Bond Activation by Nitrogen Ligated Pt(II)/Pt(IV) Complexes

by
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ABSTRACT

NATHAN M. WEST: Bond Activation by Nitrogen
Ligated Pt(II)Pt(IV) Complexes
(Under the direction of Prof. Joseph L. Templeton)

Activation and functionalization of hydrocarbons by platinum has been studied using chelating nitrogen donor ligands to stabilize Pt(II) and Pt(IV) complexes. These bidentate and tridentate ligands allowed examination of oxidative addition of R-H (R = C, Si) bonds and reductive elimination of R′-H (R′ = C, H) bonds. In addition we have investigated functionalization of hydrocarbons by dehydrogenation of alkanes and by coupling of alkynes.

Stoichiometric dehydrogenation of alkanes or simple ethers can be accomplished by stirring $Me_4Pt_2(\mu\text{-}SMe_2)_2$ and nacnacH (nacnac = bis-*N*-aryl-β-diiminate) in the solvent to be dehydrogenated. This reaction yields Pt(II) alkene hydride complexes, (nacnac)Pt(H)(η^2-alkene). The dimeric Pt reagent is protonated by nacnacH and ensuing methane elimination forms the (nacnac)PtMe fragment which then binds and cleaves a solvent C-H bond through oxidative addition to Pt. Methane elimination followed by β-H elimination from the activated solvent molecule yield the Pt alkene hydride complex, (nacnac)Pt(H)(η^2-alkene). Linear alkanes undergo selective C-H activation of primary C-H bonds to form α-olefin complexes, but ethers add selectively through the secondary C-H α to oxygen; this is due to coordination of the ether oxygen to Pt preceeding C-H activation.

The alkene hydride complex readily exchanges free and bound olefins. This facile ligand exchange has allowed us to explore the reactivity of the (nacnac)Pt(H) fragment.

Triphenylsilane displaces pentene from (nacnac)Pt(H)(1-pentene) and oxidative addition of the Si-H bond forms a stable five-coordinate Pt(IV) silyldihydride complex (nacnac)Pt(H)$_2$(SiPh$_3$). This five-coordinate complex was characterized crystallographically and appears to be a square based pyramid with the vacant coordination site *trans* to the silyl ligand. If acetylene or phosphaalkyne is mixed with the five-coordinate species the triple bond inserts across the vacant site on the Pt and the central CH on the nacnac ligand.

Alkynes easily displace pentene from (nacnac)Pt(H)(1-pentene) and rapidly undergo insertion into the Pt-H bond to initiate a reaction cascade. The identity of the final platinum product depends on the substituents on the alkyne reagent. Alkynes with propargylic protons bond favor allyl formation. Terminal silyl alkynes such as R$_3$SiC≡CH (R$_3$Si = Me$_3$Si, Ph$_3$Si, Ph$_2$MeSi) insert into the Pt-H bond in a 2,1 fashion placing the silyl group and Pt on the same carbon, subsequent C-H activation of the silicon substituents, either methyl or phenyl, forms chelated vinyl silane products. Terminal alkynes with no propargylic hydrogens such as PhC≡CH and *t*-BuC≡CH insert into the Pt-H bond in a 1,2, rather than a 2,1, fashion, placing the substituent β to the metal and precluding C-H activation of the alkyne substituent. Instead, a second alkyne binds to the metal and inserts into the Pt-vinyl bond in a 1,2 fashion forming chelated η^1-η^2-butadienyl ligands with R groups at the 2 and 4 positions.

Acid assisted reductive elimination of hydrogen from Tp'PtH$_3$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate) was examined. Loss of H$_2$ is observed from Tp'Pt(H)$_3$ upon protonation and addition of CO. No formation of hydrogen is observed if the reaction is conducted in the absence of CO. In contrast to most reductive eliminations from Pt(IV) which occur from five-coordinate intermediates, here reductive elimination occurs directly from the 6-coordinate [κ^2 -(HTp')Pt(H)$_3$(CO)][BAr'$_4$] species.

For Erin

ACKNOWLEDGEMENTS

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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 cooridination to a metal via a single atom
η^x	greek eta: denotes cooridination to a metal via x number of atoms
θ	greek theta: general angle
ν_{XY}	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 energy
$\Delta H°$	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, R_W	crystallographic refinement quality indicators
s	singlet

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

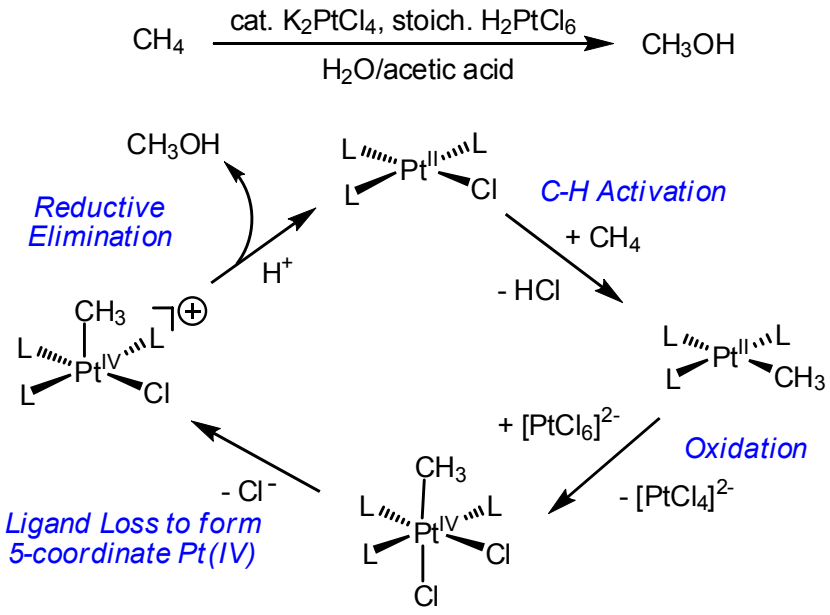
Chapter 1

Introduction to Interconversions of Organometallic Pt(II)/Pt(IV) Complexes Containing Monoanionic Chelating Nitrogen Ligands

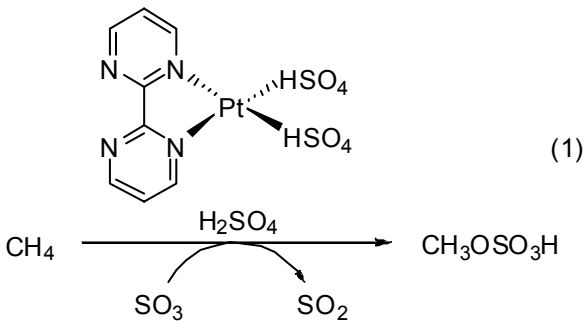
Platinum Catalyzed C-H Functionalization. Selective oxidation of alkanes has been an important goal for chemists for many years. This challenging reaction continues to grow in importance as fossil fuels are consumed and energy prices soar.[1] Even as fossil fuel supplies are exhausted, alkanes from petroleum, and particularly natural gas, remain abundant.[1-4] Alkanes are inert to acid-base reactions, and they have high C-H bond strengths.[3, 5] Radical oxidation reactions are not regioselective and furthermore, the partially oxidized products have weaker C-H bonds than the starting alkane so they are poised to undergo overoxidation.[6, 7] These chemical reactivity limitations have prevented industrial syntheses of methanol from methane; instead it is currently formed from fossil fuel based syn gas (H_2/CO).[4] Syn gas as the feedstock for methanol is preventing it from becoming a viable alternative fuel. However, organometallic reagents have the ability to selectively activate and oxidize the C-H bonds of alkanes without overoxidation.[2, 3, 5, 6, 8-18]

One of the first examples of alkane functionalization was Shilov's report of the oxidation of methane to methanol catalyzed by Pt(II) (Scheme 1.1).[18] Good selectivity for methane activation was observed, in contrast to the overoxidation of methanol and many research groups have since focused on studying d^8 metal reagents for alkane functionalization to achieve high selectivity. Recent successes have only served to intensify the research for platinum based methane oxidation catalysts.[16]

Scheme 1.1. Shilov oxidation of methane to methanol.

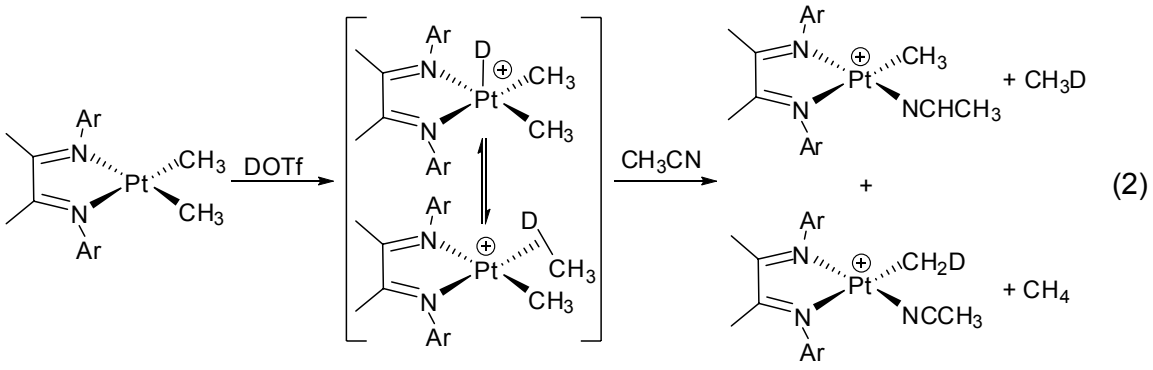


The Shilov system is impractical due to the stoichiometric consumption of Pt(IV) as the oxidant. There have been significant improvements in utilizing cheaper oxidants, but no industrially feasible process for converting methane to methanol has been discovered. The most successful methane oxidation system to date is a bipyrimidine ligated Pt(II) catalyst in fuming sulfuric acid (eq. 1), which gives high yields of the methanol analog $MeOSO_3H$. The harsh conditions, however, have prevented it from being utilized industrially.[16] Despite these considerable strides there continues to be a need to study the activation and functionalization of alkanes with organometallic complexes in the hope of developing a catalyst for selective alkane oxidation.[8, 19]



(1)

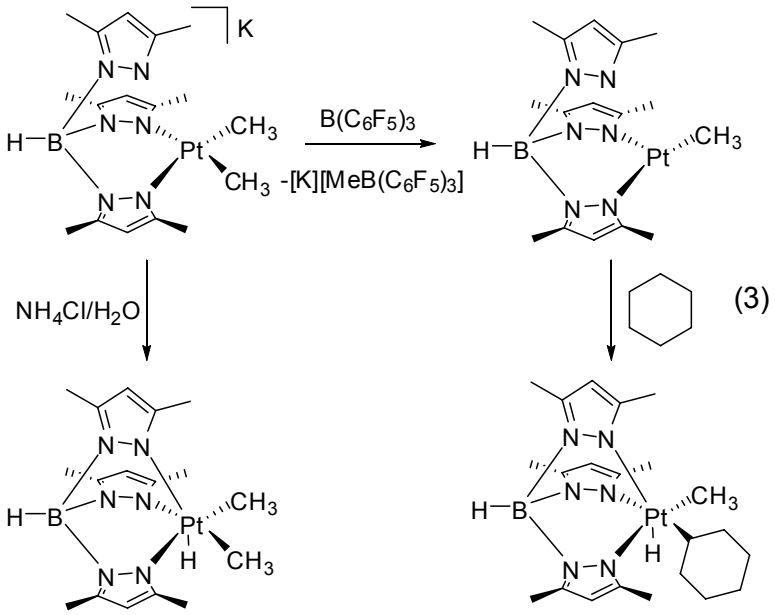
The mechanism of the Shilov oxidation, studied in depth by Bercaw and Labinger, is proposed to proceed by three key steps: oxidative addition of the C-H bond to Pt(II) followed by loss of proton, oxidation of a Pt(II)Me species to a Pt(IV)Me intermediate, then reductive elimination of C-X (X = OH, Cl).[7] Both the C-H activation and C-X formation are proposed to proceed through reactive 5-coordinate intermediates. An array of bidentate nitrogen ligands have been used to stabilize Pt(II) intermediates relevant to the Shilov oxidation. Monomethyl Pt(II) species, like the one involved in the catalytic oxidation, can be formed from protonation of the dimethyl Pt precursor. If D^+ is used instead of H^+ then scrambling of the deuterium into the Pt methyl occurs indicating that reductive elimination and oxidative addition are reversible and a σ-methane adduct must be involved (eq. 2).[20, 21]



(2)

Modeling Pt(IV) Intermediates with Tp′PtMe$_2$H. Isolation of 5-coordinate intermediates involved in C-H activation, particularly alkyl hydrides, has proven challenging due to their propensity to undergo reductive elimination. Tridentate nitrogen donor ligands have demonstrated the ability to stabilize these Pt(IV) species by inhibiting the formation of five-coordinate species. The Tp′ (Tp′ = hydrido(trispyrazolyl)borate) ligand has been particularly successful in stabilizing an array of platinum complexes including the first isolated Pt(IV) alkyl hydride complex Tp′PtMe$_2$H.[22, 23] The precursor [K][Tp′PtMe$_2$] undergoes protonation to form the 5-coordinate dialkylhydride which is immediately trapped

by the free third arm of Tp′ before elimination of methane can occur. Addition of the Lewis acid $B(C_6F_5)_3$ to the anionic dimethyl species results in methide abstraction and C-H activation of alkane solvent by the Tp′PtMe fragment (eq. 3).[24]

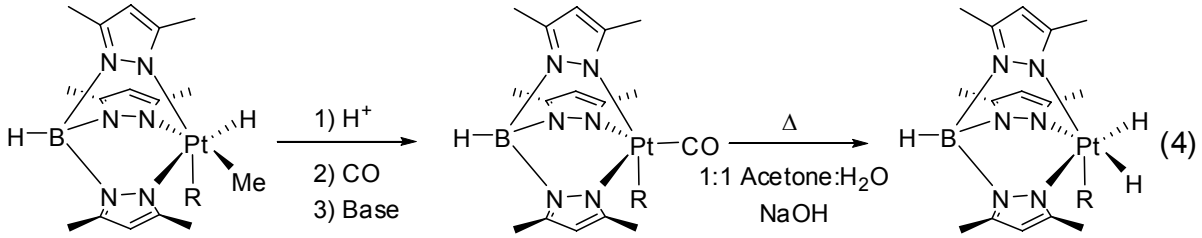


Thermolysis of $Tp'PtMe_2H$ in arene solvent resulted in loss of methane only at temperatures greater than 100°C. Methane loss leads to arene solvent C-H activation and formation of an aryl alkyl hydride Pt(IV) complex, which loses a second equivalent of methane to produce a diaryl hydride complex as the final product.[25] The high temperatures required for reductive elimination reflect the stability of the six-coordinate Pt(IV) complex that is provided by the Tp′ ligand. The thermodynamic parameters for the elimination of the first equivalent of methane are $\Delta H^{\ddagger} = 35.0 \pm 1.1$ kcal/mol and $\Delta S^{\ddagger} = 13 \pm 3$ eu.[26] If the thermolysis is done in deuterated benzene a mixture of methane isotopomers are observed. The first equivalent of methane eliminated is CH_4, but the second equivalent is a mixture of CH_3D, CH_2D_2, and CHD_3 (CD_4 may be present, but it is invisible by ^1H NMR). If reductive coupling of methane were irreversible only CH_3D would be observed; the presence of methane isotopomers indicates that reductive coupling of methane to form a sigma Pt(CH_4)

complex is reversible. This reductive coupling within the coordination sphere was examined by thermolysis of Tp′$PtMe_2D$ at temperatures well below 100°C and Tp′$PtMe(CH_2D)H$ was formed with no loss of methane. The thermodynamic parameters for this process are $\Delta H^{\ddagger}$ = 26 ± 1 kcal/mol and $\Delta S^{\ddagger}$ = 1 ± 4 eu. The significantly lower barrier to reductive coupling than for elimination suggests that dissociation of the methane is rate limiting; the activation entropy values support this proposition as well.

Reductive Elimination of Methane from Tp′$PtMe_2H$ via Protonation. Addition of strong acid to Tp′$PtMe_2H$ resulted in protonation of one of the Tp′ arms causing it to dechelate from the platinum center. The resulting 5-coordinate complex reductively eliminates methane, even at -78 °C, forming $[(Hpz^*)HB(pz^*)_2Pt(Me)(solv)]^+$ which binds a variety trapping ligands.[27] This low temperature pathway to reductive elimination of methane provided a useful alternative to high temperature thermolysis for the synthesis of Pt(II) products. The protonated Tp′ ligand is incapable of stabilizing the Pt(IV) alkyl hydride complexes, so with this one ligand we are able use acid/base chemistry to model both Pt(IV) and Pt(II) intermediates in the Shilov oxidation. Addition of D^+ to the dimethyl hydride complex resulted in no deuterium incorporation into either the Pt methyl groups or the evolved methane so protonation of the Pt-N bond is the only detectable process that had occurred. It is worth noting that protonation of Tp′$PtMe_2D$ resulted in loss of both CH_3D and CH_4 along with scrambling of the deuterium into the remaining Pt methyl group. We concluded that even when the third arm is protonated and removed, reductive coupling is rapid and reversible before methane elimination. This suggests that once again formation of a sturdy sigma adduct of methane occurs after reductive elimination forms the C-H bond.

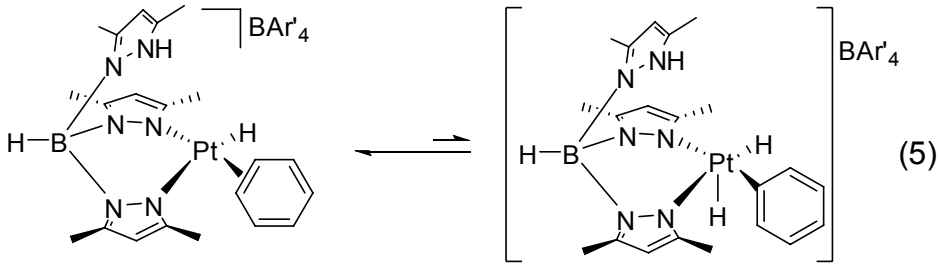
Moving from Tp′PtMe$_2$H to Tp′PtMeH$_2$ and from Tp′PtMeH$_2$ to Tp′PtH$_3$ was accomplished by heating Tp′Pt(R)CO (R = Me, H) in acetone and water in the presence of base (eq. 4).[28-30] The CO ligand is attacked by hydroxide and elimination of CO_2 reduces the metal and allows for the addition of two protons from water. Keinan first reported a similar procedure for converting TpPtMeCO to TpPtMeH$_2$.[31] Our modified procedure included the addition of base which increased the reaction rate. This reaction represents one half of the water-gas shift reaction which interconverts H_2O and CO with H_2 and CO_2. Hydrogen formation from the Pt(IV) dihydride complex would complete the water-gas shift cycle. Reductive elimination of R-H (R = Ph, Me, H) from Tp′PtRH$_2$ by reaction with acid at low temperature was studied in depth.



(4)

Reversible C-H Activation of a Coordinated Benzene Complex. We have used thermolysis experiments to study C-H activation of benzene at high temperatures, but protonation makes it possible to observe arene C-H activation at low temperatures as well. Protonation of Tp′Pt(R)(Ph)(H) (R = H, Ph) at low temperature leads to reductive elimination of benzene, and below 30 °C the benzene remains in the inner coordination sphere in an η^2 fashion as evident in the crystal structure of [κ^2-HTp′Pt(H)(C_6H_6)][BAr′$_4$].[32, 33] These coordinated benzene complexes have only recently been observed,[34] and they bear slight similarities to the highly sought after coordinated alkane adducts that precede alkane C-H activation. These coordinated η^2-benzene complexes undergo rapid and reversible C-H activation to form an unobserved five-coordinate Pt(IV) phenyl dihydride intermediate. The

equilibrium lies far toward the Pt(II) benzene complex on the left (eq. 5), but activation of the C-H bonds was confirmed by spin-saturation transfer experiments in the ^{1}H NMR that showed exchange between the platinum hydride and the benzene protons.

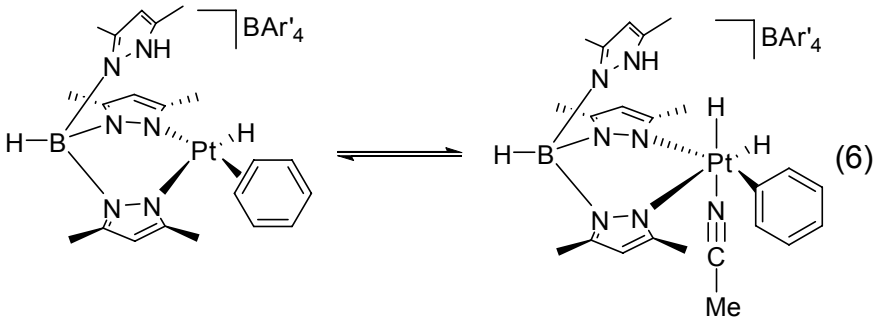


(5)

The barrier to C-H activation was determined by line broadening measurements on the platinum hydride signal and found to be 12.7 kcal/mol with $\Delta H^{\ddagger} = 11.7 \pm 0.5$ and $\Delta S^{\ddagger} = -3.8 \pm 2$ eu. It is important to note that addition of excess benzene to a solution of [κ^2-HTp′Pt(H)(C_6H_6)][BAr′$_4$] did not result in exchange of free and coordinated benzene; alkenes on the other hand easily displace the benzene *vida infra*. Furthermore, formation of [κ^2-HTp′Pt(H)(solv)][BAr′$_4$] via protonation of Tp′PtMeH_2 in the presence of benzene did not result in formation of a Pt-benzene adduct. This indicated that there was a significant activation barrier to benzene coordination to the metal, but that once it binds it forms a stable adduct. This is almost certainly due to the energetic cost of breaking the aromaticity of the benzene to coordinate it to the metal. Once the aromaticity has been broken and the metal adduct formed it is in a sufficiently deep energy well to be stable. The aromaticity is also probably the reason for the low barrier to C-H activation because even though the five-coordinate dihydride is certainly high in energy the phenyl group regaines its aromaticity during conversion from η^2 to being σ-bound to the metal.

Given the stability of the benzene hydride complex at low temperatures we hypothesized that addition of a weak ligand might allow us to trap the proposed five-

coordinate Pt(IV) phenyl dihydride, but not displace the coordinated benzene. Upon addition of acetonitrile to [κ^2-HTp′Pt(H)(C_6H_6)][BAr′$_4$] below -30 °C we observed a mixture of the six-coordinate Pt(IV) phenyl dihydride nitrile adduct [κ^2-HTp′Pt(H)$_2$(Ph)(NCCH$_3$)][BAr′$_4$], in which the two hydrides were inequivalent, and the four-coordinate [κ^2-HTp′Pt(H)(C_6H_6)][BAr′$_4$] (eq. 6).[35] In the dihydride complex, one hydride resided *trans* to acetonitrile and one was *trans* to a pyrazolyl nitrogen. The hydride *trans* to the acetonitrile resonated at -23.4 ppm and had a $^1J_{Pt\text{-}H}$ value of 1525 Hz whereas the other hydride resonated at -19.4 ppm and had $^1J_{Pt\text{-}H}$ equal to 1279 Hz; the large coupling constant of the hydride at -23.4 indicated that the acetonitrile was weakly bound. Thus, the nitrile trapping result substantiated the existence of the unobserved five-coordinate intermediate. The two compounds, square planar Pt(II) and octahedral Pt(IV), were in dynamic equilibrium with the six-coordinate acetonitrile product favored by only 0.3 kcal/mol at 230 K. Not surprisingly, as the nucleophilicity of the nitrile is increased the equilibrium shifts towards the six-coordinate species; at 201 K the K_{eq} value for *p*-OMe benzonitrile is 17.0 compared to 0.54 for *p*-CF_3 benzonitrile. The $\Delta H°$ values for CH_3CN, *p*-OMe benzonitrile, and *p*-CF_3 benzonitrile were -5.9, -5.0, and -4.0 kcal/mol respectively, indicating that the more electron rich alkyl nitriles favor the Pt(IV) more than the aryl nitriles. This coupled with the $\Delta S°$ values of around -20 eu indicate that nitrile coordination to the metal is the key element that determines the equilibrium constant.



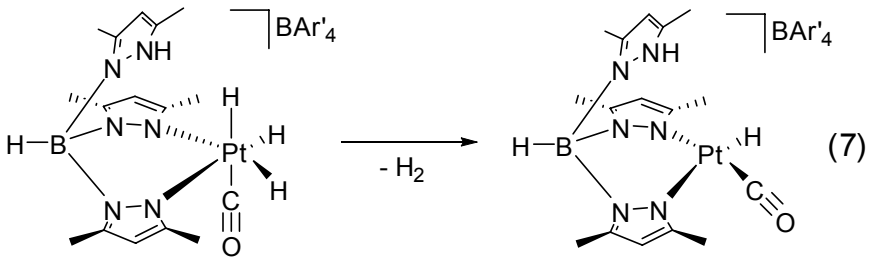
(6)

Trapping of Five-Coordinate Alkyl Dihydride and Trihydride Species with Added Ligand. We have since used similar trapping methods to study five-coordinate intermediates involved in reductive elimination of methane. Protonation of the methyl dihydride complex at low temperature followed by addition of acetonitrile resulted in trapping to form an observable six-coordinate Pt(IV) dihydride species, [κ^2-HTp′Pt(H)$_2$(Me)(NCMe)][BAr′$_4$].[30] As in the benzene case, the two hydrides were inequivalent with one *trans* to the nitrile and one *trans* to a pyrazolyl nitrogen. One hydride appeared at -20.7 ppm with a $^1J_{Pt\text{-}H}$ of 1265 Hz and the other at -24.0 ppm with a $^1J_{Pt\text{-}H}$ of 1496 Hz; these values are similar to those of the trapped phenyl dihydride species. This product was the only one formed, and while it may be in equilibrium with a σ methane adduct, we did not observe such a species. Once again, trapping with nitrile supplied evidence for the intermediacy of a five-coordinate species involved in C-H activation, and the sturdiness of the σ-methane intermediate is reinforced as it was not easily displaced by trapping ligands. If the six-coordinate Pt(IV) methyl dihydride complex was warmed above -30°C, methane elimination occured forming [κ^2-HTp′Pt(H)(NCMe)][BAr′$_4$]. We observed no elimination of dihydrogen; this was also true when Tp′PtMeH$_2$ was protonated in the absence of trapping ligand. However, if CO was used as the trapping ligand we observed elimination of both methane and hydrogen; this will be discussed in depth in Chapter 5.

One goal has been to study the reductive elimination, or lack thereof, of hydrogen from the Tp′Pt system in hopes of learning why we do not observe H_2 loss from Tp′Pt(R)(H)$_2$ (R = Me, Ph). To stack the deck in favor of H_2 elimination we began by studying the trihydride, Tp′PtH$_3$, because it has no alkane option for reductive elimination. Protonation of the trihydride complex with [H(OEt$_2$)$_2$][BAr′$_4$] does not result in reductive elimination of H_2;

rather it forms an unidentified species which decomposes to regenerate some starting material and also some Pt black. To attempt to identify the unidentified species we added acetonitrile as a trapping reagent as we had done in the other low temperature reductive elimination studies. Once again the trapping ligand worked beautifully, and the result was a quantitative yield of [κ^2-HTp′Pt(H)$_3$(NCMe)][BAr′$_4$]. The compound displays one unique and two equivalent hydrides, with chemical shifts of -24.1 ppm for the unique hydride and -20.0 ppm for the equivalent hydrides. Warming the complex does not result in the reductive elimination of hydrogen; it reverts back to starting material.

Different results are obtained if CO is used as the trapping ligand rather than acetonitrile. The CO binds to the metal forming the six-coordinate trihydride [κ^2-HTp′Pt(H)$_3$(CO)][BAr′$_4$] just as the nitrile did, but now upon warming the complex reductive elimination of hydrogen occurs and the Pt(II) hydride [κ^2-HTp′Pt(H)(CO)][BAr′$_4$] forms (eq. 7). The six-coordinate precursor species displays one unique hydride signal at -12.3 ppm with a $^1J_{Pt\text{-}H}$ of 1126 Hz and two equivalent hydrides appear at -17.5 ppm with a $^1J_{Pt\text{-}H}$ of 1114 Hz. The high field shift of the unique hydride *trans* to CO indicates that it is *trans* to a strong π-acid ligand. Mechanistic studies on the reductive elimination of H_2 from this compound will be discussed in detail in Chapter 5, but our hypothesis is that it is the π-acid nature of the CO ligand that causes hydrogen formation to occur. The nitrile adduct is too electron rich to promote elimination of H_2.

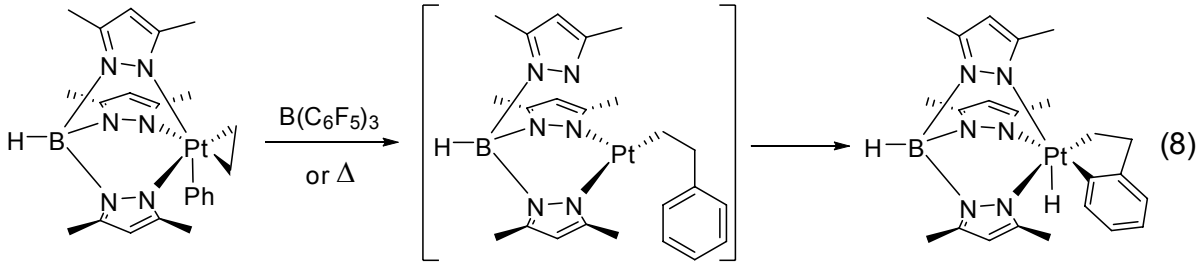


(7)

Alkene Insertion into the Pt-C_6H_5 Bond of Tp′PtPh(alkene). While mechanistic studies of C-H activation are essential for intelligent design of future catalysts, actually functionalizing molecules has proven even more challenging. We were interested in C-C bond forming reactions to functionalize hydrocarbons; to this end we sought to explore olefin insertion reactions as a mean to form new C-C bonds. Low temperature protonation/deprotonation has been used to synthesize Tp′Pt(ethylene)(Ph) complexes starting from the diphenyl hydride reagent, Tp′$PtPh_2H$. An X-ray crystal structure of the ethylene phenyl complex was obtained, and as anticipated the Tp′ ligand was found to be coordinated in a κ^3 manner.[36] The three Pt-N bond distances are 2.14, 2.17, and 2.22 Å, and the ethylene is oriented orthogonal to the Pt-C phenyl bond. The ethylene double bond has been lengthened to 1.43 Å due to back-bonding into the π^* orbital from the metal; all of these factors indicate that the compound more closely resembles a Pt(IV) octahedral compound with a metallocyclopropane ring than a Pt(II) olefin complex.

Heating this complex results in insertion of ethylene into the Pt-Ph bond, followed by oxidative addition of an *ortho* C-H bond on the phenyl ring to yield the observed product, a Pt(IV) metallacylcle hydride complex, Tp′Pt(CH_2CH_2-*o*-C_6H_4)(H) (eq. 8). The reaction can be promoted at room temperature by the addition of the Lewis acid $B(C_6F_5)_3$, which was earlier shown to facilitate dechelation of one Tp′ arm. This indicates that removal of one Tp′ arm to form a five-coordinate intermediate is critical to the insertion process. Within the Pt(IV) formalism this insertion reaction can be considered a type of reductive elimination, and reductive eliminations from Pt(IV) require formation of a five-coordinate intermediate to proceed. The crystal structure of the ethylene complex shows it to be compatible with a Pt(IV) formulation, and this is probably a factor in the relative ease of insertion. Reductive

eliminations are far more facile from Pt(IV) than from Pt(II) so one would expect a much higher barrier to insertion with a square-planar Pt(II) reagent.



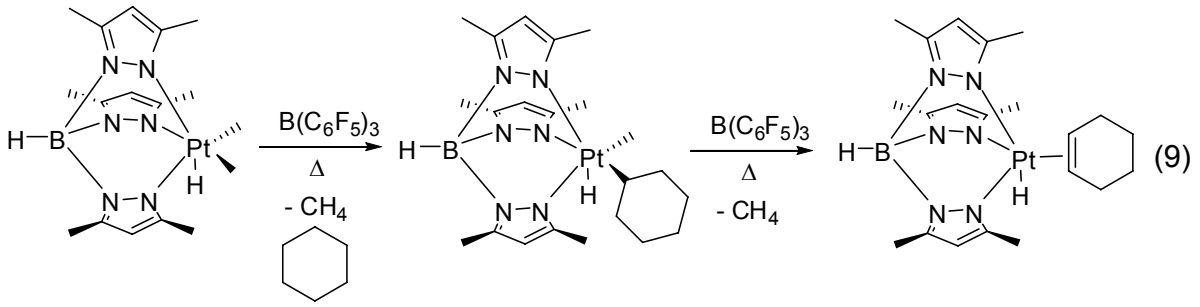
(8)

When propylene is used instead of ethylene three products are obtained: the 2,1 insertion product and both diastereomers of the 1,2 insertion product. Initially the 2,1 product is obtained as the major product, but if the mixture of products is heated to 80°C isomerization eventually yield the 1,2 insertion products as the major products. It is not surprising that the 2,1 (anti-Markovnikov) product is the kinetic product and the 1,2 (Markovnikov) product is the thermodynamic product, but it is surprising that this interconversion has a barrier of only 26.5 kcal/mol. These low barriers to C-C coupling and C-C cleavage were encouraging signs that the complex may catalyze the hydroarylation of olefins, but the thermodynamic well of the *ortho* C-H activation proved too great to overcome and catalysis did not occur. The thermodynamic stability of these metallacyclic compounds was further demonstrated by the thermolytic C-H activation of ethyl benzene derivatives. Thermolysis of Tp′$PtMe_2H$ with borane in ethyl benzene lead to formation of the same metallocyclic product formed from the insertion of ethylene into the Pt-Ph bond. The first step is arene C-H activation and then once an *ortho* C-H bond is activated the alkyl group is activated yielding the observed product. Activation of the *ortho* position is unfavorable because of steric interactions, but it occurs here because of the thermodynamic driving force for metallocycle formation.

Lewis Acid Assisted Thermal C-H activation of Alkanes. Thus far we have discussed three different ways in which Tp′Pt complexes can oxidatively add and reductively eliminate C-H bonds: high temperature thermolysis of a Pt(IV) alkyl hydride, low temperature protonation of a Pt(IV) alkyl hydride, and direct generation of Tp′PtR from a Pt(II) precursor. Another method is a hybrid of the low and high temperature routes to C-H activation following elimination of methane from a Pt(IV) alkyl hydride. Reductive elimination and C-H activation starting from Tp′PtMe(R)H is catalyzed by the Lewis acid $B(C_6F_5)_3$. The Lewis acid works in the same manner as H^+ in that it promotes formation of a reactive five-coordinate species which can eliminate methane. The difference is that the Lewis acid reversibly binds to a Tp′ arm (catalysis by trace H^+ cannot be ruled out). Following methane elimination the Lewis acid can decoordinate from Tp′ to form the reactive Tp′Pt(R) (R = Me, H, Ar) fragment which can C-H activate the solvent. Addition of the borane Lewis acid allows C-H activation of alkane and arene solvents to occur between 25 and 50 °C,[26, 37] far milder conditions than the greater than 110 °C temperatures required for direct thermal activation of arenes.[27] Stirring the borane reagent with Tp′Pt(Me)$(H)_2$ in arene solvent facilitates methane elimination and benzene C-H activation.

When high temperature thermolyses of Tp′PtMe_2H were performed in alkane solvents only Pt black was isolated, but small amounts of olefins were observed in solution indicating that some C-H activation was occurring.[27] The Lewis acid catalyzed C-H activation can be accomplished under milder conditions, and this allowed isolation of Tp′Pt(η^2-olefin)(H) complexes from the reaction with alkanes. Gentle heating of Tp′PtMe_2H in cylcohexane with $B(C_6F_5)_3$ yields Tp′Pt(η^2-cyclohexene)H (eq. 9). These products form from the oxidative addition of an alkane C-H bond to Tp′PtMe followed by reductive elimination of a second

equivalent of methane to form Tp′Pt(alkyl). This Pt alkyl fragment can then undergo β-H elimination to form the observed η^2-olefin hydride complexes. Monitoring the reactions by ^{1}H NMR allows observation of the unsymmetrical intermediate Tp′Pt(Me)(alkyl)(H) for which the hydride has a chemical shift and Pt coupling constant similar to the parent Tp′PtMe$_2$H values (Scheme 1.10). Alkane dehydrogenation is one of the simplest ways to functionalize alkanes; the alkenes formed from dehydrogenation are far more flexible reagents than the parent alkanes. Alkenes see heavy use in polymer synthesis, and in addition there are numerous basic organic reactions for the selective functionalization or oxidation of alkenes, in contrast to the few available to alkanes. In addition alkane dehydrogenation has been used as a key step in alkane metathesis as described by Goldman and Brookhart.[38] While there has been good success in catalyzing alkane dehydrogenation with Rh and Ir,[39-42] only a few examples of alkane dehydrogenation with Pt have been reported,[43-47] and only one example is catalytic.[48]



(9)

Activation of n-pentane by Tp′PtMe$_2$H/B(C$_6$F$_5$)$_3$ appears to favor oxidative addition of primary C-H bonds, initially forming the intermediate Tp′Pt(Me)(n-pentyl)(H), which has identical ^{1}H NMR resonances to the same compound formed by photolysis of Tp′Pt(Me)(CO) in n-pentane. Elimination of the second equivalent of methane from this complex and subsequent β-H elimination would yield the 1-pentene isomer of the η^2-olefin hydride complex. Selective formation of this isomer is desirable in part because the internal olefin

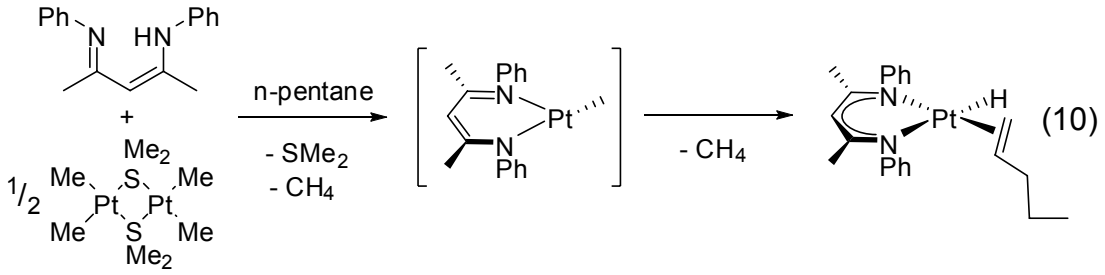
isomers are favored thermodynamically and thus it is difficult to form only the terminal isomer. In addition only the terminal isomer can be used for copolymerization with other olefins. While the major product of pentane dehydrogenation is the 1-pentene isomer, the 2-pentene isomer slowly appears. So the reaction appears to be initially selective for the formation of 1-pentene, but the α-olefin isomerizes as the reaction continues and thus cannot be isolated cleanly.

