Hydrocarbon C-H Activation with Tp′Pt Complexes

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A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry

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ABSTRACT

MARGARET G. MACDONALD:
Hydrocarbon C-H Activation by Tp' Platinum Complexes
(Under the direction of Prof. Joseph L. Templeton)

This dissertation focuses on investigations into the reactivity and regioselectivity of hydrocarbon C-H bond activation by Tp'Pt(IV) (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate) reagents via (1) thermolysis, (2) Lewis acid addition, and (3) low temperature protonation reactions. Insertion of α-olefins into a Pt-H or Pt-Ph bond has been found to occur. The synthetic and mechanistic investigations of these insertion reactions provide a starting point toward the aim of hydrocarbon functionalization.

Gentle heating of Tp'PtMe$_2$H in alkane solvents in the presence of B(C$_6$F$_5$)$_3$ results in C-H activation of the alkane solvent, R-H, to give Tp'Pt(Me)(H)(R) complexes. Further heating leads to formation of Tp'Pt(η^2-olefin)(H) complexes via methane elimination followed by β-hydride elimination, a stoichiometric alkane to olefin conversion.

The ortho-metallated phenethyl hydrido platinum(IV) complex, Tp'Pt(CH$_2$CH$_2$-o-C$_6$H$_4$)(H) has been isolated as the sole product of reaction of Tp'Pt(Me)$_2$(H) with ethylbenzene in the presence B(C$_6$F$_5$)$_3$ at 35 °C. Additional analogous Pt(IV) metallacycles, Tp'Pt(CH$_2$CH(Me)-o-C$_6$H$_4$)(H) and Tp'Pt(CH$_2$CH$_2$-o-C$_6$H$_3$Et)(H), have also been synthesized by this route. Note that heating of the dihydride reagent Tp'Pt(Me)(H)$_2$ with B(C$_6$F$_5$)$_3$ in either ethylbenzene or isopropylbenzene gave only Tp'Pt(Ar)(H)$_2$ products.

Mechanistic studies are underway to assess if initial activation occurs at an aryl or alkyl C-H bond as well as to discern any intermediate species in this intramolecular transformation.

Heating Tp'Pt(Ph)(η^2-CH_2=CH_2) in benzene forms an ortho-metallated phenethyl hydrido platinum(IV) complex, Tp'Pt(CH_2CH_2-o-C_6H_4)(H). Presumably this net reaction reflects phenyl migration to ethylene to give the insertion product, [Tp'PtCH_2CH_2Ph], as an unsaturated intermediate. Intramolecular C-H activation of an ortho phenyl proton from this intermediate would produce the metallacyle product. Low temperature protonation of the parent phenyl ethylene complex results in the formation of a cationic η^2-ethylene phenyl complex, [κ^2-(HTp')Pt(C_6H_5)(η^2-CH_2=CH_2)][BAr'$_4$]. Low temperature protonation of Tp'Pt(CH_2CH_2-o-C_6H_4)(H), followed by addition of acetonitrile leads to reductive coupling of the Pt-H and the alkyl methylene group to give a cationic Pt(II) 2-ethylphenyl complex, [κ^2-(HTp')Pt(C_6H_4-2-CH_2CH_3)($NCCH_3$)][BAr'$_4$]. Attempts to isolate an η^2-propylene phenyl complex were unsuccessful; formation of the 1,2-insertion product, Tp'Pt(CH(Me)CH_2-o-C_6H_4)(H), and two isomers of the 2,1-insertion products, Tp'Pt(CH_2CH(Me)-o-C_6H_4)(H), resulted. An in situ attempt to isolate the cationic [κ^2-(HTp')Pt(C_6H_5)(η^2-CH_2=CH(CH_3))][BF_4] resulted in the isolation of Pt(II) phenyl aqua complex, [κ^2-(HTp')Pt(C_6H_5)(OH_2)][BF_4], instead.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS AND SYMBOLS

α	greek alpha: crystallographic angle
β	greek beta: crystallographic angle
γ	greek gamma: crystallographic angle
δ	greek delta: denotes chemical shift reference scale
κ	greek kappa: denotes coordination to metal by x atoms
μ	greek mu: denotes bridging bond
π	greek pi: denotes bond
σ	greek sigma: denotes coordination to a metal via a single atom
θ	greek theta: general angle
νXY	greek nu: denotes infrared absorbance band corresponding to the stretching of the bond between atoms X and Y
Δ	greek capital delta: denotes separation between values or applied heat
a,b,c	crystallographic unit cell parameters
Å	angstrom(s)
Ar	general aromatic
BAr'4	tetrakis(3,5-trifuoromethylphenyl)borate
br	broad
t-Bu	tertiary butyl, $-C(CH_3)_3$
COSY	correlated spectroscopy
d	doublet(s)
°	degree(s)

$\Delta G°$	standard Gibbs
$\Delta H°$	standard enthalpy of reaction
$\Delta S°$	standard entropy of reaction
$\Delta G^{‡}$	Gibbs energy of activation
$\Delta H^{‡}$	enthalpy of activation
$\Delta S^{‡}$	entropy of activation
eq	equation
equiv	equivalents
Et	ethyl, $-CH_2CH_3$
Hz	Hertz
IR	infrared spectroscopy
x*J*YZ	magnetic coupling between atoms X and Y through a distance of x bonds
*K*eq	equilibrium constant
k	rate constant
L	general ligand, usually 2 e- donor
m	multiplet
Me	methyl, $-CH_3$
NMR	nuclear magnetic resonance spectroscopy
Ph	phenyl, $-C_6H_5$
q	quartet
R	general alkyl group
R, RW	crystallographic refinement quality indicators
s	singlet

t	triplet
THF	tetrahydrofuran
Tp	hydridotris(pyrazolyl)borate
Tp'	hydridotris(3,5-dimethylpyrazolyl)borate
X	general halogen atom

CHAPTER 1

INTRODUCTION TO METAL-MEDIATED C-H BOND ACTIVATION AT PLATINUM

"When you got here, even when I got here, the industrialized world was already hopelessly hooked on fossil fuels, and very soon now there won't be any more of those. Cold turkey.

Can I tell you the truth? I mean this isn't like TV news, is it?

Here's what I think the truth is: We are all addicts of fossil fuels in a state of denial, about to face cold turkey.

And like so many addicts about to face cold turkey, our leaders are now committing violent crimes to get what little is left of what we're hooked on."

– Kurt Vonnegut, Jr. *In These Times*, May 10, 2004.

Regardless of whether the prediction of an aging, antagonistic American novelist will come true, there is no disputing that our post-industrial world relies on the continual consumption of fossil fuels. We are about to face a "cold turkey" ending to our fossil fuel addiction. How much petroleum, natural gas and coal, the main fossil fuels, remain and how long we have before we may face a "cold turkey" reality is under contention. One recent estimate gives us 40 years before our oil reserves will be depleted based on our current rate of consumption.[1,2] However, with a growing world population and the recent emergence of new fossil fuel consumers, such as China and India, this could be an overestimate. The fact remains that these convenient resources, formed by nature over eons, are being depleted exponentially and irreversibly. With time, this addiction will also become more costly, with

the price we pay at the pump rising and the potential for hostility among world nations intensifying as they compete to secure what little remains.[1-6]

Fossil fuels have become a staple and we rely on them both as a principal source of energy and chemical feedstocks for chemicals and manmade materials that we are accustomed to. In the United States, we utilize fossil fuel derivatives such as gasoline and diesel oil, consumed for transportation, as well as plastics, synthetic materials and pharmaceuticals on a daily basis.[1] Comprised of mixtures of hydrocarbons, we take advantage of the high energy stored in the hydrocarbon C-H bond (bond dissociation enthalpy of 104 kcal mol^{-1} for methane at 25 ºC) and of the driving force provided by the irreversible production of CO_2 and H_2O upon combustion.[7] While fossil fuels are diminishing, however, alkanes from petroleum and natural gas still remain among the world's most abundant and low cost feedstocks.[1,6-9]

However bleak Kurt Vonnegut paints our "cold turkey" future, as scientists, we are problem solvers and prefer a proactive rather than a gloom and doom approach. Clearly the future will require the use of energy alternatives such as an oft proposed hydrogen-based economy; however such technology is not yet practical or feasible.[1,6] It is therefore important to find alternatives that are more economical and atom efficient as well as to develop greener technology for the current fossil fuel based systems we currently rely on.[2,6]

George Olah, winner of the 1994 Nobel Prize in chemistry, promotes the idea of a "methanol economy."[1,3,10] As a feedstock, methanol can be used directly as a fuel or for the formation of olefins, gasoline, dimethyl ether, methyl *tert*-butyl ether (MTBE), acetic acid, hydrogen and formaldehyde. Consequently, it is not accidental that methanol is presently among the top 10 chemicals produced globally. The current industrial synthesis of methanol

results from the reaction of syn gas (CO and H_2) (eq. 1), deriving from fossil fuels, with a Cu/ZnO-based catalyst at 220-300 ºC and 50-100 bar (eq. 2).[8]

$$CH_4 + H_2O_{(g)} \xrightarrow{[Ni]\ \Delta} CO_{(g)} + 3H_2\ (g) \qquad (1)$$

$$\Delta H^\circ = 49.3 \text{ kcal/mol}$$

$$CO_{(g)} + 2H_{2(g)} \xrightarrow{[Cu/ZnO]} CH_3OH \qquad (2)$$

$$\Delta H^\circ = -21.7 \text{ kcal/mol}$$

In advancement toward a "methanol economy," Olah and coworkers have reported the development of the direct methanol fuel cell (DMFC) which oxidizes methanol with air to produce electricity while generating carbon dioxide and water directly. In a "methanol economy," methanol could be utilized as an energy storage material, a fuel, and a feedstock for the synthesis of hydrocarbons and their products. Additionally, methanol could be prepared by either the direct oxidation of natural gas (methane) or by the reduction of carbon dioxide with hydrogen. Ideally, a "methanol economy" would incorporate the chemical recycling of CO_2 as a source of methanol, thereby also lowering the amount of CO_2 released into the atmosphere and curbing its effect on global warming (eq. 3).[1,3,11]

While our petroleum reserves are rapidly being depleted, methane gas remains an under-utilized and relatively abundant resource.[6] The direct synthesis of methanol from methane could extend the life of fossil based resources and, thereby, ease the transition

toward greener energy alternatives[1,6]. Since the early 1970s, advancements have been made in the use of organotransition metal complexes toward this aim. The development of low temperature, selective and direct oxidation of alkanes therefore remains a major research goal.[4,6,8,9,12]

Challenges and Approaches of C-H Activation.

The selective functionalization of saturated hydrocarbons (alkanes), as well as aromatic, olefinic and acetylenic hydrocarbons remains a major research challenge.[4,6,8,9,12] The C-H bonds of alkanes are notoriously inert.[7,13] These C-H bonds are extremely strong, with pKa's between 45-60 (ca. 48 for methane) and high bond dissociation enthalpies (99-104 kcal mol^{-1}), and alkanes are saturated compounds.[13] In addition, the C-H bonds of the functionalized products are typically more reactive (93 kcal mol^{-1} for CH_3OH) than the parent hydrocarbon C-H bonds, and, consequently, the initial oxidation products are prone to over-oxidation to the thermodynamically stable products, H_2O and CO_2.[7,14,15] Homolytic pathways to cleave these C-H bonds by radicals, oxidation or cracking, therefore result in a lack of selectivity in the final products or in low conversion.[14]

$$CH_{4\,(g)} + 1/2\,O_{2\,(g)} \longrightarrow CH_3OH_{(l)} \qquad (3)$$

$$\Delta H^\circ = -30.7 \text{ kcal/mol}$$

Organotransition metal complexes, however, have shown promise toward achieving this goal of the selective functionalization of hydrocarbons.[6,7,12-14,16-25] The formation of new, strong metal-hydride and metal-alkyl bonds in the intermediate R-M-H species

compensates for the high energy cost of C-H bond cleavage.[14] In addition, by cleaving the C-H bond through this inner-sphere mechanism, the metal center can mediate the transformation of the carbon moiety by controlling the rate and selectivity of the potential product.[6] (eq. 4)

$$\text{R-H} + \text{M} \longrightarrow \text{R-M-H} \longrightarrow \text{R-X} \qquad (4)$$

Notably, the selectivity preference for activating C-H bonds by transition metal reagents shows the opposite trend from that of homolytic cleavage pathways. Selectivity patterns for the homolysis of C-H bonds anticipates 3º C-H bonds to be more reactive than 2º or 1º, based on the stability of the resultant carbocations formed. However, the reverse trend has been established for transition metal complexes, 1º > 2º > 3º. In addition, aromatic C-H bonds are more reactive than their aliphatic counterparts and, remarkably, the C-H bonds of alcohols are less reactive than the alkane precursor. This overriding tendency toward activation of aryl and primary C-H bonds over secondary and tertiary C-H bonds in most systems studied gives the prospect of future control over stereoselectivity in product formation.[7,14,15,26]

C-H Activation Pathways

C-H activation reactions can be divided into five classes: (1) oxidative addition, (2) σ-bond metathesis, (3) electrophilic substitution, (4) 1,2-addition, and (5) metalloradical activation (Table 1.1).[14,15] Of these, three classes, oxidative addition, σ-bond metathesis, and electrophilic substitution, are the most common modes observed and each results in unique C-H activation patterns.[6] Some noteworthy examples will be discussed herein.

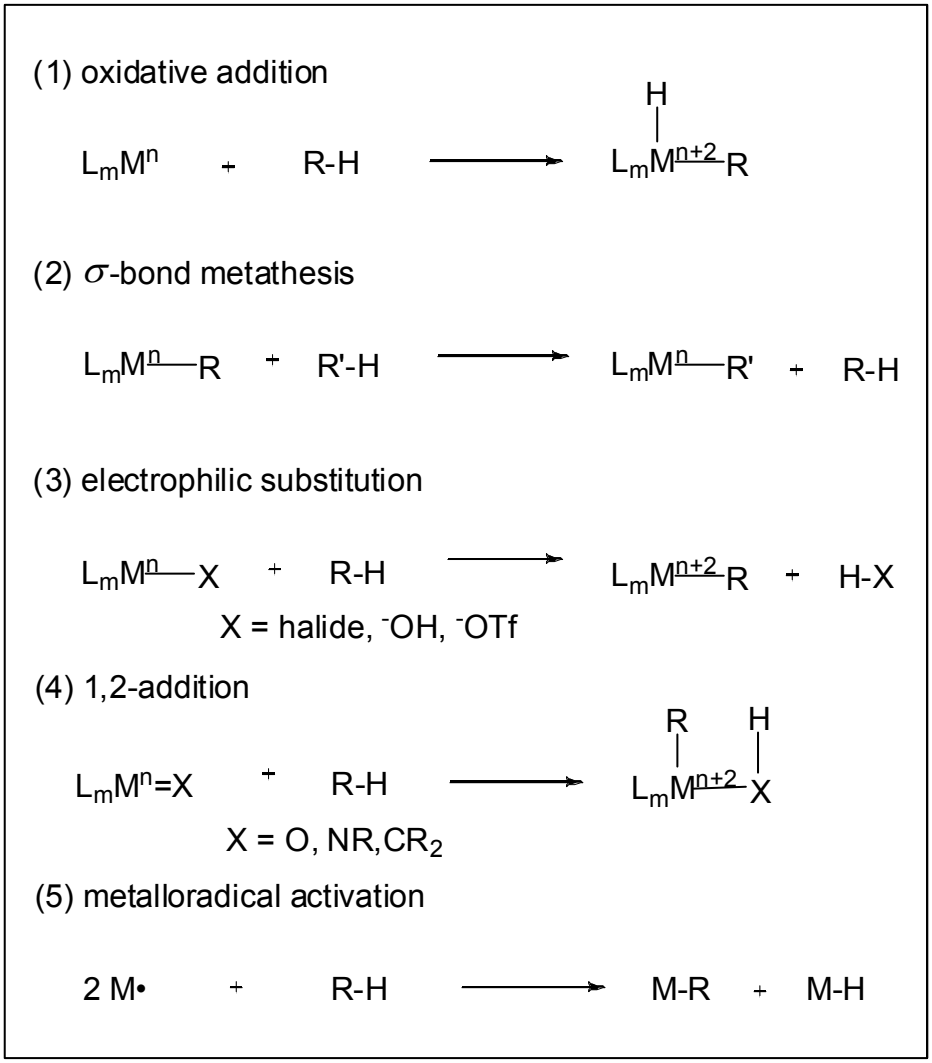
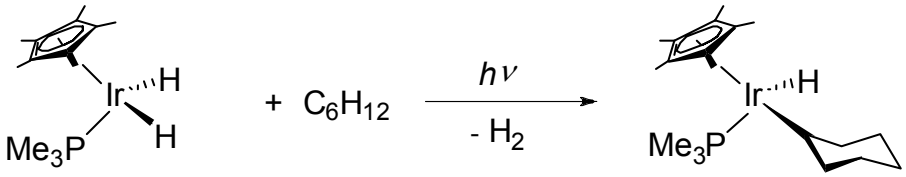


Table 1.1: C-H Activation Pathways

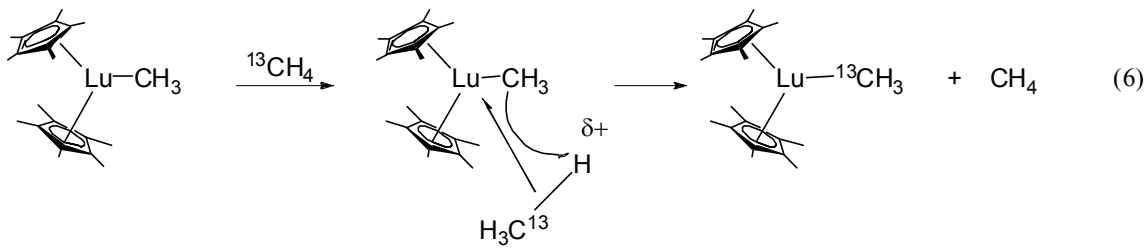
For late transition metal systems, the oxidative addition pathway is often operable for electron-rich, low oxidation state complexes, as it requires the availability of a M^{n+2} oxidation state.[14] In 1982, Bergman, and later, Graham, reported the first example of intermolecular oxidative addition of alkane C-H bonds by reagents of the type $CpIr(L)H_2$ (where Cp = Cp^* = η^5-C_5Me_5 and L = PMe_3; Cp = η^5-C_5H_5, L = CO, respectively). [27,28] Upon photolysis, the resultant 16-electron CpIr(L) fragment readily reacts with C_6H_{12} to

form the 18-electron alkyl derivative, $CpIr(L)(C_6H_{11})(H)$.[27-29] Notably, the oxidative addition of C-H bonds was found to be reversible. Heating to 60 ºC in C_6H_6 resulted in formation of the $CpIr(L)(C_6H_5)(H)$ analogue[30,31] (eq. 5). While highly reactive toward C-H bonds at relatively low temperatures, these systems however are extremely sensitive to O_2 and fall apart under the oxidizing conditions.[14]



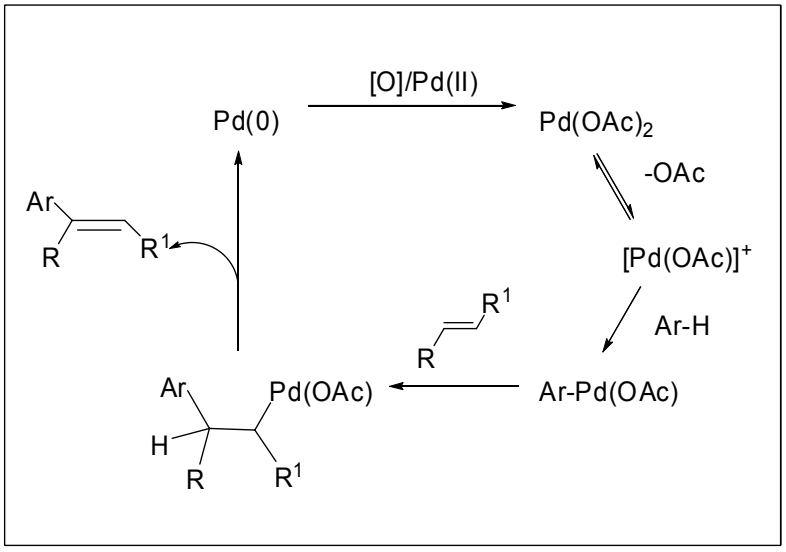
(5)

Early d^0 metal alkyl complexes have been found to undergo σ-bond metathesis pathway with unactivated alkanes. Formation of a four-centered transition state in which the bond-breaking and bond-making occur in a concerted fashion circumvents the need for an available M^{n+2} oxidation state in these systems (eq. 6).[14] An early example of this type of mechanism was reported by Watson in 1983. [32] Watson found Cp^*_2LuMe underwent exchange with isotopically labeled methane in cyclohexane solvent, as shown in eq. 6.[29,32,33] Typically only formation of a new R-H bond occurs from the σ-bond metathesis of R′-H and M-R fragments and formation of R-R′ is not observed.[29]



(6)

A prominent example of aromatic C-H bond activation via electrophilic substitution was first reported by Fujiwara and coworkers in the late 1960's.[34] Pd(II)(olefin) complexes were found to induce stoichiometric coupling of the olefin with arenes. Formation of σ-aryl-Pd complexes were later determined to be intermediates upon addition of arene C-H bonds to the cationic $[PdOAc]^+$ catalyst (Scheme 1.1).[18,35] Typically, electrophilic substitution of C-H bonds occurs on late- or post-transition metal regents in strongly polar mediums such as water or anhydrous strong acids in which the metal does not undergo a change in oxidation state.[12]

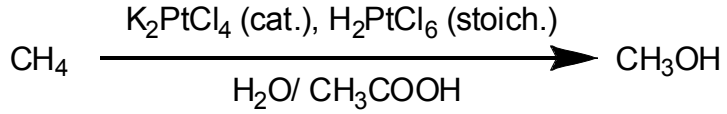


Scheme 1.1; Fujiwara Reaction

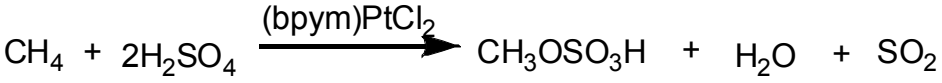
C-H Activation on Platinum

There has been a concentration on platinum-based systems for catalysts due to encouraging results such as that of Shilov Chemistry[7,25,36] (eq. 7) and, more recently, the *Catalytica* system (eq. 8).[6,23,37-39] Over 30 years ago, Shilov reported the catalytic formation

of methanol from the reaction of Pt(II) chloride salts with methane in an aqueous acidic media. While this system remains the best example of the selective transformation of methane to methanol under mild conditions, it requires the stoichiometric consumption of Pt(IV) salts as an oxidant for the Pt(II) catalyst and is therefore not a practical or economically viable solution to the problem of hydrocarbon functionalization. However, the success of the Shilov oxidation has led to the study and elucidation of its mechanism. Insight into the nature of C-H bond activation and functionalization processes on platinum therefore remains pertinent as we strive toward a more efficient catalytic system.[14,15,36]



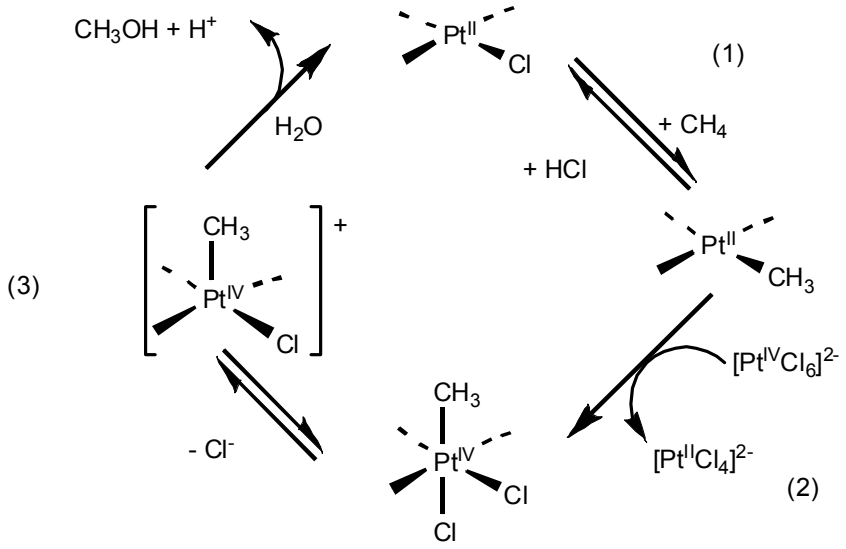
(7)



(8)

Mechanism of Shilov Oxidation

A generally accepted mechanism for the Shilov system is shown in Scheme 1.2, below:[15,40]



Scheme 1.2: Mechanism for the Shilov oxidation of methane to methanol by Pt(II)

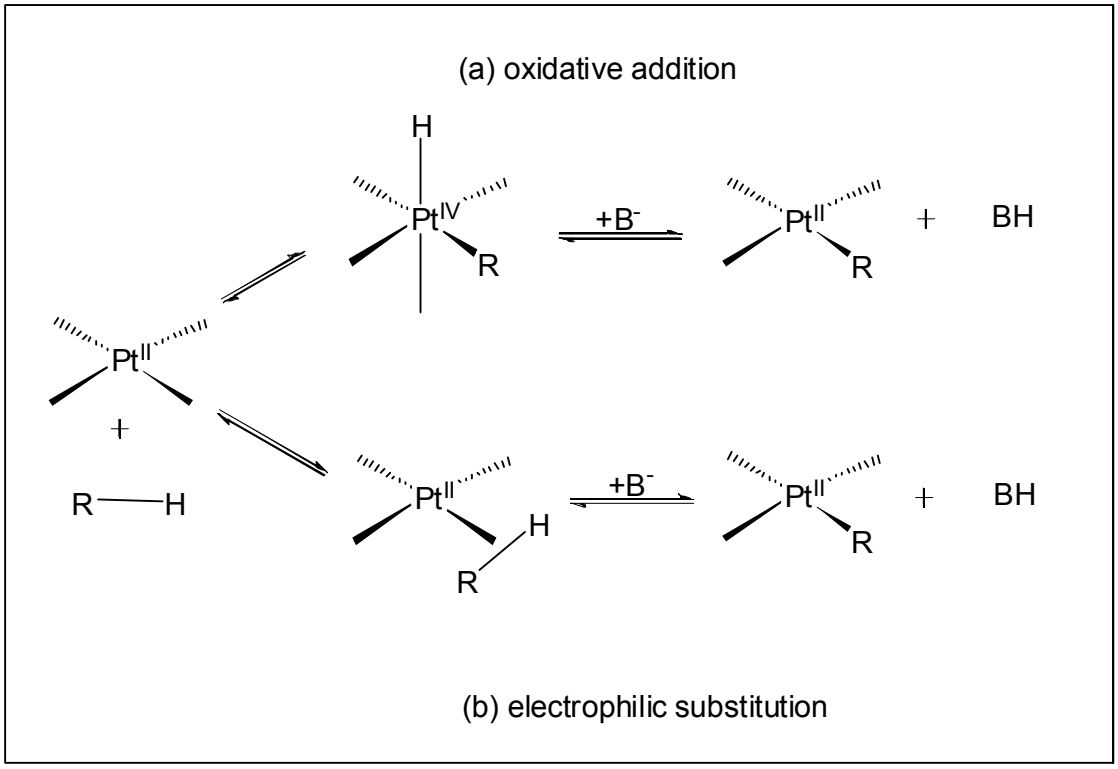
The overall process can be broken down into three major transformations: (1) initial activation of the alkane by Pt(II) and generation of an alkyl platinum intermediate, (2) oxidation of this intermediate by Pt(IV) and formation of a Pt(IV) alkyl species, and finally (3) reductive elimination to afford the functionalized product and regenerate the Pt(II) catalyst. Step 1, the C-H activation step, has received a great deal of attention because it controls the overall rate and the selectivity of the final product.[15]

Oxidative Addition or Electrophilic Substitution?

