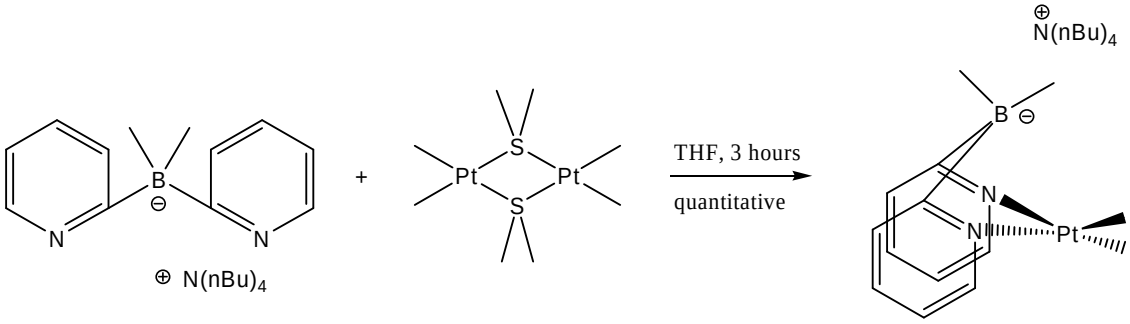
Sodium dimethyldi(2-pyridyl)boratodimethylplatinate(II), Na(dp-BMe$_2$)PtMe$_2$, 2.3



Solid Na(dp-BMe$_2$) (20.0 mg, 0.091 mmol) was added to precursor $Pt_2Me_4(SMe_2)_2$ (26.1 mg, 0.091 mmol Pt) in 1mL of THF. The bulk of the material reacted instantaneously. The yellow mixture was stirred for 3 hours after which time yield of the product quantitative and the product pure by NMR. The mixture was concentrated in vacuum and the residue was dried in vacuum for several hours to give a colorless product as an analytically pure sample, 40 mg, quantitative. If the time under vacuum was not long enough, one to two THF molecules can be detected in the residue by NMR when dissolving the freshly prepared sample in acetone-*d*6. After drying under high vacuum overnight the THF-free complex can be obtained in an analytically pure form. The compound is practically *insoluble* in water, sparingly soluble in benzene and perfectly soluble in THF or acetone. **2.3** is highly air sensitive and highly reactive with many common solvents and should at all times be stored under an inert atmosphere.

^{1}H NMR (22^{o}C, THF-d8), δ: 8.62 (d, 2H, J_{H-H} =5.6 Hz, J_{H-Pt}=26.2 Hz), 7.48 (d, 2H, J=7.9 Hz), 7.30 (t, 2H, J=7.9 Hz), 6.65 (t, 2H, J=5.4 Hz), 0.49 (s, 6H, J_{H-Pt}=75.6 Hz), 0.39 (bs, 6H).
^{13}C NMR (22^{o}C, THF-d8), δ: 150.1 (J_{C-Pt}=27.0 Hz), 132.7, 128.2, 119.5 (J_{C-Pt}=30.4 Hz), -20.3 (J_{C-Pt}=773.4 Hz). Pyridine *ipso*-carbon at 191 ppm was not always seen due to boron splitting and boron methyl groups were not seen due to both boron splitting and the fast exchange that is apparent in the ^{1}H NMR.
Anal. Calcd for $C_{14}H_{20}BN_2NaPt$: C, 37.77; H, 4.53; N, 6.29. Found: C, 37.39; H, 4.52; N, 5.87.

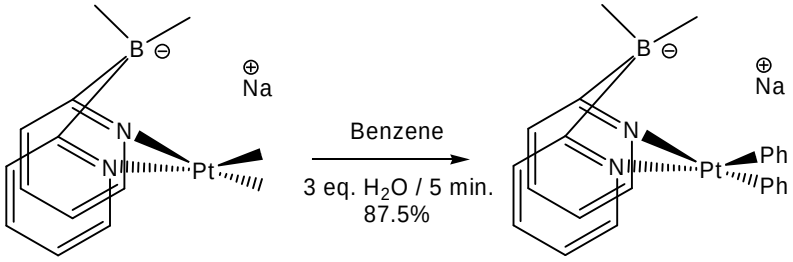
Tetra(*n*-butyl)ammonium Dimethyldi(2-pyridyl)boratodimethylplatinate(II), ^{n}Bu$_4$N(dp-BMe$_2$)PtMe$_2$, 2.4



Solid *n*Bu$_4$N(dp-BMe$_2$) (32.2 mg, 0.073 mmol) was added to precursor Pt$_2$Me$_4$(SMe$_2$)$_2$ (21 mg, 0.073 mmol Pt) in 1 mL of THF-*d*8 placed in a NMR Young tube. The bulk of the material reacted in five minutes and the mixture was stirred for a further 3 hours during which the progress of the reaction could be followed by NMR; reaction complete after 3h. The mixture was then filtered through a cotton plug and the filtrate was dried under vacuum for one hour to obtain an off color white powder (24.9 mg, 51.1% yield).

^{1}H NMR (22^{o}C, THF-d8), δ: 8.71 (dd, 2H, J_{H-H} =5.6 Hz, 1.5Hz, J_{H-Pt}=23.7 Hz), 7.44 (d, 2H, J=7.3 Hz), 7.26 (td, 2H, J=7.3 Hz, 1.5 Hz), 6.58 (vt, 2H, J=7.3 Hz), 3.16-3.20 (m, 8H), 1.53-1.62 (m, 8H), 1.26 (sextet, 8H, J=7.0 Hz), 0.89 (t, 12H, J=7.0 Hz), 0.14 (vd, 6H), 0.54 (s, 6H, J_{H-Pt}=80.8 Hz), 0.39 (bs, 6H).
^{13}C NMR (22^{o}C, THF-d8), δ: 190.6 (q, J_{C-B}= 50.2 Hz), 150.4 (J_{C-Pt}=28.4 Hz), 131.7, 127.8, 119.1 (J_{C-Pt}=29.6 Hz), 59.4, 24.9, 20.6, 14.2, 14.1 (bq, J_{C-B}= 36.0 Hz), -17.1 (J_{C-Pt}=823.1 Hz).
Anal. Calcd for $C_{30}H_{56}BN_3Pt$: C, 54.21; H, 8.51; N, 6.32. Found: C, 54.28; H, 8.26; N, 5.99.

Sodium Dimethyldi(2-pyridyl)boratodiphenylplatinate(II), Na(dp-BMe_2)$PtPh_2$, 2.5



From **2.1**, $Pt_2Me_4(SMe_2)_2$ and wet benzene.

Solid Na(dp-BMe_2) (20.0 mg, 0.091 mmol) was added to precursor $Pt_2Me_4(SMe_2)_2$ (26.1 mg, 0.091 mmol Pt) in 2 mL of deaerated, but not carefully dried, benzene. The solution was stirred and after five minutes both materials had dissolved and a fine white solid started to precipitate. The solution was left to react overnight to give a heterogeneous mixture that upon standing had white powder settle on the bottom of the reaction vessel. The residue was washed with two 1 mL portions of deaerated benzene, and dried under vacuum to give a white, powdery material (45.3 mg, 87.5%).

From **2.1**, $Pt_2Me_4(SMe_2)_2$, benzene and 2 eq. of water with partial removal of Me_2S.

Since the dryness of the benzene determined the reaction speed and it is the trace amounts of water in benzene that catalyzed the reaction whereas Me_2S liberated inhibited it, an alternative procedure was to dissolve the starting materials in 2mL of benzene, and in 10 min remove the solvent and Me_2S formed by that time under vacuum. Then another 2 mL portion of benzene and ~3μL of water (0.16 mmol) were added. Rapid evolution of methane gas was observed. After five minutes, the solvent was evaporated under high vacuum to yield complex **2.5** (pure by NMR). Yield 51.7 mg (quantitative).

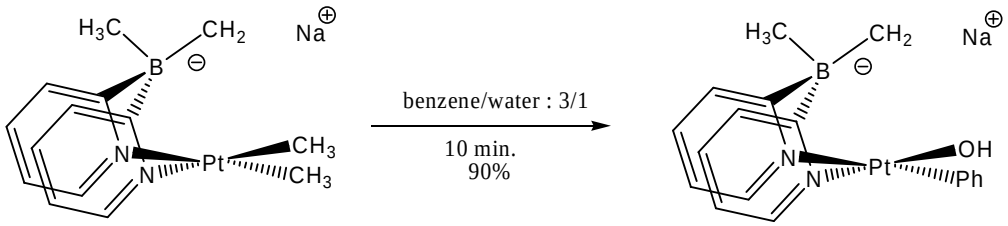
From complex **2.3**, benzene and 2 eq. of water.

Similarly, when 0.091 mmol of complex **2.3** was combined with 2 mL of benzene and ~3μL of water (0.16 mmol), a vigorous gas evolution was observed. In 2 min the solvent was removed under high vacuum to produce pure **2.5** (>90% isolated yield). The compound is sparingly *soluble* in benzene; solubility in water is slightly higher. It is perfectly soluble in THF or acetone. Solutions of **2.5** in D_2O are *basic* and show complete H/D exchange in the PtPh groups, but no signs of decomposition after 15h at room temperature. These results suggest that acidity of D_2O is sufficient to protonate **2.5** to produce $LPtPh_2D$ and form LPtPh(PhD) transient, both responsible for this slow H/D exchange in the PtPh groups at room temperature. At the same time, the energy of LPtPh(PhD) in this system is too high and its stationary concentration is too low to allow for the subsequent fast loss of PhD to produce $LPtPh(OH_2)$ and then NaLPtPh(OD). The results are consistent with the DFT-calculated reaction enthalpy profile of the PhH elimination from $LPtPh_2H$.[6a paper ref]

^{1}H NMR (22^{o}C, THF-d8), δ: 8.24 (d, 2H, J_{H-H} =4.2 Hz, J_{H-Pt}=17.4 Hz), 7.56 (d, 4H, J_{H-H}=7.3 Hz, J_{H-Pt}=66.4 Hz), 7.46 (d, 2H, *J*=7.3 Hz), 7.18 (t, 2H, *J*=7.3Hz), 6.64 (t, 4H, *J*=7.3 Hz), 6.48 (vt, 2H, *J*=7.3 Hz), 6.38 (t, 2H, *J*=6.2 Hz), 0.14-1.26 (bm, 6H).
^{13}C NMR (22^{o}C, THF-d8), δ: 152.2, 151.7, 140.7, 132.9, 129.2, 126.3, 120.3, 118.7. Pyridine *ipso*-carbon was not seen due to boron splitting and boron methyl groups were not seen due to both boron splitting and the fast exchange that is apparent in the ^{1}H NMR.
Anal. Calcd for $C_{24}H_{24}BN_2NaPt$: C, 50.63; H, 4.25; N, 4.92. Found: C, 50.20; H, 4.14; N, 4.69.

2.3.2 Reactivity of complexes in biphasic and aqueous environments and other reactivity

Experiments in biphasic 3 : 1 benzene – water mixtures. Formation of Na(dp-BMe$_2$)PtPh(OH), 2.8



Solid Na(dp-BMe_2)$PtMe_2$ (0.18 mmol) was added to a flask with 1.5 mL of benzene. Water (0.5 mL) was added to the mixture. A vigorous reaction that released methane gas occurred. The mixture was stirred for 2 minutes after which time the flask was attached to the high vacuum line where all the solvents were evacuated. The residue was dried a further ten minutes under high vacuum. The solid products dissolved completely in THF-*d*8 to give the *kinetic* product, diphenyl complex **2.5** in 80% NMR yield with 5.0 μL of acetone used as an internal standard. Another major species (15%) was (dp-BMe_2)PtPh(OH), **2.8**. Shortening the reaction time to 1 minute did not result in a higher yield of **2.5**. In a number experiments it was found that increased reaction time lead to higher fraction of complex **2.8** and lower fraction of complex **2.5**. The optimal reaction time to prepare the thermodynamically more stable product **2.8** (>90% NMR yield) free from complex **2.5** was found to be 10-12 minutes. These observations mean that complex **2.5** is a primary reaction product whereas complex **2.8** is a product of subsequent hydrolysis of **2.5**. Another important conclusion that can be made here is that PhH won the kinetic competition with H_2O. A possible explanation to this fact may be that the activation barriers corresponding to the methane for benzene and methane for aqua ligand substitution in the intermediates LPtR(MeH) (R = Me, Ph) do not differ by much. If so, the product distribution is a function of the [PhH]/[H_2O] ratio, which is close to 400 in the organic phase where

water solubility is low. The explanation is consistent with the evidence found that formation of **2.5** from **2.3** occurred in the organic phase. In turn, since both methane complexes, LPtMe(MeH) and LPtPh(MeH), are weak whereas PhH and H_2O complexes are much stronger and do not differ significantly in stability (DFT results), [6a] the MeH for PhH and MeH for H_2O substitution could have "early" transition states, where the bond order between Pt and an incoming ligand is low (assuming that the associative mechanism of ligand substitution is operative). If so, the assumption that both TS's have similar energy is reasonable. If ligand substitution follows a dissociative mechanism, the ligand substitution rate should not be a function of the incoming ligand, and the LPt(PhH)/LPt(H_2O) ratio will depend on the [PhH]/[H_2O] ratio only. We were not able to find a transition state corresponding to the associative mechanism, but this pathway cannot be ruled out. In confirmation to the observation given above and suggesting that **2.8** is the thermodynamic reaction product, pure complex **2.5** (0.18 mmol) was reacted with a mixture of 1.5 mL of benzene and 0.5 mL of water in the course of 10 min to produce **2.8** in ~90% NMR yield (5.0 μL of acetone added as an internal standard). In turn, no complex **2.5** was observed when isolated **2.8** was dissolved in wet benzene and left for 15h, so proving that the reverse reaction is slow or impossible under these conditions. These results also suggest that acidity of H_2O in the organic phase is enhanced by Na^+ ions present in it and is sufficient to protonate **2.5** and produce lipophilic LPtPh_2H. Importantly, because of the enhanced acidity, the energy level of this lipophilic transient is low enough to form quickly, eliminate PhH and form **2.8** at room temperature. Complex **2.5** is

soluble in water-saturated benzene so proving that Na^+ ions can be present in the beginning of the reaction in the organic phase in biphasic PhH-H_2O systems.

^{1}H NMR (22^{o}C, THF-d8), δ: 8.94 (dq, 1H, J_{H-H} =5.5 Hz, 0.9Hz), 8.20 (dq, 1H, J_{H-H}=5.5 Hz, 1.5Hz J_{H-Pt}=54 Hz), 7.54 (d, 1H , J_{H-H}=7.4 Hz), 7.43 (d, 1H , J_{H-H}=7.4 Hz), 7.39 (td, 1H , J_{H-H}=7.4 Hz, 1.5Hz), 6.24-7.31 (m, 3H), 6.86 (td, 1H, J_{H-H}=5.5 Hz, 1.5Hz), 6.84 (t, 2H, J_{H-H}=7.4 Hz), 6.73 (v tt, 1H , J_{H-H} =7.4 Hz, 1.5 Hz), 6.34 (v td, 1H , J_{H-H} =6.5 Hz, 1.5Hz), 0.56 (bs, 6H), -1.48 (s, 1H, J_{Pt-H}=30 Hz).
^{13}C NMR (22^{o}C, THF-d8), δ: 155.5, 148.8, 138.7 (2C), 134.1, 132.9, 129.1, 128.0, 127.7, 126.9 (2C, J_{Pt-C}=75 Hz), 122.3, 119.8, 119.3. Pyridine *ipso*-carbon (bs ~190) and boron methyl groups (bs ~12-14) were not seen due to boron splitting.

Reaction between Na(dp-BMe_2)$PtMe_2$ and C_6D_6 saturated with H_2O or D_2O

Solid complex **2.3**, Na(dp-BMe_2)$PtMe_2$, (0.23 mmol), was placed in a Young tube under argon and deuterated benzene saturated with water was added. A vigorous reaction accompanied by evolution of methane gas took place resulting in complete conversion of **2.3** to diphenyl species **2.5** by the time an NMR spectrum was taken (< 10 min). Four methane isotopologues CH_nD_{4-n} (n=1-4) in almost equimolar ratio were seen in the spectrum. An almost similar statistical ratio, 10 : 8 : 7 : 7 of CH_4 / CDH_3 / CD_2H_2 / CD_3H, was observed when C_6D_6 was combined with 3 equivalents of D_2O, shaken carefully and then complex2.3was added. Multiple deuterium scrambling is consistent with the DFT calculated reaction enthalpy profile and suggests that close-to-statistical deuterium scrambling occurred on both steps of methane elimination:

$LPt(CH_3)_2D \rightarrow$ 4/7 $LPtCH_3$ + 4/7 CDH_3 + 3/7 $LPtCH_2D$ + 3/7 CH_4
And for the loss of the second methane molecule,
4/7 possibility: $LPtCH_3 + C_6D_6 \rightarrow LPtPh$ + 4/84 CDH_3 + 30/84 CD_2H_2 + 40/84 CD_3H + 10/84 CD_4
3/7 possibility: $LPtCH_2D + C_6D_6 \rightarrow LPtPh$ + 6/36 CD_2H_2 + 20/36 CD_3H + 10/36 CD_4
In total,
CH_4 : CDH_3 : CD_2H_2 : CD_3H : CD_4 =
= (3/7) : (4/7 + 4/7(4/84)) : (4/7(30/84)+3/7(6/36)) : (4/7(40/84)+3/7(20/36)) : (4/7(10/84)+3/7(10/36)) ≈

≈ 10 : 14 : 6 : 10 : 4

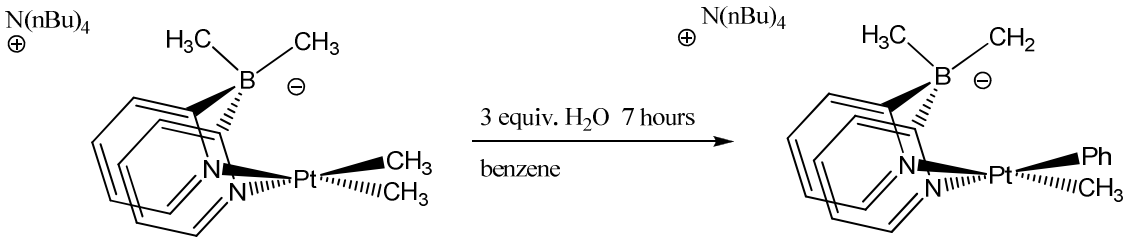
Attempted reaction between Na(dp-BMe_2)$PtMe_2$ and C_6H_6 dissolved in D_2O

Solid complex **2.3**, Na(dp-BMe_2)$PtMe_2$, (0.23 mmol), was placed in a Young tube under argon and D_2O saturated with benzene was added. After 1 day, complex 2.3did not dissolve and formation of **2.5** was not observed. The solubility of complex **2.3** and/or its reaction products in D_2O was very low, which might be the major reason of the lack of reactivity.

Attempted reaction between Na(dp-BMe_2)$PtPh_2$ and C_6D_6 saturated with H_2O or D_2O

In two separate experiments solid complex **2.5**, Na(dp-BMe_2)$PtPh_2$, (0.18 mmol), was placed in a Young tube under argon and benzene-*d6* saturated with H_2O or D_2O was introduced to produce clear solutions. After 2 days, no deuterium incorporation into the PtPh groups of **2.5** could be detected in the experiment with H_2O. Complex **2.8** did not form in this experiment either. In the second (D_2O) experiment we observed H/D exchange between the solvent and the PtC_6H_5 groups, which was noticeably faster in wet benzene than in pure D_2O (acidity of water is Na^+ - enhanced). These results suggest that basicity of **2.5** is low, but still sufficient to react with water, produce low concentrations of $LPtPh_2$(H/D) and LPtPh(PhH/PhD): transients responsible for the H/D exchange in the PtPh groups. Sodium cation binds dissolved water and so inhibits subsequent hydrolysis of LPtPh(PhH/PhD).

Tetra(*n*-butyl)ammonium dimethyldi(2-pyridyl)boratodiphenylplatinate(II), ^{n}Bu4N(dp-BMe_2)$PtPh_2$, 2.4 via tetra(*n*-butyl)ammonium dimethyldi(2-pyridyl)boratophenylmethylplatinate(II), $^{n}Bu_4N$(dp-BMe_2)PtPh(Me), 2.6



From complex **2.4**, benzene and 3 equ of water. Solid $^{n}Bu_4N(dp\text{-}BMe_2)$ (40 mg, 0.091 mmol) was added to precursor $Pt_2Me_4(SMe_2)_2$ (26.1 mg, 0.091 mmol Pt) and both solids dissolved in 2 mL of benzene as in the synthesis of **2.5** from complex **2.3**. After 10 minutes the solvent was removed under high vacuum to give dimethyl complex **2.4**, pure by NMR. Benzene and 5μL of water (0.274 mmol) were added to the solid and the mixture was stirred for 7 hours. The solvents were removed under high vacuum to afford the intermediate product **2.6**. Yield 59 mg (~90%). The complex is sparingly soluble in benzene and perfectly soluble in THF or acetone. A portion of the product was characterized by ^{1}H NMR. When 2 mL of deaerated C_6D_6 dried over molecular sieves for a few days and NaL as a promoter (0.5 equivalents) were combined with pure **2.4** (0.011 mmol), the reaction was much faster than without NaL, but much slower than in the presence of $NaBAr^F{}_4$ (see below). Complex **2.11** formed in the former case (>95% NMR yield, based on the integration of the aromatic region), with a small admixture of **2.6** (<5%) in 30 min. Pure 2.6 was evident after 1.5 hours. CH_4 and CDH_3 were detected in 3:1 ratio by ^{1}H NMR as major methane isotopologues along with traces of more deuterium-rich compounds (< 5% of all methanes). This result suggests that a deuterium scrambling occurred in the $PtMe_2$ fragment of the $PtMe_2D$ intermediate leading via LPtMe(MeD) complex to CH_4 and CDH_3.

^{1}H NMR (22^{o}C, THF-d8), δ: 8.70 (d, 1H, J_{H-H}=5.8 Hz, J_{H-Pt}=11.1 Hz), 8.15 (dd, 1H, J_{H-H}=4.4 Hz, 0.5 Hz, J_{H-Pt}=13.3 Hz), 7.49 (d, 1H, J_{H-H}=7.7 Hz), 7.44 (d, 1H, J_{H-H}=7.7 Hz), 7.30 (d, 2H, J_{H-H}=7.7 Hz, J_{H-Pt}=68.4 Hz), 7.27 (td, 1H, J_{H-H}=7.7 Hz, 0.7 Hz), 7.22 (td, 1H, J_{H-H}=8.0 Hz, 0.7 Hz), 6.62-6.70 (m, 3H), 6.60 (t, 1H, J_{H-H}=6.2 Hz), 6.37 (m, 1H), 2.98-3.02 (m, 8H), 1.41-1.51 (m, 8H), 1.23 (sextet, 8H, *J*=7.5 Hz), 0.88 (t, 12H, *J*=7.0 Hz), 0.12-0.70 (br s, 6H), 0.65 (s, 3H, J_{H-Pt}=82.6 Hz).
^{13}C NMR (22^{o}C, THF-d8), δ: 153.2, 150.5, 132.5, 132.3, 127.7, 127.3, 119.1, 118.8, 141.1, 129.1, 125.9, 119.7, 59.2, 24.6, 20.4, 14.0, -13.6. Pyridine *ipso*-carbon was not always seen and boron methyl group were not always seen due to boron splitting.

The NMR sample of **2.6** was combined with the remaining material and dried under high vacuum. Another 2 ml of benzene were added with 5μL of water (0.274 mmol). The solution was left to stir for one day. The solvent was evacuated to afford **2.11** (52mg, 72% yield based on complex **2.4**).

^{1}H NMR (22^{o}C, THF-d8), δ: 8.24 (d, 2H, J_{H-H}=5.1 Hz, J_{H-Pt}=25.0 Hz), 7.60 (d, 4H, J_{H-H}=6.9 Hz, J_{H-Pt}=59.0 Hz), 7.46 (d, 2H, *J*=7.3 Hz), 7.18 (td, 2H, *J*=6.9 Hz, 1.5 Hz), 6.69 (t, 4H, *J*=7.1 Hz), 6.54 (t, 2H, *J*=7.1 Hz), 6.37 (vt, 2H, *J*=6.9 Hz), 2.50-2.57 (m, 8H), 1.21-1.28 (m, 16H), 0.94 (t, 12H, *J*=6.5 Hz), 1.13 (bs, 3H), 0.27 (bs, 3H).
^{13}C NMR (22^{o}C, THF-d8), δ: 153.4, 153.1, 142.0, 133.8, 128.3, 127.1, 121.0, 119.6, 59.7, 25.6, 21.4, 15.0. Pyridine *ipso*-carbon and boron methyl groups were not seen due to both boron splitting and the fast exchange that is apparent in the ^{1}H NMR.
Crystals of complex **2.6** suitable for X-ray diffraction were obtained by letting the $NaBAr^F_4$ reaction mixture (see below) stand for three days in benzene.
Anal. Calcd for $C_{40}H_{60}BN_3Pt$: C, 60.90; H, 7.68; N, 5.33. Found: C, 60.74; H, 7.46; N, 5.25.

Attempted synthesis from 2.2, $Pt_2Me_4(SMe_2)_2$ and wet benzene

Solid nBu$_4$N(dp-BMe$_2$) (32.2 mg, 0.073 mmol) was added to precursor $Pt_2Me_4(SMe_2)_2$ (21 mg, 0.037 mmol) in 2 mL of deaerated but not dried benzene (the same batch as in the analogous synthesis of **2.5**). The bulk of the material reacted in five minutes. The mixture was left to stir overnight. The solvent was removed and the residue dried in vacuum for one hour to produce pure dimethyl complex **2.4**. Neither diphenyl complex **2.11** nor monophenyl complex **2.6** formed.

Reaction between (nBu)$_4$N(dp-BMe$_2$)PtMe$_2$ and wet C_6D_6 in the presence of NaBAr$^F_4$

Two NMR Young tubes were charged with solid complex **2.4** (~10mg) each in an argon-filled glovebox. Deuterated benzene (deaerated but not dried) was added to the solid in each case. The system formed a suspension due to the limited solubility of 2.4 in benzene; however, NMR data could still be obtained. 0.5 equivalent of NaB(Ar^F)$_4$ was added to the content of one of the tubes. In the time that addition of NaB(Ar^F)$_4$ took place, a vigorous reaction accompanied by release of methane gas was initiated. The suspension completely dissolved in half a minute and only complex **2.6** and all isotopomers of methane gas products in almost equal molar ratio could be detected by the time an NMR spectrum was obtained. No changes were observed in the control experiment where NaB(Ar^F)$_4$ additive was not introduced.

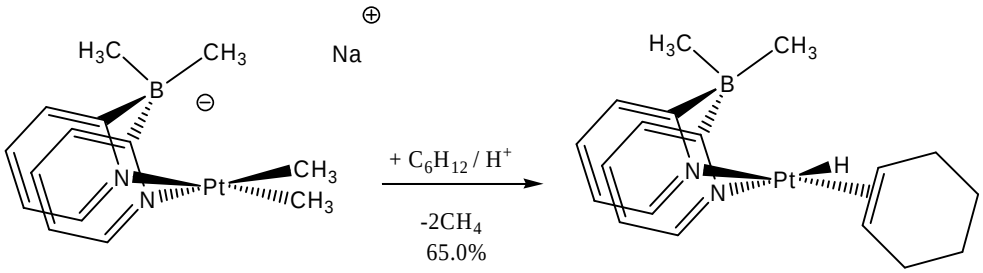
Sodium bis(2,5-difluorophenyl)dimethyldi(2-pyridyl)boratoplatinate(II), Na(dp-BMe$_2$)Pt(2,5-C$_6$H$_3$F$_2$)$_2$, 2.7

Solid Na(dp-BMe$_2$)PtMe$_2$ (0.045 mmol) was dissolved in 2mL of *p*-difluorobenzene and 3 μL of water were added via microsyringe. An immediate reaction accompanied by vigorous evolution of methane gas took place. After one hour, the solvent was evaporated under high vacuum and washed with a minimum amount of hexanes to obtain complex **2.7** (26.9mg, 92.3% yield) as an off color white solid. An analytically pure sample of **2.7**, which was also pure by ^{1}H and ^{13}C NMR could be obtained by washing the solid with 0.5 mL of benzene two times.

^{1}H NMR (22^{o}C, acetone-*d*6), δ: 8.49 (d, 2H, $J_{H\text{-}H}$=5.6 Hz, $J_{H\text{-}Pt}$=30.3 Hz), 7.53 (d, 2H, $J_{H\text{-}H}$=8.0 Hz), 7.29-7.35 (m, 4H), 6.58 (vtd, 2H, $J_{H\text{-}H}$=6.5 Hz, 1.6 Hz), 6.36-6.50 (bm, 2H), 6.24-6.30 (m, 2H), 0.16-1.22 (bm, 6H).

^{19}F NMR (22^{o}C, C6D6), δ: -110.9 (bs, $J_{F\text{-}Pt}$=430.5 Hz, 2F), -119.7 (s, 2F); CF_3CH_2OH internal standard signal set to -77.5ppm.
^{13}C NMR (22^{o}C, THF-d8), δ: 190.8 (bm), 164.9 (d, $J_{F\text{-}C}$=221.5 Hz), 159.1 (d, $J_{F\text{-}C}$=239.0 Hz), 152.1, 133.6, 128.0-128.6 (m, 4C), 119.2, 117.4 (dd, $J_{F\text{-}C}$=18.6 Hz, 13.7 Hz), 113.0 (dd $J_{F\text{-}C}$=34.9 Hz, 8.2 Hz), 107.8 (dd $J_{F\text{-}C}$=24.7 Hz, 8.1 Hz), 11.3-16.5 (m). Anal. Calcd for $C_{24}H_{20}BF_4N_2NaPt$: C, 44.95; H, 3.15; N, 4.37. Found: C, 44.87; H, 3.59; N, 4.63.

Cyclohexene hydrido dimethyldi(2-pyridyl)boratoplatinum(II), (dp-BMe_2)PtH(*cyclo*-C_6H_{10}), 2.9

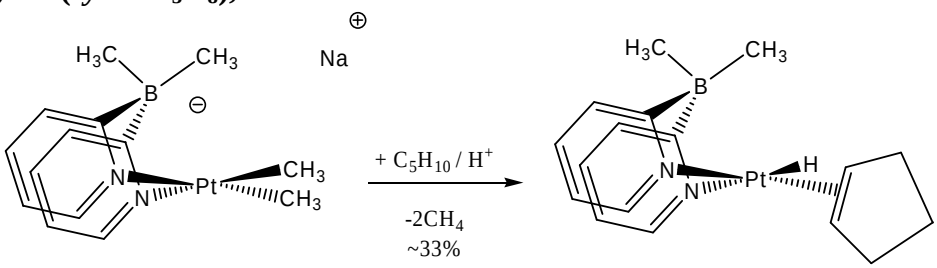


Solid Na(dp-BMe_2)PtMe_2 (0.085 mmol) was added to a flask with 2 mL of cyclohexane. Water (3 eq, 5 μL) was added by microsyringe to the suspension, upon which time a vigorous reaction occurred at the water drop/cyclohexane solvent interface, resulting in an evolution of gas. The mixture was stirred for an hour, after which the solvents were separated from the solid and evaporated. Both residues were dried under vacuum and extracted with cyclohexane to give pure complex **2.9**. Yield 17.0 mg (42%). The residue remaining after extraction produced a strongly basic solution in water consistent with formation of NaOH. A similar result was observed when solid Na(dp-BMe_2)PtMe_2 (0.85 mmol) was combined with 1.5 mL of cyclohexane and 0.5 mL of water; isolated yield 34%. The yield was essentially the same when we used a pH 7 buffer solution or 1 equivalent of dilute HBF_4 instead of pure water. When instead of water, one equivalent of H(dp-BMe_2) was used, a slow reaction occurred so that after two days **2.9** formed in 65% NMR yield (5.0 μL of acetone added as an internal standard). The major contaminant was unreacted H(dp-

BMe_2). Longer reaction times lead to lower yields. We suggest that the factors responsible for better yield of **2.9** were slower reaction times allowing for the controlled production and utilization of protonated intermediates and the absence of NaOH that would trap and destroy a reaction intermediate.

^{1}H NMR (22^{o}C, C_6D_{12}), δ: 8.64 (vd, 1H, J_{H-H}=5.1 Hz, J_{H-Pt}=63.5 Hz), 7.90 (bd, 1H, J_{H-H}=5.1 Hz), 7.75 (t, 2H, *J*=6.6 Hz), 7.30 (td, 2H, *J*=6.6 Hz, 1.7 Hz), 6.73 (m, 1H), 6.60 (m, 1H), 4.75 (bs, 2H, J_{H-Pt}=75.0 Hz), 2.74-2.26 (m, 4H), 1.90-1.80 (m, 2H), 1.38-1.28 (m, 2H), 0.49 (bs, 6H), -21.4 (s, 1H, J_{H-Pt}=1271.0 Hz).
^{13}C NMR (22^{o}C, C_6D_{12}), δ: 155.1, 144.8, 135.5, 134.8, 130.4, 129.8, 120.0, 119.1, 78.8 (bs), 27.8, 22.2. Signals of the pyridine ipso carbon and BMe_2 fragment were not seen due to boron splitting.
^{13}C NMR (22^{o}C, C_6D_6), δ: 155.2, 145.5, 136.2, 135.3, 130.3, 129.6, 120.5, 119.8 (J_{C-Pt}=64 Hz), 79.7 (bs, J_{C-Pt}=162 Hz), 30.1, 21.9, 15.7 (vb m). Signals of the pyridine *ipso*-carbon were not seen due to boron splitting.
Anal. Calcd for $C_{18}H_{25}BN_2Pt$: C, 45.48; H, 5.31; N, 5.90. Found: C, 46.30; H, 5.14; N, 5.88.

Cyclopentene hydrido dimethyldi(2-pyridyl)boratoplatinum(II), (dp-BMe_2)PtH(*cyclo*-C_5H_8), 2.10



The complex was prepared as **2.9** above utilizing 3 eq. of water added via microsyringe, with cyclopentane as the solvent. Isolated yield is ~33%. The same result was observed when solid Na(dp-BMe_2)$PtMe_2$ (0.85 mmol) was combined with 1.5 mL of cyclopentane and 0.5 mL of water.

^{1}H NMR (22^{o}C, C6D6), δ: 8.57 (d, 1H, J_{H-H}=5.6 Hz, J_{H-Pt}=60.3 Hz), 8.01 (d, 1H, J_{H-H}=7.7 Hz), 7.93 (d, 1H, *J*=7.7 Hz), 7.65 (bd, 1H, *J*=5.6 Hz), 7.05 (t, 1H, *J*=6.8 Hz), 6.90 (t, 1H, *J*=6.8 Hz), 6.40 (vt, 1H, *J*=5.7 Hz), 6.16 (vt, 1H, *J*=6.3 Hz), 4.37 (s, 2H,

$J_{H\text{-}Pt}$=73.3 Hz), 2.27-2.48 (m, 2H), 1.80-1.94 (m, 2H), 1.26-1.34 (m, 2H), 1.18 (bs, 6H), -21.2 (s, 1H, $J_{H\text{-}Pt}$=1252.9 Hz).
^{13}C NMR (22^{o}C, C_6D_6), δ: 154.9, 146.0, 136.2, 135.4, 130.4, 129.6, 120.4, 119.8, 83.5, 35.2, 21.7, 15.7 (br. m). Signals of the pyridine ipso carbon and BMe_2 fragment were not seen due to boron splitting.

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Chapter 3: Oxidatively Induced Methyl Transfer from Boron to Platinum in Dimethyldi(2-pyridyl)boratoplatinum Complexes

3.1 Introduction

3.1.1 Aerobic oxidation in Shilov-like systems

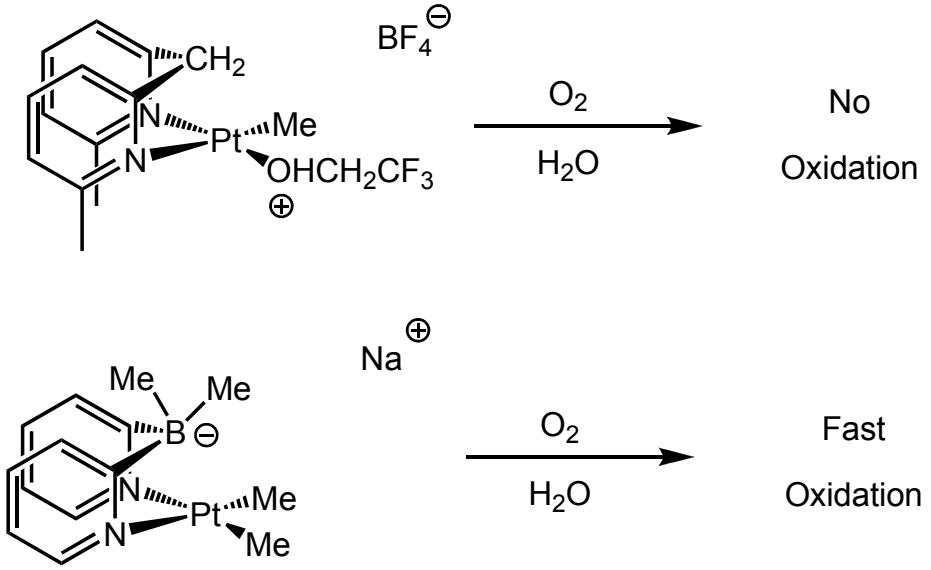
The rapid CH activation results described in Chapter 2 with dpb supported Pt complexes were encouraging not only due to the speed of reaction, but also that the products were tolerant of water and that water was a required component of the reaction. We decided to test the activity of our complexes under aerobic conditions in order to estimate the propensity of the system towards aerobic oxidatation with an eventual view towards replacing other more expensive oxidants utilized in the Shilov and Shilov-like systems[1-3] with oxygen as the terminal oxidant. In a review, Shilov explored oxidation of metals, including that of Pt^{II} alkyl systems known up to 1997.[1] There are serious drawbacks to many systems that attempted to change the oxidant from the Pt^{IV} used in the original Shilov cycle to other types of oxidants. Many systems limited the turnover and stability of the catalyst, while Wacker-like oxidation involving copper salts adversely effected selectivity.[4] Neumann has attempted to couple CH activation chemistry with oxidation by polyoxometallates that could be reoxidized by air[5] with limited success and Bercaw has studied the mechanism of oxidation at Pt^{II} centers.[6-8] However, the use of oxygen as a direct oxidant for the reaction has not received much consideration despite previous reports that showed dialkyl and other electron rich Pt^{II} complexes react rapidly with air to form Pt^{IV} specie.[9,10] This may be due to the use of neutral ligands and cationic complexes as

models for CH activation; which in turn make for very air-stable Pt^{II} monoalkyl complexes. Only recently has the use of electron rich ligands in successful and rapid CH activation become commonplace.[11-14]

3.1.2 Differences between dmdpm and dpb ligand motifs in facilitating aerobic oxidation with Pt^{II}

We were expecting rapid oxidation of dialkyl platinum complexes **2.3** and **2.5** since the anionic dipyridylborate ligand is more electron donating than neutral nitrogen based ligands. The dpm supported complexes **1.2-solvento** proved to be stable towards molecular oxygen (Scheme 3.1). While this stability was welcome for the purpose of gathering kinetic data on CH activation, it is clear that a monoalkyl complex would need to be oxidized by dioxygen as a terminal oxidant in order for systems based on the Shilov Cycle to become commercially viable. The more electron rich a Pt^{II} complex, the easier it would be to achieve a higher oxidation state. An electron releasing ligand such as dpb was synthesized for the purpose of performing CH activation experiments at the beginning, possible aerobic oxidation was an added consideration that was taken into account at the beginning of the project.