The complex Tp′Pt(H)(neohexene) was tested for catalytic activity toward the transfer dehydrogenation of alkanes in the presence of $B(C_6F_5)_3$. Neohexene was used as the hydrogen acceptor and cyclohexane as the alkane to be dehydrogenated. Stoichiometric dehydrogenation of both neohexane and cyclohexane by Tp′$PtMe_2H/B(C_6F_5)_3$ is facile. Displacement of neohexene from Tp′Pt(H)(neohexene) by cyclohexene occurs to form Tp′Pt(H)(cyclohexene). While two individual steps required for transfer dehydrogenation proceed, no transfer dehydrogenation catalysis of cyclohexane has been observed. This may be due to complications that arise from the presence of a large excess of alkene or from undesired reactions with the borane.

Alkane Dehydrogenation with a (nacnac)PtMe Fragment. To find a more active system for catalytic C-H bond functionalization we moved away from the tridentate Tp′ ligand to the monoanionic bidentate nacnac (nacnac = bis-*N*-aryl-β-diiminate) ligand. This bidentate ligand will stabilize square planar Pt(II) complexes but not octahedral Pt(IV) complexes; this should enhance catalytic activity as we want reductive elimination from Pt(IV) intermediates to be facile. Addition of an external reagent, such as borane, to remove the third Tp′ arm to generate a bidentate ligand will no longer be necessary. Goldberg has reported several derivatives of five-coordinate (nacnac)$PtMe_3$ complexes in which the nacnac

ligand contains aryl groups with bulky *ortho* substituents.[43, 49, 50] These complexes can reductively eliminate ethane under mild conditions, as opposed to Tp′$PtMe_3$ which does not eliminate ethane even at high temperatures. Once the complexes have eliminated methane they can C-H activate and dehydrogenate an alkane solvent molecule. The olefin complexes resulting from alkane dehydrogenation are not capable of undergoing associative ligand exchange due to the bulky *ortho* groups on the *N*-phenyls blocking access to the metal. This limits the utility of these compounds for catalysis.

We used a nacnac ligand with no ortho substituents on the phenyl groups to allow access to the metal and therefore suitable for facile associative ligand exchange. Stirring $Me_4Pt_2(\mu\text{-}SMe_2)_2$ with nacnacH (*N*-aryl = phenyl) in n-pentane overnight results in the C-H activation and dehydrogenation of one pentane molecule to form (nacnac)Pt(H)(1-pentene) (eq. 10).[47] Unlike the Tp′ case this 1-pentene complex does not isomerize to 2-pentene and, only the 1-pentene complex is observed. Addition of alkene results in rapid olefin exchange at room temperature. Given that olefin exchange is facile in these complexes we attempted to catalyze transfer dehydrogenation with (nacnac)Pt(H)(neohexene). The reaction was quite slow, but we were able to observe almost two turnovers in the dehydrogenation of both diethyl ether and tetrahydrofuran. While this is not the activity that we sought, it is a step in the right direction; more details are presented in chapter 2.

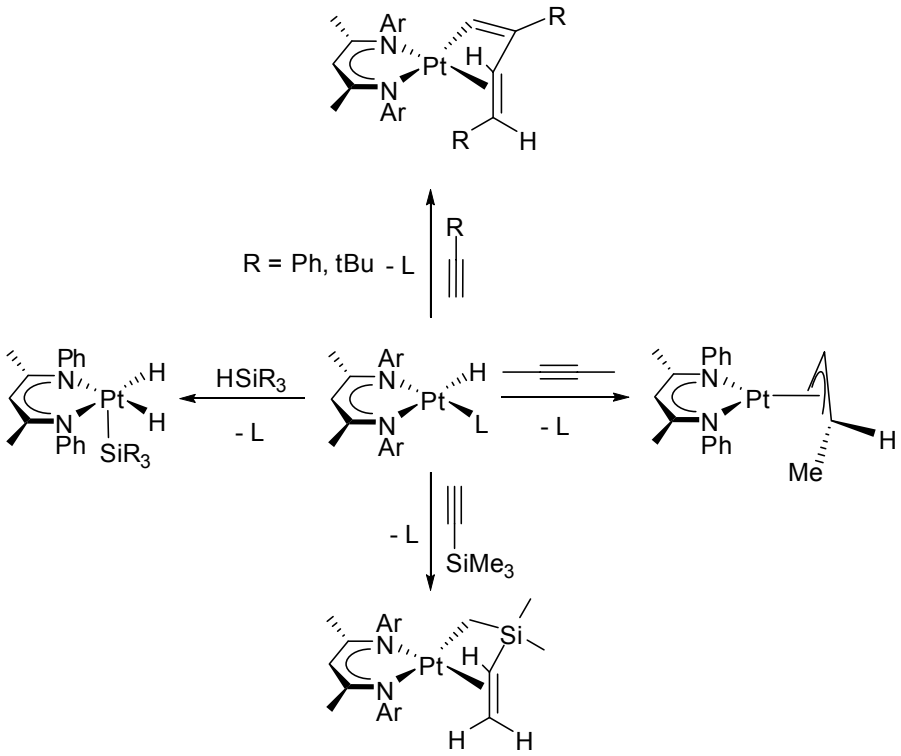


(10)

Reaction of the (nacnac)Pt(H) Fragment with Other Ligands. Now that we have a (nacnac)Pt(H)(1-pentene) framework that allows easy access to the (nacnac)Pt(H) fragment by pentene displacement we can explore the reactivity of the Pt-H bond with other ligands. In Chapter 3 we report the reactivity of this complex with $HSiR_3$ (R_3 = Ph_3, Et_3, Ph_2H). Addition of the silane to the platinum complex resulted in rapid activation of the Si-H bond to form a stable five-coordinate Pt(IV) silyl dihydride, (nacnac)Pt(SiR_3)$(H)_2$. This compound resembles the protonated Tp′Pt five-coordinate silyl dihydride, [κ^2-HTp′Pt(SiR_3)$(H)_2$][BAr′4].[51]

If alkynes are bound to the Pt-H reagent instead of alkenes rapid insertion into the Pt-H bond takes place. While all alkynes undergo rapid insertion into the Pt-H bond, the ultimate product depends on the specific alkyne used as a reagent. Alkynes with propargylic protons form Pt allyls after proton migration. Terminal silyl alkynes of the type HC≡CSiR_3 (R_3 = Ph_3, Me_3, $MePh_2$) undergo C-H activation of one of the silyl substituents after 2,1 insertion of the alkyne to form cyclometallated vinyl silanes. If carbon substituted terminal alkynes like Me_3CC≡CH and PhC≡CH are used the alkyne inserts in a 1,2 fashion, and the resulting platinum vinyl complex binds and inserts a second alkyne to form a Pt η^1-η^2-butadienyl compound with R groups at the 2 and 4 positions (Scheme 1.2). These transformations are explored in depth in Chapter 4.

Scheme 1.2. Interconversions of the (nacnac)Pt(H) Fragment.



Use of the Tp′ ligand to isolate Pt(IV) intermediates and study C-H bond activation processes has been successful and informative. We build on this knowledge to continue toward the goal of bond functionalization with platinum reagents. We have now been able to use our knowledge of C-H bond tranformations to study H-H bond formation from Tp′PtRH_2. The bidentate nacnac ligand has shown encouraging results in the catalytic dehydrogenation of hydrocarbons and has shown the ability to form C-C rapidly at room temperature.

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Chapter 2

Facile Dehydrogenation of Ethers and Alkanes with a β-Diiminate Pt Fragment

Introduction

Many transition metal complexes activate C-H bonds of alkanes, but few lead to functionalized products.[1, 2] Recent successes use d^8 transition metals for catalytic dehydrogenation of alkanes.[3-7] Progress in dehydrogenation of functionalized hydrocarbons has lagged behind alkane dehydrogenation,[8-10] and reports of C-H activation of ethers by d^8 metals are rare in comparison to alkane activation reactions.[11-15]

We report herein Pt complexes that dehydrogenate diethyl ether, THF, and alkanes, with dehydrogenation of ethers kinetically favored relative to dehydrogenation of alkanes.

Recently *β*-diiminate (nacnac) ligands with bulky *ortho*-substituents on the N-phenyl groups have become popular due to both their ease of synthesis and their ability to shield the metal center. Goldberg has used this type of ligand to stabilize five-coordinate Pt(IV) trimethyl species.[16] Thermolysis of these complexes results in reductive elimination of ethane and dehydrogenation of either the *ortho*-substituent or the alkane solvent.[17, 18] Similar results were observed by Chirik with an Ir *β*-diiminate complex.[19]

Hypothesizing that a (nacnac)Pt(olefin)(H) species with simple N-phenyl rings would facilitate associative olefin displacement, we attempted to synthesize a mono-methyl Pt(II) species capable of C-H activation that would not require the use of bulky substituents on the ligand for stability. Note that thermolysis at 85°C of p-Cl or p-OMe (nacnac)Pt(Me)(SMe_2) in benzene has been shown to form (nacnac)Pt(Ph)(SMe_2).[20]

Results and Discussion

The targeted mono-methyl Pt(II) species was formed by stirring Li(nacnac) with (Me)(Cl)Pt(SMe_2)$_2$ followed by addition of L (CO or ethylene) yielding (nacnac)Pt(Me)(L) **1** (L = C_2H_4 **1a**, CO **1b**). An analogous procedure was used to synthesize p-Cl and p-OMe

substituted (nacnac)Pt(Me(SMe_2).[20] Both **1a** and **1b** were crystallographically characterized (Figures 2.1 and 2.2). Although the bound ethylene in **1a** is static at room temperature, olefin rotation can be observed at higher temperature by ^{1}H NMR and reflects a barrier of 16.7 kcal/mol.

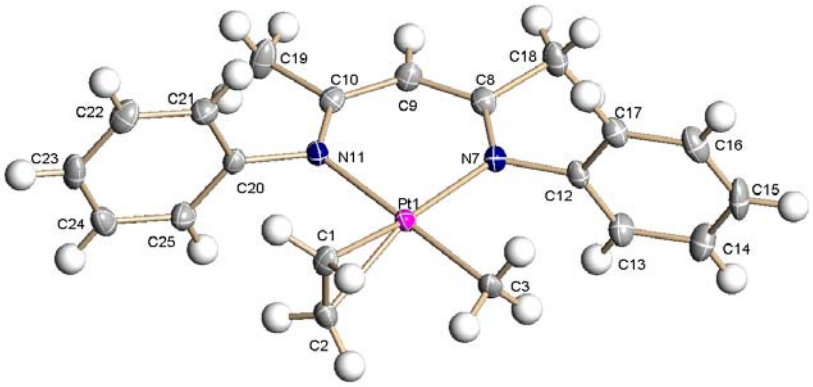


Figure 2.1. X-ray structure of (nacnac)Pt(Me)(ethylene) **1a**. Thermal ellipsoids at 30 %. Selected bond distances and angles: Pt1-C3 = 2.055 Å; Pt1-C1 = 2.118 Å; Pt1-C2 = 2.118 Å; Pt1-N7 = 2.070 Å; Pt1-N11 = 2.098 Å; N7-Pt1-N11 = 90.94 °.

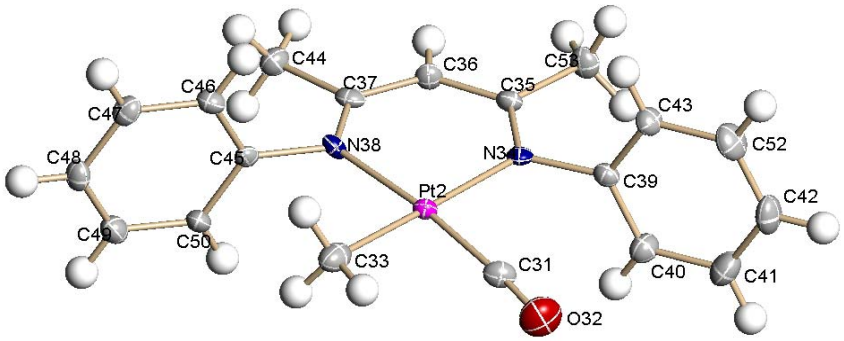
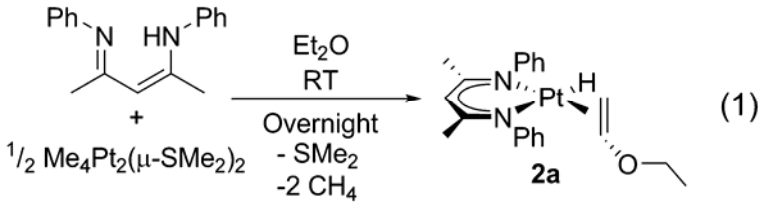


Figure 2.2. X-ray structure of (nacnac)Pt(Me)(CO) **1b**. Thermal ellipsoids at 30 %. Selected bond distances and angles: Pt2-C33 = 2.082 Å; Pt2-C31 = 1.854 Å; Pt2-N34 = 2.079 Å; Pt2-N38 = 2.053 Å; N38-Pt2-N34 = 90.55 °.

The crystal structures indicate that the metal is indeed more exposed than in related structures with *ortho*-substituents on the nacnac phenyl rings. Although we had the (nacnac)Pt^{II}(Me) framework in place, our efforts to isolate sp^3 C-H activation products by displacing L either photolytically or thermally failed. In spite of the high CO stretching

frequency of **1b** (2065 cm^{-1}, CH_2Cl_2) complexes **1a,b** were inert under the conditions we explored.

We turned to a one-pot method for generating a (nacnac)Pt^{II} species capable of C-H activation. The neutral β-enamineimine ligand (nacnacH) has an acidic proton available to react with $Me_4Pt_2(\mu\text{-}SMe_2)_2$ to form CH_4 and generate a reactive Pt(II) methyl fragment. Stirring these reagents in diethyl ether yielded no (nacnac)Pt(OEt_2)(Me), and only a small amount of (nacnac)Pt(SMe_2)(Me);[9,10] but rather the downstream dehydrogenation product (nacnac)Pt(H)(ethyl vinyl ether), **2a**, was isolated (eq. 1). This is in contrast to the reaction between the Pt dimer and 2-(N-arylimino)pyrrole which yields (N-N)Pt(Me)(SMe_2).[21] Reaction with $CH_3CD_2OCH_2CH_3$ yield a mixture of CH_4 and CH_3D as well as both (nacnac)Pt(H)(C_4H_8O) (**2a**) and (nacnac)Pt(H)(C_4H_7DO) (**2a-*d*$_1$**) indicating that the α-C is the site of initial C-H activation. Accordingly no Pt-D product was observed in this experiment. The other reported product of dehydrogenation of diethyl ether with platinum, $[(tmeda)Pt(ethyl\ vinyl\ ether)(H)]^+$, isomerizes over time to the Fischer-type carbene.[15, 22]



(1)

Conducting the reaction in THF led to the formation of the 2,3-dihydrofuran adduct with the double bond adjacent to the oxygen in (nacnac)Pt(H)(2,3-dihydrofuran) (**2b**). Metal hydride complexes of 2,3-dihydrofuran have been elusive, but here dehydrogenation of THF leads to an olefin adduct rather than to the isomeric heteroatom carbene.

Reaction of nacnacH and $Me_4Pt_2(\mu\text{-}SMe_2)_2$ in n-pentane solvent yielded (nacnac)Pt(H)(1-pentene), **2c**. Only the 1-pentene isomer adduct was observed; though the

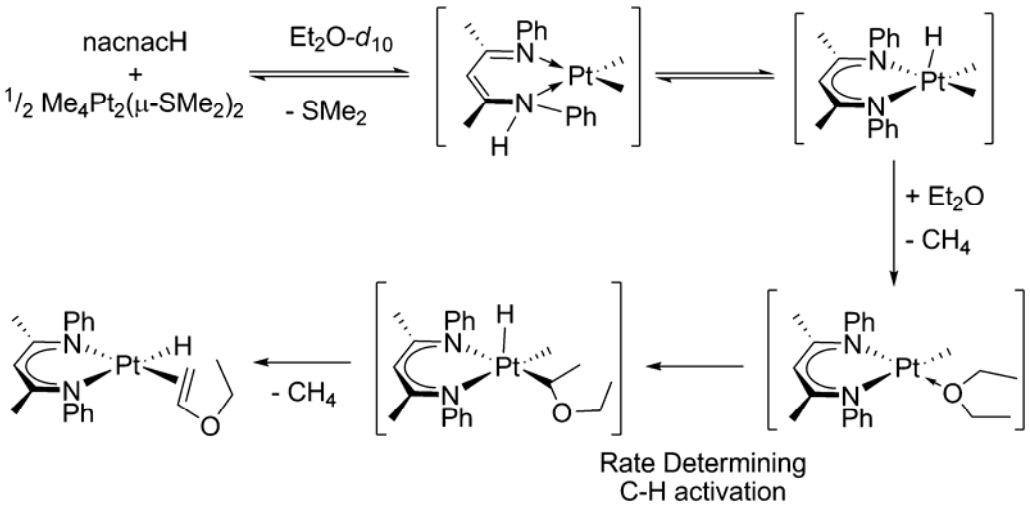
cis-2-pentene isomer can be observed after several weeks at room temperature or 48 hr at 50 °C. Acyclic alkanes yield only terminal olefins indicating a preference for terminal C-H bonds in alkanes. This is in contrast to ethers which favor activation of the C-H bond adjacent to oxygen. The differing pathways are likely due to coordination through oxygen preceding C-H activation.

Competition experiments in which mixtures of two solvents were used displayed a kinetic preference for activation of ethers over alkanes. Diethyl ether is favored 3.9:1 over pentane, Et_2O is favored 1.2:1 over THF, and n-pentane is favored 3.2:1 over cylcopentane. The kinetic preference for ethers is compatible with a mechanism involving associative displacement of methane from (nacnac)Pt(CH_3)(CH_4). Presumably ether binds more quickly than pentane to form the unobserved intermediate (nacnac)Pt(Me)(OEt_2) which then undergoes intramolecular C-H activation at the α position. A similar intramolecular C-H activation of ether was observed by Bercaw in (TMEDA)Pt(Me)(OEt_2).[15] Our results also show that straight chain alkanes are favored over cyclic alkanes. However, no similar effect favoring primary C-H activation is seen in ethers, no doubt reflecting their ability to initially bind through oxygen.

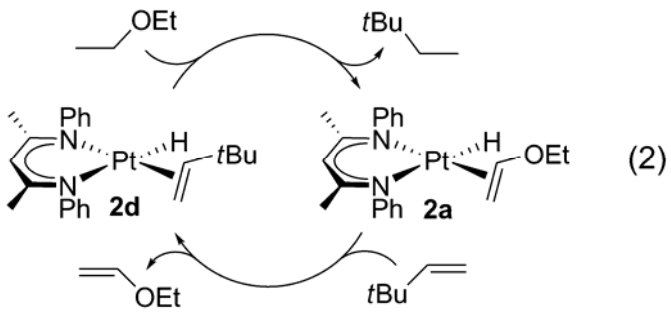
Kinetic isotope effects were determined using 1:1 ratios of protio and deutero substrates. Diethyl ether and THF both yielded k_H/k_D values of 2.2(1), while for pentane the k_H/k_D ratio was 3.8(4). The significantly lower value for the ethers is consistent with initial coordination through oxygen followed by rate limiting C-H activation at the α position (Scheme 2.1). The use of $CH_3CD_2OCH_2CH_3$ also yielded an intramolecular KIE of 2.2(1). The matching inter- and intramolecular isotope effects indicate that the ether molecule bound to Pt rapidly exchanges with free ether in solution. Rate limiting C-H activation may explain

the preference for terminal activation of alkanes. Several d^8 systems have been found to favor *coordination* of secondary C-H bonds,[23] though *activation* of primary C-H bonds is favored.[24]

Scheme 2.1. Proposed Mechanism for Et_2O Dehydrogenation.



Transfer dehydrogenations of Et_2O, THF, and n-pentane using *t*-butyl ethylene (TBE) as a hydrogen acceptor were attempted using a catalytic amount of (nacnac)Pt(H)(TBE) (**2d**) (eq. 2).[25] Formation of free olefin product (ethyl vinyl ether, 2,3-dihydrofuran and pentenes, respectively) and *t*-butyl ethane (TBA) was observed with (nacnac)Pt(H)(TBE) as the only Pt species visible by NMR. The product olefins and TBA were observed by both ^{1}H NMR and gas chromatography. A 7:1 ratio of TBE to **2d** in diethyl ether yielded 1.3 turnovers (19 % yield) after 120 hr at 50 °C. Similar conditions in THF yielded 1.1 turnovers. The low yields are due to catalyst decomposition over the course of the reaction. Increasing the temperature to 60 °C resulted in rapid catalyst decomposition. This is a rare example of catalytic dehydrogenation with Pt, and the first reported transfer dehydrogenation of Et_2O.



(2)

Hydride migration appears to be the rate-limiting step since olefin exchange is facile. Equilibrium binding ratios were measured for the olefins from worst to first: ethyl vinyl ether, neohexene, cyclopentene, 2,3-dihydrofuran, n-pentene, ethylene: 1 : 1.8 : 2.1 : 4.35 : 7.0 : 58 (Figure 2.3). Addition of olefin to the platinum hydride species results in a rapid shift to the equilibrium concentration of bound olefin. The ethylene complex (nacnac)Pt(H)(C_2H_4) (**2e**) displays rapid olefin rotation at room temperature, with a barrier to rotation of only 9.2 kcal/mol determined by low temperature ^{1}H NMR. This is 7.5 kcal/mol lower than the corresponding ethylene rotation barrier in the methyl complex and indicates a much less sterically hindered metal center which helps to explain why ligand exchange is rapid. The facile olefin exchange is in stark contrast to the *ortho*-substituted nacnac complexes reported by Goldberg; they underwent rapid hydride migration but failed to undergo efficient olefin exchange.[18]

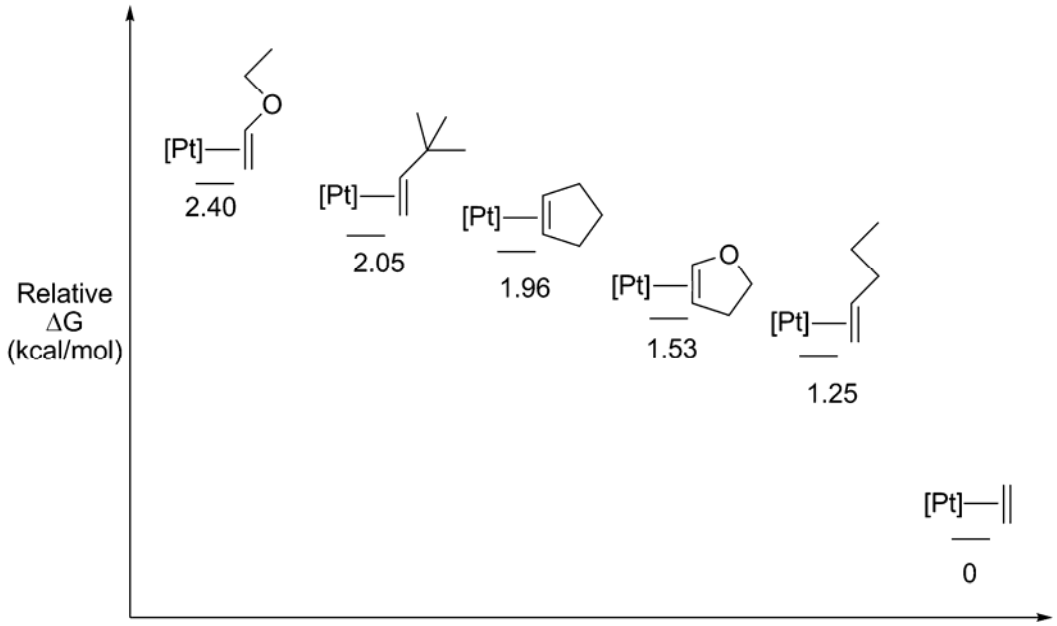


Figure 2.3. Relative binding affinities of olefins to (nacnac)Pt(H).

Conclusions

In conclusion, simple ethers and alkanes undergo facile activation by reaction with nacnacH and $Me_4Pt_2(\mu\text{-}SMe_2)_2$. Activation of ethers is kinetically favored due to the associative displacement of methane, but activation of the α C-H bond is rate limiting as demonstrated by the kinetic isotope effect. Selectivity for ether activation facilitates its dehydrogenation using neohexene as a hydrogen acceptor. The lack of bulky *ortho*-substituents on the nacnac nitrogens exposes the metal center to associative olefin exchange and allows transfer dehydrogenation to occur. Resistance to hydride migration and thermal instability limits the utility of this catalyst for transfer dehydrogenation.

Experimental

General Procedures. All reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All

glassware was flame dried under vacuum and cooled under N_2 before use. Diethyl ether, methylene chloride, toluene, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[26] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Methylene chloride-d_2 was vacuum transferred from calcium hydride and degassed by several freeze-pump-thaw cycles. Diethyl ether-d_{10}, tetrhydrofuran-d_8, and n-pentane-d_{12} were purchased from Cambridge Isotope Labs and used as received.

$Me_4Pt_2(\mu\text{-}SMe_2)_2$[27], HnacNac[28] (HNacNac = bis(N-phenyl) β-enamineimine) and CH_3CD_2OH[29] were synthesized using published procedures. Carbon monoxide was obtained from Matheson Gas Products, Inc., all other reagents were used as received.

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 MHz, Bruker Avance 400 MHz, or Bruker DRX 500MHz spectrometers. ^1H NMR and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000.

NacNacPt(Me)(ethylene) (1a). A solution of nacnacH in THF was cooled to -78 ^oC and nBuLi was added slowly. The solution was allowed to warm to room temperature. A solution of *trans*-(Me)(Cl)Pt(SMe_2)$_2$ was cannulated into the flask containing nacnacLi. The mixture was allowed to stir for 30 minutes before ethylene was bubbled into the solution. After 20 minutes the solvent was removed in vacuo. The resulting oil was chromatographed on a silica column using 100 % CH_2Cl_2. X-ray quality crystals were obtained by slow evaporation of a pentane solution of **1a** at room temperature. ^1H NMR (δ, CD_2Cl_2, 300MHz): 7.35 (4H, m, Ph-*H*), 7.16 (2H, t, Ph-*H*), 7.09 (2H, d, Ph-*H*), 6.90 (2H, d, Ph-*H*), 5.03 (1H, s, NacNac C-*H*), 2.80 (4H, m, Pt-C_2H_4, $^2J_{Pt\text{-}H}$ = 60 Hz), 1.74, 1.65 (3H, s, NacNac

C$\underline{H}_3$), -0.53 (3H, s, Pt-C$\underline{H}_3$, $^2J_{Pt\text{-}H}$ = 68 Hz). ^{13}C NMR (δ, CD_2Cl_2, 100MHz): 160.3, 157.7 (NacNac N$\underline{C}$Me), 152.8, 149.7 (Ph ipso-$\underline{C}$), 128.5, 128.5, 128.3, 128.3, 127.6, 127.6, 126.2, 126.2, 125.4, 124.8 (NacNac Ph), 99.0 (NacNac $\underline{C}$-H, $^3J_{Pt\text{-}H}$ = 50 Hz), 60.0 (Pt-$\underline{C}_2H_4$, $^2J_{Pt\text{-}H}$ = 209 Hz), 26.3, 25.9 (NacNac $\underline{C}H_3$), -3.5 (Pt-$\underline{C}H_3$, $^1J_{Pt\text{-}H}$ = 694 Hz). Anal. Calcd for $C_{20}H_{24}N_2Pt$: C, 49.28; H, 4.96; N, 5.75. Found: C, 49.20; H, 5.12; N, 5.25.

NacNacPt(Me)(CO) (1b). Same as **1a** but CO used rather than ethylene. X-ray quality crystals were obtained by slow evaporation of a pentane solution of **1b** at 0^{o}C. ^{1}H NMR (δ, CD_2Cl_2, 400MHz): 7.36 (4H, m, Ph-$\underline{H}$), 7.14 (2H, t, Ph-$\underline{H}$), 7.07 (2H, d, Ph-$\underline{H}$), 6.85 (2H, d, Ph-$\underline{H}$), 5.02 (1H, s, NacNac C-$\underline{H}$), 1.78, 1.72 (3H, s, NacNac C$\underline{H}_3$), -0.08 (3H, s, Pt-C$\underline{H}_3$, $^2J_{Pt\text{-}H}$ = 66 Hz). IR (CH_2Cl_2): ν_{CO} = 2065 cm^{-1}. Anal. Calcd for $C_{19}H_{20}N_2OPt$: C, 46.82; H, 4.13; N, 5.75. Found: C, 47.01; H, 4.14; N, 5.74.

NacNacPt(H)(1-pentene) (2c). To a schlenk flask was added 200mg (0.348 mmol) $Me_4Pt_2(\mu\text{-}SMe_2)_2$ and 209mg (0.835 mmol, 2.4 eq.) nacnacH. Methylene chloride and pentane were added and the solution was allowed to stir overnight. The bright yellow solution gradually changed to a darker orange color. The resulting oil was chromatographed on a silica column pretreated with a 3 % NEt_3 in CH_2Cl_2 solution, using 80:20 hexanes to CH_2Cl_2 solution as the mobile phase. The first yellow band contains the product and free ligand; this product was collected and rotovapped to dryness. The product was chromatographed again using an untreated silica column and 100 % CH_2Cl_2 to yield 103 mg (29 %) of pure **2b**. ^{1}H NMR (δ, CD_2Cl_2, 400MHz): 7.39 (2H, t, Ph-$\underline{H}$), 7.27 (2H, t, Ph-$\underline{H}$), 7.14 (1H, t, Ph-$\underline{H}$), 7.04 (1H, t, Ph-$\underline{H}$), 7.00 (2H, d, Ph-$\underline{H}$), 6.94 (1H, d, Ph-$\underline{H}$), 6.89 (1H, d, Ph-$\underline{H}$), 5.06 (1H, s, NacNac C-$\underline{H}$), 3.27 (1H, sextet, Pt-CH_2=C$\underline{H}$Pr, $^3J_{H\text{-}H}$ = 6.8 Hz, $^2J_{Pt\text{-}H}$ = 60 Hz), 3.03 (1H, d, *cis*-Pt-C$\underline{H}_2$=CHPr, $^3J_{H\text{-}H}$ = 12.8 Hz, $^2J_{Pt\text{-}H}$ = 46.4 Hz), 2.79 (1H, d, *trans*-Pt-

C$\underline{H_2}$=CHPr, $^3J_{H\text{-}H}$ = 7.6 Hz, $^2J_{Pt\text{-}H}$ = 63.2 Hz), 1.74, 1.69 (3H, s, NacNac C$\underline{H_3}$), 1.78, 1.54, 1.46, 1.33 (1H, m, Pt-CH$_2$=CHC$\underline{H_2}$C$\underline{H_2}$CH$_3$), 0.83 (3H, t, Pt-CH$_2$=CHCH$_2$CH$_2$C$\underline{H_3}$, $^3J_{H\text{-}H}$ = 7.4 Hz), -21.40 (1H, Pt-$\underline{H}$, $^1J_{Pt\text{-}H}$ = 1213 Hz). ^{13}C NMR (δ, CD_2Cl_2, 125MHz): 161.3 (Ph ipso-$\underline{C}$), 160.5, 156.4 (NacNac N$\underline{C}$Me), 149.4 (Ph ipso-$\underline{C}$), 128.7, 128.6, 128.3, 128.3, 125.7, 125.5, 125.5, 125.5, 125.2, 124.5 (NacNac Ph), 99.9 (NacNac $\underline{C}$-H, $^3J_{Pt\text{-}H}$ = 51 Hz), 81.7 (Pt-CH$_2$=$\underline{C}$HPr, $^2J_{Pt\text{-}H}$ = 200 Hz), 54.2 (Pt-$\underline{C}$H$_2$=CHPr, $^2J_{Pt\text{-}H}$ = 177 Hz), 41.1 (Pt-CH$_2$=CH$\underline{C}$H$_2$CH$_2$CH$_3$), 25.5 (NacNac *C*H$_3$), 24.8 (Pt-CH$_2$=CHCH$_2$$\underline{C}H_2CH_3$, $^3J_{Pt\text{-}H}$ = 57 Hz), 23.6 (NacNac $\underline{C}$H$_3$), 13.8 (Pt-CH$_2$=CHCH$_2$CH$_2$$\underline{C}H_3$). Anal. Calcd for $C_{22}H_{28}N_2Pt$: C, 51.25; H, 5.43; N, 5.47. Found: C, 51.41; H, 5.35; N, 5.33.

NacNacPt(H)(η^2-ethyl vinyl ether) (2a). Same as **2b** but diethyl ether used rather than pentane. ^{1}H NMR (δ, CD_2Cl_2, 400MHz): 7.37 (2H, t, Ph-$\underline{H}$), 7.26 (2H, t, Ph-$\underline{H}$), 7.13 (1H, t, Ph-$\underline{H}$), 7.03 (1H, t, Ph-$\underline{H}$), 6.98 (2H, d, Ph-$\underline{H}$), 6.85 (1H, d, Ph-$\underline{H}$), 6.82 (1H, d, Ph-$\underline{H}$), 5.18 (1H, dd, Pt-CH$_2$=C$\underline{H}$OEt, $^3J_{Hcis\text{-}H}$ = 4.5 Hz, $^3J_{Htrans\text{-}H}$ = 10.5 Hz, $^2J_{Pt\text{-}H}$ = 66 Hz), 5.03 (1H, s, NacNac C-$\underline{H}$), 3.78 (1H, dq, Pt-CH$_2$=CHOC$\underline{H_2}$CH$_3$, $^2J_{H\text{-}H}$ = 9.6 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz,), 3.63 (1H, dq, Pt-CH$_2$=CHOC$\underline{H_2}$CH$_3$, $^2J_{H\text{-}H}$ = 9.6 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz,), 2.85 (1H, d, *cis*-Pt-C$\underline{H_2}$=CHOEt, $^3J_{H\text{-}H}$ = 10.5 Hz, $^2J_{Pt\text{-}H}$ = 54 Hz), 2.31 (1H, dd, *trans*-Pt-C$\underline{H_2}$=CHOEt, $^3J_{H\text{-}H}$ = 12.8 Hz, $^2J_{H\text{-}H}$ = 2 Hz, $^2J_{Pt\text{-}H}$ = 68 Hz), 1.73, 1.68 (3H, s, NacNac C$\underline{H_3}$), 1.15 (3H, t, Pt-CH$_2$=CHOCH$_2$C$\underline{H_3}$, $^3J_{H\text{-}H}$ = 7.2 Hz), -21.25 (1H, Pt-$\underline{H}$, $^1J_{Pt\text{-}H}$ = 1234 Hz). ^{13}C NMR (δ, CD_2Cl_2, 125MHz): 161.1 (Ph ipso-$\underline{C}$), 160.2, 156.4 (NacNac N$\underline{C}$Me), 149.8 (Ph ipso-$\underline{C}$), 129.1, 129.1, 128.3, 128.3, 126.1, 125.5, 125.5, 125.2, 124.8, 124.4 (NacNac Ph), 112.3 (Pt-CH$_2$=$\underline{C}$HOEt, $^2J_{Pt\text{-}H}$ = 188 Hz), 99.7 (NacNac $\underline{C}$-H, $^3J_{Pt\text{-}H}$ = 49 Hz), 66.8 (Pt-CH$_2$=CHO$\underline{C}$H$_2$CH$_3$, $^3J_{Pt\text{-}H}$ = 17 Hz), 35.8 (Pt-$\underline{C}$H$_2$=CHOEt, $^2J_{Pt\text{-}H}$ = 180 Hz), 25.3, 23.5

(NacNac $\underline{C}H_3$), 14.7 (Pt-CH_2=CHO$CH_2\underline{C}H_3$). Anal. Calcd for $C_{21}H_{26}N_2OPt$: C, 48.74; H, 5.06; N, 5.41. Found: C, 48.94; H, 4.79; N, 4.53.