Each of the individual steps in the Shilov mechanism could proceed through multiple pathways.[14,15] Initial activation of the C-H bond in step 1, has been considered as either (a)

an oxidative addition of the C-H bond to the Pt(II) center, resulting in a six-coordinate Pt(IV) alkyl hydrido species or (b) an electrophilic substitution mechanism via initial formation of a σ-alkane intermediate as shown in Scheme 1.3. Subsequent deprotonation of either intermediate would generate the Pt(II) alkyl complex. These two pathways have both been implicated and extensively studied.[7,12,14,15]

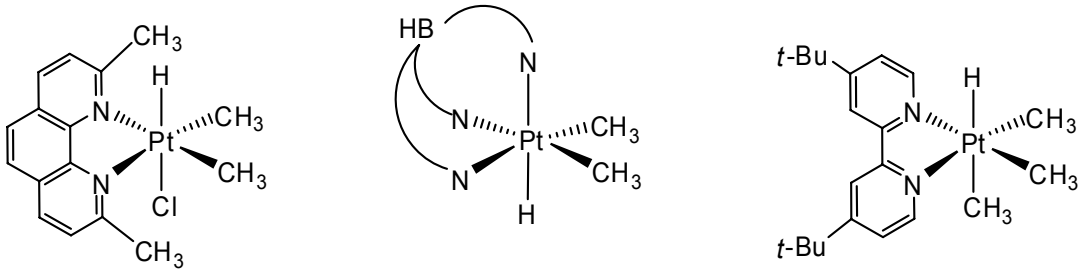
Early work by Garnett and Hodges on the Pt(II) catalyzed H/D exchange reactions in acidic media found that multiple exchanges occurred at platinum on aromatic substrates.[41] Encouraged by these results, Shilov and coworkers reported a year later that this C-H/D exchange occurs for methane and ethane in a solution containing $K_2[PtCl_4]$ in D_2O/acetic acid-d_1.[25] Shilov's work is hailed as the first homogeneous system to activate the C-H bonds of a simple alkane.[14]



Scheme 1.3: Possible modes for C-H activation in Shilov oxidation

The observation of multiple H/D reactions in acidic deuterated media has been attributed to multiple C-H bond-cleavage and bond-forming sequences on the Pt(II) center. Mechanistically these multiple H/D exchanges require the intermediacy of a σ-alkane species prior to bond cleavage/formation.[14] In 1967, Garnett[41] and Hodges[42] described such a species as one involving the delocalized molecular orbitals of the alkane. This is astonishingly similar to that of a modern σ-alkane metal complex structure. σ-Alkane complexes are now assumed as intermediates in most transition-metal mediated C-H activation reactions.[14]

Due to the thermodynamic instability associated with most Pt(IV) alkyl hydride complexes, much of the mechanistic work on the C-H activation step has been undertaken on the microscopic reverse reaction, i.e. the reductive elimination of R-H upon protonation of the stable Pt-alkyl precursor.[14,15] While Pt(IV) alkyl hydride complexes had been postulated as intermediates, it was not until 1995 that such species were observed by low temperature NMR spectroscopic studies.[40,43-45] By use of stabilizing N-donor ligands, several model Pt(IV) alkyl hydride complexes were subsequently isolated and structurally characterized, including Tp′Pt$(CH_3)_2$H from our laboratory in 1996 (Figure 1.1).[46,47]



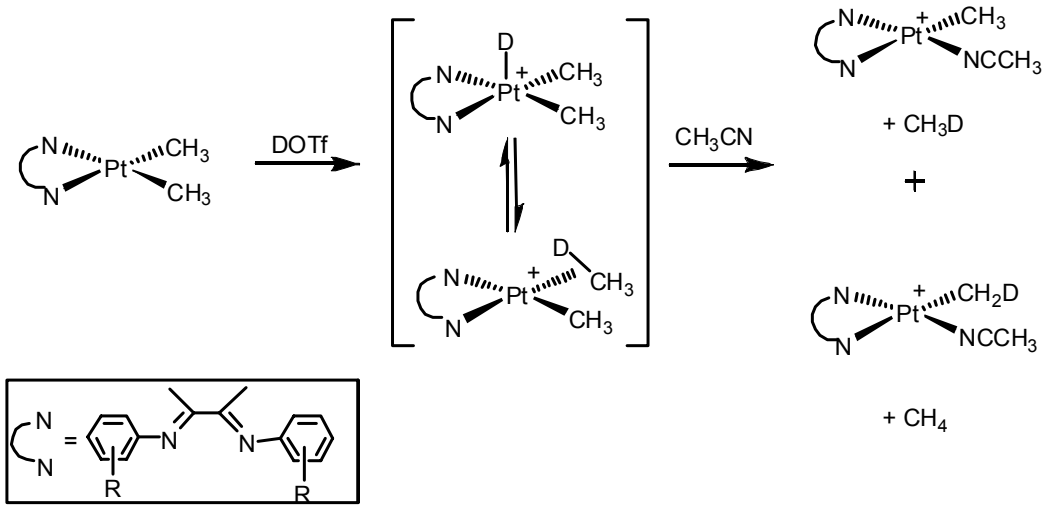
DeFelice **1995**

Templeton **1996**
Canty **1996**

Puddephatt **1996**

Figure 1.1: Early examples of stable six-coordinate Pt(IV) alkyl hydride complexes

Early mechanistic work on the protonation of Pt(II) dimethyl reagents was reported by the Bercaw group (Scheme 1.4). [14,40] Notably, these studies found deuterium scrambling between the platinum-methyl and the hydride position upon protonation with DOTf. A σ-alkane intermediate is therefore assumed to form reversibly prior to reductive elimination of methane. Zamashchikov and coworkers account for this H/D exchange by the rapid interconversion between a Pt(IV) alkyl hydride species and the Pt(II) σ-alkane complex. They contend that deprotonation to give the Pt(II) alkyl complex could occur from the Pt(IV) alkyl hydride species via the oxidative addition pathway.[14]

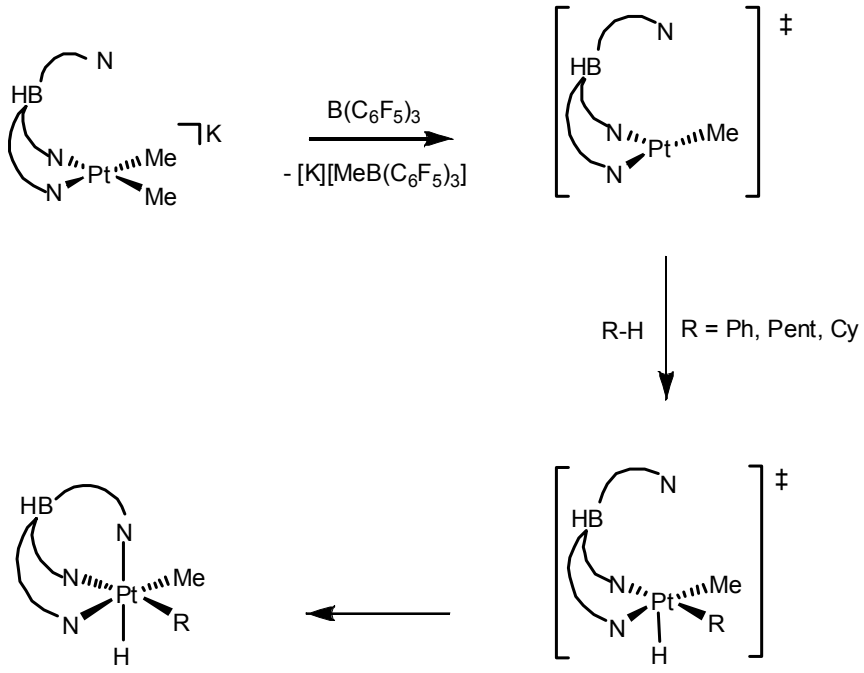


Scheme 1.4: H/D exchange and evidence for σ-methane intermediate

Bercaw and coworkers, however, favor deprotonation occuring from the σ-alkane intermediate in the Shilov system. Formation of an agostic complex, they argue, could make the agostic proton sufficiently acidic to be susceptible to direct deprotonation and, thus, generate the Pt(II) alkyl complex. The authors disfavor an oxidative addition pathway by

analogy to related Pd(II) chemistry whereby the Pd(IV) oxidation state is prohibitably high in energy.[14,15,29]

While neither the Pt(IV) alkyl hydride nor the Pt(II)σ-alkane species have been observed directly for the Shilov system, in 1997, Goldberg and Wick demonstrated the feasibility of an oxidative addition pathway by the successful addition of C-H bonds to the anionic [κ^2-Tp′Pt(II)(CH_3)]$^-$ reagent to afford Tp′Pt(IV)(CH_3)(alkyl)(H) products (Scheme 1.5).[48] Recent computational studies on the C-H activation step favor an electrophilic substitution pathway.[49] Ultimately, the evidence that has been compiled supports the intermediacy of both Pt(IV) alkyl hydride and Pt(II)σ-alkane species.[7,14,15,29]



Scheme 1.5: Reaction of KTp'$PtMe_2$ with $B(C_6F_5)_3$ in hydrocarbon solvent

Is Pt(IV) Required for Oxidation?

The second and third steps of Shilov's system have also been addressed by mechanistic studies. The second step is argued to occur as (c) an alkyl transfer from Pt(II)(alkyl) to Pt(IV) or (d) an inner-sphere two-electron transfer from Pt(II)(alkyl) to Pt(IV) (Figure 1.2). Labeling studies by Bercaw and Labinger found Pt(IV) to act as external oxidant, therefore anticipating the use of more economical oxidants than platinum for oxidation in future catalysis.[50,51] An important follow-up to this finding was the use of SO_3 as an oxidant in the *Catalytica* system (eq. 8). In the presence of a Pt(II) bipyrimidine and concentrated sulfuric acid, methane is selectively converted to methyl bisulfate (72% yield, 89% conversion, 81% selectivity).[29]

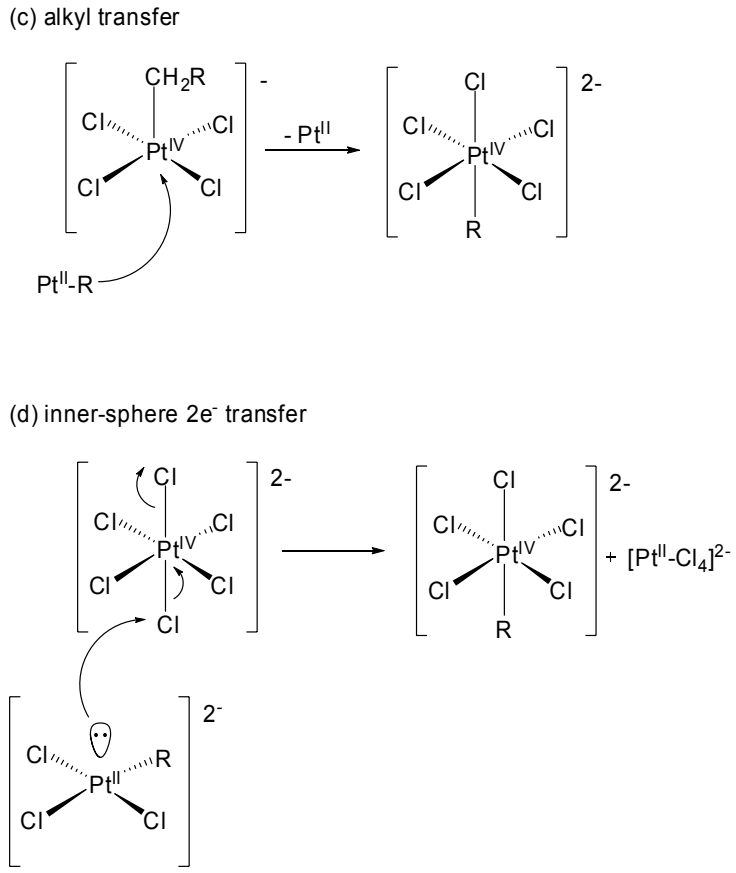


Figure 1.2: Oxidation via (c) alkyl transfer or (d) an inner-sphere two-electron transfer.

Reductive Elimination via a Proposed Five-Coordinate Intermediate

The third step, reductive elimination of the new functionalized alkane and regeneration of the Pt(II) catalyst has been proposed to occur by either (e) nucleophilic S_N2 pathway from a five-coordinate Pt(IV) intermediate or (f) in a concerted fashion directly from the six-coordinate Pt(IV) complex via a three-centered transition state (Figure 1.3).

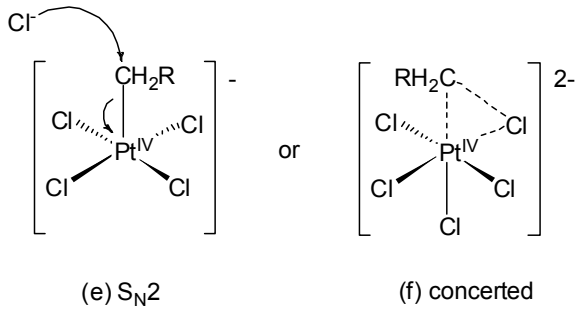


Figure 1.3. Reductive elimination by (e) nucleophilic S_N2 from a five-coordinate Pt(IV) intermediate or (f) a concerted fashion directly from the six-coordinate Pt(IV)**.**

Early findings by Zamashchikov and coworkers support formation of the proposed five-coordinate intermediate. Alkylplatinum(IV) species $[Pt(R)Cl_5]^{2-}$ (R= CH_3, CH_2CH_3, CH_2COCH_3) were found to exist in equilibrium with their monoaquo derivatives in aqueous medium and proposed to interconvert via a $[Pt(IV)(R)Cl_4]^-$ intermediate.[52-56] These results were corroborated by the subsequent report by Luinstra, et al.[57,58] Luinstra's report demonstrated that inversion of stereochemistry at carbon occurs upon reductive elimination, thereby favoring an S_N2 pathway.[59] While evidence supports the intermediacy of a five-coordinate species, such an intermediate has not been directly observed in the Shilov system.[7,15,60]

Tp′ Platinum Reagents

Recently, studies on N-ligated platinum systems have supported the formation of Pt(IV) intermediates with the isolation of Pt(IV) alkyl hydrido complexes upon the reaction of Pt(II) reagents with alkanes. Our contributions to the study of Shilov's system through the isolation of key Pt(II) and Pt(IV) analogues to these intermediates will be further discussed.

Our group has utilized the hydridotris(3,5-dimethylpyrazolyl)borate ligand (Tp′) shown in figure 1.4, to study model complexes and isolate intermediate species in the Shilov oxidation. The monoanionic, 6-electron donating Tp′ ligand is a particularly useful ligand as it acts as a NMR symmetry handle and can coordinate to the platinum center in either a bi- or tridentate fashion (Figure 1.5).[46,61] The variable denticity therefore allows access to either the d^8, Pt(II) square-planer or d^6, Pt(IV) octahedral complexes, respectively. In addition, and perhaps more notably, Tp′ has been shown to stabilize alkyl and hydride ligands in the same coordination sphere of platinum.[43,46] Thus utilization of this scorpionate ligand has allowed our group to investigate Pt(II)/Pt(IV) interconversions relevant to the Shilov system.[46,62-71]

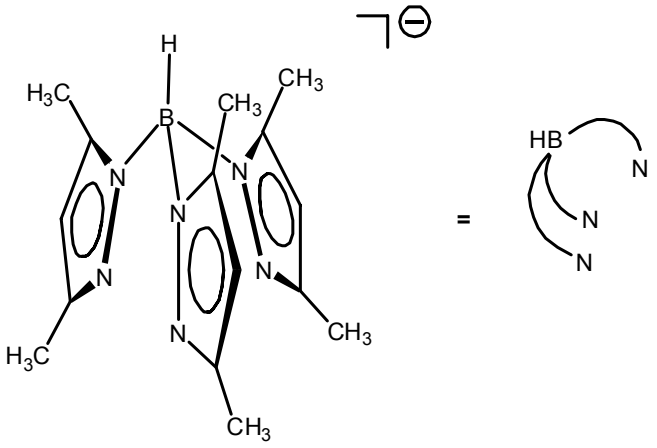


Figure 1.4 Tp′ ligand [hydridotris(3,5-dimethylpyrazolyl)borate]

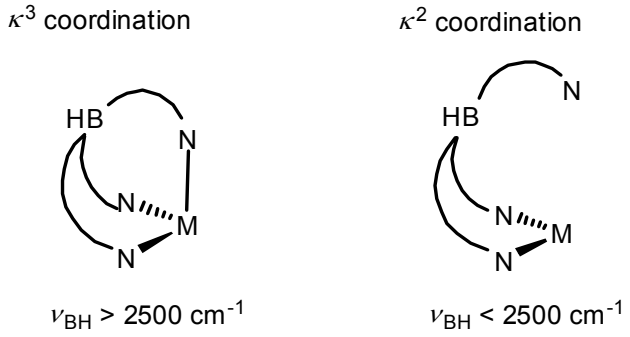
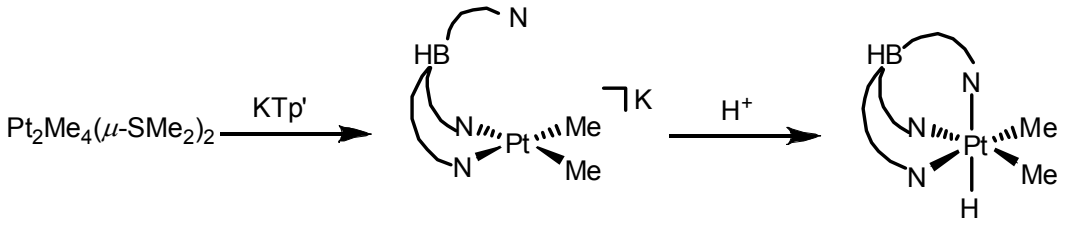


Figure 1.5 Coordination modes for Tp'

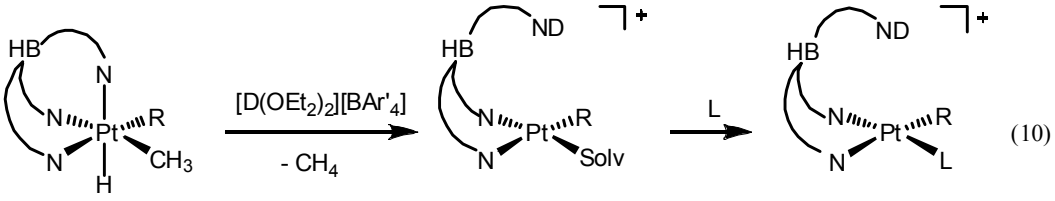
Modeling Shilov Chemistry with Tp′ Platinum Reagents

One proposed intermediate in the C-H activation step of the Shilov Oxidation is that of a six-coordinate Pt(IV) alkyl hydrido species, resulting from the oxidative addition of an alkane C-H bond to Pt(II). Our group was among the first to report the isolation of such a species with the successful synthesis and structural characterization of Tp′ $PtMe_2H$ in 1996.[46] Synthesis of the Tp′$PtMe_2H$ complex proceeds through the protonation of the κ^2-$[Tp'Pt(II)(CH_3)]^-$ reagent as shown in eq. 9 below. In this sequence, protonation occurs at the metal and promotes chelation of the third pyrazole ring to the stabilize the Pt(IV) center.



(9)

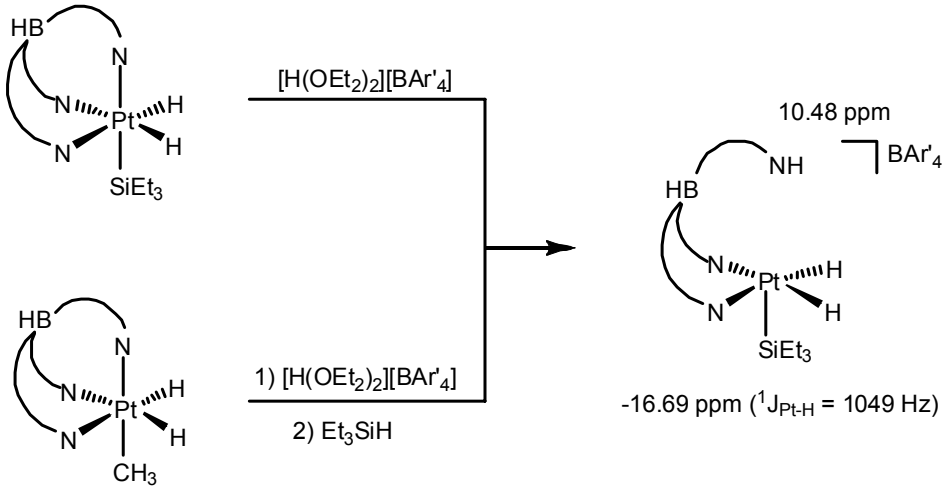
In contrast to earlier Pt(IV) *cis*-methyl hydride systems, Tp′Pt$(CH_3)_2$H does not induce reductive elimination of methane at room temperature in solution or the solid state.[46] Reductive elimination of methane from Tp′Pt$(CH_3)_2$H can be induced, however, via an acid assisted route at low temperatures. Significantly, protonation of Tp′Pt$(R)_2$H [R = CH_3 or C_6H_5] with $[H(OEt_2)_2][BAr'_4]$ was found to occur at a nitrogen atom of a coordinated pyrazole ring (eq. 10). The protonated pyrazole can easily be confirmed by ^{1}H NMR spectroscopy by the appearance of a singlet resonating downfield between 11-12 ppm. Thus, upon protonation, one Tp′ arm is released, presumably to form a five-coordinate Pt(IV) intermediate, which readily eliminates methane in the presence of a trapping ligand, L [L = CO, CH_2=CH_2, $NCCH_3$, CN^tBu, or py], to afford stable [κ^2-(H-Tp′)Pt(II)(R)(L)][BAr'_4] adducts.[72]



(10)

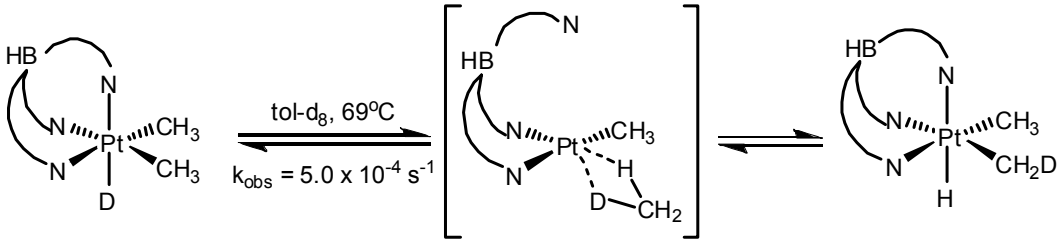
The intermediacy of a five-coordinate Pt(IV) species prior to reductive elimination had also been proposed for the Shilov system. While such a intermediate has not been directly observed for the Shilov system, our laboratory reported the isolation of the model complex, [κ^2-(H-Tp′)Pt$(H)_2(SiEt_3)$][BAr'_4] in 2001.[73] Goldberg and coworkers simultaneously reported the isolation of a related neutral five-coordinate (nacnac)$Pt^{IV}Me_3$ [nacnac = {(2,6-*i*$Pr_2C_6H_3$)NCMe}$_2$CH] complex.[74] Our five-coordinate complex can be generated either via protonation of the neutral, six-coordinate Pt(IV) precursor,

$Tp'Pt(H)_2(SiR_3)$ [R= Et, Ph or PhH] or by addition of $HSiR_3$ directly to a solution of $Tp'Pt(CH_3)(H)_2$ and $[H(OEt_2)_2][BAr'_4]$ (Scheme 1.6).[73]



Scheme 1.6 Synthesis of $[\kappa^2\text{-(H-Tp')Pt(H)}_2(SiEt_3)][BAr'_4]$

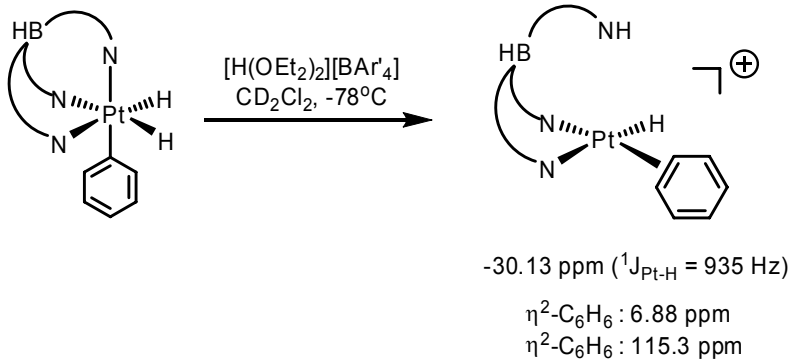
Evidence of the formation of a σ-alkane intermediate in the protonation reaction of $Tp'Pt(CH_3)_2D$ was obtained by ^1H NMR spectroscopic study at low temperature. Upon addition of $[H(OEt_2)_2][BAr'_4]$ to $Tp'Pt(CH_3)_2D$, resonances attributable to free CH_4 and CH_3D were observed in a 1:1 ratio along with resonances for two platinum bound methyl groups. This H/D scrambling was concluded to result from the rapid and reversible formation of a σ-methane intermediate prior to reductive elimination of methane (eq. 11). [63]