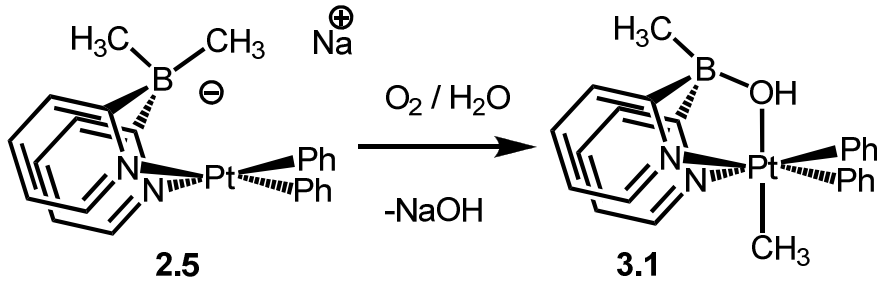
Scheme 3.1. Differences in electron density at Pt and oxidation speed



3.1.3 Introduction to initial oxidation results of complex **2.3**

In the course of CH activation studies with [dpbPt^{II}(Me)$_2$][Na] (**2.3**), we found that complex was stable under air in THF solution for a day, leading to a sluggish reaction with unidentified products after a longer time period. Analogous diphenyl complex [dpbPt^{II}(Ph)$_2$][Na] (**2.5**), proved to have similar reactivity in THF. It was also stable in water under an argon atmosphere. However, when solutions of the diphenyl complex in water were exposed to air, a very rapid oxidation of the complex towards a Pt^{IV} species was observed (Scheme 3.2). This observation suggested that coordination of O_2 to the Pt^{II} center might be a rapid and reversible process in non-hydroxylic solutions such as THF, and that coordinated dioxygen can be trapped by hydroxylic solvents. Previous work from Goldberg and Bercaw suggests that formal oxidation of the metal center occurs after protonation of coordinated dioxygen.[10]

Scheme 3.2 Aerobic oxdiation of [dpbPt^{II}(Me)$_2$][Na] in water

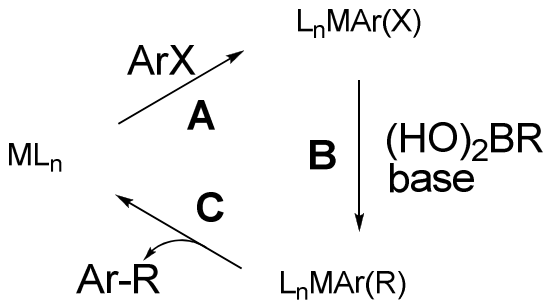


Analyzing the products of aerobic oxidation showed that B-CH_3 bond had been cleaved by the metal center. This was an undesirable development from the point of view of closing the Shilov cycle as the ligand had been formally destroyed. Concerns with regards to the stability of anionic borate ligands had been voiced by Peters earlier.[13] The Peters group synthesized a number of monoanionic borate ligands with P,P or N,N donors, but opted to use phenyl groups instead of Me. The reasons for this were voiced as greater stability towards cleavage by the metal center and greater stability of the B-C bond under acidic reaction conditions. Our study of the dpb ligand showed that the latter concern was unwarranted as the ligand was stable in mild acids such as acetic acid and aqueous HCl for long periods of time at elevated temperatures. The first concern proved valid due to the destruction of the ligand during aerobic oxidation; the short distance between the boron and platinum centers in *n*Bu_4N salt of complex **2.5** was the record short distance for all Pt^{II} complexes supported by anionic borate ligands and it played a role in putting the C-B bond in very close proximity to the metal.

3.1.4 The Suzuki-Miyaura coupling

Although destruction of the ligand is undesirable, the reaction depicted by Scheme 3.2 represents an interesting observation that may have relevance to the mechanism of Suzuki coupling (Scheme 3.3). The Suzuki-Miyaura reaction involves the coupling of an aryl halide with an alkyl or aryl boronic acid under mild conditions with Pd catalyst. It is a very widely used reaction today in the fine-chemicals and pharmaceutical industry and has supplanted other types of coupling methodologies such as Stille coupling[15] due to the low toxicity of boronic acids compared to that of the tin byproducts. Complex **3.1** can be thought of as a model of an intermediate of the Suzuki coupling reaction that is carried out by a Pd(0)/Pd(II) couple (Scheme 3.3 M=Pd). Though the oxidation state of Pt in complex **3.1** and that of Pd in the expected product of step **B** in Scheme 3.3 are different, this comparison may be useful. We sought to take a closer look at our system as a mechanistic probe that could offer insight into step **B** of the Suzuki-Miyaura coupling.

Scheme 3.3 Suzuki-Miyaura Coupling mechanism.



Although the mechanisms of C-X bond cleavage with electron-rich metal complexes (Scheme 3.3, step A)[16,17] and C-C reductive elimination from transient bis(hydrocarbyl) species (Scheme 3.3, step C) have been studied in detail for some metals,[17] less attention has been paid to boron-to-metal hydrocarbyl (alkyl or aryl)

ligand transfer (Scheme 3.3, step B).[18] This transfer has been suggested to occur as an electrophilic aromatic substitution in the case of aryl boron reagents (M=Pt), and a similar mechanism has been postulated for their alkyl analogues.[19] No information on the transfer of a hydrocarbyl group from boron to a metal atom in a high oxidation state (such as M^{IV}) is available.

3.2 Results and Discussion

When solutions of complex **2.5** in dry benzene or THF were exposed to air, a sluggish reaction was observed which led to a complex mixture of unidentified products. In contrast, a clean and fast reaction took place when water or alcohols (MeOH or EtOH) were used as a solvent. Oxidation of **2.5** in water was complete at ambient temperature after 3-5 min and led to the formation of hydroxoborato platinum(IV) complex **3.1** which was isolated from a strongly alkaline reaction mixture in an analytically pure form in 90% yield (Scheme 3.4).

Scheme 3.4 Aerobic oxidation of [dpbPt^{II}(Ph)$_2$][Na] in hydroxylic solvents

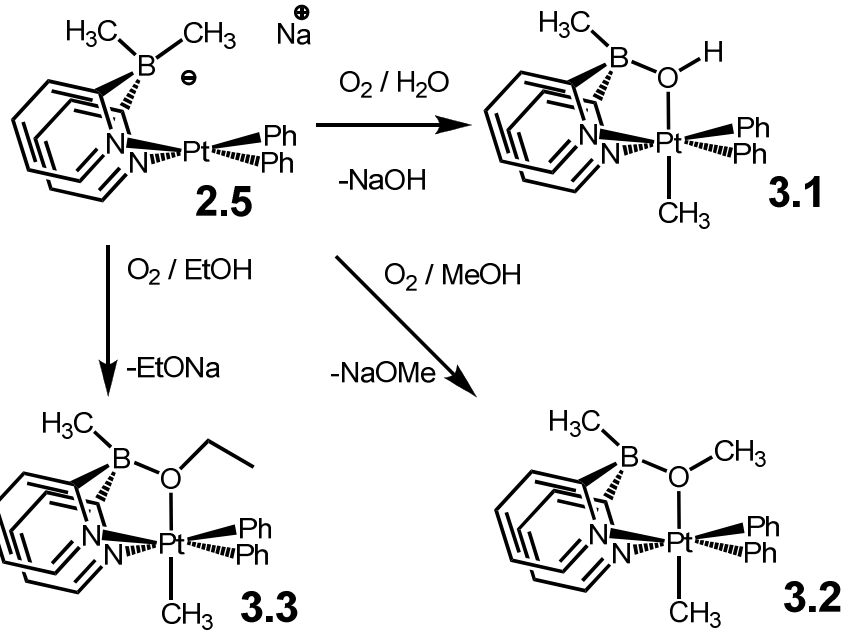
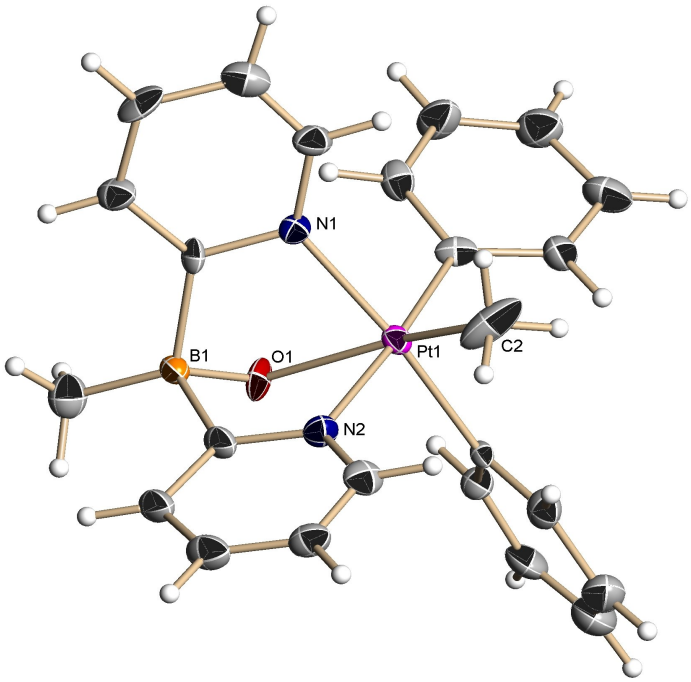


Figure 3.1 Ortep represenation (thermal ellipsoids at 50%) of complex **3.1**



According to ^{1}H, ^{13}C NMR spectroscopy and single crystal X-ray diffraction (Figure 3.1), the transformation resulted in the substitution of one of the methyl groups of the

BMe_2 on the original ligand dpb by OH and migration of the methyl to the Pt^{IV} atom. Similar to aqueous solutions, a clean and fast oxidation of **2.5** was observed when methanol or ethanol was used as a solvent to produce methoxoborato (**3.2**) or ethoxoborato (**3.3**) analogues of **3.1**, respectively, in isolated yields exceeding 90%.

Dimethylplatinum(II) complex **2.3** exhibited similar reactivity. It reacted with oxygen in ethanol to produce ethoxoborato trimethyl platinum(IV) complex **3.4** which was isolated after 5 min in an analytically pure form in 85% yield (Scheme 3.5) and characterized by NMR spectroscopy and X-ray diffraction (Figure 3.2). The use of more acidic solvents such as methanol or water led to poorer results, presumably due to competitive protonolysis of **2.3**[11].

Scheme 3.5. Aerobic oxidation of $[dpbPt^{II}(Me)_2][Na]$ in hydroxylic solvents

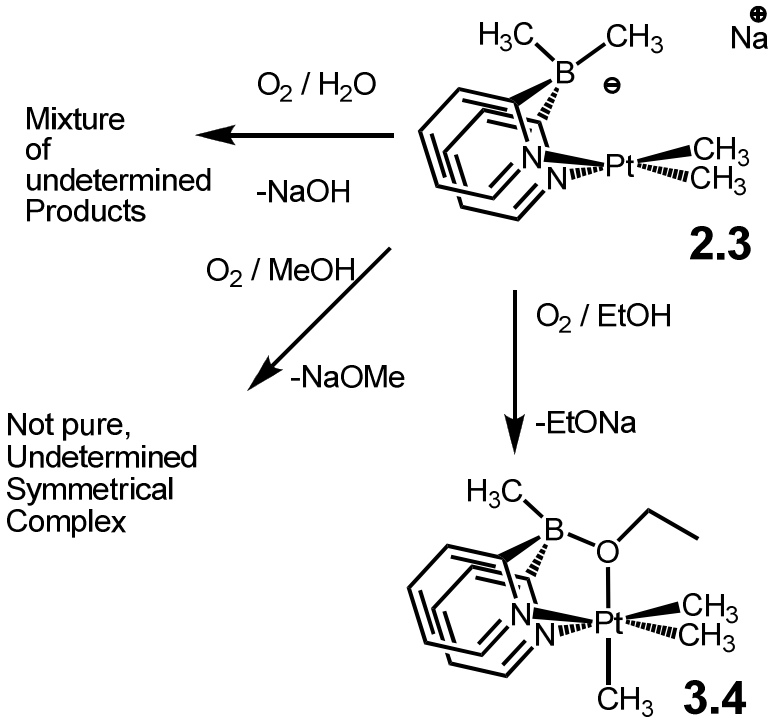
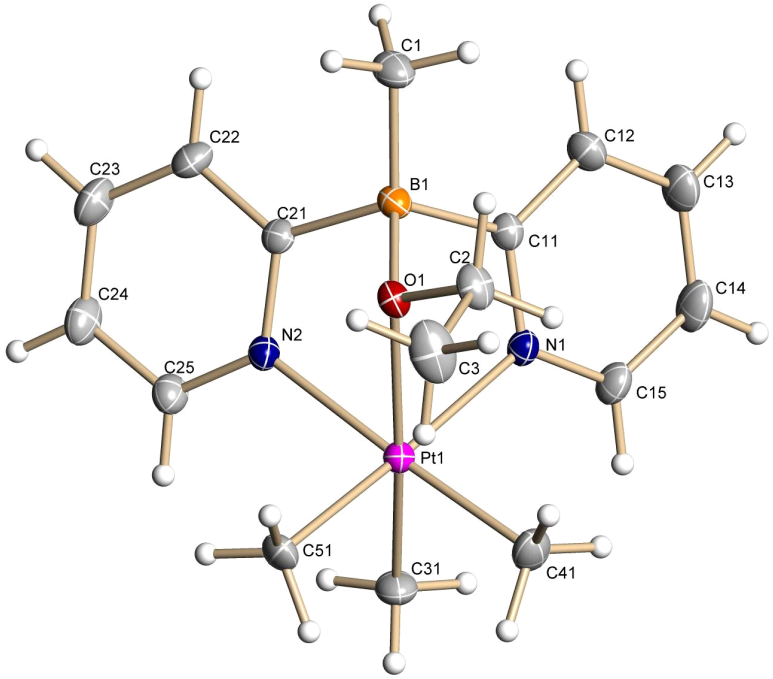


Figure 3.2 Ortep represenation (thermal ellipsoids at 50%) of complex **3.4**



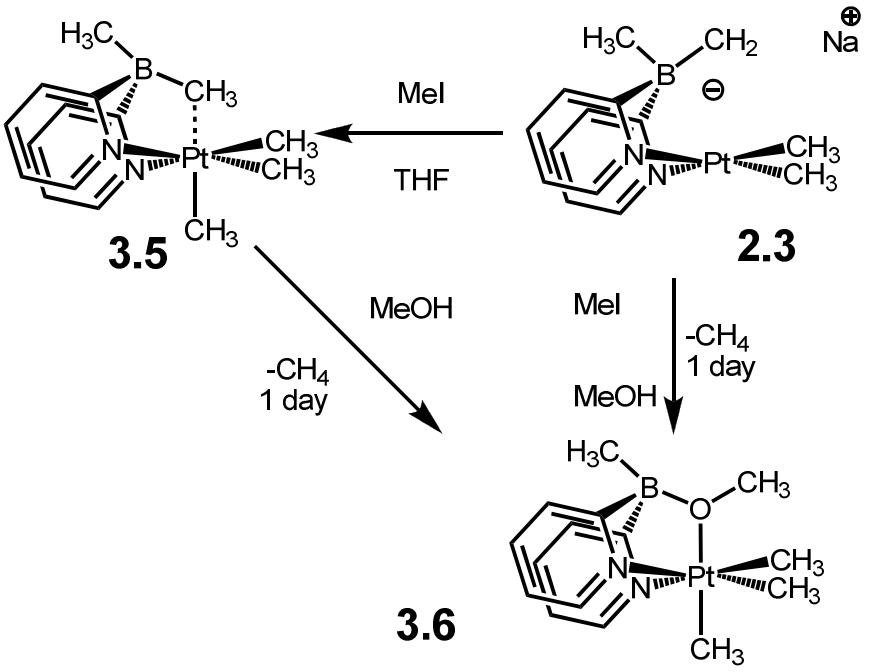
Pt1-C31	2.032(3)	Pt1-C41	2.050(3)	Pt1-C51	2.051(3)
Pt1-N2	2.137(2)	Pt1-N1	2.140(2)	Pt1-O1	2.2120(19)
B1-O1	1.547(3)	B1-C1	1.615(4)		

The experiments above suggest that the oxygen atom of the dipyridylborato ligands in complexes **3.1**-**3.4** originated from respective solvents and not from O_2. If the opposite were the case, or if two disparate reaction mechanisms were operative, OH bridged complexes should have been present in all four cases.

We decided to get a better handle on the exact mechanism of methyl group transfer by using different, easier to study oxidants which could lead to unobserved intermediates. Oxidation by dioxygen may be very complex in nature, and the solvent could play a large role in the oxidation reaction. Decoupling the oxidation and Me transfer reactions from each other should be possible with a well-behaved two-electron oxidant such as MeI.

A reaction of **2.3** with MeI attempted in aprotic THF was virtually instantaneous and led to NaI and an air stable complex **3.5** (Scheme 3.6) which, according to ^{1}H NMR, formed quantitatively and could be isolated in 75% yield.

Scheme 3.6 Oxidation of complex **2.3** with MeI and subsequent Me group transfer

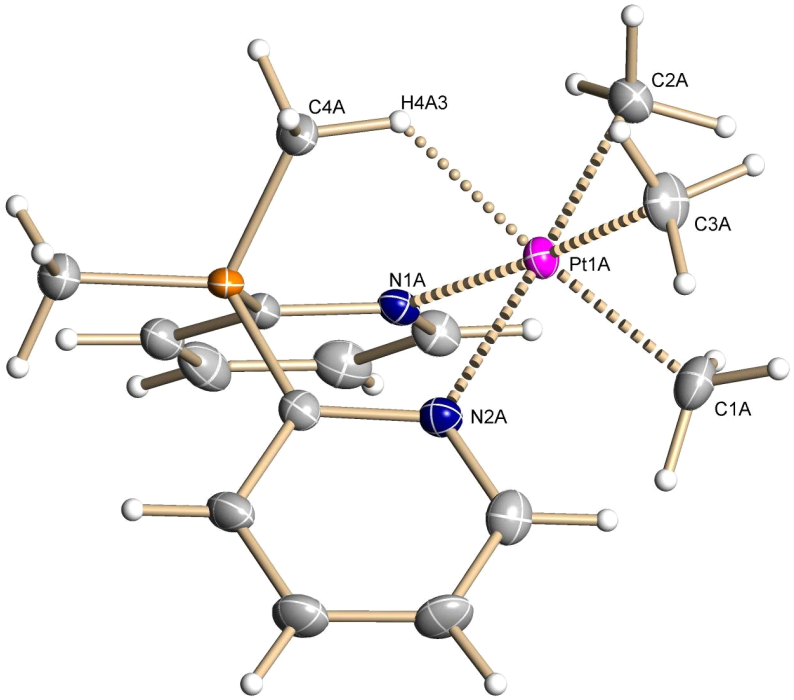


A ^{1}H NMR spectrum of **3.5** in THF-d_8 solution confirmed its mirror symmetric structure. The boron-bound methyl groups exhibited two broadened multiplets, both integrating as 3H, at 0.22 ppm (J_{BH} = 4.4 Hz), and -0.91 ppm. Remarkably, the higher field resonance at -0.91 ppm had two platinum-195 satellites with J_{PtH} = 58.1 Hz. These results suggested the presence of a five-coordinate Pt^{IV} center stabilized by a CH-agostic interaction with the boron-bound *endo*- methyl group. The hypothesis that CH bonds of one of the ligand methyl groups were coordinated to the Pt^{IV} center was supported by ^{13}C NMR spectroscopy. Specifically,

the multiplet of a “free” B-Me group at 9.0 ppm was a quartet with J_{BC} = 45.0 Hz, whereas the signal of the agostic methyl carbon at 27.1 ppm was a quartet with a smaller J_{BC} constant of 39.6 Hz and platinum-195 satellites with J_{PtC} = 60.3 Hz.

The structure of **3.5** was confirmed by single crystal X-ray diffraction (Fig. 3.3). A few five-coordinate Pt^{IV} complexes are known,[20,21] but, to the best of our knowledge, agostic CH – Pt^{IV} structures were never reported. The Pt-H distance, 2.02 Å, and the Pt-C4B separation, 2.76 Å, are shorter than those found in a three-coordinate cationic CH agostic Pt^{II} complex.[22]

Figure 3.3 Ortep represenation (thermal ellipsoids at 50%) of complex **3.5**



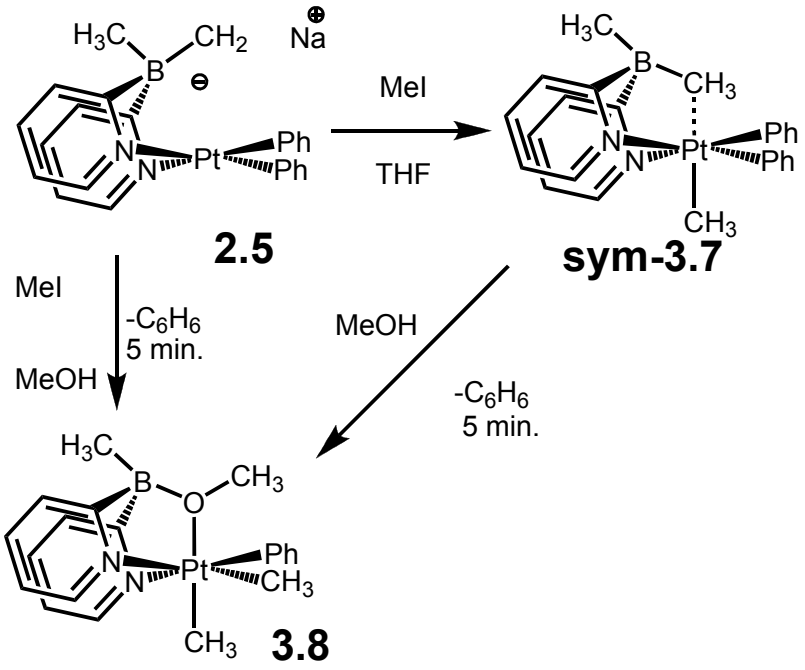
Pt1A-C1A	2.021(4)	Pt1A-C2A	2.041(5)	Pt1A-C3A	2.056(5)
Pt1A-N2A	2.139(4)	Pt1A-N1A	2.145(4)	Pt1A-H4A3	2.01(4)
B1A-C5A	1.622(6)	B1A-C4A	1.648(7)		

Interestingly, the average B-C bond length calculated for two crystallographically independent molecules of **3.5** present in the unit cell for the

endo-methyl, which is involved in the bonding to the Pt^{IV} center, 1.66(1) Å, was longer than the bond length for the *exo*-methyl group, 1.61(1) Å. This observation suggests that the B-C bond which is to be broken in the course of migration to the Pt^{IV} center might also be involved in a weak interaction with the metal. A reduced B-C coupling constant observed for **3.5** is in accordance with this suggestion.

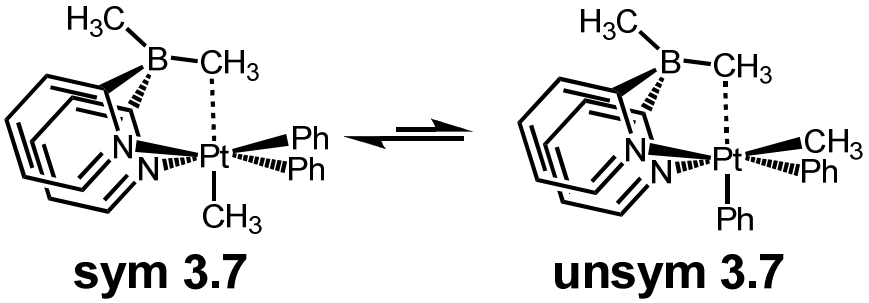
Complex **2.5** also reacted cleanly with methyl iodide to produce two isomeric CH agostic five-coordinate Ph_2Pt^{IV} complexes, *sym*-**3.7** and *unsym*-**3.7** (Figure 3.4, Scheme 3.7).

Scheme 3.7 Oxidation of complex **2.5** with MeI and subsequent Me group transfer



The reaction was quantitative by NMR. The product **3.7** could be isolated in an analytically pure form in 73% yield. According to ^{1}H NMR, the complex existed in acetone or benzene solutions as a mixture of two interconverting symmetric and unsymmetric isomers (Figure 3.4) each exhibiting distinct sharp PtMe resonances.

Figure 3.4 Equilibrium between **sym3.7** and **unsym3.7**

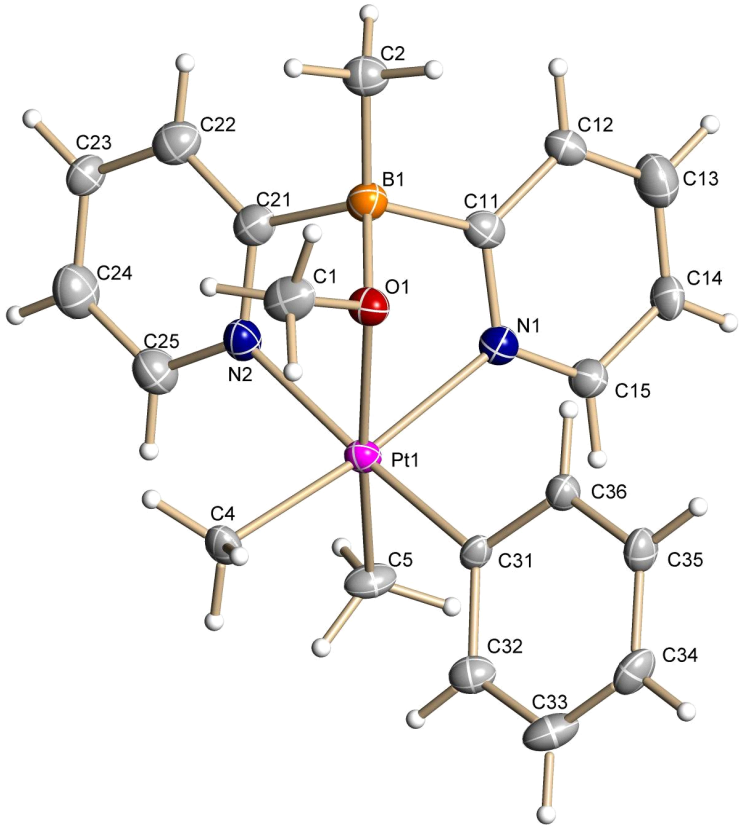


The position of the equilibrium depended on solvent, but in all cases the major isomer was the symmetrical one (3:1 ratio in acetone gave the most pronounced difference whereas the ratio was ~2:1 benzene).

Thus, no B-to-Pt^{IV} methyl group transfer was observed upon oxidative addition of methyl iodide to either **2.3** or **2.5** in THF solutions. Remarkably, this transfer was complete after 10 min when a sample of isomeric **3.7** was dissolved in methanol to produce methoxoborato complex unsym-**3.8** and benzene, quantitatively by NMR (Scheme 3.7).

According to ^{1}H, ^{13}C NMR, and X-ray diffraction, the single product **3.8** was unsymmetrical and had one $Pt^{IV}Ph$ group (Figure 3.5). Therefore, isomeric complexes **3.7** reacted selectively via protonolysis of a Pt-Ph rather than a Pt-Me bond. Accordingly, in the case of the methyl analogue **3.5**, a slow B-to-Pt^{IV} methyl group transfer accompanied by protonolysis of a Pt-Me bond led to complex **3.6** quantitatively after one day (Scheme 3.6). The methoxy bridged complex **3.6** is the analogue of ethoxy bridged **3.4** that could not be obtained by direct oxidation with O_2 in MeOH solvent earlier due to fast side-reactions.

Figure 3.5 Ortep represenation (thermal ellipsoids at 50%) of complex **3.8**



Pt1-C31	2.016(4)	Pt1-C5	2.036(4)	Pt1-C4	2.053(4)
Pt1-N2	2.133(3)	Pt1-N1	2.156(3)	Pt1-O1	2.187(3)
C1-O1	1.424(5)	O1-B1	1.544(5)	B1-C2	1.601(6)

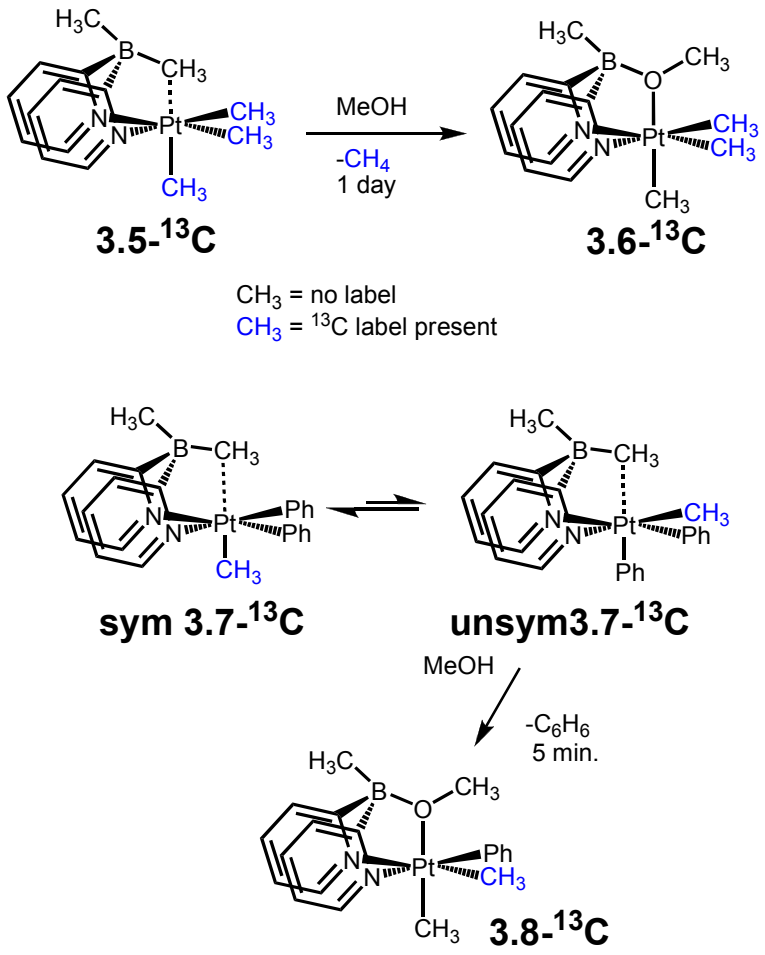
The stereochemistry of the B-to-Pt^{IV} methyl migration was revealed in experiments involving a ^{13}C-labeled complex **3.5-^{13}C** prepared using $^{13}CH_3I$. According to ^{1}H NMR spectroscopy, the complex is fluxional; the label in **3.5-^{13}C** was distributed statistically among the equatorial and the axial positions (33% ^{13}C for each of the Pt^{IV}Me groups) after 10 min upon preparation of **3.5-^{13}C** suggesting that a fast Me-group exchange in 5-coordinate Pt^{IV} complex **3.5** took place. Although the axial and equatorial Me groups of **3.5** gave distinct resonances in NMR experiments, there is precedent of very rapid equilibration in similar $Pt^{IV}(Me)_3$ complexes

supported by anionic ligands that was observed by Goldberg.[21] In their 2007 report, only one signal was observed for all three Me groups even at temperatures of 220K; however, the geometry was determined to be square planar by X-Ray crystallography. This fast exchange could be sufficiently hindered to slower than the NMR timescale by introducing a stabilizing ligand in the free sixth position of the octahedron that is favored by Pt^{IV} complexes due to the 18 electron rule. In the case of **3.5**, the sixth ligand is a CH agostic bond of the boron bound Me whereas Goldberg's complex possesses no proximate sigma bonds for such a stabilization.

Notably, reaction of **3.5-^{13}C** in CD_3OH led to the formation of a 2:1 mixture of CH_4 and $^{13}CH_4$ along with complex **3.6** which exhibited a signal of the equatorial CH_3 groups with the ^{13}C satellites corresponding to a 33% ^{13}C-enrichment and a signal of the axial CH_3 group with the intensity of the ^{13}C satellites corresponding to the natural ^{13}C abundance. Free methane observed in the reaction mixture exhibited 33% ^{13}C enrichment.

Similar behavior was exhibited by **3.7-^{13}C** (Scheme 3.8) In the latter case, ~100% ^{13}C enrichment was present at the methyl bound to Pt and no enrichment beyond the natural abundance was seen on the boron bound Me groups. It was the minor isomer, **unsym-3.7-^{13}C** that reacted to give **3.8-^{13}C** exclusively. The other product of the reaction was one equivalent of free benzene. The label was found exclusively in the equatorial position in the product while the axial Me group only had a natural abundance of ^{13}C.

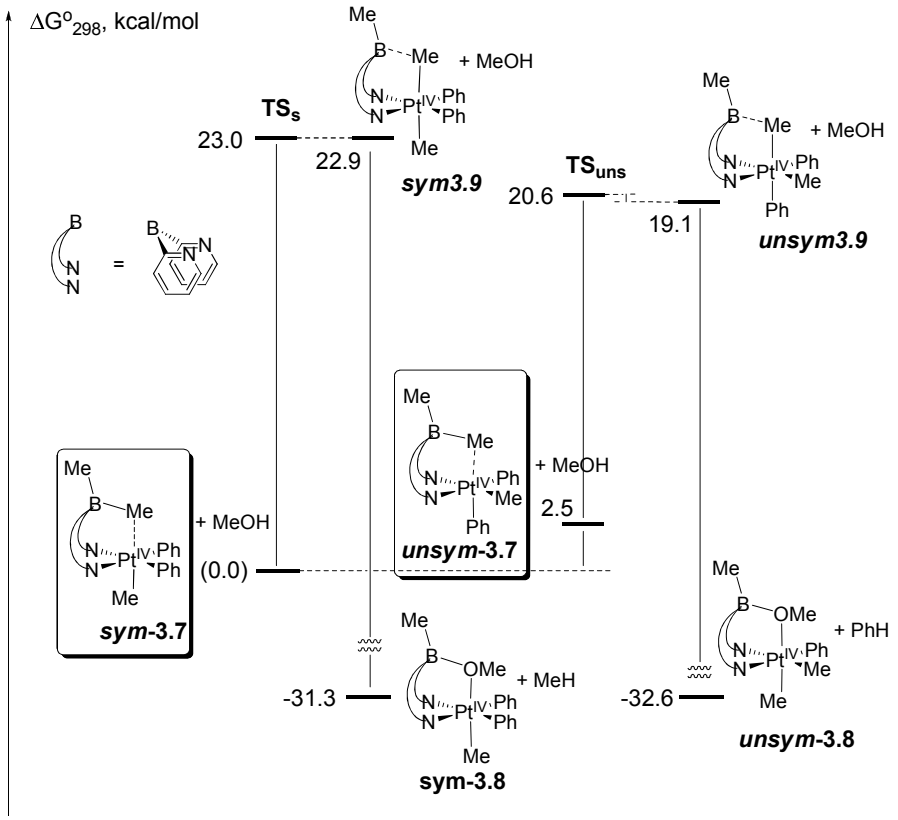
Scheme 3.8. ^{13}C label Me group transfer experiments



Thus, the methyl group transferred from the boron to the Pt^{IV} was not involved in the methanolysis. This fact is consistent with the results of our DFT calculations on the presumed six-coordinate intermediates **sym-3.9** and **unsym-3.9** (Scheme 3.9). The high-energy intermediates **3.9** might form from $Pt^{IV}MePh_2$ complexes **3.7** as a result of the B-to-Pt^{IV} methyl transfer. Then in the course of reaction they undergo protonolysis of one of the axial Pt-C bonds and after some rearrangements form the observed product **3.8**.

According to our calculations, in both isomeric complexes **3.9** the methyl transferred participates in a stabilizing B-C-H 3-center 2-electron interaction with the electron-poor boron atom and is therefore to some extent ”protected“ against attacks of another electrophile, H^+, that would be present in hydroxylic solvents such as MeOH. Protonolysis of the axial Pt^{IV}-C bond *trans*- to the methyl in *sym*-**3.9** may be facilitated by the strong *trans*-influence of the Me group. The preference for the minor unsymmetrical isomer of **3.7** with the axial Pt^{IV}-Ph to react can be due to a noticeably lower activation barrier involving $\mathbf{TS_{uns}}$ ($\Delta G^{\neq}$ = 20.6 kcal/mol) compared to $\mathbf{TS_{sym}}$ ($\Delta G^{\neq}$ = 23.0 kcal/mol). Additionally, the Pt^{IV}-Ph fragment in *unsym*-**3.9** can react with H^+ faster than the Pt^{IV}-Me fragment in *sym*-**3.9** due to the involvement of a relatively low-barrier aromatic electrophilic substitution mechanism.[1]

Scheme 3.9 DFT calculated pathways in the Me group transfer reaction



The calculated Gibbs reaction energy for the transformation of ***sym*-3.7** to ***sym*-3.9** and ***unsym*-3.9** (Scheme 3.9) is positive, 19.1-23.0 kcal/mol, with the lowest energy transition state to be $\mathbf{TS_{uns}}$, which connects *unsym*-**3.7** and *unsym*-**3.9** responsible for the formation of the observed product *unsym*-**3.8**. The DFT calculated reaction path shows that the formation of the Pt^{IV}-C bond and cleavage of the B-C bond are practically synchronous. Thus, the methyl group transfer may be viewed as an electrophilic substitution at the methyl group carbon with the Pt^{IV} atom acting as an electrophile and the three-coordinate boron playing the role of a leaving group.

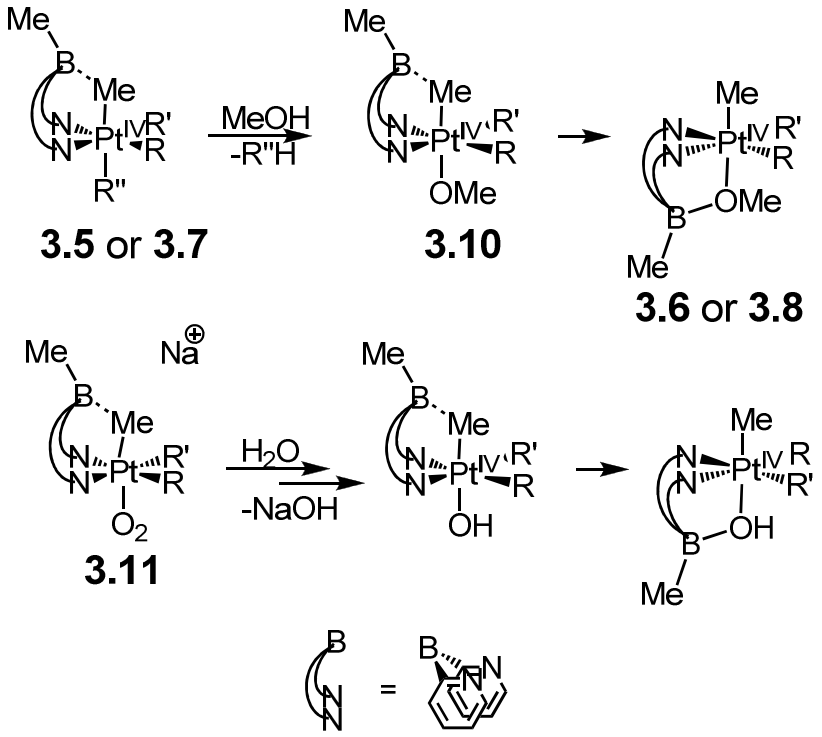
The positive energy of the methyl transfer might be diminished as a result of a nucleophilic attack of water or an alcohol at the boron atom (Scheme 3.10 top; R, R',

R“ = Me or Ph). A nucleophilic solvent molecule such as MeOH or water, can encourage methyl transfer by nucleophilically attacking the boron atom in a mechanism reminiscent of S_N2 substitution. After protonolysis of the Pt-C bond *trans*- to the methyl transferred,[23] the reaction becomes irreversible. The Gibbs energy change for methanolysis of **3.5** to produce methane and corresponding **3.10** is -11.2 kcal/mol.

