

Chapter 17

Mechanisms of Reactions Related to Selective Alkane Oxidation by Pt Complexes

Jennifer L. Look, Ulrich Fekl, and Karen I. Goldberg*

Department of Chemistry, University of Washington,
Seattle, Washington 98195-1700

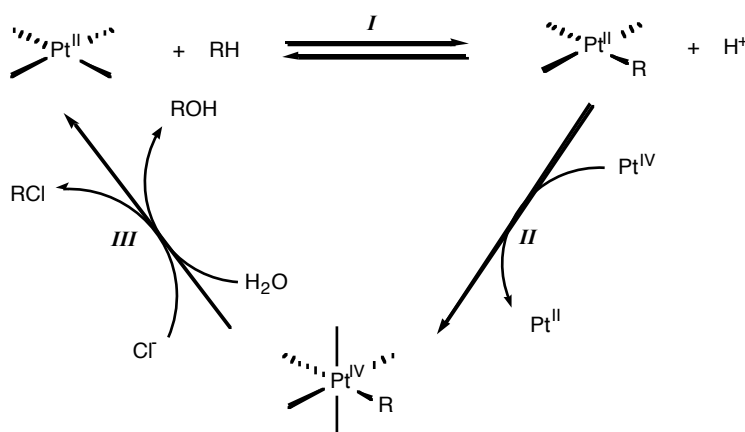
Some of the most promising homogeneous systems for the selective activation and functionalization of alkanes are based on platinum. Proposed key reaction steps at Pt(II) and Pt(IV) metal centers have been directly observed and studied using model compounds. Investigations of oxidative addition and reductive elimination reactions of carbon-hydrogen, carbon-carbon and carbon-heteroatom bonds have provided detailed information about the intermediates and kinetic barriers involved in these bond cleavage and formation reactions. In addition, reactions of platinum alkyl complexes with dioxygen, an ideal oxidant for alkane functionalization, have been studied.

Introduction

Over thirty years ago, Shilov and co-workers reported the remarkable discovery that alkanes could be selectively oxidized in aqueous solution in the presence of Pt salts (PtCl_4^{2-} and PtCl_6^{2-}); methane was converted to methanol and methyl chloride (1,2). This reaction was catalytic in Pt(II), but required Pt(IV) as a stoichiometric oxidant. Clearly, the high cost of a platinum compound as an oxidant makes this particular system impractical. However, the mere demonstration of this unprecedented transformation inspired many researchers, including us, to pursue research programs in platinum-catalyzed alkane

oxidation. Perhaps the oxidant in the Shilov system can be replaced with a more suitable oxidant and a commercially viable platinum catalyzed process can be developed. Toward this end, significant effort has been directed toward understanding the mechanistic details of Shilov's alkane oxidation system. Strong support has been presented for the pathway shown in Scheme 1 (2). In step I, a Pt(II) species activates the alkane C-H bond to generate a Pt(II) alkyl complex. Then in step II, the Pt(II) alkyl is oxidized by Pt(IV) to form a Pt(IV) alkyl complex. In step III, nucleophilic attack of either water or chloride at the Pt-bonded alkyl forms the functionalized organic product and regenerates the active catalyst. While the basic cycle pictured in Scheme 1 is now generally accepted, the intimate mechanistic details of each of these reaction steps are research topics of significant current interest. Understanding the mechanism and energetics of each step – C-H bond activation, oxidation, and C-heteroatom bond formation – is expected to aid in the development of more practical alkane functionalization processes.

Scheme 1



For the past several years, our research group has been carrying out mechanistic investigations of reactions related to those depicted in Scheme 1. Using model platinum complexes, we have directly observed and studied C-H bond oxidative addition reactions to Pt(II) and reductive elimination reactions from Pt(IV) (3-5). Thorough mechanistic studies of C-C and C-O reductive elimination reactions from Pt(IV) have also been carried out (5,6). In addition, inspired by the potential of utilizing dioxygen as a replacement for the Pt(IV) oxidant required in the Shilov system, we have explored the reactivity of Pt(II) and Pt(IV) alkyl complexes with dioxygen (7,8). In this contribution, we share the results of our investigations of these reactions and comment on some of the

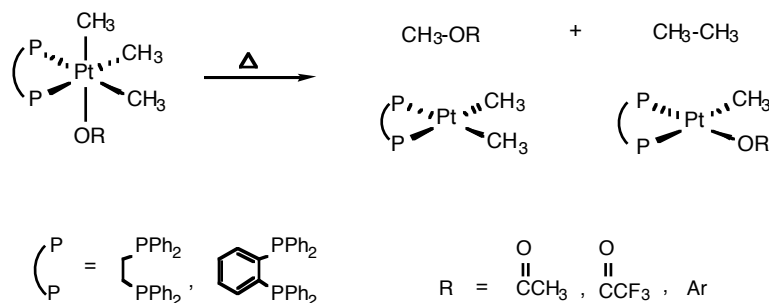
key elements to be considered in developing a Pt catalyst to convert alkanes to alcohols.

C-O Reductive Elimination

We will begin our discussion with the last reaction shown in Scheme 1 (step III). This is the product-forming step of the reaction sequence; C-X bond formation yields the alcohol or alkyl chloride product. Significant evidence has been presented for this step occurring via nucleophilic attack of a heteroatom group (Cl^- or H_2O) on an electrophilic Pt(IV) alkyl (2). In the related Catalytica process for oxidation of methane to methyl bisulfate using a platinum bipyrimidine catalyst, carbon-oxygen reductive elimination from a Pt(IV) methyl bisulfate intermediate was proposed as the product-forming step (9). Until recently (6), there were no directly observed examples of high-yield carbon-oxygen reductive elimination from Pt(IV). We were thus interested in finding examples of such reactivity and studying the intimate mechanism of these reactions. In particular, our goal was to understand some of the factors (e.g., solvent, substituents on oxygen, etc.) that favor carbon-oxygen reductive elimination from Pt(IV).