NacNacPt(H)(η^2-2,3-dihydrofuran) (2b). Same as **2b** but tetrahydrofuran used rather than pentane and CH_2Cl_2. Compound **2c** is tends to decompose on alumina so clean material is generated by displacement of 1-pentene from **2a** with 2,3-dihydrofuran. Clean **2a** is dissolved in CH2Cl2 and 5-10 eq of 2,3-dihydrofuran are added to the solution. The solvent is evacuated after 15-20 minutes of stirring yielding clean **2c**; the spectroscopic data matches exactly that observed for the product of C-H activation of THF. ^{1}H NMR (δ, CD_2Cl_2, 400MHz): 7.41 (2H, t, Ph-$\underline{H}$), 7.26 (2H, t, Ph-$\underline{H}$), 7.13 (1H, t, Ph-$\underline{H}$), 7.03 (1H, t, Ph-$\underline{H}$), 6.98 (2H, d, Ph-$\underline{H}$), 6.86 (1H, d, Ph-$\underline{H}$), 6.82 (1H, d, Ph-$\underline{H}$), 5.86 (1H, s, Pt-CH=C$\underline{H}$O$(CH_2)_2$, $^2J_{Pt\text{-}H}$ = 72 Hz), 5.02 (1H, s, NacNac C-$\underline{H}$), 3.49 (2H, m, Pt-CH=CHOC$\underline{H}_2CH_2$), 3.26 (1H, dd, Pt-C$\underline{H}$=CHO$(CH_2)_2$, $^3J_{H\text{-}H}$ = 3.4 Hz, $^3J_{H\text{-}H}$ = 2.2 Hz, $^2J_{Pt\text{-}H}$ = 78 Hz), 1.91 (2H, m, Pt-CH=CHOCH_2C$\underline{H}_2$), 1.72, 1.67 (3H, s, NacNac C$\underline{H}_3$), -20.43 (1H, Pt-$\underline{H}$, $^1J_{Pt\text{-}H}$ = 1292 Hz). ^{13}C{} NMR (δ, CD_2Cl_2, 100MHz): 161.1 (Ph ipso-$\underline{C}$), 160.3, 156.6 (NacNac N$\underline{C}$Me), 150.3 (Ph ipso-$\underline{C}$), 129.5, 129.3, 128.2, 128.2, 125.9, 125.7, 125.7, 125.3, 124.9, 124.4 (NacNac Ph), 111.8 (Pt-CH=$\underline{C}$HO$(CH_2)_2$, $^2J_{Pt\text{-}H}$ = 185 Hz), 99.6 (NacNac $\underline{C}$-H, $^3J_{Pt\text{-}H}$ = 50 Hz), 68.4 (Pt-CH=CHO$\underline{C}H_2CH_2$, $^3J_{Pt\text{-}H}$ = 33 Hz), 51.4 (Pt-$\underline{C}$H=CHO$(CH_2)_2$, $^2J_{Pt\text{-}H}$ = 214 Hz), 33.2 (Pt-CH=CHOC$H_2\underline{C}H_2$), 25.4, 23.7 (NacNac $\underline{C}H_3$). Anal. Calcd for $C_{21}H_{24}N_2OPt$: C, 48.93; H, 4.69; N, 5.43. Found: C, 49.46; H, 4.67; N, 4.89.

NacNacPt(H)(t-butyl ethylene) (2d). To a CH_2Cl_2 solution of NacNacPt(H)(1-pentene) (**2b**) was added *tert*-butyl ethylene (TBE). The solution was allowed to stir for 20 minutes before the solvent was removed in vacuo. ^{1}H NMR (δ, CD_2Cl_2, 400MHz): 7.37 (2H, t, Ph-$\underline{H}$), 7.26 (2H, t, Ph-$\underline{H}$), 7.14 (1H, t, Ph-$\underline{H}$), 7.03 (1H, t, Ph-$\underline{H}$), 6.99 (2H, d, Ph-$\underline{H}$),

6.87 (2H, m, Ph-*H*), 5.06 (1H, s, NacNac C-*H*), 3.37 (1H, dd, Pt-CH_2=C*H*$C(CH_3)_3$, $^3J_{H-H}$ = 13.5 Hz, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 63 Hz), 2.84 (1H, d, *cis*-Pt-C*H*$_2$= $CHC(CH_3)_3$, $^3J_{H-H}$ = 13.5 Hz, $^2J_{Pt-H}$ = 41.4 Hz), 2.69 (1H, d, *trans*-Pt-C*H*$_2$= $CHC(CH_3)_3$, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 61.8 Hz), 1.75, 1.70 (3H, s, NacNac C*H*$_3$), 0.85 (9H, s, Pt-CH_2= $CHC(CH_3)_3$), -21.42 (1H, Pt-*H*, $^1J_{Pt-H}$ = 1189 Hz). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 125MHz): 161.4 (Ph ipso-*C*), 160.6, 156.3 (NacNac N*C*Me), 149.0 (Ph ipso-*C*), 128.7, 128.5, 128.2, 128.2, 125.7, 125.6, 125.2, 125.2, 125.2, 124.4 (NacNac Ph), 99.8 (NacNac *C*-H, $^3J_{Pt-H}$ = 52 Hz), 94.6 (Pt-CH_2=*C*$HC(CH_3)_3$, $^2J_{Pt-H}$ = 218 Hz), 47.3 (Pt-*C*H_2=$CHC(CH_3)_3$, $^2J_{Pt-H}$ = 159 Hz), 33.9 (Pt-CH_2=CH*C*$(CH_3)_3$), 28.9 (Pt-CH_2=$CHC(CH_3)_3$, $^3J_{Pt-H}$ = 32 Hz), 25.7 (NacNac *C*H_3), 23.6 (NacNac *C*H_3). Anal. Calcd for $C_{23}H_{30}N_2Pt$: C, 52.16; H, 5.71; N, 5.29. Found: C, 51.95; H, 5.50; N, 5.44.

NacNacPt(H)(ethylene) (2e). A CH_2Cl_2 solution of NacNacPt(H)(1-pentene) (**2b**) was stirred under 1 atm of ethylene for 5 minutes. The solvent was then removed in vacuo, and the process was repeated twice, to ensure that all the pentene was removed. ^1H NMR (δ, CD_2Cl_2, 300MHz): 7.38 (2H, t, Ph-*H*), 7.27 (2H, t, Ph-*H*), 7.15 (1H, t, Ph-*H*), 7.02 (1H, t, Ph-*H*), 6.99 (2H, d, Ph-*H*), 6.86 (2H, m, Ph-*H*), 5.10 (1H, s, NacNac C-*H*), 2.99 (4H, s, Pt-C*H*$_2$=C*H*$_2$, $^2J_{Pt-H}$ = 58 Hz), 1.77, 1.71 (3H, s, NacNac C*H*$_3$), -21.14 (1H, Pt-*H*, $^1J_{Pt-H}$ = 1161 Hz). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 100MHz): 161.2 (Ph ipso-*C*), 160.7, 156.6 (NacNac N*C*Me), 148.2 (Ph ipso-*C*), 128.5, 128.5, 128.3, 128.3, 125.6, 125.6, 125.5, 125.5, 125.3, 124.6 (NacNac Ph), 100.1 (NacNac *C*-H, $^3J_{Pt-H}$ = 53 Hz), 56.1 (Pt-*C*H_2=*C*H_2, $^2J_{Pt-H}$ = 176 Hz), 25.5, 23.5 (NacNac *C*H_3).

$CH_3CD_2OCH_2CH_3$. CH_3CD_2OH (1 mL, 17.2 mmol) was placed in a Kontes tube and cooled to -78°C. Ethyl trifluoromethanesulfonate (2.34 mL, 18.0 mmol) added dropwise to solution. The solution was warmed to room temperature and stirred for 5 min. The

solution was then cooled back to -78°C and triethylamine (2.51 mL, 18.0 mmol) was added to quench the triflic acid generated by the reaction. The solution was allowed to warm back to room temperature at which time the CH_3CD_2OEt was vacuum transferred to a clean Kontes tube; 1.22g (15.5 mmol, 90% yield) of $CH_3CD_2OCH_2CH_3$ was collected. ^1H NMR (δ, CD_2Cl_2, 300MHz): 3.43 (2H, q, OC<u>*H*</u>$_2$, $^3J_{H-H}$ = 7 Hz); 1.15 (3H, t, CH_2C<u>*H*</u>$_3$, $^3J_{H-H}$ = 7 Hz); 1.13 (3H, s, CD_2C<u>*H*</u>$_3$). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 75MHz): 66.1 (O<u>*C*</u>D_2); 66.0 (O<u>*C*</u>H_2); 15.5, 15.2 (<u>*C*</u>H_3).

Solvent competition experiments. NMR tubes were prepared with 10mg (0.017 mmol) $Me_4Pt_2(\mu\text{-}SMe_2)_2$ and 11mg (2.5 eq.) Hnacnac in the drybox. To each tube was added 0.6 mL of CD_2Cl_2 and 0.2 mL of a standard solution of 1:1 molar ratio of the desired substrates (eg. 1:1 THF:Et_2O). The ^1H NMR spectrum was measured periodically over a period of 24 hours and the integration of the hydride peaks from each product was used to measure the ratio. Six runs were used to obtain the reported values and calculated standard error.

Table 2.1. Results of solvent competion experiments with standard error.

Substrates	Ratio	Standard Error (σ)
Et_2O/n-pentane	3.88 : 1	0.09
Et_2O/THF	1.22 : 1	0.04
n-pentane/cyclopentane	3.2 : 1	0.3

Kinetic isotope effect studies. Same procedure as the solvent competition experiments except that 1:1 protio to deutero solvents were used as the standard solution. The effects were calculated by measuring the integral of the Pt hydride and the nacnac methine C-H. The methine resonance was calibrated to 1 and the hydride integral was

divided by the difference in the theoretical value (0.66667 for the singlet) and the actual value (which represents the amount of Pt-D).

Catalytic transfer dehydrogenation reactions. In the drybox nacnacPt(H)(TBE) (**2d**) was dissolved in the desired solvent (Et_2O, THF, or n-pentane) and pipetted into a medium walled J-Young NMR tube. Into the tube was added TBE followed by the addition of a sealed capillary tube containing C_6D_6 for a lock signal. The tube was capped and removed from the drybox. The reaction was heated in an oil bath at 50°C for up to two weeks and the reaction was monitored by ^1H NMR periodically. After extended heating the reaction products were analyzed by gas chromatography as well. Both the product olefin and *t*-butyl ethane (TBA) were observed by GC.

Crystallographic Data for 1a and 1b.

Table 2.2. Crystal data and structure refinement for **1a** and **1b**.

Empirical Formula	$C_{20}H_{24}N_2Pt$	$C_{19}H_{20}N_2OPt$
Complex	**1a**	**1b**
Mol wt	487.50	487.46
Temperature	100(2) K	100(2) K
Wavelength	0.71703 Å	0.71703 Å
Cryst Syst	Monoclinic	Triclinic
Space Group	$P2_1/n$	P-1
a, Å	15.1323(4)	9.3350(7)
b, Å	7.9402(2)	10.3431(7)
c, Å	16.5539(4)	20.4134(18)
α, deg	90	99.0630(10)
β, deg	116.197(1)	93.3700(10)
γ, deg	90	115.3530(10)
Vol. Å3	1784.70(8)	1741.2(2)
Z	4	4
Density (calculated)	1.814 Mg/m^3	1.859 Mg/m^3
μ, mm-1	7.863	8.064
F(000)	944	936
Crystal size	0.20 x 0.20 x 0.05 mm^3	0.30 x 0.20 x 0.05 mm^3
2θ range	1.52 to 28.00°	5.58 to 30.00°
Index Ranges	-19<=h<=18 -10<=k<=10 -14<=l<=21	-13<=h<=9 -14<=k<=14 -28<=l<=28
Reflections Collected	17299	11993
Independent reflections	4315 [R(int) = 0.0248]	8418 [R(int) = 0.0188]
Data/restraints/parameters	4315/8/241	8418/9/433
Goodness-of-fit on F^2	1.036	1.024
Final R indices[I>2sigma(I)]	R1 = 0.0164 wR2 = 0.0348	R1 = 0.0357 wR2 = 0.0873
R indices (all data)	R1 = 0.0197 wR2 = 0.0358	R1 = 0.0449 wR2 = 0.0929
Largest diff. peak and hole	1.111 and -0.577 e $Å^{-3}$	4.139 and -2.202 e $Å^{-3}$

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Chapter 3

Isolation of a Five-Coordinate β-Diiminate Pt(IV) Dihydrosilyl Complex Which Undergoes Facile Cycloaddition Reactions with Terminal Alkynes and Phosphaalkynes

Introduction

Sixteen-electron five-coordinate d^6 complexes have been identified as intermediates in both bond activation and reductive elimination reactions with group 10 transition metals. In many cases formation of a five-coordinate intermediate has been shown to be the first step along the reaction pathway leading to reductive elimination from Pt(IV). Although five-coordinate d^6 species have been postulated for years, only a few examples have been isolated and structurally characterized. Several five-coordinate derivatives of the $PtMe_3$ moiety with chelating nitrogen donors such as (nacnac)$PtMe_3$, (anilide-imine)$PtMe_3$ and (pyridyl-pyrrolide)$PtMe_3$, have been reported by Goldberg since 2000.[1-4] Wang recently reported a 5-coordinate (1,2-bis(*N*-7-azaindolyl)benzene)$PtMe_3$ complex, further demonstrating the ability of the $PtMe_3$ fragment to stabilize five-coordinate complexes.[5] Cationic dihydrosilyl Pt compexes containing the protonated Tp′ (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate) ligand ([κ^2-((Hpz*)(BH(pz*)$_2$Pt(H)$_2$(SiR_3)][BAr'_4]) (Ar′ = 3,5-trifluoromethylphenyl) have been characterized.[6] A (pyridine-indolyl)Pt($SiMe_3$)$(Me)_2$ recently reported by Tilley is proposed to be five-coordinate, though no X-ray structure could be obtained.[7]

Convenient synthesis of β-diiminate Pt olefin hydride complexes, (nacnac)Pt(H)(olefin), has been accomplished by dehydrogenation of alkanes or ethers with a (nacnac)PtMe fragment formed in situ.[8] Related compounds reported by Goldberg using bulky substituents in the ortho position on the phenyl rings of the β-diiminate ligands do not readily undergo ligand exchange because access to the four-coordinate metal is sterically inhibited.[2] Our β-diiminate ligands have no *ortho*-substituents on the phenyl rings on the nitrogens, and this allows the compounds to undergo facile associative ligand exchange. We used this facile ligand exchange to our advantage in conducting catalytic transfer

dehydrogenation reactions; however, the utility of the catalyst was severely limited because of slow insertion of the olefin into the Pt-H bond. The simple synthesis of these olefin hydride complexes and the lability of the olefin provide an opportunity to explore reactions of (nacnac)Pt(H)(L) complexes. Having observed C-H activation with the (nacnac)Pt framework, we now report efforts to probe reactivity patterns of Si-H bonds.

We report herein that the olefin hydride Pt(II) reagent does indeed react with $HSiR_3$; olefin displacement leads to cleavage of the Si-H bond. The result is a stable 5-coordinate d^6 Pt(IV) silyl dihydride complex, (nacnac)Pt(SiR_3)$(H)_2$; these complexes have been characterized by NMR, IR, and X-ray crystallography. These 5-coordinate complexes are inert toward many ligands, but they do bind phosphines at the vacant site *trans* to the silyl ligand. Addition of selected alkynes or phosphaalkynes results in cycloaddition across the nacnac central CH and Pt yielding an anionic tridentate N,N,C or N,N,P ligand. It is interesting to note that in the cycloaddition products the geometry has changed from having both hydride ligands *trans* to N to having one *trans* to N and one *trans* to the new anionic ligand. The phosphaalkenyl complex represents the first report of such a ligand bound to Pt(IV). While free phosphaalkynes are polarized such that the carbon is nucleophilic and the phosphorus is electrophilic because of the respective electronegativities of the atoms,[9-11] we observe the opposite reactivity for the insertion reaction of the phosphaalkyne with the platinum(IV) nacnac reagent as the phosphorus binds to the electrophilic platinum.

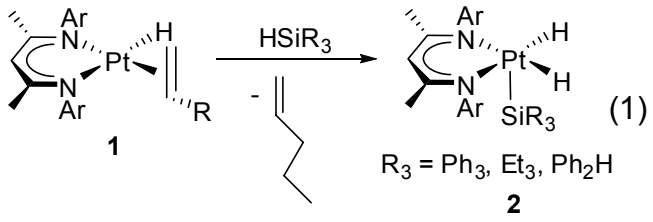
Results and Discussion

Synthesis of (nacnac)Pt$(H)_2(SiR_3)$ (2). We chose to use p-Cl substituted phenyl rings on the nacnac ligand for this study because the p-Cl substituted (nacnac)Pt(H)(1-pentene) (**1**) complex is easier to isolate in powder form than the previously reported phenyl

nacnac complex.[8] The chlorine atoms at the *para* position do not appear to influence the reactivity dramatically relative to the unsubstituted phenyl. The chloride substituents are located far away from the metal and they do not influence the steric environment. In addition the hydride resonance closely mimics the parent nacnac analog: the chemical shift changes by only 0.17 ppm and the $^1J_{Pt\text{-}H}$ changes by only 3 Hz out of 1200 Hz. Unless otherwise stated, the nacnac ligand used throughout this work is the p-Cl derivative.

Addition of triphenylsilane to the pentene hydride platinum(II) reagent **1** at room temperature resulted in disappearance of **1** and quantitative formation of a new species in less than one minute. The product was determined to be (nacnac)Pt$(H)_2(SiPh_3)$ (**2a**): it is C_S symmetric by ^{1}H NMR with a single resonance for both nacnac CH_3 groups and one resonance at -15.62 ppm ($^1J_{Pt\text{-}H}$ = 959 Hz) for the two equivalent Pt hydrides (eq. 1). The hydride ^{1}H NMR resonance is similar to the one observed for the cationic silyldihydride [κ^2-((Hpz*)(BH(pz*)$_2$Pt$(H)_2(SiPh_3)$][Bar′$_4$] for which the equivalent hydrides resonated at -15.05 ppm ($^1J_{Pt\text{-}H}$ = 986 Hz).[6] A single infrared absorption for both Pt hydrides appears at 2190 cm^{-1} in the solution IR spectrum, a frequency consistent with Pt-H stretching, and not compatible with an η^2-silane type structure. Due to the symmetric nature of the complex and the similarity to the data for the Tp′ complex, it is logical to predict that the hydrides are located in the plane with the nacnac ligand and that the open site of the octahedron is *trans* to silyl. Presumably this is the thermodynamic isomer due to the high ligand field strength of the silyl ligand.

Crystals of **2a** were grown by dissolving **1** and excess $HSiPh_3$ in a minimum volume of pentane and placing the solution in the refrigerator for 2 hr. The result was a 98 % isolated yield of air and temperature stable yellow blocks.



1

2

X-ray crystallographic analysis of **2a** (Figure 3.1) confirmed that there is no solvent coordinated to the metal. Though the hydrides were not located in the difference Fourier map the silyl ligand is roughly orthogonal to the plane of the nacnac ligand as expected for the proposed square-based pyramid structure. The C3-Pt1-Si1 angle (central nacnac methine carbon through Pt to Si) of 116.26 indicates that the silyl ligand is tilted away from the nacnac ligand, probably because of steric interactions between the silyl phenyl groups and nacnac phenyl substituents. While it is conceivable that one hydride could be *trans* to the silyl and the other hydride *trans* to a nacnac nitrogen, forming a trigonal-bipyramidal structure, we believe this is unlikely because the two hydride sites would produce dramatically different chemical shifts; furthermore there is no evidence for a fluxional process that would equilibrate the two hydrides, although of course we cannot rule out a low barrier to such a rearrangement.

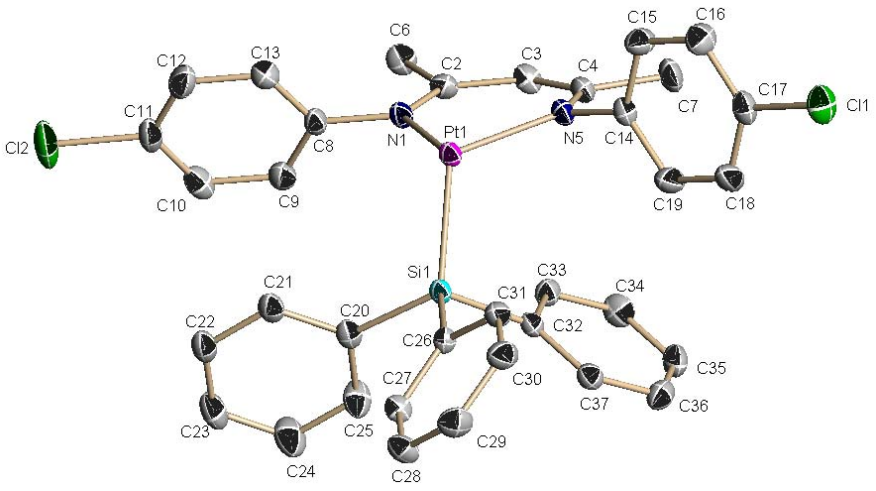


Figure 3.1. X-ray structure of (nacnac)Pt(H)$_2$(SiPh$_3$) (**2a**). Thermal ellipsoids at 50 % probability. The platinum hydrides were not located in the difference Fourier map. Selected bond distances in Angstroms (Å): Pt1-Si1 = 2.286, Pt1-N1 = 2.099, Pt1-N5 = 2.076. Selected angles in degrees (°): N1-Pt1-Si1 = 108.98, N5-Pt1-Si1 = 114.36, C3-Pt1-Si1 = 116.26, N1-Pt1-N5 = 90.41.

Reaction of **1** with HSiEt$_3$ or H$_2$SiPh$_2$ results in rapid conversion to the corresponding (nacnac)Pt(H)$_2$(SiR$_3$) (SiEt$_3$ = **2b**; SiHPh$_2$ = **2c**). The NMR data for these complexes is similar to the data for complex **2a**; the Pt-H data for all of these complexes is tabulated in Table 3.1. While **2a** and **2b** form stable solids from pentane, all three decompose to Pt black over time in CH_2Cl_2; the diphenylspecies **2c** decomposes the fastest.

Table 3.1. Platinum Hydride ^{1}H NMR Data for (nacnac)Pt(H)$_2$(SiR$_3$) Complexes.

SiR$_3$	δPt-H (ppm)	$^1J_{Pt\text{-}H}$ (Hz)	νPt-H (cm^{-1})[a]
SiPh$_3$ (**2a**)	-15.62	959	2190
SiEt$_3$ (**2b**)	-16.67	1006	2205
SiHPh$_2$ (**2c**)	-15.65	949	

[a] CH_2Cl_2 solution IR.

In this reaction the 1-pentene ligand is rapidly displaced by the silane en route to the oxidative addition reaction that yields the silyldihydride complex. It is worth noting that this synthetic method contrasts with other five-coordinate Pt(IV) complex preparations. The PtMe$_3$ derivatives are formed from an intact [PtMe$_3$]$^+$ fragment by adding the respective

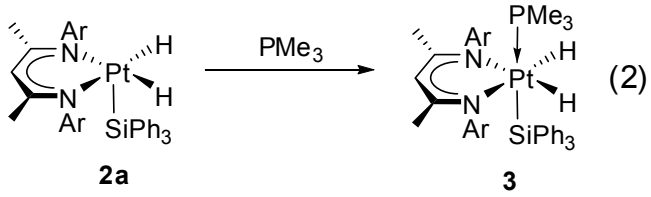
ligand.[1, 3-5] The $Pt(SiMe_3)Me_2$ complex is generated by S_N2 type reaction between an anionic Pt center and TMSOTf rather than via an Si-H bond activation process.[7] The cationic Tp′ based silyldihydrides are generated by oxidative addition of a Si-H bond, but they are formed from a $[(N\text{-}N)Pt(solvent)(H)]^+$ precursor complex, and thus the silane has only to displace a weakly coordinated solvent molecule.[6] In the present nacnac case there is a strong π-acid ligand, 1-pentene, displaced by the Si-H bond.

One might expect the displaced pentene to bind to the open coordination site on the d^6 metal in the five-coordinate product; we see no evidence for interaction between the olefin and the metal. This is true even if excess ethylene, which is a stronger binding olefin than pentene, is added to a solution of **2**. The strong *trans* influence of the silyl ligand and high oxidation state of the metal evidently disfavor binding of olefins.

Addition of mixtures of H_2SiPh_2 and D_2SiPh_2 to **1** resulted in formation of $(nacnac)Pt(H)(D)(DSiPh_2)$ (**2c-*d*$_2$**) and $(nacnac)Pt(H)_2(HSiPh_2)$ (**2c**). Complex (**2c-*d*$_2$**) exhibits a singlet for the hydride which is shifted about 0.1 ppm downfield from the corresponding dihydride chemical shift for **2c**. No H-D coupling is observed in the proton NMR, thus reinforcing the identity of the complex as a classical dihydride rather than an η^2-H_2 species. In kinetic competition experiments, the dihydride species is favored over the mixed hydride deuteride, indicating that there is a small kinetic isotope effect of about 1.3. An isotope effect of this magnitude is indicative of rate-limiting Si-H coordination to the metal.

Trimethylphosphine Addition to the Five-Coordinate Platinum(IV) Complex (2). Given that the 5-coordinate Pt(IV) complex does not bind the 1-pentene released in forming **2** from **1**, we explored interactions with other potential ligands. One would anticipate that

this electron-deficient coordinatively unsaturated Pt(IV) species would be electrophilic and bind η^1 sigma donor ligands such as nitriles. However, we have observed no indication that nitriles bind to this Pt(IV) center even upon dissolving **2a** in neat acetonitrile. Carbon monoxide typically binds strongly to Pt, significantly stronger than ethylene, but even CO does not appear to form a complex with **2a**. Only with strongly sigma donating phosphines were we able to detect ligand binding. Compound **2a** reacts with PMe_3 to form a 6-coordinate compound **3** (eq. 2). Trimethylphosphine is a strong ligand, but here it appears to be bound only weakly due to the *trans* influence of the silyl ligand. When excess PMe_3 is present we observe rapid exchange on the NMR time scale between the bound and the free phosphine. Also, the Pt-P coupling constant of 745 Hz is unusually low; a typical $^1J_{Pt\text{-}P}$ coupling constant for a Pt-PMe_3 adduct would be around 3000 Hz.



2a **3** (2)

Terminal Alkyne Addition to the Five-Coordinate Platinum(IV) Complex (2). A surprising reaction was observed when the triphenylsilane complex **2a** was exposed to acetylene in CD_2Cl_2 at room temperature. The ^1H NMR of the resulting product showed two inequivalent hydrides with $^2J_{H\text{-}H}$ coupling of about 3 Hz to each other. This was unexpected because in the PMe_3 addition reaction the phosphine simply fills the vacant octahedral site and does not perturb the fundamental framework of the reagent, thus leaving the two hydrides equivalent. With the acetylene product the two hydrides have widely disparate chemical shifts and significantly different $^1J_{Pt\text{-}H}$ coupling constants clearly indicating that they are *trans* to different ligands. One hydride resonates at -5.69 ppm with a coupling to Pt

of 773 Hz and the other resonates at -18.72 and has a $^{1}J_{Pt\text{-}H}$ coupling constant of 1242 Hz (Figure 3.2). The hydride at -5.7 is *trans* to a tremendously strong ligand as indicated by both its low coupling constant and its uncharacteristically low field signal. The other hydride ligand has a chemical shift and one-bond coupling constant typical for a hydride *trans* to nitrogen. This data suggests that the silyl ligand has moved into the plane of the nacnac along with one hydride and that the other hydride is now located cis to the nacnac ligand and is *trans* to the new ligand. Importantly, the ^{1}H NMR also contains an informative doublet at 8.14 ppm which has an H-H coupling of 8.8 Hz and Pt coupling of 74 Hz; this doublet is surely due to one of the original acetylene protons. The mated proton is difficult to observe due to overlap with Ar peaks; however it can be identified in the 2D H-H COSY NMR. The second proton resonates at 6.52 ppm, but it appears as a multiplet rather than as a simple doublet that would be indicative of an η^2-acetylene ligand. In addition to being coupled to the proton that resonates at 8.14, the hidden resonance at 6.52 ppm is coupled to a doublet at 5.36 with 16 Hz coupling. The other proton signals for this complex are assigned to Ar protons and to two inequivalent nacnac methyl groups. Note that the singlet for the central nacnac methine is no longer visible; it has presumably become the doublet at 5.36 ppm.

We postulate that cycloaddition of acetylene across platinum and the methine carbon has occurred to form a tridentate N,N,C bis-imine vinyl ligand (eq. 3). This type of reaction has been observed recently with acetylene and a ruthenium β-diiminate complex.[12] There have also been examples of cycloaddition of alkenes and alkynes across the CH and Al atoms in a coordinatively unsaturated [(nacnac)AlR]$^{+}$ complex reported by Jordan.[13] Iron, titanium, and copper nacnac complexes have been reported to add oxygen and nitrogen containing unsaturated molecules across the metal and ligand CH.[14-16] Acetylacetonate complexes of

Pd(II), Rh(I), and Ir(I) added the activated alkyne hexafluoro-2-butyne across the M and central CH as well, but unactivated alkynes did not react, and unlike our system, these are all d^8 metal reagents.[17, 18] A number of macrocyclic compounds of Co, Rh, Fe, and Ru with ligands based on multiple β-diiminate units have been reported to undergo cycloadditions.[19-24]

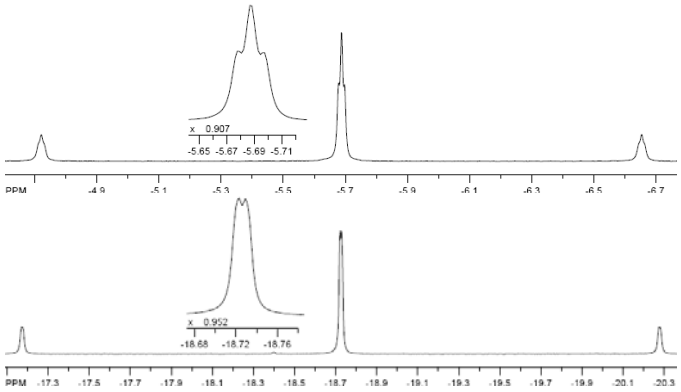
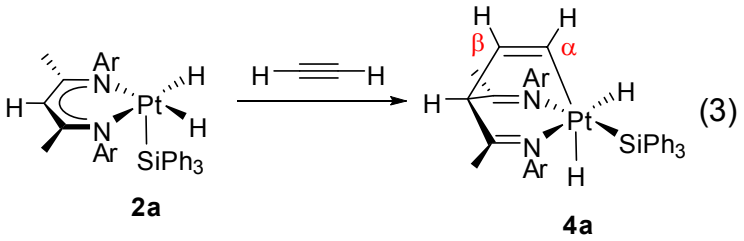


Figure 3.2: Hydride region of the ^{1}H NMR (400 MHz, 243 K) of acetylene product **4a**.

Dyson and coworkers reported that acetylene reacts with a cationic β-diiminate Ru(II) d^6 16 electron arene complex to form a cycloaddition product. Comparison of the ^{13}C NMR data for our Pt product and the Ru acetylene insertion product shows a consistency that suggests that the complexes are analogous. Complex **4a** shows ^{13}C signals at 167.2, 115.7, and 71.5 for the Pt-$\underline{C}_\alpha$, C_α=$\underline{C}_\beta$, C_β-$\underline{C}_{nacnac}$ carbons, respectively. The Ru acetylene complex displays signals at 169.4, 116.7, and 63.1 for the congruent carbons. In addition, the chemical shift for the nacnac imine carbon shifts about 30 ppm downfield because the electrons are now localized in the C=N unit of the ligand. The Pt couplings for C_α, C_β, and C_{nacnac} are 478 Hz, 44 Hz, and 64 Hz, respectively, reflecting the 1, 2, and 3 bond couplings. It is also interesting to note that we observe coupling between the hydrides and the vinyl protons. The hydride at -5.7 couples to the proton on C_β with a four bond coupling constant of 3.6 Hz, but no coupling is observed to the proton on C_α. This may reflect strong orbital

overlap between the *trans* hydride and C_α, resulting in large "*trans*-like" coupling to the C_β proton and small "geminal-like" coupling to the proton on C_α. The hydride at -18.7 exhibits a small three-bond coupling to the proton on C_α, on the order of 1 Hz, just enough to broaden the peaks and to show up in the H-H COSY NMR. All of these couplings constants support the proposed geometry of the complex. The high field strength of the vinyl ligand is presumably the reason that the complex has isomerized to the geometry with the strong silyl ligand *trans* to a weak nitrogen ligand; the observed isomer is thermodynamically more stable. In the phosphine addition case the phosphine was not a strong enough ligand to cause this isomerization.



2a **4a** (3)

The reaction with acetylene is fast and results in complete conversion of **2a** to **4a**. The compound is stable in solution below -30 °C, but it decomposes in an hour or two at room temperature. This is not surprising as it is a *cis* alkenyl hydride complex and probably undergoes facile reductive elimination. Addition of phenyl acetylene also results in cycloaddition, but the reaction is considerably slower and requires a large excess of alkyne to drive the reaction towards products. The phenylacetylene product is the isomer in which the terminal carbon binds to the Pt and the phenyl-bound carbon binds to the nacnac CH. No insertion products are observed when internal alkynes are used. Also, no reaction is observed with terminal alkyl alkynes, including propyne. We believe this is because the electron donating nature of the alkyl substituent inhibits C-C bond formation; the phenylacetylene must be just electron poor enough to react. This deactivates the alkynes towards

cycloaddition and makes the nucleophilic carbon the more substituted one which will inhibit its interaction with the sterically congested Pt. Calculations on the cycloaddition of alkynes and alkenes to $[(nacnac)AlMe]^+$ reflected the same pattern, electron-donating methyl groups on the olefins inhibit cycloaddition.[25] If the diphenylsilyl platinum species **2c** is used, analogous cycloaddition products are observed. However, if the triethylsilyl derivative **2b** is used the reaction is significantly inhibited. No reaction with phenylacetylene is observed with **2b**, and the reaction with acetylene is slow and results in only a trace amount of the cycloaddition product. It is possible that the more electron-rich triethylsilyl ligand stabilizes the electron deficient metal and decreases its Lewis acidity and thereby inhibits the reaction. Clearly the reaction is extremely sensitive to the electronic effects of both the ancillary ligands and the alkyne.

Phosphaalkyne Addition to the Five-Coordinate Platinum(IV) Complex (2). After observing the propensity for the 5-coordinate Pt(IV) complex to undergo cycloaddition reactions we turned to a more exotic ligand that has been shown to be susceptible to insertion reactions: phosphaalkynes. Phosphaalkynes readily participate in cyclization reactions with both organic substrates and transition metal complexes. Reactions of Pt complexes with phosphaalkynes have been limited to platinum in the oxidation states of 0, I, or II, and in all but one case free phosphaalkynes simply coordinate η^2 to the Pt; there is one example of a phosphaalkyne bridging across two platinum atoms.[26] Phosphorus is a soft donor atom which stabilizes low oxidation state transition metals, and π-acid ligands such as alkynes and phosphaalkynes bind more strongly to lower oxidation state metals. To date there have been no literature reports of Pt(IV) phosphaalkyne reactions.

Addition of *t*-butyl phosphaalkyne to **2a** at -78 °C results in a rapid color change from light yellow to bright red. As the solution was warmed to room temperature the color faded back to light yellow, before turning black as the compound decomposed over one hour at room temperature. Proton NMR suggested that the product, **5a**, was a cycloaddition product analogous to the one observed from insertion of acetylene. The signature of an insertion between the nacnac methine and the platinum center is two drastically different hydride signals for the complex: a doublet at -4.64 ppm which had a phosphorus coupling of 62 Hz and a Pt coupling of 929 Hz, and a singlet for the other hydride that appeared at -17.8 ppm and had a Pt coupling of 1179 Hz with no phosphorus coupling observed (Figure 3.3). There were also signals in the ^{1}H NMR for two inequivalent nacnac methyl groups, one phosphaalkyne *t*-Bu group, with the nacnac CH now appearing as a doublet at 5.24 ppm with 8 Hz coupling to phosphorus. The hydride at -4.6 was *trans* to the strong phosphaalkenyl ligand resulting in the unusual chemical shift and the low Pt-H coupling constant, and the strong coupling to P is surely due to the *trans* orientation of the ligands. The hydride at -17.8 ppm was *cis* to the new P donor atom and had a chemical shift and a Pt-H coupling constant typical for a hydride *trans* to a nitrogen; note also that there is no coupling to P due to the orthogonal orientation of the H and P donor atoms.

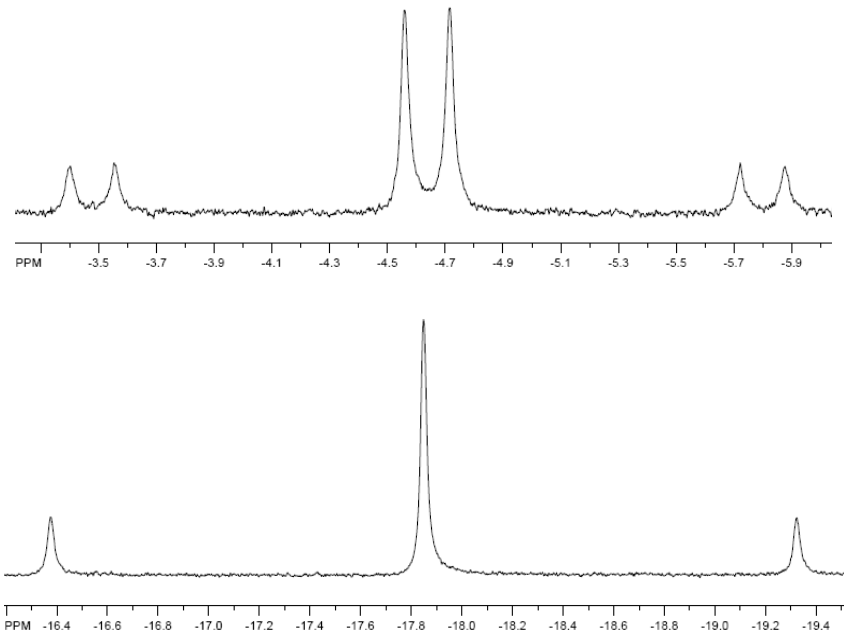


Figure 3.3: Hydride resonances of the *t*-BuC≡P addition product **5a** (^{1}H NMR, 263 K).

The ^{31}P NMR spectrum showed a signal at 371 ppm, but unfortunately the Pt satellites were not resolvable due to the broad nature of the peak. We do know that the coupling is less 200 Hz because this is the base width of the peak and no satellites fall outside of this region. The low-field chemical shift was in the range of an η^2-phosphaalkyne or an unstabilized η^1-phosphaalkene, with the small Pt coupling constant being suggestive of low s character in the P-Pt bond. This was indicative that the remaining lone pair on the P atom has mostly s character. We propose that the phosphorus coordinated to the Pt while the carbon coupled to the nacnac CH carbon.