An “inversion” of the metallacycle in the transient **3.10** might lead to the observed reaction products, RH and methoxoborates **3.6, 3.8**. According to DFT, this transformation is favored by about 30 kcal/mol overall.

The mechanism of the “inversion” might involve: i) a highly strained transition state with nearly planar dipyridylmethylborane ligand or ii) a sequence of dissociation of one of the pyridine groups from the metal, rotation of the py_2BMe (or corresponding borate) fragment about the remaining Pt-N bond by 180^o with subsequent re-coordination of the free pyridine to the transient trigonal bipyramidal Pt^{IV} center. Our DFT estimates show that the pyridine arm dissociation from the Pt^{IV} center in $Pt^{IV}R_4$ complexes such as *unsym*-**3.19** is characterized by the Gibbs energy of ~17 kcal/mol. At the same time, formation of a nearly planar dipyridylmethylborane ligand attached to the Pt^{IV} in complex **3.19** requires about 10 kcal/mol more energy. Hence, the dissociation-rotation-re-coordination mechanism might be more consistent with the observed fast reactivity of our systems.

Scheme 3.10



Based on the available observations we postulate a mechanism for aerobic reactions which is similar to the B-to-Pt^{IV} methyl migration in $dpbPtR_3$ (Scheme 3.10 lower half; and Equations 1,2). In this case the axial group is an O_2H or OH formed according to one of the mechanisms suggested for oxidation of alkyl Pt^{II} complexes by O_2 (eq 7-8):[9,24]

$$[LPt^{II}R_2]^- + H_2O + O_2 \longrightarrow LPt^{IV}R_2(O_2H) + OH^- \quad (1)$$

$$LPt^{IV}R_2(O_2H) + [LPt^{II}R_2]^- + H_2O \longrightarrow 2LPt^{IV}R_2(OH) + OH^- \quad (2)$$

The O_2 oxidation could proceed even more rapidly since protonation of coordinated O_2 is expected to be more facile than the protonation of a CH_3 or C_6H_5 from simple considerations of basicity. The weak *trans* effect of the O_2 compared to that of a hydrocarbon is expected to lower the energy of proposed intermediate **3.11** as well.

3.3 Summary

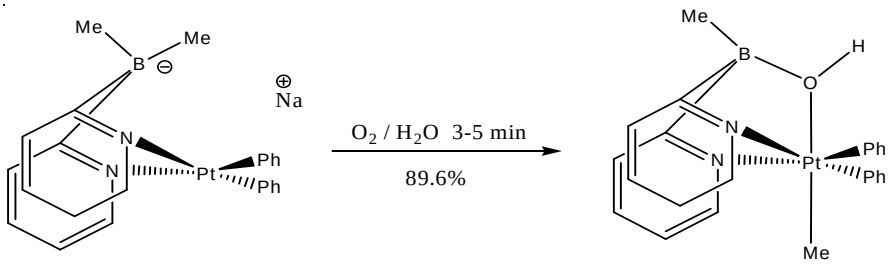
In summary, we discovered a clean intramolecular boron-to-platinum(IV) methyl group transfer which occurs as an electrophilic substitution at the methyl group carbon. The reaction involves a five-coordinate Pt^{IV} transient produced upon oxidation of a Pt^{II} precursor and is driven by coordination of a suitable protic nucleophile at the B and the Pt^{IV} atoms. If we draw a parallel between our Pt(IV)/Pt(II) reaction and the Pt(II)/Pd(0) couple active in the catalytic Suzuki cycle, this mechanism supports the observation that nucleophilic bases accelerate the Suzuki coupling reaction[25] and it leads to a conclusion that oxidation of Pd(0) to Pd(II) is necessary before group transfer from a boronic acid can take place. The reaction involves a nucleophilic substitution at the boron atom and an electrophilic substitution at the boron-bound carbon.

With regard to possible applications to the Shilov Cycle, the system was promising as it showed rapid reaction with dioxygen to give well defined products, however the destruction of the ligand scaffold becomes a significant issue that will have to be addressed with further ligand modifications.

3.4 Experimental

3.4.1 Synthesis and reactivity of (2-pyridyl)borato platinum complexes

Symmetric Diphenyl methyl-hydroxo(2-pyridyl)boratoplatinum(IV), *sym*-(dp-B(OH)(Me))Pt(Me)(Ph)$_2$, 3.1

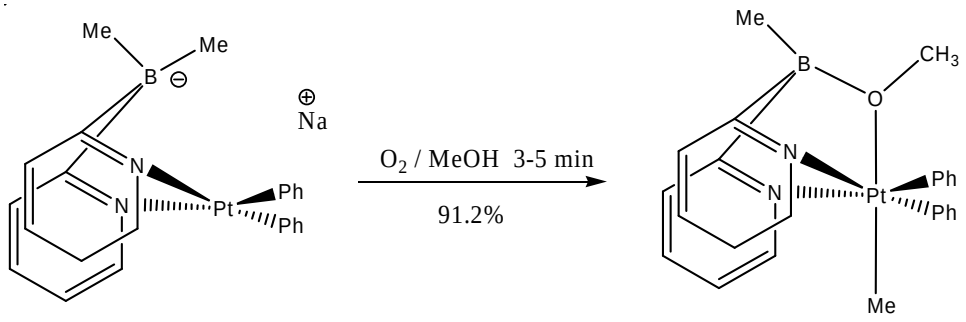


30.0 mg of Diphenyl complex **2.5** were taken out of the glove box in an 11.0 mL. vial. Immediately, 3-4mL of water were added and the vial was gently shaken for three minutes. The complex dissolved to initially give a partially clear solution, out of which after one minute, a white suspension developed. The reaction vial was left to stir for a further five minutes. 2 mL of benzene were added to the vial, the phases shaken, and then the benzene was carefully decanted. 3 mL of ether were then added and saturated NH_4Cl solution was added until the pH was 7 or less. The water layer was then removed and the ether layer was washed two more times with 3 mL of water. The combined water washings were then extracted with another 3 mL portion of ether, the ether layers were combined, dried over anhydrous $MgSO_4$, filtered through a cotton plug and evaporated under high vacuum to give pure **3.1** (26.6mg, 89.6% yield).

^{1}H NMR (22^{o}C, acetone-d$_6$), δ: 8.56 (dt, 2H, J_{H-H}=5.5 Hz, 1.0 Hz, J_{H-Pt}=20.3 Hz), 7.75 (td, 2H, J_{H-H}=7.5 Hz, 1.5 Hz), 7.66 (dq, 2H, J=7.5 Hz, 1.0 Hz), 7.21 (vtd, 2H, J=5.5 Hz, 1.6 Hz), 7.03 (dt, 4H, J_{H-H}=6.8 Hz, 1.5 Hz J_{Pt-H}=43.1 Hz), 6.77-6.89 (m, 6H), 4.72 (s, 1H, J_{Pt-H}=5.0 Hz), 1.88 (s, 3H, J_{Pt-H}= 75.9 Hz), 0.52 (s, 3H).
^{13}C NMR (22^{o}C, acetone-d6), δ: 146.9 (J_{C-Pt}=17.4 Hz), 137.4, 136.2 (J_{C-Pt}=5.1 Hz), 131.5 (J_{C-Pt}= 870.0 Hz), 127.5 (J_{C-Pt}=8.2 Hz), 127.4 (J_{C-Pt}=51.0 Hz), 124.2 (J_{C-Pt}=8.2 Hz), 122.7 (J_{C-Pt}=17.4 Hz), 0.9 (J_{C-Pt}=770.1 Hz). Signals of the pyridine ipso carbon and BMe fragment were not seen due to boron splitting.

Anal. Calcd for $C_{24}H_{25}BN_2OPt$: C, 51.16; H, 4.48; N, 4.97. Found: C, 51.50; H, 4.36; N, 5.02.

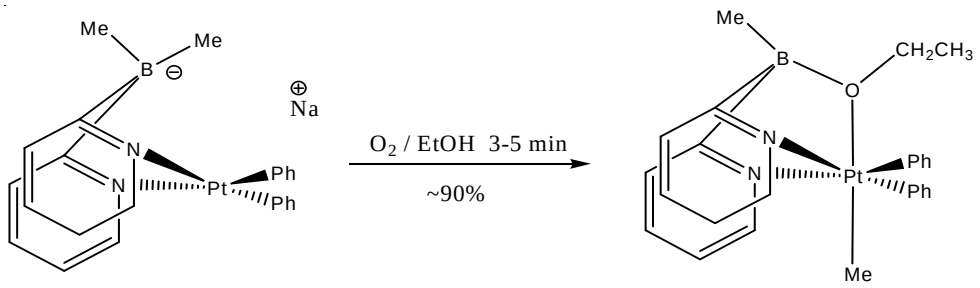
Diphenyl methyl-methoxo(2-pyridyl)boratoplatinum(IV), (dp-B(OMe)(Me))Pt(Me)(Ph)$_2$, 3.2



10.0 mg of Diphenyl complex **2.5** were taken out of the glovebox in an 11.0 mL reaction vial and 3-4 mL of methanol were immediately added. The reaction was left to stir for ten minutes, after which methanol was evaporated under vacuum. Acetone was subsequently added to the reaction vial and the solution was filtered through a cotton plug and concentrated to obtain pure **3.2**, (91.2% isolated yield).

^{1}H NMR (22^{o}C, acetone-d_6), δ: 8.53 (dt, 2H, J_{H-H}=5.5 Hz, 1.0 Hz, J_{H-Pt}=20.3 Hz), 7.77 (td, 2H, J_{H-H}=7.5 Hz, 1.4 Hz), 7.68 (dq, 2H, J=7.5 Hz, 1.0 Hz), 7.23 (vtd, 2H, J=5.4 Hz, 1.4 Hz), 7.03 (dt, 4H, J_{H-H}=7.5 Hz, 1.4 Hz J_{Pt-H}=43.0 Hz), 6.84-6.93 (m, 6H), 3.25 (s, 3H, J_{Pt-H}=10.7 Hz), 1.90 (s, 3H, J_{Pt-H}= 76.7 Hz), 0.55 (s, 3H).
^{13}C NMR (22^{o}C, acetone-d6), δ: 147.1 (J_{C-Pt}=17.2 Hz), 137.6, 136.1 (J_{C-Pt}=4.8 Hz), 132.5, 128.1, 127.7 (J_{C-Pt}=49.0 Hz), 124.5 (J_{C-Pt}=8.3 Hz), 122.7 (J_{C-Pt}=17.4 Hz), 53.9, 0.8 (J_{C-Pt}=760.4 Hz). Signals of the pyridine ipso carbon and BMe fragment were not seen due to boron splitting.
Anal. Calcd for $C_{25}H_{27}BN_2OPt$: C, 52.00; H, 4.72; N, 4.85. Found: C, 51.69; H, 5.06; N, 4.54.

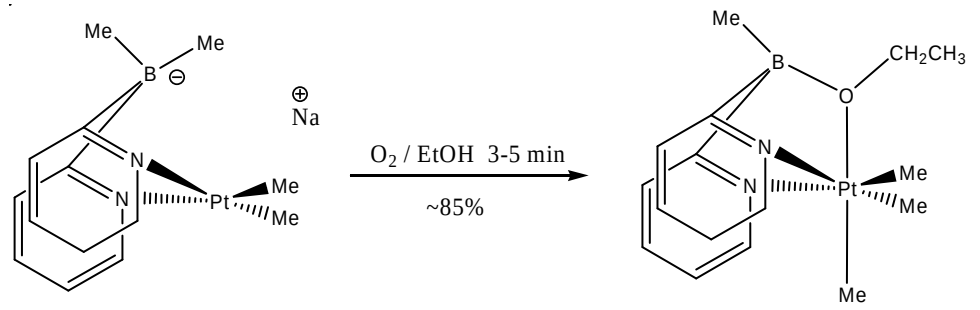
Diphenyl methyl-ethoxo(2-pyridyl)boratoplatinum(IV), (dp-B(OEt)(Me))Pt(Me)(Ph)$_2$, 3.3



The procedure followed was the same as for the complex **3.2** above. Ethanol was used instead of methanol in the synthesis. A ~90% yield was achieved.

^{1}H NMR (22^{o}C, acetone-d$_6$), δ: 8.52 (dt, 2H, J_{H-H}=5.5 Hz, 1.0 Hz, J_{H-Pt}=20.3 Hz), 7.76 (td, 2H, J_{H-H}=7.5 Hz, 1.5 Hz), 7.67 (dq, 2H, J=7.6 Hz, 1.0 Hz), 7.22 (vtd, 2H, J=5.4 Hz, 1.7 Hz), 7.02 (dt, 4H, J_{H-H}=6.8 Hz, 1.5 Hz J_{Pt-H}=43.0 Hz), 6.84-6.94 (m, 6H), 3.73 (q, 2H, J_{H-H}=7.1 Hz, J_{Pt-H}=9.0 Hz), 1.91 (s, 3H, J_{Pt-H}= 76.8 Hz), 0.74 (t, 3H, J_{H-H}=7.1 Hz), 0.60 (s, 3H).
^{13}C NMR (22^{o}C, acetone-d6), δ: 147.1 (J_{C-Pt}=17.0 Hz), 137.6, 136.4 (J_{C-Pt}=5.0 Hz), 133.0, 127.7 (J_{C-Pt}=8.2 Hz), 127.5 (J_{C-Pt}=48.9 Hz), 124.5 (J_{C-Pt}=8.3 Hz), 122.9 (J_{C-Pt}=18.3 Hz), 61.5, 18.5 (J_{C-Pt}=5.0 Hz), 0.7 (J_{C-Pt}=760.8 Hz). Signals of the pyridine ipso carbon and BMe fragment were not seen due to boron splitting.
Anal. Calcd for $C_{26}H_{29}BN_2OPt$: C, 52.80; H, 4.95; N, 4.74. Found: C, 52.32; H, 4.85; N, 4.47.

Trimethyl-ethoxo(2-pyridyl)boratoplatinum(IV), (dp-B(OEt)(Me))Pt(Me)$_3$, 3.4

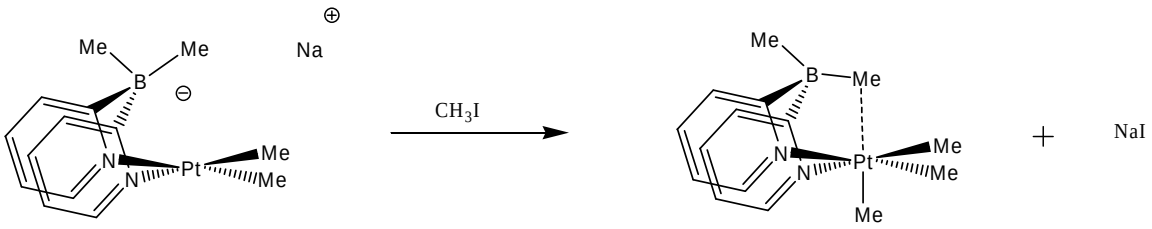


The procedure followed is identical to that for the synthesis of complex **3.3**. 10mg of dimethyl complex **2.3** was used as starting material. The yield is ~ 85%. mp 125-127^{o}C.

^{1}H NMR (22^{o}C, acetone-d6), δ: 8.43 (dt, 2H, J_{H-H}=5.4 Hz, 1.4 Hz, J_{H-Pt}=20.8 Hz), 7.74 (td, 2H, J_{H-H}=7.5 Hz, 1.5 Hz), 7.67 (dq, 2H, J=7.5 Hz, 1.0 Hz), 7.61 (vtd, 2H, J=5.4 Hz, 1.7 Hz), 7.24 (td, 2H, J_{H-H}=7.5 Hz, 1.4 Hz), 3.51 (q, 2H, J_{H-H}=7.1 Hz, J_{Pt-}

$_H$=14.6 Hz), 1.17 (s, 3H, J_{Pt-H}= 76.7 Hz), 0.96 (t, 3H, J_{H-H}=7.1 Hz), 0.83 (s, 6H, J_{Pt-H}= 67.2 Hz), 0.47 (s, 3H).
^{13}C NMR (22^{o}C, acetone-d6), δ: 145.5 (J_{C-Pt}=19.8 Hz), 136.9, 127.8, 122.9 (J_{C-Pt}=18.0 Hz), 60.4, 17.8, -9.1, -10.8. Signals of the pyridine ipso carbon and BMe fragment were not seen due to boron splitting. Some Pt couplings not observed due to high baseline.
Anal. Calcd for $C_{16}H_{25}BN_2OPt$: C, 41.12; H, 5.40; N, 6.00. Found: C, 41.01; H, 5.53; N, 5.63.

Trimethyl(2-pyridyl)boratoplatinum(IV), (dp-B(Me)$_2$)Pt(Me)$_3$, 3.5

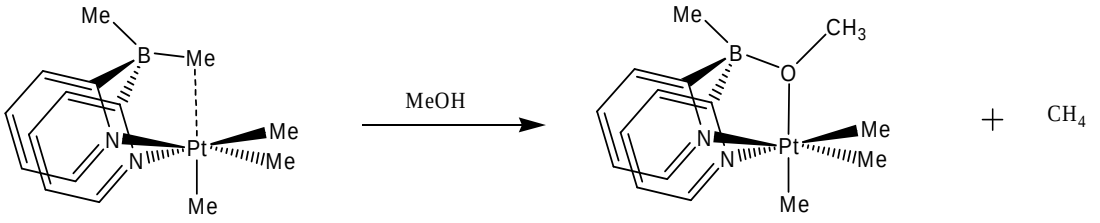


1.06 Equivalents of methyl iodide (12.0 µL) were added to the reaction flask via microsyringe that contained complex **2.3**. An immediate reaction took place, accompanied by the appearance of a fine white suspension. The product is well soluble in ether and after five minutes of stirring, it was filtered through a paper filter that was washed several times with ether to give a light yellow solution. Attempts to filter out the white suspension (assumed to be NaI) through a cotton plug or a glass frit proved to be unsuccessful. The ether solvent was evaporated under vacuum to obtain **3.5** as a flaky white solid (59.5 mg, 74.9%). A very large excess of MeI may be used for the synthesis and it was found not to affect subsequent reactivity and labeling studies when it was not removed by vacuum (NMR tube synthesis). The NMR estimated yield of **3.5** is quantitative according to a diethyl ether internal standard admitted before the reaction, meaning that 25% were lost during the filtration step to obtain an analytical sample. However, subsequently it was found that the NaI byproduct does not affect reactivity and labeling studies discussed below,

so the filtration procedure was omitted in the subsequent attempts and a sample with one equivalent of NaI was used when repeating some labeling experiments. Crystals of **3.5** were grown from such a sample by slowly evaporating ether in an NMR tube. Care must be taken when extracting the crystals as they are very soluble in ether and will be destroyed when they are scraped off the walls and put back into the mother liquor. Although this compound is stable under towards oxygen, it will react with protic solvents, including water vapor. It should be stored under an inert atmosphere.

^{1}H NMR (22^{o}C, THF-d8), δ: 8.30 (d, 2H, J_{H-H}=5.5 Hz, J_{H-Pt}=18.2 Hz), 7.62 (t, 2H, J_{H-H}=7.3 Hz), 7.58 (bd, 2H, J=7.3 Hz), 7.12 (vtd, 2H, J=5.5 Hz, 1.8 Hz), 1.67 (s, 3H, J_{Pt-H}= 84.9 Hz), 1.00 (s, 6H, J_{Pt-H}=64.1 Hz), 0.22 (bs, 3H, J_{B-H}= 4.4 Hz),
-0.91 (s, 3H, J_{Pt-H}=58.1 Hz).
^{13}C NMR (22^{o}C, THF-d8), δ: 189.8 (q, J_{B-C}=49.4 Hz), 145.4 (J_{C-Pt}=19.6 Hz), 136.5, 128.8, 121.9 (J_{C-Pt}=19.9 Hz), 27.1 (q, J_{B-C}=39.6 Hz), 9.0 (q, J_{B-C}=45.0 Hz), 2.3 (J_{C-Pt}=802.4Hz), -9.7 (J_{C-Pt}=632.9 Hz).
Anal. Calcd for $C_{15}H_{23}BN_2Pt$: C, 41.20; H, 5.31; N, 6.41. Found: C, 41.50; H, 5.29; N, 6.24.

Trimethyl-methoxo(2-pyridyl)boratoplatinum(IV), (dp-B(OMe)(Me))Pt(Me)$_3$, 3.6

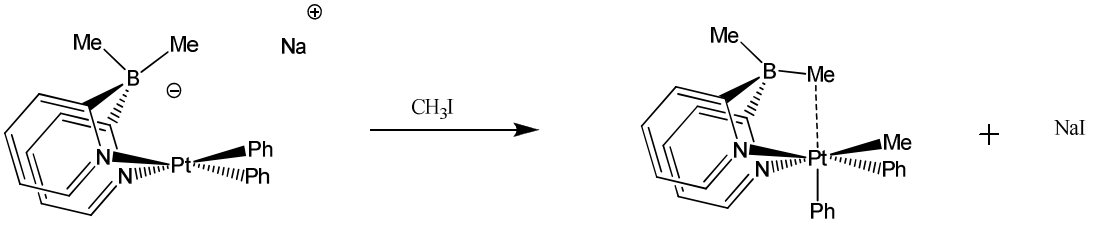


An analytically clean sample of **3.5** obtained by the method above (60.0 mg), was dissolved in 2 ml of methanol under an inert glove box atmosphere in a small reaction vial and the contents were stirred for a period of one week. Subsequently, the solvent was evaporated under vacuum to give 39.2 mg of **3.6** (63.6%) as a white, crystalline solid. In an NMR experiment with CD_3OD, quantitative yield was obtained. The reaction was monitored over time and the internal standard used was a quantity of

diethyl ether admitted into the NMR tube. It is not possible to obtain this complex, with the methoxy scorpionate tail, by the method of dissolving dimethyl compound **2.3** in methanol under air. Compound **3.6** is stable under air.

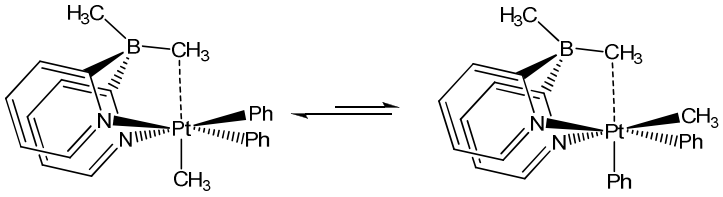
^{1}H NMR (22^{o}C, THF-d8), δ: 8.38 (d, 2H, J_{H-H}=5.5 Hz, J_{H-Pt}=15.8 Hz), 7.63 (t, 2H, J_{H-H}=7.1 Hz), 7.56 (d, 2H, J=7.1 Hz), 7.13 (vtd, 2H, J=5.4 Hz, 1.5 Hz), 3.09 (s, 3H, J_{Pt-H}=12.7 Hz), 1.14 (s, 3H, J_{Pt-H}= 77.3 Hz), 0.77 (s, 6H, J_{Pt-H}=66.7 Hz), 0.43 (s, 3H).
^{13}C NMR (22^{o}C, THF-d8), δ: 145.5 (*J*C-Pt=19.9 Hz), 136.5, 128.0, 122.6 (*J*C-Pt=18.1 Hz), 52.5, -9.1 (J_{C-Pt}=678.5 Hz), -12.0 (J_{C-Pt}=762.3 Hz). Signals of the pyridine ipso carbon and BMe fragment were not seen due to boron splitting.
Anal. Calcd for $C_{15}H_{23}BN_2OPt$: C, 39.74; H, 5.13; N, 6.18. Found: C, 39.61; H, 4.98; N, 5.96.

Diphenylmethyl(2-pyridyl)boratoplatinum(IV), (dp-B(Me)$_2$)Pt(Me)(Ph)$_2$, 3.7



A sample of diphenyl complex **2.5** (43.0mg), synthesized by the procedure described earlier, was dissolved in a few mL of ether in a small reaction vial under an inert glove box atmosphere. A 1.1 excess of methyl iodide (4.8 µL), was added to the reaction vial with stirring. An immediate reaction took place and a white suspension developed after one second. After five minutes of stirring, the solvent was filtered through a paper filter (see synthesis of **3.5**) that was washed several times with ether. The clear light yellow solution was evaporated under vacuum to give a crystalline white powder (30.9 mg, 73.0% yield). The NMR estimated yield is quantitative based on an anisole internal standard. As with the trimethyl analogue, a considerable amount of the complex is lost to the cellulose filter in order to obtain an analytically pure sample. The presence of possible OH groups in the cellulose filter is detrimental

to the sample. Since the presence of NaI was found to have no effect on reactions reported here, subsequent repetitions of the procedure utilized a non-filtered sample for low-temperature NMR and reactivity studies. Also, as with the trimethyl analogue, a large methyl iodide excess can be used without affecting subsequent reactivity. The complex exists as a mixture of two interconverting symmetric and unsymmetric (sym and unsym) isomers in solution; the NMR spectrum in the aromatic region is thus mostly second order.

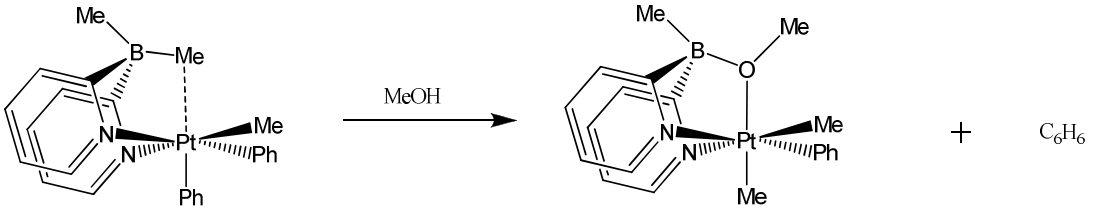


The equilibrium depends upon solvent, but the major isomer is the symmetrical one in all cases (3:1 ration in acetone), meaning that only two aromatic peaks of the unsymmetrical isomer can be assigned. The aliphatic region can be assigned for both isomers. The interconversion of the isomers was determined by first dissolving a sample of **3.7** in THF-d_8, in which a ratio of 3:1.3 sym to unsym was obtained. This same sample showed, after being dried under high vaccum, redissolved in C_6D_6, a ratio of 3:1.8 sym to unsym was observed. After drying the same sample under high vaccum and redissolving in THF-d_8, a ratio of 3:1.4 was seen after ~10 minutes. Eventually, the ratios equilibrated to the original 3:1.3 sym to unsym. This same experiment can be performed in acetone (ratio ~3:1) and benzene. Since both isomers are clearly seen at room temperature, this exchange is not fast on the NMR timescale. The compound is stable under air, but reacts rapidly with protic solvents and should

be stored under an inert atmosphere. The sensitivity of the diphenylmethyl complex to water vapor is greater than that of the trimethyl analogue.

Symmetrical isomer:
^{1}H NMR (22^{o}C, acetone-d6), δ: 8.25 (d, 2H, J_{H-H}=5.5 Hz, J_{H-Pt}=19.0 Hz), 7.73 (td, 2H, J_{H-H}=7.0 Hz, J_{H-H}=1.6 Hz), 7.68 (d, 1H, J_{H-H}=7.0 Hz), 7.12-7.17 (m, 4H), 6.91-7.00 (m, 3H), 2.58 (s, 3H, J_{Pt-H}=83.5 Hz), 0.29 (bs, 3H), -0.45 (bs, 3H, J_{Pt-H}=56.8 Hz)
Unsymmetrical isomer:
^{1}H NMR (22^{o}C, acetone-d6), δ: 8.36 (d, 1H, J_{H-H}=6.2 Hz, J_{H-Pt}=15.8 Hz), 6.53 (d, 1H, J_{H-H}=6.2 Hz, J_{H-Pt}=66.9 Hz), 1.60 (s, 3H, J_{Pt-H}=65.1 Hz), 0.31 (bs, 3H), 0.18 (bs, 3H, JP_{t-H}=60.5 Hz). Other aromatic peaks are obscured by the symmetrical isomer.
Carbon NMR peaks seen for both isomers:
^{13}C NMR (22^{o}C, THF-d8), δ: 190.1 (m, B-C (pyridine), 148.7, 148.2, 147.6, 137,7, 137.2, 136.8, 135.8, 132.2, 129.2, 129.0, 128.9, 128.2 (J_{C-Pt}=45.4 Hz), 126.2, 125.2, 124.9, 122.1, 121.8, 37.2 (m, B-CH_3, both isomers), 15.9 (J_{C-Pt}=800.7 Hz), 9.0 (m, B-CH3, both isomers), 0.5 (J_{C-Pt}=626.9 Hz).
Some Pt signals not cleanly observed due to overlaps with the major isomer; including Pt satellites.
Anal. Calcd for $C_{25}H_{27}BN_2Pt$: C, 53.48; H, 4.86; N, 4.99. Found: C, 53.78; H, 4.50; N, 5.07.

Unsymmetric-Dimethylphenyl(2-pyridyl)boratoplatinum(IV), unsym-(dp-B(OMe)(Me))Pt(Ph)(Me)$_2$, 3.8



Complex **3.7**, obtained by the method above (29.3 mg), was dissolved in methanol and allowed to stand for ten minutes. The solvent was evaporated under vacuum to give **3.8** as a crystalline, white solid in quantitative yield (27.0 mg). Formation of benzene was confirmed by NMR when carrying out the reaction in CD_3OH. Adding a known amount of benzene (3 equivalents), confirmed that ~1 equivalent of benzene had been produced. Crystals of **3.8** can be grown by slow evaporation of the methanol solvent. The compound is stable under air.

^{1}H NMR (22^{o}C, acetone-d6), δ: 8.49 (d, 1H, J_{H-H}=5.5 Hz, J_{H-Pt}=42.6 Hz), 8.12 (d, 1H, J_{H-H}=5.5 Hz, J_{H-Pt}=43.6 Hz), 7.80 (td, 1H, J_{H-H}=7.3 Hz, 1.5 Hz), 7.77 (td, 1H, J_{H-H}=7.3 Hz, 1.5 Hz), 7.70 (d of multiplets), 1H, J=7.8 Hz), 7.65 (d of multiplets), 1H, J=7.8 Hz), 7.32 (vtd, 1H, J=5.5 Hz, 1.5 Hz), 7.12 (vtd, 1H, J=5.5 Hz, 1.5 Hz), 6.93-7.06 (m, 2H), 6.87-6.92 (m, 3H), 3.10 (s, 3H, J_{Pt-H}=12.1 Hz), 1.51 (s, 3H, J_{Pt-H}= 77.2 Hz), 0.99 (s, 3H, J_{Pt-H}= 67.4 Hz), 0.52 (s, 3H).
^{13}C NMR (22^{o}C, acetone-d6), δ: 147.0, 146.5, 137.4, 137.3, 135.2, 131.5, 128.6, 127.7, 127.6 (J_{C-Pt}=47.8 Hz), 124.3, 123.5, 123.1, 52.9, -4.5, -6.2. Signals of the pyridine ipso carbon and BMe fragment were not seen due to boron splitting. Some Pt couplings not observed due to high baseline.
Anal. Calcd for $C_{20}H_{25}BN_2OPt$: C, 46.61; H, 4.90; N, 5.44. Found: C, 46.88; H, 5.17; N, 6.10. Although the complex was obtained cleanly and in high yield, and some of it was recrystallized for Xray and elemental analyses, an unsatisfactory deviation from the calculated value was obtained for nitrogen.

3.4.2 ^{13}C Isotopic Experiments

General Consideration: The presence of a small amount of ^{13}C in natural carbon samples and a small ^{12}C impurity in the sample of $^{13}CH_3I$, meant that small ^{12}C peaks and ^{13}C satellites can be observed even when it is said they are absent in the labeling study. This natural concentration of impurities is insignificant, does not affect the outcome of the experiments, and is not taken into account in the description below. All spectra referred to in this section are ^{1}H NMR spectra and the ^{13}C label was observed by proton coupling to it.

Complex **2.3**
Dimethyl complex **2.3** (10mg), was added to an NMR Young tube charged with THF-d_8 and an excess amount of $^{13}CH_3I$ (5 µL) were added. Upon taking an NMR spectrum 5 minutes later, it was found that **3.5-^{13}C** obtained by this method contained 1/3 ^{13}C labeled Me groups in the equatorial and the axial position trans to the borate moiety. Both of these NMR signals contained ^{13}C satellites that each had their own

Pt satellites with the exact same coupling as the parent ^{12}C peak. Each ^{13}C peak with its associated Pt satellites integrates as $1/6^{th}$ of the total signal intensity. Thus, by the time an NMR spectrum was taken, a statistical incorporation of the label into all three exclusively Pt bound methyl groups was obtained. Incorporation of the ^{13}C label into the B-CH_3-Pt group, as well as the exclusively boron bound Me, was not observed even after one day. Exchange with free, excess $^{13}CH_3I$ also did not occur since the $^{12}CH_3I$ peak did not increase in relation to the two $^{13}CH_3I$ satellites. A spectrum of ^{13}C labeled complex **3.5-^{13}C** is provided below.

After the above experiment was concluded, the solution in the NMR tube was collected in a small vial inside the glove box, and evaporated to dryness under high vacuum for ~3 hours. The resulting sample was dissolved in CD_3OD and put into a Young tube. The labeled complex **3.8-^{13}C** formed over the period of three days as with the unlabelled analogue and the reaction could be followed by NMR. The product contains the label only in the two equatorial Me positions. The ^{13}C label constitutes $1/3^{rd}$ of the total carbons in the two equatorial positions. The axial Me trans to the borate contains no ^{13}C label. There is no incorporation of the label into the boron bound Me group as well during the reaction. The methane formed from this reaction has two well defined ^{13}C satellites that represent ~1/3 of the total methane formed, and appears to be exclusively CD_3H with perhaps some CH_4 being present. This is difficult to distinguish due to the noise and overlapping impurities conflicting with the methane signal due its low concentration in the liquid phase. A spectrum of complex **3.8-^{13}C** formed from the labeling experiment is provided below.

Complex **2.5**

Diphenyl complex **2.5** (10 mg), was added to an NMR Young tube containing THF-d_8 and an excess amount of $^{13}CH_3I$ (5 µL) were added. The spectrum of **3.7-^{13}C**, taken five minutes after the addition of methyl iodide, contained both the symmetrical and unsymmetrical isomers as before. However, the methyl group bound exclusively to Pt in both isomers contained all of the ^{13}C label. The Me contained two ^{13}C satellites with their own Pt satellite peaks; the entire signal integrates as three protons. There was no incorporation of the ^{13}C label into the borate bound CH_3 groups even after one day. Concurrently, no exchange with free $^{13}CH_3I$ was observed. A spectrum of ^{13}C labeled complex **3.7-^{13}C** is provided below.

After the above experiment was ended, the solution in the NMR tube was emptied into a small vial inside the glove box and concentrated under high vacuum for ~3 hours. The resulting sample was dissolved in CD_3OD and put into a Young tube. Analogous to the unlabelled reaction, the labeled complex **3.8-^{13}C** formed completely by the time an NMR was obtained (5 minutes). Only one of the methyl groups of the product – the equatorial methyl – contained the ^{13}C label and no ^{12}C. The methyl group axial and trans to the borate, was entirely made up of ^{12}C carbon and no ^{13}C. A spectrum of ^{13}C labeled complex **3.8-^{13}C** is provided below.

3.5 References

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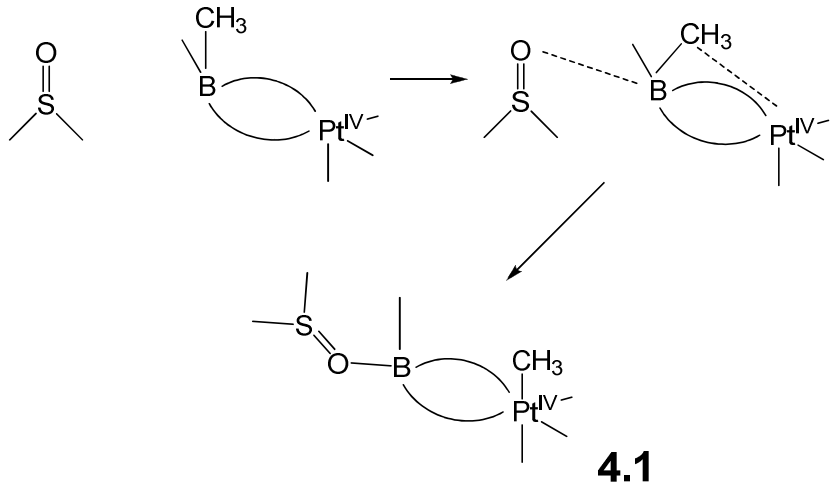
Chapter 4: Bidirectional Transfer of Phenyl and Methyl Groups between Pt^{IV} and Boron in Platinum Dipyridylborato Complexes

4.1 Introduction

This Chapter builds upon the methyl group transfer work reported in Chapter 3. Based on our proposed mechanism in Chapter 3, (Schemes 3.9-3.10), we thought to probe the formation of the proposed six coordinate tetrahydrocarbyl Pt^{IV} complexes that result in Me group transfer from B to Pt^{IV}. We reasoned that if the nucleophile was strong enough, it could bind to the B atom very strongly. If this nucleophile was also not a source of H^+ as the hydroxylic MeOH solvent utilized in previously described research (Chapter 3), then the tetrahydrocarbyl intermediate **4.1** may be isolated (Scheme 4.1 DMSO depicted as the nucleophile).

Scheme 4.1 Strategy for isolating the tetrahydrocarbyl intermediate

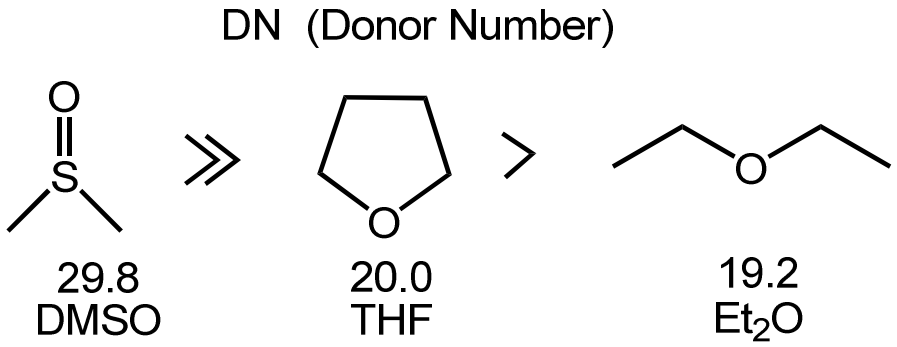


4.1

tetrahydrocarbyl intermediate

The nucleophile depicted in Scheme 4.1 is dimethylsulfoxide (DMSO) and it would be an excellent choice because of its relatively strong donicity[1] and non-acidic character. THF and Et_2O are both poorer donors than DMSO (Figure 4.1), but could be active in the reaction as well and the stability of the intermediate may reflect the nature of the nucleophile. Acetone, has a lower donicity than even diethyl ether, but it was deemed unsuitable due to the possibility of forming the acidic enol that would protonate the very basic **4.1**.