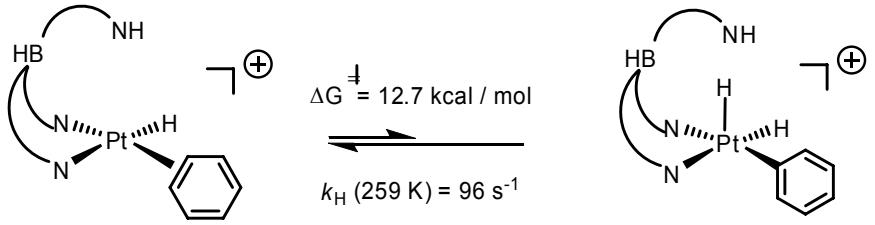
(11)

Arene C-H activation has been proposed to occur via initial formation of an η^2-arene species analogous to the σ-alkane intermediate.[15,48,75-83] Our lab has extensively studied the

microscopic reverse reaction, by inducing reductive C-H coupling to form a stable η^2-arene species upon the reaction of Tp′Pt(C_6H_5)H_2 with [H(OEt_2)$_2$][BAr′$_4$] (eq. 12).[73] The [κ^2-H-Tp′Pt(η^2-C_6H_6)H][BAr′$_4$] was characterized by x-ray crystallography[66]. In solution, this species were found to exist in dynamic equilibrium with five-coordinate platinum aryl dihydride intermediate via arene C-H oxidative addition as evidenced by scrambling of the two hydride positions (eq. 13). Barriers for arene oxidative addition were obtained ($\Delta G^{\ddagger}$ = 12.7 kcal mol^{-1} for the η^2-benzene adduct).[64,66]

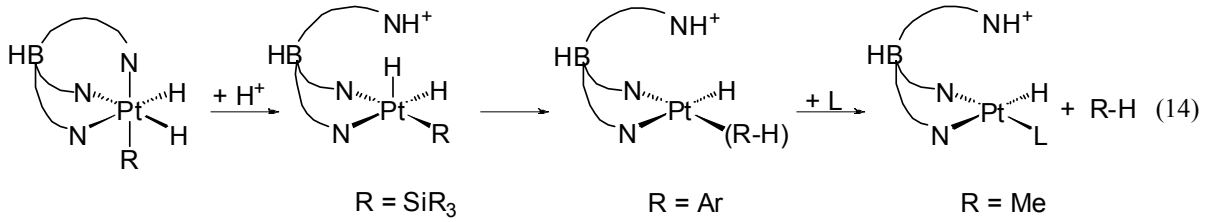


(12)



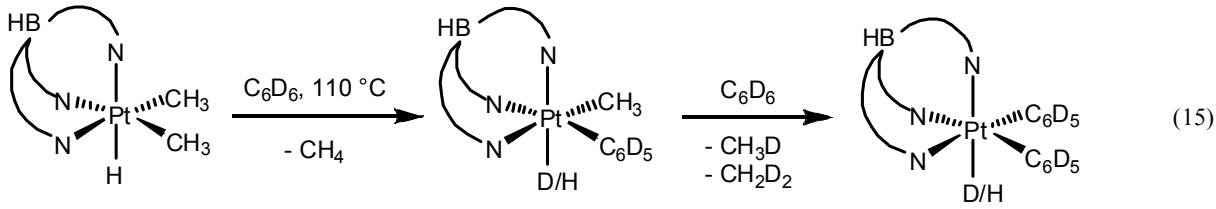
(13)

A general scheme for the identification of proposed intermediates in the Shilov oxidation by our model Tp′PtR($H)_2$ reagents is summarized below (eq. 14)[84]:



Investigations of C-H Activation of Hydrocarbons

In a collaboration with Goldberg's group, the Tp′Pt$(CH_3)_2$H reagent was found to be capable of thermally activating the C-H bonds of benzene to form Tp′Pt$(C_6H_5)_2$H through the formation of a Tp′Pt$(CH_3)(C_6H_5)$H intermediate species (eq. 15).[63] Aryl C-H activation has also been found to occur at ambient temperatures in the presence of the Lewis acid, $B(C_6F_5)_3$. Reaction of Tp′Pt$(CH_3)_2$H or Tp′Pt$(CH_3)H_2$ with substoichiometric $B(C_6F_5)_3$ in aromatic solvents generates Tp′PtPh_2H or Tp′PtPhH_2, respectively. The mechanism of this transformation may proceed via borane or trace protic acid-assisted dissociation of one of the pyrazole rings. Notably, in the case of the alkyl-substituted benzenes, toluene and xylene, only formation of the meta and para activated products was observed under these conditions.[85]



Taking the knowledge we have gleaned about Pt(II)/Pt(IV) interconversions and C-H reductive elimination from Tp′ stabilized Pt(IV) alkyl hydrido complexes, the following

chapters will discuss progress toward the goal of selective transformation of hydrocarbons by Tp′Pt(IV) regents.

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CHAPTER 2

STOICHIOMETRIC ALKANE DEHYDROGENATION WITH Tp'PtMe$_2$H TO FORM Tp'Pt(η^2-OLEFIN)(H) COMPLEXES

Introduction

The inertness of saturated hydrocarbons limits utilization of alkanes in chemical synthesis.[1-7] Although many metal reagents are now known to activate C-H bonds, few are capable of delivering productive alkane functionalization.[8-19] Alkane dehydrogenation to form the corresponding olefin is one of the simplest ways to functionalize hydrocarbons. Many transition metal catalyzed alkane dehydrogenations require stoichiometric amounts of a sacrificial olefin to accept hydrogen and effectively undergo hydrogen transfer instead of net dehydrogenation.[15,20-32] Recently progress toward developing "acceptorless" dehydrogenation catalysts has been achieved utilizing pincer-ligated iridium complexes.[33-36]

Several platinum complexes have been shown to be capable of alkane dehydrogenation. The platinum examples are stoichiometric with the exception of the catalytic dehydrogenation of cyclooctane promoted by a Pt(II)phosphite complex.[37] Examples of stoichiometric alkane dehydrogenation involving platinum complexes include: dehydrogenation of neohexane and cyclohexane with a five-coordinate Pt(IV) complex stabilized by a β-diiminate ligand;[38] dehydrogenation of various alkanes with (pyridinophane)PtMe$_2$H via methane elimination;[39] and dehydrogenation of ethers and cyclohexane with an electrophilic (tmeda)Pt(II) complex.[40]

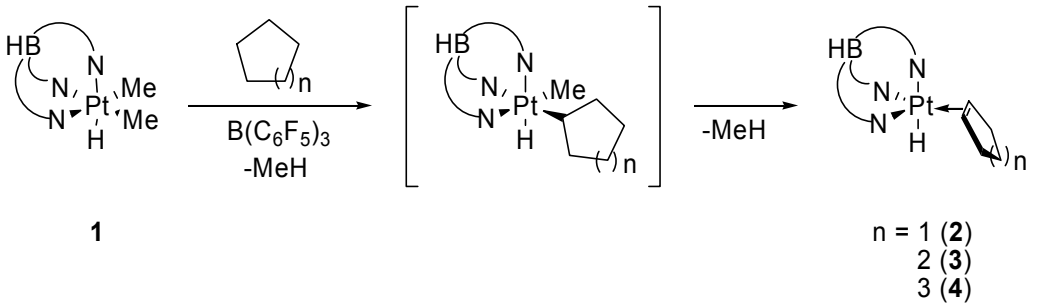
Recently, a detailed mechanistic study on the thermolysis of Tp'PtMe$_2$H (**1**) [Tp' = hydridotris(3,5-dimethylpyrazolyl)borate][41] in various solvents was reported.[42] The observation that thermolysis of **1** in cyclohexane resulted in the formation of free cyclohexene prompted us to study this reaction in more detail. The [Tp'PtMe] intermediate generated by methide abstraction from [K][Tp'PtMe$_2$] is known to activate C-H bonds to give stable Tp'Pt(Me)(H)(alkyl) complexes.[43] We now report that Tp'Pt(Me)(H)(alkyl) complexes can be generated via Lewis acid induced methane loss from Tp'PtMe$_2$H (**1**) in alkane solvents, and reductive elimination of methane from Tp'PtMe(H)(R) intermediates followed by β-H elimination forms Tp'Pt(η^2-olefin)(H) products.

Results and Discussion

Neutral η^2-Olefin Complexes. Heating Tp'PtMe$_2$H (**1**) in cycloalkane solvents (cyclopentane, cyclohexane, cyclooctane; 35-50 °C) in the presence of B(C$_6$F$_5$)$_3$ results in the loss of two equivalents of methane and formation of Tp'Pt(η^2-cycloalkene)(H) [cycloalkene = C$_5$H$_8$ (**2**), C$_6$H$_{10}$ (**3**), C$_8$H$_{14}$ (**4**)] complexes (eq. 1) after 2 days. Initial loss of methane resulted in the formation of a detectable amount of intermediate species, Tp'Pt(Me)(H)(cycloalkyl) [cycloalkane = C$_5$H$_9$ (**2a**), C$_6$H$_{11}$ (**3a**), C$_8$H$_{15}$ (**4a**)], with hydride chemical shifts similar to those previously reported.[43] When monitored by ^{1}H NMR spectroscopy in the hydride region at room temperature, the intermediates, **2a**, **3a**, and **4a** are evident. These unsymmetrical intermediates, present at a low and relatively constant concentration, are consumed to form the η^2-olefin product. The Pt-H resonances for the Tp'Pt(Me)(H)(cycloalkyl) complexes appear slightly upfield of hydridodimethyl platinum

reagent **1** (-20.90 ppm), at -21.08 ppm (**2a)**, -21.54 ppm (**3a**), and -21.66 ppm (**4a**) in CD_2Cl_2.

To probe the source of methane generated early in the reaction, complex **1** was combined with cyclohexane-d_{12} and progress was monitored by ^{1}H NMR spectroscopy at 7 ºC, just above the freezing point of the solvent. Initial methane loss was evident as a singlet appeared at δ = 0.19 ppm indicating that CH_4 formed from Tp'Pt$(CH_3)_2$H first. Upon subsequent warming to 35 ºC, scrambling to form CH_nD_{4-n} (n = 3, 2 or 1) methane isotopologues was observed. These results are consistent with previously reported findings upon thermolysis of complex **1** with cyclohexane-d_{12} at 110ºC.[42]



(1)

Considering the olefin as a neutral ligand allows one to consider a d^8 Pt configuration with either a square planar or trigonal bipyramidal Pt(II) geometry (Figure 2.1). The coordination mode of the Tp' ligand can be determined by measuring the B-H stretching frequency, and thus the geometry of the platinum complex follows indirectly from $\nu_{B\text{-}H}$.[44] A B-H stretching frequency above 2500 cm^{-1} is indicative of κ^3-Tp' coordination, while a $\nu_{B\text{-}H}$ below 2500 cm^{-1} indicates κ^2-Tp' coordination.[44] The solution IR spectrum for Tp'Pt(H)(η^2-cyclo-C_5H_8), **2**, in CH_2Cl_2 indicates κ^3 coordination for Tp' as evident by a B-H absorption at 2533 cm^{-1}. IR data for the other η^2-olefin complexes, **3** and **4**, are also consistent with κ^3 coordination. Similar neutral Tp'Pt(olefin)X complexes also exhibit κ^3 coordination of Tp',

as illustrated by the IR spectrum and ^{11}B NMR[45] chemical shift of Tp'PtMe(CH_2=CH_2) (ν_{B-H} = 2536 cm^{-1} and ^{11}B NMR δ = -8.72 ppm).[46] IR spectra for platinum olefin complexes **2** - **4** also display a platinum hydride stretch near 2270 cm^{-1} consistent with their formulation as the β-hydride elimination product.

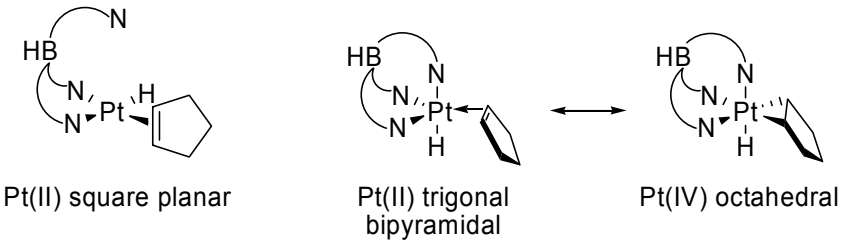


Figure 2.1: Possible geometries for Tp'Pt(η^2-cycloalkene)(H) complexes.

Both tridentate Tp' resonance structures shown in Figure 2.1 are acceptable, but the platinum(IV) octahedral metallacycloalkane depiction is particularly convenient for predicting the olefin orientation. ^{1}H NMR spectra for the Tp'Pt(η^2-cycloalkene)(H) complexes display a 2:1 pattern for the pyrazole resonances consistent with mirror symmetry in the molecule. The two olefinic protons are enantiotopic and appear as a multiplet with platinum satellites in accord with the platinum(IV) octahedral metallacycloalkane geometry. The olefin protons in the η^2-cyclohexene complex, **3**, resonate at 3.79 ppm, well upfield from free cyclohexene (δ = 6.02 ppm),[42] with $^2J_{Pt-H}$ = 100 Hz. The other η^2-cycloalkene complexes, **2** and **4**, show similar ^{1}H NMR spectra with olefinic signals at 3.64 ppm ($^2J_{Pt-H}$ = 94 Hz) and 3.36 ppm ($^2J_{Pt-H}$ = 90 Hz), respectively. The carbon atoms coordinated to the platinum center in the η^2-cyclohexene complex, **3**, resonate at 32.1 ppm with $^1J_{Pt-C}$ = 362 Hz.

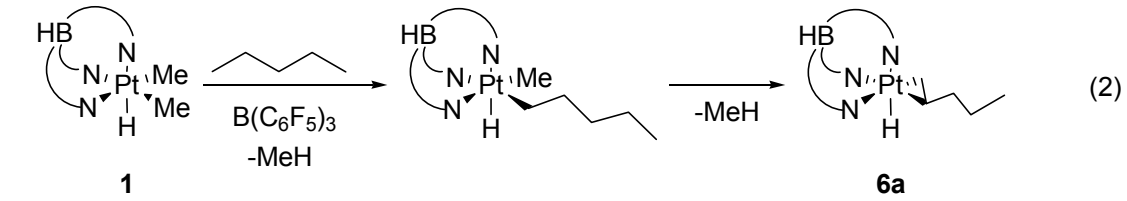
The Pt-H resonances for the Tp'Pt(η^2-cycloalkene)(H) complexes appear far upfield at -28.57 ppm (**2**, $^1J_{Pt-H}$ = 1183 Hz), -29.19 ppm (**3**, $^1J_{Pt-H}$ = 1200 Hz), and -29.12 ppm (**4**, $^1J_{Pt-H}$ = 1198 Hz) possibly due to their location in the shielding region of the adjacent pyrazole

rings. Similar Pt-H chemical shifts were observed in ([2.1.1]pyridinophane)Pt(η^2-olefin)(H) complexes.[39]

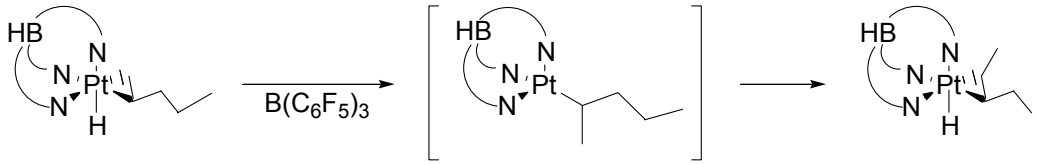
To assess the ability of Tp'PtMe$_2$H (**1**) to activate more sterically hindered C-H bonds, the reaction of **1** with *t*-butylethane in the presence of B(C_6F_5)$_3$ was studied. `The observed product formed, Tp'Pt(Me)H(CH_2CH_2($C(CH_3)_3$), upon Lewis acid induced methane elimination, arises when the less sterically hindered primary C-H bond of the ethyl group of *t*-butylethane is activated. The Pt-H resonates at –20.99 ppm ($^1J_{Pt-H}$ = 1443 Hz) in CD_2Cl_2. Continued heating results in elimination of a second equivalent of methane and formation of the β-H elimination product Tp'Pt(η^2-neohexene)(H) (**5**). The solution IR spectrum for Tp'Pt(H)(η^2-neohexene) in CH_2Cl_2 indicates κ^3 coordination for Tp' (ν_{B-H} = 2535 cm^{-1}) as was seen in the η^2-cycloalkene complexes. The three olefin protons are all distinct. The internal olefin proton resonates at 3.70 ppm with $^2J_{Pt-H}$ = 97 Hz and is easily distinguished since *cis* and *trans* couplings to the other olefin protons of $^3J_{H-H}$ = 8.4 Hz and $^3J_{H-H}$ = 10.8 Hz, respectively, are observed. The Pt-H resonates far upfield at -28.78 ppm ($^1J_{Pt-H}$ = 1154 Hz) similar to the Tp'Pt(η^2-cycloalkene)(H) complexes.

The ability of Tp'PtMe$_2$H (**1**) to activate C-H bonds regioselectively was examined by the reaction of **1** with *n*-pentane. Upon Lewis acid induced methane elimination, activation of the primary C-H bond of the solvent is indicated by the formation of Tp'Pt(1-pentyl)(Me)H as in accord with a previously reported synthesis.[43] No formation of the secondary C-H bond activation products, Tp'Pt(2-pentyl)(Me)H or Tp'Pt(3-pentyl)(Me)H, was observed under these conditions. As the reaction proceeds, elimination of a second equivalent of methane from Tp'Pt(1-pentyl)(Me)H occurs followed by β-H elimination to give the η^2-1-pentene product, Tp'Pt(η^2-CH_2=$CHCH_2CH_2CH_3$)(H) (**6a**) (Eq. 2). Increased

reaction times show the appearance of a new product formulated as the η^2-2-pentene complex, Tp'Pt(η^2-CH(Me)=CH(CH_2CH_3))(H) (**6b**). Since initial results show no formation of Tp'Pt(2-pentyl)(Me)H or Tp'Pt(3-pentyl)(Me)H which could lead directly to the η^2-2-pentene complex **6b**, formation of **6b** is most likely a result of isomerization of **6a** to the internal olefin complex via 2,1-insertion of the olefin into the Pt-H bond followed by β-H elimination (Figure 2.2). The ratio of **6a**:**6b** after 15 h was 4:1.



1 **6a** (2)



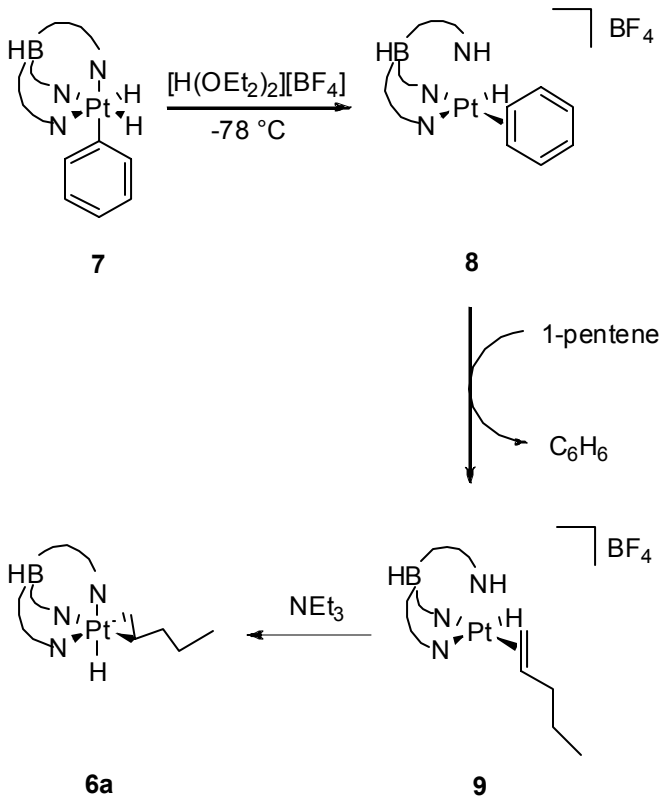
6a **6b**

Figure 2.2: Proposed mechanism for isomerization of Tp'Pt(η^2-1-pentene)(H) (**6a**) to Tp'Pt(η^2-2-pentene)(H) (**6b**).

The ^{1}H NMR spectrum for the reaction of **1** with *n*-pentane after 15 h indicated the formation of only one isomer for the η^2-1-pentene complex **6a** and one for the η^2-2-pentene complex **6b** out of the two and four possible NMR distinguishable facial isomers, respectively. Differentiation between isomers **6a** and **6b** was possible by analysis of the olefin proton resonances. Formation of the η^2-1-pentene complex **6a** was confirmed by the observation of three COSY correlated olefinic protons. The two terminal olefin protons for

6a resonate at 2.82 ppm ($^2J_{Pt-H}$ = 86 Hz, $^3J_{H-H}$ = 7.6 Hz, $^2J_{H-H}$ = 2.0 Hz) and 2.41 ppm ($^2J_{Pt-H}$ = 50 Hz, $^3J_{H-H}$ = 9.6 Hz, $^2J_{H-H}$ = 2.0 Hz) as doublets of doublets. The internal olefinic proton resonates at 3.39 ppm as a multiplet. The η^2-2-pentene isomer **6b** has only two olefinic protons, and a distinctive doublet appears for the terminal methyl group at 1.59 ppm ($^3J_{Pt-H}$ = 42 Hz).

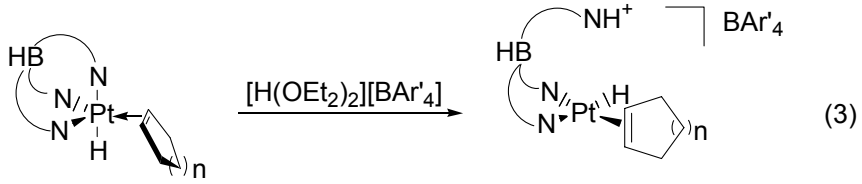
Tp'Pt(η^2-1-pentene)(H) (**6a)** has also been prepared independently via low temperature protonation of Tp'Pt(Ph)$(H)_2$ (**7**), followed by addition of 1-pentene and subsequent deprotonation (Scheme 2.1). In a previous investigation of Tp'Pt(Ar)(R)(H) complexes [Ar = aryl, R = H, C_6H_5], protonation of these aryl complexes at low temperature was found to result in the formation of cationic Pt(II) η^2-arene adducts.[47] Complex **7** was protonated with HBF_4 at -78 °C to form [κ^2-(HTp')Pt(η^2-benzene)(H)][BF_4] (**8**). Addition of excess 1-pentene to the cold solution of **8** led to formation of [κ^2-(HTp')Pt(η^2-1-pentene)(H)][BF_4] (**9**) after 5 hr. Complex **9** can be observed by ^{1}H NMR below 233 K as two isomers with platinum hydrides resonating at -22.19 ppm ($^1J_{Pt-H}$ = 1080 Hz) and -23.59 ppm ($^1J_{Pt-H}$ = 1176 Hz). The neutral, six-coordinate Tp'Pt(η^2-1-pentene)(H)(**6a**) was subsequently trapped by the deprotonation with NEt_3. Once **9** had been deprotonated the solution could be warmed and **6a** could be isolated without further isomerization to **6b**. However, if [κ^2-(HTp')Pt(η^2-1-pentene)(H)][BF_4] (**9**) was warmed prior to deprotonation, a mixture of **6a** and **6b** resulted. Synthesis of the η^2-2-pentene isomer, **6b,** by an analogous route was unsuccessful.



Scheme 2.1: Low Temperature Route to Tp'Pt(η^2-1-pentene)(H) (**6a**).

Cationic η^2-Olefin Complexes. Low temperature protonation of the Tp'Pt(η^2-cycloalkene)(H) complexes, **2** and **3**, with $[H(OEt_2)_2][BAr'_4]$ [BAr'_4 = tetrakis(3,5-trifluoromethylphenyl)borate][48] results in removal of one of the pyrazole arms from the metal center as cationic Pt(II) η^2-olefin complexes [κ^2-(HTp')Pt(η^2-cycloalkene)(H)][BAr'_4] [cycloalkene = C_5H_{10} (**10**) and C_6H_{12} (**11**)] (Eq. 3) form. The ^{1}H NMR spectra for the [κ^2-(HTp')Pt(η^2-cycloalkene)(H)][BAr'_4] complexes display N-H resonances at 9.82 (**10**) and 9.90 ppm (**11**) for the protonated pyrazole arm. The mirror symmetry of the starting neutral

platinum complexes, **2** and **3**, has been lost upon protonation as is evident in the unique signals observed for each of the three nonequivalent pyrazole arms in the ^{1}H NMR spectra.



(3)

n = 1 (**2**)
2 (**3**)

n = 1 (**10**)
2 (**11**)

The absence of symmetry in the protonated platinum complex is also reflected in the two inequivalent olefin proton resonances in the ^{1}H NMR spectra. The two distinct olefin protons for the η^2-cyclopentene complex **10** resonate at 5.37 ($^2J_{Pt\text{-}H}$ = 77 Hz) and 4.54 ppm ($^2J_{Pt\text{-}H}$ = 77 Hz), well downfield from their chemical shift in neutral analog **2**. Complex **11** shows similar resonances for the coordinated cyclohexene at 5.47 ppm ($^2J_{Pt\text{-}H}$ = 70 Hz) and 4.63 ppm ($^2J_{Pt\text{-}H}$ = 74 Hz). The carbon atoms coordinated to the cationic platinum center in the η^2-cyclohexene complex **11** are also distinct and resonate at 82.6 ppm and 81.5 ppm. The Pt-H resonances for **10** and **11** are shifted downfield from their neutral analogs to -23.25 ($^1J_{Pt\text{-}H}$ = 1182 Hz) and -23.75 ($^1J_{Pt\text{-}H}$ = 1226 Hz), respectively.

The structural features of the cationic η^2-cyclohexene platinum complex **11** were investigated by single crystal X-ray diffraction. An ORTEP diagram of **11** is shown in Figure 2.3. The Pt-N(21) distance of 2.135(6) Å is 0.1 Å longer than the Pt-N(11) distance of 2.035(6) Å *trans* to the cyclohexene ligand, indicating the stronger *trans* influence of the hydride ligand (Table 2.1). The bond distance between C1-C2 (1.366(15) Å) is significantly shorter than the single bond C-C distances in the cyclohexene ring indicating the retention of partial double bond character when coordinated to platinum(II). The tilt angle of the olefin in cyclohexene relative to the platinum square plane is 131.5°. Based on the geometries of

other square-planar platinum(II) olefin complexes, one would anticipate the orientation of the olefin in cyclohexene to be perpendicular to the platinum square plane.[46] Unfavorable steric interactions between the cyclohexene ring and the uncoordinated pyrazole ring appear to dictate the alignment of the olefin away from perpendicular relative to the platinum square plane.