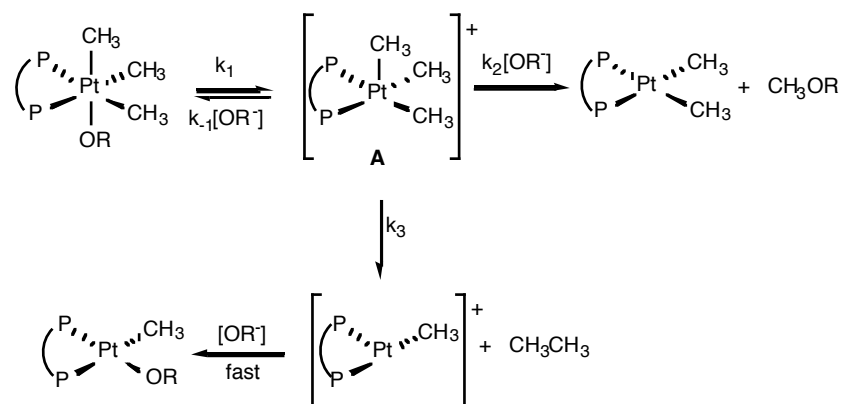
The Pt(IV) complexes $\text{fac-L}_2\text{PtMe}_3\text{OR}$ (Scheme 2, $\text{L}_2 = \text{dppe}$ (bis(diphenylphosphino)ethane), dppbz (bis(*o*-diphenylphosphino)benzene); $\text{OR} =$ carboxylate, aryloxy) were prepared and characterized (6). It was anticipated that these complexes might undergo C-O reductive elimination since they are analogous to the Pt(IV) iodide species, $\text{fac-dppePtMe}_3\text{I}$, which had been previously observed to undergo competitive C-I and C-C coupling upon thermolysis (10). Indeed, thermolysis of the $\text{fac-L}_2\text{PtMe}_3\text{OR}$ complexes proceeded to form both C-O and C-C reductive elimination products (Scheme 2), and provided us with an excellent system from which to study the intimate mechanism of C-O reductive elimination from Pt(IV) (6).

Scheme 2



The mechanisms proposed for the competitive C-O and C-C reductive elimination reactions from *fac*-L₂PtMe₃OR are shown in Scheme 3 (6). Dissociation of OR⁻ forms the five-coordinate Pt(IV) cation, L₂PtMe₃⁺ (Intermediate A). C-C coupling to form ethane proceeds directly from A in a concerted fashion. In contrast, nucleophilic attack by OR⁻ on a methyl group of the Pt(IV) intermediate A generates the methyl carboxylate or methyl aryl ether product and L₂PtMe₂. It is interesting to note that these mechanisms for C-O and C-C bond formation are analogous to those previously proposed for competing C-I and C-C reductive elimination reactions from *fac*-dppePtMe₃I (10).

Scheme 3



As expected for reactions that involve ionic intermediates, the thermolyses of these complexes show a significant solvent effect. For example, the rate of the disappearance of (dppe)PtMe₃OAc at 99 °C increased by two orders of magnitude on going from benzene-*d*₆ ($k_{\text{obs}} = 1.3 \times 10^{-5} \text{ s}^{-1}$) to nitrobenzene-*d*₅ ($k_{\text{obs}} = 1.4 \times 10^{-3} \text{ s}^{-1}$). The ratios of the products (C-O versus C-C coupling) also varied drastically with the polarity of the solvent; 90+ % C-O coupling was observed in benzene-*d*₆ and less than 1% was observed in nitrobenzene-*d*₅. When the rates of the individual reactions to form C-O or C-C bonds are examined, it can be seen that the rate of C-C reductive elimination increases substantially more with the polarity of the solvent than the C-O coupling rate. For example, the rate constant for C-O coupling from (dppe)PtMe₃OAc increased only slightly from $k_{\text{C-O}} = 1.2 \times 10^{-5} \text{ s}^{-1}$ in benzene-*d*₆ to $k_{\text{C-O}} = 4.1 \times 10^{-5} \text{ s}^{-1}$ in acetone-*d*₆, whereas the rate constant for C-C coupling increased from $1 \times 10^{-6} \text{ s}^{-1}$ to $6\text{-}10 \times 10^{-4} \text{ s}^{-1}$ in the same solvents. These solvent effects are consistent with the mechanistic scheme shown (Scheme 3). The first step of both coupling reactions (k_1 , formation of ionic intermediates A and OR⁻) should be accelerated by a more polar solvent. However, the second and rate-determining step of the C-O reductive elimination (k_2 , formation of neutral

products from charged intermediates) should be inhibited by polar solvents. In contrast, the second step of the C-C coupling reaction (k_3) occurs intramolecularly from the cationic intermediate **A**. Thus, changes in solvent polarity should have a much larger effect on C-C reductive elimination. A similar situation is observed with the addition of small amounts of the conjugate acid, HOR, to the thermolyses. Both C-O and C-C reductive elimination reactions are accelerated in the presence of HOR but the increase in the C-C coupling rate is greater. The added HOR assists the OR⁻ group in leaving the metal (k_1), but by binding to the OR⁻ group also inhibits to some extent the C-O bond-forming step (k_2).