Figure 4.1 Donor Number of various non-acidic nucleophiles

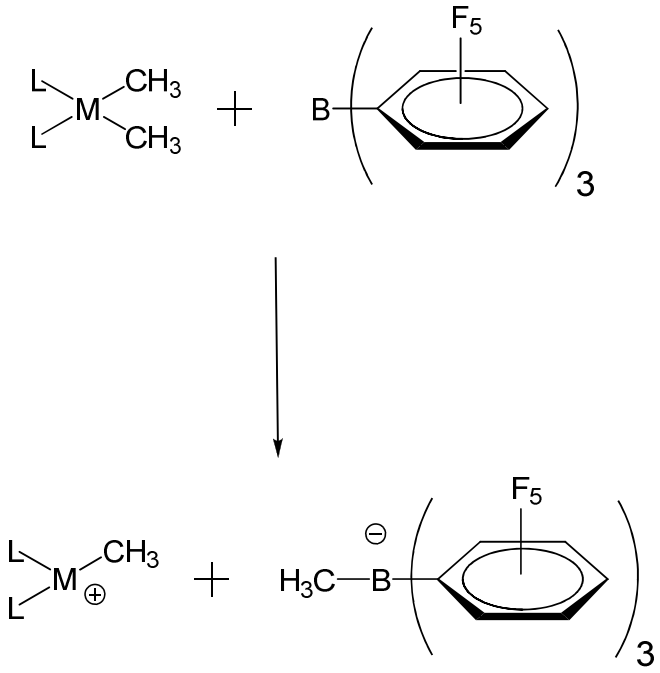


According to our proposed mechanism in Scheme 3.9, the methyl transfer from boron to platinum is energetically uphill as determined by DFT. However, the reaction energy can be diminished and even become negative if the possible stabilizational effect of the nucleophile is involved. A hydrocarbyl transfer between Pt^{IV} and B may be completely reversible unless some irreversible steps are involved in a reaction: such as protonolysis of a Pt^{IV}-C bond.

While we were unable to trap complex **4.1**, we did observe that under certain conditions, with strong and non-hydroxylic nucleophiles, reversible methyl transfer between Pt^{IV} and B could occur. This was a new reaction that has never before, to our

knowledge, been documented. Boron to metal hydrocarbyl transfer (transmetallation) is very common. It occurs in a number of important catalytic processes such as Suzuki Coupling (Scheme 3.3)[2]. The reverse reaction, metal to boron hydrocarbyl group transfer is also common. Electron poor aryl boranes have been used as Me group abstractors from metals in order to create a vacant coordination site or to activate a catalyst (Scheme 4.2).[9,10] The novelty of our observations lie in being able to observe *reversible* transfer between Pt^{IV} and B. These observations imply, in particular, that under certain conditions there might be an additional pathway leading to products of homocoupling of organoboron compounds[11] occurring along with the desired cross-coupling between a boron reagent and an aryl halide.

Scheme 4.2 Me group abstraction with an electron poor triarylborane

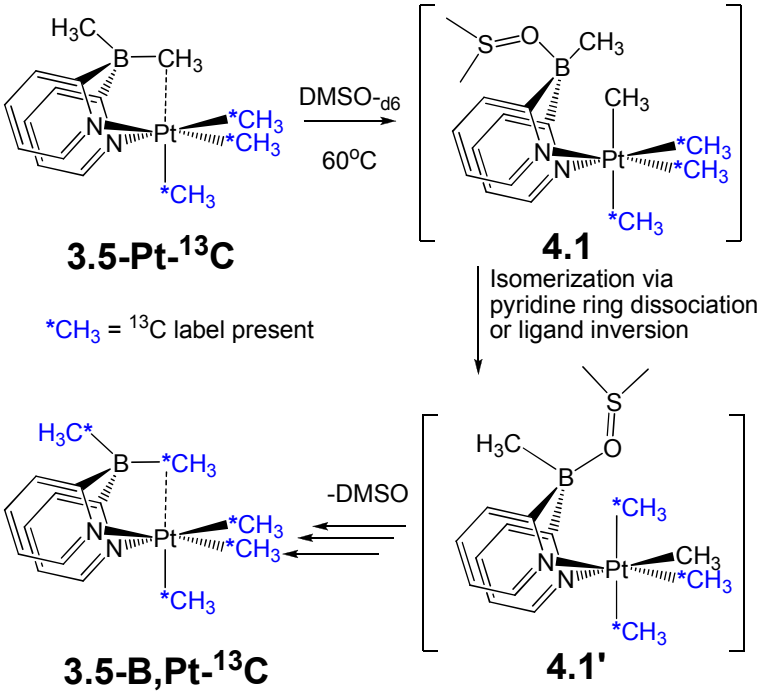


4.2 Results and Discussion

To probe reversibility of methyl transfer in **3.5** the Pt-^{13}C-labeled complex $(Me_2Bpy_2)Pt^{IV}(^*Me)_3$, **3.5-^{13}C**, prepared from **2.4** and one equivalent of *MeI (*Me = $^{13}CH_3$) was utilized (Scheme 3.6). Five minutes after mixing the reagents, a statistical distribution of the label among the three Pt-bound methyl ligands was reached resulting in their effective 33% ^{13}C-enrichment (see Chapter 3). We have shown that the labeled complex **3.5-Pt-^{13}C** is stable in benzene-d_6 or THF-d_8 in the temperature range of 20^o-60^{o}C for at least two weeks and shows no sign of ^{13}C-label incorporation in the BMe_2 moiety (Chapter 3).

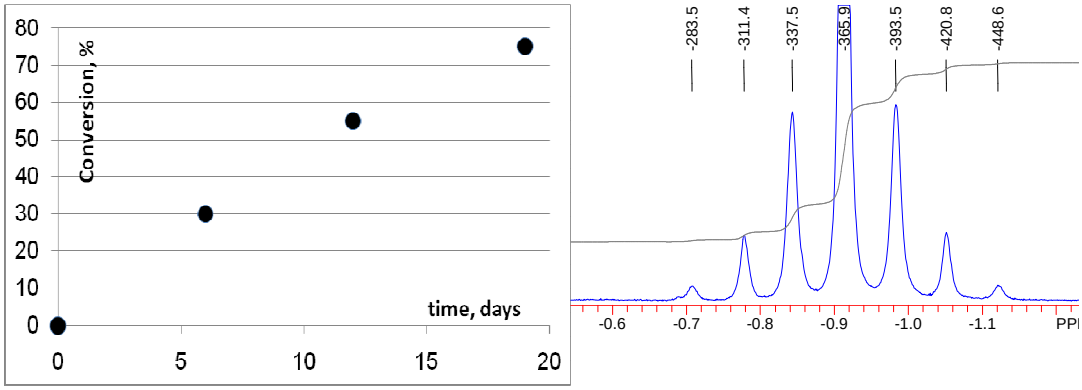
This situation changed when we used DMSO-d_6, a stronger non-hydroxylic Lewis base compared to THF, as the solvent. Slow formation of **3.5-B,Pt-^{13}C** isotopologues with ^{13}C-label incorporated in both methyl groups of the BMe_2 fragment could be observed at 60^{o}C (Scheme 4.3; note that DMSO coordinates boranes typically though the oxygen atom[13]). The ^{13}C-enrichment of the BMe_2 group was 75% of the expected purely statistical value of 20% after 19 days (Figure 4.2).

Scheme 4.3 Conversion of **3.5-Pt-^{13}C** to **3.5-B,Pt-^{13}C** via **4.1**



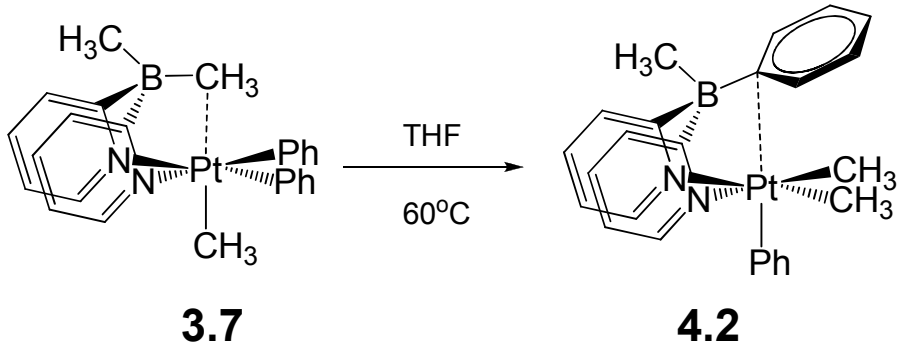
To account for these observations we suggest the following mechanism (Scheme 4.3). The first step involves B-to-Pt^{IV} migration leading to a tetrahydrocarbyl Pt^{IV} species **4.1** that is facilitated by concurrent nucleophilic attack of solvent at the B atom. Dissociation of one of the pyridine nitrogens from Pt^{IV}Me(R)$_2$R' in **4.1** with subsequent scrambling of hydrocarbyl groups in the resulting five coordinate metal intermediate leading to transient **4.1'**, re-coordination of the pyridyl group and *Me group transfer from Pt^{IV} to B leads to a species with a ^{13}C-labeled BMe$_2$ group, **3.5-B,Pt-^{13}C**. An alternative pathway from **4.1** to **4.1'** might include platinum chelate ring inversion, but ring strain build-up may render this pathway impractical (see Experimental and Chapter 3).

Figure 4.2 Transformation of **2-Pt-^{13}C** to **2-B,Pt-^{13}C** in DMSO-d_6 solution at 60°C: left) plot of conversion vs. time; right) high-field region of ^{1}H NMR spectrum of **2-B,Pt-^{13}C** with ^{195}Pt and ^{13}C satellites after 19 days.



Similar experiments were performed with the diphenyl analogue of **3.5**, dpbPt^{IV}Ph$_2$Me, **3.7**. No reaction was seen in benzene solutions of **3.7** at 60°C after 3 days. By contrast, isomerization of **3.7** to C_s-symmetricl methylphenylborato complex [MeBPh(py)$_2$]Pt^{IV}PhMe$_2$ **4.2,** involving Pt^{IV}-to-B phenyl migration, was complete at 60°C after 24h in THF solution (Scheme 4.4). As in the case of trimethyl Pt^{IV} complex **3.5**, the use of more Lewis basic solvent DMSO allowed for faster, but less clean, transformation. In DMSO solution, isomerization of **3.7** to **4.2** was possible already at 22°C, however **4.2** was just one of a complex mixture of products whereas the transformation in THF gave only one major product that could be easily isolated.

Scheme 4.4 Transformation of **3.7** to **4.2**; Ph group transfer from Pt to B



3.7 **4.2**

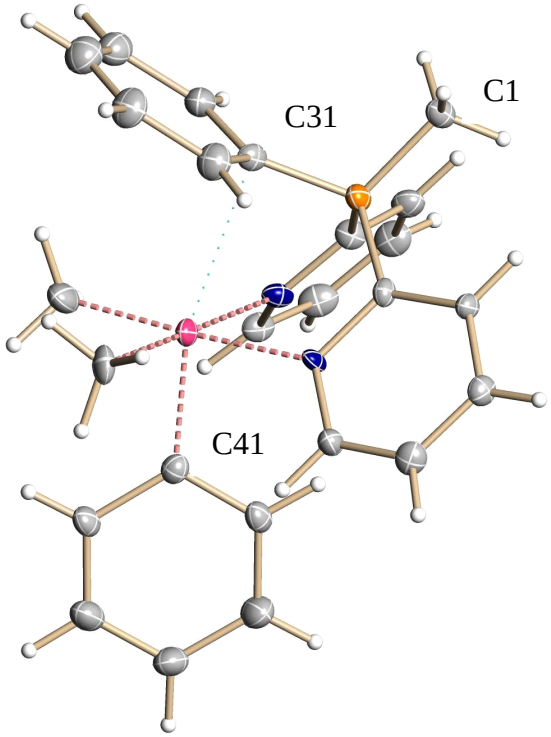
These observations suggest that **4.2** has a higher thermodynamic stability compared to **3.7**. According to our DFT estimates, the standard Gibbs energy of isomerization of **3.7** to **4.2** is -3.1 kcal/mol. The effect of the boron-bound Ph group on the position of the hydrocarbyl transfer equilibrium may be due to a better ability of the B-Ph fragment to donate to the Pt^{IV} center compared to the B-Me group in **3.7** and it could have to do with the better ability of the π system of the phenyl ring to stabilize the Pt^{IV} center compared to an agostic CH bond of CH_3.

Complex **4.2** could be isolated from the solution in THF in pure form in 89% yield and was fully characterized by NMR, elemental analysis, and single crystal X-ray diffraction analysis (Figure 4.3). The compound features a phenyl group attached to B with the B1-C31 distance of 1.654(4) Å. The B-bound phenyl *ipso*-carbon atom is involved in a weak interaction with the Pt^{IV} with Pt1-C31 separation of 2.646(3) Å. The other carbon atoms of the boron bound phenyl ring are more than 3 Å removed from the metal center.

Interestingly, compared to the relatively slow methyl group exchange between B and Pt^{IV} in **3.5**, a similar methyl for phenyl group exchange in **3.7** is more facile under the same conditions. While one product is favored by ~4kcal/mol

thermodynamically, the kinetic barrier towards forming the intermediate **4.1** is not affected by these considerations. This faster kinetic behavior might stem from the weaker *trans*-influence of phenyl vs. methyl, affecting the relative kinetic accessibility of intermediate **4.1**. Isomerization to **unsym 3.7**, with the phenyl group in the axial position, would lower the energy needed for Me transfer from B to Pt as seen in Scheme 3.9. Additionally, if one assumes that the isomerization such as of **4.1** and **4.1'**s is the rate limiting step that involves the pyridyl dissociation mechanism, the presence of a bulky Ph group in the equatorial plane of **3.7** would diminish the energy required for dissociation of an adjacent pyridyl.

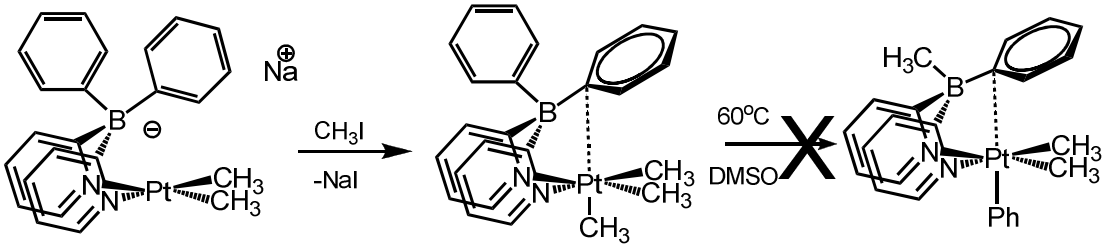
Figure 4.3 Crystal structure of **4.2** and selected bond distances



Pt-C41(Ph) 2.014(3) Pt-C31(Ph-B) 2.646(3) B-C1(Me) 1.634(4)
B-C31(Ph) 1.654(4)

To probe the reverse option of B-to-Pt^{IV} Ph group transfer we attempted transformation of diphenyldipyridylborato (L') complex L'$Pt^{IV}Me_3$, **4.4** to its isomer **4.2**. We synthesized the diphenyldipyridylborate ligand (dphdpb) and the associated [dphdpb$Pt^{II}(Me)_2$][Na] **4.3** which could be converted to the corresponding trimethyl Pt^{IV} complex by the addition of MeI (Scheme 4.5).

Scheme 4.5 Synthesis of **4.4** and attempted isomerization to **4.2**

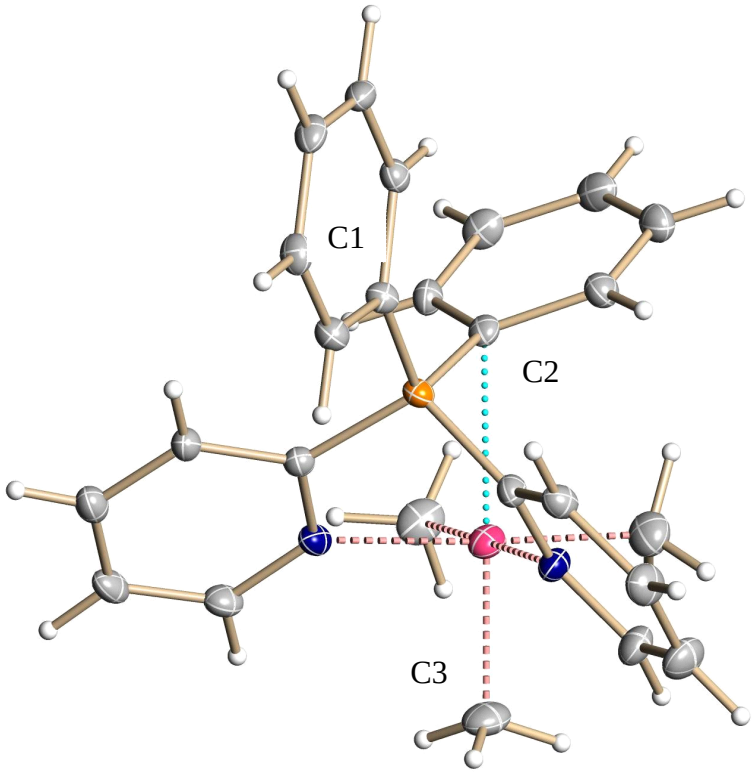


4.3 **4.4** **4.2**

Complex **4.4** was characterized by ^1H and ^{13}C NMR spectroscopy and by X-ray diffraction (Figure 4.4). Similar to **4.2**, one of the boron-bound phenyl groups in **4.4** is involved in stabilization of Pt^{IV} center with B1-C31 distance of 1.643(7) Å and Pt1-C31 distance of 2.624(4) Å. According to our DFT calculations, the thermodynamic stability of **4.2** and **4.4** is not very different; the Gibbs energy of isomerization of **4.4** to **4.2** is -0.4 kcal/mol. In spite of that, no changes were seen in ^1H NMR spectra of **4.4** in both THF-d_8 and DMSO-d_6 after 5 days at 60°C. We presume that the stability of this diphenylborato Pt^{IV} species **4.4** might be of kinetic origin and solvent nucleophilicity is not sufficient to decrease the reaction barrier. An argument based on trans effects of the Me vs. Ph can also be made here since the stronger *trans* effect of the methyl ligand may prevent it from forming a **4.1**-like tetrahydrocarbyl

intermediate when it has to compete with the trans effect of the methyl group. This situation is reversed when **4.2** is synthesized from **3.7**.

Figure 4.4 Crystal structure of **4.4** and selected bond distances



Pt-C3(ax)	2.078(5)	Pt-C2 (ph)	2.660(4)
B-C1 (ph)	1.626(7)	B-C2 (ph-Pt)	1.649(7)

It is still possible to transfer the phenyl group from B to Pt^{IV} under certain conditions. The viability of this transfer in Pt – dipyridylborate systems was demonstrated in a reaction of [dphdpb$Pt^{II}(Me)_2$][Na], **4.3** with O_2 in *i*-PrOH solution leading to isopropoxo-bridged $Pt^{IV}Me_2Ph$ complex **4.5** (Scheme 4.6). In this case, the ligand trans to phenyl is coordinated O_2H, which has a much weaker trans effect than Me and allows for the formation of **4.1**-like intermediate, in this case a

trihydrocarbyl/hydroperoxo (or hydroxo) complex that goes on to give product **4.5** by the mechanism laid out in Scheme 3.10. Strongly nucleophilic *i*-PrO$^-$ present in reaction mixture also plays a role by potentially nucleophilically attacking boron via an S_N2 pathway and diminishing the activation barrier for the B-to-Pt^{IV} phenyl group transfer.

Scheme 4.6 Formation of complex **4.5** and Ph group transfer from B to Pt^{IV}

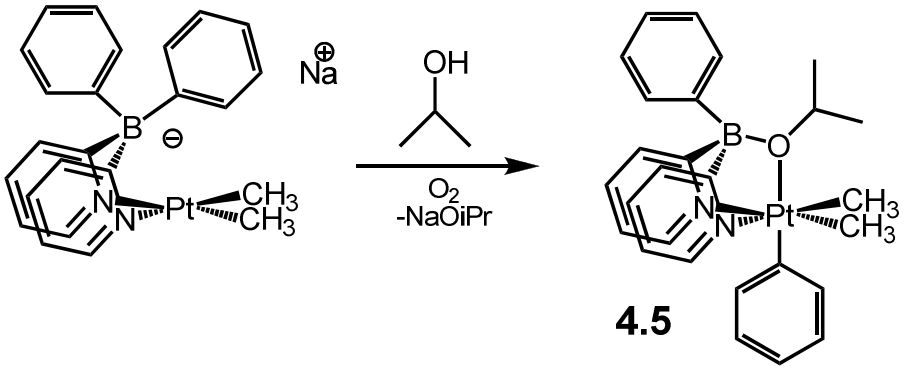
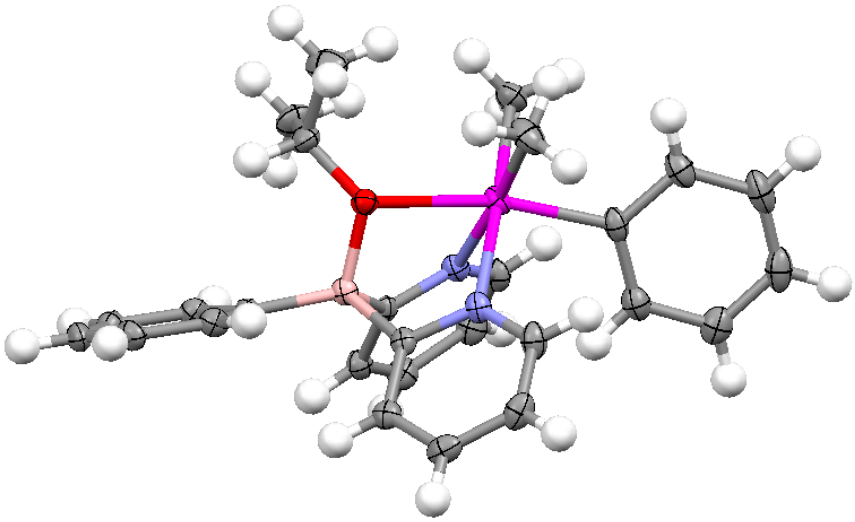


Figure 4.5 Mercury drawing (ellipsoids at 50% probability level) of **4.5**



4.3 Conclusion

In summary, we showed that phenyl group migration between Pt^{IV} and B centers can occur in both directions and is accelerated by Lewis bases. To our knowledge, this is a previously undescribed transformation in Organometallic chemistry. In the case of phenyl for methyl group exchange, the prevailing product is determined by a stronger donor group bridging Lewis acidic B and Pt^{IV} centers. In the case the attempted isomerization of **4.4** to **4.2**, the activation barrier is kinetically inaccessible at 60^{o}C. According to DFT, this transformation is thermodynamically allowed.

In the case of dimethylborato trimethyl Pt^{IV} complex **3.5** and the use of aprotic weakly nucleophilic DMSO, degenerate methyl migration between Pt^{IV} and B centers is reversible. These results may explain why many Suzuki coupling processes suffer from undesirable homocoupling sideproducts that may result after transfer of an aryl from an electrophilic aryl-halide starting material, to a unit of $B(OH)_2(OR)$ (where R=H, Me, Et) that is formed during the reaction. Subsequent coupling of this boronic acid with another equivalent of aryl-halide would form the homocoupling product. This must now be considered as one of the possible pathways that results in these undesirable byproducts. Moreover, our results show that this pathway could be utilized for the selective synthesis of novel organoboron compounds. We are currently working on a way to exploit our system for this purpose.

4.4 Experimental

4.4.1 Preparation of Complexes

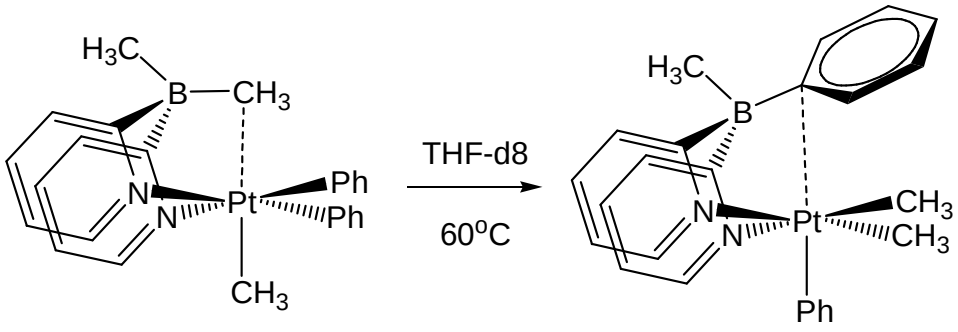
Preparation of dimethyl-di(2-pyridyl)borato trimethylplatinum(IV)-^{13}C, (dp-BMe$_2$)Pt^{IV}Me$_2$*Me, 3.5-Pt-^{13}C

The complex was prepared as described before (Chapter 3) for non-labeled complex **3.5**[2] from complex **2.3** and $^{13}CH_3I$ in THF solution.

^{1}H and ^{13}C NMR spectra for unlabeled complex **3.5** were reported previously (Chapter 3).

^{1}H NMR (22^{o}C, DMSO-d_6), δ: 1.68 (axial Pt$^{IV}CH_3$, $J_{C\text{-}H}$= 139.2Hz), 0.96 (equatorial Pt$^{IV}CH_3$, $J_{C\text{-}H}$= 131.2Hz).

Symmetrical (methyl)phenyl-di(2-pyridyl)borato phenyldimethylplatinum(IV), (dp-BMe(μ-Ph))Pt^{IV}Me$_2$Ph, 4.2



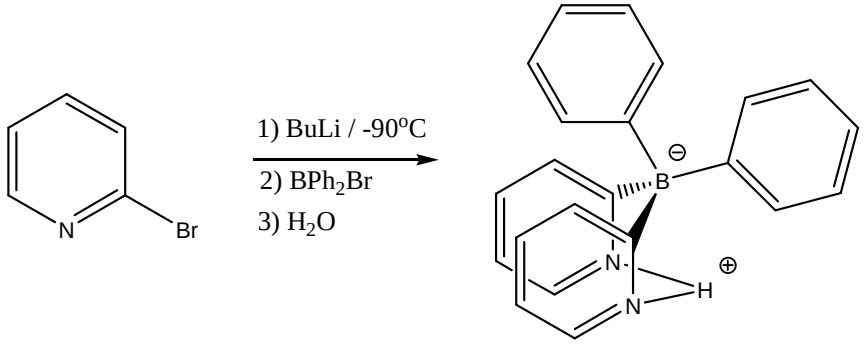
Compound **3.7** was prepared as described in Chapter 3. 40.0 mg of **3.7** were put into a Young tube and dissolved in 0.6 mL of THF-d_8. The Young tube was heated for 3 days at 65 ^{o}C and an NMR was periodically taken to check the reaction progress. Most of the reaction was complete after two days, but three days are required for complete disappearance of starting material. Solution of compound **4.2** was filtered

through Celite. The Young tube and filter were washed two times with 1 mL of THF, which was then evaporated under high vacuum. The resulting slightly yellow solid was further dried under high vacuum for 8 hours to get pure **4.2** (35.5mg, 88.8%). Crystals of **4.2** can be grown by slow evaporation of THF solvent.

^{1}H NMR (22^{o}C, THF-d_8), δ: 7.76-7.81 (m, 4H), 7.72 (dt, 2H, *J*H-H=7.5Hz, 1.5Hz), 7.28 (t, 1H, *J*H-H=7.4Hz), 7.05 (t, 2H, *J*H-H=7.5Hz), 7.02 (vt, 2H, *J*H-H=5.8Hz), 6.91 (t, 1H, *J*H-H=7.2Hz), 6.72-6.81 (m, 4H), 6.27 (bd, 2H, *J*H-H=7.5Hz, *J*H-Pt=66.8Hz), 0.62 (s, 6H, *J*H-Pt=64.8Hz), 0.34 (bs, 3H).
^{13}C NMR (22^{o}C, THF-$d_{8)}$, δ: 188.1 (q, *J*B-C=40.9 Hz), 154.1 (q, *J*B-C=53.0 Hz), 148.9 (*J*C-Pt=16.2Hz), 138.4, 136.7, 136.4, 135.2 (*J*C-Pt=13.4Hz), 129.9, 129.4, 129.2, 128.3 (*J*C-Pt=73.4Hz), 125.4 (*J*C-Pt=12.8Hz), 122.2 (*J*C-Pt=20.0Hz), 10.4 (q, *J*B-C=49.2 Hz), 0.0 (*J*C-Pt=650.4Hz).

Preparation of diphenyl-di(2-pyridyl)borato trimethylplatinum(IV), (dp-BPh_2)$Pt^{IV}Me_3$,

dphdpbH Hydrogen diphenyl-di(2-pyridyl)borate



Diphenylboron bromide was synthesized by the method of Haubold et al.[9] and was used without further purification. Following the original procedure, two equivalents of trimethylphenylsilane and one equivalent of tribromoboron were mixed in a Schlenk flask and sealed. With very large 50 ml total volume the flask needs to be kept cool during initial mixing of reagents before it is sealed. After sealing the flask, it was heated at 180 ^{o}C anywhere from 18 to 40 hours with extra reaction times having no apparent effect on reaction outcome. After reaction, the flask was cooled

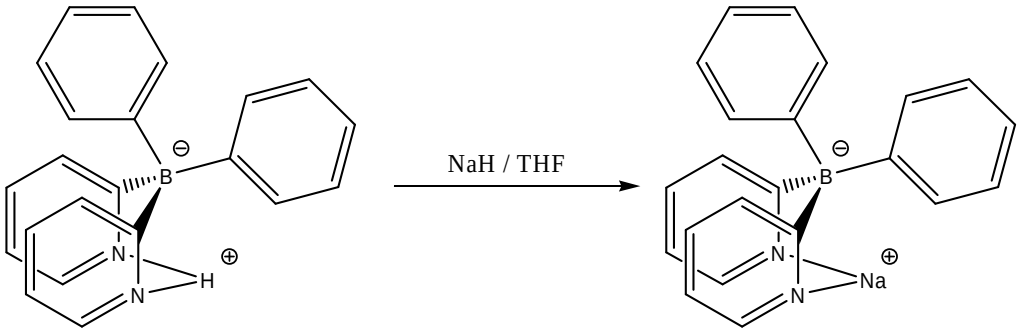
and attached to a high vacuum line. All the byproducts and potential unreacted material are conveniently distilled out at 0.3 Torr at room temperature after 1 hour. It is advised to use a series of two liquid nitrogen traps to protect the vacuum pump.

Following a slightly modified procedure of Hodgkins and Powell,[12] 2-bromopyridine (13.5 g. 85.4 mmol) was loaded into a dry reaction flask under argon and 150 mL. of anhydrous THF were added. The solution was cooled to -90 ^{o}C and 2.5 M *n*-BuLi (34.2 mL. 85.4mmol) was added over a one minute period. The color changed immediately to deep red, but the reaction was allowed to stir for another half an hour during which the temperature was not allowed to rise above -78 ^{o}C. After half an hour, diphenylboron bromide (42.7 mmol based on BBr_3) was added via cannula from the Schlenk flask, in which it was made, in entirety. The reaction was stirred for a further half an hour at -78 ^{o}C and then the temperature was allowed to rise to room temperature and quenched with water after another 18 hours. The aqueous layer was drained and about 0.20 grams of solid material, which proved to be pure (dp-BPh_2)H, was filtered out of the aqueous layer. The organic layer was washed with two 75 ml. portions of 1M acetic acid and the acid washings were collected. The remaining organic layer contained a black solid mass that was collected by filtering off the organic liquid, recrystallized from acetone over activated charcoal two times, and purified by washing with cold acetone to give an additional 2.85 grams of light brown colored (dp-BPh_2)H. The acetic acid washings were made basic with 75 mL of 6M NaOH solution, upon the addition of which a black liquid rose to the surface and solidified after a day. The solid was filtered out of solution and washed with cold

water and dried. It was recrystallized from acetone to give a yet another additional 1.15 grams of **dphdpb** (total weight 4.20 g. 30.5% yield).

^{1}H NMR (22^{o}C, C_6D_6), δ: 7.53-7.60 (m, 4H), 7.47 (bd, 4H, *J*=6.1Hz), 7.34 (t, 4H, *J*=7.5Hz), 7.18-7.25 (m, 2H), 6.88 (dt, 2H, *J*=7.5Hz, 1.7Hz), 6.31 (ddd, 2H, *J*=7.1Hz, 5.5Hz, 1.3Hz), 1.54 (s, 1H).
^{13}C NMR (22^{o}C, C_6D_6), δ: 187.0 (q, $J_{C\text{-}B}$=51.2Hz), 157.1 (q, $J_{C\text{-}B}$=50.2Hz), 140.1, 137.0, 135.5, 132.9, 127.6, 124.8, 119.5.
Anal. Calcd. for $C_{22}H_{19}BN_2$: C, 82.01; H, 5.94; N, 8.69. Found: C, 81.80; H, 5.94; N, 8.63.

Sodium diphenyl-di(2-pyridyl)borate, dphdpbNa

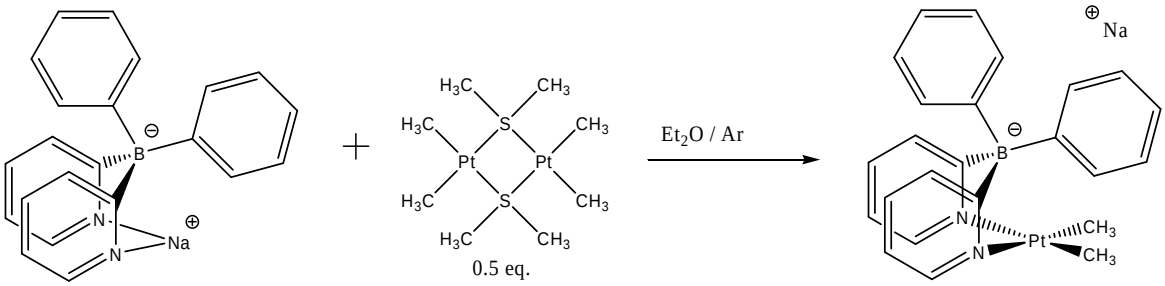


The protonated diphenyldi(2-pyridyl)borate ligand, **dphdpbH**, was added to a small vial in the glove box (100 mg, 0.31mmol) and dissolved in 4 mL of THF. To this solution, sodium hydride (37 mg, 1.55mmol) was slowly added to control gas evolution. The reaction was left to stir overnight, after which time the resulting brown solution was filtered through a Celite plug and the filter washed 2 times with 1 mL of THF. The solvent was evaporated under high vacuum to give an off color white solid that can be washed with cyclohexane or a 4:1 hexane/ether mixture and dried under high vacuum overnight to give white **dphdpbNa** (105mg, 98% yield).

^{1}H NMR (22^{o}C, acetone-d_6), δ: 8.31 (d, 2H, *J*=4.3Hz), 7.53 (bd, 2H, *J*=7.6Hz), 7.28 (dt, 2H, *J*=7.6Hz, 1.6Hz), 7.21 (bm, 4H), 7.01 (t, 4H, *J*=7.2Hz), 6.86 (bt, 2H, *J*=7.2Hz), 6.76 (bt, 2H, *J*=6.1Hz).

^{13}C NMR (22^{o}C, acetone-d_6), δ: 187.9 (q, J_{C-B}=53.9Hz), 161.8 (q, J_{C-B}=50.1Hz), 148.6, 136.2, 132.8, 129.8, 126.5, 123.0, 117.7.
Anal. Calcd. for $C_{22}H_{19}BN_2$: C, 76.77; H, 5.27; N, 8.14. Found: C, 76.56; H, 5.27; N, 7.84.

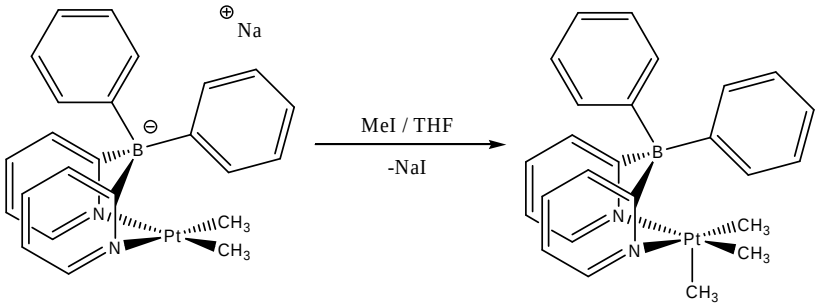
Sodium diphenyl-di(2-pyridyl)borato dimethylplatinate(II), dphdpbPtMe$_2$, 4.3



dphdpbNa (20 mg, 0.058 mmol) was put into a small reaction vial and the tetramethylbis(dimethylsulfide)diplatinum(II) precursor (16.9mg, 0.021mmol) was added. The solids were placed in 3 ml of diethyl ether and stirred. After five minutes, the reactants had dissolved and a new, distinct precipitate fell out of solution. The reaction mixture was stirred for a further 4 hours, after which time the solvent was evacuated under high vacuum and the resulting off color white solid dried for 10 hours to get pure target complex (33 mg, quantitative yield).

^{1}H NMR (22^{o}C, THF-d_8), δ: 8.69 (d, 2H, J_{H-H}=5.5Hz, J_{H-Pt}=18.6Hz), 7.35 (td, 2H, J_{H-H}=7.8Hz, 1.4Hz), 7.24 (bd, 2H, J_{H-H}=7.8Hz), 6.50-7.14 (m, 10H), 6.86 (t, 2H, J_{H-H}=7.3Hz), 0.21 (s, 6H, J_{H-Pt}=73.9Hz).
^{13}C NMR (22^{o}C, THF-d_8), δ: 150.7, 132.9, 132.8, 127.1, 120.8, -19.1. *Ipso*-carbon groups to Boron were not seen due to boron splitting and some of the signals were not observed due to low solubility and eventual significant decomposition of the sample after one day inside the NMR tube.
Anal. Calcd for $C_{24}H_{24}BN_2NaPt$: C, 50.63; H, 4.25; N, 4.92. Found: C, 50.96; H, 4.62; N, 4.56.

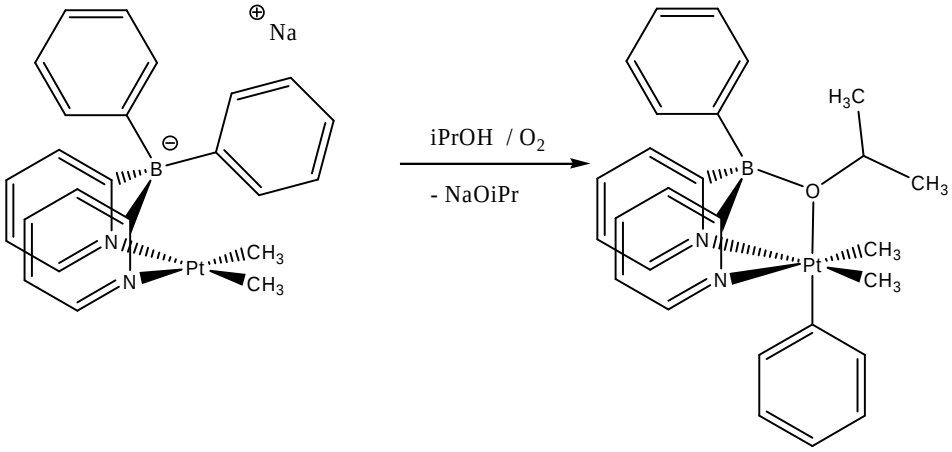
Diphenyl-di(2-pyridyl)borato trimethylplatinum(IV), (dp-BPh$_2$)PtMe$_3$, 4.4



51.8 mg of **4.3** (0.091 mmol) were put into a reaction vial and 4 mL of THF were added. A large excess of MeI (8eq, 10.0 μL) was added to the vial with a microsyringe. Immediately the suspension changed color to a brighter white. The mixture was stirred for a further five minutes, after which time the solution was filtered through Celite and cotton, and the filter washed two times with 2 mL portions of THF. The solvent was evaporated off under vacuum and the resulting white solid dried under high vacuum overnight to get pure complex **4.4** (36.7mg, 71.9 % yield). Crystals of **4.4** were grown by slow evaporation of THF or by layering THF with cyclohexane.