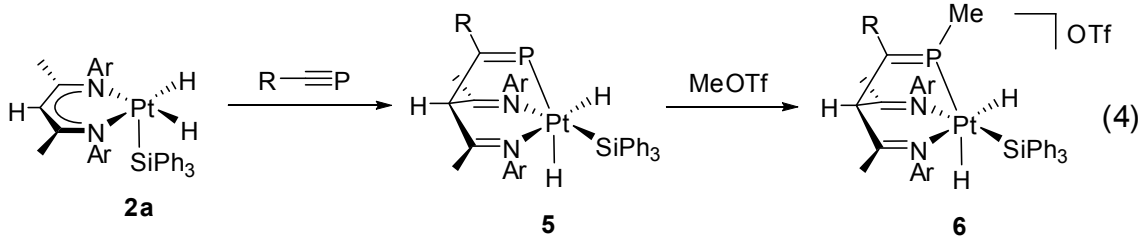
Free phosphaalkynes are typically polarized with the phosphorus being electrophilic and the carbon nucleophilic, $RC^{\delta-}\equiv P^{\delta+}$, due to the greater electronegativity of carbon.[9-11] This polarization is manifested in the addition of hydrohalogens across the triple bond such that the carbon becomes protonated and the halogen nucleophile attacks the phosphorus forming products of the type (R)(H)C=PX.[10, 11, 27, 28] Thus one might expect the phosphorus to bind to

the CH and the carbon to bind to the metal, but this is not the result. The 62 Hz coupling to the *trans* hydride at -4.6 ppm is too large to be three-bond coupling and is large even for two-bond coupling due to the strong orbital overlap because of the *trans* nature of the ligands. The platinum coupling constant to the hydride at -4.6 ppm is about 140 Hz larger than the analogus hydride in the alkyne addition product **4**. The larger coupling indicates that the hydride is *trans* to a weaker ligand which again suggests that the P atom is bound to Pt as it is typically a weaker ligand than a C atom; also if the C of the phosphaalkyne was bound to Pt the hydride should have a similar one-bond Pt coupling to the alkyne addition product. While one would expect the harder carbon atom to better stabilize the hard Pt(IV) atom, the strong *trans* influence of the hydride ligands will cause the compound to favor binding of the softer and weaker phosphorus atom to the metal to reduce the unfavorable interaction of two strong field ligands *trans* to one another. Thus the strong nature of the hydride ligands may cause the polarity reversal of the phosphaalkyne and lead to formation of the observed product. The newly formed C-C bond from the C≡P carbon to the nacnac methine carbon is likely stronger than the C-P bond that would be formed in the other isomer; yet another reason why this isomer is thermodynamically favorable over the other. Additional anecdotal evidence for this isomer is the fact that the compound is relatively stable at temperatures below 0 °C, while the other isomer would have the P bound to the nacnac CH which would provide little stabilization to the low-coordinate phosphorus and it would likely degrade rapidly.

Reaction of the five-coordinate Pt(IV) reagent **2a** with the bulky adamantyl phosphaalkyne (AdC≡P) resulted in cycloaddition to form the six-coordinate phosphaalkenyl species (**5d**) in analogy to the reaction with *t*-BuC≡P (Scheme 3.4). The NMR data for this

species is similar to that of the *t*-Bu analog. The rate of reaction was also comparable to the *t*-Bu analog, indicating little steric inhibition from the adamantyl group.

We probed the nucleophilicity of the lone pair on the phosphorus atom of the 6-coordinate phosphaalkenyl species, **5a**, by adding MeOTf (OTf = $-OS(O)_2CF_3$) at 250 K; methylation of the phosphorus occurred rapidly. The product was [{(κ^3-(tBu)C=P(Me)(C=NAr)$_2$(CH))}Pt(SiPh$_3$)(H)$_2$][OTf] (**6a**) (eq. 4). Rapid alkylation of the phosphorus atom indicated that the lone pair is nucleophilic. This suggests that the polarity of the C=P still places most of the electron density on P rather than on C due to coordination to Pt. Phosphaalkenes, like phosphaalkynes, typically favor polarization of the electron density towards carbon ((R)(R′)C$^{\delta-}$=P$^{\delta+}$(R″)), except in cases where R or R′ is a good pi-donor group such as NMe_2 which reverses the polarization ((NMe$_2$)(R)C$^{\delta+}$=P$^{\delta-}$(R′)).[29] Phosphaalkenes bound to transition metals in a bent fashion, as in complex **5**, have also been shown to be nucleophilic at phosphorus.[9, 11, 30, 31]



(4)

The ^{1}H NMR of **6a** displayed a doublet at 1.78 ppm with 16.4 Hz phosphorus coupling due to the C=P-CH_3. The hydride resonance *trans* to P shifted up-field to -7.78 ppm and displayed a two-bond phosphorus coupling of 266 Hz, more than 4 times the coupling constant of the neutral species **5a**, and the platinum coupling constant increased to 1143 Hz. The *cis* hydride resonance shifted slightly downfield to -17.33 ppm and had 8.8 Hz phosphorus coupling as well as 1154 Hz coupling to platinum. The only other example of a Pt hydride trans to a phosphaalkene ligand is the platinum(II) compound

(DPCB)Pt(H)($SiMe_2Ph$) (DPCB = diphosphinidenecyclobutene) and it displayed a $^2J_{P\text{-}H}$ of 230 Hz, similar to the value observed for our cationic Pt(IV) species **6a**.[32] The platinum coupling constants for the two hydrides were virtually identical reflecting the fact that they were both *trans* to neutral two-electron donor ligands. The platinum coupling constants to the hydrides provided a quantitative comparison of the *trans* influence of the η^1-phospaalkenyl and η^1-phospaalkene ligands compared to the more heavily studied η^1-vinyl ligand. The ordering from highest to lowest field strength is η^1-vinyl > η^1-phosphaalkenyl >> η^1-phosphaalkene. Anecdotal evidence for a strong *trans* effect of η^1-phosphaalkenyl ligands has been reported, but quantitative comparisons were lacking.[30] The large phosphorus coupling to the *trans* hydride and the observable phosphorus coupling to the *cis* hydride indicated a great deal more s character to the Pt-P bond after methylation at phosphorus, likely due to the fact that that bond can now be considered a dative bond made using the lone pair on the phosphorus. The phosphorus signal in the ^{31}P NMR shifted from 371 ppm in neutral **5a** to 217 ppm in methylated **6a** which is compatible with a report of the methylation of the Ru η^1-phosphaalkenyl complex (CO)(Cl)(PPh_3)$_2$Ru(P=C(H)(tBu)) with MeI to yield (CO)(Cl)(PPh_3)$_2$Ru((Me)P=C(H)(tBu))(I) in which the phosphorus resonance shifts from 450 ppm to 225 ppm.[31] Of course both Ru(II) and Pt(IV) systems are d^6 metals.

To the best of our knowledge these Pt(IV) phosphaalkenyl complexes are only the second examples of Pt phosphaalkenyl compounds, and the first in the Pt(IV) oxidation state. The previous example was formed by oxidative addition of the P-I bond in (Me_3Si)$_2$C=P-I to (Ph_3P)$_2$Pt(0)(C_2H_4).[33] There are many examples of neutral phosphaalkene complexes of Pt(0) or Pt(II) though virtually all of them are kinetically stabilized by bulky groups, most commonly the super mesityl group, bound to phosphorus.[32, 34-44] We are not aware of any

other Pt(IV) complexes with neutral phosphaalkenes. This is consistent with fact that soft phosphine ligands typically stabilize softer low valent metals whereas harder nitrogen ligands typically stabilize high valent metal atoms.

Conclusions

The (nacnac)Pt(H)(1-pentene) complex (**1**) is a useful starting material to assess the reactivity of the (nacnac)Pt(H) fragment since the 1-pentene ligand is easily displaced. Complex **1** reacted with $HSiR_3$ to activate the Si-H bond and form stable 5-coordinate Pt(IV) silyldihydride species which, perhaps surprisingly, did not react with the free 1-pentene in solution despite having a vacant site on Pt. The complex only weakly interacted with the strong sigma donor ligand PMe_3. On the other hand, acetylene or phospaalkynes reacted rapidly with the 5-coordinate complex adding across the nacnac CH and Pt to form new monoanionic N,N,C or N,N,P ligands containing either a vinyl or a phosphaalkenyl group. We believe that the alkyne addition reaction occurs because of the Lewis acidic nature of the Pt and Lewis basic nature of the nacnac CH. The phosphaalkyne addition product is counterintuitive based on the polarization of free phosphaalkynes in which the carbon is nucleophilic. We believe the isomer with phosphorus bound to platinum is the thermodynamically preferred one. This may be because phosphorus is the weaker donor ligand and is better suited to reside *trans* to the strong hydride ligand than is a carbon donor. The C-C versus C-P bond strength to the nacnac methine carbon may play an important role in the thermodynamics also. The phosphaalkenyl lone pair showed significant nucleophilicity and reacted cleanly with MeOTf to form a cationic methyl phosphaalkene complex. The *trans* influence of the phosphaalkene ligand in the cationic complex was

significantly lower than that of the phosphaalkenyl ligand in the neutral complex as assessed by the platinum hydride coupling constant values for the corresponding *trans* hydrides.

Experimental

General Procedures. Unless otherwise stated all reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was flame dried under vacuum and cooled under N_2 before use. Diethyl ether, methylene chloride, toluene, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[45] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Methylene chloride-d_2 was vacuum transferred from calcium hydride and degassed by several freeze-pump-thaw cycles. $Me_4Pt_2(\mu\text{-}SMe_2)_2$[46] and p-Cl-nacnacH[47] (Hnacnac = bis(N-(p-Cl-phenyl)) β-enamineimine) were synthesized via published procedures. All other reagents were used as received from Sigma Aldrich.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 MHz, Bruker Avance 400 MHz, or Bruker DRX 500MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000.

p-Cl-nacnacPt(H)(1-pentene) (1). The complex was synthesized in analogous manner to nacnacPt(H)(1-pentene). To a schlenk flask was added 200 mg (0.348 mmol) $Me_4Pt_2(\mu\text{-}SMe_2)_2$ and 245 mg (0.766 mmol, 2.2 eq.) nacnacH. Methylene chloride and pentane were added and the solution was allowed to stir overnight. The bright yellow solution gradually changed to a darker orange color. The resulting oil was chromatographed

on a silica column pretreated with a 3 % NEt_3 in CH_2Cl_2 solution, using 80:20 hexanes to CH_2Cl_2 solution as the mobile phase. The first yellow band contains the product and free ligand; this product was collected and rotovapped to dryness. The product was chromatographed again using an untreated silica column and 100 % CH_2Cl_2 to yield 106 mg (30 %) of pure **1**. IR (CH_2Cl_2): $\nu_{Pt\text{-}H}$ = 2217 cm^{-1}. ^1H NMR (δ, CD_2Cl_2, 400MHz): 7.34 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacPh); 7.23 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacPh); 6.93 (d, 2H, $^3J_{H\text{-}H}$ = 8.0 Hz, *o*-nacnacPh); 6.83 (d, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, *o*-nacnacPh); 6.79 (d, 1H, $^3J_{H\text{-}H}$ = 8.4 Hz, *o*-nacnacPh); 5.06 (s, 1H, nacnac-C*H*); 3.24 (1H, sextet, Pt-CH_2=C*H*Pr, $^3J_{H\text{-}H}$ = 6.8 Hz); 3.06 (1H, d, *cis*-Pt-C*H*$_2$=CHPr, $^3J_{H\text{-}H\,trans}$ = 12.8 Hz, $^2J_{Pt\text{-}H}$ = 48 Hz); 2.75 (1H, d, *trans*-Pt-C*H*$_2$=CHPr, $^3J_{H\text{-}H\,cis}$ = 7.6 Hz, $^2J_{Pt\text{-}H}$ = 62.4 Hz); 1.74 (s, 3H, nacnac-C*H*$_3$); 1.68 (s, 3H, nacnac-C*H*$_3$); 1.71, 1.58, 1.46, 1.33 (1H, m, Pt-CH_2=CHC*H*$_2$C*H*$_2$$CH_3$); 0.83 (3H, t, Pt-$CH_2$=$CHCH_2CH_2$C*H*$_3$, $^3J_{H\text{-}H}$ = 7.4 Hz); -21.57 (s, 1H, $^1J_{Pt\text{-}H}$ = 1216 Hz, Pt-H). Anal. Calcd for $C_{22}H_{26}N_2Cl_2Pt$: C, 45.21; H, 4.48; N, 4.79. Found: C, 45.31; H, 4.28; N, 4.68.

p-Cl-nacnacPt($SiPh_3$)$(H)_2$ (2a). In a vial in open air 30 mg (0.0514 mmol) of 1 and 16 mg (0.0617 mmol, 1.2 eq.) $HSiPh_3$ were dissolved in 3 mL pentane. The vial was capped and placed in the refrigerator for 2 hrs yielding 39 mg (0.0503 mmol, 98 % yield) of yellow block crystals suitable for x-ray diffraction. IR (CH_2Cl_2): $\nu_{Pt\text{-}H}$ = 2190 cm^{-1} (br). ^1H NMR (δ, CD_2Cl_2, 300MHz): 7.31 (t, 3H, $^3J_{H\text{-}H}$ = 7.4 Hz, *p*-$SiPh_3$); 7.19 (t, 6H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-$SiPh_3$); 7.05 (d, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz, *o*-$SiPh_3$); 6.95 (d, 4H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacPh); 6.23 (d, 4H, $^3J_{H\text{-}H}$ = 8.4 Hz, *o*-nacnacPh); 5.25 (s, 1H, nacnac-C*H*); 1.75 (s, 6H, nacnac-C*H*$_3$); -15.62 (s, 2H, $^1J_{Pt\text{-}H}$ = 959 Hz, Pt-$(H)_2$). Anal. Calcd for $C_{35}H_{32}N_2Cl_2PtSi$: C, 54.26; H, 4.16; N, 3.62. Found: C, 54.99; H, 4.12; N, 3.45.

p-Cl-nacnacPt(SiEt$_3$)(H)$_2$ (2b). The same procedure was used as for **2a**, but $HSiEt_3$ was used instead of $HSiPh_3$. A yellow solid was obtained from a pentane solution of **2b** at -30 °C. IR (CH_2Cl_2): $\nu_{Pt\text{-}H}$ = 2205 cm^{-1} (br). ^{1}H NMR (δ, CD_2Cl_2, 300MHz): 7.25 (d, 4H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacPh); 6.96 (d, 4H, $^3J_{H\text{-}H}$ = 8.4 Hz, *o*-nacnacPh); 5.14 (s, 1H, nacnac-C*H*); 1.84 (s, 6H, nacnac-CH_3); 0.56 (s, 15H, Si(CH_2CH_3)$_3$); -16.73 (s, 2H, $^1J_{Pt\text{-}H}$ = 1006 Hz, Pt-(H)$_2$). Anal. Calcd for $C_{23}H_{32}N_2Cl_2PtSi$: C, 43.81; H, 5.11; N, 4.44. Found: C, 43.85; H, 4.84; N, 4.35.

p-Cl-nacnacPt(SiHPh$_2$)(H)$_2$ (2c). The same procedure was used as for **2a**, but H_2SiPh_2 was used instead of $HSiPh_3$. A yellow solid was obtained from a pentane solution of **2c** at -30 °C. ^{1}H NMR (δ, CD_2Cl_2, 300MHz): 7.17 (d, 4H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacPh); 6.61 (d, 4H, $^3J_{H\text{-}H}$ = 8.4 Hz, *o*-nacnacPh); 5.23 (s, 1H, nacnac-C*H*); 1.79 (s, 6H, nacnac-CH_3); -15.66 (s, 2H, $^1J_{Pt\text{-}H}$ = 948 Hz, Pt-(H)$_2$).

p-Cl-nacnacPt(PMe$_3$)(SiPh$_3$)(H)$_2$ (3a). ^{1}H NMR (δ, CD_2Cl_2, 400MHz): 7.59 (d, 2H $^3J_{H\text{-}H}$ = 8.0 Hz, nacnacPh); 7.49 (d, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, nacnacPh); 7.40 (m, 4H, nacnacPh); 7.28 (t, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, nacnacPh); 7.18 (t, 3H, $^3J_{H\text{-}H}$ = 7.2 Hz, *p*-SiPh$_3$); 7.07 (t, 6H, $^3J_{H\text{-}H}$ = 7.2 Hz, *m*-SiPh$_3$); 6.96 (d, 6H, $^3J_{H\text{-}H}$ = 7.2 Hz, *o*-SiPh); 4.63 (s, 1H, nacnac-C*H*); 1.61 (s, 6H, nacnac-CH_3); 1.56 (d, 9H, $^2J_{P\text{-}H}$ = 7.2 Hz, P(CH_3)$_3$); -19.26 (s, 2H, $^1J_{Pt\text{-}H}$ = 1038 Hz, Pt-(H)$_2$). ^{31}P NMR(δ, CD_2Cl_2, 162MHz): -27.73 (s, $J_{Pt\text{-}P}$ = 745 Hz, PMe_3).

(κ^3-CH=CH-p-Cl-nacnac)Pt(SiPh$_3$)(H)$_2$ (4a). In a J-Young NMR tube was dissolved 10mg (0.013 mmol) **2a** in 0.6 mL CD_2Cl_2. The solvent was freeze pump thawed and 0.13 mmol (10 eq.) acetylene was condensed into the tube at 77 K. The tube was thawed out and shaken at room temperature before being placed in the NMR probe cooled to 243 K. ^{1}H NMR (δ, CD_2Cl_2, 400MHz, 243 K): 8.14 (d, 1H, $^3J_{H\text{-}H}$ = 8.8 Hz, $^2J_{Pt\text{-}H}$ = 74 Hz,

CHC=C*H*Pt); 7.54 (d, 1H, $^{3}J_{H\text{-}H}$ = 6.4 Hz, nacnacPh); 7.5-7.3 (m, 5H, nacnacPh); 7.23 (m, 3H, $SiPh_3$); 7.16 (m, 12H, $SiPh_3$); 6.94 (d, 2H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, nacnacPh); 6.52 (m, 1H, C*H*C=CHPt); 5.36 (d, 1H, $^{3}J_{H\text{-}Hacetylene}$ = 16 Hz, nacnac-C*H*); 2.24, 2.11 (s, 3H, nacnac-CH_3); -5.69 (dd, 1H, $^{1}J_{Pt\text{-}H}$ = 773 Hz, Pt-$H_{trans\text{-}C}$); -18.72 (d, 1H, $^{2}J_{H\text{-}H}$ = 2.8 Hz, $^{1}J_{Pt\text{-}H}$ = 1242 Hz, Pt-$H_{trans\text{-}N}$). ^{13}C NMR (δ, CD_2Cl_2, 100MHz, 243 K): 172.4 ($^{2}J_{Pt\text{-}C}$ = 16 Hz, (Me)(CH)*C*=NAr); 172.4 ($^{2}J_{Pt\text{-}C}$ = 22 Hz, (Me)(CH)*C*=NAr); 167.2 ($^{1}J_{Pt\text{-}C}$ = 478 Hz, C=*C*(H)(Pt)); 150.1 (N-Ph ipso *C*); 148.4 ($^{2}J_{Pt\text{-}C}$ = 11 Hz, N-Ph ipso *C*); 141.1 ($^{2}J_{Pt\text{-}C}$ = 48 Hz, Si-Ph ipso *C*); 136.1 ($^{3}J_{Pt\text{-}C}$ = 17 Hz, Si-Ph ipso *C*); 135.9, 130.9, 130.5, 129.7, 129.0, 128.7, 128.7, 128.0 (N-Ph *C*); 127.6 (Si-Ph *p*-*C*); 126.8 (Si-Ph *m*-*C*); 122.9, 122.9 (N-Ph *C*-Cl); 115.7 ($^{2}J_{Pt\text{-}C}$ = 44 Hz, (H)(C)*C*=C(H)(Pt)); 71.5 ($^{3}J_{Pt\text{-}C}$ = 64 Hz, (*C*)(H)C=C); 24.9, 24.0 ((H_3*C*)C=N).

(κ^3-(Ph)C=CH-p-Cl-nacnac)Pt($SiPh_3$)$(H)_2$ (4d) in situ. To a sample of 10 mg (0.013 mmol) of **2a** in 0.6 mL of CD_2Cl_2 in an NMR tube was added several equivalences of phenylacetylene. The tube was shaken and the NMR recorded. ^{1}H NMR (δ, CD_2Cl_2, 400MHz, RT): 8.41 (s, 1H, $^{2}J_{Pt\text{-}H}$ = 71 Hz, (HC)(Ph)C=C*H*Pt); 7.6-6.9 (m, 28H, Ph); 5.83 (s, 1H, nacnac-C*H*); 2.36, 2.17 (s, 3H, nacnac-CH_3); -5.74 (d, 1H, $^{1}J_{Pt\text{-}H}$ = 762 Hz, Pt-$H_{trans\text{-}C}$); -18.57 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1252 Hz, Pt-$H_{trans\text{-}N}$).

(κ^3-(Ph)C=CH-p-Cl-nacnac)Pt($SiHPh_2$)$(H)_2$ (4e) in situ. To a sample of 10 mg (0.013 mmol) of **2c** in 0.6 mL of CD_2Cl_2 in an NMR tube was added several equivalences of phenylacetylene. The tube was shaken and the NMR recorded. ^{1}H NMR (δ, CD_2Cl_2, 500MHz, 260 K): 8.25 (s, 1H, $^{2}J_{Pt\text{-}H}$ = 70 Hz, (HC)(Ph)C=C*H*Pt); 7.6-6.9 (m, 23H, Ph); 5.80 (s, 1H, nacnac-C*H*); 2.30, 2.27 (s, 3H, nacnac-CH_3); -6.01 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 760 Hz, Pt-$H_{trans\text{-}C}$); -18.52 (s, 1H, $^{1}J_{Pt\text{-}H}$ = 1260 Hz, Pt-$H_{trans\text{-}N}$).

(κ^3-(tBu)C=P-p-Cl-nacnac)Pt($SiPh_3$)$(H)_2$ (5a). In the drybox 10 mg (0.013 mmol) **2a** was placed in an NMR tube and 0.6 mL CD_2Cl_2 was added. The tube was capped with a septum and removed from the box. The tube was cooled to -78 °C and 2.1 μL of tBuCP was syringed in. The tube was shaken at which time it rapidly turned from a light yellow to bright red solution. The sample was placed in an NMR probe pre-cooled to 213 K. NMR spectra were taken as the sample was warmed to 263 K. Upon removal of the sample after complete conversion to **5a** the solution had become light yellow. ^{1}H NMR (δ, CD_2Cl_2, 400MHz, 263 K): 7.27 (br m, 3H, Ph); 7.18 (br d, 4H, Ph) 7.11 (m, 12H, Ph); 6.75 (br, 2H, Ph); 6.42 (d, 1H, Ph); 6.38 (s, 1H, Ph); 5.24 (d, 1H, $^3J_{P\text{-}H}$ = 8 Hz, nacnac-C*H*); 2.20 (s, 3H, nacnac-CH_3); 2.13 (s, 3H, nacnac-CH_3); 1.42 (s, 9H, (CH_3)$_3$CP); -4.64 (d, 1H, $^2J_{P\text{-}H}$ = 62.4 Hz, $^1J_{Pt\text{-}H}$ = 929 Hz, Pt-$H_{trans\text{-}P}$); -17.85 (s, 1H, $^1J_{Pt\text{-}H}$ = 1179 Hz, Pt-$H_{trans\text{-}N}$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 162 MHz, 263 K): 371.5 (s, 1P, $^1J_{Pt\text{-}P}$ = 90 Hz, *t*-BuC*P*).

(κ^3-(adamantyl)C=P-p-Cl-nacnac)Pt($SiPh_3$)$(H)_2$ (5d). In the drybox 10 mg (0.013 mmol) **2a** and 2.5 mg (0.014 mmol, 1.1 eq.) adamantyl phosphaalkyne were placed in an NMR tube. The tube was capped with a septum and removed from the box. The tube was cooled to -78 °C and 0.6 mL CD_2Cl_2 was syringed in. The tube was shaken at which time it rapidly turned from a light yellow to bright red solution. The sample was placed in an NMR probe pre-cooled to 213 K. NMR spectra were taken as the sample was warmed to 263 K. Upon removal of the sample after complete conversion to **5a** the solution became light yellow. ^{1}H NMR (δ, CD_2Cl_2, 300MHz, RT): 7.16 (d, 2H, Ph); 7.08 (m, 19H, Ph) 6.64 (d, 2H, Ph); 5.20 (s, 1H, , nacnac-C*H*); 2.06 (s, 3H, nacnac-CH_3); 2.01 (s, 3H, nacnac-CH_3); 2.01 (s, 3H, (C*H*)$_3$AdCP); 1.89 (s, 6H, (CH_2)$_3$AdCP); 1.66 (s, 6H, (CH_2)$_3$AdCP); -4.60 (d, 1H, $^2J_{P\text{-}}$

$_H$ = 62.1 Hz, $^1J_{Pt\text{-}H}$ = 930 Hz, Pt-$H_{trans\text{-}P}$); -17.99 (s, 1H, $^1J_{Pt\text{-}H}$ = 1181 Hz, Pt-$H_{trans\text{-}N}$). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 162 MHz, RT): 383.5 (s, 1P, AdC*P*).

[(κ^3-(tBu)C=P(Me)-p-Cl-nacnac)Pt($SiPh_3$)$(H)_2$][OTf] (6a). To an NMR solution of **5a** (0.013 mmol) in CD_2Cl_2 was added 2.5 uL of MeOTf at 195 K. The tube was shaken and placed in an NMR probe pre-cooled to 250 K. ^1H NMR (δ, CD_2Cl_2, 400MHz, 250 K): 7.41 (d, 2H, Ph); 7.34 (t, 3H, Ph) 7.21 (t, 7H, Ph); 7.05 (d, 6H, Ph); 7.01 (m, 2H, Ph); 6.92 (s, 1H, Ph); 6.63 (s, 1H, Ph); 6.05 (s, 1H, Ph); 5.99 (d, 1H, $^3J_{P\text{-}H}$ = 18.4 Hz, nacnac-C*H*); 2.41, 2.38 (s, 3H, nacnac-CH_3); 1.78 (d, 3H, $^2J_{Pt\text{-}H}$ = 16.4 Hz, C=P(CH_3)); 1.45 (s, 9H, (CH_3)$_3$C=P); -7.78 (d, 1H, $^2J_{P\text{-}H}$ = 266.4 Hz, $^1J_{Pt\text{-}H}$ = 1142.6 Hz, Pt-$H_{trans\text{-}P}$); -17.33 (s, 1H, $^2J_{P\text{-}H}$ = 8.8 Hz, $^1J_{Pt\text{-}H}$ = 1154 Hz, Pt-$H_{trans\text{-}N}$). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 162 MHz, 250 K): 216.9 (s, 1P, *t*-BuC=*P*(Me)).

Crystallographic Data for 2a.

Table 3.2. Crystal data and structure refinement for **2a**.

Complex	**2a**
Empirical Formula	$C_{35}H_{32}Cl_2N_2PtSi$
Mol wt	774.71
Temperature	100(2) K
Wavelength	1.54178 Å
Cryst Syst	Triclinic
Space Group	P-1
a, Å	9.841(2)
b, Å	11.172(2)
c, Å	14.862(3)
α, deg	88.797(9)
β, deg	82.253(7)
γ, deg	73.627(6)
Vol. Å3	1553.2(6)
Z	2
Density (calculated)	1.657 Mg/m^3
μ, mm^{-1}	10.606
F(000)	764
Crystal size	0.20 x 0.10 x 0.10 mm^3
2θ range	3.00 to 70.06°
Index Ranges	-11<=h<=11 -13<=k<=13 -15<=l<=17
Reflections Collected	33592
Independent reflections	5693 [R(int) = 0.0389]
Data/restraints/parameters	5693/2/380
Goodness-of-fit on F^2	1.126
Final R indices[I>2sigma(I)]	R1 = 0.0236 wR2 = 0.0756
R indices (all data)	R1 = 0.0250 wR2 = 0.0875
Largest diff. peak and hole	1.127 and -0.628 e $Å^{-3}$

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Chapter 4

Insertion Products Resulting from Addition of Alkynes to β-Diiminate Pt(H)(1-pentene) Reagents

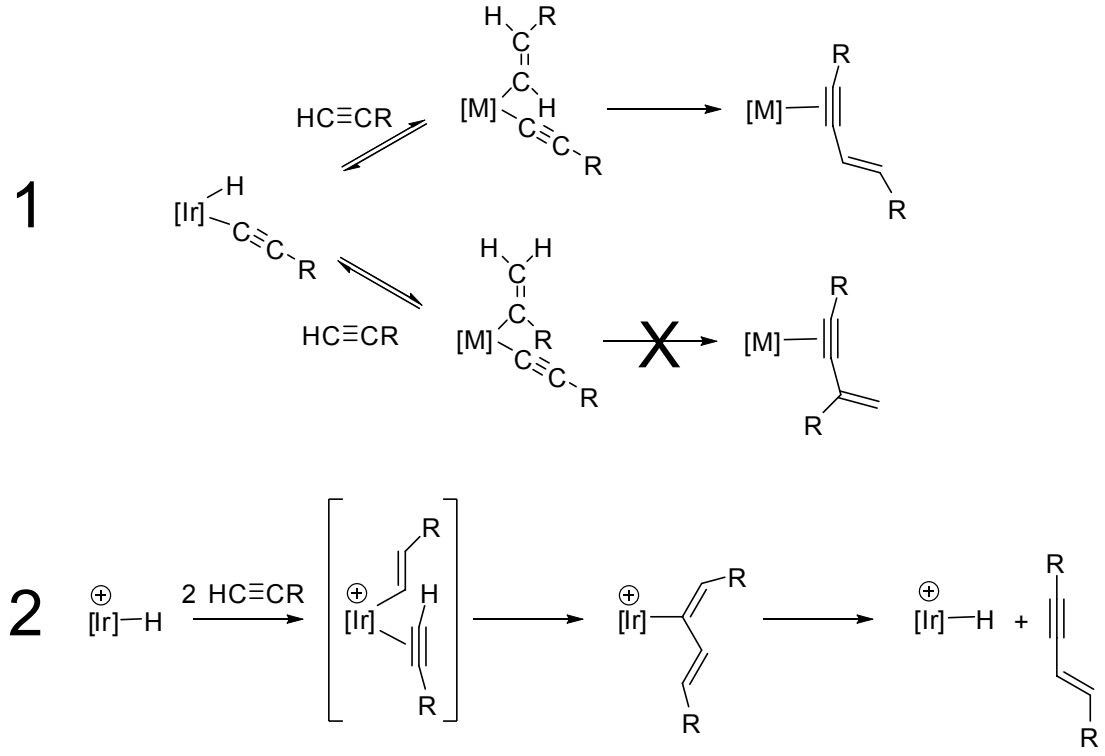
Introduction

Dehydrogenation of n-pentane with a (nacnac)PtMe fragment formed in situ provides a convient route to (nacnac)Pt(H)(1-pentene), and the pentene ligand is labile.[1] The *β*-diiminate ligands used here have phenyl rings on the nitrogens with no substituents at the *ortho* positions, and the absence of bulky ortho substituents allows facile ligand exchange. Similar compounds reported by Goldberg used bulky substituents in the ortho position on the phenyl rings of the *β*-diiminate ligands, which inhibited ligand exchange because the metal was too sterically crowded to undergo associative ligand exchange.[2] The simple synthesis of these olefin hydride complexes coupled with the ease of displacing the *α*-olefin ligand to allow access to a range of (nacnac)Pt(H)(L) complexes. Given the propensity for alkynes to insert into M-H bonds, we have undertaken a systematic study of alkyne reactions with (nacnac)Pt(H)(1-pentene).

Though many transition complexes have been shown to dimerize terminal alkynes, few favor coupling in a head-to-tail fashion.[3-6] Reductive dimerization of terminal alkynes to yield 1,3-butadienes is somewhat less common, but once again head-to-tail coupling is rare.[7-9] Most couplings favor head-to-head coupling so that the R groups from RC≡CH reside at the 1 and 4 positions in the organic product.[7, 8, 10-18] Regardless of whether the new C-C bond is formed via reductive elimination or alkyne insertion into an M-C bond, the head-to-head product is usually heavily favored due to the steric bulk of the R group on the tail carbon of the alkyne. A recent report by Goldman showed that even though migration of the hydride to the terminal carbon of phenylacetylene was favored, no reductive elimination with C-C bond formation occurred from the phenylacetylide intermediate due to the steric bulk (Mechanism 1; Scheme 1).[13] Reductive elimination occurred only when the opposite alkyne insertion

product was formed as an intermediate. Terminal alkyne dimerization has been accomplished with an Ir-H reagent and it occurs by migration of the hydride to the most substituted alkyne position yielding the less sterically hindered metal bound vinyl group which then migrates to a second alkyne, but the second migration goes to the least substituted carbon and so the head-to-head product is formed upon *β*-H elimination (Mechanism 2; Scheme 4.1).[12] Thus 1,3-disubstituted 1,3-butadienes or enynes have proven far more elusive than than the 1,4-disubstituted analogs. As described in detail in this article, our results are particularly surprising because we observe only head-to-tail coupling even with the bulky *t*-butyl substituent on the alkyne. Aside from dimerization, alkynes can be used to synthesize more complex unsaturated compounds via reductive coupling to heteroatom containing unsaturated molecules.[9, 19]

Scheme 4.1. Alkyne coupling pathways favoring head-to-head coupling products.



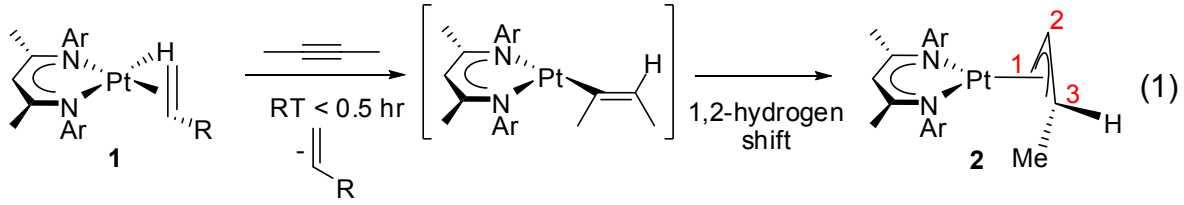
Alkynes react rapidly with the olefin hydride Pt(II) reagent, and they then undergo rapid insertion into the Pt-H bond. Products depend on alkyne identity. Internal alkynes with protons on the carbons adjacent to the triple bond, such as 2-butyne, form Pt allyls. Terminal alkynes with no protons adjacent to the triple bond form one of two products depending on the R group of the alkyne. Silyl acetylenes, such as triphenylsilylacetylene and trimethylsilylacetylene, produce a cyclometallated vinyl silane where the alkyne has been reduced to an alkene and C-H activation of either the silyl methyl or phenyl has occurred. Carbon substituted alkynes, such as phenylacetylene and *t*-butylacetylene, couple in a head-to-tail fashion forming η^1-η^2-butadienyl complexes with substituents on the 2 and 4 carbons. The products of terminal alkyne addition reflect reversal from 1,2 to 2,1 insertion into the Pt-H bond when switching from C to Si atoms adjacent to the C≡C unit. Multiple insertions of alkynes into metal hydride bonds are rare because the second insertion, C-C forming step, is usually significantly higher in energy than the first insertion, C-H forming step; only a few examples of these multiple insertions have been reported.[16-18, 20-23]

Results and Discussion

Reaction of (p-Cl-nacnac)Pt(H)(1-pentene) (1) with $CH_3C{\equiv}CCH_3$. For this study we chose to use p-Cl substituted aryl rings on the nacnac ligand due to their slightly lower solubility in non-polar solvents.[24] Use of aryl rings that are unsubstituted at the *ortho* position on the nacnac ligand allows access to the platinum center and promotes facile ligand displacement. Thus, reactivity patterns of ligands other than olefins can be explored. We previously reported that olefin insertion into the Pt-H bond of (nacnac)Pt(H)(olefin) wass surprisingly slow. To further explore the insertion chemistry of the Pt-H bond we chose to probe the ability of alkynes to insert into the bond. The thermodynamic driving force for

reduction of alkynes is much higher than alkenes, so the driving force for alkyne insertion should be similarly greater than for alkenes.

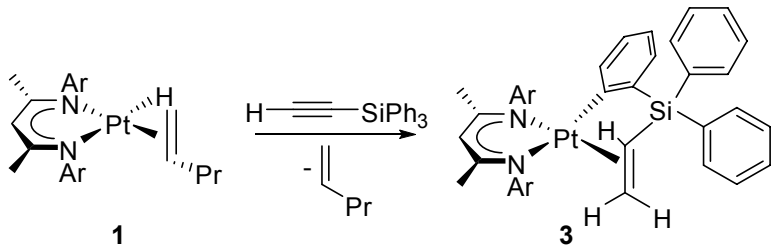
We first tested the reactivity of the pentene hydride complex **1** with 2-butyne, and found that hydride migration was indeed rapid. Addition of one equivalent of 2-butyne to a CD_2Cl_2 solution of **1** at room temperature resulted in a rapid color change from yellow to light orange. The ^1H NMR showed free 1-pentene and no hydride signals were evident. The product was identified as the 1-methyl-allyl adduct, (nacnac)Pt(1-Me-allyl) **2** (eq. 1). The ^1H NMR displayed signals indicative of one methylallyl isomer: a doublet of triplets at 4.6 ppm, a pseudo quintet at 2.4 ppm, and doublet at 1.9 ppm, all with Pt satellites. These signals correspond to the central proton on C2, the proton on C3, and both protons on C1 respectively. The two protons one C1 appear as one doublet with an averaged coupling constant between the syn and anti values. The equivalence of the syn and anti protons on C1 reflects rapid η^1-η^3 interconversions. The proton on C3 exhibits a syn coupling of 6.6 Hz to the central CH proton, so the methyl on C3 must reside in the anti position. Typically only the anti isomer is observed when allyls are formed via alkyne insertion into a metal-hydride bond since the alkyne insertion step is stereoselective for *cis* so the vinyl geometry is poised to form the anti allyl product.[25] The 1,2 proton shift then probably occurs by C-H activation of the methyl group adjacent to platinum and reductive elimination of the vinyl C-H.