When OR⁻ anion is added to the thermolysis reaction, the rate of the C-O reductive elimination is unaffected. In contrast, the C-C elimination is completely inhibited. This behavior is to be expected based on the mechanisms shown in Scheme 3. The first step (k_1) of the C-O and C-C reductive eliminations is inhibited by OR⁻. For the C-O reductive elimination, this inhibition in the presence of OR⁻ is balanced by an equal acceleration of the second step. In the case of C-C reductive elimination, the second step is unaffected by the added OR⁻ and so an overall inhibition by added OR⁻ is observed. Additional support for the two-step mechanisms involving initial OR⁻ dissociation is that the reductive elimination reactions are significantly affected by modifying the electron-withdrawing ability of the OR⁻ group. More electron-withdrawing groups accelerate both C-O and C-C reductive elimination reactions, albeit to different extents. For example, replacing acetate with trifluoroacetate (dpppPtMe₃(O₂CCF₃)), leads to a 12-fold increase in the rate of C-O reductive elimination and a 200-fold increase in the rate of C-C reductive elimination. The C-O reductive elimination experiences a lesser acceleration because unlike the C-C reductive elimination, the second step involves nucleophilic attack (k_2) and as such would be inhibited by the presence of electron-withdrawing groups on OR⁻.

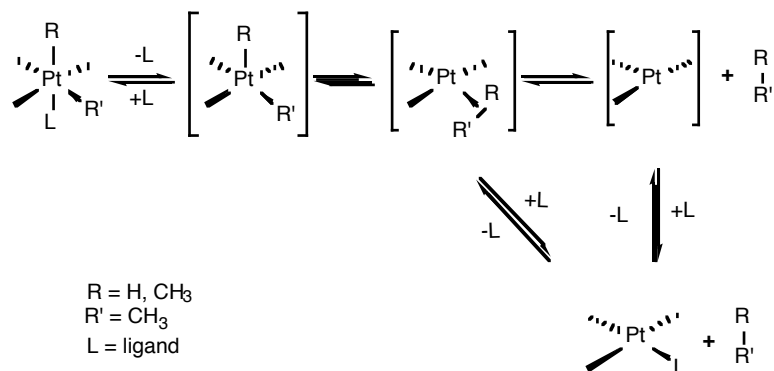
In summary, our results support the formation of a five-coordinate cationic intermediate **A** in both the C-O and C-C coupling reactions from Pt(IV). Thus, circumstances that accelerate formation of this five-coordinate intermediate – polar solvents, acids, and electron-withdrawing groups on OR⁻ – act to increase the rates of both C-O and C-C reductive elimination. Of note is that the successful Pt alkane oxidation systems reported to date do in fact operate in polar, acidic media (2,9,11). The increase in rate observed with electron-withdrawing groups on R may at first seem counterintuitive for a mechanism involving a nucleophilic attack by OR⁻ (Scheme 1). However, this effect is a direct consequence of the involvement of the five-coordinate intermediate (Scheme 3), and leads to the suggestion that most useful coupling reactions in platinum-catalyzed alkane functionalization processes may be those involving good leaving groups such as trifluoroacetate, sulfonates and bisulfates. Particularly interesting in this regard is that the use of such groups is also

attracting attention as a methodology for preventing overoxidation of the alcohol derivative product (2*b*,9,12).

C-H Bond Activation and Related Reactions

The first step of the reaction sequence for platinum-catalyzed alkane functionalization, as shown in Scheme 1, is the activation of the C-H bond by a Pt(II) species (2). Studying this reaction directly has been challenging as model Pt(II) complexes, which are capable of activating alkane C-H bonds, have only recently been prepared (13). However, a significant amount of insight into the mechanism of C-H bond activation reactions by Pt(II) centers has been garnered from the study of alkane C-H reductive elimination reactions from Pt(IV) and the application of the principle of microscopic reversibility (2,4,5,14,-16). Over the past 30 years, considerable mechanistic evidence has been collected on C-C and C-H reductive elimination reactions from Pt(IV) centers. In almost every case (vide infra for the first exception (5)), the data have supported dissociation of a ligand from the six-coordinate starting complex to form a five-coordinate Pt(IV) intermediate prior to C-C or C-H bond formation. This general mechanism is shown in Scheme 4. C-C or C-H coupling occurs from the five-coordinate Pt(IV) intermediate to form a σ -C-H alkane species. The observation of isotopic scrambling and inverse kinetic isotope effects in C-H reductive elimination from Pt(IV) has been offered as support for such σ -alkane intermediates in Pt(IV) C-H reductive elimination reactions (4,14*a,c*,17,18). The alkane product is released from the σ -alkane species by either a dissociative or associative ligand substitution to form the final Pt(II) product (19). Thus, although it may seem that a very simple coupling of R-R' could take place from

Scheme 4



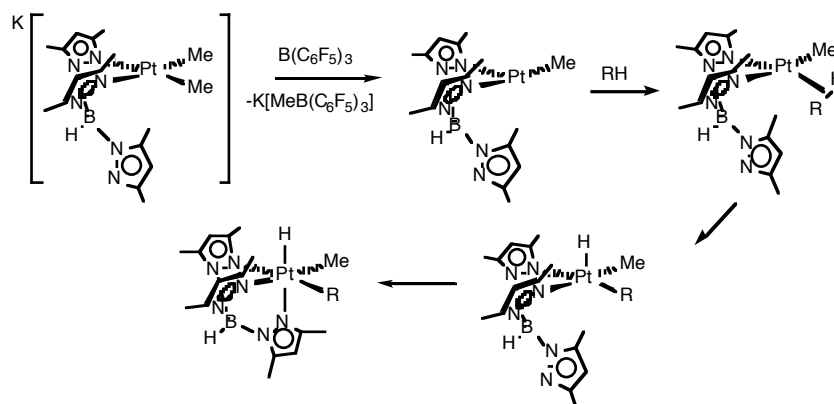
the starting six-coordinate Pt(IV) complex to form the Pt(II) product and alkane, the most common mechanism for this reaction instead involves initial loss of ligand followed by recoordination of ligand at the end of the reaction.