^{1}H NMR (22^{o}C, THF-d_8), δ: 8.41 (d, 2H, J_{H-H}=5.4Hz, J_{H-Pt}=13.6Hz), 7.84 (d, 2H, J_{H-H}=7.8Hz),
7.63 (td, 2H, J=7.8Hz, 1.Hz), 7.36 (vt, 1H, J_{H-H}=7.4Hz), 7.19-7.34 (m, 2H), 7.17 (t, 2H, J_{H-H}=7.4Hz), 7.04-7.09 (m, 3H), 6.95-7.00 (bm, 2H), 6.51-6.56 (bm, 2H), 1.59 (s, 3H, J_{H-Pt}=82.7Hz), 0.23 (s, 6H, J_{H-Pt}=63.1Hz).
^{13}C NMR (22^{o}C, THF-d_8), δ: 186.3 (q, J_{B-C}=51.3Hz), 154.4 (J_{B-C}=55.9Hz), 148.9 (J_{B-C}=51.6Hz), 146.9 (J_{C-Pt}=19.5Hz), 141.3, 136.4, 136.2, 131.4, 130.1, 128.6, 127.6, 125.2, 122.6 (J_{C-Pt}=18.6Hz), 4.8 (J_{C-Pt}=804.1Hz), -4.1 (J_{C-Pt}=650.4Hz).

Preparation of (μ-isopropoxo)-phenyl-di(2-pyridyl)borato dimethylphenylplatinum(IV), (dp-BPh(μ-O-*i*-Pr))PtMe$_2$, 4.5



Complex **4.3** that was prepared from 50.0 mg (0.145 mmol) of ligand **dphdpbNa** and corresponding amount of Pt precursor by the method outlined above, was used without isolation. The product was exposed to air and isopropanol (2-3mL) was added to the reaction vial as soon as possible after exposure. The solution was stirred for 3 minutes, after which time the murky, white solution was dried under high vacuum to get a grayish solid. The solids were re-dissolved in benzene and filtered through Celite and cotton and the filter washed 2 times with 2 mL of benzene. After the benzene was evaporated on the rotovap, pure complex **4.5** was obtained as a yellow tinged white solid (31.7 mg, 33.8% yield based on **dphdpb**).

^{1}H NMR (22^{o}C, C_6D_6), δ: 8.04 (d, 2H, J_{H-H}=6.7Hz), 7.92 (d, 2H, J_{H-H}=5.7Hz, J_{H-Pt}=12.8Hz), 7.69 (d, 2H, J_{H-H}=7.7Hz), 7.49 (t, 2H, J_{H-H}=7.3Hz), 7.40 (t, 1H, $J_{H-H=}$7.3Hz), 7.08 (t, 1H, J_{H-H}=7.3Hz), 6.99 (bd, 2H, J_{H-H}=7.3Hz), 6.90 (td, 2H, J_{H-H}=7.7Hz, 1.5Hz), 6.77 (d, 2H, J_{H-H}=7.3Hz, J_{H-Pt}=51.4Hz), 6.22-6.27 (m, 2H), 3.85 (sep, 1H, J_{H-H}=6.5 Hz, J_{H-Pt}=12.8Hz), 1.75 (s, 6H, J_{H-Pt}=68.2Hz), 0.98 (d, 6H, J_{H-H}=6.5Hz).
^{13}C NMR (22^{o}C, C_6D_6), δ: 179.0-180.3 (m), 148.0 (J_{C-Pt}=20.0Hz), 145.2-146.9 (bm), 136.5, 136.0, 135.3, 128.3, 127.9, 127.6, 127.0, 125.9, 124.0 (J_{C-Pt}=10.0Hz), 121.4 (J_{C-Pt}=18.5Hz), 71.7, 23.4, -4.8 (J_{C-Pt}=667.5 Hz).

4.4.2 Isomerization experiments

Transformation of 3.5-Pt-^{13}C to 3.5-B-Pt-^{13}C

In THF solution. As reported in Chapter 2, complex **3.5-Pt-^{13}C** contained the ^{13}C label on the Pt bound methyl groups, where the label made up 33% of the total. The equatorial and the axial position are in equilibrium, and 5 minutes after the synthesis of the complex, there is a perfect statistical distribution of the label. The complex was heated in THF-d_8 at 60^{o}C for two weeks, after which time no ^{13}C incorporation into the boron bound methyl groups was observed.

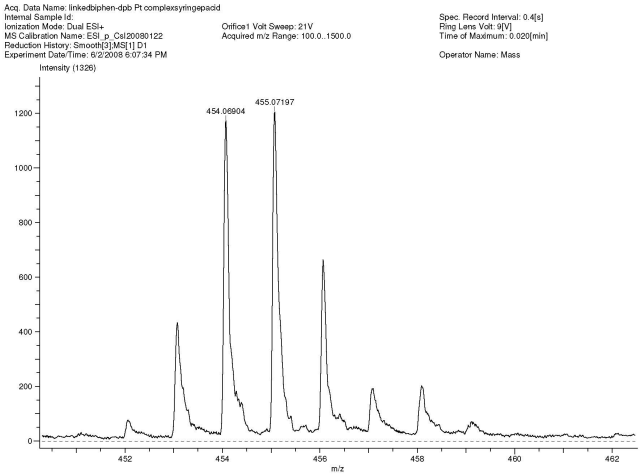
In DMSO solution. A stronger Lewis base, DMSO-d_6, was used as a solvent for complex **3.5-Pt-^{13}C** at 60^{o}C. Conveniently, the *endo*-B-Me group whose resonance appears at -0.91 ppm and its Pt and C satellites can be cleanly observed (see Fig. 1b). For the *exo*-B-Me group whose resonance was centered at 0.18 ppm the high-field ^{13}C-satellite was clearly observable, whereas the downfield one was also seen but overlapped with other signals.

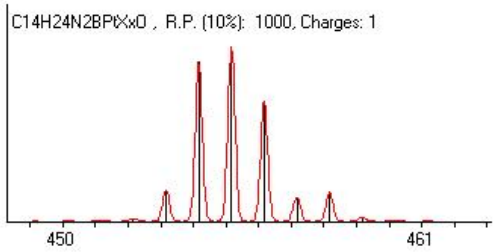
After 6 days of heating, the carbon satellites around the *endo*-B-Me and the *exo*-B-Me were ~6% each (12% total), or a 30% possible incorporation. After 12 days the satellites were ~11% for each of the BMe groups (22% total), or a 55% possible incorporation and after 19 days; the satellites totaled ~15% for each of the B-Me groups, or a 75% of the purely statistical distribution that was possible.

Importantly, no noticeable incorporation of two ^{13}C-labels and/or formation of unlabeled complex **3.5** was detected. This conclusion can be made based on ESI-mass-spectrometry of the solution resulting from methanolysis of the product:

$(Me_2Bpy_2)PtMe_3$ + MeOH → $(MeBPy_2)(\mu\text{-}OMe)PtMe_3$ + MeH

Simulated and experimentally observed mass spectra of $[(MeBPy_2)(\mu\text{-}OMe)PtMe_2{}^{13}CH_3]\cdot H^+$ matched; m/z calcd for $C_{14}{}^{13}CH_{24}N_2{}^{11}B^{195}PtO$, 455.167, found 455.072:





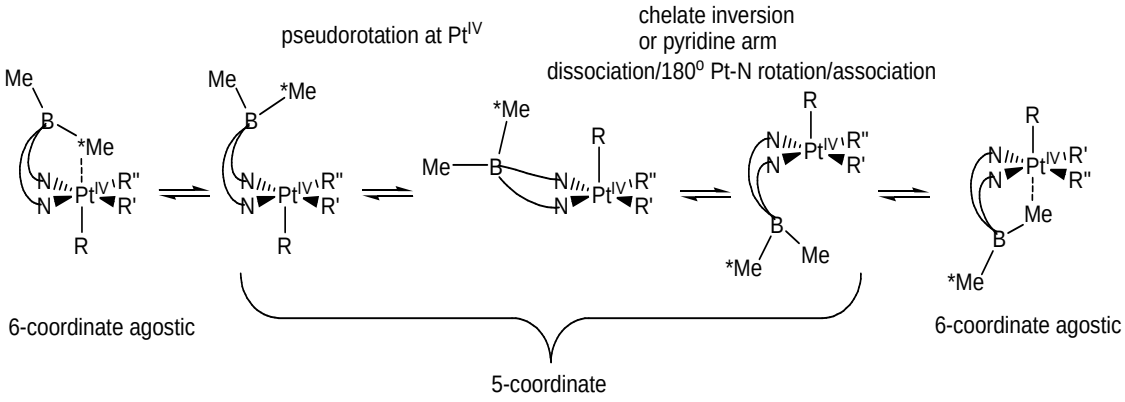
Theoretical Isotope Distribution
Composition: C14 H24 N2 B1 Pt1 Xx1 O1
Unsaturation: 5.5

m/z	Rel. abundance	
449.165090	0.0074	
450.161719	0.0310	
451.166178	0.4190	
452.162825	1.7341	*
453.167793	17.7312	*********
454.165533	91.0245	**********
455.167138	100.0000	**********
456.167267	68.9179	**********
457.170844	13.8113	*******
458.169820	16.7332	********
459.172715	2.5796	*
460.175466	0.2248	
461.178089	0.0142	
462.180749	0.0007	

Calculated average molecular weight: 455.245950
First isotope moment: 455.078880
Second isotope moment: 1.614011

^{1}H and ^{13}C NMR spectra for unlabeled complex **3.5** were reported in Chapter 3
^{1}H NMR (22^{o}C, DMSO-d_6), δ: 1.68 (axial $Pt^{IV}CH_3$, $J_{C\text{-}H}$= 139.2Hz), 0.96 (equatorial $Pt^{IV}CH_3$, $J_{C\text{-}H}$= 131.2Hz), 0.18 (endo-B-CH_3, $J_{C\text{-}H}$= 115 Hz), -0.87 (exo-B-CH_3, $J_{C\text{-}H}$= 109.4 Hz).

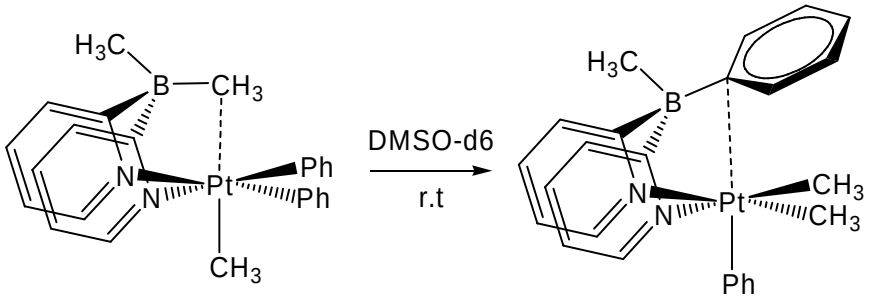
A possible mechanism of the ^{13}C-label migration between the *endo*- and *exo*-positions in the BMe_2 fragment of **3.5-B-^{13}C** is shown below.



Isomerization of complex 3.7 to 4.2

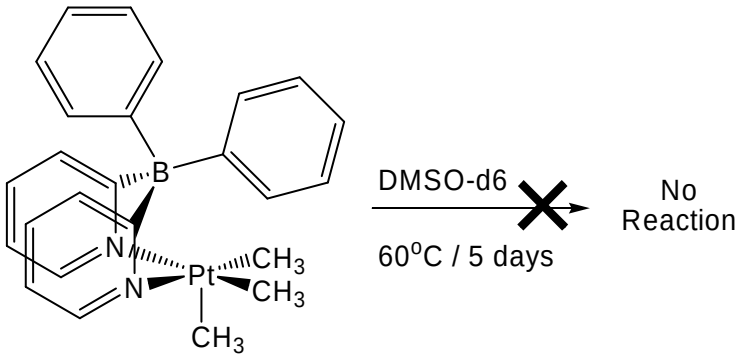
In THF solution was described above.

In DMSO solution



Complex **3.7** (10mg) was dissolved in DMSO-d_6 in a Young tube under argon. An NMR spectrum of the mixture taken a few hours after mixing revealed mostly starting material. The solution was monitored over a period of two weeks at 20^{o}C. The last spectrum revealed a mixture of products and just a little of starting materials (~10%) remaining. Major byproduct resulted from the reaction of trace amounts of water with complex **3.7**. However, it was possible to tell that complex **4.2** did indeed form (~30%) due to tell-tale peaks whose coupling constants matched exactly the values obtained in THF-d_8 where the transformation occurred cleanly at elevated temperature. The chemical shifts were closely mirrored as well. These peaks were the equatorial CH_3-Pt peaks and the ortho protons of the axial Pt bound phenyl that are located in the unique ~6.30 ppm region and have a Pt coupling constant of 66.8Hz (see spectral data for **4.2**). The other aromatic peaks are obscured by byproducts.

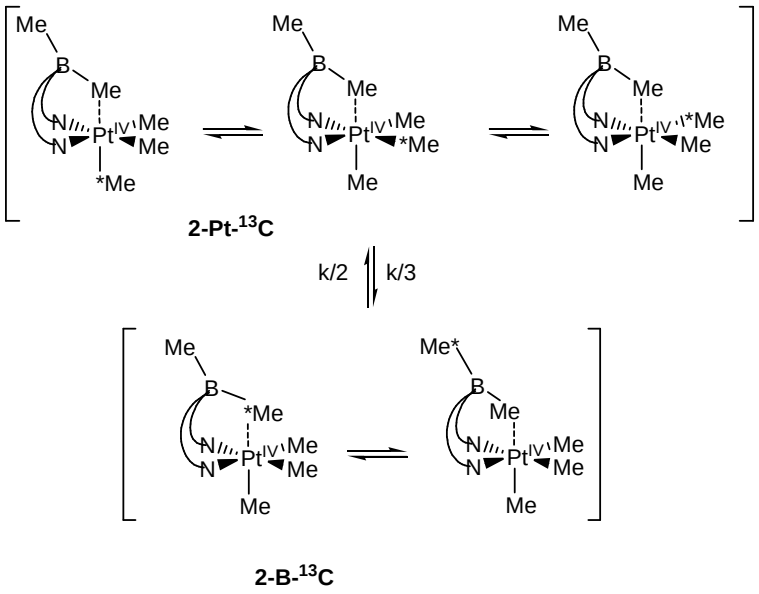
Attempted isomerization of complex 4.4 to 4.2



Complex **4.4** (10mg) was dissolved in 0.4 mL of DMSO-d_6 in a Young tube under argon. The solution was heated at 60^{o}C over a period of 5 days and an NMR spectrum

was acquired every day. Throughout this time, no changes were observed in the NMR spectrum.

4.4.3 Kinetics of transformation of 3.5-Pt-^{13}C to 3.5-B-Pt-^{13}C



For degenerate methyl group transfer between B and Pt^{IV} (*Me = regular methyl) rate constants for the direct and reverse reactions are identical (k). When one of the methyl groups in the $Pt^{IV}Me_3$ fragment is $^{13}CH_3$, the rate constant for its transfer to B is k/3. For the reverse reaction involving B to Pt^{IV} transfer of the single label $^{13}CH_3$ the rate constant is k/2. Hence, the equilibrium constant K for the reaction above is 2/3 what corresponds to 40% **3.5-B-Pt-^{13}C** and 60% **3.5-Pt-^{13}C** at equilibrium.

If C_0 is the total concentration of all labeled complexes **3.5** in solution, [Pt] is the concentration of complex **3.5-Pt-^{13}C** and [B] is the concentration of complex **3.5-B-^{13}C**, then the rate of approaching to equilibrium is

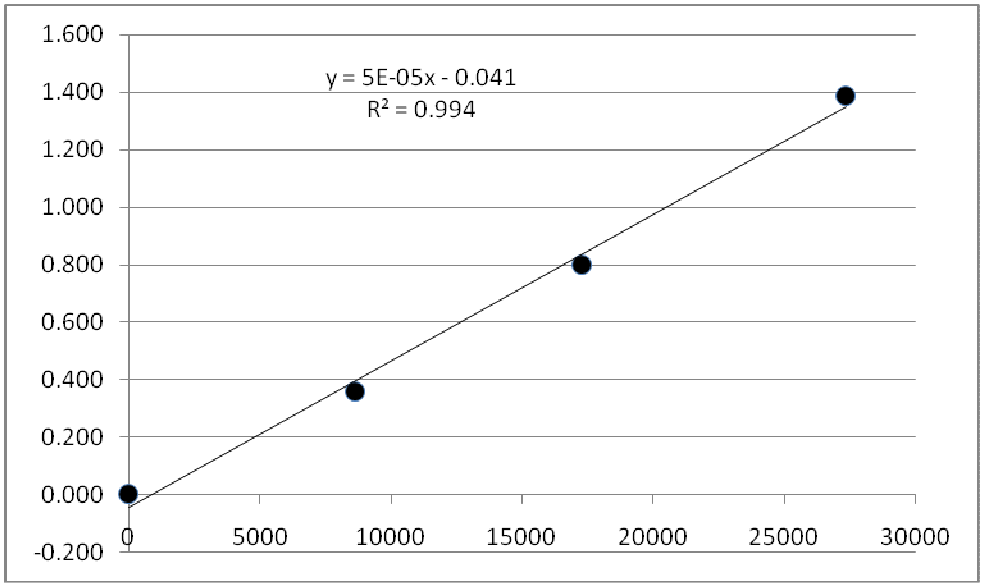
$$d[B]/dt = k/3[Pt] - k/2[B] = k(C_0 - 5/6[B]) \quad \text{(S1)}$$

Integration of equation (S1) gives

$\ln[1/(1-5/2([B]/C_0))] = (5/6)kt$

time, min	all B(*Me)/C_0	ln[1/(1-2.5[all B(*Me)/C_0])]
0	0	0
8640	0.12	0.356675
17280	0.22	0.798508
27360	0.30	1.386294

Data in the Table above allows to find the observed pseudo-first order rate constant (solvent role is not taken into account):



Finally, the rate constant k is $(5.1\pm0.2)\cdot10^{-5}$ min^{-1} at 60°C in DMSO-d_6 solution.

4.5 References

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Chapter 5: Oxidation of monoalkyl Pt^{II} complexes supported by dipyridylborate (dpb) and diphenyldipyridylborate (dphdpb) ligands

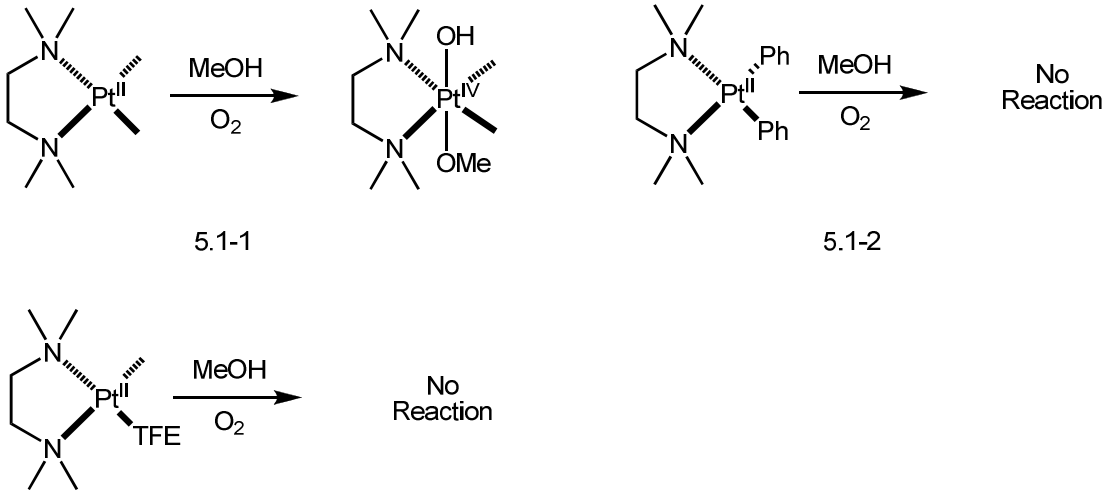
5.1 Introduction

Oxidation of monoalkyl Pt^{II} complexes represents the second, oxidative step of the Shilov catalytic cycle (Scheme 1.1). One of the goals of our research is to substitute expensive oxidants and indirect dioxygen activation via metal salt,[1] polyoxometalate (POM),[2] benzoquinone mediators by direct O_2 oxidation. Indirect oxidation with mediators can lead to undesirable results such as low selectivity and catalyst decomposition.[3,4] By modifying the ligand environment, it should be possible to achieve direct oxidation of monoalkyl species by dioxygen.

An early report by Goldberg and Bercaw showed that oxidation of dimethyl Pt^{II} complexes supported by neutral ligands is very facile.[5] However, changing the two strongly donating Me groups for two phenyl ligands, shut down the oxidation reaction (Scheme 5.1).[6] Removing electron density from the Pt^{II} complex, by substituting one Me ligand for solvent (TFE, aqua, MeOH), shuts down the direct oxidation reaction as well (Scheme 5.1; 5.1-3). Similarly, it is known that cationic Pt^{II} monoalkyl species supported by bidentate ligands do not react with dioxygen, including the diketimine motif, and the dipyridyl methane ligand that was utilized in Chapter 1 for CH activation studies in hydroxylic solvents (Scheme 5.2). A dinuclear complex **1.10** that is formed as a byproduct in CH activation reactions, would be even more stable towards direct oxidation since it possesses a positive charge and no

strongly donating ligands. By contrast, dmdpm$Pt^{II}(Me)_2$ **1.6**, did react readily with O_2 (our unpublished results; also see ref 7),[7] but the products of oxidation were not characterized.

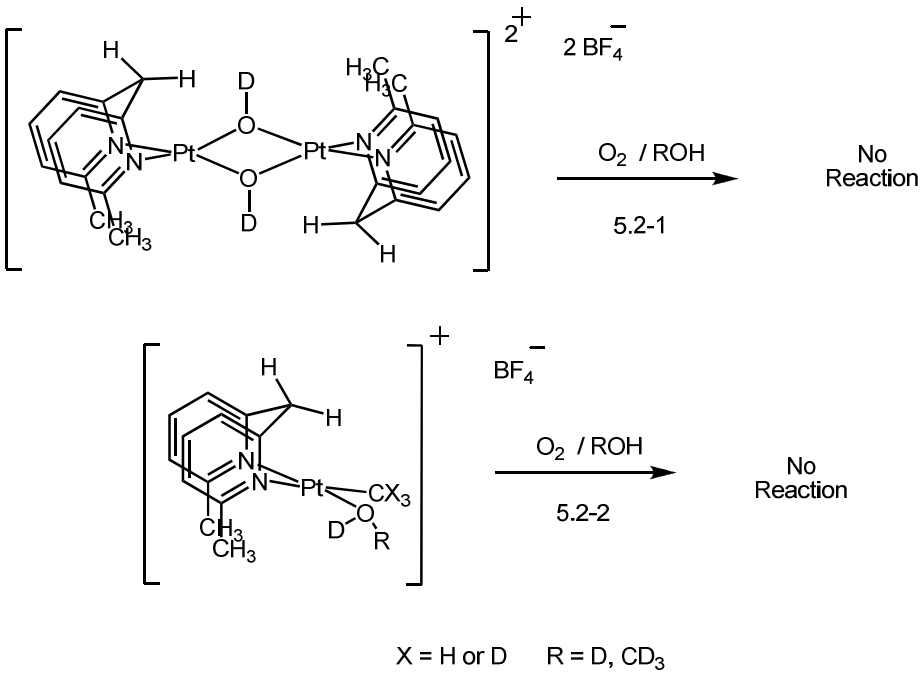
Scheme 5.1 Oxidation of electron rich Pt^{II} complexes



5.1-1 5.1-2

5.1-3

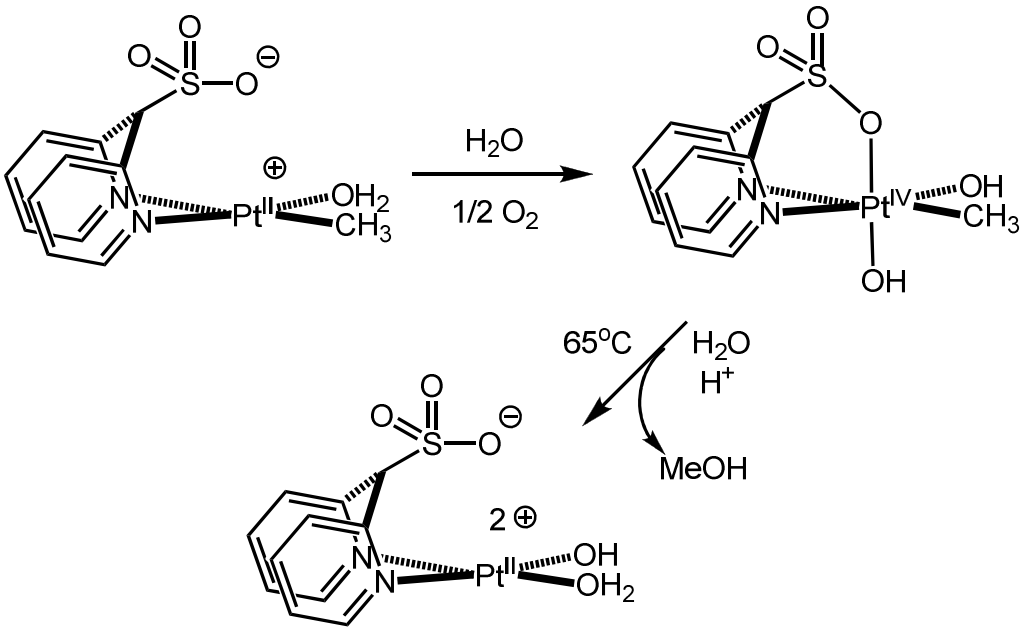
Scheme 5.2 Stability of dmdpm supported Pt^{II} complexes towards O_2



5.2-1 5.2-2

By contrast, Pt^{II} complexes supported by the dipyridylborate ligand (dpb) introduced in Chapter 2 (for oxidation reactions see Chapter 3) and the diphenyldipyridylborate (dphdpb Chapter 4), that both can be viewed as analogues of dpms with an even poorer third donor instead the sulfonate, the boron-bound Me of Ph group (see Fig. 2.11, 3.1 and 4.6), are reactive with dioxygen. Unlike the TMEDA complexes in Scheme 5.1, $dpbPt^{II}(Ph)_2$ does react with dioxygen virtually as rapidly as its dimethyl analogue (Scheme 3.2). This activity can be rationalized by the electron releasing character of the dpb ligand and the ability of the boron-bound methyl to stabilize the emerging Pt^{IV} center. Although the ligand is altered during the oxidation process via methyl group transfer from boron to platinum, we were hopeful to observe oxidation of monomethyl Pt^{II} complexes as a proof of concept that the oxidation reaction could be promoted by anionic, tripod ligands, or even by a relatively poor donor such as an agostic bond arising from a methyl or phenyl group. Reports with the anionic dpms ligand show that this anionic ligand can mediate oxidation of $Pt^{II}(Me)(OH)$ to a Pt^{IV} complex that eventually eliminates MeOH under mild conditions (Scheme 5.3).[8,9] The analogous disolvento $dpmsPt^{II}$ complex that remains after methanol elimination, is stable towards oxidation.

Scheme 5.3 Oxidation of dpmsPt^{II}(Me)(OH_2) complex and MeOH elimination



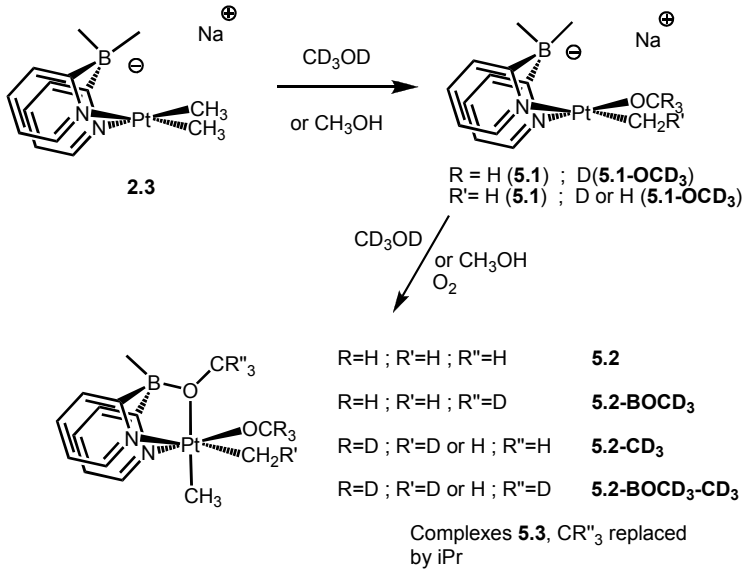
Thus, anionic ligands may represent a perfect scaffold for Shilov type catalytic mechanisms with regard to oxidation potential. They do not promote oxidation of the disolvento complexes that must activate a CH bond, but after the formation of a monomethyl complex, fast oxidation can occur. We decided to examine the reaction of monoalkyl complexes supported by the dpb and dphdpb ligand with dioxygen and were gratified to learn that the oxidation reaction occurs rapidly in hydroxylic solvents just as was shown in Chapter 3. Although undesirable Me group transfer from B to Pt occurs during oxidation in the case of monomethyl complexes as well, by modifying the dpb ligand, we hope to prevent the transfer without altering the rapid CH activation and oxidation reactions. At the end of this Chapter, possible modifications of the dpb ligand motif will be discussed in detail.

5.2 Results and Discussion

When dpb supported dimethyl Pt^{II} compelx **2.3** was added to a methanol solution, an immediate reaction took place, followed by vigorous evolution of methane gas to give monomethyl methoxo complex **5.1** in quantitative yield. The deuterated form of complex **5.1**-OCD_3 was made by dissolving **2.3** in CD_3OD. This led to deuterium incorporation into the remaining Me ligand.

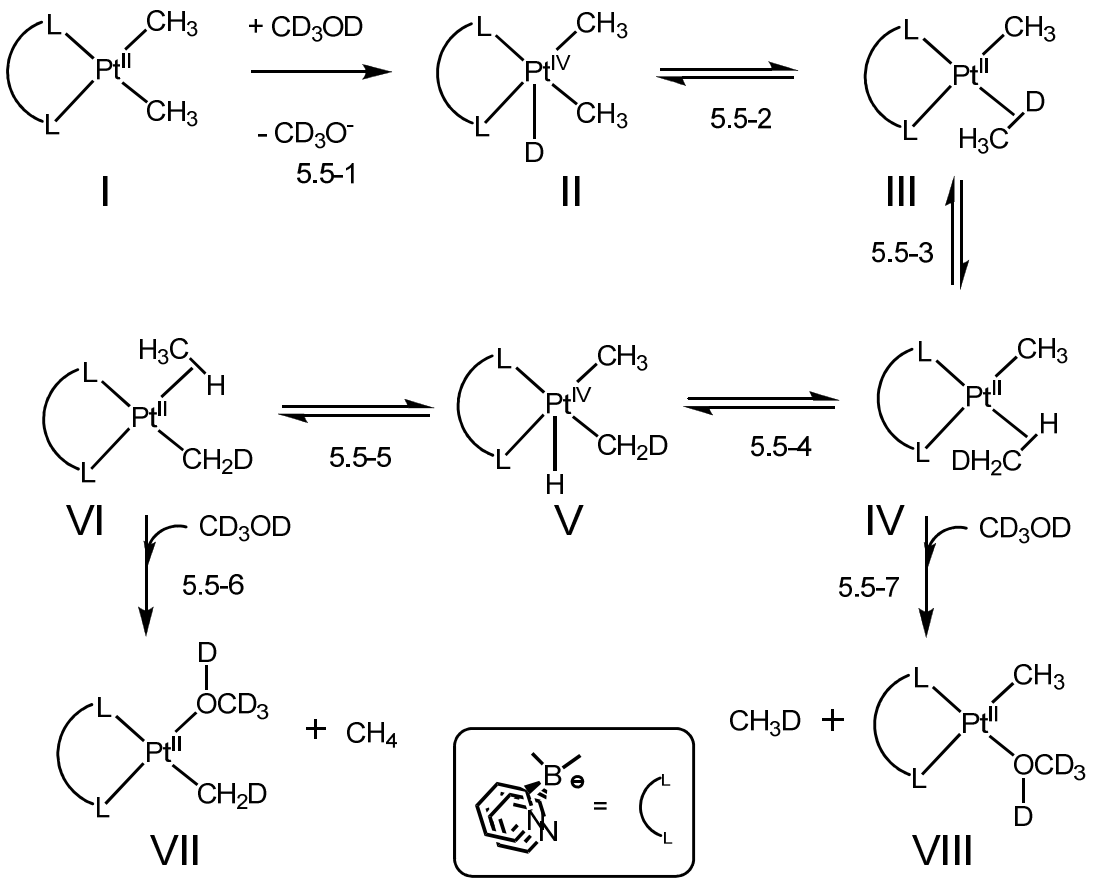
Exposure of CD_3OD solutions of **5.1** or **5.1**-OCD_3 to air led to a change in the NMR spectrum towards deuterated complex **5.2**-$BOCD_3$ or **5.2**-$BOCD_3$-OCD_3 respectively. These complexes were formed by methyl group transfer from B to Pt^{IV} (see Chapters 3,4) upon oxidation of the Pt^{II} center. A deprotonated molecule of solvent that is ^1H NMR silent is incorporated into the final product (Scheme 5.4). Isolation of complex **5.1** by concentrating solutions, and subsequent oxidation in CH_3OH leads to the formation of completely non-deuterated **5.2**. Cross experiments with isolating the deuterated **5.1**-OCD_3 lead to the same set of results.

Scheme 5.4 Aerobic Oxidation of $dpbPt^{II}(Me)(OMe)$



The NMR spectra of **5.1** and **5.2** were not clean in the aromatic region, presumably due to activation of MeOH solvent and formation of byproducts during the methanolysis step to form **5.1**. However, the relevant information regarding methanolysis and oxidation could be extracted via deuterium labeling studies by observing the aliphatic region. The elimination of the first methyl group from **2.3** to form complexes **5.1** occurs by protonation of **2.3** to form an intermediate Pt^{IV} hydride or deuteride (Scheme 5.5; I), that then undergoes reversible reductive coupling / oxidative cleavage in a series of reversible steps that span intermediates II to VI before loss of a coordinated methane molecule from either intermediate IV or VI.[10]

Scheme 5.5 Reaction sequence leading to formation of complexes **5.1-OCD$_3$**



That the barrier for reductive coupling 5.5-2 and 5.5-5 and oxidative cleavage 5.5-4 are less than that for loss of coordinated methane 5.5-6 and 5.5-7 is reflected in the presence of unlabeled methane molecules CH_4 in the product mixture when protonation with CD_3OD is carried out. The presence of CH_4 can be explained by substitution of coordinated CH_4 in intermediate VI by a solvent molecule to form VII, which is eventually deprotonated to give complex **5.1** with one deuterium in the remaining Pt coordinated Me group. Alternatively, substitution of coordinated CH_3D can take place in intermediate IV to give VIII (Scheme 5.5; 5.5-7), which is deprotonated to give a molecule of complex **5.1** that has a non-labeled Me ligand coordinated to the Pt.

If no reversible oxidative cleavage and CH bond scrambling occurred before methane dissociation from the complex, then only CH_3D would be observed in the NMR spectrum. The observation of only CH_3D would not give information on the reversibility of transformation II to III (Scheme 5.5; 5.5-2) and it would suggest that an alternative mechanism of direct protonation of the Pt bound CH_3 was functional. This is not as likely with an electron rich metal center.

Since CH_4 is observed, the accessibility of intermediates IV, V, and VI is verified. If reductive coupling (5.5-2) were irreversible and CH bond slippage (5.5-3) was reversible, intermediates III and IV would become the only occupied states and solvent substitution of coordinated methane from these complexes can only lead to CH_3D. However, the presence of CH_4 suggests that all steps (5.5-2 to 5.5-5 are reversible). Moreover, the ratios of CH_4 and CH_3D are close to the statistical value of

3:4, implying that equilibrium is reached before coordinated methane substitution by the solvent and that rapid interconversion between intermediates II to VI is observed.

Moreover, free CH_2D_2 and/or CHD_3 were not observed in the spectra above baseline noise and they may not be present in the solution at all along with CD_4. Coordinated CH_3 or CH_2D remaining after deprotonation from VII and VIII integrates as just less than 3 protons against the ortho pyridine ligand signals and is seen as a single peak with a small upfield shoulder, suggesting that Pt-CHD_2 and Pt-CD_3 are not significant byproducts of the reaction. These results point to the practical irreversibility of the protonation step 5.5-1 (or, more likely, very slow deprotonation of II) before coordinated methane substitution. If protonation equilibria were fast, then intermediate V could be deprotonated and then re-protonated by another molecule of CD_3OD to yield multiply deuterated methane and Pt-Me species. In contrast, reversible protonation of $[(dpms)PtMe_2]^-$ by D_2O is much faster compared to methane loss leading $[(dpms)PtMe(OD)]^-$ to so that complete deuteration of the methyl ligands was observed well before any significant degree of hydrolysis could be achieved in that dpms-system.[11] Hence, once again, dpb complexes showed much faster ligand (methane) substitution at Pt^{II} center compared to their dpms analogues.

Similar reversible behavior was observed with this system in Chapter 2: The complexes were protonated by D_2O and coordinated methane in intermediates IV and VI was substituted by a deuterated benzene (C_6D_6) ligand. The isotopic distribution of the final free methane molecules was more complex due to the fact that double CD activation in benzene-d_6 had occurred and six deuterides (from C_6D_6) had to be

accounted for in the case of the second molecule of methane lost, but experimental data closely matched the calculated statistical equilibrium.