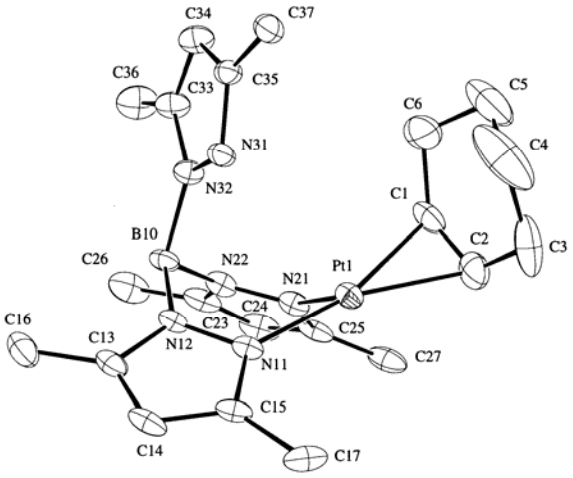


Figure 2.3: ORTEP diagram of [κ^2-(HTp')Pt(η^2-cyclo-C_6H_{10})(H)][BAr'$_4$] (**11**). Ellipsoids are drawn at the 50% probability level, and the [BAr'$_4$] counterion is omitted for clarity.

Table 2.1: Selected Bond Distances (Å)and Angles(°) for Complex **11**

Pt-C1	2.189(8)	C1-C2	1.366(15)
Pt-C2	2.204(9)	C1-C6	1.510(14)
Pt-N11	2.035(6)	C2-C3	1.503(16)
Pt-N21	2.135(6)	C4-C5	1.47(3)
C1-Pt-C2	36.2(4)	C2-Pt-N21	110.0(3)
C1-Pt-N11	164.1(3)	N11-Pt-N21	85.71(22)
C1-Pt-N21	86.2(3)	Pt-C1-C2	72.5(5)
C2-Pt-N11	159.1(3)	Pt-C2-C1	71.3(5)

Summary

Stoichiometric alkane dehydrogenation was observed when Tp'PtMe$_2$H was treated with Lewis acid in alkane solvents. The reaction is proposed to proceed via borane-induced methane elimination and subsequent C-H activation of the solvent to give a Tp'Pt(Me)(alkyl)H intermediate. Upon further heating, elimination of a second equivalent of methane occurs followed by β-H elimination to give Tp'Pt(η^2-olefin)(H) complexes. Although the selective conversion of *n*-pentane to 1-pentene was not achieved, initial results indicate regioselective activation of the stronger primary C-H bond over the weaker secondary C-H bond of *n*-pentane. Protonation of neutral Tp'Pt(η^2-cycloalkene)(H) complexes results in release of one pyrazole arm from the platinum center and formation of cationic Pt(II) η^2-cycloalkene complexes.

Experimental Section

Materials and Methods. Reactions were performed under an atmosphere of dry nitrogen or argon using standard drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was oven-dried prior to use. Methylene chloride and pentane were purified under an argon atmosphere by passage through a column packed with activated alumina.[49] Cyclopentane (Aldrich, sure seal), cyclohexane (Aldrich, sure seal), cyclooctane, and tert-butylethane were used as purchased. Deuterated methylene chloride was vacuum transferred from P_2O_5 and degassed by several freeze-pump-thaw cycles.

Tp'PtMe$_2$H,[50] Tp'PtPhH$_2$[47] and [H(OEt$_2$)$_2$][BAr'$_4$][48] were synthesized according to published procedures. B(C$_6$F$_5$)$_3$ was used as obtained from Strem. [H(OEt$_2$)$_2$][BF$_4$] was obtained from Aldrich and used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 or 300 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Chemical analyses were performed by Atlantic Microlabs of Norcross, GA.

Representative Synthesis of Tp'Pt(η^2-olefin)(H). In a typical experiment, Tp'PtMe$_2$H (1) (0.100 g, 0.191 mmol) and 1 equivalent of B(C_6F_5)$_3$ (0.098 g) were weighed into a 100 mL Schlenk flask. Then 15 mL of the alkane solvent were added via syringe through the septum. The reaction mixture was heated at 35-50 ºC and stirred for two days. After solvent was removed in vacuo, the residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a white solid was obtained which was recrystallized from CH_2Cl_2/methanol at -30 °C.

Tp'Pt(η^2-cyclo-C_5H_8)(H) (2). Anhydrous cyclopentane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 2.5 days at 35 °C. Yield: 85 mg (79 %). IR (CH_2Cl_2): $\nu_{B\text{-}H}$ = 2533 cm^{-1}, $\nu_{Pt\text{-}H}$ = 2265 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 253K, δ): 5.83, 5.64 (s, 2H, 1H, Tp'C*H*), 3.64 (m, 2H, $^{2}J_{Pt\text{-}H}$ = 94 Hz, Pt(C*H*=C*H*$CH_2CH_2CH_2$)), 2.32, 2.30, 2.16, 2.15 (s, 6H, 3H, 6H, 3H, Tp'CH_3), 2.00, 1.71, 1.16 (m, m, m, 6H, Pt(CH=CHCH_2CH_2CH_2), -28.57 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1183 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 253K, δ): 148.9, 144.5, 143.9 (3C, 1C, 2C, Tp'*C*CH_3), 107.8, 104.9 (1C, 2C, Tp'*C*H), 38.4, 32.2, 22.0 (2C, 2C, 1C, Pt(*C*H=*C*HCH_2CH_2CH_2), 14.6, 13.2, 12.4, 12.2 (2C, 1C, 2C, 1C, Tp'C*C*H_3). Anal. Calcd. for $PtBN_6C_{20}H_{31}\cdot CH_2Cl_2$: C, 39.03; H, 5.15; N, 13.00; Found: C, 40.03; H, 5.15; N, 12.79.

Tp'Pt(η^2-cyclo-C_6H_{10})(H) (3). Anhydrous cyclohexane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 2 days at 50 °C. Yield: 70 mg (64 %). IR (KBr): $\nu_{B\text{-}H}$ = 2516 cm^{-1}, $\nu_{Pt\text{-}H}$ = 2269 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 263K, δ): 5.83, 5.64

(s, 2H, 1H, Tp'C*H*), 3.79 (m, 2H, $^{2}J_{Pt\text{-}H}$ = 100 Hz, Pt(C*H*=C*H*$CH_2CH_2CH_2CH_2$)), 2.32, 2.31, 2.21, 2.19 (s, 6H, 3H, 6H, 3H, Tp'CH_3), 2.09, 1.62, 1.28 (m, m, m 8H, Pt(CH=CHCH_2CH_2CH_2CH_2)), -29.19 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1200 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 263K, δ): 150.8, 149.0, 144.5, 143.9 (1C, 2C, 1C, 2C, Tp'*C*CH_3), 108.3, 105.1 (1C, 2C, Tp'*C*H), 32.1 (2C, $^{1}J_{Pt\text{-}C}$ = 362 Hz, Pt(*C*H=*C*H$CH_2CH_2CH_2CH_2$), 29.6, 22.1 (2C, 2C, Pt(CH=CH*C*H_2*C*H_2*C*H_2*C*H_2),) 14.7, 12.6, 12.5, 11.8 (2C, 1C, 2C, 1C, Tp'C*C*H_3). Anal. Calcd for $PtBN_6C_{21}H_{33}\cdot 0.5\ CH_3OH$: C, 43.66; H, 5.96; N, 14.21; Found: C, 43.13; H, 5.66; N, 14.34.

Tp'Pt(η^2-cyclo-C_8H_{14})(H) (4). Cyclooctane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 2 days at 50 °C. Yield: 91 mg (79 %). IR (CH_2Cl_2): $\nu_{B\text{-}H}$ = 2533 cm^{-1}, $\nu_{Pt\text{-}H}$ = 2275 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 263K, δ): 5.82, 5.67 (s, 2H, 1H, Tp'C*H*), 3.36 (m, 2H, $^{2}J_{Pt\text{-}H}$ = 90 Hz, Pt(C*H*=C*H*$CH_2CH_2CH_2CH_2CH_2CH_2$), 2.32, 2.31, 2.20, 2.19 (s, 3H, 6H, 6H, 3H, Tp'CH_3), 1.66-1.41 (m, 12H, Pt(CH=CHCH_2CH_2CH_2CH_2CH_2CH_2), -29.12 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1198 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 263K, δ): 151.0, 148.9, 144.0, 143.9 (1C, 2C, 1C, 2C, Tp'*C*CH_3), 108.4, 105.0 (1C, 2C, Tp'*C*H), 37.5 (2C, $^{1}J_{Pt\text{-}C}$ = 362 Hz, Pt(*C*H=*C*H$CH_2CH_2CH_2CH_2CH_2CH_2$), 33.5, 31.7, 26.6 (2C, 2C, 2C, Pt(CH=CH*C*H_2*C*H_2*C*H_2*C*H_2*C*H_2*C*H_2),) 14.9, 12.6, 12.5, 12.0 (2C, 1C, 2C, 1C, Tp'C*C*H_3). Anal. Calcd for $PtBN_6C_{23}H_{37}\cdot CH_2Cl_2$: C, 41.87; H, 5.71; N, 12.21; Found: C, 42.17; H, 5.80; N, 12.39.

Tp'Pt(η^2-neohexene)(H) (5). Anhydrous *tert*-butylethane (15 mL) was added to the solids as described above. The reaction mixture was stirred for 3 days at 35 °C. Yield: 72 mg (65 %). IR (CH_2Cl_2): $\nu_{B\text{-}H}$ = 2535 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 240K, δ): 5.82, 5.67 (s, 2H, 1H, Tp'C*H*), 3.70 (dd, 1H, $^{2}J_{Pt\text{-}H}$ = 97 Hz, $^{3}J_{H\text{-}H}$ = 8.4 Hz, $^{3}J_{H\text{-}H}$ = 10.8 Hz, Pt-CH_2=C*H*($C(CH_3)_3$),

2.45 (dd, 1H, Pt-CH_2=CH(C$(CH_3)_3$), 2.35, 2.27, 2.18 (s, 9H, 3H, 6H, Tp'CH_3), 1.05 (s, 9H, Pt-CH_2=CH(C(CH_3)$_3$), -28.78 (s, 1H, $^1J_{Pt-H}$ = 1154 Hz, Pt-*H*). The other inequivalent olefin proton resonance is obscured by the Tp'(CH_3) resonances in the range from 2.35 - 2.18 ppm. Satisfactory analytical data was not obtained.

Tp'Pt(η^2-pentene)(H). Anhydrous *n*-pentane (20 mL) was added to the solids as described above. The reaction mixture was stirred for 15 hours at 30 °C. The ratio of Tp'Pt(η^2-1-pentene)(H) (**6a**) to Tp'Pt(η^2-2-pentene)(H) (**6b**) was 4:1 with a yield of 34 mg (63 %). IR (CH_2Cl_2): ν_{B-H} = 2535 cm^{-1}. ^{1}H NMR for **6a** (CD_2Cl_2, 298 K, δ): 5.83, 5.67 (s, 2H, 1H, Tp'C*H*), 3.39 (m, 1H, Pt-CH_2=C*H*$CH_2CH_2CH_3$), 2.82 (dd, 1H, $^2J_{Pt-H}$ = 86 Hz, $^3J_{H-H}$ = 7.6 Hz, $^2J_{H-H}$ = 2.0 Hz, Pt-CH_2=C$HCH_2CH_2CH_3$ (*trans*-H)), 2.41 (dd, 1H, $^2J_{Pt-H}$ = 50 Hz, $^3J_{H-H}$ = 9.6 Hz, $^2J_{H-H}$ = 2.0 Hz, Pt-CH_2=C$HCH_2CH_2CH_3$ (*cis*-H)), 2.38 - 2.12 (s, 18H, Tp'CH_3), 1.71, 1.32 (m, 2H, 2H, Pt-CH_2=CHCH_2C$H_2$$CH_3$), 0.99 (t, Pt-$CH_2$=$CHCH_2CH_2CH_3$), -29.14 (s, 1H, $^1J_{Pt-H}$ = 1144 Hz, Pt-*H*). ^{1}H NMR for **6b** (CD_2Cl_2, 298 K, δ): 5.83, 5.67 (s, 2H, 1H, Tp'C*H*), 3.45 (m, 2H, Pt-C*H*(CH_3)=C*H*(CH_2CH_3), 2.38 - 2.12 (s, 18H, Tp'CH_3), 1.59 (d, 3H, $^3J_{Pt-H}$ = 42 Hz, Pt-CH(CH_3)=CH(CH_2CH_3)), 1.45 (m, 2H, Pt-CH(CH_3)=CH(C$H_2$$CH_3$)), 1.07 (t, 3H, Pt-CH($CH_3$)=CH($CH_2CH_3$)), -29.50 (s, 1H, $^1J_{Pt-H}$ = 1208 Hz, Pt-*H*).

Synthesis of Tp'Pt(η^2-1-pentene)(H) (6a). Tp'Pt(Ph)$(H)_2$ (**7**) (85mg, 0.148 mmol) was placed in a 50 mL Schlenk flask under N_2 and dissolved in 15 mL CH_2Cl_2. The solution was cooled to -78 °C and 1.1 equivelents of HBF_4 (22 μL, 0.162 mmol) were added via syringe. After 15 minutes, 190 μL (1.48 mmol) of cold 1-pentene were added to the solution. After 5 h, NEt_3 (22 μL, 0.148 mmol) was added to the cold solution to depronate. After 1.5 h, the cold bath was removed and solvent pulled off in vacuo, resulting in an oily yellow product. The product was taken up in minimal CH_2Cl_2 and 5x hexanes were added to crash out the

salts. The liquid was filtered away from the salts via canula transfer and the filtrate condensed to a white powder by rotoevaporation. Yield: 69 mg (83 %).

[κ^2-(HTp')Pt(η^2-1-pentene)(H)][BF_4] (9). An NMR tube was charged with 15 mg of Tp'Pt(η^2-1-pentene)(H) (**6a)** (0.0266 mmol) and the solids dissolved in 0.7 ml anhydrous CD_2Cl_2 in the drybox. Outside the drybox, the tube was cooled to -78 °C and 3.6 μL [$H(OEt_2)_2$][BF_4] (0.0266 mmol) were added. The sample was kept below 233 K. ^{1}H NMR (CD_2Cl_2, 233 K, δ): -22.19 (s, 1H, $^1J_{Pt\text{-}H}$ = 1080 Hz, Pt-*H*), -23.59 (s, 1H, $^1J_{Pt\text{-}H}$ = 1176 Hz, Pt-*H*).

Representative [BAr'$_4$]$^-$ NMR Data. ^{1}H and ^{13}C NMR data for the [BAr'$_4$]$^-$ counterion are reported separately for simplicity. ^{1}H NMR (CD_2Cl_2, 193K, δ): 7.77 (br, 8H, o-Ar'), 7.60 (br, 4H, p-Ar'). ^{13}C NMR (CD_2Cl_2, 193K, δ): 162.2 (1:1:1:1 pattern, $^1J_{B\text{-}C}$ = 50 Hz, C_{ipso}), 135.3 (C_{ortho}), 129.4 (qq, $^2J_{C\text{-}F}$ = 30 Hz, $^4J_{C\text{-}F}$ = 5 Hz, C_{meta}), 125.1 (q, $^1J_{C\text{-}F}$ = 270 Hz, CF_3), 117.9 (C_{para}).

[κ^2-(HTp')Pt(η^2-cyclo-C_5H_8)(H)][BAr'$_4$] (10). Tp'Pt(η^2-C_5H_8)(H) (2) (0.125 g, 0.239 mmol) and [$H(OEt_2)_2$][BAr'$_4$] (0.290 g, 0.287 mmol) were weighed into a 100 mL Schlenk flask in the drybox. The flask was cooled to -78 °C outside the drybox. CH_2Cl_2 (20 mL) was slowly added through the septum, and the reaction mixture was stirred for 10 minutes. The cold bath was removed, and the reaction was stirred for 30 minutes while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. Colorless crystals were obtained from CH_2Cl_2/pentane at -30 °C. Yield: 66 mg (20 %). ^{1}H NMR (CD_2Cl_2, 293K, δ): 9.82 (s, 1H, pz'N*H*), 6.24, 6.09, 6.00 (s, 1H each, HTp'C*H*), 5.37 (m, 1H, $^2J_{Pt\text{-}H}$ = 77 Hz, Pt(C*H*=C*H*$CH_2CH_2CH_2$)), 4.54 (m, 1H, $^2J_{Pt\text{-}H}$ = 77 Hz, Pt(C*H*=C*H*$CH_2CH_2CH_2$)), 2.37, 2.36, 2.27, 2.22, 1.83 (s, 6H, 3H, 3H, 3H, 3H, HTp'CH_3),

2.09, 1.65, 1.42 (m, 2H each, Pt(CH=CHCH_2CH_2CH_2)), -23.25 (s, 1H, $^1J_{Pt\text{-}H}$ = 1182 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 293K, δ): 153.8, 153.2, 150.2, 149.2, 148.7, 144.3 (HTp'*C*CH_3), 110.2, 109.4, 108.1 (HTp'*C*H), 86.9, 85.7 (Pt(*C*H=*C*HCH_2CH_2CH_2), 35.6, 34.3, 21.0 (Pt(CH=CHCH_2CH_2CH_2) 16.4, 14.2, 13.3, 11.6, 11.4 (Tp'C*C*H_3). Anal. Calcd for $PtB_2F_{24}N_6C_{52}H_{44}$: C, 43.81; H, 3.11; N, 5.89; Found: C, 44.01; H, 3.12; N, 5.61.

[κ^2-(HTp')Pt(η^2-cyclo-C_6H_{10})(H)][BAr'$_4$] (11). Tp'Pt(η^2-C_6H_{10})(H) (3) (0.042 g, 0.072 mmol) and [H(OEt_2)$_2$][BAr'$_4$] (0.089 g, 0.088 mmol) were weighed into a 50 mL Schlenk flask in the drybox. The flask was cooled to -78 °C outside the drybox. CH_2Cl_2 (10 mL) was slowly added through the septum, and the reaction mixture was stirred for 10 minutes. The cold bath was removed, and the reaction was stirred for 30 minutes while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. Colorless crystals were obtained from CH_2Cl_2/pentane at -30 °C. Yield: 67 mg (73 %). ^{1}H NMR (CD_2Cl_2, 293K, δ): 9.90 (s, 1H, pz'N*H*), 6.25, 6.10, 6.00 (s, 1H each, HTp'C*H*), 5.47 (m, 1H, $^2J_{Pt\text{-}H}$ = 70 Hz, Pt(C*H*=C*H*CH_2CH_2CH_2CH_2)), 4.63 (m, 1H, $^2J_{Pt\text{-}H}$ = 74 Hz, Pt(C*H*=C*H*CH_2CH_2CH_2CH_2)), 2.39, 2.38, 2.36, 2.26, 2.24, 1.80 (s, 3H each, HTp'CH_3), 1.70-1.27 (m, 8H, Pt(CH=CHCH_2CH_2CH_2CH_2)), -23.75 (s, 1H, $^1J_{Pt\text{-}H}$ = 1226 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 293K, δ): 153.7, 153.3, 150.2, 149.1, 148.8, 144.3 (HTp'*C*CH_3), 110.3, 109.5, 108.0 (HTp'*C*H), 82.6, 81.5 (Pt(*C*H=*C*HCH_2CH_2CH_2CH_2)), 30.3, 29.6, 21.3, 20.9 (Pt(CH=CHCH_2CH_2CH_2CH_2)), 14.5, 14.1, 13.3, 11.6, 11.5 (Tp'C*C*H_3). Anal. Calcd for $PtB_2F_{24}N_6C_{53}H_{46}$: C, 44.22; H, 3.22; N, 5.84; Found: C, 44.26; H, 3.09; N, 5.78.

Structural Data for 11. Crystals from CH_2Cl_2/pentane; $C_{53}H_{45.34}N_6F_{24}B_2Pt$, M = 1438.98; triclinic, space group P –1; Z = 2; a = 12.6222(4), b = 12.6738(4), c = 18.3604(5) Å; α = 87.648(1), β = 82.375(1), γ = 83.164(1)°; U = 2889.52(15) Å^3; D_c = 1.654 Mg m^{-3}; T = -

100°C; max 2θ: 50°; Mo-K_α radiation (λ = 0.71073 Å); 10163 unique reflections were obtained and 8156 of these with I > 2.5σ(I) were used in the refinement; data were collected on a Bruker SMART diffractometer, using the omega scan method. For significant reflections merging R-value: 0.032; Residuals: R_F: 0.050; R_W: 0.060 (significant reflections); GoF: 1.7330.

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CHAPTER 3

ETHYLENE INSERTION IN Tp'Pt(Ph)(η^2-CH_2=CH_2) AND C-H ACTIVATION OF ETHYLBENZENE TO FORM A Pt(IV) ORTHO-METALLATED PHENETHYL COMPLEX

Introduction

Generation of useful chemicals from readily available and inexpensive chemical feedstocks, such as saturated hydrocarbons, remains a major research challenge. Transition metal-mediated activation of C-H bonds is a promising approach to achieve this goal, and significant effort has been directed at understanding these processes.[1-8] While many metal reagents are capable of activating C-H bonds, few lead to catalytic formation of new C-C or C-X bonds, a prerequisite for the production of organic molecules.[9,10] Substantive advances in C-H activation of arenes with subsequent C-C bond formation have been made, although they are primarily limited to arenes with heteroatom functionality.[11] The heteroatom typically allows coordination of the arene to the metal center thus positioning the C-H bond to be cleaved. One of the most useful transformations of this type is the ruthenium-[12-14] or rhodium-catalyzed[15] selective *ortho* alkylation of aromatic ketones with olefins.

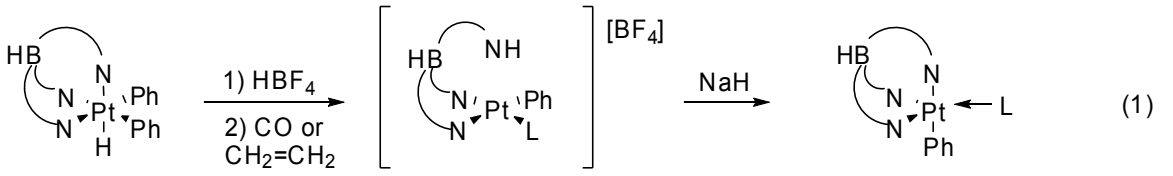
Transformations with unactivated C-H bonds by transition metal complexes, such as hydroarylation of olefins, are rare.[16-23] A few homogeneous catalysts have been reported recently to catalyze the intermolecular hydroarylation of unactivated arenes with unactivated olefins via a C-H activation reaction. Periana and co-workers, for example, have described the regioselective hydroarylation of olefins by O-donor ligated Ir(III) catalysts, specifically,

$(acac\text{-}O,O)_2Ir(R)(py)$ and, more recently, $(trop\text{-}O,O)_2Ir(Ph)(py)$ (acac-O,O = κ^2-O,O-acetylacetonate, trop-O,O = κ^2-O,O-tropolonato, R = CH_3, C_2H_5, Ph, CH_2CH_2Ph). [24-30] Gunnoe and co-workers[31-33] have reported a related Ru(II) catalyst, TpRu(CO)(NCMe)Me (Tp = hydridotris(pyrazolyl)borate), that is ~200 times faster than previous systems[34] for the catalytic conversion of benzene and ethylene to ethylbenzene at 90 °C. These Ir(III) and Ru(II) systems preferentially undergo 2,1-insertion to form straight-chain alkylarenes. Theoretical studies suggest that these systems react through a common mechanism which includes insertion of the π bond of the metal coordinated ethylene into the metal-aryl bond and C-H activation/hydrogen transfer of an unactivated benzene.[26,27,34] Of the various systems that have been reported as active catalysts for the hydroarylation of unactivated olefins, none have proven to be sufficiently active and/or selective to be commercially viable.[27]

The synthesis of Tp'Pt(Ph)(η^2-CH_2=CH_2) (**5**) was undertaken in order to explore its potential as a catalyst in ethylbenzene formation, perhaps via a catalytic cycle analogous to that of the previously reported systems.[27,30,33,34] Thermolysis of complex (**5**) in C_6D_6, however, leads to formation of a stable platinum(IV) *ortho*-metallated complex, Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (**7**). While our system undergoes C-C bond formation via insertion of ethylene into the platinum phenyl linkage, subsequent intramolecular C-H activation of an *ortho*-aryl proton, yielding the metallacycle, occurs rather than intermolecular C-H activation of solvent. This *ortho*-metallated platinum hydride complex, **7**, has also been independently prepared as the sole product in the reaction of Tp'$PtMe_2H$ (**2**) with ethylbenzene.

Results and Discussion

Tp'PtLR Complexes. The synthesis of a variety of neutral Tp'PtLMe complexes via protonation of Tp'PtMe$_2$H (**2**), addition of a neutral trapping ligand and subsequent deprotonation has been reported.[35] This reaction sequence has now been used to prepare analogous Tp'Pt(Ph)(L) complexes, Tp'Pt(Ph)(CO) (**4**) and Tp'Pt(Ph)(η^2-CH$_2$=CH$_2$) (**5**), via a protonation/ligand addition/deprotonation sequence with Tp'PtPh$_2$H (**1**) as the metal precursor. Low temperature addition of HBF$_4$·Et$_2$O to a solution of Tp'PtPh$_2$H (**2**) results in the formation of the phenyl benzene adduct [κ^2-(HTp')Pt(C$_6$H$_5$)(η^2-C$_6$H$_6$)][BF$_4$][36] as indicated by the yellow solution color. Addition of ethylene or CO and warming to room temperature results in loss of the η^2-benzene ligand and formation of a Pt(II) cation, [κ^2-(HTp')Pt(C$_6$H$_5$)(L)][BF$_4$] (L = CO or CH$_2$=CH$_2$). Deprotonation of the free pyrazole ring with NaH in THF results in the formation of the desired neutral complexes, Tp'Pt(Ph)(CO) (**4**) and Tp'Pt(Ph)(η^2-CH$_2$=CH$_2$) (**5**) (eq. 1).