For alkane functionalization, the critical reaction step is clearly not C-H reductive elimination from Pt(IV), but rather C-H activation by Pt(II). Yet, the principle of microscopic reversibility tells us that a C-H oxidative addition pathway will involve the same intermediates and transition states as the reverse reductive elimination reaction (Scheme 4). Thus, a Pt(II) complex expected to undergo facile C-H bond oxidative addition should have at least one weakly bound ligand. Indeed, this appears to be the case, as the examples of Pt(II) complexes exhibiting C-H bond activation reactivity do in fact contain a weakly coordinating ligand (e.g. OTf^- , NC_5D_5 , H_2O) (13,20). Yet most of these examples of model Pt(II) complexes which activate hydrocarbons simply exchange one hydrocarbyl group for another, and only Pt(II) (and not Pt(IV)) species are detected. The five-coordinate Pt(IV) intermediate shown in Scheme 4 would be expected to be highly reactive toward reductive elimination. A good ligand, however, should be able to trap this species to form a six-coordinate Pt(IV) alkyl hydride. The key would be to use a trapping ligand that would not be an effective ligand to Pt(II) so as not to inhibit the initial hydrocarbon coordination and activation steps. Such a strategy is described in the following section.

Investigations With Tp^{Me_2} Ligands

As shown in Scheme 5, when the potentially facially coordinating ligand Tp^{Me_2} (Tp^{Me_2} = hydridotris((3,5-dimethyl)pyrazolyl)borate) is employed, alkanes

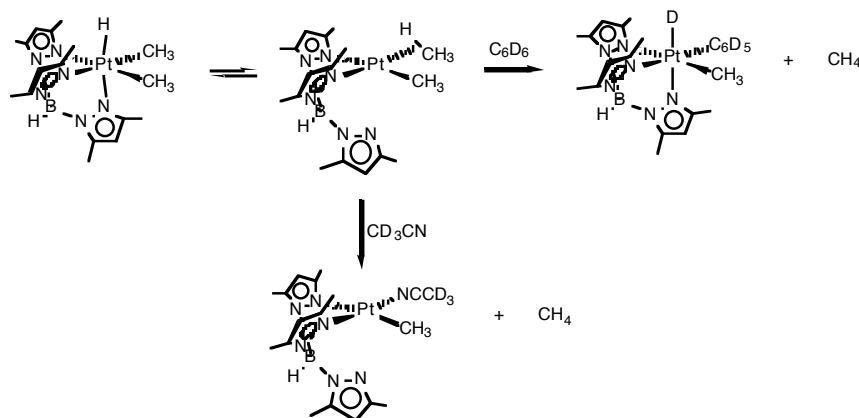
Scheme 5



can add to a Pt(II) center to produce stable octahedral Pt(IV) alkyl hydride complexes (3). The initially pendent pyrazolyl “arm” coordinates in the Pt(IV) product. As detailed in Scheme 5, it was proposed that methide abstraction from $\text{KTp}^{\text{Me}_2}\text{PtMe}_2$ using $\text{B}(\text{C}_6\text{F}_5)_3$ generates the open site needed for alkane coordination. Then oxidative addition of RH from the σ -alkane complex intermediate yields a five-coordinate Pt(IV) alkyl hydride, which is trapped by the free pyrazolyl arm. However, while the observation of Pt(IV) alkyl hydride products directly demonstrated that alkanes can oxidatively add to Pt(II) centers, support for the proposed mechanism was lacking. Mechanistic studies were hampered by the low solubility of the anionic Pt(II) precursor in hydrocarbon solvents, the requisite bimolecular activation step with $\text{B}(\text{C}_6\text{F}_5)_3$, and the occurrence of competing side reactions. Instead, detailed information about C-H bond cleavage in this Tp^{Me_2} system was obtained from studies of the microscopic reverse reaction, reductive elimination from $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ (4).

Thermolysis of $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ in benzene at 110 °C results in reductive elimination of methane and oxidative addition of benzene to form $\text{Tp}^{\text{Me}_2}\text{Pt}(\text{Me})(\text{Ph})\text{H}$. Reductive elimination of a second equivalent of methane then leads to activation of a second equivalent of benzene to yield $\text{Tp}^{\text{Me}_2}\text{PtPh}_2\text{H}$. An inverse kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 0.8$) for the C-H reductive elimination reaction was observed. It was also demonstrated that thermolysis of $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{D}$ at 60 °C leads to scrambling of deuterium into the methyl positions, without loss of methane. The observations of an inverse kinetic isotope effect and H/D scrambling can be most directly accommodated by the involvement of a σ - CH_4 complex intermediate prior to methane elimination (18) (Scheme 6).

Scheme 6



When $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ is heated at 110 °C in the presence of acetonitrile, the Pt(II) species resulting from methane loss is trapped (Scheme 6). The rate of formation of $\kappa^2\text{-Tp}^{\text{Me}_2}\text{PtMe}(\text{CD}_3\text{CN})$ is independent of the concentration of acetonitrile and is much slower than the rate of H/D scrambling (see above), indicating that methane loss from the $\sigma\text{-CH}_4$ complex is dissociative (19,21). Combining this mechanistic information with the activation parameters obtained for both the scrambling and the reductive elimination reactions allows construction of an energy profile of the reaction (Figure 1) and the calculation that the enthalpy of alkane dissociation from the σ -complex must be at least 9 kcal/mol (4).