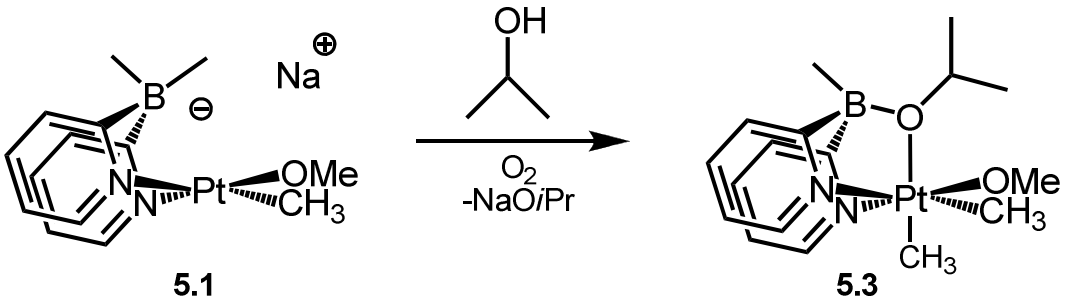
Oxidation experiments that included the transformation of labeled and non-labeled **5.1** to various labeled **5.2** complexes with CD_3OD show that the MeO ligand in **5.1**, does not form a bridging ligand between Pt and B in the synthesis of **5.2**, but that a second solvent molecule fulfills this role. The non-labeled Pt-OCH_3 in **5.1** can be differentiated from the solvent molecule that forms the bridging ligand between Pt and B if CD_3OD is used in oxidation. OCH_3 remains as an anionic ligand in the equatorial position while OCD_3 forms the bridging species. If **5.1-OCD_3** is used, then the ^{1}H NMR signal of the remaining Pt bound Me group has a shoulder from the presence of CH_2D. This labeled group remains in the equatorial position, while the Me group that is transferred from boron ends up in the axial position trans to the boron moiety.

After Me group transfer from B to Pt^{IV} occurs, coordination of the second MeO and formation of the B-O-Pt bridge is faster than isomerization of the intermediate (see Chapter 4). This result might suggest an inversion of the boron ligand as opposed to pyridine arm dissociation (that could be accompanied by isomerization) as the operative mechanism that explains why the boron moiety ends up trans to the Me group that was transferred from it. Alternatively, pyridine arm dissociation-rotation-re-coordination is a much faster process than ligand scrambling at five-coordinate metal center in $LPt^{IV}Me(OMe)_2$ intermediate.

Although the information obtained from isotopic labeling studies in CD_3OD was invaluable, the formation of **5.1** and **5.2** was not clean. In order to obtain a clean

sample of Pt^{IV} complex after aerobic oxidation of a monoalkyl species, methanol solvent was substituted for isopropyl alcohol. Switiching to a more lipophilic and bulky alcohol gave a much cleaner oxidized product **5.3** with a well-definied aromatic region in the ^{1}H NMR spectrum (Scheme 5.6). Isotopologous complexes **5.3** were used as surrogates to investigate the mechanism in Scheme 5.5 after it was determined that the reactivity pattern was identical and **5.2** proved too difficult to isolate and observe by ^{1}H NMR.

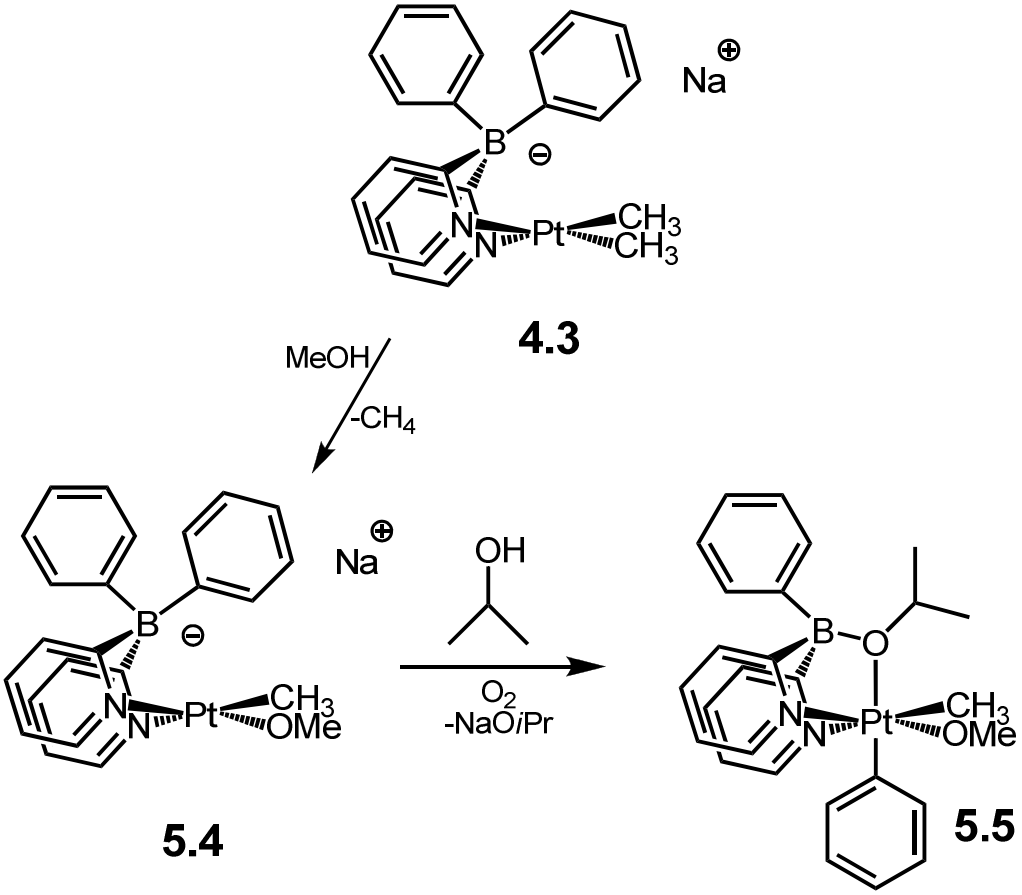
Scheme 5.6



5.1 **5.3**

Similar reactivity was observed with the related monomethyl complexes supported by dphdpb ligand. Loss of only one Pt^{II}-coordinated Me ligand of **4.3** was observed to give complex **5.4** cleanly, unlike in the case of **5.2**. Subsequent aerobic oxidation in the presence of isopropyl alcohol gave the corresponding product of Ph group transfer **5.5** (Scheme 5.7).

Scheme 5.7 Aerobic oxidation of dphdpbPt^{II}(Me)(OMe)



The two CH_3 groups of the coordinated *i*-PrO moiety are diastereotopic. Overall, reactions with the bulky dphdpb scaffold gave much cleaner products in higher yields, and this effect may be attributed to the higher lipophilicity of the Pt complexes supported by this ligand.

5.3 Conclusion

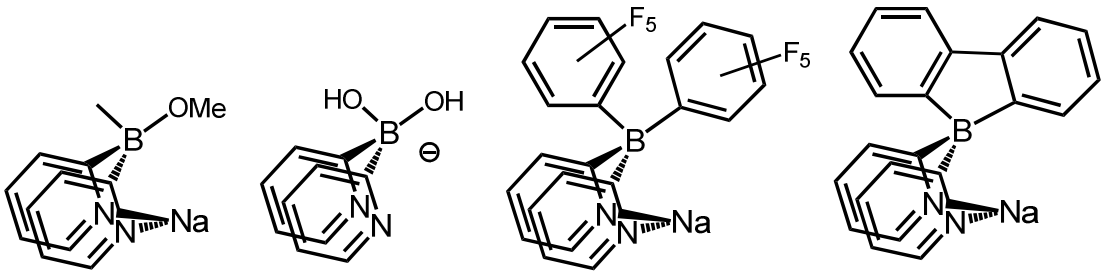
Although fast aerobic oxidation of monoalkyl complexes was observed in hydroxylic solvents, the process is unsatisfactory from the point of view of Shilov chemistry as the ligand is destroyed in the process via methyl or phenyl transfer. In addition, it is very difficult to achieve reductive elimination from dialkyl Pt^{IV} complexes resulting

from these oxidation reactions; the products of oxidation are stable after heating at 80^{o}C in MeOD for prolonged periods. This behavior is similar to the well documented stability of (dpms)PtMe$_2$(OH) toward reductive elimination. C-C reductive elimination was observed with the similar trimethyl Pt^{IV} complex **3.5** to give ethane accompanied by decomposition of some part of the remaining organometallic species. In the case of **3.5** however, the complex was predisposed towards C-C reductive elimination since it was five coordinate, with a weak stabilizing agostic CH bond interaction in the sixth coordination site. Direct C-C reductive elimination from unsupported, true square pyramidal trimethyl Pt^{IV} complexes has been reported by the Goldberg group.[12-14] The trimethyl complexes utilized by Goldberg were precursors that eliminated ethane upon gentle heating to form a (presumed) three coordinate intermediate that was very active in intra and inter-molecular CH activation reactions.

In the case of complexes **5.3** and **5.5**, the isopropoxo bridging unit is bonded too strongly to the Pt center. It is possible to de-coordinate the isopropoxo unit in trimethyl Pt^{IV} complex **5.3** by introducing one equivalent of strong acid such as HBF$_4$ (unpublished results), but reductive elimination studies in the presence of strong acids have not been performed yet. Direct, acid promoted reductive elimination from **5.3** or **5.5** may lead to ethane or toluene respectively, and nucleophilic attack on coordinated Me groups from solvent or another equivalent of Pt complex[8,9] would lead to MeOH. We believe that a better route towards coupling aerobic oxidation and reductive elimination is to modify the ligand. Since reductive elimination from **5.3** would leave to a complex supported by a dipyridylborate with alkoxo and alkyl arms (ligand **5.6**),

we might expect that ligands such as **5.7** would carry out oxidation of Pt^{II} complexes and not be destroyed in the process (Figure 5.1).

Figure 5.1 Proposed ligands for promoting aerobic oxidation

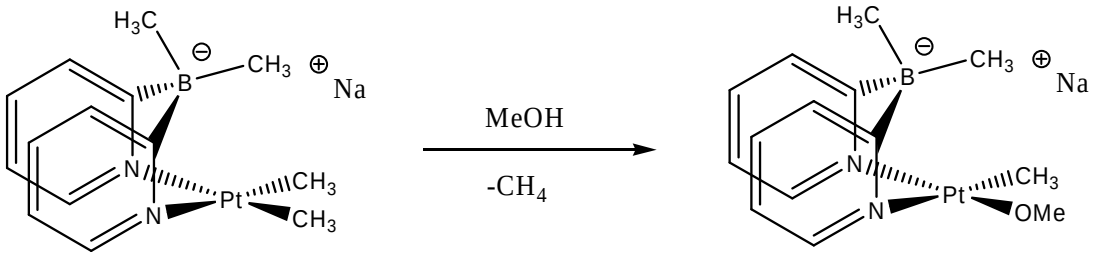


5.6 **5.7** **5.8** **5.9**

Alternative strategies include decreasing electron density on the aryl rings coordinated to the boron atom. There is precedent that electron poor bonds between B and electron poor C are more stable than bonds between B and electron rich C. This is documented in the stability of the $B(ArF_5)_4^-$ anion[15] as opposed to BPh_4^- anion that is often used for Ph transfer.[16,17] There are reports of the splitting of electron poor B-C bonds by organometallic reagents,[18] and this effect could be exacerbated by the proximity of that bond in **5.8** to the Pt center. The solution may be to make phenyl group transfer impossible via sterics as in proposed ligand **5.9**. Attempts to synthesize the proposed ligands and studies of their potential in aerobic oxidation of Pt^{II} complexes are currently underway.

5.4 Experimental

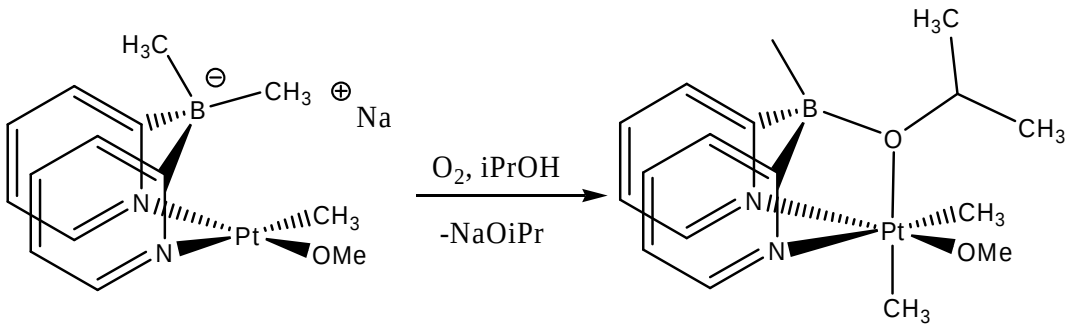
Sodium dimethyldi(2-pyridyl)boratomethylmethoxyplatinate(II), Na(dp-BMe$_2$)Pt(OMe)(Me), 5.1



Previously reported[3] Na(dp-BMe$_2$)PtMe$_2$ **2.3**, (60.0mg, 0.135mmol) was weighed out into a vial in the glove box, and one mL of MeOH was added and the contents stirred. Immediate gas evolution was observed and lasted for half a minute. Two minutes later, MeOH was evacuated under high vacuum and the grey-yellow solid was washed several times with pentane and dried under vacuum overnight. **5.1** was obtained in 95.2% yield (59.2 mg).

^{1}H NMR (22^{o}C, acetone-d$_6$), δ: 8.95 (dq, 1H, J_{H-H}=5.5Hz, 0.8Hz), 8.61 (d, 1H, J_{H-H}=5.9Hz, J_{H-Pt}=48.5Hz), 7.46 (d, 1H, J_{H-H}=8.2Hz), 7.38-7.41 (m, 2H), 7.35 (td, 1H, J_{H-H}=7.8Hz, 1.6Hz), 6.84 (m, 1H), 6.59 (m, 1H), 3.41 (s, 3H, J_{H-Pt}=46.6Hz), 0.82 (s, 3H, J_{H-Pt}=76.0Hz), 0.48 (bs, 6H).
^{13}C NMR (22^{o}C, acetone-d$_6$), δ: 154.1, 148.8, 133.3, 132.2, 127.9, 127.1, 120.0, 119.0, 59.0, 13.5 (q, J_{B-C}=41.9 Hz), -15.7.
Some *Ipso*-carbon groups to Boron were not seen due to boron splitting.

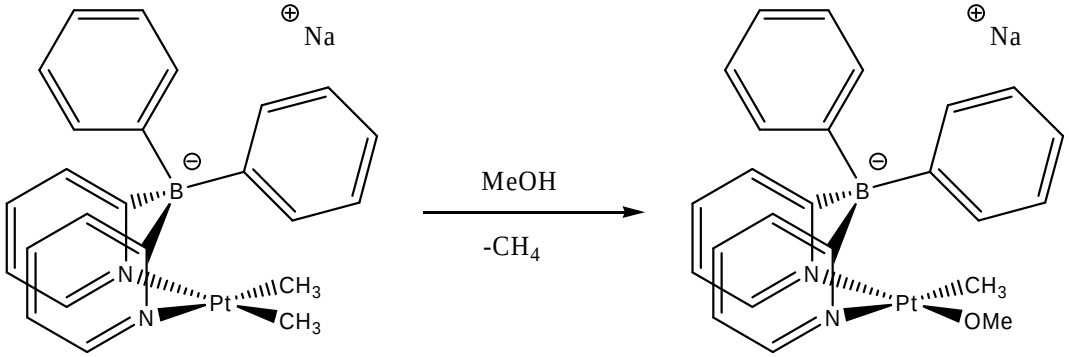
Dimethylmethoxo-isopropoxo(2-pyridyl, methyl)boratoplatinum(IV), (dp-B(OiPr)(Me))Pt(Me)$_2$(OMe), 5.3 versus 5.2



The procedure for the synthesis of complex **5.3** was the same as the one used for the synthesis of complex **4.5**. The complex was not obtained in a completely pure form and was not recrystallized to purity. However, the spectral data was unambiguous. The aromatic region had impurities and the aliphatic region was pure just as in associated complexes **5.2** that were obtained in labeled and non-labeled methanol mediated aerobic oxidation. However, the aromatic signals accounted for ~65% of the total aromatic signals in **5.3** as opposed to ~30% of the total signals in **5.2**.

^{1}H NMR (22^{o}C, C_6D_6), δ: 8.46 (d, 1H, J_{H-H}=5.8Hz, J_{Pt-H}=10.1Hz), 7.58 (d, 1H, J_{H-H}=5.8Hz, J_{Pt-H}=33.0Hz), 7.45 (d, 1H, J_{H-H}=7.7Hz), 7.26 (d, 1H, J_{H-H}=7.7Hz), 6.97 (td, 1H, J_{H-H}=7.7Hz;1.4Hz), 6.76 (td, 1H, J_{H-H}=7.7Hz; 1.4Hz), 6.50 (ddd, 1H, J_{H-H}=7.7Hz; 5.8Hz; 1.4Hz), 6.13 (ddd, 1H, J_{H-H}=7.7Hz; 5.8Hz; 1.4Hz), 4.54 (sep, 1H, J_{H-H}=6.2Hz, J_{Pt-H}=12.2Hz), 3.56 (s, 3H, J_{Pt-H}=45.1Hz), 1.78 (s, 3H, J_{Pt-H}=78.3Hz), 1.75 (s, 3H, J_{Pt-H}=68.3Hz), 1.47 (d, 3H, J_{H-H}=6.2Hz), 1.07 (d, 3H, J_{H-H}=6.2Hz), 0.77 (s, 3H).

Sodium diphenyldi(2-pyridyl)boratomethylmethoxoplatinate(II), Na(dp-BPh$_2$)Pt(OMe)(Me), 5.4

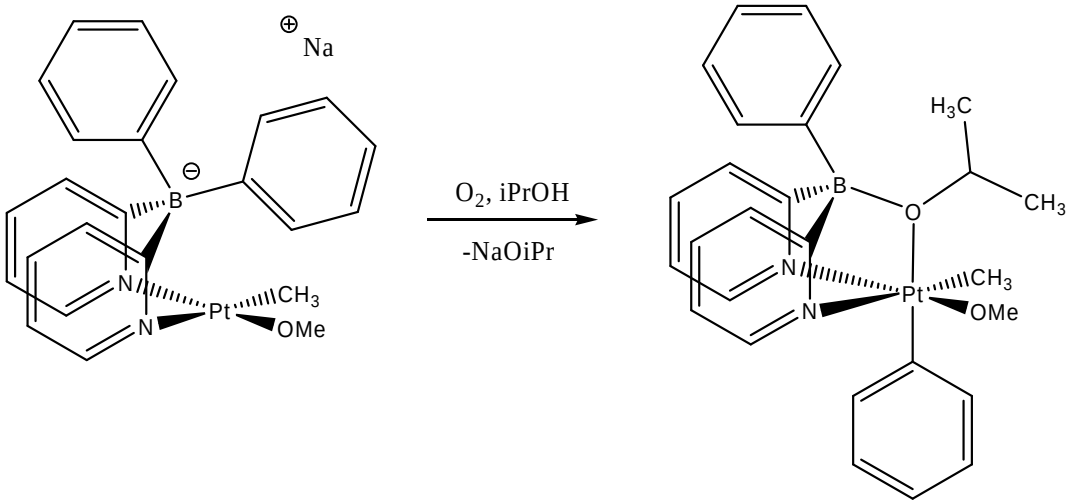


9.1 mg of **4.3** were used to prepare **5.4** in quantitative isolated yield (9.1mg). The procedure used was exactly the same as that for the synthesis of **5.1** above. **5.4** was obtained as a dark gray solid.

^{1}H NMR (22^{o}C, acetone-d_6), δ: 8.97 (d, 1H, J_{H-H}=5.5Hz), 8.71 (d, 1H, J_{H-H}=5.9Hz, J_{H-Pt}=44.9Hz), 7.42 (td, 1H, J_{H-H}=7.5Hz, 1.6Hz), 7.34 (td, 1H, J_{H-H}=7.5Hz, 1.4Hz), 7.31 (d, 1H, J_{H-H}=78.2H), 7.00-7.04 (m, 6H), 6.93-6.96 (m, 6H), 6.70-6.73 (m, 1H), 2.81 (s, 3H, J_{H-Pt}=39.1Hz), 0.51 (s, 3H, J_{H-Pt}=73.9Hz).

^{13}C NMR (22^{o}C, acetone-d_6), δ: 186.7 (q, J_{B-C}=52.2 Hz), 183.6 (q, J_{B-C}=47.2 Hz), 159.7 (q, J_{B-C}=51.0 Hz), 153.4, 149.5, 136.8, 133.1, 132.3, 132.0, 130.9, 126.7, 123.7, 120.7, 119.9, 58.0, -13.7 (q, J_{Pt-C}=858.6Hz).

Dimethylphenyl-isopropoxo(2-pyridyl, phenyl)boratoplatinum(IV), (dp-B(OiPr)(Ph))Pt(Me)$_2$(Ph), 5.5



The reaction was performed following the protocol for the synthesis of **4.5**. 29.4 mg (5.02e-5mol) of **5.4** gave 25.8mg of **5.5** as a yellow tinged white solid (82.7% yield).

^{1}H NMR (22^{o}C, C_6D_6), δ: 8.36 (d, 1H, J_{H-H}=5.0Hz), 8.03 (d, 1H, J_{H-H}=7.8Hz), 7.94 (d, 2H, J_{H-H}=7.5Hz), 7.62 (d, 1H, J_{H-H}=5.2Hz J_{H-Pt}=30.1Hz), 7.52 (t, 2H, J_{H-H}=7.3Hz), 7.42 (t, 1H, J_{H-H}=7.5Hz), 7.33 (d, 1H, J_{H-H}=7.7Hz), 7.09-7.24 (m, 5H), 6.95 (t, 1H, J_{H-H}=7.8Hz), 6.68 (t, 1H, J_{H-H}=7.5Hz), 6.63 (t, 1H, J_{H-H}=5.2Hz), 5.98 (t, 1H, J_{H-H}=5.0Hz), 4.06 (sept, 1H, J_{H-H}=6.2Hz), 3.42 (s, 3H, J_{H-Pt}=41.9Hz), 2.29 (s, 3H, J_{H-Pt}=67.9Hz), 1.51 (d, 3H, J_{H-H}=6.2Hz), 1.13 (d, 3H, J_{H-H}=6.2Hz).
^{13}C NMR (22^{o}C, C_6D_6), δ: 149.9 (J_{Pt-C}=25.3Hz), 149.2, 136.3, 136.2, 136.0, 134.9, 129.2, 128.7, 128.6, 128.4, 127.4, 125.3, 121.9 (J_{Pt-C}=39.8Hz), 121.0 (J_{Pt-C}=12.9Hz), 72.3, 59.1 (J_{Pt-C}=21.1Hz), 23.5, 21.8, 5.1 (J_{Pt-C}=640.2Hz).
Ipso-carbon groups to Boron were not seen due to boron splitting and one signal not seen due to overlap with solvent.

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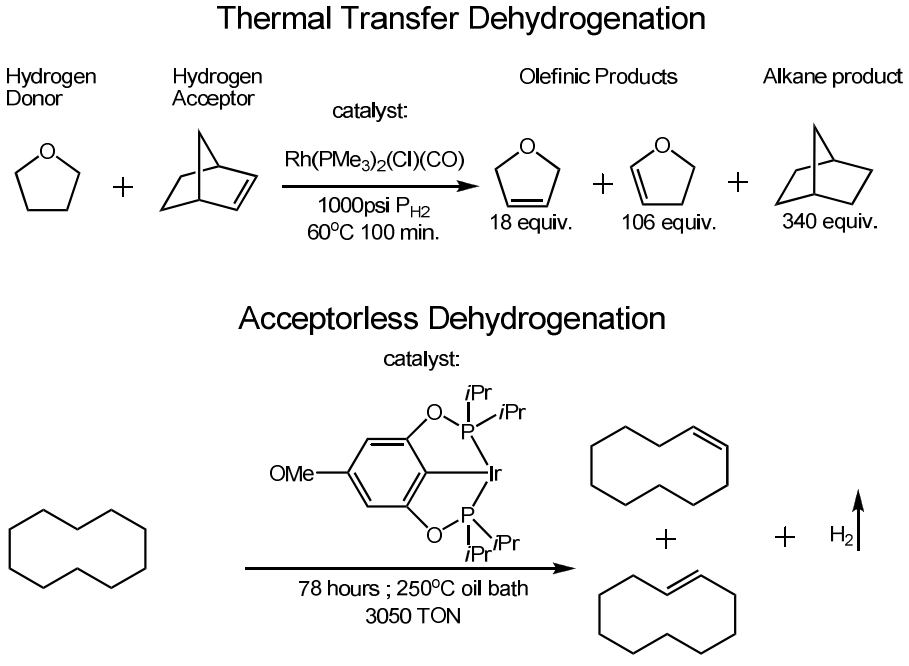
Chapter 6: Catalytic Transfer Dehydrogenation of Cyclic Alkanes Promoted by Pt^{II} complexes supported by a lipophilic anionic borate ligand

6.1 Introduction

6.1.1 Alkane dehydrogenation as a CH bond functionalization strategy

Dehydrogenating alkanes towards olefins is a viable CH bond functionalization strategy.[1] A double bond is a lot easier to modify by further mild catalytic oxidation methods such as Wacker oxidation or olefin epoxidation[3] or via olefin metathesis.[4] Catalytic dehydrogenation by homogenous metallic species was first reported by Crabtree,[5-7] and in the 90s, well defined organometallic species with group 9 metal centers have proven to be active in catalytic transfer dehydrogentation[8-10] and acceptorless dehydrogenation of alkanes[11,12] (Scheme 6.1).

Scheme 6.1 Examples of catalytic transfer and acceptorless dehydrogenation



The systems shown in Scheme 6.1, operate at elevated temperatures, but are effective in terms of large turnover numbers (TONs). Systems that operate with *tert*-butylethene (TBE) acting as a sacrificial hydrogen acceptor generally have higher TONs and are easier to quantify since the system is closed. The transfer of hydrogen to a sacrificial olefin has to be thermodynamically feasible for the reactions to work, thus TBE is often utilized in this role, but the conditions for transfer dehydrogenation are often milder than in its acceptorless counterpart. Acceptorless dehydrogenation is desirable from the point of view of converting alkanes directly to functionalized products without wasting one equivalent of sacrificial olefin for each equivalent of product produced. The drawbacks of acceptorless dehydrogenation include the need to utilize an open system (to drive off the H_2 produced) and a much higher temperature required for the reaction. The iridium catalyst in Scheme 6.1 is also active in transfer dehydrogenation at lower temperatures.

A variant of this catalyst has been used in tandem with Schrock's olefin metathesis catalyst to perform alkane metathesis in a closed system, where H_2 gas is recombined with olefins, at 125^{o}C.[13] The limiting factor for alkane metathesis was believed to be the instability of the olefin metathesis catalyst. Other systems that utilize early transition metal hydrides adsorbed on silica are also effective for alkane metathesis[14-17] and have been recently shown to operate via a similar dehydrogenation / olefin meathesis / hydrogenation pathway.[18] Another possible use of acceptorless dehydrogenation catalysts may be in hydrogen storage since an alkane can be considered as a hydrogen reservoir.[5-7] For this and other applications to become

practical, the hurdles of catalyst stability and low operational temperature have to be overcome.

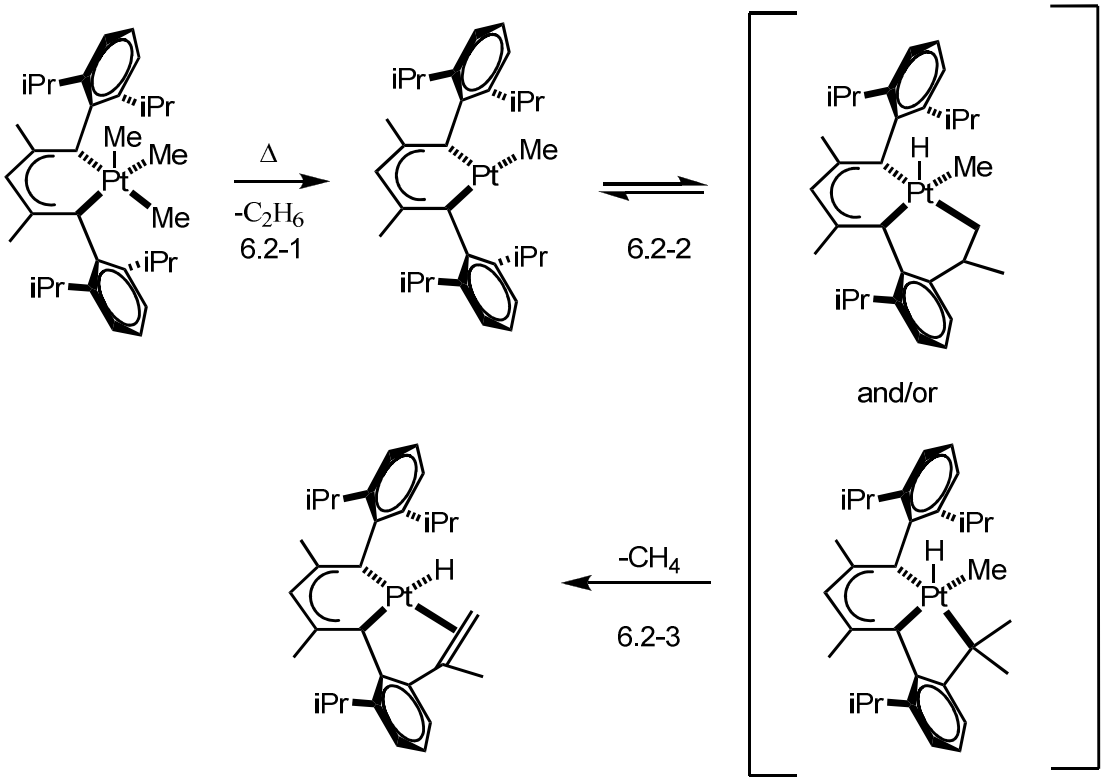
6.1.2 Alkane dehydrogenation with Pt complexes

Group 10 metals have been shown to stoichiometrically dehydrogenate alkanes,[19] including our own results discussed in Chapter 2, but there has been no report of catalytic dehydrogenation mediated by homogenous, organometallic, Pt based catalysts. It is not readily apparent why group 10 metals should be less active than their group 9 counterparts in this reaction, as both are extensively studied in CH bond activation reactions[20], and the breaking of a CH bond of an alkane often is the rate determining step in a catalytic process with both group 9 and group 10 metal systems involved in rapid CH bond breaking reactions.[3,19]

Intriguing results that hint at the possibility of transfer dehydrogenation at a Pt center have been obtained by Goldberg and Fekl at the early part of this decade. The system utilized was a trimethyl Pt^{IV} complexes supported by a diketiminate (also termed 'nacnac') ligands.[21-23] Unusually, the Pt^{IV} complexes were of a five-coordinate square pyramidal geometry and predisposed toward ethane elimination at elevated temperature of about 150^{o}C (a subsequent study in 2007 found that lower temperatures could be utilizied).[24] In the case of our trimethyl Pt^{IV} complex **3.5**, the geometry can be classified as square pyramidal, but there is a weak, stabilizing, agostic CH bond interaction in the sixths coordination site that may be responsible for the high temperature required for ethane elimination (120^{o}C / THF) at which decomposition of the complex is also observed (unpublished results). In 2002, Goldberg and Fekl reported that trimethyl Pt^{IV} supported by a diketiminate ligand

with isopropyl moieties on the aryl arms, underwent clean reductive elimination of ethane (Scheme 6.2; 6.2-1) and subsequent intramolecular CH activation of one of the isopropyl groups.[22] After activation, a cyclometalated Pt^{IV} hydride would presumably be formed (6.2-2), and it undergoes reductive coupling and elimination of methane. After the formation of coordinated CH_4 or a vacant coordination site, the cyclometalated complex undergoes β-hydride elimination to give the final olefin hydride product (6.2-3).

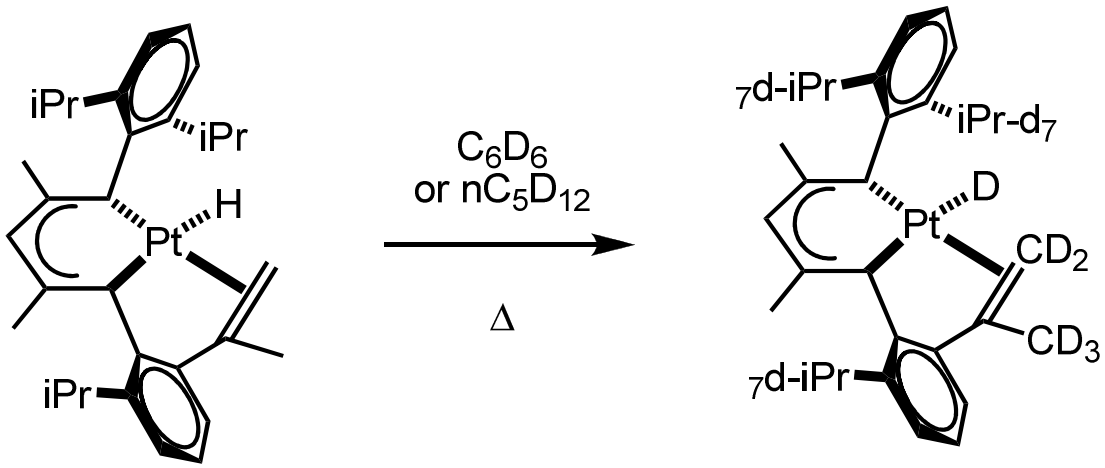
Scheme 6.2 Intramolecular CH activation and dehydrogenation with diketiminate supported Pt complex



Remarkably, reaction 6.2-3 could be rendered reversible by choosing the right alkane. The coordinated olefin formally inserts into Pt-H bond to form a three coordinate intermediate that then could bind an alkane CH bond, subsequently splitting it.

Although the olefin hydride complex failed to activate methane, *n*-pentane-d_{12} activation was evident at elevated temperatures. The reaction led to complete H/D exchange between the deuterated alkane and isopropyl groups of the partially dehydrogenate nacnac ligand L in LPtH after 62h at 85°C. The use of C_6D_6 allowed for the observation of deuterium incorporation at lower temperatures (Scheme 6.3). β–Hydride elimination at coordinated pentane give pentene hydrides, but these products were not seen because of a preference of the complex to bind the side-arm rather than an external olefin. Thus pentene hydrides were presumed intermediates in the H/D exchange reaction with *n*-pentane-d_{12}.

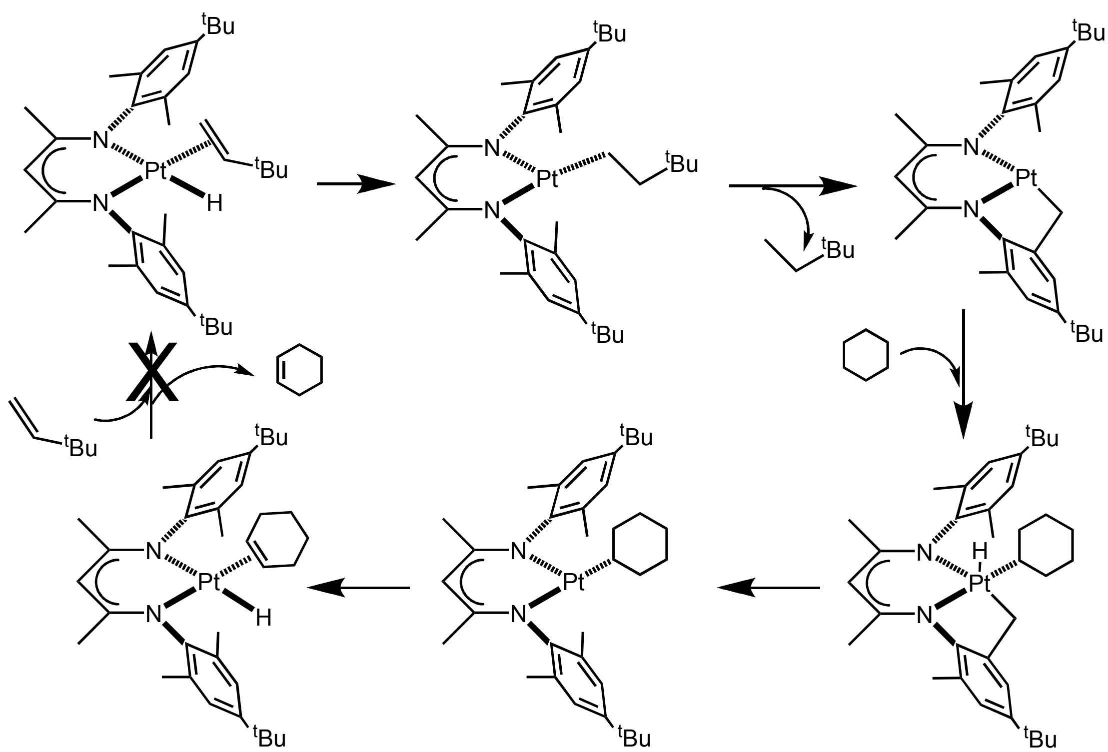
Scheme 6.3 Activation of alkanes and arenes with diketiminate Pt^{II} olefin hydride



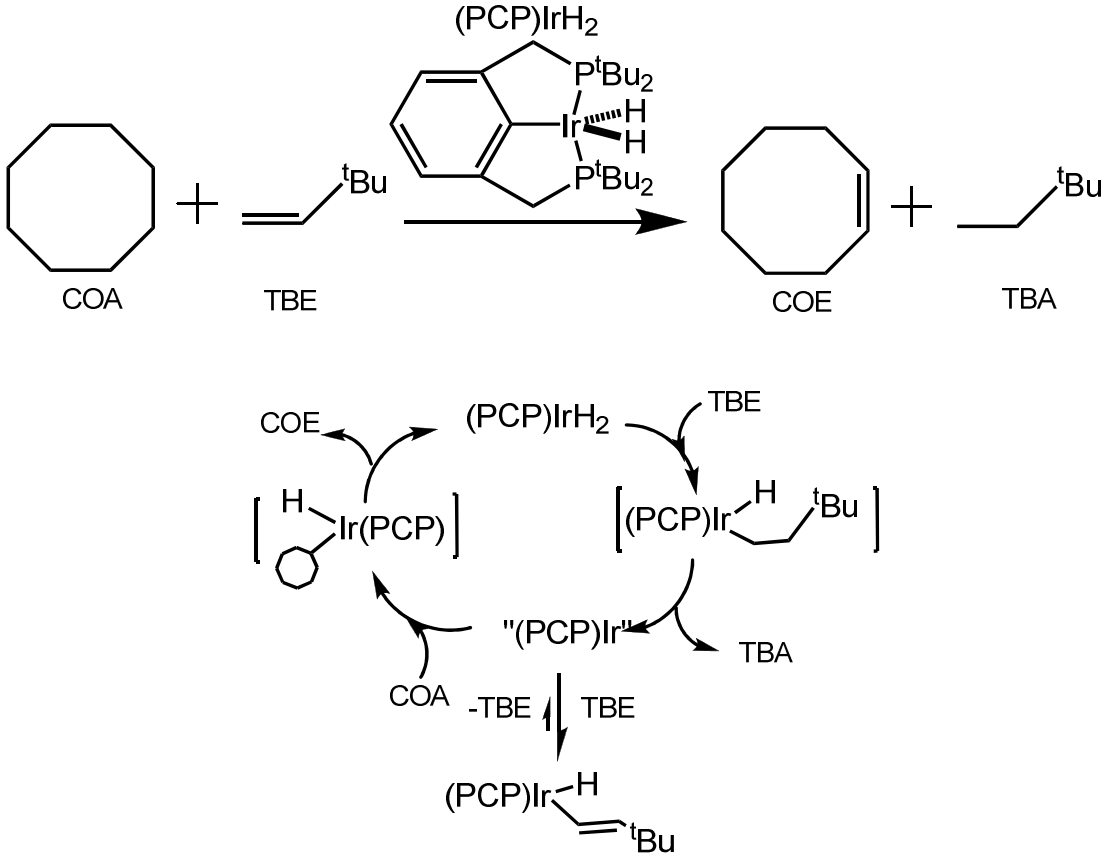
Substituting the isopropyls on the pendant aryl groups by methyl groups that would not undergo β–hydride elimination after intramolecular CH activation, allowed for observation of alkane dehydrogenation products with a coordinated external olefin (Scheme 6.4).[23] Free cyclohexane and *tert*-butylethane (TBA) could be dehydrogenated to give corresponding olefin hydrides. The TBE hydride complex can

undergo olefin insertion and will activate cyclohexane. Eventually, all TBE will be converted to TBA and a cyclohexene hydride complex forms. The mechanism shown in Scheme 6.4 is also believed to be the one operative in transfer dehydrogenation catalyzed by Ir complexes and was the first proposed mechanism (Scheme 6.5).[12] Unlike the latter case however, the cyclohexene hydride complexes reported by Goldberg were not catalytically active as the last reaction to close the catalytic cycle, substitution of coordinated cyclohexene by TBE, was not possible. This may be due to the steric demands imposed by the relatively large pendant aryls and cyclohexene itself.