1 L = CO (**4**), CH$_2$=CH$_2$ (**5**) (1)

The geometries of analogous Tp'Pt(Me)(L) complexes depend on the identity of the neutral trapping ligand.[35] Complexes containing σ-donor ligands, such as NCMe or SMe$_2$, display simple square-planar Pt(II) geometries with one free Tp' pyrazolyl arm, while complexes with π-acid ligands, such as CO or ethylene, bind all three Tp' rings to the platinum center (Figure 3.1). Both resonance structures shown in Figure 1 for κ^3-Tp' platinum complexes

with olefin ligands are applicable. The octahedral Pt(IV) metallacyclopropane depiction is particularly useful for representing olefin orientation and for predicting coupling constants. The coordination mode of the Tp' ligand can be determined by measuring the B-H stretching frequency, and this indirectly indicates the geometry of the platinum complex. A B-H stretching frequency above 2500 cm^{-1} is indicative of κ^3-Tp' coordination, while a B-H stretch below 2500 cm^{-1} indicates κ^2-Tp' coordination.[37] The methyl ethylene complex, Tp'Pt(Me)(η^2-CH_2=CH_2), displays a five-coordinate trigonal-bipyramidal geometry, whereas, the methyl carbonyl complex, Tp'Pt(Me)(CO), undergoes rapid interconversion between trigonal-bipyramidal and square-planar geometries on the NMR time scale. The analogous Tp'Pt(Ph)(CO) complex **4** displays a similar solution IR spectrum to the methyl carbonyl complex with two absorptions for both the B-H stretch (2528, 2485 cm^{-1}) and CO stretch (2092, 2082 cm^{-1}). This data is consistent with rapid interconversion of the Pt(II) κ^3-Tp' ($\nu_{B\text{-}H}$ 2528 cm^{-1}, ν_{CO} 2082 cm^{-1}) and Pt(II) κ^2-Tp' ($\nu_{B\text{-}H}$ 2485 cm^{-1}, ν_{CO} 2092 cm^{-1}) geometries in solution.[35,38,39]

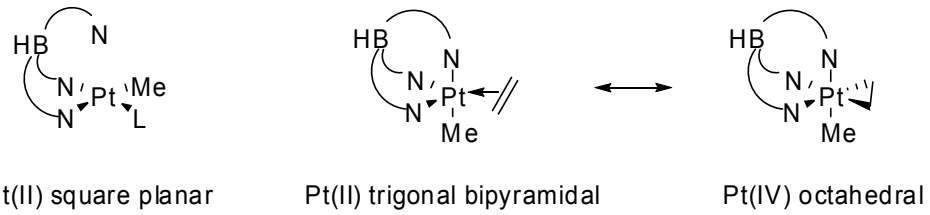


Figure 3.1; Possible geometries for neutral Tp'Pt complexes.

The mirror symmetry observed in the ^1H NMR spectrum for the phenyl carbonyl complex **4** is consistent with a rapid equilibration between square-planar and trigonal bipyramidal geometries in solution. The NMR timescale is too slow to resolve this dynamic process, but both geometries are evident in the infrared spectrum. The carbonyl carbon for complex **4**

resonates at 163.7 ppm in the ^{13}C NMR spectrum, close to the CO chemical shift in the Tp'Pt(Me)(CO) complex.[35]

Proton NMR spectra for neutral Tp'Pt(Ph)(L) complexes display a 2:1 pattern for the pyrazole resonances consistent with mirror symmetry in the Pt(II) trigonal bipyramidal geometry. The four olefinic protons for the phenyl ethylene complex **5** are equivalent at room temperature due to a combination of mirror symmetry and rapid olefin rotation (Figure 3.2). At 253 K, olefin rotation is slow on the NMR time scale, and doublets are observed at 3.31 ppm ($^2J_{Pt\text{-}H}$ = 80 Hz and $^3J_{H\text{-}H}$ = 7.2 Hz) and 2.44 ppm ($^2J_{Pt\text{-}H}$ = 56 Hz and $^3J_{H\text{-}H}$ = 7.2 Hz) reflecting the AA'XX' pattern of the static C_s structure. The carbon atoms in the coordinated ethylene are isochronous and resonate at 24.2 ppm.

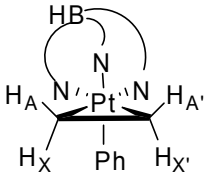


Figure 3.2: Olefin orientation in Tp'Pt(Ph)(η^2-CH_2=CH_2) (**5**).

The structural features of the neutral phenyl ethylene platinum complex **5** were investigated by X-ray structural analysis. An ORTEP diagram of **5** shows κ^3-coordination of the Tp' ligand (Figure 3.3). The platinum atom exhibits a trigonal-bipyramidal coordination geometry (Table 3.1). One coordinated pyrazole ring and the phenyl ligand occupy the axial positions (C3-Pt-N21 = 171.7(6)°) while the other pyrazole rings and ethylene ligand are in the equatorial plane (C2-Pt-N11 = 117.1(8)° and C1-Pt-N31 = 115.6(6)°). The ethylene ligand is oriented perpendicular to the Pt-Ph bond (C1-Pt-C3 = 90.4(7)° and C2-Pt-C3 = 92.0(8)°) with a C1-C2 bond distance of 1.43(3) Å. This coordinated olefin C-C bond

distance is similar to other C-C bond lengths observed in neutral Pt(II) ethylene complexes.[40,41]

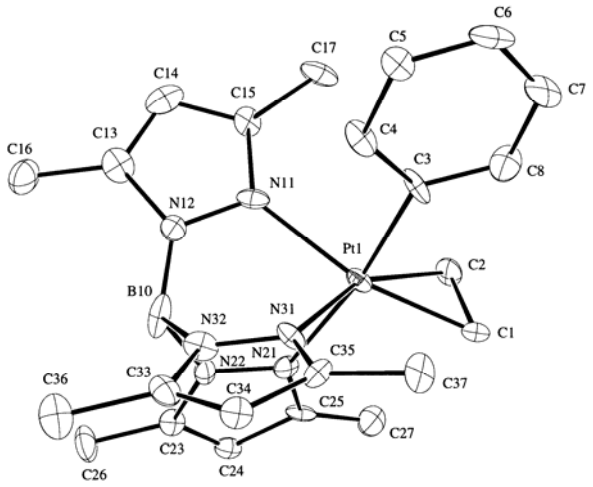


Figure 3.3: ORTEP diagram of Tp'Pt(Ph)(η^2-CH_2=CH_2) (**5**). Ellipsoids are drawn at the 50% probability level.

Table 3.1; Selected bond distances (Å) and angles (°) for complex **5**.

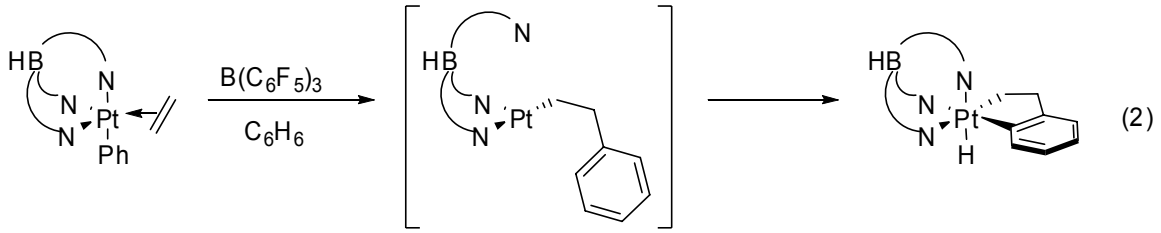
Bond angles			
C1-Pt-C2	40.2(9)	Pt-C2-C1	71.4(10)
C1-Pt-C3	90.4(7)	Pt-C1-C2	68.4(10)
C2-Pt-C3	92.0(8)	C3-Pt-N11	89.4(6)
C1-Pt-N11	157.3(6)	C3-Pt-N21	171.7(6)
C1-Pt-N21	97.7(6)	C3-Pt-N31	90.8(6)
C1-Pt-N31	115.6(6)	N11-Pt-N21	83.8(5)
C2-Pt-N11	117.1(8)	N11-Pt-N31	87.1(5)
C2-Pt-N21	95.3(7)	N21-Pt-N31	84.1(5)
C2-Pt-N31	155.6(9)		

Bond distances			
Pt-C1	2.104(18)	Pt-N11	2.168(15)
Pt-C2	2.064(16)	Pt-N21	2.220(12)
Pt-C3	2.052(14)	Pt-N31	2.140(12)
C1-C2	1.43(3)		

The intermediate cationic Pt(II) η^2-ethylene phenyl complex, [κ^2-(HTp')Pt(η^2-CH_2=CH_2)(Ph)][BAr'$_4$] (**6**) could be detected by low temperature ^{1}H NMR spectroscopy. Protonation of complex **5** with [H(OEt_2)$_2$][BAr'$_4$] resulted in the release of one pyrazole ring from the metal center and formation of complex **6**. The ^{1}H NMR spectrum for complex **6** displays an N-H resonance at 10.36 ppm for the protonated pyrazole ring. The mirror symmetry of the starting neutral platinum complex **5** has been lost, as is evident by the unique signal for each of the three nonequivalent pyrazole rings observed in the ^{1}H NMR spectra. Rapid rotation of the ethylene ligand around the midpoint of the platinum-ethylene bond at room temperature is indicated by the two multiplets observed at 4.21 and 3.77 ppm with broad platinum satellites for the ethylene protons. Similar NMR data has been reported for the analogous methyl complex, [κ^2-(HTp')Pt(η^2-CH_2=CH_2)(Me)][BAr'$_4$].[35]

Olefin Insertion. The addition of Lewis acids to Tp'PtMe_2H (**2**) and Tp'PtMeH_2 (**3**) has been proposed to induce dissociation of one of the pyrazole rings from the platinum center to generate a reactive five-coordinate intermediate at ambient temperatures.[42] In an effort to uncover arene and alkane functionalization routes, the Lewis acid, B(C_6F_5)$_3$, has been used to induce ethylene insertion into the platinum phenyl bond of the phenyl ethylene complex **5** at ambient temperatures (eq. 2). This transformation may proceed by borane-assisted dissociation of one of the pyrazole rings or perhaps trace protic acid is responsible for the

observed reaction. In the presence of borane, insertion occurs readily at 60 °C and is followed by rapid intramolecular C-H activation of an *ortho* phenyl proton to form a Pt(IV) *ortho*-metallated phenethyl hydride complex, Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (**7**). Formation of complex **7** was also observed from the thermolysis of **5** at temperatures above 80 °C in the absence of borane. The appearance of four distinct aromatic proton signals and an upfield Pt-H resonance in the ^{1}H NMR spectrum suggested the metallacyclic structure of complex **7**. Heating the phenyl carbonyl complex **4** to 90 °C in the presence of $B(C_6F_5)_3$ did not result in a similar insertion to form an acyl product, but only led to decomposition.



5 **7**

The preferred formation of complex **7** leads to the question of how the Tp'Pt system differs from the previously reported catalytic systems with Ir(III) and Ru(II). A key difference in the Tp'Pt system and the Ir(III) and Ru(II) systems is the ability of Tp'Pt species to access and stabilize both Pt(II) and Pt(IV) oxidation states. Formation of the Pt(IV) metallacylo hydride complex **7** from Tp'Pt(Ph)(η^2-CH_2=CH_2) (**5**) results from insertion of ethylene into the Pt-Ph bond, followed by oxidative addition of an aryl C-H bond. In contrast, for the Ir(III) and Ru(II) systems, DFT studies suggest that following insertion and η^2-coordination of benzene, a σ-bond metathesis or a oxidative hydrogen migration pathway (OHM) – a concerted transfer of a hydrogen from the aryl carbon to the aliphatic carbon – is operative due to the absence of an easily accessible M^{n+2} oxidation state required for an oxidative addition pathway.[27,33,34] In addition, the Ir(III) and Ru(II) systems are coordinatively

saturated and formation of a seven-coordinate metallacycle hydride species may be unfavorable.

The chirality of complex **7** is evident in the three nonequivalent pyrazole rings observed in the ^{1}H NMR spectrum. The four aromatic protons are all distinct with one doublet at 6.76 ppm with $^{3}J_{Pt\text{-}H}$ = 38 Hz, indicative of the one aromatic proton coupled to platinum. The four bridging CH_2CH_2 methylene protons are diastereotopic and appear as multiplets between 3.18 and 2.63 ppm with broad platinum satellites. The platinum hydride resonates at -19.63 ppm with $^{1}J_{Pt\text{-}H}$ = 1391 Hz. The internal carbon of the methylene bridge resonates at 43.98 ppm and the platinum bound methylene carbon resonates far upfield at 8.54 ppm ($^{1}J_{Pt\text{-}C}$ = 601 Hz).

Clear, colorless block crystals of complex **7** were obtained, and the structure was investigated by single crystal X-ray analysis. The hydride ligand on platinum was placed in a calculated position. Figure 3.4 shows the ORTEP diagram of **7**, which displays an octahedral geometry with a κ^3 coordination mode of the Tp' ligand. The metallacycle lies in the equatorial plane opposite two pyrazole rings (C1-Pt-N11 = 177.85(5)° and C8-Pt-N21 = 178.54(4)°, Table 3.2) and is twisted into an envelope conformation with C2 folded toward the platinum hydride position. The Pt-N (Pt-N31 = 2.205(1) Å) bond *trans* to the hydride is longer than the two Pt-N bonds in the equatorial plane, which have similar lengths (Pt-N11 = 2.166(1) Å and Pt-N21 = 2.155(1) Å), indicating the stronger *trans* influence of the hydride ligand. The bond distance from platinum to the methylene carbon is longer than to the arene carbon by 0.059 Å (Pt-C1 = 2.076(1) Å and Pt-C8 = 2.018(1) Å). This difference is consistent with the hybridization of the two carbons; M-C(sp^2) bonds are shorter than M-C(sp^3) bonds.

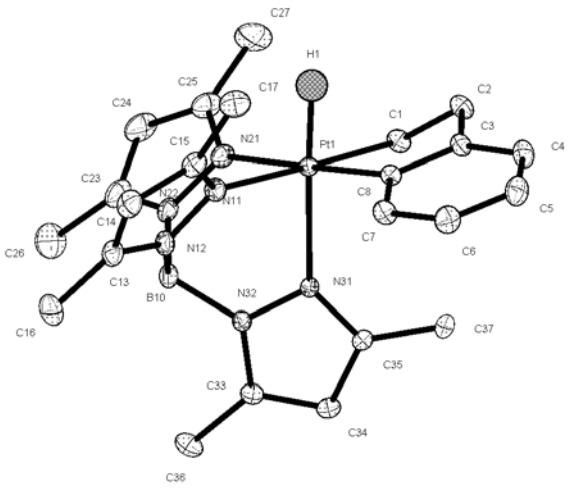
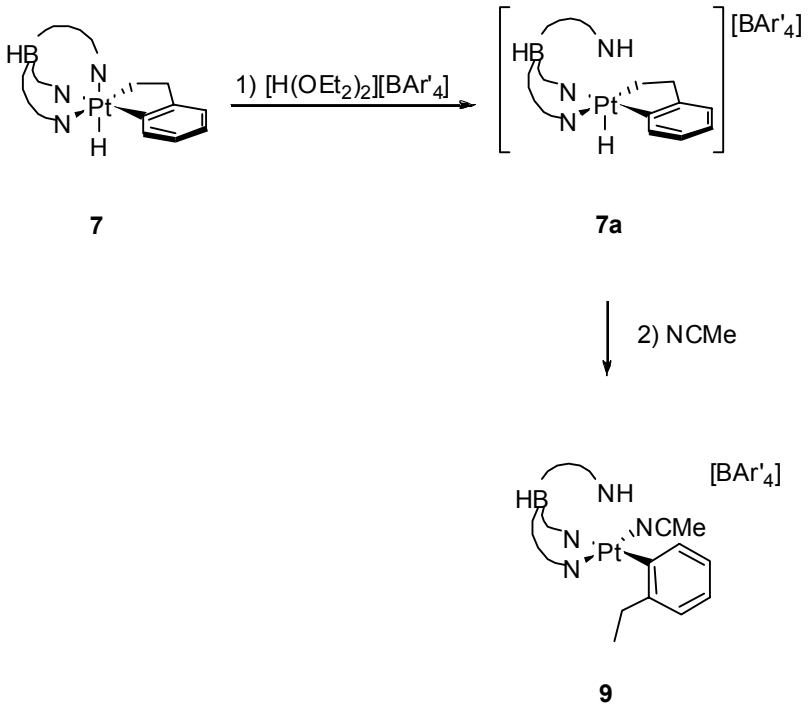


Figure 3.4; ORTEP diagram of Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (**7**). Ellipsoids are drawn at the 50% probability level. C_6H_5Et and Et_2O molecules omitted for clarity.

Table 3.2; Selected bond distances (Å) and angles (°) for complex **7**.

Bond distances			
Pt-C8	2.0176(12)	C3-C4	1.4031(19)
Pt-C1	2.0762(11)	C3-C8	1.4160(15)
Pt-N21	2.1549(11)	C4-C5	1.402(2)
Pt-N11	2.1662(10)	C5-C6	1.399(2)
Pt-N31	2.2053(9)	C6-C7	1.4060(19)
C1-C2	1.5468(19)	C7-C8	1.4055(16)
C2-C3	1.5086(18)		
Bond angles			
C8-Pt-C1	81.33(5)	N21-Pt-N31	87.32(4)
C8-Pt-N21	178.54(4)	N11-Pt-N31	86.71(4)
C1-Pt-N21	97.29(5)	C2-C1-Pt	108.98(8)
C8-Pt-N11	97.68(4)	C3-C2-C1	108.07(9)
C1-Pt-N11	177.85(5)	C4-C3-C2	124.73(11)
N21-Pt-N11	83.69(4)	C8-C3-C2	115.12(11)
C8-Pt-N31	93.25(4)	C7-C8-Pt	125.10(9)
C1-Pt-N31	95.25(4)	C3-C8-Pt	115.61(8)

Low temperature protonation of the platinum(IV) *ortho*-metallated phenethyl hydride complex, Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (**7**), resulted in release of one pyrazole ring from the metal center to presumably generate a reactive five-coordinate intermediate, **7a** (eq. 3). Intermediate **7a** has two possible reductive elimination pathways: the Pt-H can couple with either an aromatic or an aliphatic carbon leaving the other end of the original metallacycle bound to platinum. Reductive elimination of the alkyl group gives exclusively a Pt(II) 2-ethylphenyl ether cation, [κ^2-(HTp')Pt(C_6H_4-2-CH_2CH_3)(OEt_2)][BAr'_4] (**8**). Addition of NCMe converts this complex to the more stable acetonitrile adduct, [κ^2-(HTp')Pt(C_6H_4-2-CH_2CH_3)(NCMe)][BAr'_4] (**9**) (eq. 3). Reductive elimination of the alkyl group was detected by the appearance of an ethyl group in the ^{1}H NMR spectrum. The diastereotopic methylene protons appear as a complex AB portion of an ABX_3 pattern at 3.25 ppm, and the methyl group resonates as a triplet at 1.37 ppm.



(3)

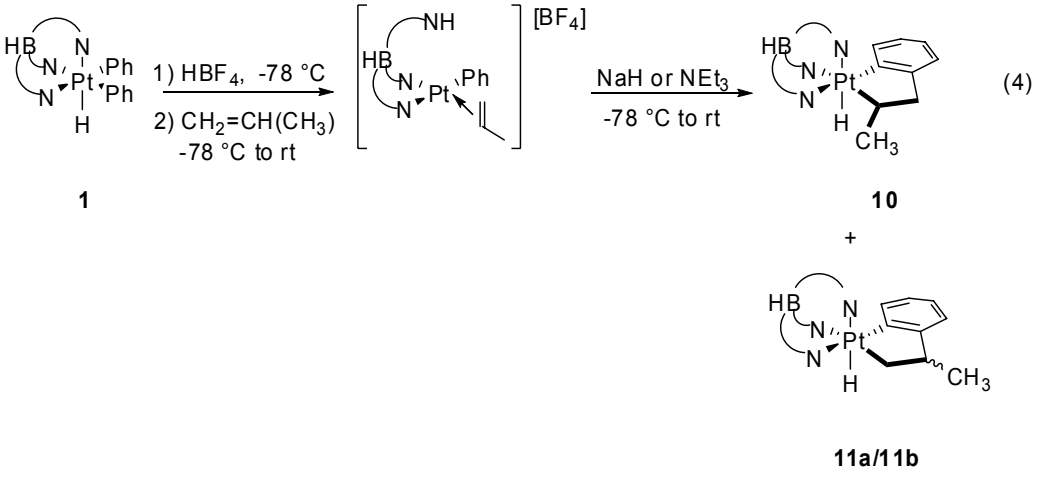
7 **7a** **9**

The preference for alkyl elimination can be attributed to the relative stabilities of the products formed since M-aryl bonds are stronger than M-alkyl bonds.[43-46] Factors other than M-C bond strengths have been shown to be involved in controlling the relative rates of alkyl/aryl reductive elimination,[47] but in this system the products are consistent with relative M-C bond strengths. It is possible that aryl elimination also occurs, but that the product formed rapidly rearranges to the observed 2-ethylphenyl derivative. For example, in the related (diimine)Pt(Me)(Ph)(H)(solv) system Me-H and Ph-H formation and elimination have been shown to be competitive.[48-51]

A similar rearrangement has also been studied for a related Pd system, $\overline{\text{Pd}(CH_2CMe_2\text{–}o\text{-}C_6H_4)}(PMe_3)_2$, synthesized from the base-induced metallation of the neophyl derivatives *trans*-$[Pd(CH_2CMe_2Ph)X(PMe_3)_2]$ (X = Cl, OAc or OTf). When the metallacyle was protonated with HX, the reaction was reversed and the alkyl-bound complex, the neophyl derivative, was reformed via an observed π,η^1-arene intermediate, the π,η^1 designation reflecting coordination of the *ipso* carbon to palladium. Protonation of the metallacycle with $[H(OEt_2)_2][BAr'_4]$ at low temperature resulted in initial formation the π,η^1-arene species which, upon warming in Et_2O or THF, gave the aryl-bound $[Pd(C_6H_5\text{-}2\text{-}CMe_3)(PMe_3)][BAr'_4]$ derivative. Notably, the π,η^1-arene intermediate is proposed to isomerize to the aryl-bound species through a solvent-assisted rearrangement that could produce a Pd(IV) metallacycle hydrido intermediate.[46,52] The Pt(IV) metallacycle hydride complexes synthesized in this work support the feasibility of such an intermediate.

Propylene Insertion. In attempts to prepare the propylene analogue of **5**, Tp'Pt(Ph)(η^2-CH_2=$CH(CH_3)$), by the same low temperature route used to synthesize **4** and **5**, metallacycle

hydride products comparable to **7** were observed after deprotonation. Following addition of $HBF_4 \cdot Et_2O$ at -78 °C to Tp'$PtPh_2H$ (**1**), propylene was sparged into the reaction flask as the solution slowly warmed to room temperature. After 30 min., deprotonation led to one major platinum species, as determined by the ^1H NMR spectrum of the crude reaction product, with a hydride resonating at -19.48 ppm ($^1J_{Pt\text{-}H}$ =1368 Hz) and a multiplet with platinum satellites at 5.03 ppm ($^3J_{H\text{-}H}$ = 6 Hz, $^3J_{H\text{-}H}$ = 15 Hz, $^2J_{Pt\text{-}H}$ = 50 Hz), as well as multiple new aryl peaks. When the propylene sparge was continued for 2 hours prior to deprotonation, however, additional platinum hydride resonances appeared at -19.40 ppm ($^1J_{Pt\text{-}H}$ =1385 Hz) and -19.78 ppm ($^1J_{Pt\text{-}H}$ =1393 Hz), along with olefinic signals between 2.4-3.5 ppm and new aryl peaks. The first product is formulated as the metallacycle Tp'Pt(CH(CH_3)CH_2-*o*-C_6H_4)(H) (**10**), resulting from the 2,1-insertion of olefin into the phenyl-platinum bond. The other two species observed can be identified as diastereomers of Tp'Pt(CH_2CH(CH_3)-*o*-C_6H_4)(H) (**11a/11b**), the 1,2-insertion product (eq. 4).



(4)

Low temperature ^1H NMR experiments were conducted to confirm complex **10** as the kinetic product of insertion and complexes **11a** and **11b** as the thermodynamic products.

Upon addition of NEt_3 to the reaction of propylene and $[(HTp')Pt(C_6H_5)(\eta^2\text{-}C_6H_6)][BF_4]$, the 2,1-insertion product, **10**, was trapped as the major species, as evidenced by the platinum hydride signal at -19.48 ppm. The product was then separated from the salts and excess propylene, redissolved in 1,1,2,2-tetrachloroethane-d_2, and subsequently heated in the NMR probe. At 80 ºC, formation of the 1,2-insertion products, **11a** and **11b**, and consumption of the 2,1-insertion product, **10**, was clearly evident by changes in the hydride region of the spectrum. No intermediate species was observed.

It may be that isomerization of the 1,2-insertion product, **10**, to the 2,1-insertion products, **11a** and **11b,** proceeds through the elusive $Tp'Pt(Ph)(\eta^2\text{-}CH_2{=}CH(CH_3))$ complex as an intermediate. This would indicate that propylene insertion into the Pt-Ph bond and formation of a C-C bond is reversible. A possible reaction coordinate is shown in Figure 3.5. NMR experiments at 80 ºC indicate a $\Delta G^{\ddagger}$ for the conversion of **10** to **11a** and **11b** of 26.5 kcal/mol (eq. 5 and Figure 3.6).