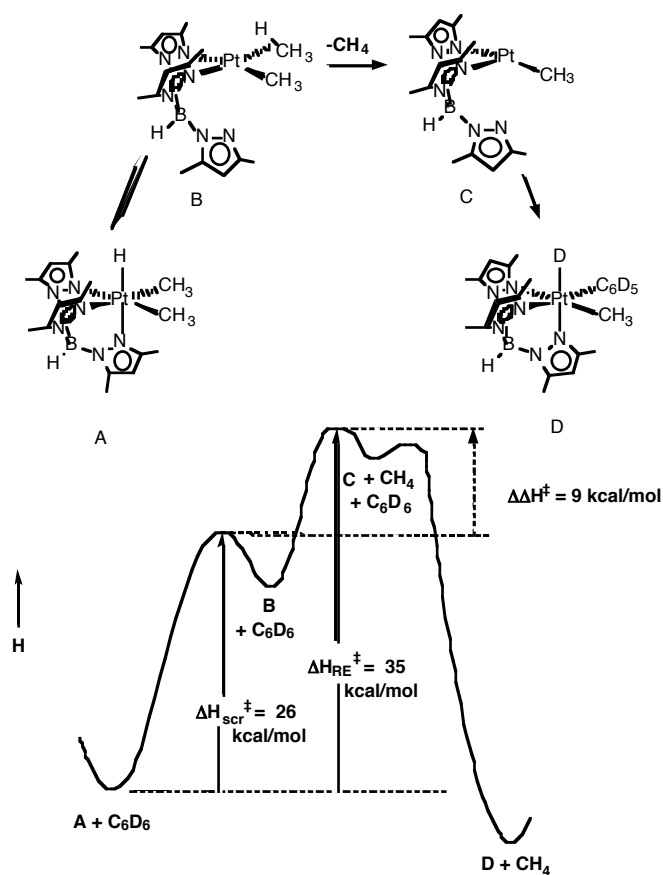


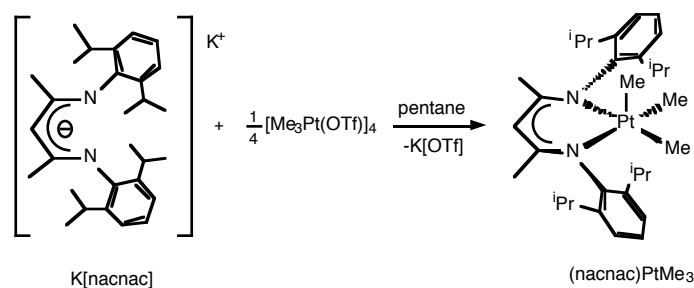
Figure 1. Enthalpy diagram for the reductive elimination of methane from $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$

This study of C-H bond formation and cleavage from $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ emphasizes the importance of unsaturated species in oxidative addition/reductive elimination at Pt(II)/Pt(IV). Earlier studies of both C-C and C-H reductive elimination from Pt(IV) have found support for the involvement of five-coordinate Pt(IV) intermediates. Here we find evidence, in a particular Pt system, for the involvement of an unsaturated three-coordinate Pt(II) intermediate ($\kappa^2\text{-Tp}^{\text{Me}_2}\text{PtMe}$) on the reaction pathway (22).

Investigations With ‘nacnac’ Ligands

The virtually ubiquitous nature of five-coordinate Pt(IV) intermediates in platinum(II)/(IV) bond cleavage and formation reactions led us to search for stable five-coordinate Pt(IV) complexes to model these proposed intermediate species. Bis(*o*-diisopropylaryl) β -diketiminate (nacnac) was employed to synthesize the first stable five-coordinate Pt(IV) alkyl complex (Scheme 7) (23). Our strategy was to use a chelating anionic ligand to produce a charge neutral complex. In this way, we would avoid coordination of a counterion in the sixth position, as had been previously observed (24). In addition, bulky groups on the aryl rings were incorporated to shield the open site to some extent and also to allow solubility in alkanes. The new compound was fully characterized and was shown to have a square pyramidal structure in the solid state by X-ray crystallography (23).

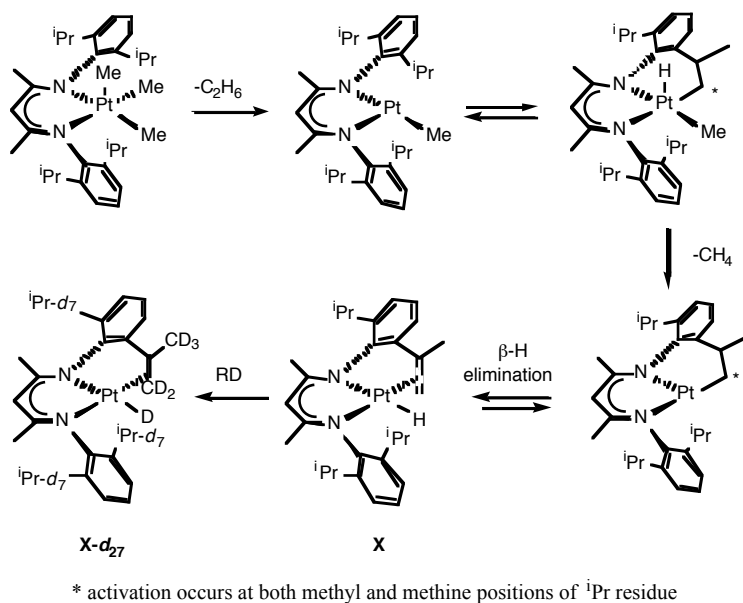
Scheme 7



The next question was whether this compound would serve as a model for the intermediates in reductive elimination from Pt(IV) and actually undergo C-C coupling. Indeed, reductive elimination of ethane from $(\text{nacnac})\text{PtMe}_3$ was observed at elevated temperature in hydrocarbon solvent (25). Methane and a Pt(II) product, a cyclometallated olefin hydride (**X** in Scheme 8), were also produced in this reaction. The formation of these products is readily explained

in the proposed mechanism shown in Scheme 8. Reductive elimination of ethane from (nacnac)PtMe₃ leads to a three-coordinate Pt(II) species (26). As discussed above, this unsaturated intermediate should readily activate C-H bonds. The proximity of the isopropyl groups results in intramolecular activation to produce a five-coordinate cyclometallated Pt(IV) methyl hydride complex. The five-coordinate Pt(IV) methyl hydride intermediate undergoes facile reductive elimination of methane. β -Hydrogen elimination from the cyclometalated group then leads to the Pt(II) olefin hydride complex **X**. Intermolecular C-H bond activation of benzene and alkane solvents by the Pt(II) olefin hydride complex **X** was also demonstrated. Deuterium incorporation into all of the isopropyl positions, the isopropenyl group, and the hydride position formed **X-d₂₇** when **X** was heated in benzene-*d*₆ or pentane-*d*₁₂. Deuterium labeling studies showed an 85% selectivity for the labeling of the terminal positions of pentane. The mechanism suggested for this process is that reversible β -hydride elimination allows olefin insertion from **X** to generate a three-coordinate Pt(II) species which undergoes intermolecular C-H activation (25).