Scheme 6.4 Attempt at transfer dehydrogenation with diketiminate Pt^{II} olefin hydride



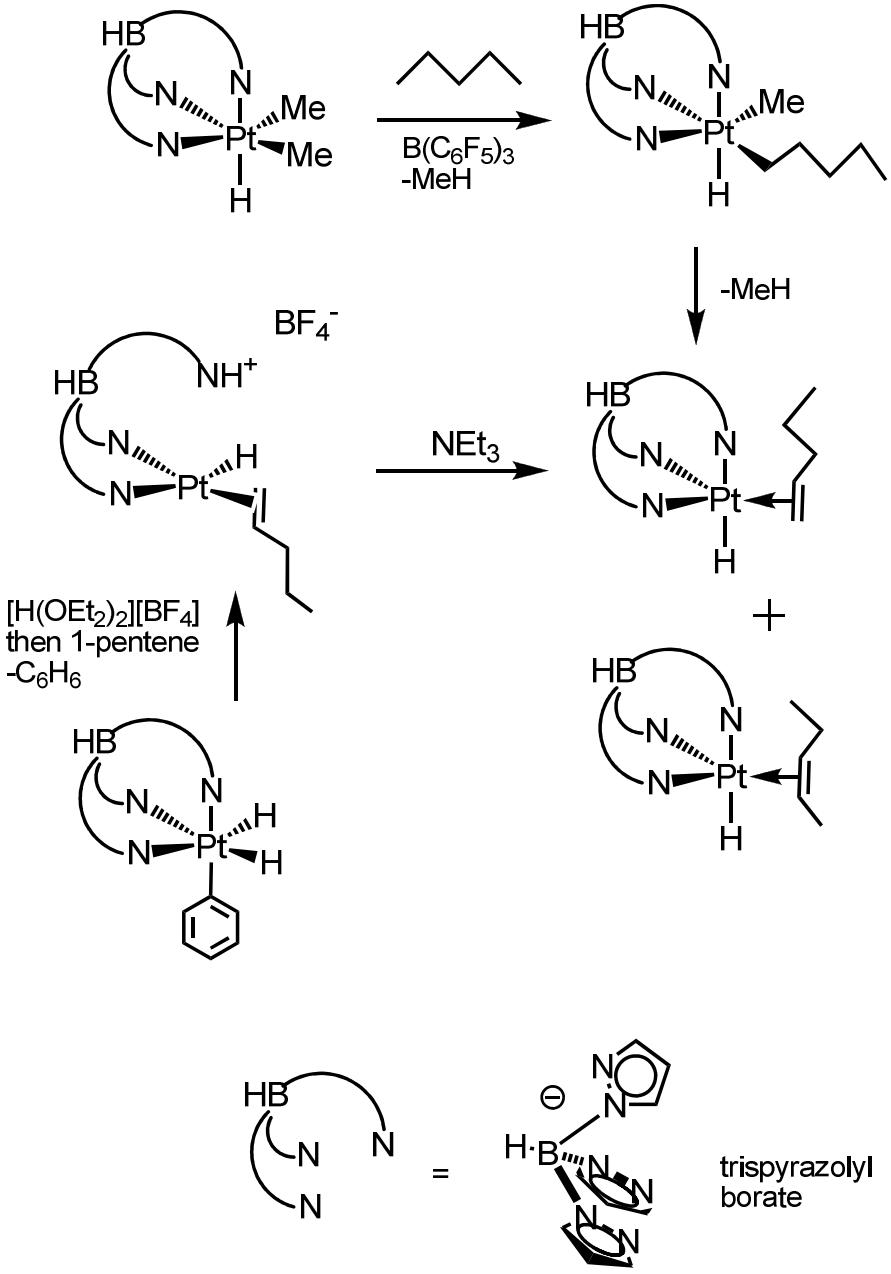
Scheme 6.5 First proposed mechanism for transfer dehydrogenation catalysis with Ir pincer complexes



In 2006, Templeton observed alkane dehydrogenation with Pt complexes supported by a trispyrazolylborate (TPB) motif (Scheme 6.6).[25] Recently, transfer dehydrogenation was attempted with this system and catalytic turnover was reported for the case of diethylether and THF dehydrogenation (1.1-1.3 TONs).[26] However, a clear case has yet to be made for catalysis, as the complex decomposed even at 60^{o}C and the reactions were accompanied by large amounts of Pt black formation. The TONs were also limited and may well fall within experimental error that was not reported in the original manuscript. Nonetheless, it appears possible that the

trispyrazolyl motif can in fact be active in catalytic transfer dehydrogenation as it is an electron rich anionic ligand just as in the case of the diketiminates, that can stabilize the Pt^{IV} hydride intermediates (Scheme 6.3) to a greater extent than the diketiminate.

Scheme 6.6 Alkane dehydrogenation with TPB supported Pt complexes



6.1.3 Alkane dehydrogenation with t-bu-dpb supported Pt complexes

There were other reports of note in stoichiometric dehydrogenation with Pt^{II} centers that were not subsequently pursued for possible use in catalytic transfer dehydrogenation, or in acceptorless dehydrogenation. In 1997 Bercaw reported dehydrogenation of Et_2O, THF and cyclohexane by (tmeda)PtMe(pyridine-F_5)$^+$ complex[27] and Vedernikov and Caulton reported mild and clean dehydrogenation of ethane, propane, *n*-butane, cyclopentane and cyclohexane with (2.1.1-pyridinophane)$PtMe_2H^+$ complex in dichloromethane solutions at room temperature.[28,29]

Encouraged by alkane dehydrogenation results obtained by others, we decided to see if olefin hydride complexes that we obtained as a result of stoichiometric alkane dehydrogenation in biphasic water/alkane mixtures with the dpb ligand, **2.9** and **2.10**, would be active in transfer dehydrogenation. Unlike the bulky diketiminate motif, these olefin hydrides were relatively sterically unhindered. The resonances of the olefinic protons in the NMR spectra ~5 ppm were downfield shifted and close to the signals of free olefins, hinting that substitution by TBE should be more facile than in diketiminates. We were hindered in exploring the reactivity of **2.9** and **2.10** by the low yields (30-40%) and the low purity of the resultant complexes in the majority of the reactions. We reasoned that both problems may have been an artifact of the relatively short half-life of Pt^{IV} hydride complexes with these ligands. After protonation of **2.3** in benzene, the clean double CH activation that ensued may have been a factor of the solubility of the Pt^{IV} hydrides in the reaction medium. Complex **2.3** was soluble in benzene, but it was not at all soluble in cyclohexane and

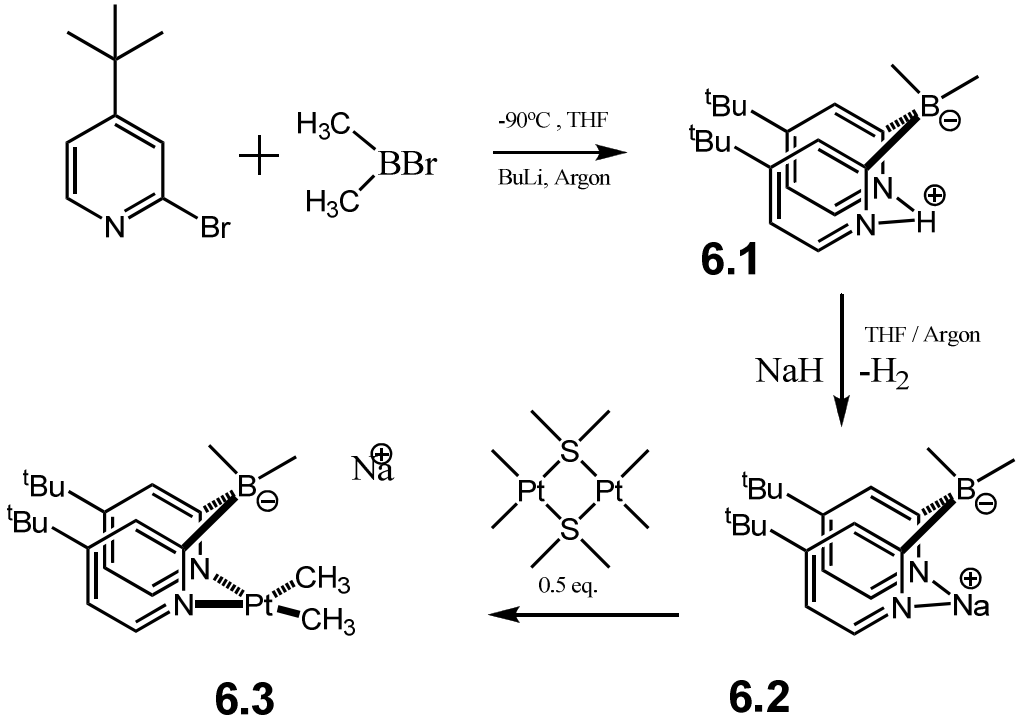
cyclopentane, and the reaction appeared to take place at the water/alkane interface. In order to transfer the short-lived Pt^{IV} hydride intermediates to the hydrocarbon phase more effectively, we decided to make the dpb ligand more lipophilic by introducing two *t*-butyl groups onto the pyridine rings in the para positions away from the metal. While these groups are electron donating, the modest electronic change would be easy to separate from effects conferred by better solubility. Gratifyingly, sodium dimethyl Pt^{II} borate complexes produced with the new lipophilic *tert*-butyldipyridylborate (*t*-bu-dpb) ligand proved to be soluble in alkane mixtures. Upon addition of water, a fast CH activation reaction occurred to give much cleaner olefin hydride products in quantitative yield. These complexes were active in alkane transfer dehydrogenation of cyclic alkanes C_nH_{2n} (n=5,6,8) at 80-100^oC with TBE acting as the sacrificial olefin.

6.2 Results and Discussion

6.2.1 Synthesis of lipophilic complexes and alkane dehydrogenation

4-*t*-Bu-2-bromopyridine was prepared by a slightly modified[32] literature procedure. It was lithiated at -90^oC and reacted with BMe_2Br to give the protonated form of the t-Budpb ligand **6.1** (Scheme 6.7). The ligand was deprotonated under an inert atmosphere with sodium hydride to produce the sodium form of the ligand **6.2** as a white, flaky, hydroscopic solid. Reacting with half an equivalent of Pt precursor gave the dimethyl complex **6.3**, an analogue of **2.3** as a light yellow powder.

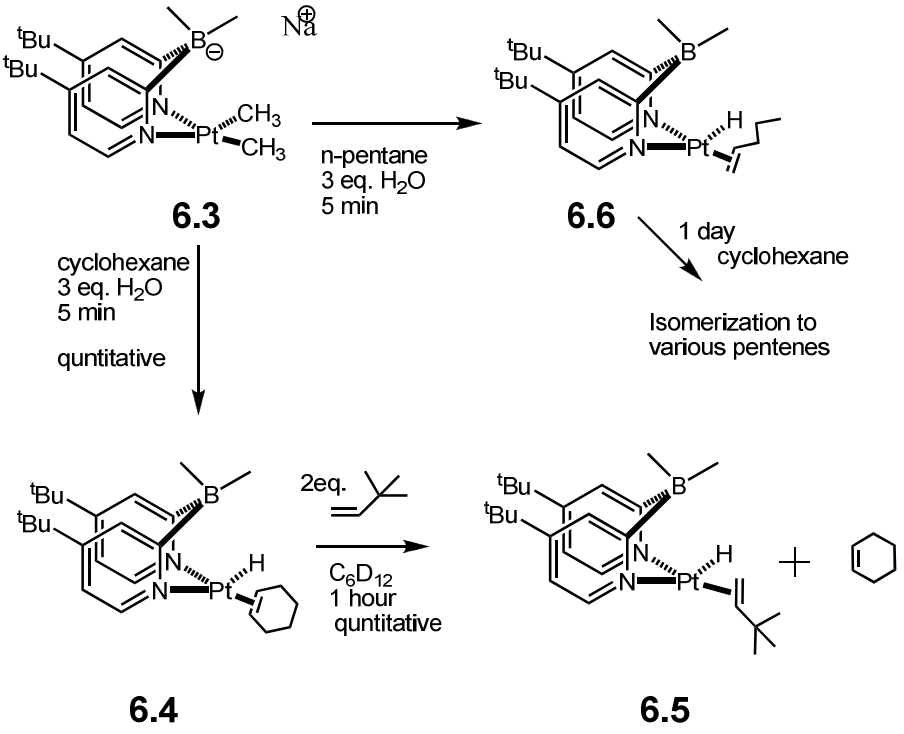
Scheme 6.7 Synthesis of [*t*-Bu-dpbPt^{II}(Me)$_2$][Na]



Complex **6.3** is soluble in alkanes to an appreciable extent (10 mg/ml cyclohexane), unlike **2.3** which did not dissolve in cyclohexane at all. Upon adding a few equivalents of water to cyclohexane mixtures of **6.3**, rapid methane gas evolution was observed. After five minutes, gas evolution had stopped and the solution turned a deeper, yellow color. There was not as much precipitate as in the analogous reaction with **2.3**, suggesting that decomposition was minimal. After filtering the solution through celite, and concentrating under vacuum, cyclohexene hydride complex **6.4** was obtained in quantitative yield (Scheme 6.8). The olefinic protons are present at 4.92 ppm in the NMR spectrum, close to the value of free cyclohexene in deuterated acetone (5.6ppm). This suggests that the olefin may be weakly bound and susceptible to substitution. Indeed, adding an equivalent of TBE cleanly displaced cyclohexene and formed the associated TBE complex, **6.5** (Scheme 6.8). This was the reaction that

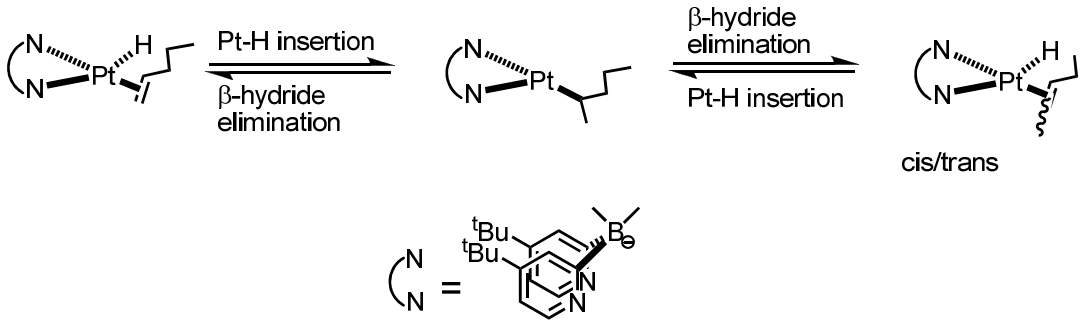
could not be accomplished by diketiminate complexes and suggested that transfer dehydrogenation may be possible in our system.

Scheme 6.8 Stoichiometric alkane dehydrogenation and subsequent alkene substitution in dtBudpb supported Pt^{II} complex



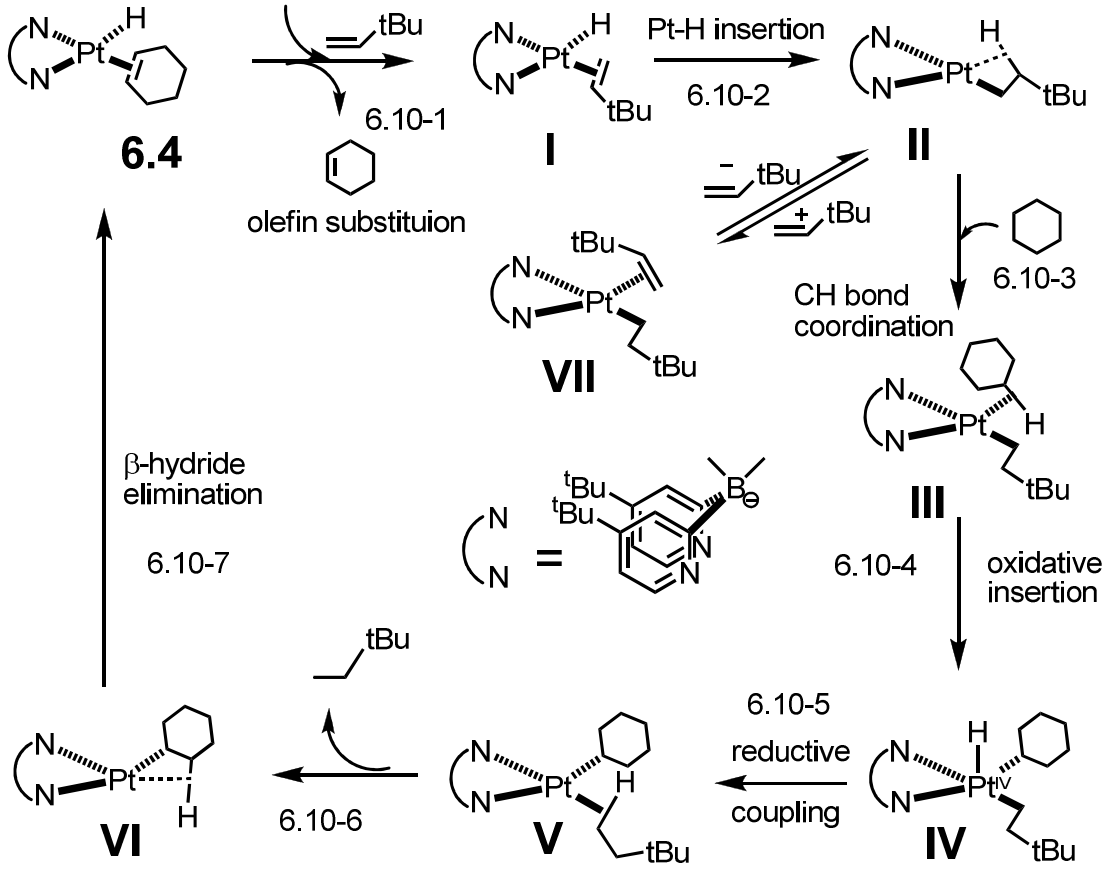
Complex **6.6** also showed evidence of chain walking (Scheme 6.9), suggesting that rapid enough insertion of olefin into the Pt-H bond could occur even at room temperature. Bercaw and Labinger observed this phenomenon in the activation of linear alkanes by diketimine supported Pt^{II} complexes.[30] They were not only able to isolate internal olefins from reaction mixtures, but were able to infer from deuterium labeling studies that initial activation took place at the terminal carbon. When activating n-pentane with **6.3** and leaving the mixture to stir for half an hour, we observed a mixture of various hydrides that we assumed were various cis/trans and regio isomers.

Scheme 6.9 Mechanism of 1-pentene isomerization via olefin 'chain-walking'



Due to the multitude of products, it was difficult to analyze the aromatic region and the hydride region proved the most informative. However, if the reaction was quickly filtered less than 5 minutes after addition of H_2O and rapidly dried under high vacuum, we were able to observe only one hydride signal (complex **6.6**), that we assumed was the product of primary CH bond activation. Leaving the complex in cyclo-C_6D_{12} over a period of a few days, led to isomerization and the reemergence of a similar hydride pattern, that was seen in the reaction that was left to stir in n-pentane for half an hour. Since ability to form a three-coordinate intermediate after olefin insertion was considered crucial in our proposed mechanism (Scheme 6.10), we decided that **6.4**-**6.6** had a very good chance to be active catalysts for transfer dehydrogenation and we decided to settle on **6.4** as our catalyst of choice as it was the most easily obtained complex with a simple NMR pattern.

Scheme 6.10 Proposed mechanism of catalytic transfer dehydrogenation with tBudpbPt^{II} cyclohexene hydride complex



6.2.2 Catalytic transfer dehydrogenation and evaluation of alternative sacrificial olefins

Indeed, preliminary results with TBE as the sacrificial olefin, cyclohexane as the solvent, showed that catalysis was already possible even at 60^{o}C, although the TON number was limited to 2-3 even after long reaction times. We eventually settled on the optimum temperature of 100^{o}C for the reaction, which gave the most TONs, but resulted in a fast decomposition of the catalyst complex towards undetermined organometallic species after 1 day. Analysis of the dark yellow residues revealed a mixture of complexes as determined by the multitude of aromatic signals and the disappearance of all hydride signals. Stopping the catalytic reaction after 6 hours

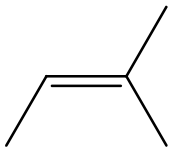
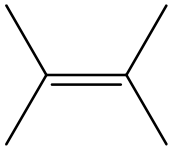
revealed that only a little starting complex remained with regard to aromatic signals, and that a new small hydride signal at -17 ppm was evident that had coupling of ~560Hz. We are unsure of the nature of this complex, but based on reports with other metal dihydrides,[31] we suggest that this may be a Pt^{IV} dihydride that undergoes further decomposition. No Pt black was observed to form during the reaction.

Based on the mechanism in Scheme 6.10, we reasoned that we may be able to improve the outcome of the catalytic reaction by increasing the rate of 6.10-2 and 6.10-5. Since 6.10-1 occurs very readily a bulkier olefin should be able to accomplish this reaction as well. Insertion and reductive coupling in the 6.10-2 and 6.10-5 will be driven by relieving steric strain with a disubstituted or trisubstituted sacrificial olefin. Steric strain may also prevent sacrificial olefin binding to intermediate **II**, which could be a significant alternative reaction route that lowers the overall rate of reaction by forming stable intermediate **VII**. This same reasoning would increase the barrier for reactions 6.10-1 and 6.10-3, but the overall outcome will be based on which of the steps is rate determining and the thermodynamic stability of intermediate **VII**. Certainly, **VII** is believed to play a large role since the optimum TONs were found when only 20 equivalents of TBE (5% catalyst) were used. Larger amounts of TBE led to lower TONs, with the reaction being completely suppressed when 100 equivalents of TBE were used; lower amounts of TBE limited maximum (and overall) TON to the maximum amounts of TBE utilized. We attempted to use trimethyl and tetramethyl ethylene as bulkier olefins. Thermodynamically, the transfer of hydrogen from cyclohexane to these two olefins is favorable. However, we were unable to observe clear cut cases of catalysis with the latter olefin. Trimethylethylene gave

lower TONs than TBE as sacrificial olefin, and clear isomerization to the terminal olefin position (towards 3-methyl-1-butene) was evident in a large part of the remaining unreacted olefin.

The most remarkable conclusion that we could extract from our attempt to utilize alternative sacrificial olefins, was in equilibrium experiments of **6.4** mixed with trimethylethylene and tetramethylethylene. Despite our initial assumption that cyclohexene, being a less bulky disubstituted alkane, would be a much better ligand for Pt than even trimethylethylene, a surprising K_{eq} of 0.36 (average of two experiments) was measured at room temperature. Even more remarkable, was that we could detect by NMR, the tetramethylethylene complex with Pt in the presence of cyclohexene. Although the equilibrium lies far on the cyclohexene complex side, it is possible to clearly observe the Pt-H signal of the new complex (Table 6.1). These results suggest that sterics is not a crucial factor in olefin binding to the Pt complex, possibly due to the relaxed steric environment around the metal centre that is supported by the dpb ligand motif. Secondly, these results suggest that reaction 6.10-1 is reversible and may play a larger role in the overall catalytic process; ready olefin substitution in dtBudpb complexes on the other hand, is the feature that enables catalysis in this system and not in the system reported by Goldberg (Scheme 6.4).

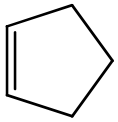
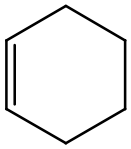
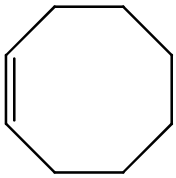
Table 6.1 Equilibrium constants for the reaction of **6.4** with sterically bulky olefins

Olefin	K_{eq}	Hydride shift (δ) and coupling
	3.64e-1	-22.19 ppm J_{PtH}=1312.9Hz
	2.06e-4	-21.89 ppm J_{PtH}=1279.6Hz

Ultimately, the optimal conditions for catalytic transfer dehydrogenation with **6.4** as the catalyst were found to be 1 day of heating at 100^{o}C in a closed Schlenk flask. The amount of cycloalkane utilized was 3 mL in all cases and the amount of TBE sacrificial olefin was 20 equivalents with regard to catalyst amount, 5mg (8.51e-5 mol). Unlike previous reports by Goldman and Templeton, the amount of olefin produced was quantified via ^{1}H NMR and not by GC/MS. Accurate measurements were obtained by adding an external standard (10 eq of mesitylene or anisole) after completion of reaction and dissolving a sample of the reaction mixture in $CDCl_3$. Table 6.2 contains a summary of the optimized results and TONs for three different cyclic olefins – products of dehydrogenation of respective cycloalkanes. The numbers are an average of two good runs and the catalysis is reproducible in every single case. There is discrepancy between conversion and TON for cyclopentane substrate. The

conversion represents equivalents of TBA produced, and the latter the equivalents of cycloolefin formed. Although relaxation delay was taken into account when calculating both numbers, the discrepancy may be due to experimental error when measuring effects of T_1 relaxation on free cyclohexene and the assumption made that this would be the same for cyclopentene and cyclooctene.

Table 6.2 Conversion of *tert*-butylethene, TON and yield of products of catalytic transfer dehydrogenation, TON with 5% **6.4** after 24h. at 100°C

Product	Conversion	TON
	11	6.6
	15	13[a]
	7.5	8

a. For cyclohexene, 2 protons were subtracted from the product to account for 1 equivalent formed from the release of cyclohexene from the catalyst. In other cases, free cyclohexene was observed.

It is surprising that the least strained cycloalkane is most reactive towards transfer dehydrogenation and for now, we do not have a satisfactory explanation of this selectivity, except to note that the reaction outcome probably depends more on the

energetics of the CH bond being cleaved (6.10-4; Scheme 6.10) than on the ring strain of the parent alkane. This would suggest that linear alkanes with easily accessible primary CH bonds would give better results. However, initial transfer dehydrogenation results are inconclusive since the method of analysis (^{1}H NMR) does not lend itself well towards separating and quantifying large numbers of alkane isomers. Another possibility is the stability of the resulting olefin hydrides toward ligand substittion (step 6.10-1): more strained olefins (cyclopentene, *cis*-cyclooctene) are known to be better ligands for Pt, compared to unstrained cyclohexene, and therefore, less prone to substitution by TBE. At 100^{o}C however, substitution by TBE is expected to be rapid for all disubsituted cyclic substrates. In the future, we plan to carry out transfer dehydrogenation of relatively simple *n*-alkanes such as pentane, and will quantify the results via GC/MS. Acceptorless dehydrogenation will also be attempted.

6.3 Summary

In conclusion, we were able to show the first, unambiguous case of alkane transfer dehydrogenation that could be carried out with a group 10 metal acting as the homogenous catalyst: complex **6.4**. The catalyst decomposes after 1 day of reaction time, but only towards organometallic products. We could not identify any of the decomposition products or prove if they are catalytically active. However, based on earlier reports regarding the mechanism of transfer dehydrogenation, we propose the mechanism outlined in Scheme 6.10 as the one that is active in our system. We were able to demonstrate equilibrium between Pt bound and free olefins in solution and

suggest that the existence of this equilibrium even with sterically hindered olefins plays a large role in the overall catalytic success of the system.

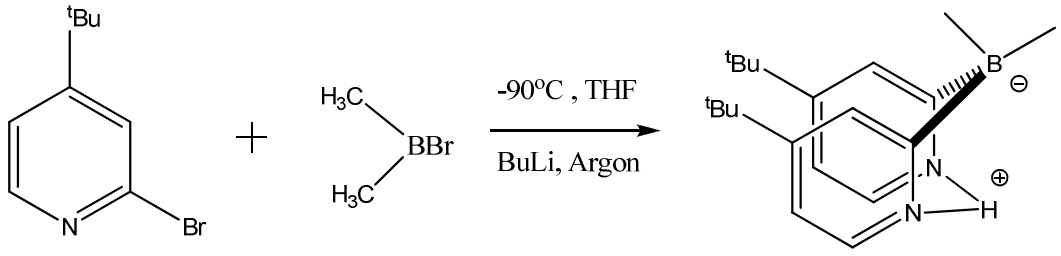
An advantage of our system is that slightly lower temperatures can be used for the reaction than those used with group 9 catalysts by the Goldman group. Indeed, our system is already active at 80°C while Goldman's Ir systems need an operating temperature of at least 120°C. This may lead to more effective alkane metathesis catalysts since the main drawback of the tandem alkane metathesis system (Ir alkane dehydrogenation / Mo olefin metathesis) reported by Goldman[13] was the instability of the olefin metathesis catalyst at the high temperatures ($\geq$120°C) required for catalysis. Operational temperatures also have to be lowered if olefins are to be seriously considered as repositories for hydrogen gas storage.

Although the number of TONs is limited in our system, the case for catalysis is unambiguous;[26] these first results point towards including group 10 metals in the toolkit of the very promising alkane dehydrogenation reaction.

6.4 Experimental

6.4.1 Synthesis of ligands and complexes

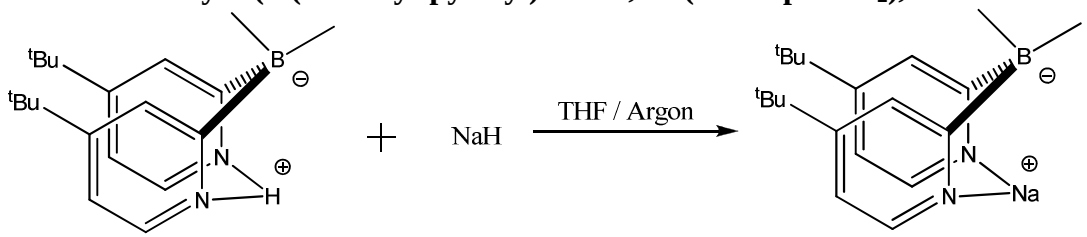
Hydrogen dimethyldi(2-(4-*t*-butyl-pyridyl)borate, H(dt-Bu-p-BMe$_2$), 6.1



The known compound, 2-bromo-4-*t*-butyl-pyridine, was prepared via Chichibabin amination[32] of 4-*t*-butyl-pyridine followed by its subsequent bromination following the method of Adams and Miyano[33]. After amine purification via column chromatography or recrystallization, bromination usually affords pure product via the published procedure (>95%), and no further purification is required. Pure (by ^{1}H NMR) 2-bromo-4-*t*-butyl-pyridine is a dark red solid/liquid dual phase mixture at room temperature. The procedure for the preparation of **6.1** is similar to the published procedure of Hodgkins[34]. 9.60 grams (4.48e-2 mol) of the Bromide were put into a flame dried flask under an argon atmosphere and 150 mL of dry diethyl ether were added. The temperature was lowered to -90 ^{o}C and 17.9 mL of 2.5 M solution of BuLi (4.48e-2 mol) were added dropwise with vigorous stirring. The temperature was allowed to slowly rise to -80 ^{o}C over the span of the next half an hour. Raising the temperature further usually results in the decomposition of the metalated pyridine and subsequent lower yields. After half an hour, the temperature was again lowered to -90 ^{o}C and 2.19 mL of dimethylboronbromide (2.24e-2 mol) were added dropwise to the solution, which took on a dark black color. The reaction was continued for a further 18 hours, during which time it was allowed to come to room temperature. It was quenched with water and the organic layer washed with 2x100 mL of 1M Acetic acid. To the aqueous washings, 100 mL. of 6M NaOH were added and a black solid formed at the top of the liquid after a few hours. The black solid was collected and washed with cold water, then recrystallized from hexane, to obtain 1.40g. of **6.1** (10.1% yield).

^{1}H NMR (22^{o}C, acetone-d_6, 400MHz), δ: 14.31 (bs, 1H), 8.45 (d, J=5.92Hz, 2H), 7.79 (s, 2H), 7.26 (dd, J=5.92, 2.17Hz, 2H), 1.35 (s, 18H), 0.05 (bs, 6H).
^{13}C NMR (22^{o}C, acetone-d_6, 400MHz), δ: 191.7 (quartet, $J_{C\text{-}B}$=47.2Hz), 161.2, 141.5, 125.8, 117.4, 35.7, 30.8, 14.65 (quartet, $J_{C\text{-}B}$=40.85 Hz).
Anal. Calcd. for $C_{20}H_{31}BN_2$: C, 77.42; H, 10.07; N, 9.03. Found: C, 77.42; H, 10.36; N, 9.11.

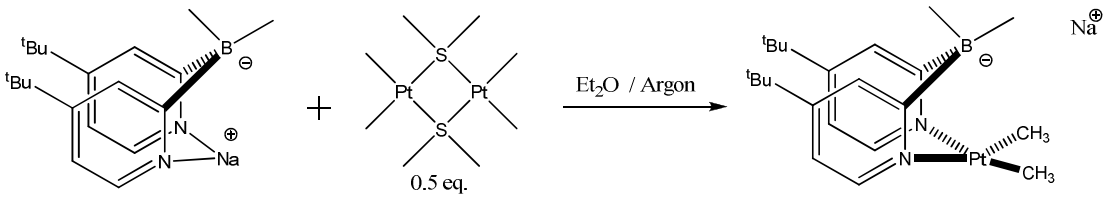
Sodium dimethyldi(2-(4-*t*-butyl-pyridyl)borate, Na(d-t-Bup-BMe$_2$), 6.2



100 mg. of H(d^{t}Bup-BMe$_2$), **6.1** (3.22e-4 mol), was dissolved in 3-4mL. of THF in a small vial in the glove box and 50 mg. of dry NaH (3.5x excess) was added slowly accompanied by vigorous evolution of hydrogen gas. The reaction was allowed to stir overnight, after which time it was filtered through celite and washed two times with 1mL. of THF. The solution was dried under high vacuum and washed two times with a minimum amount of benzene. After the washings, the remaining solids were once again dried under high vaccum to give 61.2 mg. of **6.2** as a flaky, white solid (57.2% yield). The benzene washings can be omitted to obtain, yellowish **6.2** in quantitative yield that is >95% pure. The product is highly hydrolysable and thus should be stored and used under an inert atmosphere.

^{1}H NMR (22^{o}C, THF-d_8, 500MHz), δ: 8.19 (d, J=5.5Hz, 2H), 7.59 (s, 2H), 6.69 (d, J=5.5Hz, 2H), 1.24 (s, 18H), 0.42 (bs, 6H).
^{13}C NMR (22^{o}C, THF-d_8, 125MHz), δ: 194.06 (quartet, $J_{C\text{-}B}$=50.7Hz), 155.65, 147.52, 123.61, 114.62, 35.02, 31.26, 13.56 (quartet, $J_{C\text{-}B}$=42.3Hz).
Anal. Calcd. for $C_{20}H_{30}BN_2Na$: C, 72.30; H, 9.10; N, 8.43. Found: C, 72.05; H, 9.39; N, 7.99.

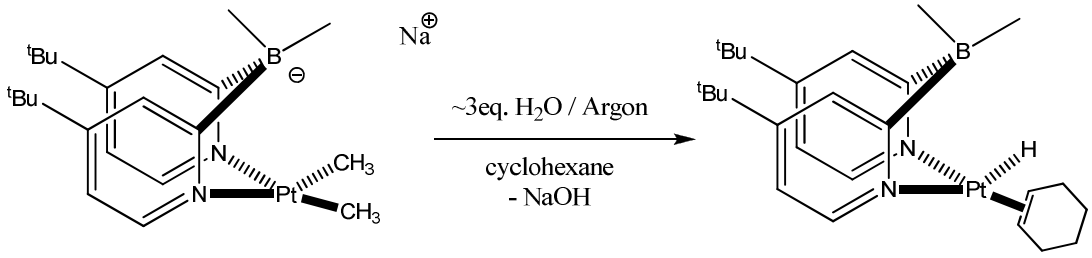
Sodium dimethyldi(2-(4-*t*-butyl-pyridyl)boratodimethylplatinate(II), Na(d-t-Bup-BMe$_2$)PtMe$_2$, 6.3



100 mg of **6.2** (3.01e-4 mol), and 86.5 mg of Platinum dimethyl precursor (1.50e-4 mol) were added to a vial inside the glove box containing 4 mL of diethyl ether. The reaction mixture was stirred overnight, then dried for under high vacuum, washed with heptanes and further dried under high vacuum 12 hours to obtain **6.3** (163.7 mg; 99.0% yield) as an air sensitive white solid.

^{1}H NMR (22^{o}C, THF-d$_8$, 500MHz), δ: 8.52 (d, J_{H-H}=6.3Hz, J_{Pt-H}=22.0Hz, 2H), 7.58 (d, J_{H-H}=2.4Hz, 2H), 6.71 (dd, J_{H-H}=6.3, 2.4Hz, 2H), 1.25 (s, 18H), 0.46 (bs, 6H), 0.24-0.46 (bs, 6H).
^{13}C NMR (22^{o}C, THF-d$_8$, 125MHz), δ: 189.15 (quartet, J_{C-B}=51.8Hz), 155.40, 149.54, 124.60, 116.74 (J_{Pt-C}=24.5Hz), 35.18, 30.96, 13.0-15.0 (bs), -20.61 (J_{Pt-C}=768.0Hz).
Anal. Calcd. for $C_{22}H_{36}BN_2NaPt$: C, 47.40; H, 6.51; N, 5.03. Found: C, 47.46; H, 6.94; N, 4.85.

Cyclohexene hydrido dimethyldi(2-(4-*t*-butyl-pyridyl)boratoplatinum(II), (d-*t*-Bup-BMe$_2$)PtH(*cyclo*-C$_6$H$_{10}$), 6.4

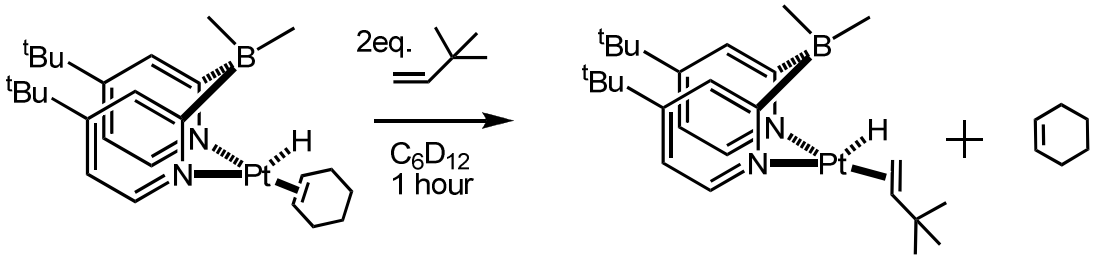


40.2 mg. of **3** (7.21e-5 mol) was added to a reaction vial in the glove box and 4 mL of cyclohexane were added to the vial and the contents stirred vigorously. Most of the

dimethyl complex dissolved, with the rest forming a fine, light-yellow suspension. 5 µL of H_2O Were added to the solution, after which a vigorous evolution of methane gas occurred. The suspension became a clear, yellow liquid with large particulates after five minutes. After half an hour, the contents of the vial were filtered through celite and washed two times with 1mL of cyclohexane. The clear, yellow liquid was dried overnight under high vacuum to obtain **6.4** (42.0 mg, quantitative yield).