(1)

Reaction of (nacnac)Pt(H)(1-pentene) (1) with $R_3SiC{\equiv}H$ (R_3 = Me_3, Ph_3, $MePh_2$). What products will result from alkyne insertion if there are no propargylic protons on the

carbon adjacent to the triple bond? Reaction of one equivalent of $Ph_3SiC{\equiv}CH$ with a CD_2Cl_2 solution of **1** resulted in formation of a complex, **3**, that did not contain a platinum hydride. The reaction was complete in less than one hour and formed a single product quantitatively as monitored by ^1H NMR. Complex **3** displayed diagnostic ^1H NMR signals characteristic of a Pt bound terminal olefin. Compound **3** has a doublet of doublets at 3.7 ppm (J = 10.8 and 14.4 Hz), a doublet at 3.2 (J = 10.8 Hz) and a doublet at 3.1 ppm (J = 14.4 Hz); each signal displays a $^2J_{Pt\text{-}H}$ coupling in the 50-70 Hz range. The $^3J_{H\text{-}H}$ values are indicative of *cis* and *trans* couplings. This classic terminal olefin pattern reflects addition of another hydrogen besides the original Pt-H in order to generate $(R_3Si)HC{=}CH_2$ from $R_3SiC{\equiv}CH$. The hydrogen does not originate in another equivalent of alkyne as only one alkyne equivalent was consumed in the reaction. The platinum complex was be purified by silica gel chromatography yielding a yellow solid of pure **3**. After purification the aromatic region of the ^1H NMR was clean, and it was clear that the 3 Ph's on the $SiPh_3$ group have been desymmetrized. Besides the aromatic nacnac *p*-C_6H_4Cl signals, two distinct C_6H_5 groups were observed, and there were also two doublets and two triplets in this region with each of the signals integrating for one proton. This indicates that one of the phenyls lost an *ortho* proton and each of the four remaining protons was unique in the product. Fitting these pieces together, it appeared that after alkyne insertion into the Pt-H bond the Pt activated an aromatic C-H bond on one of the $SiPh_3$ phenyl groups and then reductively eliminated the vinyl group to form a chelated vinyl triphenylsilane complex (eq. 2).



(2)

Recrystallization of **3** from pentane at -30 °C yielded yellow crystals suitable for X-ray crystallography, and the resulting structure confirms the proposed geometry of **3** (Figure 4.1). The structure of (nacnac)Pt((*o*-C_6H_4)Si(Ph)$_2$(CH=CH_2)), **3**, shows the Pt geometry deviates only slightly from an ideal square planar geometry. The olefin is aligned virtually orthogonal to the square plane as is typical for such Pt(II) complexes, but the olefin is not centered along the z-axis. The olefin location is constrained by ring limitations as evidenced by the N1-Pt1-C21 and N1-Pt-C20 angles of 151.0° and 169.3°; ideally these two angles would be the same. The C34-Si1-C21 bond angle is compressed to 100.2° reflecting a small amount of ring strain. The Pt1-C39-C34-Si1-C21 ring exhibits a classic envelope structure with the Pt1, C39, C34, and Si1 atoms virtually coplanar and C21 out of the plane. The nacnac ligand is somewhat twisted to place the nitrogens as close to directly *trans* to the aryl and olefin ligands as possible; this is evidenced by a torsion angle of 19.2° between the two nacnac methyl bonds (C6-C2 and C4-C7). The aryl-Pt bond distance, C39-Pt1, is 2.03Å and the olefin-Pt bond lengths, C21-Pt1 and C20-Pt1, are 2.14 and 2.14 Å, respectively. The Pt1-N5 bond *trans* to the phenyl is 2.12 Å while the Pt1-N1 bond *trans* to the olefin is only 2.04 Å indicating the stronger *trans* influence of the aryl group relative to the olefin. The nacnac Ar and the Pt bound aryl adjacent to each other are stacked parallel to one another, and the distance between the two *ipso* carbons is only 2.94 Å which rationalizes hindered rotation of one nacnac Ar group evident in the ^{1}H NMR.

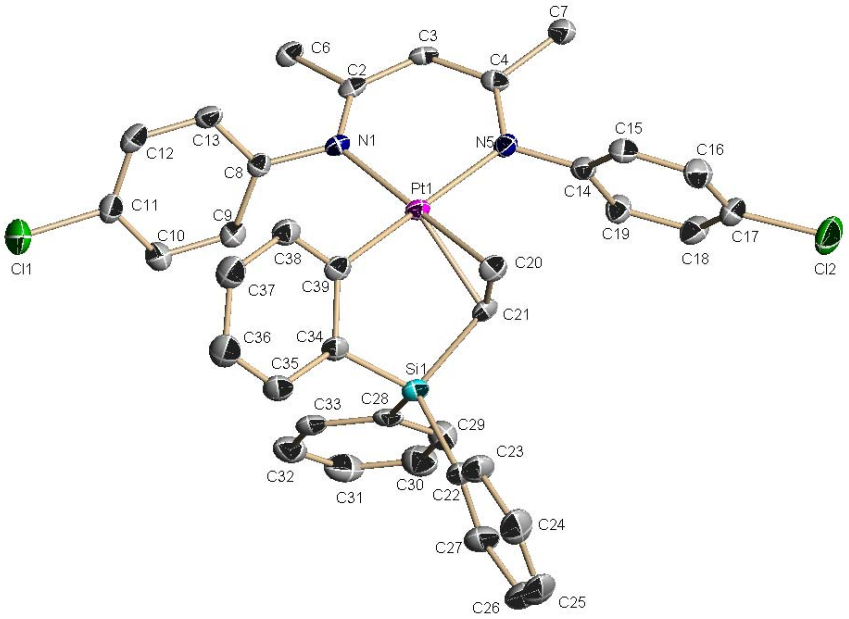


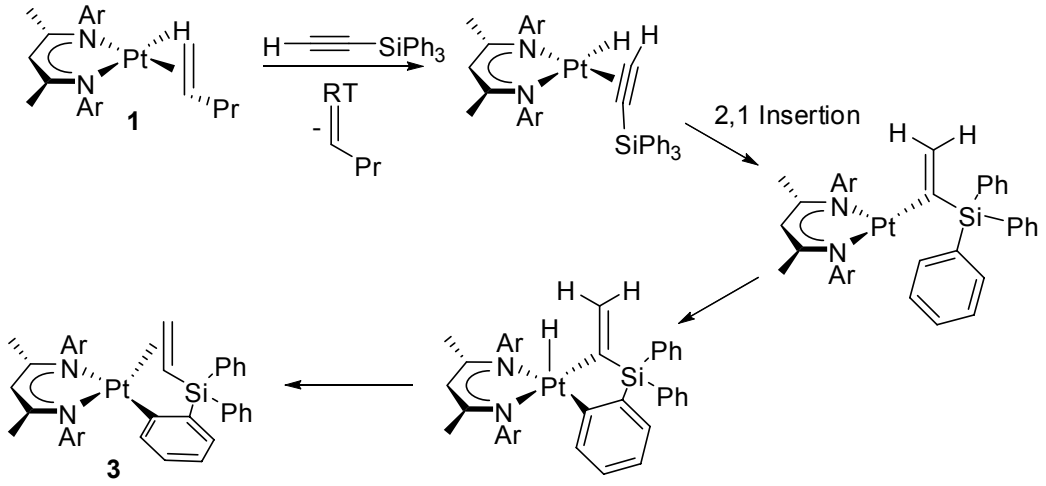
Figure 4.1: X-ray crystal structure of $Ph_3SiC{\equiv}CH$ product **3**. Selected bond distances and angles: Pt1-C39 = 2.031 Å; Pt1-C20 = 2.142 Å; Pt1-C21 = 2.140 Å; Pt1-N1 = 2.044 Å; Pt1-N5 = 2.120 Å; C20-C21 = 1.404 Å; C39-Pt1-C20 = 82.62°; C39-Pt1-C21 = 86.12°; C34-Si1-C21 = 100.2°; N1-Pt1-C20 = 150.97°; N1-Pt1-C21 = 169.33°; N1-Pt1-N5 = 91.02°.

If CO is bubbled into a solution of **3** the coordinated olefin tail is rapidly replaced by CO. The reaction proceeds quantitatively by ^{1}H NMR in less than five minutes to produce (nacnac)Pt(CO)((*o*-C_6H_4)Si(Ph)$_2$(CH=CH_2)) (**4**). The dechelated vinyl silane olefinic protons appear at 7.2, 6.2, and 5.6 ppm and display *trans*, *cis*, and *geminal* coupling constants of 20.0, 14.4, and 3.6 Hz, respectively. The Pt bound aryl resonances shift only slightly and still appear as four distinct signals, two doublets and two triplets. The CO stretch for **4** appears at 2080 cm^{-1} in hexanes.

An attractive hypothesis is that reaction of $Ph_3SiC{\equiv}CH$ with **1** results in formation of the arene activation product **3** following 2,1 insertion into the Pt-H bond. A 1,2 insertion of the alkyne into the Pt-H bond would leave Pt bound to the terminal carbon of the vinyl group. A 1,2 insertion would also place the $SiPh_3$ group γ to the metal and arene C-H activation would be unlikely. On the other hand, a 2,1 insertion places both Pt and Si on the same

carbon. This would in turn position the $SiPh_3$ phenyls close to the metal and allow for facile arene C-H activation (Scheme 4.2).

Scheme 4.2: Formation of **3** via 2,1 insertion of $Ph_3SiC{\equiv}CH$ into the Pt-H bond of **1**.



To probe whether this change in insertion selectivity is due to steric factors or electronic factors, $Me_3SiC{\equiv}CH$ was reacted **1** because it is sterically similar to $Me_3CC{\equiv}CH$ but electronically more similar to $Ph_3SiC{\equiv}CH$. Addition of two equivalents of $Me_3SiC{\equiv}CH$ to a CD_2Cl_2 solution of **1** resulted in a reaction that formed a new product, **5**, quantitatively in less than one hour as monitored by ^1H NMR. Only one equivalent of acetylene was consumed in the reaction. The product contained several signals integrating for a total of 3 protons in the chemical shift region indicative of bound olefins; one signal appeared as a doublet of doublets with 13.2 and 3.2 Hz coupling constants and with 66 Hz Pt satellites. The other two protons resonated on top of one another. Surprising the ^1H NMR spectrum also displays four inequivalent methyl signals, two due to the nacnac ligand; the other two appeared upfield at 0.16 and -0.26 ppm. Matched doublets with 12.4 Hz coupling appeared at -0.89 and -1.34 ppm, and they exhibit 68 and 78 Hz Pt coupling, respectively (Figure 4.2). These Pt coupling constants are typical for two-bond coupling values and these unique

signals were assigned to diastereotopic protons on a Pt bound methylene group. This assignment was consistent with both the chemical shifts and the large H-H coupling. It appeared that the alkyne had inserted into the Pt-H bond and then activated a C-H bond of one of the silyl methyl groups to form a chelated alkyl olefin complex, (nacnac)Pt($CH_2SiMe_2CH{=}CH_2$) (**5**). The two remaining methyl groups became diastereotopic exactly as observed by ^{1}H NMR. The methylene fragment of the activated methyl group became the diastereotopic methylene group which displays high field signals due to coordination to platinum and to shielding from the nacnac Ar group. Like the $SiPh_3$ analog, $Me_3SiC{\equiv}CH$ must undergo 2,1 insertion prior to C-H activation of one of the silyl methyl groups (eq. 3); a 1,2 insertion would place the methyl hydrogens too far from the metal to react. Related chelated dimethylvinylsilane complexes of Pt(II) have been made by Young via metathesis of the Grignard reagent $ClMgCH_2SiMe_2CH{=}CH_2$ with Pt(II) chlorides; they exhibit similar ^{1}H NMR signals.[26, 27]

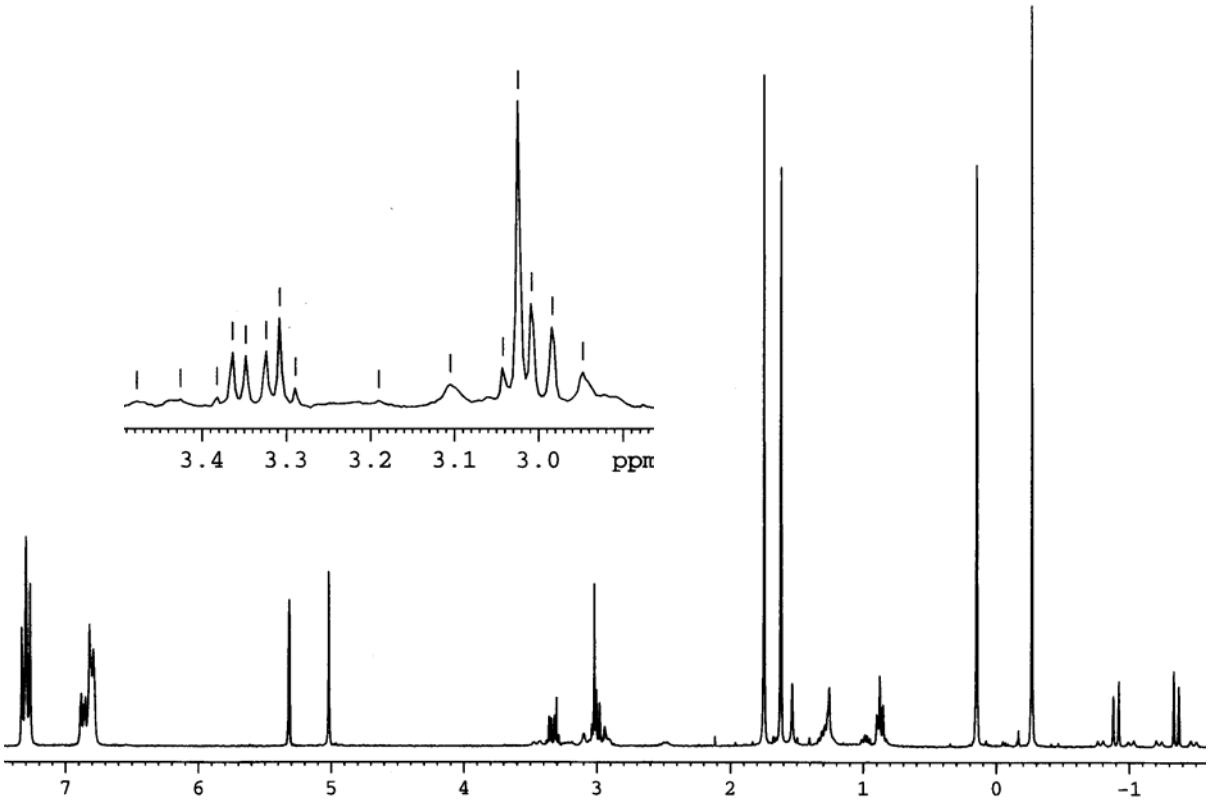
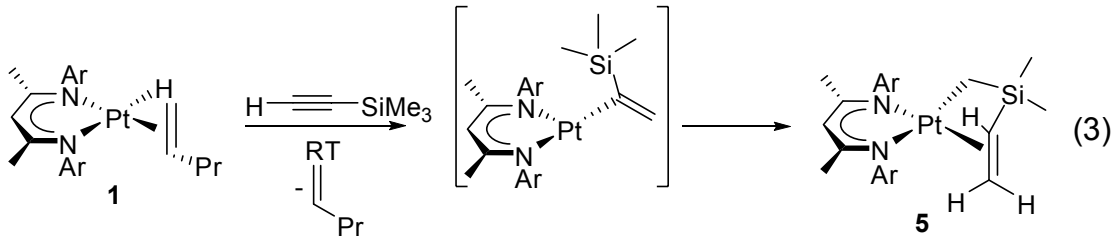


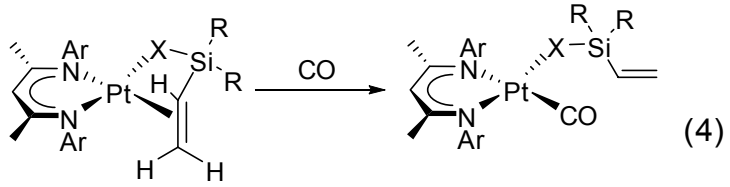
Figure 4.2. ^{1}H NMR of (nacnac)Pt(CH$_2$SiMe$_2$CH=CH$_2$), **5**.



(3)

Addition of CO to a solution of **5** resulted in displacement of the chelating olefin and replacement by CO to form (nacnac)Pt(CO)(CH$_2$SiMe$_2$CH=CH$_2$) (**6**) quantitatively by ^{1}H NMR in less than five minutes (eq. 4). The ^{1}H NMR of **6** displays terminal olefin signals at 6.10, 5.82, and 5.51 ppm with *trans*, *cis*, and geminal coupling constants of 20.1, 14.6, and 3.9 Hz, respectively. As a result of dechelation the two silyl methyls are equivalent and appear at -0.1 ppm. The Pt bound methylene protons are no longer diastereotopic since they are related by a mirror plane in the C_s complex, and they appear as a singlet at -0.08 ppm

with 78 Hz Pt coupling. The CO stretch appears at 2072 cm^{-1} in hexanes indicating that the chelated alkyl group donates more electron density to the metal than the chelated arene in **4** where the CO stretch is slightly higher at 2080 cm^{-1}.



(4)

X = *o*-C_6H_4, **3**, R = Ph
X = CH_2, **5**, R = Me

X = *o*-C_6H_4, **4**, R = Ph
X = CH_2, **6**, R = Me

We hoped to compare phenyl activation and methyl activation processes by employing $Ph_2MeSiC{\equiv}CH$ as a reagent. Reaction of $Ph_2MeSiC{\equiv}CH$ with labile Pt(II) pentene reagent **1** results in formation of a mixture of all three possible products namely, the methyl activation product and both diastereomers of the phenyl activation products. The two diastereomers resulting from phenyl activation are present in equal amounts indicating that, as expected, there is no preference for one phenyl relative to the other. Perhaps, unexpectedly the complex reflecting methyl activation is present in about a 1:1 ratio with the two phenyl activation isomers combined. This product ratio indicates that methyl activation is about twice as likely as phenyl activation. We expected that the five-membered chelate structure would be significantly more stable than the four-membered ring and that this would thermodynamically favor phenyl activation. Platinum(II) aryl bonds have been reported to be stronger than platinum(II) methyl bonds which would add further thermodynamic stability to the arene activation product.[28] The reaction products are probably determined kinetically, in which case the methyl activation may be favored because this conformer would have the large phenyl groups rotated away from the metal and avoid unfavorable steric interactions with the nacnac Ar groups.

Reaction of (nacnac)Pt(H)(1-pentene) (1) with RC≡CH (R = *t*-Bu, Ph). Reactions with terminal alkynes lacking propargylic protons were also explored. Addition of one equivalent of *t*-BuC≡CH to a CD_2Cl_2 solution of pentene hydride complex **1** at room temperature resulted in a color change from yellow to light orange. After about an hour the ^{1}H NMR spectrum showed a 1:1 ratio of unreacted **1** and a (nacnac)Pt product that contained no hydride ligand. Addition of a second equivalent of alkyne promotes complete conversion of **1** to the new Pt product, **7a**. Note that 1-pentene was displaced during the reaction and did not react with the product. The ^{1}H NMR spectrum for **7a** exhibits a singlet at 4.01 ppm with 32 Hz Pt coupling in addition to two coupled doublets, one at 3.50 ppm and the other at 2.89 ppm with 53 and 47 Hz Pt coupling, respectively, as well as 8.8 Hz $^3J_{H\text{-}H}$ coupling (Figure 4.3). The ^{1}H NMR spectrum also displayed two distinct *t*-butyl groups, confirming that two equivalents of alkyne are incorporated into **7a**. We postulated that the vinyl formed by 1,2 insertion into the Pt-H bond coupled in a head-to-tail fashion to a second equivalent of alkyne to yield an η^1-butadienyl ligand which could then chelate to Pt through the second double bond to form an η^1-η^2-butadienyl complex (Scheme 4.3). A similar η^1-η^2-butadienyl complex was observed for the insertion of diphenylacetylene into a Pt-H bond followed by insertion of the resulting vinyl into a second equivalent of diphenylacetylene; this complex was characterized crystallographically.[29] The η^1-η^2-butadienyl complex **7a,** (nacnac)Pt((H)C=C(*t*Bu)-(H)C=C(H)(*t*Bu)), would contain three olefinic hydrogens, two of which would couple to one another and one that would stand alone, as observed. To confirm the identity of the product ^{13}C{^{1}H}, HMQC, and HMBC ^{13}C experiments were conducted. The olefinic signals at 4.0, 3.5, and 2.9 ppm correlated with carbons at 114, 64, and 104 ppm; the ^{13}C signal at 114 had a Pt coupling of 740 Hz and the signal at 104 ppm had a Pt coupling

of 248 Hz. A $^{1}J_{Pt\text{-}C}$ coupling constant of 740 Hz is typical of a Pt-C sigma bond and is consistent with an η^1-vinyl ligand; the coupling of 248 Hz is typical of $^{1}J_{Pt\text{-}C}$ for a Pt-(η^2-olefin), further supporting the proposed η^1-η^2-butadienyl structure. The ^{13}C resonance at 64 ppm had a Pt coupling constant of only 24 Hz indicating that the η^2-olefin coordination was not symmetrical because it was constrained by the ring size. The remaining vinyl carbon, with no protons attached, was found via HMBC to resonate at 151 ppm, compatible with our formulation of this product. The *tertiary*-butyl alkyne is sterically similar to $Me_3SiC{\equiv}CH$, so the regiochemistry of the insertion appears to be dominated by the electronic effect of the atom bound to the C≡CH fragment atom. The silicon atom makes the adjacent Pt-C bond stronger and thus the selectivity reverses, just as observed by Trost.[3] Such a complete reversal from 1,2 to 2,1 insertion indicates that there is a subtle balance between the two pathways, and thermodynamics of the vinyl intermediates formed from the initial insertion into the Pt-H bond likely determine which direction the insertion occurs. This simple insertion guideline could be useful in tailoring catalysts for alkyne reduction and/or alkyne coupling since replacement of C by Si would reverse the product geometry. Few catalysts can be modified to yield either 1,4 or 1,3 disubstituted alkynes, but they usually produce a mixture of isomers.[30-32]

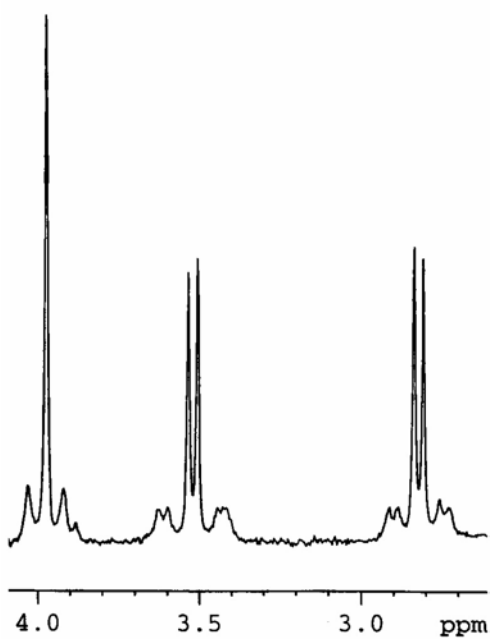
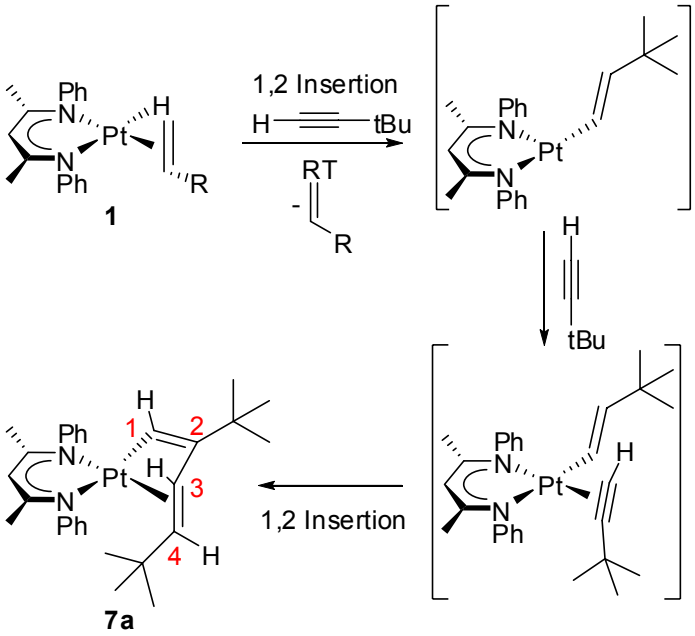


Figure 4.3: Olefinic region of the ^{1}H NMR of **7a**.

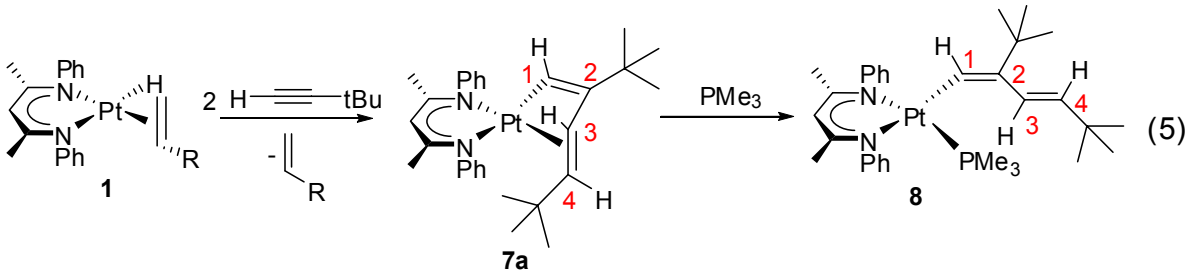
When phenyl acetylene was reacted with **1** the analogous coupled product, **7b**, was observed. The three olefinic protons displayed the same pattern, with two doublets and one singlet (all with Pt satellites), but they were shifted about 1 ppm downfield relative to **7a**. This product was less stable than the *t*-butyl analog and degraded over a day in solution to an unidentified product. The *t*-butyl analog on the other hand was stable in solution and was purified via silica gel chromatography yielding a yellow solid.

Scheme 4.3: Reductive coupling of two equivalents of *t*-BuC≡CH.



For further proof of the compound's identity and to explore its reactivity we attempted to displace the η^2-olefin tail by addition of another ligand, thereby forming an η^1-butadienyl complex. Compound **7a** was found to be unreactive towards most ligands, including CO which usually displaces olefins rapidly and irreversibly, but trimethylphosphine did displace the olefin and yielded (nacnac)Pt(PMe_3)(η^1-butadienyl), **8**, quantitatively by NMR spectroscopy (eq. 5). The vinyl proton on C1 in **8** shifted down 1.4 ppm from 4.0 ppm in **7a** to 5.4 ppm but retained an almost identical $^2J_{Pt\text{-}H}$ coupling of 34 Hz. The downfield shift of this proton was probably due to the fact that in the chelated species this proton would be oriented directly toward the nacnac aryl ring and thus was heavily shielded resulting the high field signal at 4 ppm; once the ligand was dechelated it could rotate away from the aryl and out of the shielding cone. The olefinic hydrogens on C3 and C4 shifted down to 5.2 and 5.5 ppm, respectively, and they no longer exhibited Pt coupling. The coupling between these two protons increased to 13.2 Hz indicative of a *trans* geometry

in accord with Pt-H addition to the triple bond. The carbon signals for C3 and C4 shifted downfield to 130 and 140 ppm respectively, again with loss of Pt coupling; they were no longer coordinated to the metal. The resonance for C1 shifted only slightly downfield to 120 ppm and now phosphorus coupling of 15 Hz was evident; C2 also underwent a small shift (to 144 ppm) and exhibited a 3 Hz $^{3}J_{P\text{-}C}$ coupling. The ^{1}H NMR for the butadienyl ligand resembles that of the free 1,3-di-*t*-Bu-1,3-butadiene.[33]

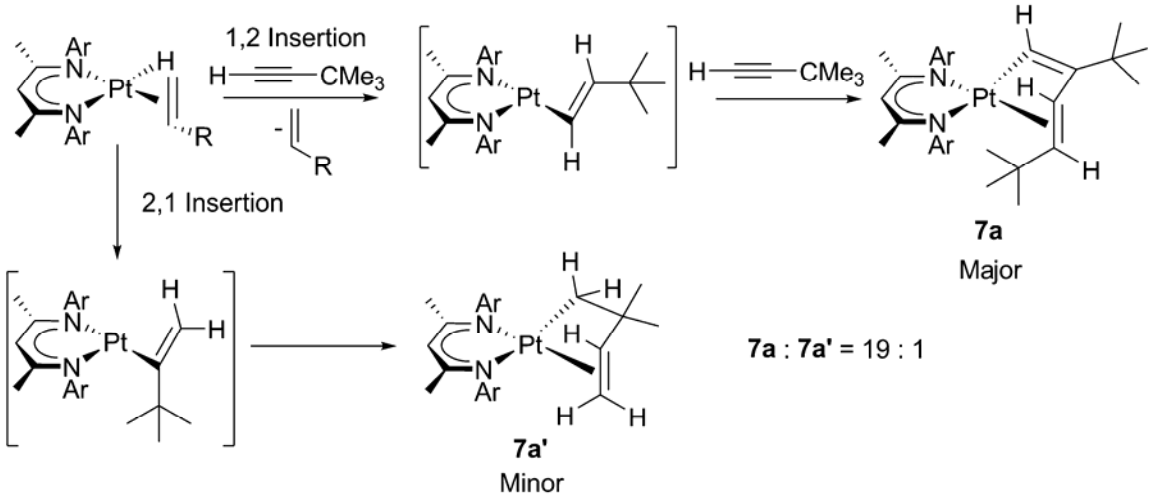


(5)

We noticed that during the synthesis of the *t*-BuC≡CH coupled product, **7a**, a minor product formed in about 5 % yield as assessed by ^{1}H NMR. This minor product displayed Pt coupled doublets at -0.22 and -0.74 ppm with 8 Hz $J_{H\text{-}H}$ coupling and Pt satellites with approximately 70 Hz coupling. We were not able to isolate this compound for further characterization, but it was clear that these doublets were due to the same type of species as the $Me_3SiC{\equiv}CH$ product **5**. So it appears that a small amount of the $Me_3CC{\equiv}CH$ underwent 2,1 insertion before C-H activation of one of the *t*-butyl methyl groups to form a chelated neohexenyl compound **7a′**. It appears that when 2,1 insertion occurs C-H activation of the R group, either methyl or phenyl, is faster than coordination and insertion of a second alkyne. When 1,2 insertion occurs there is no alkyne substituent in position to be easily activated, so the unsaturated vinyl intermediate binds a second alkyne and C-C coupling occurs. A similar mechanism is probably operative for the insertion of internal alkynes like 2-butyne; once insertion occurs the metal can rapidly activate the C-H bonds of the methyl group. This

would yield a Pt allene hydride intermediate which would rapidly undergo hydride migration to the central carbon to form the observed Pt allyl complex.

Scheme 4.4: Two possible insertion pathways for *t*-BuC≡CH.



It is worth noting that the structures of **7a′** and **5** are similar to the geometry of the vinyl-alkyne coupling products, **7**. Both products link the internal olefin carbon to the metal through four-membered chelate rings. Also, both products are bound in an η^1-η^2-fashion through one Pt-C sigma bond and one η^2-olefin. The only difference between the four atom skeleton of the ligands, equating Si and C, is the double bond between C1 and C2 in **7**. The sp^2 hybridized carbons in **7** are more rigid than the sp^3 atoms in **7a′** and **5** which probably increase the ring strain somewhat. While it seems like the four membered rings would have substantial ring strain, the experimental evidence indicates that it is quite stable. All of the products funnel down to this type of structure. The chelated nature of these products appears to be a thermodynamic sink as the products from different types of reactions all converge to remarkably similar structures.

Mechanistic Considerations for Head-to-Tail Coupling of RC≡CH (R = t-Bu, Ph). To form the observed head-to-tail coupled product the first alkyne must insert into the

Pt-H bond in a 1,2 fashion giving a Pt vinyl intermediate in which the R group is distal from the metal. A 1,2 insertion is not only required to yield the observed head-to-tail coupling, but it also prohibits C-H activation of the *t*-Bu substituent, indirectly allowing alkyne coupling to occur. We believe that the electropositive nature of the Si atom is the cause for the reversal between 2,1 and 1,2 insertion. Steric factors are not likely to dictate 2,1 insertion of the silyl alkynes, because the $SiMe_3$ group on the 2 carbon is sterically similar to the CMe_3 group of *t*-BuC≡CH, an alkyne that favors 1,2 insertion. The silyl group will stabilize the Pt-C bond formed by 2,1 insertion of the alkyne into the Pt-H, favoring this product thermodynamically even though it is more sterically crowded relative to the 1,2 insertion product. There is no significant electronic stabilization of the Pt-C bond from C based groups such as *t*-Bu or Ph, so in those cases the most stable Pt-C bond is the one with the bulky group away from the metal. A switch from 1,2 insertion to 2,1 insertion on moving from CMe_3 to $SiMe_3$ was observed for the $Pd(OAc)_2$ catlyzed alkyne dimerization reaction by Trost.[3]

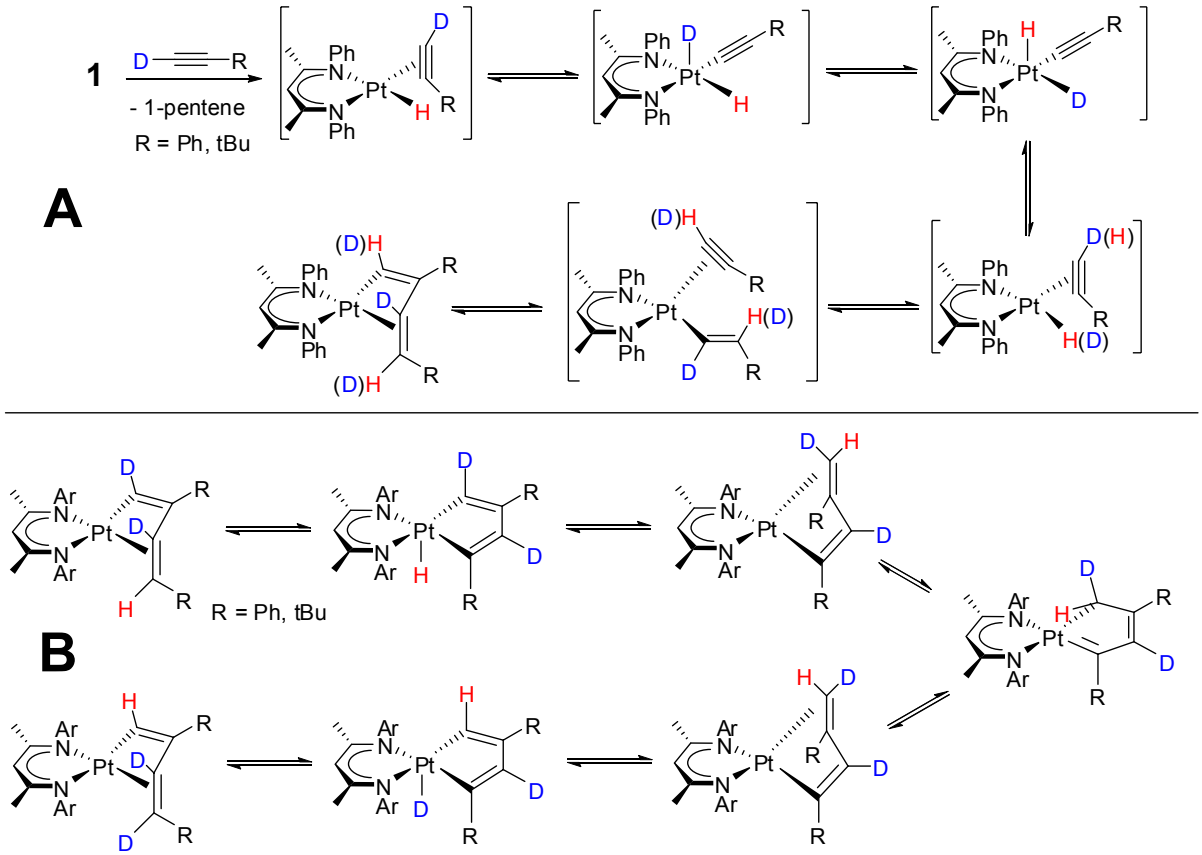
Once the alkyne has inserted into the Pt-H bond a second alkyne coordinates to the metal and a 1,2 insertion of the alkyne into the Pt-C bond to the vinyl group occurs, yielding the complex that places the R group of the alkyne farther from the metal. It is notable that while 1-pentene was available to trap the vinyl intermediate we did not observe any pentene binding. Attempts to observe reaction intermediates via low temperature ^1H NMR failed. The reaction of the phenyl acetylene with **1** was monitored by VT ^1H NMR but only loss of **1** and appearance of **7b** and 1-pentene were observed. This indicates that displacement of 1-pentene is rate-limiting. We observed earlier that the second alkyne addition is faster than the first by adding one equivalent of alkyne to **1** and getting a 1:1 ratio of **1** to **7**; so rate-limiting olefin displacement is not surprising because hydride migration should be rapid.

Considering that olefin displacement is fairly rapid, the barrier to C-C bond formation in this system is quite low for a Pt species.

Deuterium labeling studies were conducted to test for scrambling between the Pt-H and the acetylenic protons. Two equivalents of PhCCH were added to a CD_2Cl_2 solution of (nacnac)Pt(D)(1-pentene-d_{10}) (**1-*d*$_{11}$**) and the resulting η^1-η^2-butadienyl complex exhibited integrations for the protons on C1, C3, and C4 as follows: singlet ~ 0.5 H, doublet over singlet ~ 1H, and doublet ~ 0.5 H. This indicates that the Pt-D is scrambled between the C1 and C4 positions. When PhCCD was reacted with (nacnac)Pt(H)(1-pentene) (**1**) the ^{1}H NMR spectrum showed a singlet integrating for about half a proton for the C1 and C4 signals and no signal is seen for the C3 proton. This again shows that the original Pt-H is ultimately scrambled between the C1 and C4 sites. Reaction of *t*BuCCD with **1** yielded slightly different results. In this case the initial ^{1}H NMR showed only a small amount of scrambling between the positions on C1 and C4; ~ 20% H at C1 and ~ 20 % D at C4. Upon standing in solution for several hours the spectrum showed complete scrambling; ~ 50 % H at C1 and ~50 % D at C4.

This indicates that the protons do not have to scramble on the way to forming **7**, but that they can scramble once the product is formed. This is probably true for the phenyl acetylene product as well; in that case the scrambling just happens too fast to catch it before it completion. There are several plausible mechanisms for C1-C4 proton scrambling. The protons could be scrambled via acetylenic C-H activation before the alkynes are coupled and if the coupling step is reversible then scrambling after **7** is formed would occur. Alternatively, the protons could scramble after alkyne coupling via some type of vinylic C-H activation mechanism.