Scheme 8



This work involving the preparation, characterization and reactivity studies of the first stable five-coordinate Pt(IV) alkyl complex has provided further

insight into C-H activation chemistry at Pt(II). Support has again been put forth for the involvement of unsaturated five-coordinate Pt(IV) and three-coordinate Pt(II) species in C-H activation reactions. A unique and successful approach to generating the requisite site for alkane coordination (and activation) at Pt(II) via olefin insertion was introduced.

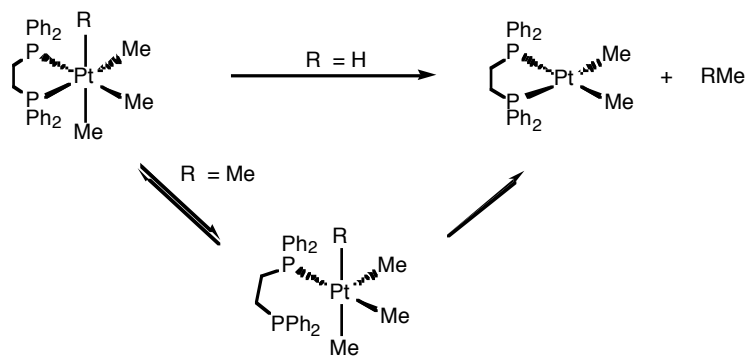
Investigations With Phosphine Ligands

Although we have detailed the importance of five-coordinate Pt(IV) intermediates in reductive elimination reactions from Pt(IV), we have also found that one must exercise caution in presuming that all such reactions involve five-coordinate Pt(IV) intermediates. We have recently presented the first evidence for a C-H reductive elimination from octahedral Pt(IV) that proceeds directly without ligand dissociation (5). The novel phosphine-ligated Pt(IV) alkyl hydride complexes, L_2PtMe_3H ($L_2 = dppe$ (bis(diphenylphosphino)ethane), $dppbz$ (bis(*o*-diphenylphosphino)benzene)) were prepared and characterized. These complexes undergo C-H reductive elimination to form methane at room temperature (Scheme 9). The complexes, which bear chelating phosphine ligands of very different rigidity, react at virtually the same rate (at 50 °C, $k_{obs} = 1.3(1) \times 10^{-4} s^{-1}$ and $1.2(1) \times 10^{-4} s^{-1}$ for the $dppe$ and $dppbz$ derivatives, respectively). The activation parameters are also very similar. No H/D scrambling into the methyl groups or the methane is observed when the complexes L_2PtMe_3D are subjected to thermolysis, and normal kinetic isotope effects are observed for the reactions of both complexes. The lack of any difference between the reaction rates for the $dppe$ derivative versus the more rigid $dppbz$ complex is not consistent with a mechanistic pathway involving phosphine predissociation. Instead, reductive elimination directly from a six-coordinate Pt(IV) complex is the favored mechanism.

In contrast, the mechanism for C-C reductive elimination from the analogous $dppe$ complex, $(dppe)PtMe_4$ is consistent with a phosphine dissociation pathway to form a five-coordinate intermediate prior to C-C coupling. The $dppbz$ analog, $dppbzPtMe_4$ eliminated methane at 165 °C with a rate at least two orders of magnitude slower than the $dppe$ complex. It was also shown that phosphine chelate opening is kinetically viable at high temperatures. When the related complex $dppePtMe_3Et$ is heated at 165 °C, β -hydride elimination occurs to produce ethylene. This indicates that an open site, generated by phosphine arm dissociation, must be accessible.

These studies of C-C and C-H reductive elimination from Pt(IV) mark the first time that Me-Me and Me-H coupling reactions from the same metal-ligand environment have been directly compared (5). To achieve comparable rates of reaction, a temperature difference of almost 150 °C was required. Perhaps even

Scheme 9



more significant, however, is that the C-C and C-H reductive eliminations proceed via different mechanisms. C-H reductive elimination proceeds via a direct pathway and C-C reductive elimination proceeds via ligand dissociation and a five-coordinate intermediate (Scheme 9). The observation of these distinct mechanisms in such closely related systems emphasizes the need for caution when making analogies between C-C and C-H bond-forming reactions.

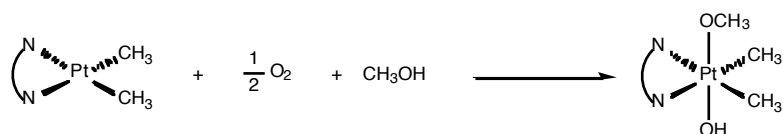
Oxidation by O₂

Activation of C-H bonds is necessary, but not sufficient for alkane functionalization. Oxidation of the platinum alkyl complex must precede elimination of the functionalized product. In the original Shilov system, Pt(IV) is consumed as a stoichiometric oxidant (Scheme 1, step II). More recently, systems which use Cl₂, SO₃, and H₂O₂ as oxidants have been explored (9,11a,b). The use of O₂ and co-catalysts like CuCl₂ or heteropolyacids has also been reported (11c,d). Despite some progress with these alternative oxidants, a commercially viable system for selective alkane functionalization has yet to emerge. When one considers economic, environmental, and availability issues, the best oxidant for this reaction would certainly be molecular oxygen from air. We have been investigating the concept of using oxygen directly (without a co-catalyst) for this alkane functionalization and have been studying the reaction chemistry between platinum alkyl complexes and O₂.