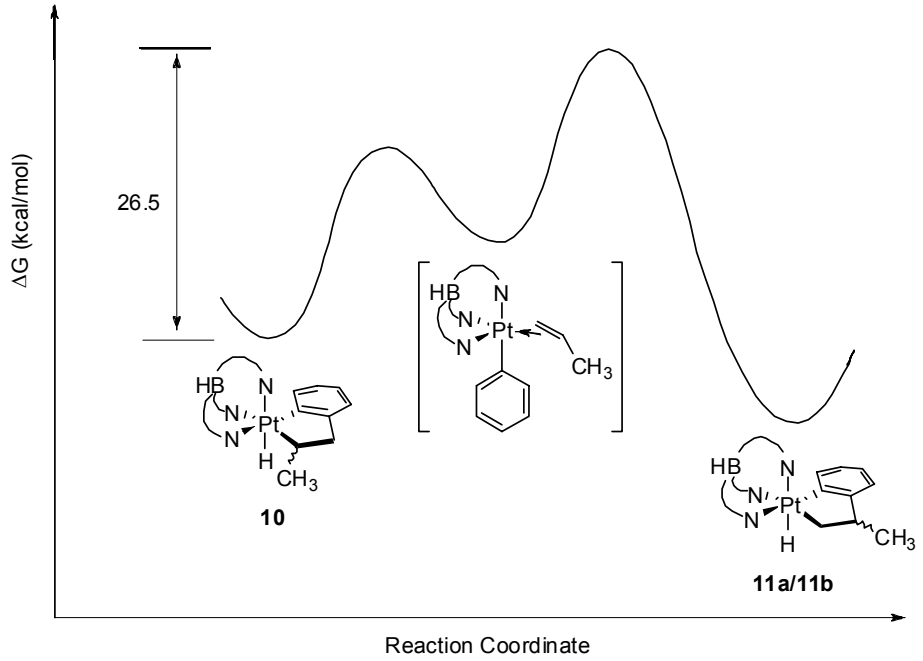


Figure 3.5; Conversion of complex **10** to complexes **11a** and **11b.**

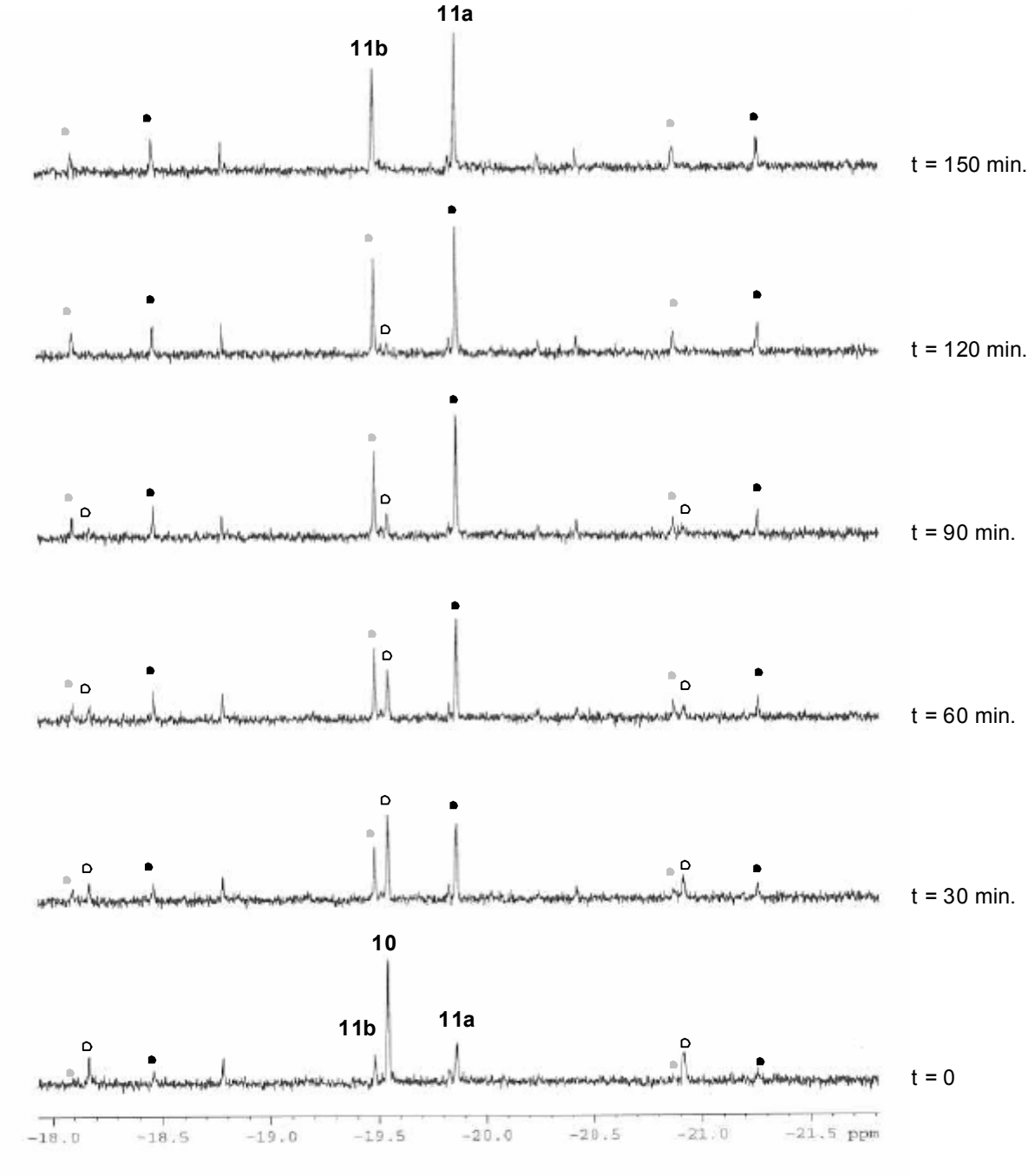
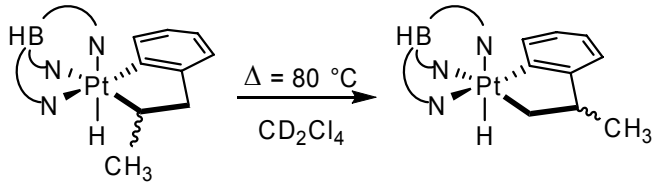


Figure 3.6; Conversion of 10 to 11a and 11b at 80 °C as monitored by ^{1}H NMR Spectroscopy (500 MHz, $C_2D_2Cl_4$) of hydride region.



(5)

10 **11a/11b**

In a related system with cationic Pt(II) complexes of the type $[Pt(aryl)(N\text{-}N)(L)]^+$ (N-N = bidentate nitrogen ligand), α-olefins were found to insert into the Pt-aryl bond in the presence of $AgBF_4$ to form either an alkyl-bound [Pt]-CH_2-CHR-aryl species or an aryl-bound [Pt]-aryl-2-(CHR-CH_3) derivative.[43,45,53] The alkyl-bound product was formed when donor ligands, such as excess olefin, pyridine, or triphenylphosphine, were available in solution, while the aryl-bound derivative was preferred in the absence of donor ligands and is presumed to form from an intramolecular rearrangement of the alkyl-bound species.[45] The metallacycle hydride complexes here represent one type of proposed intermediate in the earlier study.[43]

Low temperature attempts to isolate the cationic Pt(II) η^2-propylene phenyl complex, [κ^2-(HTp')Pt(η^2-CH_2=$CH(CH_3)$)(Ph)][BF_4], were unsuccessful. Instead a stable cationic Pt(II) phenyl aqua complex [κ^2-(HTp')Pt(Ph)(OH_2)][BF_4] (**12**) was isolated, presumably from adventitious water present in the $HBF_4 \cdot Et_2O$ solution. The ^{1}H NMR spectrum for complex **12** displays a N-H resonance at 11.62 ppm for the protonated pyrazole ring, and a broad singlet at 4.97 ppm for the coordinated water molecule. Similar cationic (diimine)Pt aqua complexes have been reported previously, and it is noteworthy that they activate benzene and methane C-H bonds under mild conditions.[48,54]

The structural features of the cationic phenyl aqua complex **12** were investigated by X-ray structural analysis. An ORTEP diagram of **12** is shown in Figure 3.7. The protonated pyrazole nitrogen atom is turned away from the platinum square plane, an orientation seen in similar cationic (Tp'-H)Pt(II) complexes.[35] The Pt-N(21) distance of 2.095(5) Å is 0.10 Å longer than the Pt-N(31) distance of 1.987(5) Å *trans* to the water ligand indicating the stronger trans influence of the phenyl ligand (Table 3.3). The Pt-O distance of 2.075(1) Å is similar to other Pt(II)-OH_2 bond distances *trans* to nitrogen ligands.[55-58]

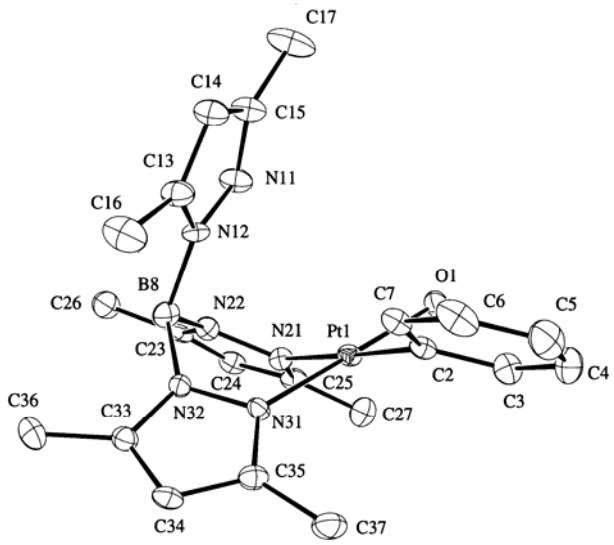


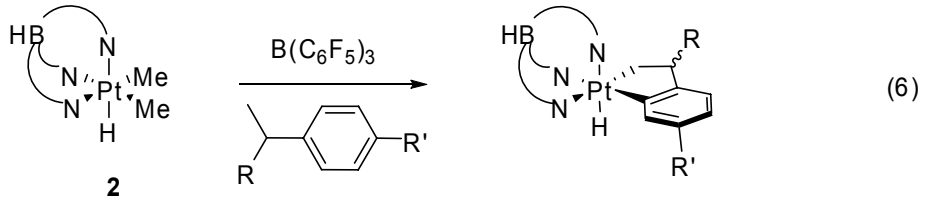
Figure 3.7; ORTEP diagram of [κ^2-(HTp')Pt(Ph)(OH_2)][BF_4] (**12**). Ellipsoids are drawn at the 50% probability level, and the [BF_4] counterion is omitted for clarity.

Table 3.3; Selected bond distances (Å) and angles (°) for complex **12**.

Bond distances			
Pt-O1	2.075(1)	Pt-N21	2.095(5)
Pt-C2	1.997(6)	Pt-N31	1.987(5)

Bond angles			
O1-Pt-C2	88.95(23)	C2-Pt-N21	178.58(24)
O1-Pt-N21	89.82(19)	C2-Pt-N31	93.46(24)
O1-Pt-N31	177.58(20)	N21-Pt-N31	87.78(21)

C-H Activation of Alkylarenes. Mild heating of Tp'PtMe$_2$H (**2**) in neat ethylbenzene in the presence of B(C_6F_5)$_3$ resulted in the loss of two equivalents of methane and formation of metallacyclic complex **7** as the sole product (eq. 6). When monitored by NMR, the reaction proceeded to completion at room temperature within 15 minutes after the addition of ethylbenzene. The diarylhydride platinum intermediate complex, Tp'Pt(C_6H_4Et)$_2$H, was not observed. Analogous reactions of **2** with either isopropyl- or 1,4-diethylbenzene also yield clean *ortho*-metallated platinum hydride complexes, Tp'Pt(CH$_2$CH(Me)-*o*-C_6H_4)(H) (**11a/11b**) and Tp'Pt(CH$_2$CH$_2$-*o*-C_6H_3(Et))(H) (**13**), respectively.



(6)

R = H; R' = H (**7**)
R = Me; R' = H (**11a**/**11b**)
R = H; R' = Et (**13**)

The ^{1}H NMR spectrum for the platinum metallacycle derived from isopropylbenzene, complexes **11a** and **11b**, shows hydride resonances at -19.78 ($^1J_{Pt-H}$ = 1393 Hz) and -19.40 ($^1J_{Pt-H}$ = 1385 Hz) in a ratio of 2.7:1, reflecting a major, **11a**, and a minor, **11b**, isomer. These hydrides are the same as the 1,2-insertion products observed in attempts to isolate Tp'Pt(Ph)(η^2-CH$_2$=CH(CH$_3$)), *vide supra*. While the products are chiral and formally contain

only nonequivalent pyrazole rings, two of the pyrazole rings are incidentally isochronous in the room temperature ^{1}H NMR spectrum. The identity of the bridging -$CH_2CH(CH_3)$- protons was revealed by 2D NMR. For the major species, **11a**, the methine proton of the saturated bridge appears as a multiplet, resonating the furthest downfield among the bridge hydrogens at 3.20 ppm. One of the other two bridging metallacycle protons can be found at 2.77 ppm with Pt satellites ($^2J_{Pt\text{-}H}$ = 63 Hz), and the third proton is hidden under the Tp' methyl peaks around 2.40 ppm. In the minor species, the methine proton signal is located at 2.95 ppm, upfield from the corresponding proton in the major isomer. The two methylene protons of **11b** are concealed by signals at 3.20 ppm and 2.40 ppm. The methyl protons for both isomers appear as doublets between 1.31 and 1.34 ppm among the Tp' methyl peaks.

Honey-colored crystals of what is assumed to be the major diastereomer, complex **11a,** were obtained and the framework structure indicated by NMR studies was confirmed by X-ray analysis. Figure 3.8 shows the ORTEP diagram of isomer **11a**, with the methyl group positioned in an equatorial position of the five-membered ring. The solid state structure displays an octahedral geometry with a κ^3 coordination mode of the Tp' ligand. The platinum hydride was found from the difference map and refined, indicating a Pt-H bond length of 1.493(5) Å (Table 3.4). The metallacycle lies in the equatorial plane opposite two pyrazole rings (C1-Pt-N31 = 178.76(13)° and C9-Pt-N11 = 177.83(11)°) and, as seen in complex **7**, the PtC_4 ring is puckered into an envelope conformation with C2, bearing the methyl substituent, folded towards the platinum hydride. As found for complex **7**, all three Pt-N bonds have similar lengths, although the pyrazole ring located in the axial position *trans* to hydride is again slightly longer (Pt-N21 = 2.180(3) Å) than the two Pt-N bond lengths in the equatorial plane (Pt-N11 = 2.146(2) Å and Pt-N31 = 2.144(3) Å). The bond distance from

platinum to the methylene carbon is longer than to the arene carbon by 0.043 Å (Pt-C1 = 2.054(3) Å and Pt-C9 = 2.011(3) Å). These bond distances are similar to those reported for Tp'Pd(CH_2CMe_2-*o*-C_6H_4)(NO).[59]

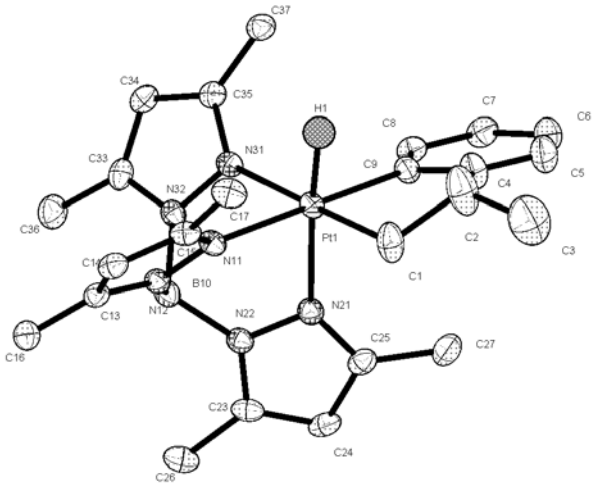


Figure 3.8; ORTEP diagram of Tp'Pt(CH_2CHMe-*o*-C_6H_4)(H) (**11a**). Ellipsoids are drawn at the 50% probability level. CH_2Cl_2 molecule omitted for clarity.

Table 3.4; Selected bond distances (Å) and angles (°) for complex **11a**.

Bond distances			
Pt-C9	2.011(3)	C2-C4	1.518(5)
Pt-C1	2.054(3)	C4-C5	1.396(5)
Pt-H1	1.493(5)	C4-C9	1.401(5)
Pt-N31	2.144(3)	C5-C6	1.383(5)
Pt-N11	2.146(2)	C6-C7	1.381(5)
Pt-N21	2.180(3)	C7-C8	1.400(5)
C1-C2	1.558(5)	C8-C9	1.388(4)
C2-C3	1.459(6)		

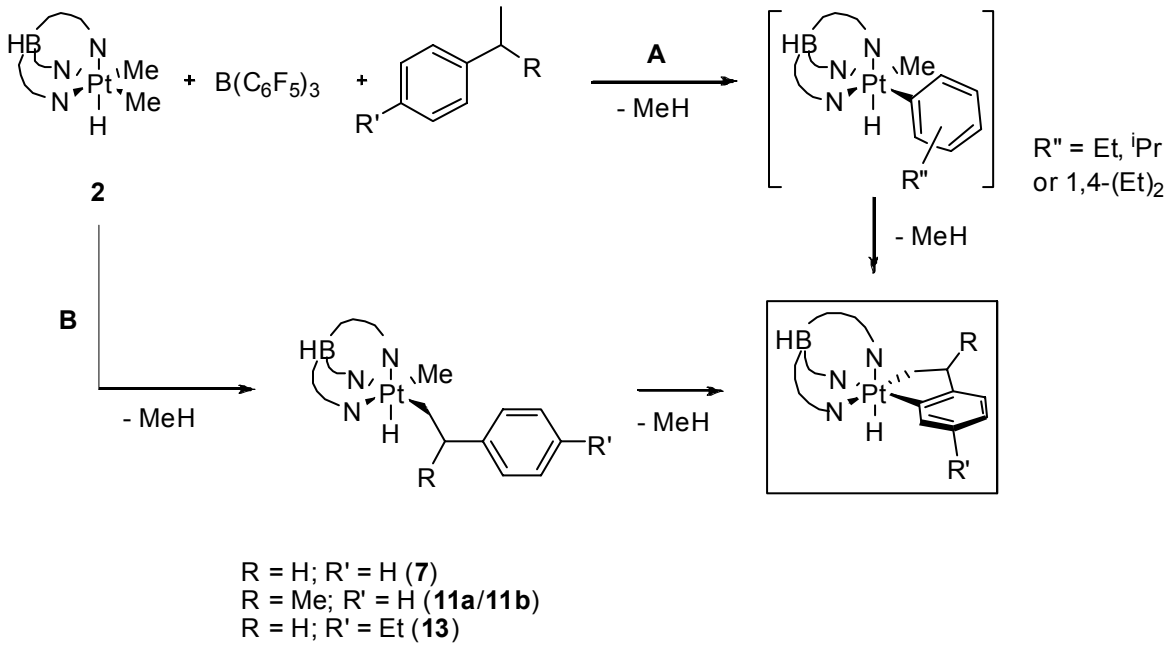
Bond angles			
C9-Pt-C1	81.31(13)	C2-C1-Pt	109.4(2)
C9-Pt-N31	98.75(11)	C3-C2-C4	116.0(4)
C1-Pt-N31	178.76(13)	C3-C2-C1	114.9(4)
C9-Pt-N11	177.83(11)	C4-C2-C1	106.0(3)
C1-Pt-N11	96.72(12)	C5-C4-C9	119.8(3)
C9-Pt-N21	91.76(11)	C5-C4-C2	124.8(3)
C1-Pt-N21	95.04(13)	C9-C4-C2	115.4(3)
N11-Pt-N21	89.29(9)	C8-C9-Pt	124.9(2)
N31-Pt-N11	83.21(9)	C4-C9-Pt	115.7(2)
N31-Pt-N21	86.20(9)		

Only one pair of enantiomers is possible for the 1,4-diethylbenzene derivative, complex **13**. The C_1 symmetry of complex **13** is evident by the three nonequivalent pyrazole rings in the ^{1}H NMR spectrum. The three aromatic protons are unique, with two doublets at 6.98 ($^3J_{H\text{-}H}$ = 6.8 Hz, $^4J_{Pt\text{-}H}$ = 18 Hz) and 6.74 ppm (d, $^3J_{H\text{-}H}$ = 6.8 Hz) and a singlet at 6.73 ppm ($^3J_{Pt\text{-}H}$ = 37 Hz). The chemical shifts for the four diastereotopic methylene protons are nearly identical to those of the ethylbenzene derivative, complex **7**. The two methylene protons of the aryl-CH_2CH_3 substituent are now diastereotopic, resonating at 2.70 and 2.45 ppm and the methyl triplet at 1.08 ppm is shifted slightly upfield from that of free 1,4-diethylbenzene. The aryl-C_{ipso} carbon resonates at 133.2 ppm with $^1J_{Pt\text{-}C}$ = 859 Hz. Similar coupling has been reported previously for Tp'Pt(IV)(aryl) complexes.[42,60] As found for the ethylbenzene derivative, complex **7**, the bridging methylene carbons for **13** resonate at 43.5 ppm ($^2J_{Pt\text{-}C}$ = 54 Hz) and 8.8 ppm ($^1J_{Pt\text{-}C}$ = 604 Hz).

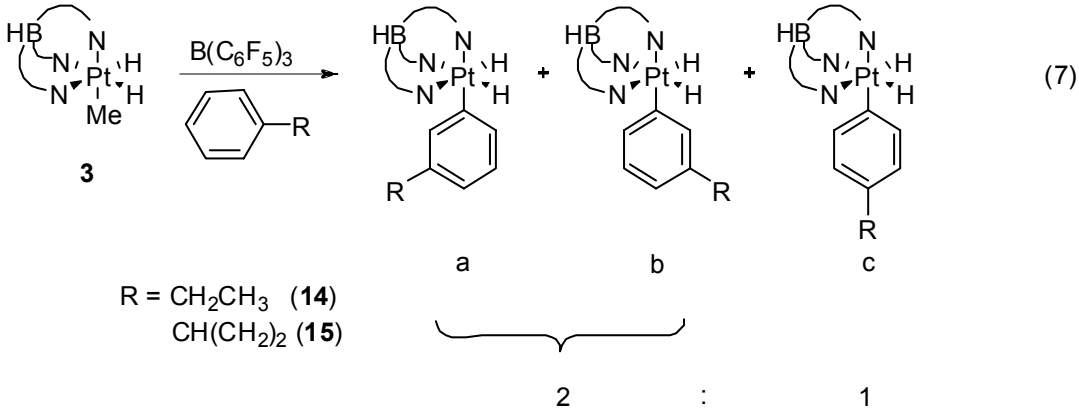
Mechanistic Possibilities for C-H Activation Route. Two discrete mechanistic categories can be delineated for formation of platinum hydride complexes **7, 11a**/**11b,** and **13**

from alkyl-substituted benzenes (Scheme 3.1). Following Lewis acid induced loss of methane, initial activation could take place at either an aryl (**A**) or an alkyl (**B**) C-H bond. Oxidative addition of an arene C-H bond to a metal center can be favored over alkane C-H oxidative addition both thermodynamically, due to the strength of the resultant metal-aryl bond formed, and kinetically, by lowering the barrier for C-H activation through initial π-coordination of the arene to the metal center.[36,61,62] By analogy, path **A** is probably favored here. In addition, when the dihydride analogue, Tp'PtMeH_2, was reacted with either ethyl- or isopropylbenzene in the presence of Lewis acid, only the aryl C-H activated products, Tp'PtArH_2 (Ar = ethylphenyl (**14)** and isopropylphenyl (**15)**), resulted (eq. 7). These results fit the pattern of previous findings for the reactivity of Tp'PtMeH_2 with toluene and xylenes, in which no benzylic C-H activated products were observed.[36]

Support for path **A** comes from work by Labinger, Bercaw and co-workers which details the reactivity of diimine platinum(II) methyl cations towards alkyl-substituted benzenes. In the case of ethylbenzene, initial aryl C-H bond activation occurs exclusively, and reversibly, and the kinetic product converts intramolecularly to an η^3-benzyl product. They propose that this conversion takes place once ethylbenzene is *ortho*-activated since then it can pass through a platinum(IV) metallacycle hydride intermediate, similar to complex **7**, on the way to the final η^3-benzyl product.[63,64]



Scheme 3.1; Possible C-H Activation Pathway for Formation of Metallacyclic Complexes **7**, **11a/11b**, and **13.**



Although there is no evidence that Tp'Pt intermediates preferentially activate alkyl C-H bonds of alkylarenes, there are reports of C-H oxidative addition in other systems that are selective for alkyl over aryl C-H bonds, so, path **B** in Scheme 1 deserves

consideration as a viable alternative. In systems favoring alkyl C-H activation this reactivity is often explained by steric effects. For example, Tilset and coworkers found benzylic C-H bond activation of toluene and *p*-xylene by Pt(II) diimine complexes was favored when a sterically congested diimine ligand (Ar-N=CMe=N-Ar; Ar = 2,6-$(CH_3)_2C_6H_3$) was employed.[65] Direct activation of an ethyl C-H bond of triethylbenzene has been observed when the system contained a bulky, sterically crowded diimine ligand (Ar = 2,4,6-$Me_3C_6H_2$).[64] If path **B** is operational in our system, then the alkyl-bound alkylarene complex could go on to the final benzometallacycle. It is noteworthy that upon thermolysis, neophyl complexes $Pt(CH_2CMe_2Ph)_2L_2$ (L = N-donor or P-donor ligands) generate benzometallacycle derivatives, $Pt(CH_2CMe_2\text{-}o\text{-}C_6H_4)L_2$, and tert-butylbenzene. This rearrangement proceeds via intramolecular activation of the arene C-H bond.[66,67]

Conclusion

In summary, the neutral Pt(II) phenyl ethylene complex **5** displays a five-coordinate trigonal-bipyramidal geometry, whereas, the analogous Pt(II) phenyl carbonyl complex **4** undergoes rapid interconversion between the trigonal-bipyramidal and square-planar geometries in solution. Upon ethylene insertion into the Pt-phenyl bond in complex **5** at 60 °C, intramolecular C-H activation of an *ortho* proton occurs to give a stable Pt(IV) metallacyclo hydride complex **7**. Low temperature protonation of **7** resulted in reductive elimination of the alkyl ligand to form a cationic Pt(II) 2-ethylphenyl complex. Attempts to isolate the neutral Pt(II) phenyl propylene or the cationic Pt(II) η^2-propylene phenyl complexes were unsuccessful, leading to a mixture of Pt(IV) metallacyclo hydride adducts (**7** and **11a**/**11b**) or a cationic Pt(II) phenyl aqua complex (**12**), respectively.

Several Pt(IV) hydridometallacycle complexes (**7**, **11a**/**11b**, and **13**) have been synthesized through Lewis acid assisted C-H oxidative addition of alkyl-substituted arenes to Tp'$PtMe_2H$ (**2**). The formation of these metallacycles is believed to take place via initial activation of an arene C-H bond rather then initial alkyl C-H activation. In the comparative reaction of the dihydrido reagent, Tp'$PtMeH_2$ (**3**), with alkyl-substituted arenes, only Tp'$PtArH_2$ products (**14** and **15**) resulted. While a detailed mechanism of formation of these platinum metallacycles has yet to be determined, these results indicate that an *intramolecular* rearrangement to form an *ortho*-activated aryl complex is favored over an *intermolecular* C-H activation pathway.