Scheme 4.5: Possible mechanisms for proton scrambling in **7**.



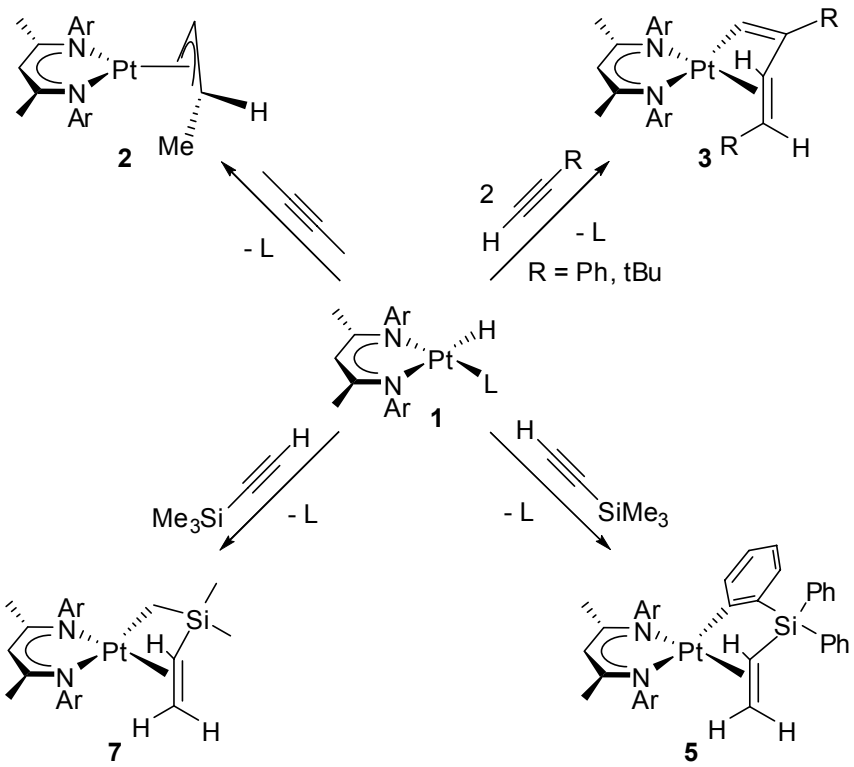
Mechanism A (Scheme 4.5) involves C-H activation of the first alkyne rather than insertion into the Pt-H bond. This yields a five-coordinate Pt(IV) dihydride which could rapidly equilibrate the hydrides. Reductive elimination of the alkyne will reform the Pt(II) hydride alkyne adduct with the hydride and acetylide protons scrambled. From here the second alkyne will insert into the Pt-H(D) bond to yield a Pt(II) vinyl alkyne intermediate. This Pt(II) vinyl alkyne species will then undergo migratory insertion to give the η^1-η^2-butadienyl product **7**. This mechanism would be reasonable if all of the scrambling occurred before formation of **7**, but since we observed scrambling of the protons in the already formed product when *t*-BuC≡CD is used it does not seem likely. The alkyne coupling could conceivably be reversible, but it seems unlikely. Note that alkyne deinsertion from the Pt-H

would be necessary to scramble the protons. There is a large thermodynamic driving force to reduce the alkyne, so it seems unlikely to deinsert. Though there are a vast number of reports of alkyne insertion into metal hydrides there are few examples of alkyne deinsertion to generate a metal hydride.[13, 34]

Mechanism B (Scheme 4.5) involves scrambling of the C1 and C4 protons in **7** via isomerization of the butadienyl ligand. Activation of the C4-H bond would yield a Pt(IV) hydride metallacyclopentadiene species. Reductive elimination of the hydride with C1 instead of C4 would form the opposite isomer of the η^1-η^2-butadienyl in which C1 and C2 are now bound as the η^2-olefin. The compound could isomerize to a carbene metallacyclopentadiene where C1 is now an sp^3 hybridized methylene group. Because this ligand is planar the complex is C_s symmetric with the mirror plane splitting the protons on C1 and thus equilibrating them. Isomerization back to the original geometry of **7** then results in scrambling of the original C1 and C4 protons in **7**. A possible variant of this mechanism is rehybridization to form the alkyl carbene metallacyclopentadiene with the proton and *t*Bu group on the C4 methylene carbon and a 1,3 proton shift from C4 to C1 yielding the same C_s symmetric intermediate for proton equilibration; it is not possible to distinguish between these two variants experimentally. Mechanism B seems more attractive because it does not require C-C bond cleavage or alkyne deinsertion to regenerate a Pt-H unit. There are a fairly large number of metallacyclopentadiene complexes of d^8 transition metals in the literature,[35-40] so postulating such species as an intermediate has precedence. A Rh(I) catalyst was recently reported to C-H activate the terminal vinyl C-H bond in a η^1-η^2-eneiminyl ligand to form a Rh(III) metallapyrrole hydride species;[41] this transformation is analogous to the Pt(II) η^1-η^2-butadienyl to Pt(IV) metallacylclopentadiene transformation proposed here. A similar

transformation has been proposed for a Rh(I) η^1-butadienyl complex.[21] One might hope to observe some of the other isomer in solution, but we believe that the isomer in which C1 and C2 form the η^2-olefin will be energetically less favorable than the observed isomer. Even though a terminal olefin typically binds more tightly to Pt than an internal olefin, here the *t*Bu group on C4 would be forced to point directly toward the nacnac aryl ring and the result would be an unfavorable steric interaction.

Scheme 4.6: Addition of various alkynes to (nacnac)Pt(H)(1-pentene) (**1**).



Conclusions

The (nacnac)Pt(H)(1-pentene) complex (**1**) is a useful starting material to assess the reactivity of the (nacnac)Pt(H) fragment as the 1-pentene is easily displaced by other ligands. Complex **1** reacts with alkynes to displace 1-pentene followed by rapid insertion of the alkyne into the Pt-H bond. Once insertion occurs the electron rich Pt reacts with alkyl or aryl

C-H bonds on the newly formed vinyl group if they are in close proximity to the metal. This results in the formation of Pt allyls when alkynes with protons on the C adjacent to the triple bond, such as 2-butyne, are used. Alternatively, chelating alkyl/aryl olefins are formed when there are no protons adjacent to the triple bond, such as with $Ph_3SiC{\equiv}CH$ or $Me_3SiC{\equiv}CH$ (Scheme 4.6). If alkyne insertion occurs in such a way that no C-H bonds are in the vicinity of the metal, such as the 1,2 insertion of *t*-BuC≡CH, the metal will bind another alkyne and a second 1,2 insertion will occur yielding a η^1-η^2-butadienyl complex. This product is the result of head-to-tail reductive dimerization of the alkynes which is typically less favorable that head-to-head dimerization. We also observed that if silyl alkynes such as $Me_3SiC{\equiv}CH$ are used the initial insertion of the alkyne reverses from 1,2 to 2,1 insertion probably because the Si atom stabilizes the Pt-C bond when the silicon is β to the metal. This complete reversal of insertion selectivity with a simple change to the substrate could prove useful in finding a catalyst that can selectively form different isomers of coupling products with a slight adjustment to the substrate.

Experimental

General Procedures. Unless otherwise stated all reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was flame dried under vacuum and cooled under N_2 before use. Diethyl ether, methylene chloride, toluene, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[42] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Methylene chloride-d_2 was vacuum transferred from calcium hydride and degassed by several freeze-pump-thaw cycles.

Compound **1**, (p-Cl-nacnac)Pt(H)(1-pentene), wa synthesized via published procedure.[24] Silyl alkynes $Ph_3SiC{\equiv}CH$ and $Ph_2MeSiC{\equiv}CH$ were synthesized via published procedures.[43] The *t*-BuC≡CD was formed by stirring *t*-BuC≡CH in $NaOD/D_2O$ for two days. All other reagents were used as received from Sigma Aldrich.

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 MHz, Bruker Avance 400 MHz, or Bruker DRX 500MHz spectrometers. ^1H NMR and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000.

(p-Cl-nacnac)Pt(1-methylallyl) 2. In a vial was dissolved 30 mg (0.051 mmol) of **1** in 2 mL of pentane. To the solution was added 5.0 μL (3.5 mg, 0.065 mmol, 1.1 eq) of 2-butyne. The vial was capped and shaken; after 30 minutes the solvent was evacuated yielding **2** as a yellow solid in quantitative yield. Product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2:NEt_3 and a mobile phase of 4:1 Hexanes:CH_2Cl_2. ^1H NMR (δ, CD_2Cl_2, 400MHz, RT): 7.30 (m, 4H, nacnacPh); 7.1-6.9 (m, 6H, nacnacPh); 4.90 (s, 1H, nacnac-C<u>*H*</u>); 4.62 (dt, 1H, $^3J_{H\text{-}Hsyn}$ = 6.6 Hz, $^3J_{H\text{-}Hanti}$ = 10.8 Hz, $^2J_{Pt\text{-}H}$ = 78 Hz, $H_2CC\underline{H}C(H)(Me)$); 2.39 (quin, 1H, $^3J_{H\text{-}Hsyn}$ = $^3J_{H\text{-}H(Me)}$ = 6.6 Hz, $^2J_{Pt\text{-}H}$ = 40 Hz, $H_2CCHC(\underline{H})(Me)$); 1.85 (d, 2H, $^3J_{H\text{-}Hobs}$ = 9.2 Hz, $^2J_{Pt\text{-}H}$ = 24 Hz, $\underline{H}_2CCHC(H)(Me)$); 1.65, 1.64 (s, 3H, nacnac-C$\underline{H}_3$); 0.57 (d, 3H, $^3J_{H\text{-}H}$ = 6.4 Hz, $^3J_{Pt\text{-}H}$ = 13.6 Hz, $H_2CCHC(H)(C\underline{H}_3)$). ^{13}C NMR (δ, CD_2Cl_2, 100MHz, RT): 158.5, 156.2 ((Me)(CH)<u>*C*</u>=NAr); 156.7, 156.3 (N-Ph ipso <u>*C*</u>); 128.3, 128.3, 128.3, 128.3, 124.8, 124.8, 124.6, 124.6, 124.3, 124.1 (N-Ph <u>*C*</u>); 98.7 ($^3J_{Pt\text{-}C}$ = 61 Hz, nacnac <u>*C*</u>H); 98.1 ($^1J_{Pt\text{-}C}$ = 63 Hz, $H_2C\underline{C}HC(H)Me$)); 59.3 ($^1J_{Pt\text{-}C}$ = 242 Hz, $H_2\underline{C}CHC(H)Me$)); 40.1 ($^1J_{Pt\text{-}C}$ = 253 Hz, $H_2CCH\underline{C}(H)Me$)); 23.9, 23.6 ($(H_3\underline{C})C{=}N$); 14.0 ($^2J_{Pt\text{-}C}$ = 49 Hz, $H_2CCHC(H)(\underline{C}H_3)$).

(p-Cl-nacnac)Pt(*o*-C_6H_4-$SiPh_2$-CH=CH_2) 3. In a vial was dissolved 30 mg (0.058 mmol) **1** in 2 mL pentane. To the solution was added 1 eq. of $Ph_3SiC{\equiv}CH$. The vial was capped and shaken, then after 1 hour the solvent was evacuated yielding compound **3**. Product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2:NEt_3 and a mobile phase of 4:1 Hexanes:CH_2Cl_2. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, RT): 7.82 (m, 2H, *o*-SiPh); 7.54 (m, 3H, *m*,*p*-SiPh); 7.34 (br d, 2H, *m*-nacnacAr); 7.31 (m, 1H, *p*-SiPh′); 7.23 (m, 4H, *o*,*m*-SiPh′); 7.03 (br, 1H, *o*-nacnacAr); 6.95 (br, 1H, *o*-nacnacAr); 6.84 (d, 1H, $^3J_{H\text{-}H}$ = 6.8 Hz, C3-*H* Pt-Ph-Si); 6.74 (d, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, C6-*H* Pt-Ph-Si); 6.70 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacAr′); 6.61 (t, 1H, $^3J_{H\text{-}H}$ = 7.2 Hz, C5-*H* Pt-Ph-Si); 6.54 (t, 1H, $^3J_{H\text{-}H}$ = 7.2 Hz, C4-*H* Pt-Ph-Si); 6.28 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, *o*-nacnacAr′); 5.08 (s, 1H, nacnac-C*H*); 3.70 (dd, 1H, $^3J_{H\text{-}H\textit{cis}}$ = 10.8 Hz, $^3J_{H\text{-}H\textit{trans}}$ = 14.8 Hz, (SiR_3)*H*C=CH_2); 3.24 (d, 1H, $^3J_{H\text{-}H\textit{cis}}$ = 10.8 Hz, (SiR_3)HC=C*H*$_2$); 3.07 (d, 1H, $^3J_{H\text{-}H\textit{trans}}$ = 14.8 Hz, (SiR_3)HC=C*H*$_2$); 1.75, 1.72 (s, 3H, nacnac-C*H*$_3$).

(p-Cl-nacnac)Pt(CO)(*o*-C_6H_4-$SiPh_2$-CH=CH_2) 4. In an NMR tube was dissolved 10 mg (0.013 mmol) **3** in 2 mL pentane. To the solution was bubbled CO gas then the tube was shaken yielding compound **4** in quantitative yield by ^{1}H NMR. IR (Hexanes, RT) ν_{CO} = 2080 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, RT): 7.46 (d, 4H, $^3J_{H\text{-}H}$ = 6.8 Hz, *o*-$SiPh_2$); 7.38 (m, 4H, *m*-$SiPh_2$); 7.30 (m, 2H, *p*-$SiPh_2$); 7.24 (dd, 1H, $^3J_{H\text{-}H\textit{cis}}$ = 14.4 Hz, $^3J_{H\text{-}H\textit{trans}}$ = 20.0 Hz, (SiR_3)*H*C=CH_2); 7.23 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacAr); 7.03 (d, 1H, $^3J_{H\text{-}H}$ = 6.8 Hz, C6-*H* Pt-Ph-Si); 6.86 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, *m*-nacnacAr); 6.74 (d, 1H, $^3J_{H\text{-}H}$ = 7.2 Hz, C3-*H* Pt-Ph-Si); 6.69 (t, 1H, $^3J_{H\text{-}H}$ = 7.2 Hz, C5-*H* Pt-Ph-Si); 6.62 (br, 2H, *m*-nacnacAr′); 6.51 (t, 1H, $^3J_{H\text{-}H}$ = 7.0 Hz, C4-*H* Pt-Ph-Si); 6.23 (dd, 1H, $^3J_{H\text{-}H\textit{cis}}$ = 14.4 Hz, $^3J_{H\text{-}H\textit{gem}}$ = 3.6 Hz,

(SiR_3)HC=C$\underline{H_2}$); 6.20 (br, 2H, *o*-nacnacAr′); 5.57 (dd, 1H, $^3J_{H\text{-}Htrans}$ = 20.0 Hz, $^3J_{H\text{-}Hgem}$ = 3.6 Hz, (SiR_3)HC=C$\underline{H_2}$); 5.07 (s, 1H, nacnac-C$\underline{H}$); 1.81, 1.62 (s, 3H, nacnac-C$\underline{H_3}$).

(p-Cl-nacnac)Pt(CH$_2$-SiMe$_2$-CH=CH$_2$) 5. In a vial was dissolved 30 mg (0.058 mmol) **1** in 2 mL pentane. To the solution was added 1 eq. $Me_3SiC{\equiv}CH$. The vial was capped and shaken, then after 1 hour the solvent was evacuated yielding compound **5**. Product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2:NEt_3 and a mobile phase of 4:1 Hexanes:CH_2Cl_2. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, RT): 7.3 (m, 4H, nacnacAr); 6.87 (m, 1H, nacnacAr); 6.81 (m, 3H, nacnacAr); 5.02 (s, 1H, nacnac-C$\underline{H}$); 3.34 (m, 1H, $^2J_{Pt\text{-}H}$ = 68 Hz, (SiR_3)HC=C$\underline{H_{2cis}}$); 3.02 (m, 2H, (SiR_3)$\underline{H}$C=C$\underline{H_{2trans}}$ (simulated *J* values: $^3J_{H\text{-}Htrans}$ = 15.2 Hz, $^3J_{H\text{-}Hcis}$ = 10.2 Hz, $^2J_{H\text{-}H}$ = 3.2 Hz,)); 1.75, 1.63 (s, 3H, nacnac-C$\underline{H_3}$); 0.16, (s, 3H, $Si(Me_2)_{up}$); -0.26 (s, 3H, $Si(Me_2)_{down}$); -0.89 (d, 1H, $^2J_{H\text{-}H}$ = 12.4 Hz, $^2J_{Pt\text{-}H}$ = 67.6 Hz, Pt-(C$\underline{H_2}$)$_{down}$-Si); -1.34 (d, 1H, $^2J_{H\text{-}H}$ = 12.4 Hz, $^2J_{Pt\text{-}H}$ = 77.6 Hz, Pt-(C$\underline{H_2}$)$_{up}$-Si). ^{13}C NMR (δ, CD_2Cl_2, 125 MHz, RT): 159.6, 156.9 (nacnac $\underline{C}$=N); 152.4, 148.1 (N-Ar *ipso*-$\underline{C}$); 130.6, 129.8, 128.2, 128.2, 128.1, 128.1, 127.6, 127.6, 127.2, 127.2 (nacnac Ar $\underline{C}$); 99.4 (nacnac $\underline{C}$H, $^3J_{Pt\text{-}C}$ = 48 Hz); 75.3 ($SiMe_2$-CH=$\underline{C}H_2$, $^1J_{Pt\text{-}C}$ = 242 Hz); 63.9 ($SiMe_2$-$\underline{C}$H=CH_2, $^1J_{Pt\text{-}C}$ = 75 Hz); 26.0, 25.7 (nacnac $\underline{C}H_3$); 7.6 ($SiMe(\underline{C}H_3)_{down}$); -2.3 ($SiMe(\underline{C}H_3)_{up}$); -14.1 ($(CH_2)SiMe_2$, $^1J_{Pt\text{-}C}$ = 504 Hz).

(p-Cl-nacnac)Pt(CO)(CH$_2$-SiMe$_2$-CH=CH$_2$) 6. In an NMR tube was dissolved 10 mg (0.016 mmol) **5** in 2 mL pentane. To the solution was bubbled CO gas then the tube was shaken yielding compound **6** in quantitative yield by ^{1}H NMR. ^{1}H NMR (δ, CD_2Cl_2, 300 MHz, RT): 7.35 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, nacnacAr); 7.31 (d, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, nacnacAr); 7.02 (d, 2H, $^3J_{H\text{-}H}$ = 8.7 Hz, nacnacAr); 6.86 (d, 2H, $^3J_{H\text{-}H}$ = 8.7 Hz, nacnacAr); 6.10 (dd, 1H, $^3J_{H\text{-}Htrans}$ = 20.1 Hz, $^3J_{H\text{-}Hcis}$ = 14.6 Hz, (SiR_3)$\underline{H}$C=CH_2); 5.81 (dd, 1H, $^3J_{H\text{-}Hcis}$ = 14.6 Hz, $^3J_{H\text{-}}$

$_{Hgem}$ = 3.2 Hz, (SiR_3)HC=C$\underline{H_2}$); 5.51 (dd, 1H, $^3J_{H\text{-}Htrans}$ = 20.1 Hz, $^3J_{H\text{-}Hgem}$ = 3.2 Hz, (SiR_3)HC=C$\underline{H_2}$); 5.01 (s, 1H, nacnac-C$\underline{H}$); 1.78, 1.71 (s, 3H, nacnac-C$\underline{H_3}$); -0.08 (s, 2H, $^2J_{Pt\text{-}H}$ = 78 Hz, Pt-C$\underline{H_2}$-Si); -0.10 (s, 6H, $SiMe_2$). IR (Hexanes, RT) ν_{CO} = 2072 cm^{-1}.

(p-Cl-nacnac)Pt(η^1-η^2-C(H)=C(tBu)-C(H)=C(H)(tBu)) 7a. In a vial was dissolved 30 mg (0.058 mmol) **1** in 2 mL pentane. To the solution was added 21.4 μL (14.2 mg, 3 eq.) of 3,3-dimethyl-1-butyne. The vial was capped and shaken, then after 3 hours the solvent was evacuated yielding compound **7a**. Product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2:NEt_3 and a mobile phase of 4:1 Hexanes:CH_2Cl_2. ^{1}H NMR (δ, CD_2Cl_2, 300 MHz, RT): 7.32 (d, 2H, $^3J_{H\text{-}H}$ = 8 Hz, nacnacAr); 7.30 (d, 2H, $^3J_{H\text{-}H}$ = 8 Hz, nacnacAr); 6.86 (br d, 2H, nacnacPh); 6.80 (d, 2H, $^3J_{H\text{-}H}$ = 8.1 Hz, nacnacPh); 4.91 (s, 1H, nacnac-C$\underline{H}$); 4.01 (s, 1H, $^2J_{Pt\text{-}H}$ = 32 Hz, Pt-C($\underline{H}$)=C(tBu)-); 3.50 (d, 1H, $^3J_{H\text{-}H}$ = 8.8 Hz, $^2J_{Pt\text{-}H}$ = 53 Hz, -C($\underline{H}$)=C(H)(tBu)); 2.89 (d, 1H, $^3J_{H\text{-}H}$ = 8.8 Hz, $^2J_{Pt\text{-}H}$ = 47 Hz, -C(H)=C($\underline{H}$)(tBu)); 1.73, 1.67 (s, 3H, nacnac-C$\underline{H_3}$); 0.87 (s, 9H, -C(H)=C(H)(C(C$\underline{H_3}$)$_3$)); 0.82 (s, 9H, -C(H)=C(C(C$\underline{H_3}$)$_3$)-). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, RT): 160.0, 156.2 ((Me)(CH)$\underline{C}$=NAr); 152.2, 151.2 (N-Ph ipso $\underline{C}$); 151.2 (Pt-C(H)=$\underline{C}$(tBu)-); 130.2, 129.9, 128.5, 128.5, 128.5, 128.5, 128.2, 128.2, 127.3, 127.3 (N-Ar $\underline{C}$); 113.7 ($^1J_{Pt\text{-}C}$ = 740 Hz, Pt-$\underline{C}$(H)=C(tBu)-); 104.0 ($^1J_{Pt\text{-}C}$ = 248 Hz, -C(H)=$\underline{C}$(H)(tBu)); 98.9 ($^3J_{Pt\text{-}C}$ = 50 Hz, nacnac $\underline{C}$H); 63.7 ($^1J_{Pt\text{-}C}$ = 24 Hz, -$\underline{C}$(H)=C(H)(tBu)); 37.3 ($^3J_{Pt\text{-}C}$ = 77 Hz, Pt-C(H)=C($\underline{C}$Me$_3$)-); 36.0 ($^2J_{Pt\text{-}C}$ = 21 Hz, -C(H)=C(H)($\underline{C}$Me$_3$)); 32.0 ($^3J_{Pt\text{-}C}$ = 24 Hz, -C(H)=C(H)(C($\underline{C}$H$_3$)$_3$)-); 28.3 (Pt-C(H)=C(C($\underline{C}$H$_3$)$_3$)-); 25.3, 25.0 ((H$_3\underline{C}$)C=N).

(p-Cl-nacnac)Pt(η^1-η^2-C(H)=C(Ph)-C(H)=C(H)(Ph)) 7b. In an NMR tube was dissolved 10 mg (0.017 mmol) **1** in 0.6 mL CD_2Cl_2. To the solution was added 3.8 μL (3.5 mg, 2 eq.) of phenylacetylene. The tube was capped, shaken, and the ^{1}H NMR spectrum

recorded after 20 min displayed complex **7b**. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, RT): 7.6-6.9 (18H, Ph); 5.22 (s, 1H, $^{2}J_{Pt-H}$ = 34 Hz, Pt-C(*H*)=C(Ph)-); 5.10 (s, 1H, nacnac-C*H*); 4.41 (d, 1H, $^{3}J_{H-H}$ = 7.6 Hz, $^{2}J_{Pt-H}$ = 46 Hz, -C(H)=C(*H*)(Ph)); 4.29 (d, 1H, $^{3}J_{H-H}$ = 7.6 Hz, $^{2}J_{Pt-H}$ = 50 Hz, -C(*H*)=C(H)(Ph)); 1.85, 1.84 (s, 3H, nacnac-CH_3). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, RT): 160.1, 156.4 ((Me)(CH)*C*=NAr); 153.6, 152.6 (N-Ph ipso *C*); 142.7 (Pt-C(H)=*C*(Ph)-); 140.0, 138.6 (C-Ph ipso *C*); 129-122 (15C, Ph *C*); 123.4 (Pt-*C*(H)=C(Ph)-); 99.0 (nacnac *C*H); 92.5 (-C(H)=*C*(H)(Ph)); 63.7 (-*C*(H)=C(H)(Ph)); 25.3, 24.9 ((H$_3$*C*)C=N).

(p-Cl-nacnac)Pt(η^1-C(H)=C(tBu)-C(H)=C(H)(tBu))(PMe$_3$) 8. A CH_2Cl_2 solution of butadienyl complex **7** was placed in a flask in the dry box. The flask was removed from the box and placed under positive N_2 pressure. Trimethylphosphine was added via microliter syringe, upon addition the light orange solution turned bright yellow. After 30 minutes the solvent was removed and the product triturated with pentane yielding **8** in quantitative yield. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, RT): 7.24 (d, 2H, $^{3}J_{H-H}$ = 8.8 Hz, nacnacPh); 7.22 (d, 2H, $^{3}J_{H-H}$ = 8.8 Hz, nacnacPh); 7.03 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, nacnacPh); 6.96 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, nacnacPh); 5.50 (d, 1H, $^{3}J_{H-H}$ = 13 Hz, -C(H)=C(*H*)(tBu)); 5.39 (s, 1H, $^{2}J_{Pt-H}$ = 34 Hz, Pt-C(*H*)=C(tBu)-); 5.23 (d, 1H, $^{3}J_{H-H}$ = 13 Hz, -C(*H*)=C(H)(tBu)); 4.70 (s, 1H, nacnac-C*H*); 1.59, 1.57 (s, 3H, nacnac-CH_3); 1.21, (s, 9H, -C(H)=C(C(CH_3)$_3$)-); 0.87 (d, 9H, $^{2}J_{P-H}$ = 10.4 Hz, $^{3}J_{Pt-H}$ = 30 Hz, P(CH_3)$_3$); 0.73 (s, 9H, -C(H)=C(H)(C(CH_3)$_3$)). ^{31}P NMR (δ, CD_2Cl_2, 162 MHz, RT): -39.5 (s, $^{1}J_{Pt-P}$ = 4164 Hz, PMe_3). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, RT): 158.2, 157.5 ((Me)(CH)*C*=NAr); 155.0, 150.1 (N-Ph ipso *C*); 143.6 ($^{3}J_{P-C}$ = 3 Hz, Pt-C(H)=*C*(tBu)-); 140.4 (-C(H)=*C*(H)(tBu)); 129.9 (-*C*(H)=C(H)(tBu)); 129.3, 129.1, 129.1, 129.0, 129.0, 128.1, 128.1, 127.6, 127.6, 124.1 (N-Ph *C*); 120.1 ($^{2}J_{P-C}$ = 15 Hz, Pt-*C*(H)=C(tBu)-); 99.4 ($^{3}J_{Pt-C}$ = 43 Hz, nacnac *C*H); 38.4 ($^{3}J_{Pt-C}$ = 70 Hz, Pt-C(H)=C(*C*Me$_3$)-); 32.6 (-

C(H)=C(H)(<u>*C*</u>Me$_3$)); 30.9 (Pt-C(H)=C(C(<u>*C*</u>H$_3$)$_3$)-); 30.1 (-C(H)=C(H)(C(<u>*C*</u>H$_3$)$_3$)); 25. 0, 25.0 ((H$_3$<u>*C*</u>)C=N); 16.8 ($^1J_{P\text{-}C}$ = 40 Hz, $^2J_{Pt\text{-}C}$ = 53 Hz, P(<u>*C*</u>H$_3$)$_3$).

Crystallographic Data for 3.

Table 4.1. Crystal data and structure refinement for **3**.

Complex	**3**
Empirical Formula	$C_{37}H_{32}Cl_2N_2PtSi$
Mol wt	798.73
Temperature	100(2) K
Wavelength	0.71073 Å
Cryst Syst	Triclinic
Space Group	P-1
a, Å	10.2345(2)
b, Å	11.6447(2)
c, Å	14.6854(3)
α, deg	97.484(1)
β, deg	90.520(1)
γ, deg	91.588(1)
Vol. Å3	1734.45(6)
Z	2
Density (calculated)	1.529 Mg/m^3
μ, mm^{-1}	4.261
F(000)	788
Crystal size	0.59 x 0.12 x 0.10 mm^3
2θ range	1.40 to 25.68°
Index Ranges	-12<=h<=12 -13<=k<=14 -17<=l<=11
Reflections Collected	15681
Independent reflections	6559 [R(int) = 0.0330]
Data/restraints/parameters	6559/0/390
Goodness-of-fit on F^2	1.101
Final R indices[I>2sigma(I)]	R1 = 0.0274 wR2 = 0.0733
R indices (all data)	R1 = 0.0314 wR2 = 0.0751
Largest diff. peak and hole	1.291 and -0.693 e $Å^{-3}$

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Chapter 5

Carbon Monoxide Promoted Reductive Elimination of Hydrogen from Tp' Platinum Complexes

Introduction

Activation of H_2 by and reductive elimination of H_2 from transition metal complexes are two fundamental reactions in organometallic chemistry; these are crucial steps in many catalytic reactions.[1-5] Of the two processes, H_2 activation has been more widely investigated than has hydrogen elimination.[6-9]

Hydrogen production currently involves steam reformation of hydrocarbons produced from fossil fuels, and consequences of this are high cost and dependence on a limited resource. Significant research has focused on the synthesis of catalysts capable of producing hydrogen from biomass, water, or other renewable resources.[10-14] In order to move toward a hydrogen economy an inexpensive route for the production of hydrogen is needed.

One well known method of either producing or purifying H_2 is the water gas shift reaction (WGSR). This reaction is thermodynamically favorable at standard temperature and pressure, but without a catalyst high temperatures and high pressures are required for rapid reaction.[2, 15] Some homogeneous catalysts accomplish this process under mild conditions, but they have not been adapted to industrial processes.[15-19] Lowering both temperature and pressure for WGSR conversion of water and CO to hydrogen and CO_2 is highly desirable.

Here we report initial studies of CO-assisted, acid-induced elimination of hydrogen from Tp′Pt di- and trihydride complexes (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) (Figure 5.1) which are in turn synthesized by WGS chemistry. The resulting Pt(II) carbonyl complexes can then be reoxidized to Pt(IV) polyhydrides thus completing the WGSR in stepwise fashion. Examination of the individual steps of this reaction may provide insight for future catalyst development in the growing field of aqueous organoplatinum chemistry.[20]

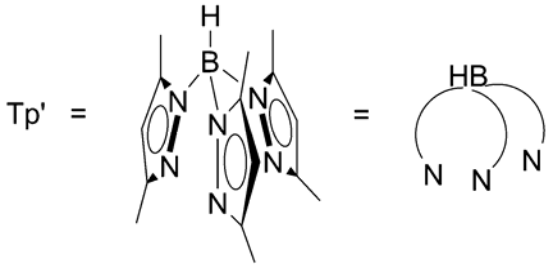
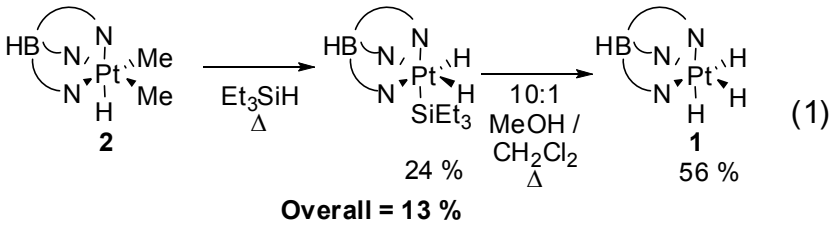


Figure 5.1: Tp′ ligand (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate).

Results and Discussion

Synthesis of Tp′PtH$_3$ (1). In the original synthesis of the Tp′PtH$_3$ (**1**)[21] (eq. 1) heating Tp′PtMe$_2$H (**2**)[22] in HSiEt$_3$ produced the key intermediate Tp′Pt(SiEt$_3$)(H)$_2$ in ca. 20 % yield. Replacement of the triethylsilyl group by a proton was effected by refluxing in MeOH/CH$_2$Cl$_2$. While this method required only two steps from reagent **2**, the product was obtained in a 13 % overall yield. An alternative synthetic route was therefore sought in order to make **1** a viable starting material for future reactions.



A sequence of clean reactions converts Tp′PtMe$_2$H (**2**) into Tp′PtMeH$_2$ (**3**),[23] (eq. 2) and we hypothesized that it might be possible to repeat this sequence to access the trihydride (**1**). This method required the synthesis of Tp′Pt(H)(CO) (**5**) followed by oxidation of **5** in H$_2$O/acetone to form the trihydride **1** in a manner similar to that used by Keinan to synthesize TpPtMeH$_2$ from TpPt(Me)(CO).[24]

Tp′Pt(H)(CO) (**5**) is synthesized by protonation of Tp′PtMeH$_2$ with [H(OEt$_2$)$_2$][BAr′$_4$] [BAr′$_4$ = tetrakis(3,5-trifluoromethylphenyl)borate] at -78 ^{o}C in CH$_2$Cl$_2$ followed by purging the reaction mixture with CO while warming to room temperature. Loss of methane and

trapping with CO generates [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**), which is then deprotonated *in situ* by reaction with NEt_3 at -78 ^oC to form Tp′Pt(H)(CO) (**5**).

Solution phase IR (CH_2Cl_2) for **5** shows one B-H absorption at 2526 cm^{-1} indicating that the Tp′ ligand is bound in κ^3 fashion,[25] one Pt-H absorption at 2216 cm^{-1}, and one CO absorption at 2070 cm^{-1}, suggesting the presence of only one geometric isomer. Most platinum(II) complexes are square planar and hence 4-coordinate, but the π acidity of the CO ligand makes the metal center sufficiently electron deficient here that it adopts a 5-coordinate structure. The closely related complex Tp′Pt(Me)(CO) was shown to present in both κ^2 and κ^3 forms in solution.[26] The analogous TpPt(Me)(CO) complex with no methyls on the pyrazole rings also is fluxional in solution with both 4-coordinate and 5-coordinate geometries easily accessible,[24, 27, 28] but has a solid state structure that is square planar with the Tp binding in a bidentate fashion.[29] X-ray quality crystals of the neutral Tp′Pt(H)(CO) complex **5** were obtained by layering a CH_2Cl_2 solution of **5** with hexanes at 4 °C. The X-ray crystal structure shows Tp′ to be tridentate, and thus the complex is 5-coordinate. The three Pt-N bond lengths of 2.088, 2.139, and 2.489 Å (Figure 5.2) reflect weak binding of the third Tp′ arm and suggest that the geometry of the complex lies between square planar and trigonal bipyramidal. The hydride ligand position was not refined.

Note that the weakly bound third Tp′ arm is approximately *trans* to the vacant site. In other words the weak interaction is positioned axially relative to a square-planar point of departure for this d^8 complex. The strong *trans* influence of the CO ligand produces a Pt-N bond distance of 2.088 Å while the strong *trans* influence of the hydride ligand produces a Pt-N bond distance of 2.139 Å.

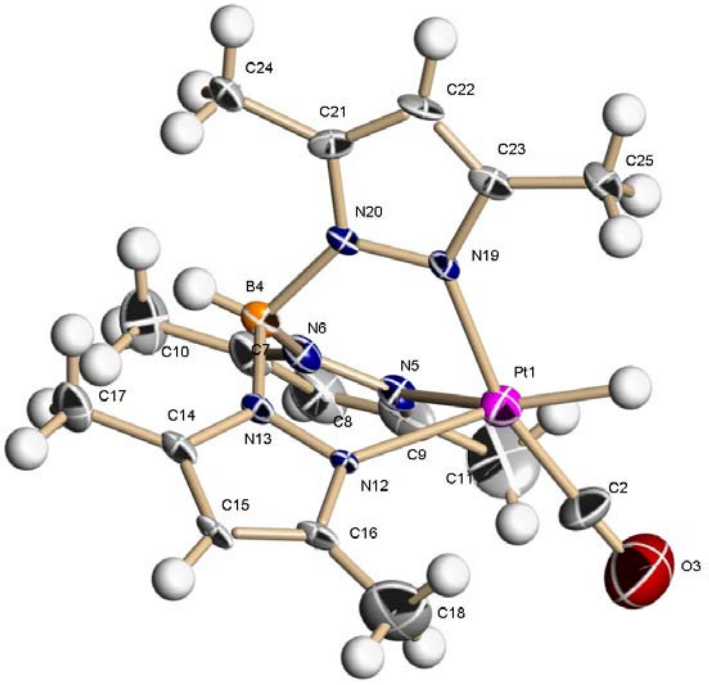
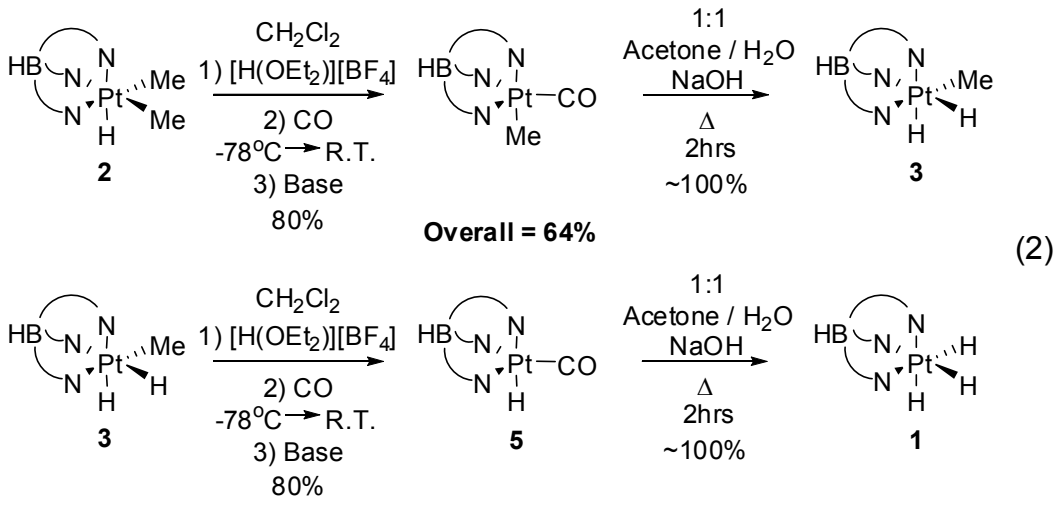


Figure 5.2: X-ray structure of Tp′Pt(H)(CO) (**5**). Ellipsoids are drawn with 50 % probability. Selected bond distances in Angstroms (Å): Pt1-C2 = 1.827, Pt1-N5 = 2.139, Pt1-N12 = 2.489, Pt1-N19 = 2.088, C2-O3 = 1.138. Selected bond angles in degrees (deg): C2-Pt1-N5 = 102.0, C2-Pt1-N12 = 115.4, N5-Pt1-N12 = 81.5, C2-Pt1-N19 = 163.6, N5-Pt1-N19 = 85.5, N12-Pt1-N19 = 79.8.