^{1}H NMR (22^{o}C, acetone-d_6, 400MHz), δ: 8.68 (d, J_{H-H}=6.16Hz; J_{Pt-H}=61.18Hz, 1H), 8.06 (d, J_{H-H}=6.06Hz; J_{Pt-H}=23.8Hz, 1H), 7.73 (bs, 2H), 7.06 (dd, J_{H-H}=6.16, 2.33Hz, 1H), 6.96 (dd, J_{H-H}=6.16, 2.33 Hz,1H), 4.92 (bs, J_{Pt-H}=71.69Hz, 2H), 2.40-2.62 (bm, 4H), 1.73-1.84 (bm, 2H), 1.38-1.29 (bm, 2H), 1.26 (s, 9H), 1.25 (s, 9H), 0.46 (bs, 6H), -21.27 (s, J_{Pt-H}=1269.35Hz, 1H).
Anal. Calcd. for $C_{26}H_{41}BN_2Pt$: C, 53.15; H, 7.03; N, 4.77. Found: C, 53.47; H, 7.17; N, 4.71.

***t*-Butylethene hydrido dimethyldi(2-(4-*t*-butyl-pyridyl)boratoplatinum(II), (d-*t*-Bup-BMe_2)PtH(*TBE*-C_6H_{12}), 6.5**

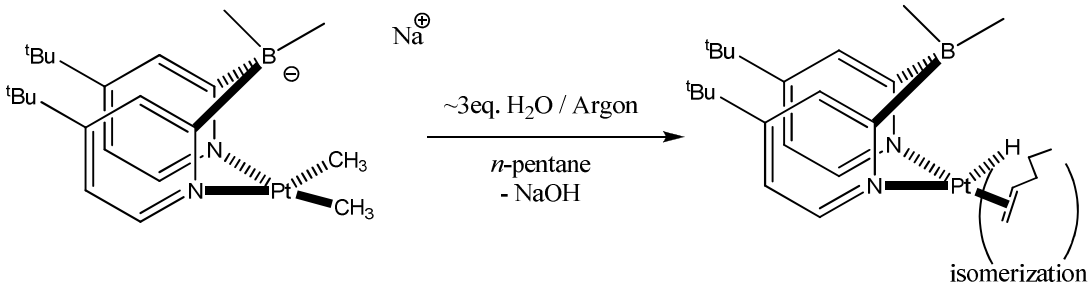


Complex **6.4** (5.0 mg, 8.5e-5 mmol) was dissolved in 0.5 mL of deuterated cyclohexane in a Young tube under Argon and 2 eq. of TBE (2.3 µL) were added to ensure an excess of TBE. Although the reaction was relatively slow at room temperature and both the starting material and the product could be observed even half an hour after mixing at room temperature, complete olefin exchange took place 90 minutes after addition.

^{1}H NMR (22^{o}C, C_6D_{12}), δ: 8.58 (d, J_{H-H}=6.1Hz; J_{Pt-H}=56.7Hz, 1H), 7.86 (bd, J_{H-H}=6.1Hz, 1H), 7.81 (bs, 2H), 6.82 (m, 1H), 6.70 (m,1H), 4.32 (dd, J_{H-H}=13.5, 8.2Hz; J_{Pt-H}=66.5Hz, 1H), 3.64 (d, J_{H-H}=13.5Hz; J_{Pt-H}=60.4Hz, 1H), 3.47 (d, J_{H-H}=8.2Hz; J_{Pt-H}=61.4Hz, 1H), 1.26 (s, 9H overlapping), 1.20 (s, 9H), 1.00 (s, 9H), 0.43-0.46 (bd, 6H), -21.82 (s, J_{Pt-H}=1151.0Hz, 1H).

6.4.2 Dehydrogenation and catalytic experiments

***n*-Pentane dehydrogenation experiment with 6.3**



The reaction with n-pentane was performed in the same manner as with the formation of complex **6.4** detailed above. However, a clean, single complex was not formed when stopping the reaction after half an hour, giving rise to a complex spectrum and a number of Pt hydride signals. When the reaction was stopped after 5 minutes, a single major hydride could be observed while the aliphatic and aromatic region still exhibited considerable complexity. A single complex tentatively assigned as 1-pentene bound complex could be assigned as the major species. The metal hydride signal appears at -20.98 as the major hydride with J_{Pt-H}=1189.0 Hz at ~90%. Thereafter, the complex was observed by ^{1}HNMR every three days.

^{1}H NMR (22^{o}C, C_6D_6), δ: 8.73 (d, J_{H-H}=6.7Hz, 1H), 8.20-8.25 (m, 2H), 7.72-7.80 (m, 1H), 6.61 (m, 1H), 6.41 (m,1H), 3.90-4.20 (m, 2H), 3.62 (d, J_{H-H}=7.7Hz; J_{Pt-H}=71.2Hz, 1H), 2.44 (m, J_{Pt-H}=88.1Hz, 1H), 1.09 (s, 9H overlapping), 1.00 (s, 9H, overlapping), -20.98 (s, J_{Pt-H}=1189.0Hz, 1H).
Not all NMR signals could be assigned due to large overlap of signals in the aliphatic region and some isomerization that had already taken place. See spectrum (Figure E2) below.

Transfer dehydrogenation experiments with 6.4 as catalyst; sample procedure for cyclohexane dehydrogenation.

In a 50 mL Schlenk flask under an inert atmosphere, 5.0 mg of **6.4** (8.5e-5 mol) were added to 3mL of cyclohexane. 23 µL of 3,3-dimethylbutene (1.7e-4 mol, 20eq.) were then added and the flask sealed. The contents were heated in an oil bath at 100^{o}C for 24 hours, after which time the flask was opened, 10 equivalents of mesytilene internal standard were added, and an NMR spectrum was obtained in $CDCl_3$ or acetone-d_6. Conversion was based on the integration of remaining 3,3-dimethylbutene and TON is based on the signals of olefinic protons of the cycloalkene formed. Since these signals were found to be underestimated by a factor of 2 in a spectrum of cyclohexene with standard at a delay time of two seconds, they are multiplied by 2. This also results in a better agreement with the conversion number. The runs were found to give catalytic turnover at least three times for each olefin; results summarized in the table are an average of 2 best runs. A large excess of sacrificial olefin was found to be detrimental for the reaction. For example, 100 eq. of 3,3-dimethylbutene gave no catalysis with the same amount of substrate and catalyst.

An experiment was set up to determine the fate of the catalyst. After 24 hours of reaction at 100 ^{o}C, all the volatiles were removed under high vacuum, and the resulting dark orange solid was dissolved in acetone-d_6 and an NMR spectrum was taken. A large number of complex decomposition products, many of them still containing Pt (as evidenced by Pt-H pyridine ortho couplings), and one hydride peak at ~-17ppm were observed. The presumed catalyst, or catalytic precursor, does not survive under the reaction conditions. This explains why higher yields were not observed, when the reaction was stopped after >24 hours.

6.4.3 Equilibrium constant measurements

Equilibrium constants measurements with 2methyl-2-butene and tetramethylethylene.

6.6 mg of **6.4** (1.1e-5 mol) were added to a Teflon valve NMR tube in the glove box and dissolved in acetone-d_6. 5 Equivalents of 2-methyl-2-butene were added to the NMR tube, after which it was sealed. The system comes to equilibrium after two days, after which the Keq was measured. It is reported here as an average of two runs. For tetramethylethylene, 10 equivalents of olefin were used.

In transfer dehydrogenation reactions with cyclohexane as substrate, no catalytic (tetramethylethylene), or poor in the case of 2-methyl-2-butene (~2eq.), turnover was observed when using 20 equivalents of these olefins. Minor isomerization of free olefin to 1-butenes was also observed at the end of these reactions. Measuring accurate Keq for the disubstituted olefin, 2-butene, was problematic since it is a gas at room temperature. It was also not active in catalytic transfer dehydrogenation (~100 equivalents).

6.4.3 ^{1}HNMR spectra

Figure 6.1 ^{1}HNMR spectrum of Cyclohexene hydrido dimethyldi(2-(4tertbutyl-pyridyl)boratoplatinum(II), (d^{t}Bup-BMe_2)PtH(*cyclo*-C_6H_{10}) (6.4) in acetone-d_6

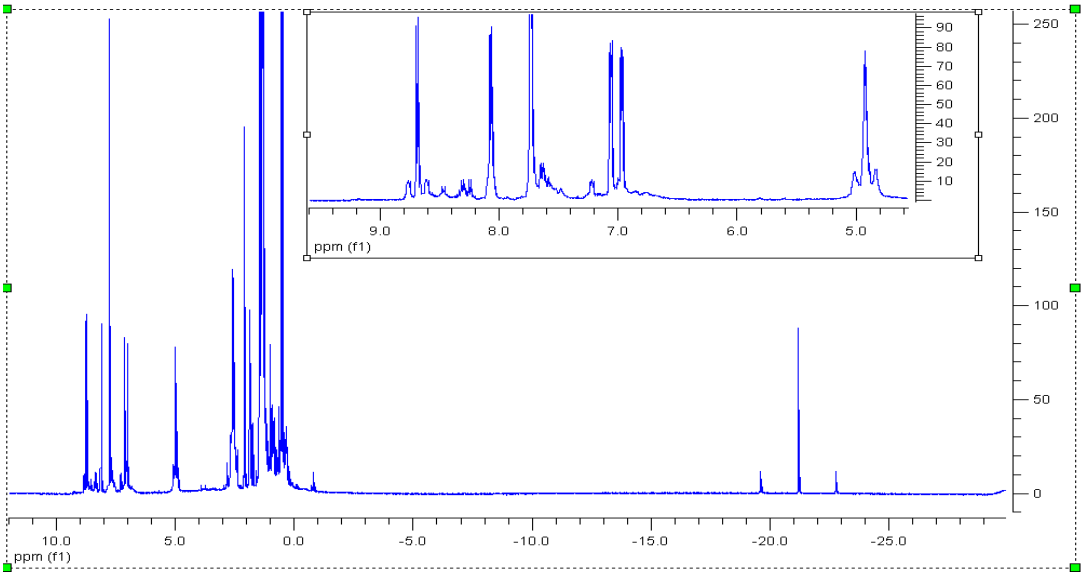
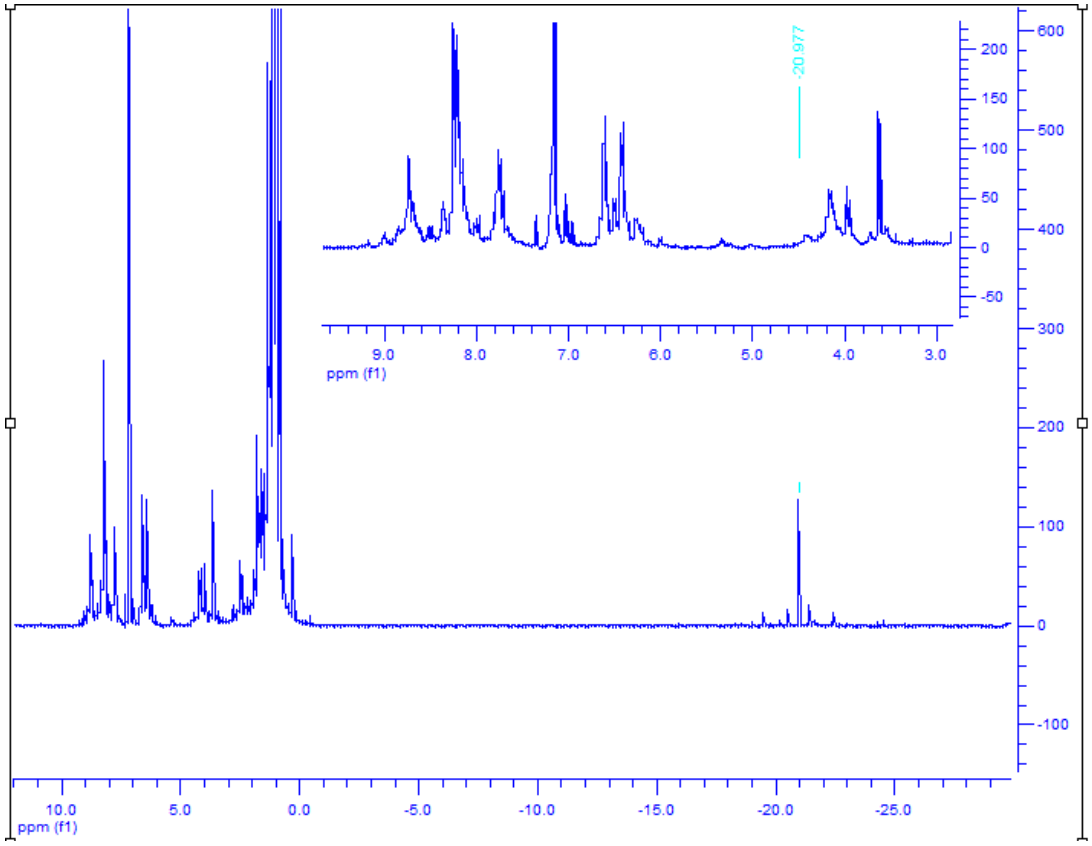


Figure 6.2 Spectrum of presumed 1-pentene Pt-H complex when quenching the reaction after a short time.



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Appendix

General Specifications

All manipulations were carried out under purified argon using standard Schlenk and glove box techniques. All reagents for which synthesis is not given are commercially available from Aldrich, Acros, or Alfa-Aesar and were used as received without further purification. Tetramethylbis(dimethylsulfide)diplatinum(II) ($Pt(CH_3)_2(SMe_2)]_2$) complex[1] was synthesized according to published procedure. Water was deaerated by repeating freezing – pumping cycles and stored under argon in a Teflon-sealed Schlenk flask in a glove box. Tetrahydrofuran-d_8, cyclohexane-d_{12} from Cambridge Isotope Laboratories were dried with $LiAlH_4$ or CaH_2, vacuum-transferred and stored in Teflon-sealed flasks in an argon-filled glove box. Labelled methyl iodide ($^{13}CH_3I$) was also obtained from Cambridge Isotope Laboratories; it was dearated via repeating freezing – pumping cycles and stored inside the glove box freezer at -23^oC over a copper wire. ^1H (400.132 MHz) and ^{13}C NMR (100.625 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. NMR experiments were carried out in NMR tubes fitted with Teflon stopcocks (J. Young tubes). Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. Elemental analyses were carried out by Chemisar Laboratories Inc., Guelph, Canada.

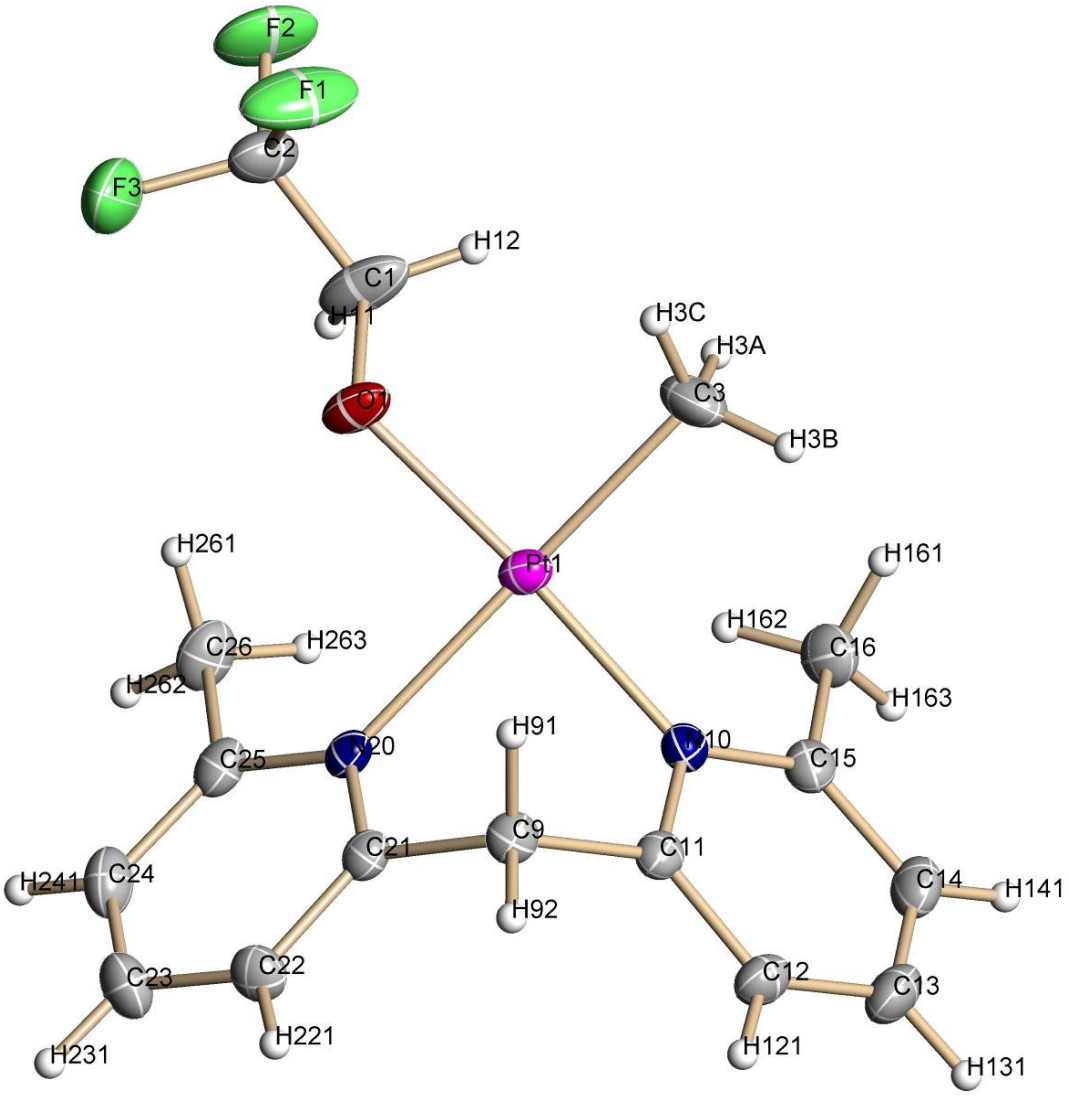
Computational details

Theoretical calculations in this work have been performed using density functional theory (DFT) method,[2] specifically functional PBE,[3] implemented in an original program package "Priroda".[4,5] In PBE calculations relativistic Stevens-Basch-Krauss (SBK) effective core potentials (ECP)[6] optimized for DFT-calculations have been used. Basis set was 311-split for main group elements with one additional polarization p-function for hydrogen, additional two polarization d-functions for elements of higher periods. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation frequency analysis has been carried out. All minima have been checked for the absence of imaginary frequencies. All transition states possessed just one imaginary frequency.

Computational work in Chapters 2-4 and the Appendix was performed by Dr. Andrei Vedernikov and computations in Chapter 1 were performed by Eugene Khaskin and Dr. Andrei Vedernikov.

X-Ray Structure Determination for Complex ***1.3***

Figure A1 A view of $(CF_3CH_2O)(CH_3)Pt(dpy)$ showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.



A colorless needle of $C_{16}H_{19}F_3N_2OPt$, approximate dimensions 0.11 × 0.22 × 0.44 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 223(2) K on a three-circle diffractometer system equipped with Bruker Smart1000 CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å) operated at 50 kV and 40 mA. The detector was placed at a distance of 4.958 cm from the crystal.

A total of 1045 frames were collected with a scan width of 0.3° in ω and an exposure time of 13 sec/frame using SMART.[7] The total data collection time was 5.85 hours. The frames were integrated with SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 8142 reflections to a maximum θ angle of 27.50°, of which 3759 were independent (completeness = 97.2%, R_{int} = 2.57%, R_{sig} = 3.17%) and 3229 were greater than 2σ(I). The final cell dimensions of *a* = 8.1907(13) Å, *b* = 10.7192(17) Å, *c* = 19.390(3) Å, α= 90°, β= 98.623(3)°, γ= 90°, *V* = 1683.1(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 5370 reflections with 2.1 < θ < 29.0° using SAINT. Analysis of the data showed 0.00 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS.[8] The minimum and maximum transmission coefficients were 0.113 and 0.398.

The structure was solved and refined using the SHELXS-97 [9] and SHELXL-97 [10] software in the space group $P2_1/n$ with $Z = 4$ for the formula unit $C_{16}H_{19}F_3N_2OPt$. The final anisotropic full-matrix least-squares refinement on F^2 with 268 variables converged at R_1 = 2.45 % for the observed data and wR_2 = 6.71 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 1.802 $\bar{e}/Å^3$ and the largest hole was -1.478 $\bar{e}/Å^3$. On the basis of the final model, the calculated density was 2.002 g/cm^3 and F(000), 968 $\bar{e}$.

Table A1 Bond lengths (Å), $(CF_3CH_2O)(CH_3)Pt(dpy)$.

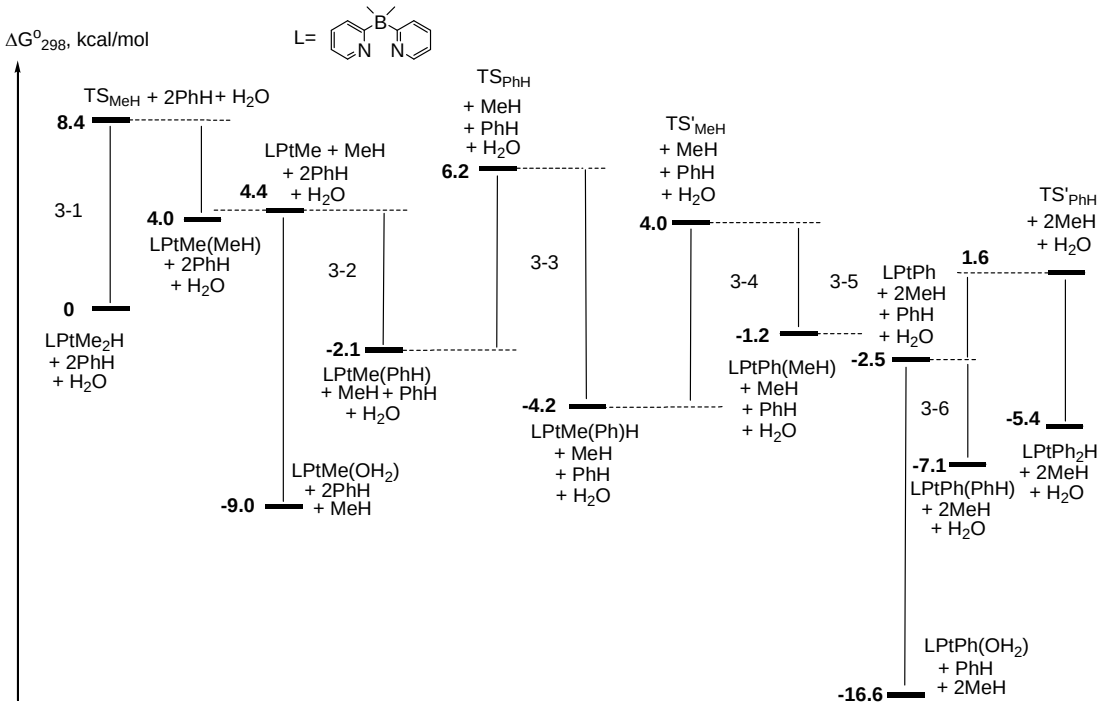
Pt1-O1	1.999(3)	Pt1-N10	2.016(3)
C9-C11	1.505(5)	C9-C21	1.511(5)
C11-C12	1.387(5)	C12-C13	1.371(6)
C15-C16	1.487(6)	N20-C21	1.343(5)
C22-C23	1.385(6)	C23-C24	1.378(6)
O1-C1	1.396(6)	C1-C2	1.459(8)
C2-F2	1.355(7)	C1A-C2A	1.462(11)
C2A-F2A	1.352(10)	O1-Pt1-N10	174.97(12)
Pt1-C3	2.048(5)	Pt1-N20	2.155(3)
N10-C11	1.355(5)	N10-C15	1.360(5)
C13-C14	1.371(7)	C14-C15	1.384(5)
N20-C25	1.366(5)	C21-C22	1.381(5)
C24-C25	1.378(6)	C25-C26	1.500(6)
C2-F1	1.291(8)	C2-F3	1.327(8)
C2A-F1A	1.291(11)	C2A-F3A	1.326(12)

Chapter 2

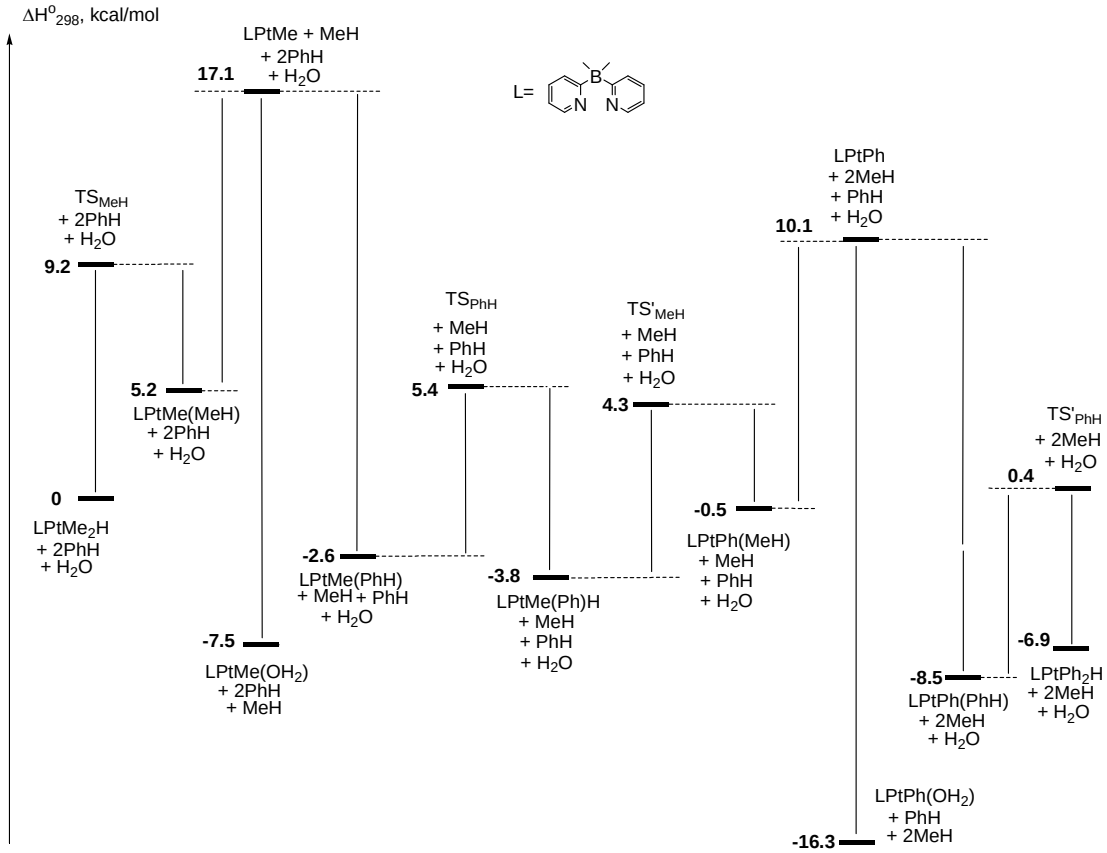
DFT-calculated structures of $LPtMe_2H$, $LPtMe(CH_4)$, $LPtMe(OH_2)$, LPtMe, $LPtMe(\eta^2\text{-}C_6H_6)$, LPtMe(Ph)H, LPtPh(MeH), LPtPh, $LPtPh(OH_2)$, $LPtPh_2H$, $LPtPh_2^-$, $LPtPh(OH)^-$ and the transitions states for the reductive coupling of $LPtMe_2H$, LPtMe(Ph)H, and $LPtPh_2H$

More complete Schemes representing the DFT-calculated mechanism of $LPtMe_2H$ to $LPtPh_2H$ transformation are given below:

Scheme A1



Scheme A2

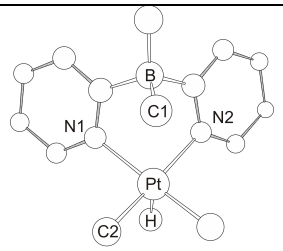
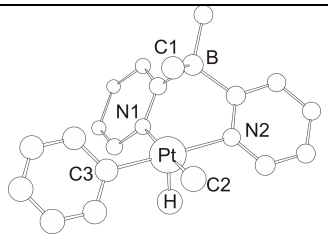
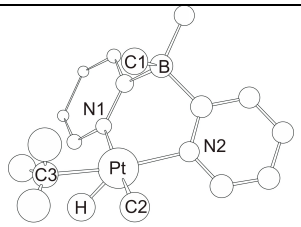
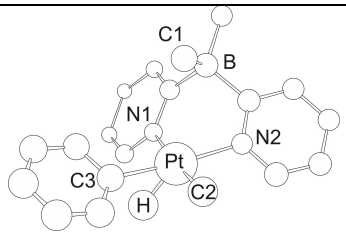
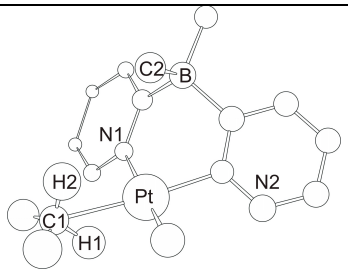
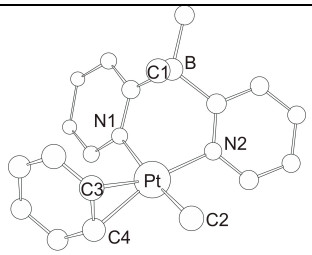


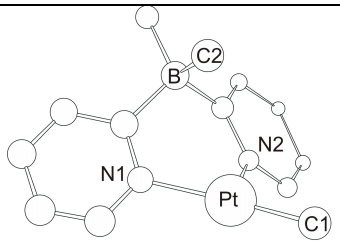
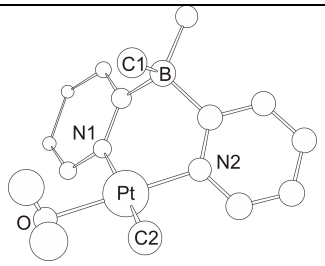
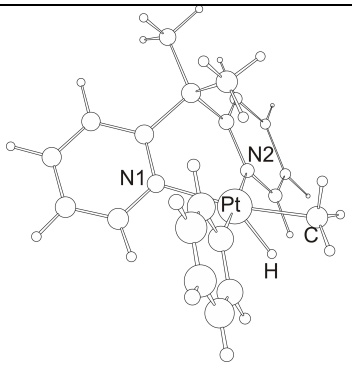
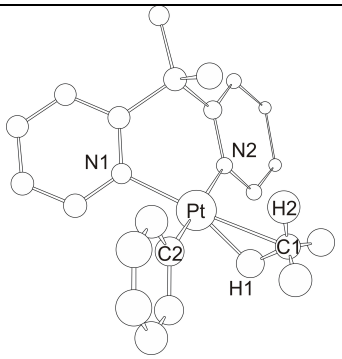
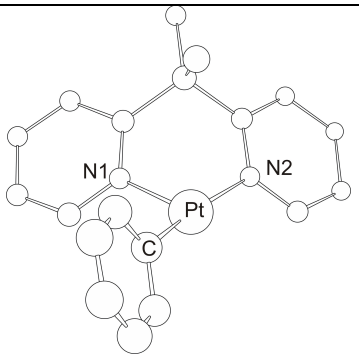
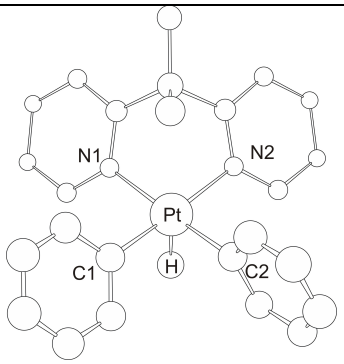
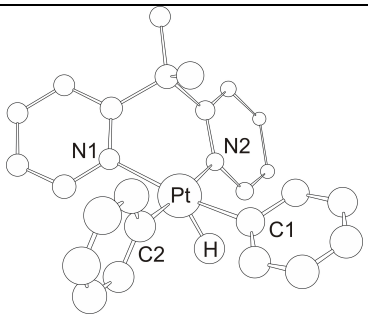
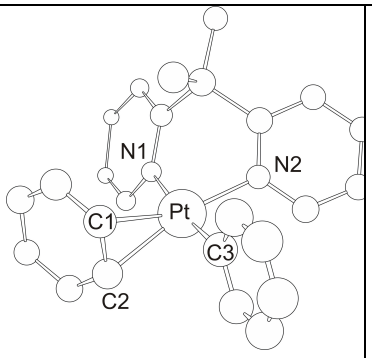
An attempt to locate a transition state corresponding to an <u>associative</u> MeH for PhH substitution failed.

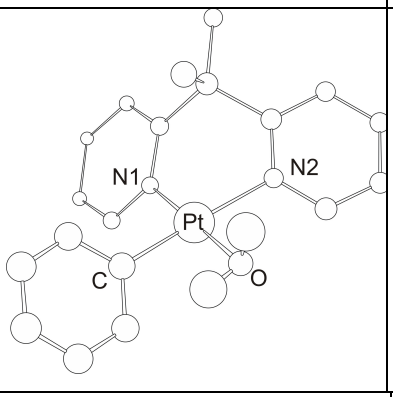
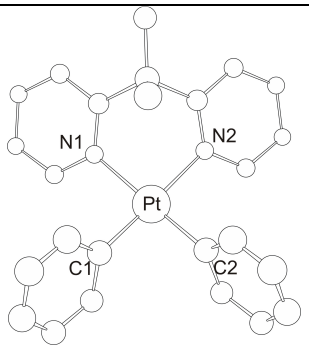
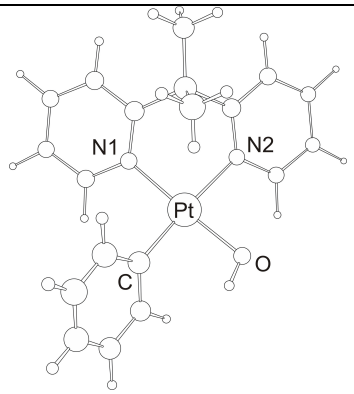
Since the basicity of $LPtR(R')^-$ is expected to decrease in the row of, R': Me,Me > Me,Ph > Ph,Ph, actually, loss of the second mole of methane does not occur faster than of the first one.

This reduced basicity adds to the relative stabilization of $LPtR(R')^-$ and an effective increase of barriers of C-H reductive elimination.

DFT optimized structures with selected distances (Å) and reaction standard Gibbs energies (kcal/mol, 298K) are given below. Most hydrogen atoms are omitted for clarity.

2PhH + (dp-BMe$_2$)PtMe$_2$H (0)		**MeH + PhH + (dp-BMe$_2$)PtMe(Ph)H (-4.2)**	
Pt-H, 1.538 Pt-C1, 2.740 Pt-B, 3.075 Pt-N1, 2.168 Pt-N2, 2.168 C2-H, 2.469			Pt-H, 1.537 Pt-C1, 2.749 Pt-B, 3.082 Pt-N1, 2.171 Pt-N2, 2.164 Pt-C2, 2.088 Pt-C3, 2.051
2PhH + TS$_{MeH}$ (8.4)		**MeH + PhH + TS$_{PhH}$ (6.2)**	
Pt-H, 1.569 Pt-C1, 3.196 Pt-B, 3.253 Pt-N1, 2.162 Pt-N2, 2.105 Pt-C3, 2.152 C3-H, 1.583			Pt-H, 1.579 Pt-C1, 3.139 Pt-B, 3.243 Pt-N1, 2.173 Pt-N2, 2.118 Pt-C2, 2.084 Pt-C3, 2.104 C3-H, 1.581
2PhH + (dp-BMe$_2$)PtMe(MeH) (4.0)		**MeH + PhH + (dp-BMe$_2$)PtMe(PhH) (-2.1)**	
Pt-H1, 1.822 Pt-H2, 2.316 Pt-C1, 2.397 Pt-C2, 3.325 Pt-B, 3.257 Pt-N1, 2.152 Pt-N2, 2.013 C1-H1, 1.166			Pt-C1, 3.305 Pt-B, 3.259 Pt-N1, 2.168 Pt-N2, 2.062 Pt-C2, 2.082 Pt-C3, 2.259 Pt-C4, 2.304 C3-C4, 1.431

2PhH + MeH + (dp-BMe_2)PtMe (4.4)		**(dp-BMe_2)PtMe(OH_2)**	
Pt-C1, 2.049 Pt-C2, 3.360 Pt-B, 3.264 Pt-N1, 2.132 Pt-N2, 1.968			Pt-C1, 3.358 Pt-B, 3.266 Pt-N1, 2.131 Pt-N2, 1.993 Pt-C2, 2.070 Pt-O, 2.167
MeH + PhH + TS'_{MeH} (4.0)		**MeH + PhH + (dp-BMe_2)PtPh(MeH) (-1.2)**	
Pt-C, 2.152 Pt-H, 1.566 C-H, 1.611 Pt-N1, 2.113 Pt-N2, 2.163			Pt-C1, 2.408 Pt-H1, 1.832 C1-H1, 1.163 Pt-N1, 2.020 Pt-N2, 2.150
2MeH + PhH + (dp-BMe_2)PtPh (-2.5)		**2MeH + (dp-BMe_2)$PtPh_2H$ (-5.4)**	
Pt-C, 2.003 Pt-N1, 1.984 Pt-N2, 2.129			Pt-C1, 2.058 Pt-C2, 2.056 Pt-N1, 2.170 Pt-N2, 2.175 Pt-H, 1.535 C1-H, 2.450
2MeH + TS'_{PhH} (1.6)		**2MeH + (dp-BMe_2)PtPh(PhH) (-7.1)**	
Pt-C1, 2.103 Pt-C2, 2.046 Pt-H, 1.575 C1-H, 1.642 Pt-N1, 2.136 Pt-N2, 2.173			Pt-C1, 2.276 Pt-C2, 2.327 Pt-C3, 2.045 Pt-N1, 2.164 Pt-N2, 2.069

<table>
<tr><td colspan="2">(dp-BMe₂)PtPh(OH₂)</td><td colspan="2"></td></tr>
<tr><td>Pt-C, 2.027
Pt-O, 2.171
Pt-N1, 2.001
Pt-N2, 2.130</td><td> 
</td><td colspan="2"></td></tr>
<tr><td colspan="2">H₂O + (dp-BMe₂)PtPh₂⁻ (0)</td><td colspan="2">PhH + (dp-BMe₂)PtPh(OH)⁻ (0.4)</td></tr>
<tr><td>Pt-C1, 2.027
Pt-C2, 2.026
Pt-N1, 2.150
Pt-N2, 2.153</td><td> 
</td><td> 
</td><td>Pt-C, 2.020
Pt-O, 2.025
Pt-N1, 2.049
Pt-N2, 2.133</td></tr>
</table>

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