Alkane activation by Pt(II) species can produce Pt(II) alkyl or Pt(IV) alkyl hydride products. Thus, the reaction of each type of Pt alkyl product with O₂ merits investigation. Several years ago, together with Bercaw, Labinger and co-workers, our group reported that L₂PtMe₂ complexes (L₂ = tmeda, bpy, phen) react with oxygen in methanol to form Pt(IV) methyl hydroxide methoxide

complexes (Scheme 10) (7). This reaction is similar to the oxidation step in the Shilov system in that a Pt(II) alkyl is directly oxidized by the oxidant, in this case dioxygen, to a Pt(IV) species. Bercaw, Labinger and co-workers have recently investigated the mechanism of this reaction with O_2 and have identified a Pt(IV) hydroperoxide intermediate that reacts with starting material to ultimately produce two equivalents of Pt(IV) hydroxide product (27).

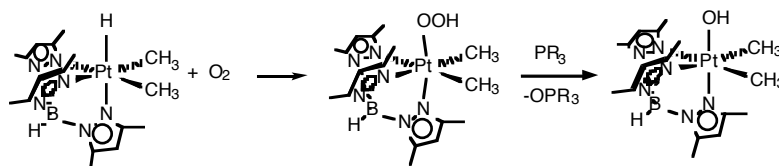
Scheme 10



NN = bpy, phen, tmeda

Another potentially useful reaction with dioxygen that we recently discovered is shown in Scheme 11. Formal insertion of dioxygen into the Pt-H bond of $Tp^{Me_2}PtMe_2H$ cleanly generates the hydroperoxide complex, $Tp^{Me_2}PtMe_2OOH$ (8). This is exciting because oxidative addition of C-H bonds has been observed with this same $Tp^{Me_2}Pt$ system (see above) (3,4). Now two of the three desired steps – C-H bond activation and utilization of O_2 – have been observed within the same type of ligand environment.

Scheme 11

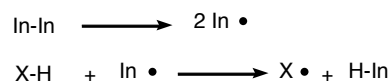


The rate of the reaction of $Tp^{Me_2}PtMe_2H$ with O_2 increases in the presence of light or AIBN (azobisisobutyronitrile, a radical initiator) and decreases in the presence of radical inhibitors (e.g. 1,4-cyclohexadiene). These observations suggest a mechanism involving radical species. A mechanism analogous to the well-studied radical chain pathway for autoxidation of hydrocarbons (28) was initially proposed (Scheme 12). The initiation step generates a radical, which abstracts the hydrogen atom attached to platinum. The Pt-based radical reacts with oxygen to form a platinum peroxy radical. This species abstracts a hydrogen atom from another molecule of starting material to form the

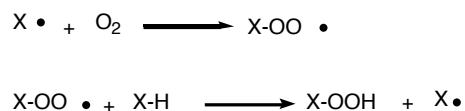
hydroperoxide complex and the chain-carrying Pt-based radical. Eventually, two radicals combine and terminate the chain.

Scheme 12

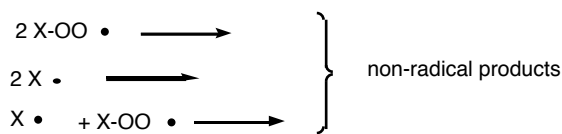
Initiation



Propagation



Termination



Consistent with the proposal of a Pt-based radical intermediate, radical-based substitution at Pt(IV) can be observed under photolytic conditions. When $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ is dissolved in CCl_4 and exposed to light, $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{Cl}$ is formed cleanly and quantitatively (29). Furthermore, benzyl radicals generated in the presence of $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ abstract a hydrogen atom to form toluene (30). At sufficient O_2 pressure, the rate of oxidation is independent of O_2 concentration. The kinetic behavior of the reaction is also consistent with autocatalysis by the product $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{OOH}$ (29). Similar observations have also been noted in the autoxidation of hydrocarbons, but a detailed kinetic analysis of the reaction of $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{H}$ and O_2 indicates that a more complex mechanism than that presented in Scheme 12 may be operating (29).

When the Pt(IV) hydroperoxide species $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{OOH}$ is allowed to react with a good oxygen atom acceptor such as trimethylphosphine, the Pt(IV) hydroxide complex $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{OH}$ is formed (Scheme 11). $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{OH}$ is also obtained by thermolysis of the hydroperoxide complex. Note that if carbon-oxygen reductive elimination were to take place from the Pt(IV)

hydroxide complex $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{OH}$, the product would be methanol. Since C-H activation and oxygen incorporation, the first two steps of the desired alkane functionalization cycle, were observed with this same ligand set, this is an exciting possibility as a methane to methanol transformation can be envisaged. However, such C-O bond formation is not observed to take place from $\text{Tp}^{\text{Me}_2}\text{PtMe}_2\text{OH}$. Yet, our earlier work on C-O reductive elimination from Pt(IV) (6) may shed some light on why this is the case. Note that if the oxygen group were to dissociate, it would not be possible to attack a methyl group that is trans to an open site. Thus, although the facially coordinating Tp^{Me_2} ligand supports the first two steps of C-H activation and O_2 consumption, the C-O reductive elimination step is problematic in this environment.

Summary

Key reaction steps for platinum systems capable of oxidatively functionalizing alkanes have been examined. We have found Pt(II) complexes which can oxidatively add alkane C-H bonds and studied the mechanism of this reaction via investigation of C-H reductive elimination from Pt(IV). Reactions of Pt(II) alkyl and Pt(IV) alkyl hydride complexes with dioxygen have also been discovered. Finally, the mechanism of C-O reductive elimination reaction from Pt(IV) has been investigated. These studies have emphasized the importance of unsaturated intermediates in both bond-forming and bond-cleavage reactions at platinum.