Reflux of Tp′Pt(H)(CO) (**5**) in acetone/water (1:1) under slightly basic conditions yields Tp′PtH_3 (**1**) quantitatively. This method is analogous to that used to synthesize Tp′$PtMeH_2$ from Tp′Pt(Me)(CO).[23, 24] This reaction likely occurs by a WGS type mechanism in which water or a hydroxide ion attacks the carbonyl carbon forming a CO_2 linkage so that the complex can then lose CO_2 and form the [Tp′Pt(R)H] anion, such that addition of a proton yields Tp′Pt(R)H_2 (R = Me, H). Heating Tp′Pt(H)(^{13}CO) (**5***) in acetone-d_6/D_2O with catalytic NaOH in an NMR tube yielded Na$^{13}CO_3H$ which was converted to $^{13}CO_2$ which was observed by ^{13}C NMR after addition of one drop of HBF_4·Et_2O.

The new synthesis of **1** (Scheme 5.2), a simple extension of the synthesis of the dihydride (**3**), requires four steps, but the overall yield from **1** (64 %) is significantly improved from the two step route (13 %). Many dihydride complexes have been reported in

the literature; most of them are synthesized from hydride sources or from activation of H_2.[6, 30-33] The fact that the hydrides in complexes **3** and **1** come from H_2O is significant because H_2 elimination from these complexes would represent completion of the water gas shift reaction.



(2)

Protonation of Tp′PtH$_3$ (1). In the absence of added ligands, reaction of Tp′PtH$_3$ (**1**) with [H(OEt$_2$)$_2$][BAr′$_4$] at -78 °C in CD_2Cl_2 results in a color change from colorless to light orange, but ^{1}H NMR analysis shows no signals corresponding either to dihydrogen or to the hydride associated with the [κ^2-(HTp′)Pt(H)(solv)][BAr′$_4$] complex which is visible by NMR after loss of methane from the methyl dihydride (**3**).[23] The only species visible by ^{1}H NMR at low temperature is the neutral trihydride reagent. Upon warming to room temperature some dihydrogen loss was detected along with formation of Tp′H and platinum black. The observed H_2 must be formed after dissociation of Tp′H from Pt otherwise the Tp′Pt(II) monohydride cation would be observed. NMR suggests that Tp′PtH$_3$ is difficult to protonate and only a small amount of [HTp′PtH$_3$]$^+$ is ever generated. Typically, not more than 50 % of the starting material is consumed in this reaction.

Dramatically different results are obtained if protonation of Tp′PtH_3 (**1**) is conducted under a CO atmosphere. This reaction ultimately yields [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**), a product compatible with loss of H_2. This result resembles reactivity observed by Keinan and coworkers in their study of $TpPtMeH_2$.[34] They reported H_2 loss from $TpPtMeH_2$ upon addition of PMe_3 at room temperature, but no loss of H_2 without added phosphine even when heated to 70 ^oC. They proposed two possible mechanisms for this process, both involving an initial dissociation of one Tp arm. In one pathway subsequent PMe_3 coordination forms a 6-coordinate species which then eliminates H_2. The second pathway involves formation of a 4-coordinate η^2-H_2 species followed by loss of H_2 and coordination of PMe_3.

Low Temperature NMR Studies. Efforts to probe the mechanism of hydrogen formation in the Tp′PtH_3 system were undertaken. Proton NMR experiments under a CO atmosphere at 193 K show a single initial product upon protonation of the trihydride (**1**): coupled hydride signals appear at δ -12.33 ppm (t, 1H, $^2J_{H\text{-}H}$ = 4.4 Hz, $^1J_{Pt\text{-}H}$ = 1120 Hz) and δ = -17.51 ppm (d, 2H, $^2J_{H\text{-}H}$ = 4.4 Hz, $^1J_{Pt\text{-}H}$ = 1108 Hz) (Figure 5.3). Given the presence of three hydride ligands reflected in the NMR data, we formulate the product as 6-coordinate Pt(IV) carbonyl complex [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (**6**) in which the unique hydride is *trans* to CO and the two equivalent hydrides are *cis* to CO. Similar types of trapping experiments using nitriles have been used to access other cationic Pt(IV) hydride species.[35, 36] Experiments using ^{13}CO gas yield [κ^2-(HTp′)Pt(H)$_3$(^{13}CO)][BAr′$_4$] (**6***). The hydrides of **6*** appear as a doublet of triplets at δ -12.33 ppm (dt, 1H, $^2J_{C\text{-}H}$ = 90 Hz, $^2J_{H\text{-}H}$ = 4.4 Hz, $^1J_{Pt\text{-}H}$ = 1120 Hz) and a doublet of doublets at δ -17.51 ppm (dd, 2H, $^2J_{C\text{-}H}$ = 6 Hz, $^2J_{H\text{-}H}$ = 4.4 Hz, $^1J_{Pt\text{-}H}$ = 1108 Hz). The large $^2J_{C\text{-}H}$ coupling for the hydride at δ -12.33 ppm reinforces the notion that it is located *trans* to CO, and the small ^{13}CO coupling to the hydrides at δ -17.51 ppm

indicates that they are *cis* to CO. As the reaction mixture warms to room temperature, loss of dihydrogen can be detected by ^{1}H NMR spectroscopy as a singlet appears at δ 4.57 ppm, the chemical shift where H_2 appears in CD_2Cl_2 (eq. 3). If the solution is subjected to a freeze pump thaw cycle, this peak disappears. Formation of the H_2 elimination product [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) can be detected by the growth of a hydride peak at -14.64 ppm ($^1J_{Pt\text{-}H}$ = 1122 Hz); the yield is ca. 90%. At low temperatures this process is slow, making it possible to monitor the reaction by NMR.

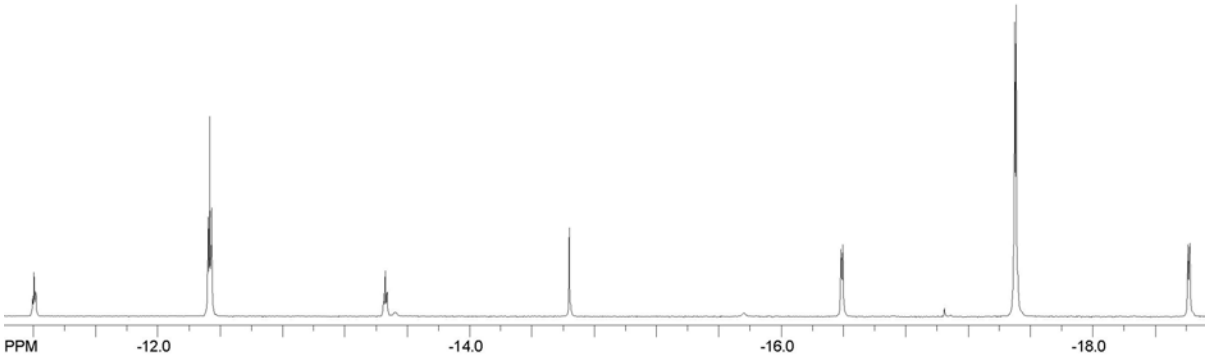
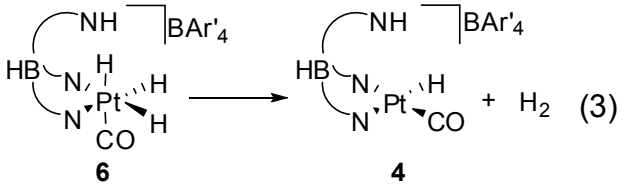


Figure 5.3: 500 MHz ^{1}H NMR spectra (193 K) showing hydride signals for [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (**6**) (t, -12.33; d, -17.51) and [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) (s, -14.64).



6 **4**

Trapping Ligands Other than CO. When similar NMR experiments are performed with α-olefins (ethylene, propylene, 1-butene, or 1-pentene) added to the solution instead of CO gas, H_2 loss is observed at even lower temperatures. No 6-coordinate olefin bound species, analogous to [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′4], is observed by NMR even at 150 K; the observed products are H_2 and [κ^2-(HTp′)Pt(H)(L)][BAr′$_4$] (L = $H_2C{=}CH_2$,[23] $H_2C{=}CHCH_3$, $H_2C{=}CHCH_2CH_3$, $H_2C{=}CHCH_2CH_2CH_3$). With these olefins no 6-coordinate cationic

trihydride adducts are detected as stable intermediates; likely the olefin trihydride cations are higher in energy than the CO trihydride cation and cannot be seen by NMR. This change in reaction coordinate precludes a kinetic study of the rate of disappearance of an intermediate. No reaction with internal olefins is observed, probably because of their increased steric bulk.

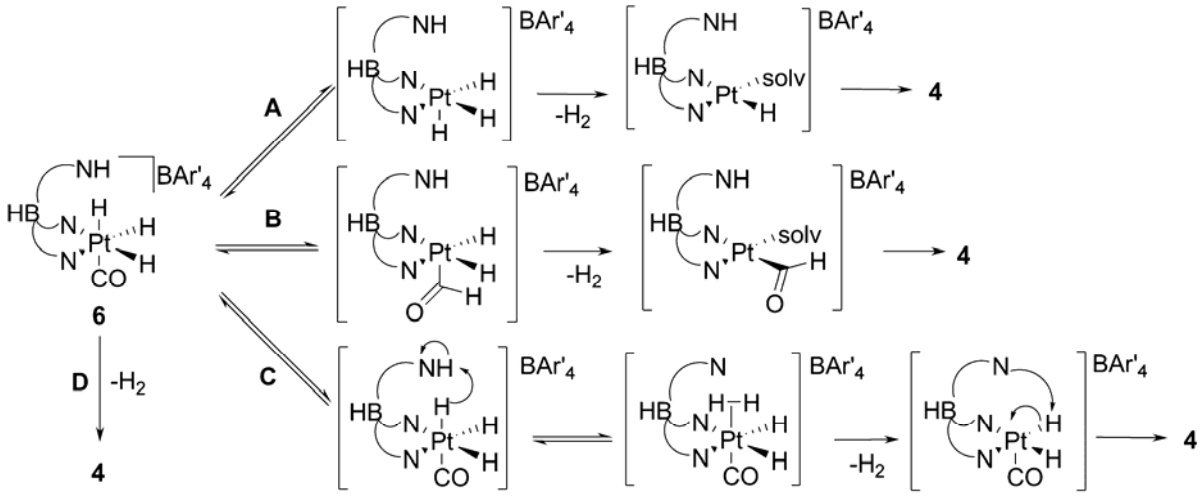
When acetonitrile is used as a trapping ligand after protonation, the 6-coordinate nitrile-bound species, [κ^2-(HTp′)Pt(H)$_3$(NCMe)][BAr′$_4$] (**7**), is observed by NMR at low temperature. The cationic acetonitrile adduct has hydride signals in the ^{1}H NMR spectrum at δ -19.94 ppm (s, $^1J_{Pt\text{-}H}$ = 1166 Hz, 2H, Pt-*H*), and at δ -24.08 ppm (s, $^1J_{Pt\text{-}H}$ = 1423 Hz, 1H, Pt-*H*). Upon warming to room temperature no H_2 loss is observed and the only platinum species visible by NMR is the starting material, neutral Tp′PtH$_3$ (ca. 50%) with the rest of the material having undergone decomposition.

Addition of either PMe_3 or PMe_2Ph as the trapping reagent results in a small but detectable amount of H_2 loss, but undesirable side reactions of the phosphines with acid precluded detailed study. Use of 3,5-dimethylphenyl isocyanide or isopropyl isocyanide as trapping ligands after protonation results in observation of a 6-coordinate species. Upon warming only a small amount of hydrogen loss is observed; the major species observable at room temperature is starting material. The isocyanide ligands may be too bulky to coordinate to the metal strongly, or they may be sufficiently basic to buffer the solution acidity.

Mechanistic Studies. Although we have shown that CO binds to the trihydride before H_2 elimination to form complex **6,** there are still several pathways by which H_2 elimination could occur from this complex (scheme 5.1). Most reductive eliminations from octahedral Pt(IV) occur via coordinatively unsaturated 5-coordinate intermediates;[26, 37-44]

there are multiple ways in which a 5-coordinate intermediate could be implicated here. Pathway **A** is pre-dissociation of CO from **6**, elimination of H_2, then recoordination of CO; pathway **B** is migration of a hydride to CO, elimination of H_2, followed by deinsertion of the CO from the formyl ligand to yield the Pt(II) product **4**. Another possibility which does not involve direct reductive elimination from Pt(IV) is pathway **C** in which one of the hydrides couples with the proton on nitrogen, H_2 is lost, and the Pt(IV) dihydride is deprotonated by nitrogen yielding complex **4**. The simplest possibility is direct elimination of H_2 from the 6-coordinate complex **6**, pathway **D**. Yet another possibility is dechelation of a Tp′ arm from **6** resulting in a 5-coordinate intermediate which could eliminate H_2, followed by coordination of the arm.

Scheme 5.1: Possible pathways for H_2 elimination from trihydride carbonyl cation (**6**).



Experiments were conducted to probe whether or not CO binding is reversible. Protonation of **1** under ^{12}CO followed by removal of gas via three freeze, pump, thaw cycles and refilling with ^{13}CO yields a significant amount of the 6-coordinate trihydride-^{13}CO complex, indicating facile exchange between bound and free CO gas in solution. The reversibility of the hydrogen elimination reaction was also investigated. Protonation of

Tp′PtD_3 (**1-*d*$_3$**) at low temperature under CO and H_2 leads to elimination of D_2 with no incorporation of H into the platinum product. No HD or Pt-D formation is detected from stirring [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) in CD_2Cl_2 under D_2 at room temperature, indicating that H_2 loss is irreversible.

Experiments at various CO pressures and constant temperature provide further support for facile reversible loss of CO. An increase in the rate of hydrogen production with increasing CO pressure is observed. Elimination of hydrogen from the five coordinate product of CO loss from **6** would yield an inverse rate relationship with CO pressure. This qualitative rate data, coupled with the fact that no H_2 loss is seen in the absence of CO, allows us to rule out pathway **A** as a possibility. Protonation of Tp′PtH_3 (**1**) with [$D(OEt_2)_2$][BAr′$_4$] or protonation of Tp′PtD_3 (**1-*d*$_3$**) with [$H(OEt_2)_2$][BAr′$_4$] under CO resulted in no elimination of HD, ruling out Pathway **C**.

Pathway **B**, the insertion-deinsertion pathway, could explain why H_2 loss is faster using olefins than CO. Insertion of olefins into metal hydride bonds to form alkyl ligands is typically facile,[45, 46] while CO insertion to form stable formyl ligands is unlikely.[47, 48] Attempted synthesis of Tp′$Pt(H)_2$(CHO) from Tp′Pt(H)(CO) by stepwise H^-, H^+ addition yielded the desired product along with Tp′PtH_3 as determined by ^{1}H NMR spectroscopy. This illustrates that Tp′$Pt(H)_2$(CHO) does not lose H_2 but rather can lose CO to form the neutral trihydride **3**. The formyl hydride anion [Tp′Pt(H)(CHO)][K] displays coupled formyl proton and hydride signals at 13.93 ($^2J_{Pt\text{-}H}$ = 268 Hz, $^3J_{H\text{-}H}$ = 7 Hz), and -16.09 ($^2J_{Pt\text{-}H}$ = 1620 Hz, $^3J_{H\text{-}H}$ = 7 Hz) respectively (ppm, THF-d_8, 283K). The neutral formyl dihydride Tp′$Pt(H)_2$(CHO) displays coupled formyl proton and hydride signals at 12.85 ($^2J_{Pt\text{-}H}$ = 182

Hz, $^{3}J_{H\text{-}H}$ = 4 Hz), and -17.96 ($^{2}J_{Pt\text{-}H}$ = 1340 Hz, $^{3}J_{H\text{-}H}$ = 4 Hz) respectively (ppm, THF-d_8, RT).

In the case of ethylene addition, if a 6-coordinate trihydride olefin cation is formed it could undergo insertion leading to a five coordinate ethyl dihydride cation. This intermediate would seem more likely to lose ethane than hydrogen, based on known reactions with $[HTp'PtMeH_2]^+$.[23] The NMR for $Tp'PtH_3$ plus acid and ethylene contains a large signal due to hydrogen, but no signal for ethane is detected, so an ethyl dihydride intermediate seems unlikely. If a 3-coordinate platinum ethyl species resulted from H_2 elimination, it could be trapped by excess ethylene, but we see no evidence for a platinum ethyl ethylene complex. Reaction of $[D(OEt_2)_2][BAr'_4]$ with $Tp'PtD_3$ (**1-*d*$_3$**) under C_2H_4 ethylene resulted in $[Tp'DPt(D)(C_2H_4)][BAr'_4]$ with no incorporation of D into the ethylene ligand and no formation of a platinum hydride. This evidence rules out pathway **B** as a viable mechanism for H_2 loss. Dechelation of a Tp′ arm to form a reactive 5-coordinate intermediate is kinetically indistinguishable from direct elimination; however dechelation of Tp′ from Pt(IV) is unprecedented at the low temperatures used in these reactions. Since the platinum center is electron deficient (ν_{co} = 2130 cm^{-1}) the Tp′ arms are probably tightly bound. Direct elimination of H_2 from the cationic 6-coordinate intermediate **6,** pathway **D**, remains the mechanism of choice.

Kinetic Studies. Kinetic experiments performed with ^{1}H NMR spectroscopy between 225 K and 245 K monitored the disappearance of the hydride signals of the platinum(IV)(CO) adduct (**6**). Disappearance of intermediate **6** and formation of platinum(II) product **4** display first order kinetics over several half-lives, probably because the concentration of CO in solution is effectively constant. The rate at 239 K under 18.7 psi CO

was found to be 4 x 10^{-4} s^{-1}, giving rise to a $\Delta G^{\ddagger}$ value of 17.2 (± 0.1) kcal/mol. An Eyring plot (Figure 5.4) was constructed using rate constants from this admittedly narrow temperature range at 18.7 psi CO; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 23.0 (± 1) kcal/mol and 24.5 (± 4) eu, respectively.

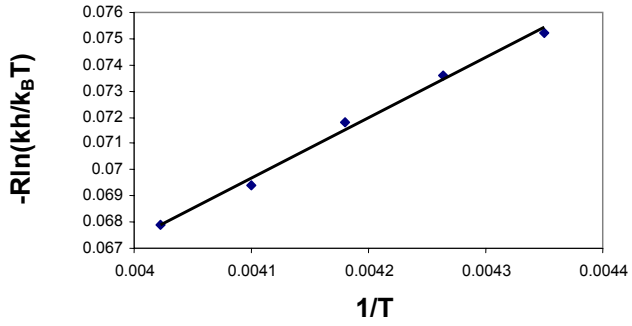


Figure 5.4: Eyring plot of H_2 loss from **6** under 18.7 psi CO.

Measurement of the rate of D_2 loss from [κ^2-(HTp′)Pt(D)$_3$(CO)][BAr′$_4$] (**6-*d*$_3$**), formed by protonation of Tp′PtD$_3$ (**1-*d*$_3$**), at 239 K under 18.7 psi CO allows for calculation of an isotope effect of k_H/k_D = 2.2 (± 0.1) by comparison with the rate of H_2 loss from **6** under the same conditions. Isotope effects of similar magnitude have been reported for H_2 elimination from other systems.[6, 49, 50] It has been demonstrated previously that oxidative addition of H_2 to a metal center results in an *inverse* equilibrium isotope effect,[49-55] and this has also been shown to hold for the coordination of H_2 in η^2-H_2 complexes.[56-59] Because of the stronger affinity of the metal to bind D_2 than H_2 a *normal* isotope would be expected for dissociation of D_2 relative to H_2 as is observed in this case.

The normal isotope effect and positive entropy of transition state formation suggest that the barrier to reductive coupling of H_2 is lower than the barrier to dissociation of H_2 (Figure 5.5). In such a case the transition state is becoming less ordered resulting in positive

entropy of activation. It has been shown that dissociation of H_2 can account for a normal isotope effect of this magnitude (*vida supra*). A lower barrier for reductive coupling to form H_2 in the coordination sphere than for dissociation of H_2 is consistent with the mechanism proposed for elimination of CH_4 from Tp′Pt systems. The barrier for reductive coupling of methane was previously found to be lower than the energy barrier for dissociation of methane.[23, 26, 34, 41, 60] A reaction profile of this type would indicate that the observed isotope effect of 2.2 is a combination of a kinetic isotope effect due to the irreversible dissociation of H_2, a secondary kinetic effect due to the additional M-D bond, and an equilibrium effect from the reversible reductive coupling.

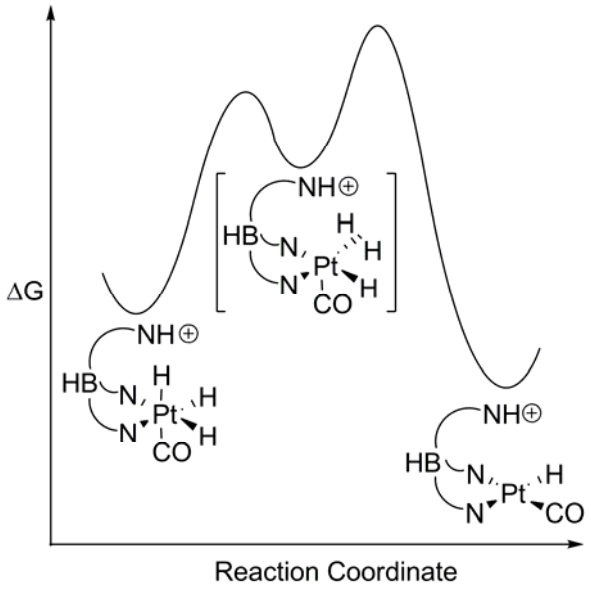


Figure 5.5: Possible reaction coordinate diagram for elimination of H_2 from **6**.

π-Acid Induced H_2 Elimination? A possible explanation for generation of hydrogen in the presence of CO is that with an electron-withdrawing CO ligand bound to platinum there may be too little electron density at the metal to maintain a Pt(IV) dihydride formulation, and formation of an η^2-H_2 Pt(II) species is favored. If the metal is electron rich a dihydride will be favored, but with decreasing electron density an η^2-H_2 ligand will be more

likely to form. The protonated CO trihydride complex [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (**6**) is highly electron-deficient as judged by the C-O stretching frequency determined by *in situ* FTIR spectroscopy (ν_{CO} = 2130 cm^{-1}).

The surprising low temperature hydrogen generation with ethylene present could be due to the larger size of ethylene relative to CO, perhaps increasing unfavorable steric interactions with the Tp′ ligand and increasing the energy of the 6-coordinate adduct. It could also be that the ethylene π* orbitals have more effective overlap with a single filled metal dπ orbital, thus making ethylene a single faced π-acid uniquely suited to increase the rate of H_2 elimination. There is relevant experimental evidence regarding ethylene as a strong single-faced π-acid. The complexes Tp′Pt(Me)(CO)[26] and Tp′Pt(Ph)(CO)[61] both exhibit solution IR and NMR data consistent with rapid interconversion between κ^2 and κ^3 binding modes of Tp′. However, the analogous ethylene complexes, Tp′Pt(Me)(H_2C=CH_2)[26] and Tp′Pt(Ph)(H_2C=CH_2)[61], have spectroscopic data consistent with only κ^3 bound Tp′. These complexes are aptly described as octahedral Pt(IV) metallocyclopropane complexes,[26] and this is reflected in the crystal structure of Tp′Pt(Ph)(H_2C=CH_2) that has Pt-N bond lengths of 2.140, 2.168, and 2.220 Å.[61] In comparison the bond lengths for Tp′Pt(H)(CO) are 2.088, 2.139, and 2.489 Å clearly showing that the third pyrazolyl is bound much more weakly, and thus indicating that this complex is more similar to square planar d^8 Pt(II), than to octahedral Pt(IV).

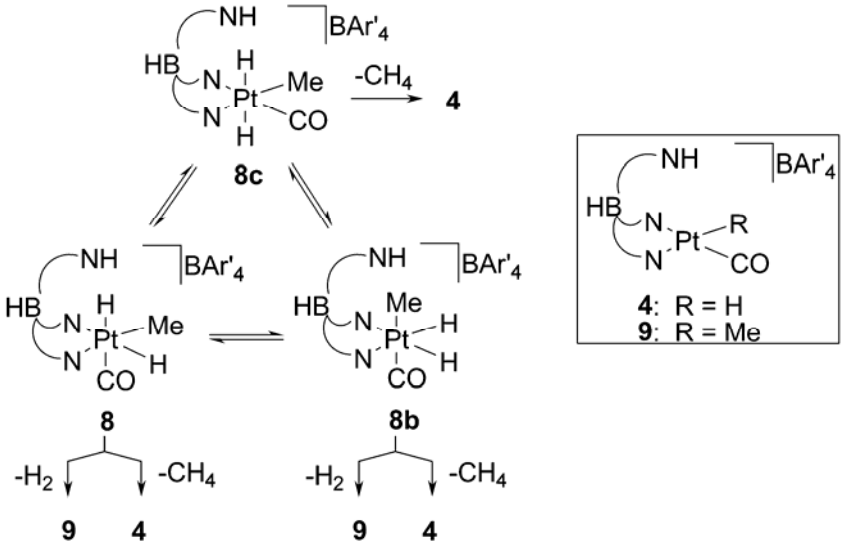
Protonation of Tp′PtMeH$_2$ (3). When reactions analogous to the protonation of trihydride (**1**) are performed with the methyl dihydride (**3**) under CO, it is possible to observe similar 6-coordinate species, namely [κ^2-(HTp′)Pt(Me)(H)$_2$(CO)][BAr′$_4$] (**8**) and [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8***). In the absence of added ligand, protonation of

Tp′PtMeH$_2$ induces rapid methane loss even at 193 K.[26] However, by having CO in solution before acidification it was possible to trap the 5-coordinate intermediate that leads to methane loss. Complex **8** has hydride signals at δ -12.33 (d, $^2J_{H\text{-}H}$ = 5.5 Hz, $^1J_{Pt\text{-}H}$ = 1166 Hz) and δ -17.84 (d, $^2J_{H\text{-}H}$ = 5.5 Hz, $^1J_{Pt\text{-}H}$ = 1193 Hz). The ^{13}C labeled carbonyl complex **8*** resembles complex **6*** in that the downfield hydride has a 94 Hz $^2J_{C\text{-}H}$ coupling while the upfield signal has only a 3.2 Hz ^{13}C-H coupling. No ^3J coupling to the CO carbon is detected for the methyl protons. This data indicates that **8** has one hydride *trans* to CO, leaving the other hydride and the methyl ligand *cis* to CO. This octahedral species, **8**, appears to lose either H_2 or CH_4 to form either **4** or [κ^2-(HTp′)Pt(Me)(CO)][BAr′$_4$] (**9**)[26]. This result is surprising because in previous experiments we observed only loss of CH_4 from Tp′PtMeH$_2$ (**3**) upon protonation and trapping with an added ligand. However, the solution of protonated **3** in those experiments was allowed to warm slightly before trapping ligand was added. It has been shown previously that complex **3** will easily lose methane from the 5-coordinate species when protonated in the absence of trapping ligand.[23] When CO is present, the protonated species is trapped. Either CH_4 or H_2 can be eliminated from the resulting cationic 6-coordinate species, with a ratio of CH_4 to H_2 loss about ~5:1. Complex **8** has a carbonyl *trans* to hydride configuration that is similar to the (dppe)Ir(Et)(H)$_2$(CO) complex reported by Eisenberg and coworkers, from which C-H and H-H coupling and elimination are competitive,[6] as in this case.

There is a small amount of another isomer of **8** present (**8b**) (Scheme 5.5) which has a hydride signal at δ -16.72 (s, $^1J_{Pt\text{-}H}$ = 1201 Hz) and a methyl signal at δ 0.53 (s, $^2J_{Pt\text{-}H}$ = 55 Hz). Presumably this is the isomer with CO *trans* to methyl. This isomer formulation is further confirmed when ^{13}CO is used: the $^2J_{C\text{-}H}$ coupling from the ^{13}CO to the two equivalent

hydrides is only 4 Hz, indicating that they are both located *cis* to CO. Complexes **8** and **8b** slowly convert to a third species which has a single hydride signal at δ -17.05 (s, $^{1}J_{Pt\text{-}H}$ = 1212 Hz). This third species (**8c**), the most thermodynamically stable of the three isomers, eventually becomes the major species in solution. Methane loss, but not dihydrogen loss, is observed from complex **8c**. The hydride signal for **8c** shows 4 Hz $^{2}J_{C\text{-}H}$ coupling when ^{13}CO is used so *cis* CO, hydride ligands are indicated. An attractive geometry with CO *trans* to N for **8c** is presented in Scheme 5.2. There is precedence for a *trans* dihydride carbonyl structure being thermodynamically favored over a *cis* dihydride carbonyl structure,[62] but this formulation requires coincidental equivalence of the *trans* hydride NMR signals in order to fit the limited data available for **8c** at this point. Only methane loss seems feasible from a trans-dihydride isomer in accord with our observations.

Scheme 5.2: Isomerization following protonation of Tp′PtMeH$_2$ (**3**) under CO.



Protonation of Tp′PtMeD$_2$ under CO at 193K results in immediate isotope scrambling in the 6-coordinate cationic carbonyl species. Observation of CH_3, CH_2D, and CHD_2 isotopomers of the H_2 loss product [κ^2-(HTp′)Pt(Me)(CO)][BAr′$_4$] (**9**) upon warming

indicates that this scrambling is a result of reversible reductive coupling to form methane in the coordination sphere. The isotope scrambling is complete in the initial ^{1}H NMR, thus it was not possible to monitor this process by NMR.

If the methyl dihydride is protonated at 193K and CH_3CN is quickly added it is again possible to trap the 5-coordinate methyl dihydride cation and form the 6-coordinate cation [κ^2-(HTp′)Pt(Me)(H)$_2$(NCMe)][BAr′$_4$] (**10**) which has inequivalent hydride signals at -20.67 (s, $^1J_{Pt\text{-}H}$ = 1265 Hz, 2H, Pt-*H*) and -24.08 (s, $^1J_{Pt\text{-}H}$ = 1496 Hz, 1H, Pt-*H*). Warming of this complex results in elimination of methane only and formation of [κ^2-(HTp′)Pt(H)(NCMe)][BAr′$_4$][23], once again showing the necessity of a π-acid for the elimination of H_2.

Conclusions

Low temperature NMR spectra reported here show that after protonation opens a coordination site carbon monoxide adds to Pt, and reductive elimination of H_2 occurs from the resulting 6-coordinate complex. The isotope effect (2.2 ± 0.1) and reaction entropy (24.5 ± 4 eu) are consistent with a mechanism involving reversible reductive coupling to form coordinated dihydrogen followed by rate limiting irreversible dissociation of dihydrogen. Significant hydrogen elimination occurs when either CO or ethylene is used as a trapping ligand. We postulate that the π-acid character of these ligands withdraws sufficient electron density from the metal so that it is reluctant to support the platinum(IV) dihydride structure. Surprisingly, elimination of H_2 occurs at lower temperatures with ethylene than with CO even though CO would typically be considered the stronger π-acid. However, examination of the structures of Tp′Pt(R)CO (R = Me, H) complexes compared to the structures of Tp′Pt(R)(H_2C=CH_2) (R = Me, Ph) provides relevant data. The Pt(II) carbonyl complexes

have only weak coordination of the third Tp′ arm and are thus more similar to Pt(II) square planar complexes. The Tp′Pt(II) ethylene complexes have strong coordination of all three Tp′ arms and resemble octahedral Pt(IV) complexes. For these Tp′Pt complexes the single faced π-acid ethylene ligand seems to be a uniquely effective π-acid. This feature may explain why it facilitates H_2 loss at such low temperatures compared to the cylindrically symmetrical CO π-acid. Also, it is important to note that the neutral hydride complexes were generated by WGS chemistry and thus elimination of H_2 from $Tp'PtH_3$ represents net production of H_2 from H_2O and CO, a stoichiometric water gas shift reaction.

Experimental

Materials and Methods. All reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was flame dried under vacuum and cooled under N_2 before use. Diethyl ether, methylene chloride, acetonitrile, toluene, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[63] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Methylene chloride-d_2 was vacuum transferred from calcium hydride and degassed by several freeze-pump-thaw cycles.

$Tp'PtMe_2H$ (**1**)[22], $Tp'PtMeH_2$ (**2**)[23], $Tp'PtMeD_2$ (**2-*d*$_2$**)[23], $Tp'PtPhH_2$[64], $[HTp'Pt(SiEt_3)H_2][BAr'4]$[65], and $[H(OEt_2)_2][BAr'_4]$[66] were synthesized using published procedures. Carbon monoxide was obtained from Matheson Gas Products, Inc. and ^{13}C labeled carbon monoxide from Cambridge Isotope Laboratories, Inc. All other reagents were used as received.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 MHz, Bruker Avance 400 MHz, or Bruker DRX 500MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000.

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, 193 K, δ): 7.77 (br, 8H, *o*-Ar'), 7.60 (br, 4H, *p*-Ar'). ^{13}C NMR (CD_2Cl_2, 193 K, 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}).

Tp′PtH$_3$ (1). Tp′Pt(H)(CO) (**5**) (78 mg, 0.149 mmol) was placed in a Schlenk flask and purged with N_2. A 1:1 mixture of acetone/H_2O (50 mL) was then added along with NaOH (5 drops). The solution was refluxed for 2 hours and then cooled to 0 °C. A white powder of Tp′PtH$_3$ was filtered from the mixture and dried under vacuum. Yield: 73 mg (98 %). Tp′PtD$_3$ (**1-*d*$_3$**) was synthesized in an analogous fashion using D_2O/acetone-d_6. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 5.85 (s, 3H, Tp′C*H*), 2.38, 2.12 (s, 9H, Tp′CH_3), -20.03 (s, $^1J_{Pt\text{-}H}$ = 1168 Hz, 1H, Pt-*H*).

[κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (4). In the drybox, Tp′PtMeH$_2$ (**3**) (100 mg, 0.196 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (223 mg, .213 mmol) were added to a 100 mL Schlenk flask. The flask was capped with a septum, removed from the box, and cooled to -78 °C. CH_2Cl_2 (15 mL) was syringed into the flask and was allowed to stir for 5 minutes. The cold bath was removed and CO was bubbled into solution for 30 minutes. The solvent was removed in vacuo. The product was recrystallized from CH_2Cl_2/pentane at -30°C, yielding colorless crystals. Yield: 217 mg (80 %). [κ^2-(HTp′)Pt(H)(^{13}CO)][BAr′$_4$] (**4***) was synthesized in an

analogous fashion using ^{13}CO gas. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 9.59 (s, 1H, pz′N*H*), 6.8 6.14, 6.14 (s, 1H each, Tp′C*H*), 2.42, 2.42, 2.34, 2.32, 2.32, 1.77 (s, 3H each, Tp′CH_3), -14.69 (s, $^{1}J_{Pt\text{-}H}$ = 1120 Hz, 1H, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 298 K, δ): 163.0 ($^{1}J_{Pt\text{-}C$ = 1790Hz, Pt-*C*O); 155.6, 154.0, 150.8, 150.8, 149.8, 145.3 (HTp′*C*CH_3); 110.6, 108.9, 108.8 (HTp′*C*H); 16.7, 15.2, 13.3, 13.0, 11.5, 11.3 (HTp′*C*H_3). IR (CH_2Cl_2): ν_{BH} = 2524 cm^{-1}, ν_{PtH} = 2225 cm^{-1}, ν_{CO} = 2107 cm^{-1}. Anal. Calcd for $C_{48}H_{36}N_6F_{24}B_2OPt$: C, 41.61; H, 2.62; N, 6.07. Found: C, 41.62; H, 2.66; N, 6.18.

Tp′Pt(H)(CO) (5). [κ^2-(HTp′)Pt(H)(CO)][BAr′$_4$] (**4**) (217 mg, 0.157 mmol) was dissolved in CH_2Cl_2 mixture and run down an alumina column. The solvent was removed and the resulting white powder was crystallized in 10:1 hexanes/CH_2Cl_2 giving colorless X-ray quality crystals. Yield: 78 mg (95 %). ^{1}H NMR (CD_2Cl_2, 298 K, δ): 5.85 (s, 3H, Tp′C*H*), 2.33, 2.26 (s, 9H, Tp′CH_3), -15.95 (s, $^{1}J_{Pt\text{-}H}$ = 1057 Hz, 1H, Pt-*H*). IR (CH_2Cl_2): ν_{BH} = 2526 cm^{-1}.,$\nu_{Pt\text{-}H}$ = 2216 cm^{-1}, ν_{CO} = 2070 cm^{-1}. ^{13}C NMR (CD_2Cl_2, 193 K, δ): 165.1 (Pt-*C*O), 149.4 ($J_{Pt\text{-}C}$ = 38 Hz, Tp′*C*CH_3), 144.9 (Tp′*C*CH_3), 105.9 ($^{3}J_{Pt\text{-}C}$ = 14 Hz, Tp′*C*H), 15.3 ($J_{Pt\text{-}C}$ = 28 Hz, Tp′C*C*H_3), 12.8 (Tp′C*C*H_3). Anal. Calcd for $C_{16}H_{23}N_6BOPt$: C, 36.86; H, 4.45; N, 16.12. Found: C, 36.74; H, 4.46; N, 15.88.