Experimental Section

Materials and Methods. Reactions were performed under an atmosphere of dry nitrogen or argon using standard drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was oven-dried prior to use. Methylene chloride and pentane were purified under an argon atmosphere by passage through a column packed with activated alumina.[68] Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl prior to use. Deuterated methylene chloride was vacuum transferred from P_2O_5 and degassed by several freeze-pump-thaw cycles and deuterated 1,1,2,2-tetrachloroethane was used without further purification. Ethylbenzene, isopropylbenzene, and 1,4-diethylbenzene were purchased from Sigma-Aldrich and dried over molecular sieves prior to use. Tris(pentfluorophenyl)borane was obtained from Strem and used without further purification.

Tp'PtPh$_2$H (**1**), Tp'PtMe$_2$H[60] (**2**), Tp'PtMeH$_2$[69] (**3**), and [H(OEt$_2$)$_2$][BAr'$_4$][70] were synthesized according to published procedures. Carbon monoxide and ethylene were obtained from Matheson Gas Products, Inc. and propylene was obtained from National Specialty Gases.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 500, 400, or 300 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Chemical analyses were performed by Atlantic Microlabs of Norcross, GA.

Tp'Pt(C$_6$H$_5$)(CO) (4). Tp'PtPh$_2$H (**1**) (0.057 g, 0.088 mmol) was placed in a 100 mL Schlenk flask under nitrogen. CH_2Cl_2 (15 mL) was added through the septum, and the reaction mixture was cooled to -78 °C. $HBF_4 \cdot Et_2O$ (16 μL, 0.114 mmol) was added dropwise and the reaction was stirred for 10 minutes. The cold bath was removed and $CO_{(g)}$ was purged through the solution for 30 minutes while warming to room temperature. After the solvent was removed in vacuo, NaH (0.003 g, 0.114 mmol) was added to the flask which was then cooled to -78 °C. THF (15 mL) was slowly added, the cold bath was removed, and the solution was stirred for one hour. After solvent was removed by rotary evaporation, the residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a white solid was obtained. Yield: 35 mg (67 %). IR (CH_2Cl_2): $\nu_{B\text{-}H}$ = 2528, 2485 cm^{-1}, ν_{CO} = 2092, 2082 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298K, δ): 7.25 (d, 2H$_{ortho}$, $^3J_{Pt\text{-}H}$ = 54 Hz, Pt-C$_6$*H$_5$*), 6.97 (m, 2H$_{meta}$ and 1H$_{para}$, Pt-C$_6$*H$_5$*), 5.99, 5.78 (s, 1H, 2H, Tp'C*H*), 2.41, 2.40, 2.25, 1.80 (s, 3H, 3H, 6H, 6H, Tp'C*H$_3$*). ^{13}C NMR (CD_2Cl_2, 298K, δ): 163.7 (Pt-*C*≡O), 150.0, 149.8, 144.9, 144.6 (1C, 2C, 2C, 1C, Tp'*C*CH$_3$), 138.9 (C$_{meta}$, Pt-*C$_6$*H$_5$), 127.9 (C$_{ortho}$, $^1J_{Pt\text{-}C}$ = 54 Hz, Pt-*C$_6$*H$_5$), 124.7

(C_{para}, Pt-C_6H_5), 106.7, 106.6 (1C, 2C, Tp'*C*H), 15.2, 14.1, 13.3, 12.8 (1C, 2C, 1C, 2C, Tp'C*C*H_3).

Tp'Pt(C_6H_5)(η^2-CH_2=CH_2) (5). Tp'$PtPh_2H$ (**1**) (0.150 g, 0.232 mmol) was placed in a 100 mL Schlenk flask under nitrogen. CH_2Cl_2 (15 mL) was added through the septum, and the reaction mixture was cooled to -78 °C. $HBF_4{\cdot}Et_2O$ (42 μL, 0.301 mmol) was added dropwise and the reaction was stirred for 10 minutes. The cold bath was removed and ethylene was purged through the solution for 30 minutes while warming to room temperature. After the solvent was removed in vacuo, NaH (0.007 g, 0.301 mmol) was added to the flask which was then cooled to -78 °C. THF (20 mL) was slowly added, the cold bath was removed, and the solution was stirred for one hour. After solvent was removed by rotary evaporation, the residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a white solid was obtained which was recrystallized from CH_2Cl_2/methanol at -30 °C. Yield: 30 mg (22 %). ^{1}H NMR (CD_2Cl_2, 253K, δ): 6.76 (t, 1H$_{para}$, Pt-C_6H_5), 6.69 (t, 2H$_{meta}$, Pt-C_6H_5), 6.23 (d, 2H$_{ortho}$, $^3J_{Pt\text{-}H}$ = 39 Hz, Pt-C_6H_5), 5.79, 5.65 (s, 2H, 1H, Tp'C*H*), 3.31 (d, 2H, $^2J_{Pt\text{-}H}$ = 80 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz, Pt-CH_2=CH_2), 2.44 (d, 2H, $^2J_{Pt\text{-}H}$ = 56 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz, Pt-CH_2=CH_2), 2.42, 2.30, 2.22, 1.48 (s, 6H, 3H, 3H, 6H, Tp'CH_3). ^{13}C NMR (CD_2Cl_2, 253K, δ): 151.1, 149.2, 144.7, 143.7 (1C, 2C, 1C, 2C, Tp'*C*CH_3), 125.8, 122.8 (C_{meta}, C_{ortho}, Pt-C_6H_5), 118.8 (C_{para}, Pt-C_6H_5), 114.5 (C_{ipso}, Pt-C_6H_5), 108.5, 105.6 (1C, 2C, Tp'*C*H), 24.2 (Pt-*C*H_2=*C*H_2), 13.8, 13.4, 12.4, 12.1 (2C, 1C, 2C, 1C, Tp'C*C*H_3). Anal. Calcd for $PtBN_6C_{23}H_{31}{\cdot}CH_2Cl_2$: C, 42.25; H, 4.87; N, 12.32; Found: C, 43.12; H, 4.59; N, 12.05.

Representative [BAr'$_4$]$^-$ NMR Data. ^{1}H and ^{13}C NMR data for the [BAr'$_4$]$^-$ counterion for ionic products **6**, **8**, and **9** are reported separately for simplicity. ^{1}H NMR (CD_2Cl_2, 193K, δ): 7.77 (br, 8H, o-Ar'), 7.60 (br, 4H, p-Ar'). ^{13}C NMR (CD_2Cl_2, 193K, δ): 162.2 (1:1:1:1

pattern, $^{1}J_{B\text{-}C}$ = 50 Hz, C_{ipso}), 135.3 (C_{ortho}), 129.4 (qq, $^{2}J_{C\text{-}F}$ = 30 Hz, $^{4}J_{C\text{-}F}$ = 5 Hz, C_{meta}), 125.1 (q, $^{1}J_{C\text{-}F}$ = 270 Hz, CF_3), 117.9 (C_{para}).

[κ^2-(HTp')Pt(C_6H_5)(η^2-CH_2=CH_2)][BAr'$_4$] (6). Tp'PtPh$_2$H (**1**) (0.100 g, 0.154 mmol) and [H(OEt_2)$_2$][BAr'$_4$] (0.172 g, 0.169 mmol) were weighed into a 100 mL Schlenk flask in the drybox. The flask was cooled to -78 °C outside the drybox. CH_2Cl_2 (15 mL) was slowly added through the septum, and the reaction mixture was stirred for 10 minutes. The cold bath was removed and ethylene was purged through the solution for 30 minutes while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. ^{1}H NMR (CD_2Cl_2, 293K, δ): 10.36 (s, 1H, pz'NH), 7.10 - 6.78 (m, 5H, Pt-C_6H_5), 6.36, 6.07, 5.93 (s, 1H each, HTp'C*H*), 4.21, 3.77 (m, 2H each, broad Pt satellites, Pt-CH_2=CH_2), 2.45, 2.43, 2.38, 2.33, 2.09, 1.60 (s, 3H each, HTp'CH_3).

Tp'Pt(CH$_2$CH$_2$-*o*-C$_6$H$_4$)(H) (7) by Ethylene Insertion. Tp'Pt(Ph)(η^2-CH_2=CH_2) (**5**) (0.224 g, 0.375 mmol) and 1 equivalent of B(C_6F_5)$_3$ (0.192 g) were placed in a 100 mL Schlenk flask under nitrogen. Toluene (25 mL) was added, and the reaction mixture was stirred for 1 hour at 60 °C. After solvent was removed in vacuo, the residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a white solid was obtained. Yield: 111 mg (50 %). ^{1}H NMR (CD_2Cl_2, 253K, δ): 7.05 (d, 1H, Pt-CH_2CH_2-*o*-C_6H_4), 6.88 (t, 1H, Pt-CH_2CH_2-*o*-C_6H_4), 6.76 (d, 1H$_{ortho}$, $^{3}J_{Pt\text{-}H}$ = 38 Hz, Pt-CH_2CH_2-*o*-C_6H_4), 6.69 (t, 1H, Pt-CH_2CH_2-*o*-C_6H_4), 5.89, 5.69 (s, 2H, 1H, Tp'C*H*), 3.18 (m, 1H, Pt-CH_2CH_2-*o*-C_6H_4), 2.84 (dd, 1H, $^{3}J_{H\text{-}H}$ = 16.0 Hz, $^{2}J_{H\text{-}H}$ = 5.0 Hz, $^{2}J_{Pt\text{-}H}$ = 114 Hz, Pt-CH_2CH_2-*o*-C_6H_4), 2.75 (m, 1H, Pt-CH_2CH_2-*o*-C_6H_4), 2.69 (m, 1H, Pt-CH_2CH_2-*o*-C_6H_4), 2.37, 2.35, 2.34, 2.07, 1.31 (s, 6H, 3H, 3H, 3H, 3H, Tp'CH_3), -19.63 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1391 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 253K, δ): 157.6 (1C, Pt-CH_2CH_2-*o*-*C*$_6$H$_4$), 150.7, 150.5, 149.4, 145.2, 144.8, 144.1 (1C, 1C, 1C,

1C, 1C, 1C, Tp'*C*CH_3), 133.8, 133.4 (C_{ipso}), 124.3, 124.0, 122.1 (1C, 1C, 1C, 1C, 1C, Pt-CH_2CH_2-*o*-*C*$_6H_4$), 107.9, 106.6, 106.3 (Tp'*C*H), 44.0 (Pt-CH_2*C*H_2-*o*-C_6H_4), 15.2, 14.9, 12.8, 11.8 (1C, 1C, 3C, 1C, Tp'C*C*H_3), 8.5 (1C, $^1J_{Pt-H}$ = 601 Hz, Pt-*C*H_2CH_2-*o*-C_6H_4). Anal. Calcd for $PtBN_6C_{23}H_{31}\cdot ½CH_2Cl_2$: C, 44.11; H, 5.04; N, 13.13; Found: C, 44.34; H, 5.16; N, 13.04.

[κ^2-(HTp')Pt(C_6H_4-2-CH_2CH_3)(O(CH_2CH_3)$_2$)][BAr'$_4$] (8). Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (**7**) (0.010 g, 0.017 mmol) and [H(OEt_2)$_2$][BAr'$_4$] (0.022 g, 0.022 mmol) were weighed into an NMR tube in the drybox. The NMR tube was cooled to -78 °C outside the drybox. CD_2Cl_2 (0.7 mL) was slowly added through the septum, and the reaction mixture was inverted several times to insure complete mixing. ^{1}H NMR (CD_2Cl_2, 203K, δ): 11.35 (s, 1H, pz'NH), 6.92 (d, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.85 (t, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.63 (t, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.20 (d, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.29, 5.99, 5.83 (s, 1H each, HTp'C*H*), 3.96 (q, 4H, Pt-O(C$H_2$$CH_3$)$_2$), 3.29 (dq, 2H, Pt-$C_6H_4$-2-C$H_2$$CH_3$), 2.37, 2.34, 2.30, 2.25, 1.79, 1.50 (s, 3H each, HTp'C*H*$_3$), 1.33 (t, 6H, Pt-O(CH_2C*H*$_3$)$_2$), 1.25 (t, 3H, Pt-C_6H_4-2-CH_2C*H*$_3$).

[κ^2-(HTp')Pt(C_6H_4-2-CH_2CH_3)($NCCH_3$)][BAr'$_4$] (9). Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (**7**) (0.010 g, 0.017 mmol) and [H(OEt_2)$_2$][BAr'$_4$] (0.022 g, 0.022 mmol) were weighed into an NMR tube in the drybox. The NMR tube was cooled to -78 °C outside the drybox. CD_2Cl_2 (0.7 mL) was slowly added through the septum, and the reaction mixture was inverted several times to insure complete mixing. $NCCH_3$ (2 μL, 0.034 mmol) was added via syringe. ^{1}H NMR (CD_2Cl_2, 273K, δ): 11.90 (s, 1H, pz'NH), 7.00 (d, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.89 (t, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.64 (t, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.28 (d, 1H, Pt-C_6H_4-2-CH_2CH_3), 6.27, 6.04, 5.81 (s, 1H each, HTp'C*H*), 3.25 (dq, 2H, Pt-C_6H_4-2-C$H_2$$CH_3$), 2.42, 2.37, 2.35, 2.34, 2.32, 2.19, 1.44 (s, 3H each, HTp'C*H*$_3$ and Pt-NCC*H*$_3$), 1.37 (t, 3H, Pt-C_6H_4-2-CH_2C*H*$_3$).

Tp'Pt(CH(CH$_3$)CH$_2$-*o*-C$_6$H$_4$)(H) (10) by Propylene Insertion. Tp'PtPh$_2$H (**1**) (150 mg, 0.232 mmol) was placed in a 100 mL Schlenk flask under nitrogen. CH_2Cl_2 (20 mL) was added through the septum, and the reaction mixture was cooled to -78 °C. $HBF_4{\cdot}Et_2O$ (42 μL, 0.301 mmol) was added dropwise and the reaction was stirred for 10 minutes. The cold bath was removed and propylene sparged into the flask for 30 minutes as the solution warmed slowly to rt. After the solvent was removed in vacuo, NaH (0.007 g, 0.301 mmol) was added to the flask which was then cooled to -78 °C. THF (20 mL) was slowly added, the cold bath was removed, and the solution was stirred for one hour. After solvent was removed by rotary evaporation, the residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a colorless oil was obtained. Major product (**10**) ^{1}H NMR (CD_2Cl_2, 303K, δ): 6.75, 6.69 (m,1H, 2H, Pt-CH(CH$_3$)CH$_2$-*o*-C$_6$*H*$_4$) 6.55 (1H, $^3J_{H\text{-}H}$ = 15 Hz, $^2J_{H\text{-}H}$ = 2.0 Hz, $^3J_{Pt\text{-}H}$ = 44 Hz, Pt-CH(CH$_3$)C*H*$_2$-*o*-C$_6$H$_4$), 6.69 (m,1H, $^2J_{Pt\text{-}H}$ = 40 Hz, Pt-CH(CH$_3$)CH$_2$-*o*-C$_6$*H*$_4$) 5.84, 5.71 (s, 2H, 1H, Tp'C*H*), 5.03 (m, 1H, $^3J_{H\text{-}H}$ = 6 Hz, $^3J_{H\text{-}H}$ = 15 Hz, $^2J_{Pt\text{-}H}$ = 57 Hz, Pt-C*H*(CH$_3$)CH$_2$-*o*-C$_6$H$_4$), 2.48, 2.40, 2.39, 2.24, 1.69, 1.41 (s, 3H, 3H, 3H, 3H,, 3H, 3H, Tp'C*H*$_3$), 1.71 (dd, 3H, $^3J_{H\text{-}H}$ = 6 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, $^2J_{Pt\text{-}H}$ = 10 Hz, Pt-CH(C*H*$_3$)CH$_2$-*o*-C$_6$H$_4$), -19.48 (s, 1H, $^1J_{Pt\text{-}H}$ = 1368 Hz, Pt-*H*)

Tp'Pt(CH(CH$_3$)CH$_2$-*o*-C$_6$H$_4$)(H) (10) and Tp'Pt(CH$_2$CH(CH$_3$)-*o*-C$_6$H$_4$)(H) (11a/11b) Mixture by Propylene Insertion. Tp'PtPh$_2$H (**1**) (100 mg, 0.154 mmol) was placed in a 100 mL Schlenk flask under nitrogen. CH_2Cl_2 (20 mL) was added through the septum, and the reaction mixture was cooled to -78 °C. $HBF_4{\cdot}Et_2O$ (28 μL, 0.200 mmol) was added dropwise and the reaction was stirred for 10 minutes. Propylene was condensed into the solution and allowed to stir for one hour at -78 °C. The cold bath was removed and solution warmed slowly to rt under propylene. After one hour, the propylene purge was stopped and the flask

again cooled to -78 °C. NEt_3 (28 μL, 0.200 mmol) was slowly added and the solution was left to stir for 90 minutes at -78 °C. The solution was allowed to warm as solvent was removed in vacuo. The residue was taken up in CH_2Cl_2/hexanes (3/20 mL) and solution transferred away from the salts via canula. The product was chromatographed on silica (CH_2Cl_2 as eluent) and a white powder obtained. ^{1}H NMR (CD_2Cl_2, 293K, δ): -19.40 (s, 1H, $^1J_{Pt\text{-}H}$=1385 Hz, Pt-*H*, **11b**), -19.48 (s, 1H, $^1J_{Pt\text{-}H}$=1368 Hz, Pt-*H*, **10**) and -19.78 (s, 1H, $^1J_{Pt\text{-}H}$=1393 Hz, Pt-H, **11a**), ratio of products: **11b** (1.3):**10** (1.0):**11a** (1.3).

[κ^2-(HTp')Pt(C_6H_5)(OH_2)][BF_4] (12). Tp'PtPh_2H (**1**) (0.150 g, 0.232 mmol) was placed in a 100 mL Schlenk flask under nitrogen. CH_2Cl_2 (30 mL) was added through the septum, and the reaction mixture was cooled to -78 °C. $HBF_4{\cdot}Et_2O$ (35 μL, 0.254 mmol) was added dropwise and the reaction was stirred for 10 minutes. The cold bath was removed and propylene was purged through the solution for 30 minutes while warming to room temperature. The solvent was removed in vacuo, and the residue was triturated with pentane. A white solid was obtained which was recrystallized from CH_2Cl_2/pentane at -30 °C. Yield: 148 mg (95 %). ^{1}H NMR (CD_2Cl_2, 293K, δ): 11.62 (s, 1H, pz'NH), 6.89 (m, 3H, Pt-C_6H_5), 6.71 (d, 2H$_{ortho}$, Pt-C_6H_5), 6.25, 6.09, 5.83 (s, 1H each, HTp'C*H*), 4.97 (s, 2H, Pt-OH_2), 2.43, 2.42, 2.38, 2.35, 2.13, 1.56 (s, 3H each, HTp'CH_3).

General C-H Activation of Alkylarene (7, 11a/11b and 13). Tp'Pt$(Me)_2$(H)(**2**) (0.075 g, 0.143 mmol) and 1 equivalent of $B(C_6F_5)_3$ (0.073 g) were placed in a 100 mL Schlenk flask under nitrogen. An alkyl substituted benzene (20 mL) was added, and the reaction mixture was stirred for overnight at 35 °C. After solvent was removed in vacuo, the resultant brown residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a yellow oil was collected. A white solid was obtained upon recrystallization in CH_2Cl_2/methanol at -30 °C.

Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (7) Tp'Pt(Me)$_2$(H) (**2**) (0.075 g, 0.143 mmol) and 1 equivalent of $B(C_6F_5)_3$ (0.073 g) were combined as described with 20 mL of ethylbenzene. Recrystallized in ethylbenzene at 0°C. Yield: 55 mg (64 %).

Tp'Pt($CH_2CH(CH_3)$-*o*-C_6H_4)(H) (11a/11b). Tp'Pt(Me)$_2$(H) (**2**) (0.075 g, 0.143 mmol) and 1 equivalent of $B(C_6F_5)_3$ (0.073 g) were combined as described with 20 mL of isopropylbenzene. ^{1}H NMR **11a** (CD_2Cl_2, 298 K, δ): 7.05-6.65 (4H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 5.89, 5.69 (s, 2H, 1H, Tp'C*H*), 3.19 (m, 1H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 2.79 (dd, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^2J_{Pt\text{-}H}$ = 63 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 2.4 (m, 1H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 2.44-2.35 (s, 12H, Tp'CH_3), 2.09 (s, 3H, Tp'CH_3), 1.33 (d, 3H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 1.30 (s, 3H, Tp'CH_3), -19.78 (s, 1H, $^1J_{Pt\text{-}H}$ = 1393 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 298K, δ): 159.0 (s, 1C, $^2J_{Pt\text{-}C}$ = 90 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 150.5 (s, 1C, $^2J_{Pt\text{-}C}$ = 21 Hz, Tp'*C*CH_3), 150.4 (1C, $^2J_{Pt\text{-}C}$ = 26 Hz, Tp'*C*CH_3) 149.4 (1C, $^2J_{Pt\text{-}C}$ = 16 Hz, Tp'*C*CH_3), 145.2, 144.7, 144.1 (s, 1C, 1C, 1C, Tp'*C*CH_3), 133.7 (s, 1C, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 133.0 (s, 1C, $^1J_{Pt\text{-}C}$ = 837 Hz, C_{ipso}) 124.9 (s, 1C, $J_{Pt\text{-}C}$ = 43 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 124.0 ($J_{Pt\text{-}C}$ = 7 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 122.7 (1C, $J_{Pt\text{-}C}$ = 54 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 107.9, 106.6 ($^3J_{Pt\text{-}C}$ = 11.5 Hz), 106.2 ($^3J_{Pt\text{-}C}$ = 9.8 Hz) (1C, 1C, 1C, Tp'*C*H), 47.9 (1C, $^2J_{Pt\text{-}C}$ = 64 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 20.7 ($^3J_{Pt\text{-}C}$ = 83 Hz., Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 18.4 (d, $^1J_{Pt\text{-}C}$ = 601 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 15.15 ($^3J_{Pt\text{-}C}$ = 17 Hz), 14.92 ($^3J_{Pt\text{-}C}$ = 17 Hz), 12.82, 12.8, 12.79, 12.17 (1C, 1C, 1C, 1C, 1C, 1C, Tp'CCH_3).

1H NMR **11b** (CD_2Cl_2, 243 K, δ): 7.05-6.65 (4H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 5.89, 5.69 (s, 2H, 1H, Tp'C*H*), 3.12 (m, 1H, $^2J_{Pt\text{-}H}$ = 108 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 2.92 (dd, 1H, $^3J_{H\text{-}H}$ = 6.5 Hz, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 2.4 (m, 1H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4) 2.44-2.35 (s, 12H, Tp'CH_3), 2.11 (s, 3H, Tp'CH_3), 1.31 (d, 3H, Pt-$CH_2CH(CH_3)$-*o*-C_6H_4), 1.26 (s, 3H, Tp'CH_3),

-19.4 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1385 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 298K, δ): 162.5 (s, 1C, Pt-$CH_2CH(CH_3)$-*o*-*C*$_6H_4$), 150.5, 150.3, 149.4, 145.2, 144.8, 144.1 (s, 1C, 1C, 1C, 1C, 1C, 1C, Tp'*C*CH_3), 134.0 (s, 1C, Pt-$CH_2CH(CH_3)$-*o*-*C*$_6H_4$), 131.0 (s, 1C, C_{ipso}) 124.6 (s, 1C, $J_{Pt\text{-}C}$ = 40 Hz, Pt-$CH_2CH(CH_3)$-*o*-*C*$_6H_4$), 124.2 ($J_{Pt\text{-}C}$ = 7 Hz, Pt-$CH_2CH(CH_3)$-*o*-*C*$_6H_4$), 122.1 (1C, $J_{Pt\text{-}C}$ = 46 Hz, Pt-$CH_2CH(CH_3)$-*o*-*C*$_6H_4$), 107.9, 106.6, 106.2 (1C, 1C, 1C, Tp'*C*H), 46.5 (1C, $^{2}J_{Pt\text{-}C}$ = 34 Hz, Pt-CH_2*C*H(CH_3)-*o*-C_6H_4), 23.5 (1C, Pt-CH_2CH(*C*H_3)-*o*-C_6H_4), 18.1 (d, $^{1}J_{Pt\text{-}C}$ = 612 Hz, Pt-*C*$H_2CH(CH_3)$-*o*-C_6H_4), 15.2 ($^{3}J_{Pt\text{-}C}$ = 17 Hz), 15.1 ($^{3}J_{Pt\text{-}C}$ = 17 Hz), 12.82, 12.8, 12.79, 11.6 (1C, 1C, 1C, 1C, 1C, Tp'C*C*H_3). Anal. Calcd for $PtBN_6C_{24}H_{33}\cdot CH_2Cl_2$: C, 43.12; H, 5.07; N, 12.35; Found: C, 43.79; H, 5.20; N, 12.35.