Coordination of alkane to form a Pt(II) σ -complex appears to be an important prerequisite for hydrocarbon activation. This σ -complex can either be formed by the reaction of alkane with a three-coordinate Pt(II) species or by an associative substitution reaction at a four-coordinate Pt(II) complex. Oxidative addition of the C-H bond then occurs from the σ -alkane species to form a five-coordinate Pt(IV) alkyl hydride complex. The five-coordinate intermediate can be trapped by ligand to generate a stable Pt(IV) alkyl hydride. Alternatively, deprotonation of the five-coordinate Pt(IV) alkyl hydride would form a Pt(II) alkyl.

Examples of both Pt(II) alkyls and Pt(IV) alkyl hydrides have been shown to react directly with dioxygen to yield Pt(IV) complexes. In the case of Pt(II) dimethyl complexes, Pt(IV) dimethyl methoxide hydroxide complexes are formed in methanol solution. With a Pt(IV) dimethyl hydride complex, we found that the reaction with O_2 leads to a Pt(IV) dimethyl hydroperoxide complex, which can subsequently be converted to a Pt(IV) dimethyl hydroxide species. Finally the reductive elimination of C-O bonds from Pt(IV) occurs via a two-step process. Dissociation of the oxygen group is followed by

nucleophilic attack at a five-coordinate Pt(IV) alkyl to form the C-O coupled product.

It is anticipated that a detailed understanding of these important reactions at Pt(II)/Pt(IV) centers will allow the design of a ligand capable of stabilizing the required intermediates such that a complete cycle for efficient alkane functionalization can be realized.

Acknowledgements

We gratefully acknowledge the graduate students, postdoctoral research associates, visiting professors and undergraduate researchers in our laboratory who have contributed to this research project: Scott Williams, Dawn Crumpton-Bregel, April Getty, Nicole Smythe, Andy Pawlikowski, Douglas Wick, Mike Jensen, William Dasher, Tami Lasseter, Andy Holland and Darcie Porter. We also thank Professor Joe Templeton and Stefan Reinartz (University of North Carolina) for an enjoyable and productive collaboration (reference 4). Finally, we thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for funding of this work.

References

1. (a) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem.* **1972**, *46*, 785. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (c) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729.
2. Recent reviews: (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem. Int. Ed.* **1998**, *37*, 2180. (c) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Boston, 2000. (d) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259.
3. Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235.
4. Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I.; *J. Am. Chem. Soc.* **2003**, *125*, 8614.
5. Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442.

6. (a) Williams, B. S.; Holland, A. W.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 252. (b) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576.
7. Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530.
8. Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1999**, *121*, 11900.
9. Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fuji, H. *Science* **1998**, *280*, 560.
10. (a) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.*, **1995**, *117*, 6889. (b) Goldberg, K. I.; Yan, J. Y.; Winter, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 1573.
11. (a) Horváth, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8. (b) DeVries, N.; Roe, D. C.; Thorn, D. L. *J. Mol. Catal. A* **2002**, *189*, 17. (c) Lin, M.; Shen, C.; Garcia-Zayas, E. A.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 1000. (d) Geletii, Y. V.; Shilov, A. E. *Kinet. Catal.* **1983**, *24*, 413.
12. Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550.
13. (a) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (b) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (c) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467. (d) Johansson, L.; Ryan, O. B.; Tilset, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 1974. (e) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831. (f) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (g) Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 6579. (h) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378.
14. (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (b) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946. (c) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156. (d) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854. (e) Reinartz, S.; Baik, M.-H.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2001**, *40*, 4726. (f) Norris, C.M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649. (g) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 787. (h) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. (i) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, *20*, 1709. (j) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 563.

15. (a) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966. (b) Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 563. (c) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739. (d) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116.
16. Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219-221*, 157.
17. (a) Lo, H. C.; Haskel, A.; Kapon, M.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 3226. (b) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041.
18. The interpretation of kinetic isotope effects reported in ref 17 has been reexamined. (a) Churchill, D.G.; Janak, K. E.; Wittenberg, J.S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403. (b) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140.
19. In contrast to the results of our study (4), substitutions at Pt(II) are generally found to proceed via associative mechanisms. For evidence of associative substitution mechanisms involving hydrocarbons as ligands at Pt(II) centers, see: (a) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739. (b) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808.
20. (a) Brainard, R. L.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100. (c) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753. (d) Konze, W. V.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 12550.
21. It is possible that the uncoordinated pyrazolyl ring provides anchimeric assistance in the loss of methane from $\kappa_2\text{-Tp}^{\text{Me}_2}\text{PtMe}(\text{CH}_4)$. Such an interaction would not be detected in our kinetic experiments.
22. The “uncoordinated” pyrazolyl ring may interact with the Pt center to provide some additional stabilization to the “three-coordinate” Pt(II) species.
23. (a) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423. (b) Simultaneous discovery of a five-coordinate Pt(IV) dihydrido silyl complex: Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6425.
24. Counterion coordination to cationic complexes has been prohibitive for the synthesis of five-coordinate cationic Pt(IV) alkyls. Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408.
25. Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804.
26. Three-coordinate intermediates pictured in Scheme 8 may be stabilized by agostic donations from ligand C-H bonds to the open site.

27. Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608.
28. (a) Foote, C. S.; Valentine, J. S.; Greenberg, A.; Liebman, J. F.; Editors *Active Oxygen in Chemistry. [In: Struct. Energ. React. Chem. Ser., 1995; 2]*, **1995**. (b) Kochi, J. K.; Editor *Free Radicals, Vol. 2*, **1973**. (c) Howard, J. A. *Advan. Free-Radical Chem.* **1972**, *4*, 49-173.
29. Look, J. L.; Goldberg, K. I., manuscript in preparation.
30. (a) Kolwaite, D.S.; Franz, J.A. unpublished results. (b) methodology similar to Franz, J. A. L., J.C.; Birnbaum, J.C.; Hicks, K. W.; Alnajjar, M.S. *J. Am. Chem. Soc.* **1999**, *121*, 9824-9830.