In Situ Generation of [κ^2-(HTp′)Pt(H)$_3$(CO)][BAr′$_4$] (6). Tp′PtH_3 (**1**) (10 mg, 0.02 mmol) and [H(OEt_2)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. The tube was purged and filled with the desired pressure of CO 3 times. It was cooled to -78 ^{o}C and CD_2Cl_2 (0.7 mL) was added. It was then placed in the NMR with the probe cooled to 193 K. [κ^2-(HTp′)Pt(D)$_3$(CO)][BAr′$_4$] (**6-*d*$_3$**) was synthesized in an analogous fashion using Tp′PtD_3 (**1-*d*$_3$**). [κ^2-(HTp′)Pt(H)$_3$(^{13}CO)][BAr′$_4$] (**6***) was synthesized in an analogous fashion using

^{13}CO gas. ^{1}H NMR (CD_2Cl_2, 193 K, δ): 9.76 (s, 1H, pz′N*H*), 6.15, 6.15, 6.07 (s, 1H, Tp′C*H*), 2.40, 2.40, 2.24, 2.20, 2.20, 1.46 (s, 3H, Tp′CH_3), -12.33 (t, $^{2}J_{H\text{-}H}$ = 5 Hz, $^{1}J_{Pt\text{-}H}$ = 1126 Hz, 1H, Pt-*H*), -17.51 (d, $^{2}J_{H\text{-}H}$ = 5 Hz, $^{1}J_{Pt\text{-}H}$ = 1114 Hz, 1H, Pt-*H*). IR (CH_2Cl_2): ν_{BH} = 2522 cm^{-1}, ν_{CO} = 2130 cm^{-1}. Spectral data for [κ^2-(HTp′)Pt(D)$_3$(CO)][BAr′$_4$] (**6-*d*$_3$**). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 9.76 (s, 1H, pz′N*H*), 6.15, 6.15, 6.07 (s, 1H, Tp′C*H*), 2.40, 2.40, 2.24, 2.20, 2.20, 1.46 (s, 3H, Tp′CH_3), -12.33 (t, $^{2}J_{H\text{-}H}$ = 5 Hz, $^{1}J_{Pt\text{-}H}$ = 1126 Hz, 1H, Pt-*H*), -17.51 (d, $^{2}J_{H\text{-}H}$ = 5 Hz, $^{1}J_{Pt\text{-}H}$ = 1114 Hz, 1H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(H)$_3$(^{13}CO)][BAr′$_4$] (**6***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 9.76 (s, 1H, pz′N*H*), 6.15, 6.15, 6.07 (s, 1H, Tp′C*H*), 2.40, 2.40, 2.24, 2.20, 2.20, 1.46 (s, 3H, Tp′CH_3), -12.33 (dt, $^{2}J_{C\text{-}H}$ = 90 Hz, $^{2}J_{H\text{-}H}$ = 5 Hz, $^{1}J_{Pt\text{-}H}$ = 1126 Hz, 1H, Pt-*H*), -17.51 (dd, $^{2}J_{C\text{-}H}$ = 4 Hz, $^{2}J_{H\text{-}H}$ = 5 Hz, $^{1}J_{Pt\text{-}H}$ = 1114 Hz, 1H, Pt-*H*). ^{13}C NMR (CD_2Cl_2, 193 K, δ): 171.0 (dt, $^{1}J_{Pt\text{-}C}$ = 570 Hz, $^{2}J_{C\text{-}H\ trans}$ = 90 Hz, $^{2}J_{C\text{-}H\ cis}$ = 4 Hz, *C*O).

In Situ Generation of [κ^2-(HTp′)Pt(H)$_3$(NCCH$_3$)][BAr′$_4$] (7). Tp′PtH$_3$ (**1**) (10 mg, 0.02 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. It was then cooled to -78 °C and CD_2Cl_2 (0.7 mL) was added. Acetonitrile (6.5 μL, 0.2 mmol) was syringed in and the tube was shaken, it was then placed in the NMR at 193 K. ^{1}H NMR (CD_2Cl_2, 193 K, δ): 9.77 (s, 1H, pz′N*H*), 6.10, 6.10, 6.04 (s, 1H, Tp′C*H*), 2.39, 2.39, 2.26, 2.26, 2.22, 2.17, 1.48 (s, 3H, Tp′CH_3, NCCH_3), -19.94 (s, $^{1}J_{Pt\text{-}H}$ = 1166 Hz, 2H, Pt-*H*), -24.08 (s, $^{1}J_{Pt\text{-}H}$ = 1423 Hz, 1H, Pt-*H*).

In Situ Generation of [κ^2-(HTp′)Pt(Me)(H)$_2$(CO)][BAr′$_4$] (8). Tp′PtMeH$_2$ (**3**) (10 mg, 0.02 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. The tube was

purged and filled with the desired pressure of CO 3 times. It was cooled to -78 °C and CD_2Cl_2 (0.7 mL) was added. It was then placed in the NMR with the probe cooled to 193 K. [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8***) was synthesized in an analogous fashion using ^{13}CO gas. ^{1}H NMR (CD_2Cl_2, 193 K, δ): 10.01 (s, 1H, pz′N*H*), 6.10, 6.09, 6.09 (s, 1H, Tp′C*H*), 2.37, 2.36, 2.27, 2.26, 2.15, 1.49 (s, 3H, Tp′CH_3), -12.33 (d, $^2J_{H\text{-}H}$ = 5.5 Hz, $^1J_{Pt\text{-}H}$ = 1166 Hz, 1H, Pt-*H*), -17.84 (d, $^2J_{H\text{-}H}$ = 5.5 Hz, $^1J_{Pt\text{-}H}$ = 1193 Hz, 1H, Pt-*H*). IR (CH_2Cl_2): ν_{BH} = 2522 cm^{-1}, ν_{CO} = 2124 cm^{-1}. Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 10.01 (s, 1H, pz′N*H*), 6.10, 6.09, 6.09 (s, 1H, Tp′C*H*), 2.37, 2.36, 2.27, 2.26, 2.15, 1.49 (s, 3H, Tp′CH_3), -12.33 (dd, $^2J_{C\text{-}H}$ = 94 Hz, $^2J_{H\text{-}H}$ = 5.5 Hz, $^1J_{Pt\text{-}H}$ = 1166 Hz, 1H, Pt-*H*), -17.84 (dd, $^2J_{C\text{-}H}$ = 3.2 Hz, $^2J_{H\text{-}H}$ = 5.5 Hz, $^1J_{Pt\text{-}H}$ = 1193 Hz, 1H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(CO)][BAr′$_4$] (**8b**). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 0.53 (s, $^2J_{Pt\text{-}H}$ = 55 Hz, 3H, Pt-Me), -16.72 (s, $^1J_{Pt\text{-}H}$ = 1201 Hz, 2H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8b***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): 0.53 (s, $^2J_{Pt\text{-}H}$ = 55 Hz, 3H, Pt-Me), -16.72 (d, $^2J_{C\text{-}H}$ = 4 Hz, $^1J_{Pt\text{-}H}$ = 1201 Hz, 2H, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(CO)][BAr′$_4$] (**8c**). ^{1}H NMR (CD_2Cl_2, 193 K, δ): -17.05 (s, $^1J_{Pt\text{-}H}$ = 1212 Hz, Pt-*H*). Spectral data for [κ^2-(HTp′)Pt(Me)(H)$_2$(^{13}CO)][BAr′$_4$] (**8c***). ^{1}H NMR (CD_2Cl_2, 193 K, δ): -17.05 (d, $^2J_{C\text{-}H}$ = 3.7 Hz, $^1J_{Pt\text{-}H}$ = 1212 Hz, Pt-*H*).

In Situ Generation of [κ^2-(HTp′)Pt(Me)(H)$_2$(NCCH$_3$)][BAr′$_4$] (10). Tp′PtMeH$_2$ (**3**) (10 mg, 0.02 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (23 mg, 0.02 mmol) were added to an NMR tube in the drybox. The tube was capped with a septum and removed from the box. It was then cooled to -78 °C and CD_2Cl_2 (0.7 mL) was added. Acetonitrile (6.5 μL, 0.2 mmol) was syringed in and the tube was shaken, it was then placed in the NMR at 193 K. ^{1}H NMR (CD_2Cl_2, 193 K, δ): 10.56 (s, 1H, pz′N*H*), 6.04, 6.03, 6.03 (s, 1H, Tp′C*H*), 2.34, 2.34, 2.30,

2.30, 2.22, 2.20, 1.45 (s, 3H, Tp′CH_3, NCCH_3), -20.67 (s, $^1J_{Pt\text{-}H}$ = 1265 Hz, 1H, Pt-*H*), -24.08 (s, $^1J_{Pt\text{-}H}$ = 1496 Hz, 1H, Pt-*H*).

Kinetic Studies. Complex **6** was prepared in situ as described above, then the NMR spectrometer was adjusted to the desired temperature and ^{1}H NMR spectra were taken after specific time intervals. The hydride peaks for 6 were integrated relative to the solvent peak. The data were plotted as a function of ln(integration)/(initial integration) vs. time and resulted in a straight line from which the pseudo first order rate constant was determined. The kinetic isotope effect was determined by comparison of the rate of decay of **6** and **6-*d*$_3$** at 239 K and 18.7 psi CO. The rate of decay of **6-*d*$_3$** was monitored by integration of one of the Tp′ methyl peaks relative to the solvent peak.

Crystallographic Data for 5.

Table 5.1. Crystal data and structure refinement for **5**.

Complex	**5**
Empirical Formula	$C_{16}H_{23}BN_6OPt$
Mol wt	521.30
Temperature	173 K
Wavelength	0.71073 Å
Cryst Syst	Monoclinic
Space Group	$P2_1/n$
a, Å	13.5767 (5)
b, Å	7.8292 (3)
c, Å	18.9222 (6)
α, deg	90
β, deg	110.744 (2)
γ, deg	90
Vol. Å3	1880.94 (12)
Z	4
Density (calculated)	1.84 Mg/m^3
μ, mm^{-1}	7.476
F(000)	1008
Crystal size	0.15 x 0.20 x 0.20 mm^3
2θ range	3.00 to 56.00°
Index Ranges	-17<=h<=16 0<=k<=10 0<=l<=25
Reflections Collected	4538
Independent reflections	4538 [R(int) = 0.0006]
Data/restraints/parameters	4538/2/228
Goodness-of-fit on F^2	1.092
Final R indices[I>2sigma(I)]	R1 = 0.065 wR2 = 0.170
R indices (all data)	R1 = 0.065 wR2 = 0.170
Largest diff. peak and hole	4.61 and -2.66 e $Å^{-3}$

APPENDIX A

Complete list of bond distances and angles for (nacnac)Pt(Me)(ethylene) (Chapter 2, **1a**).

Pt(1)-C(6)	2.055(4)	C(6)-Pt(1)-C(5)	86.1(4)
Pt(1)-C(3)	2.055(4)	C(3)-Pt(1)-C(5)	17.41(19)
Pt(1)-N(7)	2.070(2)	N(7)-Pt(1)-C(5)	93.2(3)
Pt(1)-N(11)	2.0977(19)	N(11)-Pt(1)-C(5)	163.1(2)
Pt(1)-C(1)	2.118(3)	C(1)-Pt(1)-C(5)	87.4(4)
Pt(1)-C(5)	2.118(3)	C(6)-Pt(1)-C(2)	22.1(3)
Pt(1)-C(2)	2.118(3)	C(3)-Pt(1)-C(2)	85.91(19)
Pt(1)-C(4)	2.118(3)	N(7)-Pt(1)-C(2)	158.27(15)
C(1)-C(2)	1.391(6)	N(11)-Pt(1)-C(2)	93.47(13)
C(4)-C(5)	1.390(6)	C(1)-Pt(1)-C(2)	38.33(15)
N(7)-C(8)	1.336(3)	C(5)-Pt(1)-C(2)	76.9(3)
N(7)-C(12)	1.440(3)	C(6)-Pt(1)-C(4)	85.2(4)
C(8)-C(9)	1.398(3)	C(3)-Pt(1)-C(4)	21.6(2)
C(8)-C(18)	1.517(4)	N(7)-Pt(1)-C(4)	93.7(3)
C(9)-C(10)	1.388(3)	N(11)-Pt(1)-C(4)	157.6(3)
C(10)-N(11)	1.335(3)	C(1)-Pt(1)-C(4)	75.9(3)
C(10)-C(19)	1.516(3)	C(5)-Pt(1)-C(4)	38.32(16)
N(11)-C(20)	1.446(3)	C(2)-Pt(1)-C(4)	90.3(3)
C(12)-C(13)	1.383(3)	C(2)-C(1)-Pt(1)	70.84(9)
C(12)-C(17)	1.394(3)	C(1)-C(2)-Pt(1)	70.83(9)
C(13)-C(14)	1.391(4)	C(5)-C(4)-Pt(1)	70.83(9)
C(14)-C(15)	1.385(4)	C(4)-C(5)-Pt(1)	70.85(9)
C(15)-C(16)	1.381(4)	C(8)-N(7)-C(12)	115.0(2)
C(16)-C(17)	1.388(4)	C(8)-N(7)-Pt(1)	125.09(16)
C(20)-C(25)	1.387(3)	C(12)-N(7)-Pt(1)	119.80(15)
C(20)-C(21)	1.391(3)	N(7)-C(8)-C(9)	124.7(2)
C(21)-C(22)	1.383(4)	N(7)-C(8)-C(18)	119.4(2)
C(22)-C(23)	1.383(4)	C(9)-C(8)-C(18)	115.9(2)
C(23)-C(24)	1.380(4)	C(10)-C(9)-C(8)	129.8(2)
C(24)-C(25)	1.389(4)	N(11)-C(10)-C(9)	124.7(2)
C(6)-Pt(1)-C(3)	89.0(3)	N(11)-C(10)-C(19)	119.7(2)
C(6)-Pt(1)-N(7)	178.9(3)	C(9)-C(10)-C(19)	115.5(2)
C(3)-Pt(1)-N(7)	89.99(16)	C(10)-N(11)-C(20)	115.74(19)
C(6)-Pt(1)-N(11)	90.0(3)	C(10)-N(11)-Pt(1)	124.47(16)
C(3)-Pt(1)-N(11)	178.84(18)	C(20)-N(11)-Pt(1)	119.74(15)
N(7)-Pt(1)-N(11)	90.94(8)	C(13)-C(12)-C(17)	119.6(2)
C(6)-Pt(1)-C(1)	17.0(3)	C(13)-C(12)-N(7)	120.5(2)
C(3)-Pt(1)-C(1)	85.2(2)	C(17)-C(12)-N(7)	119.9(2)
N(7)-Pt(1)-C(1)	162.28(16)	C(12)-C(13)-C(14)	120.3(2)
N(11)-Pt(1)-C(1)	93.66(17)	C(15)-C(14)-C(13)	119.8(3)

C(16)-C(15)-C(14)	120.2(2)	C(22)-C(21)-C(20)	120.3(2)
C(15)-C(16)-C(17)	120.1(2)	C(21)-C(22)-C(23)	120.5(3)
C(16)-C(17)-C(12)	120.0(2)	C(24)-C(23)-C(22)	119.4(2)
C(25)-C(20)-C(21)	119.1(2)	C(23)-C(24)-C(25)	120.5(2)
C(25)-C(20)-N(11)	122.0(2)	C(20)-C(25)-C(24)	120.2(2)
C(21)-C(20)-N(11)	118.9(2)		

APPENDIX B

Complete list of bond distances and angles for (nacnac)Pt(Me)(CO) (Chapter 2, **1b**).

Pt(1)-C(1)	1.848(8)	C(39)-C(40)	1.384(7)
Pt(1)-N(8)	2.065(4)	C(40)-C(41)	1.390(8)
Pt(1)-N(4)	2.069(4)	C(41)-C(42)	1.393(9)
Pt(1)-C(3)	2.079(8)	C(42)-C(52)	1.376(9)
C(1)-O(2)	1.119(9)	C(43)-C(52)	1.407(8)
C(1A)-O(2A)	1.124(9)	C(45)-C(50)	1.395(7)
N(4)-C(5)	1.341(7)	C(45)-C(46)	1.399(7)
N(4)-C(9)	1.434(6)	C(46)-C(47)	1.389(7)
C(5)-C(6)	1.380(7)	C(47)-C(48)	1.401(8)
C(5)-C(15)	1.516(7)	C(48)-C(49)	1.382(8)
C(6)-C(7)	1.408(6)	C(49)-C(50)	1.391(7)
C(7)-N(8)	1.338(6)	C(1)-Pt(1)-N(8)	174.6(7)
C(7)-C(16)	1.501(8)	C(1)-Pt(1)-N(4)	94.3(8)
N(8)-C(17)	1.452(6)	N(8)-Pt(1)-N(4)	90.49(17)
C(9)-C(10)	1.391(7)	C(1)-Pt(1)-C(3)	84.2(6)
C(9)-C(14)	1.397(7)	N(8)-Pt(1)-C(3)	91.2(7)
C(10)-C(11)	1.390(7)	N(4)-Pt(1)-C(3)	176.0(8)
C(11)-C(12)	1.397(8)	O(2)-C(1)-Pt(1)	176(2)
C(12)-C(13)	1.382(8)	C(5)-N(4)-C(9)	116.8(4)
C(13)-C(14)	1.392(7)	C(5)-N(4)-Pt(1)	125.5(3)
C(17)-C(22)	1.379(7)	C(9)-N(4)-Pt(1)	117.5(3)
C(17)-C(18)	1.394(7)	N(4)-C(5)-C(6)	124.2(4)
C(18)-C(19)	1.393(7)	N(4)-C(5)-C(15)	118.8(5)
C(19)-C(55)	1.382(7)	C(6)-C(5)-C(15)	117.0(5)
C(21)-C(22)	1.386(7)	C(5)-C(6)-C(7)	130.1(5)
C(21)-C(55)	1.395(8)	N(8)-C(7)-C(6)	123.1(5)
Pt(2)-C(31)	1.854(5)	N(8)-C(7)-C(16)	119.4(4)
Pt(2)-N(38)	2.053(4)	C(6)-C(7)-C(16)	117.5(5)
Pt(2)-N(34)	2.079(4)	C(7)-N(8)-C(17)	115.3(4)
Pt(2)-C(33)	2.082(6)	C(7)-N(8)-Pt(1)	126.3(3)
C(31)-O(32)	1.126(6)	C(17)-N(8)-Pt(1)	118.4(3)
N(34)-C(35)	1.331(7)	C(10)-C(9)-C(14)	119.3(5)
N(34)-C(39)	1.450(6)	C(10)-C(9)-N(4)	121.2(4)
C(35)-C(36)	1.410(7)	C(14)-C(9)-N(4)	119.5(4)
C(35)-C(53)	1.513(7)	C(11)-C(10)-C(9)	120.9(5)
C(36)-C(37)	1.383(6)	C(10)-C(11)-C(12)	119.5(5)
C(37)-N(38)	1.321(7)	C(13)-C(12)-C(11)	119.6(5)
C(37)-C(44)	1.538(8)	C(12)-C(13)-C(14)	121.0(5)
N(38)-C(45)	1.454(6)	C(13)-C(14)-C(9)	119.6(5)
C(39)-C(43)	1.383(7)	C(22)-C(17)-C(18)	119.4(4)

C(22)-C(17)-N(8)	120.3(4)	C(36)-C(37)-C(44)	115.3(5)
C(18)-C(17)-N(8)	120.3(4)	C(37)-N(38)-C(45)	116.6(4)
C(19)-C(18)-C(17)	119.6(5)	C(37)-N(38)-Pt(2)	124.9(3)
C(55)-C(19)-C(18)	120.8(5)	C(45)-N(38)-Pt(2)	118.4(3)
C(22)-C(21)-C(55)	119.7(5)	C(43)-C(39)-C(40)	120.3(5)
C(17)-C(22)-C(21)	121.1(5)	C(43)-C(39)-N(34)	119.5(4)
C(31)-Pt(2)-N(38)	174.33(19)	C(40)-C(39)-N(34)	120.2(4)
C(31)-Pt(2)-N(34)	93.7(2)	C(39)-C(40)-C(41)	120.3(5)
N(38)-Pt(2)-N(34)	90.55(16)	C(40)-C(41)-C(42)	119.5(5)
C(31)-Pt(2)-C(33)	84.1(2)	C(52)-C(42)-C(41)	120.5(5)
N(38)-Pt(2)-C(33)	91.9(2)	C(39)-C(43)-C(52)	119.5(5)
N(34)-Pt(2)-C(33)	175.1(2)	C(50)-C(45)-C(46)	120.3(4)
O(32)-C(31)-Pt(2)	175.5(5)	C(50)-C(45)-N(38)	119.8(4)
C(35)-N(34)-C(39)	116.9(4)	C(46)-C(45)-N(38)	119.9(4)
C(35)-N(34)-Pt(2)	126.2(3)	C(47)-C(46)-C(45)	119.4(5)
C(39)-N(34)-Pt(2)	116.6(3)	C(46)-C(47)-C(48)	120.3(5)
N(34)-C(35)-C(36)	122.9(4)	C(49)-C(48)-C(47)	119.7(4)
N(34)-C(35)-C(53)	120.2(4)	C(48)-C(49)-C(50)	120.6(5)
C(36)-C(35)-C(53)	116.9(5)	C(49)-C(50)-C(45)	119.6(5)
C(37)-C(36)-C(35)	128.7(5)	C(42)-C(52)-C(43)	119.9(5)
N(38)-C(37)-C(36)	126.4(5)	C(19)-C(55)-C(21)	119.4(5)
N(38)-C(37)-C(44)	118.3(4)		

APPENDIX C

Complete list of bond distances and angles for (nacnac)Pt(H)$_2$(SiPh$_3$) (Chapter 3, **2a**).

Pt(1)-N(5)	2.076(3)	C(32)-C(37)	1.405(6)
Pt(1)-N(1)	2.099(4)	C(33)-C(34)	1.392(6)
Pt(1)-Si(1)	2.2862(11)	C(34)-C(35)	1.374(7)
Si(1)-C(32)	1.880(4)	C(35)-C(36)	1.394(7)
Si(1)-C(20)	1.883(4)	C(36)-C(37)	1.390(6)
Si(1)-C(26)	1.887(4)	N(5)-Pt(1)-N(1)	90.41(14)
Cl(1)-C(17)	1.747(5)	N(5)-Pt(1)-Si(1)	114.36(10)
Cl(2)-C(11)	1.745(5)	N(1)-Pt(1)-Si(1)	108.98(10)
N(1)-C(2)	1.319(6)	C(32)-Si(1)-C(20)	108.22(19)
N(1)-C(8)	1.435(5)	C(32)-Si(1)-C(26)	107.53(18)
C(2)-C(3)	1.398(6)	C(20)-Si(1)-C(26)	106.47(18)
C(2)-C(6)	1.538(6)	C(32)-Si(1)-Pt(1)	101.95(13)
C(3)-C(4)	1.399(6)	C(20)-Si(1)-Pt(1)	114.10(14)
C(4)-N(5)	1.313(6)	C(26)-Si(1)-Pt(1)	117.99(14)
C(4)-C(7)	1.520(6)	C(2)-N(1)-C(8)	118.7(4)
N(5)-C(14)	1.442(5)	C(2)-N(1)-Pt(1)	124.5(3)
C(8)-C(9)	1.388(7)	C(8)-N(1)-Pt(1)	116.9(3)
C(8)-C(13)	1.401(6)	N(1)-C(2)-C(3)	124.5(4)
C(9)-C(10)	1.389(7)	N(1)-C(2)-C(6)	119.9(4)
C(10)-C(11)	1.378(8)	C(3)-C(2)-C(6)	115.6(4)
C(11)-C(12)	1.385(8)	C(2)-C(3)-C(4)	129.8(4)
C(12)-C(13)	1.385(7)	N(5)-C(4)-C(3)	124.2(4)
C(14)-C(19)	1.384(6)	N(5)-C(4)-C(7)	119.6(4)
C(14)-C(15)	1.390(6)	C(3)-C(4)-C(7)	116.2(4)
C(15)-C(16)	1.385(7)	C(4)-N(5)-C(14)	117.6(3)
C(16)-C(17)	1.377(7)	C(4)-N(5)-Pt(1)	125.2(3)
C(17)-C(18)	1.372(7)	C(14)-N(5)-Pt(1)	117.1(3)
C(18)-C(19)	1.391(7)	C(9)-C(8)-C(13)	119.6(4)
C(20)-C(21)	1.397(6)	C(9)-C(8)-N(1)	120.9(4)
C(20)-C(25)	1.397(7)	C(13)-C(8)-N(1)	119.4(4)
C(21)-C(22)	1.401(6)	C(8)-C(9)-C(10)	120.2(5)
C(22)-C(23)	1.374(8)	C(11)-C(10)-C(9)	119.4(5)
C(23)-C(24)	1.380(8)	C(10)-C(11)-C(12)	121.6(4)
C(24)-C(25)	1.398(7)	C(10)-C(11)-Cl(2)	119.4(4)
C(26)-C(27)	1.395(6)	C(12)-C(11)-Cl(2)	119.0(4)
C(26)-C(31)	1.403(6)	C(11)-C(12)-C(13)	119.0(5)
C(27)-C(28)	1.393(6)	C(12)-C(13)-C(8)	120.2(4)
C(28)-C(29)	1.382(7)	C(19)-C(14)-C(15)	119.3(4)
C(29)-C(30)	1.385(7)	C(19)-C(14)-N(5)	120.9(4)
C(30)-C(31)	1.390(7)	C(15)-C(14)-N(5)	119.8(4)
C(32)-C(33)	1.403(6)	C(16)-C(15)-C(14)	120.8(4)

C(17)-C(16)-C(15)	119.2(4)
C(18)-C(17)-C(16)	120.8(4)
C(18)-C(17)-Cl(1)	119.9(4)
C(16)-C(17)-Cl(1)	119.3(4)
C(17)-C(18)-C(19)	120.2(5)
C(14)-C(19)-C(18)	119.7(5)
C(21)-C(20)-C(25)	117.7(4)
C(21)-C(20)-Si(1)	122.1(4)
C(25)-C(20)-Si(1)	119.9(3)
C(20)-C(21)-C(22)	120.4(4)
C(23)-C(22)-C(21)	120.8(4)
C(22)-C(23)-C(24)	119.8(4)
C(23)-C(24)-C(25)	119.7(5)
C(20)-C(25)-C(24)	121.6(5)
C(27)-C(26)-C(31)	117.6(4)
C(27)-C(26)-Si(1)	119.6(3)
C(31)-C(26)-Si(1)	122.6(3)
C(28)-C(27)-C(26)	121.5(4)
C(29)-C(28)-C(27)	120.2(4)
C(28)-C(29)-C(30)	119.2(4)
C(29)-C(30)-C(31)	120.9(4)
C(30)-C(31)-C(26)	120.7(4)
C(33)-C(32)-C(37)	117.5(4)
C(33)-C(32)-Si(1)	119.9(3)
C(37)-C(32)-Si(1)	122.4(3)
C(34)-C(33)-C(32)	121.0(4)
C(35)-C(34)-C(33)	120.6(4)
C(34)-C(35)-C(36)	119.7(4)
C(37)-C(36)-C(35)	120.0(4)
C(36)-C(37)-C(32)	121.2(4)

APPENDIX D

Complete list of bond distances and angles for (p-Cl-nacnac)Pt(*o*-C_6H_4-$SiPh_2CH{=}CH_2$) (Chapter 4, **3**).

Pt(1)-C(39)	2.031(5)	C(29)-C(30)	1.404(7)
Pt(1)-N(1)	2.044(3)	C(30)-C(31)	1.372(7)
Pt(1)-N(5)	2.120(3)	C(31)-C(32)	1.385(7)
Pt(1)-C(21)	2.140(4)	C(32)-C(33)	1.387(7)
Pt(1)-C(20)	2.142(4)	C(34)-C(35)	1.396(6)
Cl(1)-C(11)	1.753(5)	C(34)-C(39)	1.424(6)
Cl(2)-C(17)	1.750(4)	C(35)-C(36)	1.379(7)
Si(1)-C(34)	1.844(5)	C(36)-C(37)	1.399(7)
Si(1)-C(22)	1.874(4)	C(37)-C(38)	1.372(6)
Si(1)-C(21)	1.875(4)	C(38)-C(39)	1.407(6)
Si(1)-C(28)	1.881(5)	C(39)-Pt(1)-N(1)	92.11(15)
N(1)-C(2)	1.351(5)	C(39)-Pt(1)-N(5)	174.09(14)
N(1)-C(8)	1.433(5)	N(1)-Pt(1)-N(5)	91.02(13)
C(2)-C(3)	1.393(6)	C(39)-Pt(1)-C(21)	86.12(17)
C(2)-C(6)	1.511(6)	N(1)-Pt(1)-C(21)	150.97(15)
C(3)-C(4)	1.403(6)	N(5)-Pt(1)-C(21)	93.57(15)
C(4)-N(5)	1.341(5)	C(39)-Pt(1)-C(20)	82.62(17)
C(4)-C(7)	1.514(6)	N(1)-Pt(1)-C(20)	169.33(15)
N(5)-C(14)	1.445(5)	N(5)-Pt(1)-C(20)	93.47(16)
C(8)-C(9)	1.386(6)	C(21)-Pt(1)-C(20)	38.29(17)
C(8)-C(13)	1.393(6)	C(34)-Si(1)-C(22)	113.8(2)
C(9)-C(10)	1.388(6)	C(34)-Si(1)-C(21)	100.2(2)
C(10)-C(11)	1.379(6)	C(22)-Si(1)-C(21)	107.23(19)
C(11)-C(12)	1.371(6)	C(34)-Si(1)-C(28)	111.8(2)
C(12)-C(13)	1.385(6)	C(22)-Si(1)-C(28)	109.4(2)
C(14)-C(19)	1.379(6)	C(21)-Si(1)-C(28)	114.1(2)
C(14)-C(15)	1.393(6)	C(2)-N(1)-C(8)	115.8(3)
C(15)-C(16)	1.382(6)	C(2)-N(1)-Pt(1)	124.8(3)
C(16)-C(17)	1.386(6)	C(8)-N(1)-Pt(1)	119.2(2)
C(17)-C(18)	1.375(6)	N(1)-C(2)-C(3)	125.2(4)
C(18)-C(19)	1.403(6)	N(1)-C(2)-C(6)	119.8(4)
C(20)-C(21)	1.404(6)	C(3)-C(2)-C(6)	115.0(4)
C(22)-C(23)	1.391(7)	C(2)-C(3)-C(4)	129.6(4)
C(22)-C(27)	1.403(7)	N(5)-C(4)-C(3)	123.3(4)
C(23)-C(24)	1.398(6)	N(5)-C(4)-C(7)	120.2(4)
C(24)-C(25)	1.373(9)	C(3)-C(4)-C(7)	116.5(4)
C(25)-C(26)	1.382(9)	C(4)-N(5)-C(14)	115.0(3)
C(26)-C(27)	1.389(7)	C(4)-N(5)-Pt(1)	124.4(3)
C(28)-C(33)	1.400(6)	C(14)-N(5)-Pt(1)	120.6(3)
C(28)-C(29)	1.406(7)	C(9)-C(8)-C(13)	118.6(4)

C(9)-C(8)-N(1)	120.2(4)	C(38)-C(39)-C(34)	117.6(4)
C(13)-C(8)-N(1)	121.1(4)	C(38)-C(39)-Pt(1)	122.1(3)
C(8)-C(9)-C(10)	121.0(4)	C(34)-C(39)-Pt(1)	120.2(3)
C(11)-C(10)-C(9)	118.7(4)		
C(12)-C(11)-C(10)	121.7(4)		
C(12)-C(11)-Cl(1)	118.6(3)		
C(10)-C(11)-Cl(1)	119.8(3)		
C(11)-C(12)-C(13)	119.0(4)		
C(12)-C(13)-C(8)	120.9(4)		
C(19)-C(14)-C(15)	119.9(4)		
C(19)-C(14)-N(5)	119.6(4)		
C(15)-C(14)-N(5)	120.4(4)		
C(16)-C(15)-C(14)	120.3(4)		
C(15)-C(16)-C(17)	119.1(4)		
C(18)-C(17)-C(16)	121.6(4)		
C(18)-C(17)-Cl(2)	119.0(4)		
C(16)-C(17)-Cl(2)	119.3(4)		
C(17)-C(18)-C(19)	118.8(4)		
C(14)-C(19)-C(18)	120.2(4)		
C(21)-C(20)-Pt(1)	70.8(2)		
C(20)-C(21)-Si(1)	120.4(4)		
C(20)-C(21)-Pt(1)	70.9(2)		
Si(1)-C(21)-Pt(1)	105.0(2)		
C(23)-C(22)-C(27)	117.6(4)		
C(23)-C(22)-Si(1)	119.6(3)		
C(27)-C(22)-Si(1)	122.6(4)		
C(22)-C(23)-C(24)	121.8(5)		
C(25)-C(24)-C(23)	119.4(6)		
C(24)-C(25)-C(26)	120.2(5)		
C(25)-C(26)-C(27)	120.5(5)		
C(26)-C(27)-C(22)	120.5(5)		
C(33)-C(28)-C(29)	118.4(4)		
C(33)-C(28)-Si(1)	119.4(4)		
C(29)-C(28)-Si(1)	122.1(3)		
C(30)-C(29)-C(28)	120.2(5)		
C(31)-C(30)-C(29)	120.1(5)		
C(30)-C(31)-C(32)	120.4(5)		
C(31)-C(32)-C(33)	120.2(5)		
C(32)-C(33)-C(28)	120.7(5)		
C(35)-C(34)-C(39)	119.8(4)		
C(35)-C(34)-Si(1)	126.5(3)		
C(39)-C(34)-Si(1)	113.6(3)		
C(36)-C(35)-C(34)	121.1(4)		
C(35)-C(36)-C(37)	119.1(4)		
C(38)-C(37)-C(36)	120.7(4)		
C(37)-C(38)-C(39)	121.2(4)		

APPENDIX E

Complete list of bond distances and angles for
(Tp′)Pt(H)(CO) (Chapter 5, **5**).

Pt(1)-C(2)	1.827(11)	Pt(1)-N(5)-C(9)	131.6(8)
Pt(1)-N(5)	2.139(8)	N(6)-N(5)-C(9)	106.9(9)
Pt(1)-N(12)	2.489(9)	B(4)-N(6)-N(5)	122.5(8)
Pt(1)-N(19)	2.088(9)	B(4)-N(6)-C(7)	127.1(9)
C(2)-O(3)	1.138(18)	N(5)-N(6)-C(7)	110.4(8)
B(4)-N(6)	1.569(14)	N(6)-C(7)-C(8)	105.9(9)
B(4)-N(13)	1.536(15)	N(6)-C(7)-C(10)	123.8(10)
B(4)-N(20)	1.605(15)	C(8)-C(7)-C(10)	130.3(10)
N(5)-N(6)	1.371(12)	C(7)-C(8)-C(9)	107.7(10)
N(5)-C(9)	1.350(13)	N(5)-C(9)-C(8)	109.2(10)
N(6)-C(7)	1.356(13)	N(5)-C(9)-C(11)	121.0(12)
C(7)-C(8)	1.400(16)	C(8)-C(9)-C(11)	129.7(11)
C(7)-C(10)	1.477(15)	Pt(1)-N(12)-N(13)	117.1(6)
C(8)-C(9)	1.369(17)	Pt(1)-N(12)-C(16)	136.9(8)
C(9)-C(11)	1.487(18)	N(13)-N(12)-C(16)	106.0(9)
N(12)-N(13)	1.359(13)	B(4)-N(13)-N(12)	119.7(9)
N(12)-C(16)	1.334(14)	B(4)-N(13)-C(14)	129.2(10)
N(13)-C(14)	1.338(14)	N(12)-N(13)-C(14)	111.1(10)
C(14)-C(15)	1.402(19)	N(13)-C(14)-C(15)	107.0(11)
C(14)-C(17)	1.50(2)	N(13)-C(14)-C(17)	123.5(12)
C(15)-C(16)	1.383(18)	C(15)-C(14)-C(17)	129.4(11)
C(16)-C(18)	1.505(19)	C(14)-C(15)-C(16)	104.9(10)
N(19)-N(20)	1.373(13)	N(12)-C(16)-C(15)	111.0(11)
N(19)-C(23)	1.359(14)	N(12)-C(16)-C(18)	120.1(11)
N(20)-C(21)	1.357(14)	C(15)-C(16)-C(18)	128.8(11)
C(21)-C(22)	1.348(17)	Pt(1)-N(19)-N(20)	122.5(7)
C(21)-C(24)	1.529(19)	Pt(1)-N(19)-C(23)	131.5(9)
C(22)-C(23)	1.372(19)	N(20)-N(19)-C(23)	106.0(10)
C(23)-C(25)	1.501(19)	B(4)-N(20)-N(19)	122.0(9)
C(2)-Pt(1)-N(5)	102.0(5)	B(4)-N(20)-C(21)	129.6(10)
C(2)-Pt(1)-N(12)	115.4(5)	N(19)-N(20)-C(21)	108.4(9)
N(5)-Pt(1)-N(12)	81.5(3)	N(20)-C(21)-C(22)	109.4(11)
C(2)-Pt(1)-N(19)	163.6(5)	N(20)-C(21)-C(24)	121.6(11)
N(5)-Pt(1)-N(19)	85.5(3)	C(22)-C(21)-C(24)	129.0(11)
N(12)-Pt(1)-N(19)	79.8(3)	C(21)-C(22)-C(23)	106.2(10)
Pt(1)-C(2)-O(3)	177.1(13)	N(19)-C(23)-C(22)	110.0(11)
N(6)-B(4)-N(13)	110.6(9)	N(19)-C(23)-C(25)	120.6(12)
N(6)-B(4)-N(20)	105.2(8)	C(22)-C(23)-C(25)	129.3(11)
N(13)-B(4)-N(20)	107.1(8)		
Pt(1)-N(5)-N(6)	121.5(6)		

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