Tp'Pt(CH$_2$CH$_2$-*o*-C$_6$H$_3$(CH$_2$CH$_3$))(H) (13). Tp'Pt(Me)$_2$(H) (**2**) (0.075 g, 0.143 mmol) and 1 equivalent of $B(C_6F_5)_3$ (0.073 g) were combined as described with 20 mL of 1,4-diethylbenzene. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 6.98 (d, 1H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, $^{4}J_{Pt\text{-}H}$ = 18 Hz, Pt-CH_2CH_2–*o*-$C_6H_3(CH_2CH_3)$), 6.74 (d, 1H, $^{3}J_{H\text{-}H}$ = 6.8 Hz, Pt-CH_2CH_2–*o*-$C_6H_3(CH_2CH_3)$), 6.73 (s, 1H$_{ortho}$, $^{3}J_{Pt\text{-}H}$ = 37 Hz, Pt-CH_2CH_2–*o*-$C_6H_3(CH_2CH_3)$), 6.16, 5.90 (d, 1H$_{para}$, 1H$_{meta}$, $^{3}J_{H\text{-}H}$ = 3.3 Hz, Pt-CH_2CH_2–*o*-$C_6H_3(CH_2CH_3)$), 5.90, 5.89, 5.71 (s, 1H, 1H, 1H, Tp'C*H*), 3.18 (m, 1H, Pt-CH_2C*H*$_2$–*o*-$C_6H_3(CH_2CH_3)$), 2.85 (dd, 1H, $^{2}J_{H\text{-}H}$ = 5.6, $^{2}J_{H\text{-}H}$ = 15.2, $^{2}J_{Pt\text{-}H}$ = 114 Hz, Pt-C*H*$_2CH_2$–*o*-$C_6H_3(CH_2CH_3)$), 2.76 (m, 1H Pt-CH_2C*H*$_2$–*o*-$C_6H_3(CH_2CH_3)$ 2.70 (1H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Pt-CH_2CH_2–o-C_6H_3(C*H*$_2CH_3$)), 1.08 (t, 3H, $^{3}J_{H\text{-}H}$ = 7.6 Hz, Pt-CH_2CH_2–*o*-$C_6H_3(CH_2CH_3)$), -19.73 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1395 Hz, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 298K, δ): 154.6 (1C, $^{2}J_{Pt\text{-}C}$ = 108 Hz, Pt-CH_2CH_2-*o*-*C*$_6H_3(CH_2CH_3)$), 150.8 ($^{2}J_{Pt\text{-}C}$ = 22.0 Hz), 150.4 ($^{2}J_{Pt\text{-}C}$ = 25.0 Hz), 149.3 ($^{2}J_{Pt\text{-}C}$ = 19.0 Hz), 145.1, 144.7, 144.1 (1C, 1C, 1C, 1C, 1C, 1C, Tp'*C*CH_3), 140.4 ($J_{Pt\text{-}C}$ = 46 Hz), 133.4, 133.2 (1C$_{ipso}$, $^{1}J_{Pt\text{-}C}$ = 859 Hz, Pt-CH_2CH_2-*o*-*C*$_6H_3(CH_2CH_3)$), 123.6, 121.8 ($^{2}J_{Pt\text{-}C}$ = 46 Hz), (1C, 1C, 1C, 1C, 1C, Pt-CH_2CH_2-*o*-*C*$_6H_3(CH_2CH_3)$), 107.9

($^3J_{Pt-C}$ = 11.6 Hz), 106.6 ($^3J_{Pt-C}$ = 11.4 Hz), 106.3 ($^3J_{Pt-C}$ = 9.0 Hz) (1C, 1C, 1C, Tp'*C*H), 43.5 (1C, $^2J_{Pt-C}$ = 54.0 Hz, Pt-CH_2*C*H_2-*o*-$C_6H_3(CH_2CH_3)$), 29.1 (1C, Pt-CH_2*C*H_2-*o*-C_6H_3(*C*H_2CH_3)) 16.8, 15.2 ($^3J_{Pt-C}$ = 16.6 Hz), 14.9 ($^3J_{Pt-C}$ = 16.4 Hz), 12.85, 12.78 (1C, 1C, 1C, 2C, 1C, Tp'C*C*H_3), 11.8 (1C, $^2J_{C-C}$ = 2Hz, Pt-CH_2CH_2-*o*-C_6H_3(CH_2*C*H_3)), 8.8 (1C, $^1J_{Pt-C}$ = 604 Hz, Pt-*C*H_2CH_2-*o*-$C_6H_3(CH_2CH_3)$). Anal. Calcd for $PtBN_6C_{25}H_{35}\cdot CH_2Cl_2$: C, 48.00; H, 5.67; N, 13.44; Found: C, 47.06; H, 5.64; N, 12.70.

General Procedure for the synthesis of Tp'Pt(Ar)(H)$_2$ Complexes (14-15). Tp'PtMe(H)$_2$ (**3**) (0.075 g, 0.147 mmol) and 1 equivalent of $B(C_6F_5)_3$ (0.075 g) were placed in a 100 mL Schlenk flask under nitrogen. Aromatic solvent (15 mL) was subsequently added and the reaction mixture was stirred overnight at 35 °C. After solvent removal in vacuo, the resultant residue was chromatographed on alumina (CH_2Cl_2 as eluent) and a white solid was obtained, which was recrystallized from pentanes at -30 °C.

Tp'Pt($C_6H_4CH_2CH_3$)(H)$_2$ (14). Tp'PtMe(H)$_2$ (**3**) (0.050 g, 0.098 mmol) and $B(C_6F_5)_3$ (0.050 g, 0.098 mmol) were combined as described above with 15 ml anhydrous ethylbenzene. ^{1}H NMR (CD_2Cl_2, 298K, δ): 6.76, 6.72 (br, Pt-C_6*H*$_4$Et), 5.87, 5.84 (s, 1H, 2H, Tp'-C*H*), 2.47, 2.41, 2.40, 2.24, 2.22, 2.09 (Tp'-CH_3) 2.54, 1.43 (m, 1H, 1H, $C_6H_4CH_2CH_3$), 1.19 (t, 3H, $^3J_{H-H}$ = 7.5 Hz, $C_6H_4CH_2CH_3$), -18.74, -18.77 (s, 2H, ca. 2:1, $^1J_{Pt-H}$ =1290 Hz, $^1J_{Pt-H}$ =1289, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 298K, δ): 149.6 (s, 2C, $^2J_{Pt-C}$ = 21 Hz, Tp'*C*CH_3), 149.4 (s, 1C, $^2J_{Pt-C}$ = 25 Hz, Tp'*C*CH_3), 144.5, 143.9 (s, 1C, 2C, Tp'*C*CH_3), 126.3, 122.2, 121.4 (s, Pt-*C*$_6$H$_4$Et) 105.6 (s, 2C, $^2J_{Pt-C}$ = 9.8 Hz, Tp'*C*H) 104.9 (s, 1C, $^2J_{Pt-C}$ = 10 Hz, Tp'*C*H), 31.5, 29.2, 15.4 (s, 1C, $^2J_{Pt-C}$ = 33 Hz, Tp'C*C*H_3), 13.8 (s, 2C, $^2J_{Pt-C}$ = 18 Hz, Tp'C*C*H_3) 13.7, 12.1 (s, 1C, 2C, Tp'C*C*H_3).

Tp'Pt($C_6H_4CH(CH_3)_2$)$(H)_2$ (15). Tp'PtMe$(H)_2$ (**3**) (0.050 g, 0.098 mmol) and $B(C_6F_5)_3$ (0.050 g, 0.098 mmol) were combined as described above with 15 mL isopropylbenzene. ^{1}H NMR (CD_2Cl_2, 298K, δ): 6.76, 6.71 (br, Pt-C_6H_4^{i}Pr), 5.85, 5.82 (s, 1H, 2H, Tp'-C*H*), 2.45, 2.39, 2.22, 2.07 (Tp'-CH_3) 2.73 (m, 1H, Pt-$C_6H_4CH(CH_3)_2$), 1.18 (d, 6H, Pt-$C_6H_4CH(CH_3)_2$) -18.78, -18.80 (s, 2H, ca. 2:1, $^1J_{Pt-H}$=1292, $^1J_{Pt-H}$=1289 Hz, Pt-*H*).

Structural Data for 5. Crystals from CH_2Cl_2/methanol; $C_{23}H_{31}N_6BPt$, M = 597.43; orthorhombic, space group $P2_1nb$; Z = 4; a = 7.9063(4), b = 11.9371(6), c = 25.2697(12) Å; α = 90, β = 90, γ = 90°; U = 2384.91(20) Å^3; D_c = 1.664 Mg m^{-3}; T = -100°C; max 2θ: 50°; Mo-K_α radiation (λ = 0.71073 Å); 4011 unique reflections were obtained and 2493 of these with I > 2.5σ(I) were used in the refinement; data were collected on a Bruker SMART diffractometer, using the omega scan method. For significant reflections merging R-value: 0.044; Residuals: R_F: 0.043; R_W: 0.045 (significant reflections); GoF: 1.0495.

Structural Data for 7. Crystals were obtained from ethylbenzene; $C_{27}H_{36}N_6BPt$, M = 650.52; monoclinic, space group $P2_1/c$; Z = 4; a = 8.0135(8), b = 24.027(3), c = 14.0296(14) Å; α = 90, β = 99.090 (4), γ = 90°; U = 2667.3(5) Å^3; D_c = 1.620 Mg m^{-3}; T = 100(2) K; max 2θ: 50°; Mo-K_α radiation (λ = 0.71073 Å); 202152 unique reflections were obtained and 27982 of these with I > 2σ(I) were used in the refinement; data were collected on a Bruker SMART APEX-II diffractometer, using the omega scan method. For significant reflections merging R-value: 0.0604; Residuals: R_F: 0.0297; R_W: 0.0613 (significant reflections); GoF: 1.120.

Structural Data for 11. Crystals were obtained from CH_2Cl_2/methanol; $C_{25}H_{35}N_6Cl_2BPt$, M = 696.39; monoclinic, space group C2/c; Z = 8; a = 28.0057(6), b = 12.4619(3), c = 15.5140(3) Å; α = 90, β = 94.3510 (10), γ = 90°; U = 5398.8(2) Å^3; D_c = 1.714 Mg m^{-3}; T =

100(2) K; max 2θ: 50°; Mo-K_α radiation (λ = 0.71073 Å); 56961 unique reflections were obtained and 6519 of these with I > 2.5σ(I) were used in the refinement; data were collected on a Bruker SMART APEX-II diffractometer, using the omega scan method. For significant reflections merging R-value: 0.0296; Residuals: R_F: 0.0251; R_W: 0.0518 (significant reflections); GoF: 1.041.

Structural Data for 12. Crystals from CH_2Cl_2/pentane; $C_{21.5}H_{31}N_6ClF_4B_2OPt$, M = 717.67; triclinic, space group P –1; Z = 4; a = 9.1331(2), b = 12.6495(3), c = 24.9106(5) Å; α = 102.218(1), β = 95.437(1), γ = 96.559(1)°; U = 2773.27(11) $Å^3$; D_c = 1.719 Mg m^{-3}; T = -100°C; max 2θ: 50°; Mo-K_α radiation (λ = 0.71073 Å); 9783 unique reflections were obtained and 7764 of these with I > 2.5σ(I) were used in the refinement; data were collected on a Bruker SMART diffractometer, using the omega scan method. For significant reflections merging R-value: 0.039; Residuals: R_F: 0.037; R_W: 0.038 (significant reflections); GoF: 1.8003.

Appendix A

Bond Distances (Å) and Angles (deg) for Tp'Pt(CH_2CH_2-*o*-C_6H_4)(H) (Chapter 3, **7**).

Pt(1)-C(8)	2.0176(12)
Pt(1)-C(1)	2.0762(11)
Pt(1)-N(21)	2.1549(11)
Pt(1)-N(11)	2.1662(10)
Pt(1)-N(31)	2.2053(9)
C(1)-C(2)	1.5468(19)
C(2)-C(3)	1.5086(18)
C(3)-C(4)	1.4031(19)
C(3)-C(8)	1.4160(15)
C(4)-C(5)	1.402(2)
C(5)-C(6)	1.399(2)
C(6)-C(7)	1.4060(19)
C(7)-C(8)	1.4055(16)
B(10)-N(32)	1.5483(17)
B(10)-N(12)	1.5569(19)
B(10)-N(22)	1.557(2)
N(11)-C(15)	1.3488(16)
N(11)-N(12)	1.3743(16)
N(12)-C(13)	1.3638(16)
C(13)-C(14)	1.391(2)
C(13)-C(16)	1.501(2)
C(14)-C(15)	1.411(2)
C(15)-C(17)	1.501(2)

N(21)-C(25)	1.3494(18)
N(21)-N(22)	1.3779(17)
N(22)-C(23)	1.3600(19)
C(23)-C(24)	1.390(3)
C(23)-C(26)	1.503(3)
C(24)-C(25)	1.409(3)
C(25)-C(27)	1.503(3)
N(31)-C(35)	1.3522(14)
N(31)-N(32)	1.3754(14)
N(32)-C(33)	1.3608(15)
C(33)-C(34)	1.3924(18)
C(33)-C(36)	1.5040(19)
C(34)-C(35)	1.4090(18)
C(35)-C(37)	1.4979(18)
C(41)-C(42)	1.533(5)
C(42)-C(43)	1.512(5)
C(43)-C(44)	1.395(4)
C(43)-C(48)	1.405(4)
C(44)-C(45)	1.406(5)
C(45)-C(46)	1.406(6)
C(46)-C(47)	1.386(7)
C(47)-C(48)	1.400(6)

C(8)-Pt(1)-C(1)	81.33(5)
C(8)-Pt(1)-N(21)	178.54(4)
C(1)-Pt(1)-N(21)	97.29(5)
C(8)-Pt(1)-N(11)	97.68(4)
C(1)-Pt(1)-N(11)	177.85(5)
N(21)-Pt(1)-N(11)	83.69(4)
C(8)-Pt(1)-N(31)	93.25(4)
C(1)-Pt(1)-N(31)	95.25(4)
N(21)-Pt(1)-N(31)	87.32(4)
N(11)-Pt(1)-N(31)	86.71(4)
C(2)-C(1)-Pt(1)	108.98(8)
C(3)-C(2)-C(1)	108.07(9)
C(4)-C(3)-C(8)	120.12(11)
C(4)-C(3)-C(2)	124.73(11)
C(8)-C(3)-C(2)	115.12(11)
C(5)-C(4)-C(3)	120.35(12)
C(6)-C(5)-C(4)	119.69(13)
C(5)-C(6)-C(7)	120.37(13)
C(8)-C(7)-C(6)	120.31(12)
C(7)-C(8)-C(3)	119.12(11)
C(7)-C(8)-Pt(1)	125.10(9)
C(3)-C(8)-Pt(1)	115.61(8)
N(32)-B(10)-N(12)	109.42(11)
N(32)-B(10)-N(22)	109.27(10)
N(12)-B(10)-N(22)	108.81(11)
C(15)-N(11)-N(12)	107.73(10)
C(15)-N(11)-Pt(1)	134.61(9)
N(12)-N(11)-Pt(1)	117.62(7)
C(13)-N(12)-N(11)	109.62(11)
C(13)-N(12)-B(10)	130.04(12)

C(14)-C(15)-C(17)	128.38(12)
C(25)-N(21)-N(22)	107.49(12)
C(25)-N(21)-Pt(1)	134.74(11)
N(22)-N(21)-Pt(1)	117.74(8)
C(23)-N(22)-N(21)	109.44(12)
C(23)-N(22)-B(10)	130.14(13)
N(21)-N(22)-B(10)	120.39(10)
N(22)-C(23)-C(24)	107.94(15)
N(22)-C(23)-C(26)	122.69(18)
C(24)-C(23)-C(26)	129.35(17)
C(23)-C(24)-C(25)	106.04(13)
N(21)-C(25)-C(24)	109.09(15)
N(21)-C(25)-C(27)	122.81(15)
C(24)-C(25)-C(27)	128.09(15)
C(35)-N(31)-N(32)	106.78(9)
C(35)-N(31)-Pt(1)	135.93(8)
N(32)-N(31)-Pt(1)	117.14(7)
C(33)-N(32)-N(31)	110.17(9)
C(33)-N(32)-B(10)	129.87(10)
N(31)-N(32)-B(10)	119.95(9)
N(32)-C(33)-C(34)	107.61(11)
N(32)-C(33)-C(36)	123.28(12)
C(34)-C(33)-C(36)	129.09(12)
C(33)-C(34)-C(35)	105.84(10)
N(31)-C(35)-C(34)	109.61(10)
N(31)-C(35)-C(37)	123.95(11)
C(34)-C(35)-C(37)	126.44(11)
C(43)-C(42)-C(41)	113.8(3)
C(44)-C(43)-C(48)	118.7(3)
C(44)-C(43)-C(42)	120.0(3)

N(11)-N(12)-B(10)	119.96(10)
N(12)-C(13)-C(14)	107.52(12)
N(12)-C(13)-C(16)	123.19(14)
C(14)-C(13)-C(16)	129.26(13)
C(13)-C(14)-C(15)	106.34(11)
N(11)-C(15)-C(14)	108.78(13)
N(11)-C(15)-C(17)	122.83(12)

C(48)-C(43)-C(42)	121.3(3)
C(43)-C(44)-C(45)	121.1(3)
C(44)-C(45)-C(46)	119.2(4)
C(47)-C(46)-C(45)	120.2(3)
C(46)-C(47)-C(48)	120.1(3)
C(47)-C(48)-C(43)	120.7(3)

Atomic parameters x,y,z and Biso for complex **7**

atom	x	y	z	U(eq)
Pt(1)	3669(1)	8053(1)	1710(1)	10(1)
C(1)	2245(2)	8071(1)	338(1)	14(1)
C(2)	1991(2)	7468(1)	-44(1)	16(1)
C(3)	1822(2)	7094(1)	798(1)	14(1)
C(4)	919(2)	6591(1)	730(1)	18(1)
C(5)	828(2)	6274(1)	1560(1)	20(1)
C(6)	1625(2)	6464(1)	2460(1)	19(1)
C(7)	2503(2)	6973(1)	2538(1)	16(1)
C(8)	2611(1)	7291(1)	1710(1)	12(1)
B(10)	4139(2)	8984(1)	3381(1)	15(1)
N(11)	5208(1)	8009(1)	3123(1)	14(1)
N(12)	5104(1)	8444(1)	3748(1)	15(1)
C(13)	6079(2)	8332(1)	4614(1)	18(1)
C(14)	6841(2)	7818(1)	4536(1)	20(1)
C(15)	6274(2)	7628(1)	3589(1)	16(1)
C(16)	6191(2)	8713(1)	5471(1)	27(1)
C(17)	6741(2)	7102(1)	3118(1)	22(1)
N(21)	4783(1)	8868(1)	1670(1)	15(1)
N(22)	4844(1)	9200(1)	2476(1)	16(1)
C(23)	5614(2)	9689(1)	2327(2)	24(1)
C(24)	6059(2)	9674(1)	1409(2)	28(1)
C(25)	5525(2)	9151(1)	1020(1)	22(1)
C(26)	5906(4)	10140(1)	3078(2)	43(1)
C(27)	5728(3)	8915(1)	53(2)	34(1)
N(31)	1714(1)	8444(1)	2433(1)	12(1)
N(32)	2233(1)	8853(1)	3099(1)	13(1)
C(33)	876(2)	9079(1)	3429(1)	15(1)
C(34)	-563(2)	8806(1)	2970(1)	16(1)
C(35)	13(1)	8412(1)	2354(1)	14(1)
C(36)	1014(2)	9551(1)	4142(1)	24(1)
C(37)	-1060(2)	8020(1)	1689(1)	22(1)
C(41)	7978(5)	9360(2)	8069(3)	27(1)
C(42)	9236(5)	9844(1)	8247(2)	25(1)
C(43)	9791(4)	9977(1)	9303(2)	19(1)
C(44)	9559(4)	10511(1)	9648(2)	21(1)
C(45)	10125(5)	10651(2)	10618(3)	28(1)
C(46)	10875(5)	10238(2)	11256(3)	30(1)
C(47)	11100(5)	9705(2)	10923(3)	29(1)
C(48)	10564(5)	9573(2)	9951(3)	24(1)

Appendix B

Bond Distances (Å) and Angles (deg) for Tp'Pt(CH_2CHMe-*o*-C_6H_4)(H) (Chapter 3, **11a**).

Pt(1)-C(9)	2.011(3)
Pt(1)-C(1)	2.054(3)
Pt(1)-N(31)	2.144(3)
Pt(1)-N(11)	2.146(2)
Pt(1)-N(21)	2.180(3)
C(1)-C(2)	1.558(5)
C(2)-C(3)	1.459(6)
C(2)-C(4)	1.518(5)
C(4)-C(5)	1.396(5)
C(4)-C(9)	1.401(5)
C(5)-C(6)	1.383(5)
C(6)-C(7)	1.381(5)
C(7)-C(8)	1.400(5)
C(8)-C(9)	1.388(4)
B(10)-N(12)	1.537(4)
B(10)-N(22)	1.548(4)
B(10)-N(32)	1.549(4)
N(11)-C(15)	1.343(4)
N(11)-N(12)	1.375(3)
N(12)-C(13)	1.356(4)

C(13)-C(14)	1.375(4)
C(13)-C(16)	1.492(4)
C(14)-C(15)	1.396(4)
C(15)-C(17)	1.490(4)
N(21)-C(25)	1.341(4)
N(21)-N(22)	1.375(4)
N(22)-C(23)	1.357(4)
C(23)-C(24)	1.378(5)
C(23)-C(26)	1.493(4)
C(24)-C(25)	1.394(5)
C(25)-C(27)	1.500(5)
N(31)-C(35)	1.338(4)
N(31)-N(32)	1.373(3)
N(32)-C(33)	1.358(4)
C(33)-C(34)	1.379(5)
C(33)-C(36)	1.493(5)
C(34)-C(35)	1.406(4)
C(35)-C(37)	1.489(4)
C(41)-Cl(1)	1.767(4)
C(41)-Cl(2)	1.772(4)

C(9)-Pt(1)-C(1)	81.31(13)
C(9)-Pt(1)-N(31)	98.75(11)
C(1)-Pt(1)-N(31)	178.76(13)
C(9)-Pt(1)-N(11)	177.83(11)
C(1)-Pt(1)-N(11)	96.72(12)
N(31)-Pt(1)-N(11)	83.21(9)
C(9)-Pt(1)-N(21)	91.76(11)
C(1)-Pt(1)-N(21)	95.04(13)
N(31)-Pt(1)-N(21)	86.20(9)
N(11)-Pt(1)-N(21)	89.29(9)
C(2)-C(1)-Pt(1)	109.4(2)
C(3)-C(2)-C(4)	116.0(4)
C(3)-C(2)-C(1)	114.9(4)
C(4)-C(2)-C(1)	106.0(3)
C(5)-C(4)-C(9)	119.8(3)

N(12)-C(13)-C(16)	122.9(3)
C(14)-C(13)-C(16)	129.6(3)
C(13)-C(14)-C(15)	106.8(3)
N(11)-C(15)-C(14)	109.0(3)
N(11)-C(15)-C(17)	122.9(3)
C(14)-C(15)-C(17)	128.1(3)
C(25)-N(21)-N(22)	107.0(2)
C(25)-N(21)-Pt(1)	136.6(2)
N(22)-N(21)-Pt(1)	116.06(18)
C(23)-N(22)-N(21)	109.7(2)
C(23)-N(22)-B(10)	129.7(3)
N(21)-N(22)-B(10)	120.5(2)
N(22)-C(23)-C(24)	107.3(3)
N(22)-C(23)-C(26)	122.9(3)
C(24)-C(23)-C(26)	129.7(3)

C(5)-C(4)-C(2)	124.8(3)
C(9)-C(4)-C(2)	115.4(3)
C(6)-C(5)-C(4)	120.4(3)
C(7)-C(6)-C(5)	120.1(3)
C(6)-C(7)-C(8)	120.0(3)
C(9)-C(8)-C(7)	120.3(3)
C(8)-C(9)-C(4)	119.3(3)
C(8)-C(9)-Pt(1)	124.9(2)
C(4)-C(9)-Pt(1)	115.7(2)
N(12)-B(10)-N(22)	109.4(3)
N(12)-B(10)-N(32)	107.7(2)
N(22)-B(10)-N(32)	110.6(2)
C(15)-N(11)-N(12)	107.2(2)
C(15)-N(11)-Pt(1)	134.9(2)
N(12)-N(11)-Pt(1)	117.73(18)
C(13)-N(12)-N(11)	109.5(2)
C(13)-N(12)-B(10)	130.1(3)
N(11)-N(12)-B(10)	120.0(2)
N(12)-C(13)-C(14)	107.6(3)

C(23)-C(24)-C(25)	106.8(3)
N(21)-C(25)-C(24)	109.2(3)
N(21)-C(25)-C(27)	124.3(3)
C(24)-C(25)-C(27)	126.4(3)
C(35)-N(31)-N(32)	107.9(2)
C(35)-N(31)-Pt(1)	133.3(2)
N(32)-N(31)-Pt(1)	118.05(18)
C(33)-N(32)-N(31)	109.2(2)
C(33)-N(32)-B(10)	129.4(3)
N(31)-N(32)-B(10)	119.4(2)
N(32)-C(33)-C(34)	107.8(3)
N(32)-C(33)-C(36)	122.4(3)
C(34)-C(33)-C(36)	129.8(3)
C(33)-C(34)-C(35)	106.4(3)
N(31)-C(35)-C(34)	108.8(3)
N(31)-C(35)-C(37)	122.1(3)
C(34)-C(35)-C(37)	129.1(3)
Cl(1)-C(41)-Cl(2)	111.69(18)

Atomic parameters x,y,z and Biso for complex **11a**.

	x	y	z	U(eq)
Pt(1)	920(1)	7047(1)	2114(1)	17(1)
C(1)	976(2)	8678(3)	2289(2)	33(1)
C(2)	629(2)	9258(3)	1608(3)	46(1)
C(3)	710(2)	10409(4)	1529(3)	61(1)
C(4)	638(1)	8611(3)	780(2)	29(1)
C(5)	553(1)	9029(3)	-52(2)	34(1)
C(6)	556(1)	8365(3)	-765(2)	31(1)
C(7)	645(1)	7281(3)	-659(2)	27(1)
C(8)	736(1)	6854(3)	172(2)	23(1)
C(9)	739(1)	7516(3)	892(2)	21(1)
B(10)	1635(1)	5203(3)	2828(2)	20(1)
N(11)	1104(1)	6606(2)	3434(2)	18(1)
N(12)	1430(1)	5791(2)	3589(2)	19(1)
C(13)	1473(1)	5564(3)	4446(2)	20(1)
C(14)	1175(1)	6250(3)	4846(2)	22(1)
C(15)	947(1)	6885(3)	4199(2)	21(1)
C(16)	1798(1)	4710(3)	4827(2)	26(1)
C(17)	583(1)	7742(3)	4292(2)	27(1)
N(21)	1665(1)	6823(2)	1840(2)	20(1)
N(22)	1907(1)	6013(2)	2288(2)	19(1)
C(23)	2376(1)	6037(3)	2126(2)	22(1)
C(24)	2433(1)	6863(3)	1551(2)	24(1)
C(25)	1984(1)	7336(3)	1387(2)	22(1)
C(26)	2742(1)	5307(3)	2561(2)	28(1)
C(27)	1861(1)	8234(3)	765(2)	30(1)
N(31)	845(1)	5347(2)	1938(2)	17(1)
N(32)	1210(1)	4699(2)	2273(2)	18(1)
C(33)	1067(1)	3659(3)	2214(2)	21(1)
C(34)	606(1)	3641(3)	1831(2)	22(1)
C(35)	477(1)	4716(3)	1668(2)	19(1)
C(36)	1386(1)	2752(3)	2514(2)	30(1)
C(37)	15(1)	5161(3)	1285(2)	23(1)
C(41)	2010(1)	8123(3)	3996(2)	29(1)
Cl(1)	1813(1)	9283(1)	4519(1)	43(1)
Cl(2)	2642(1)	8102(1)	3971(1)	35(1)

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