Mechanistic Studies of Alkane Activation by Platinum(II) Complexes

Thesis by

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In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1997

(Submitted May 19, 1997)

For Mom and Dad

and

Tom and Jody

Acknowledgments

The past five years in graduate school have been some of the best years of my life. I've been blessed to interact with numerous wonderful people, many of whom have had a tremendous influence on my life. At the risk of being a bit "sappy," I'd like to use a few pages to share a few things I've thought and felt but, unfortunately, often left unsaid.

Where can I start but at the foundation? To an Awesome God, whose providential care and grace I continue to experience, I live indebted to You and Your Son for the Hope extending far beyond this life. Ups and downs, twists and turns... thanks for Your patience! I've got so much to learn!! (Philippians 3:10-14)

Mom and Dad, Raelynn and Craig, Penny and Blake, you've been a rock! It's an incredible comfort knowing that wherever I go and whatever I do, you're still there, ready to welcome me back. Hopefully, in some way, I can repay what you've given me. I love you all!

And to one of the greatest advisors a student could ask for... thanks John!! The scientific benefits and training that all of us reap while in your group are obvious. But you've taught me much about scientific "character" as well. In many ways, I value this even more. I hope that I can mimic a fraction of these qualities if I have a chance to be on my own someday.

Jay and Harry, thanks for your role in my training here. Jay, your attention to details combined with an ability to see the big picture, as well as your diversity of interests is inspiring. Harry, your capacity to provide so many students with personal attention and encouragement is remarkable; I'm thankful to have been one of the recipients. And your group meetings,

with their blend of entertainment and rigorous science, are an indelible memory from my experience at Caltech.

Although, as graduate students at Caltech, we often take our funding for granted (no pun intended), I sincerely appreciate and acknowledge both personal and project money provided by the National Science Foundation, the Office of Naval Research, and the Army Research Office. It still amazes me (and quite a few of my non-scientific friends and family) that I can actually be paid to go to school.

Pat and Dian, you make the world go 'round. What more can I say?

Tom and Jody, Jim, John, Suzanne and Joseph... where would I be without you? Thanks so much for answering "the call," and providing me with a place to live and "grow up." Perhaps only God knows the profound influence you've had on my life; you'll forever have a special place in my heart! (I'll try to forget most of the "Klotzle four-wallers" that I've accumulated.) To the entire John Klotzle family, I've really appreciated being part of your family with holiday get-togethers, birthdays, beach trips, etc. (And I'd love to hold on to the "cuncle" title, if I may.)

I would never have gone anywhere (literally!), without a host of willing (and sometimes, not-so-willing) chauffeurs: Dave, Rebecca, Chris, Carol, Elaine, and Mike, may your wheels roll on forever. I think I'll always feel a touch of home when I think about all of you in the Altadena A. C. church family. You've been a tremendous support and encouragement over the past five years. You make it incredibly difficult to leave!

I've also enjoyed a phenomenal group of friends and co-workers while here: you're a major reason that I've had such a great time in grad school! It

started off with Mary, Amy and Justin in "first-year land." What a great way to embark on a graduate career.

The Bercaw group has been host to a multitude of memories. Thanks to the organizational prowess of Tim and Mike, I enjoyed my first backpacking experiences in the Sierras, including one infamous turkey-dinner preparation with EQG (may we never have to work that closely together again!), or laughing at yet another joke from Chris Karp, or choking down Dario's split pea soup, or rejecting yet another of his many attempts to promote the use of squeeze "mar-gar-EEN," or starting the hike with a horrible cold and unknowingly sneezing and coughing all over Jeff at night in the tent (I still feel bad about that one Jeff), or losing our way on the final 6000 foot descent and running in nettles trying to return to the trail (EQG sure was ticked!)... never to be forgotten!

And then there was Hogball: from Andy, perhaps the best coach of all-time, (although we never could quite win the championship); to Wiener, angering and then continuing to fight with "the Duchess;" to Cory, who could cover basically the entire left side of the infield by himself; to Fenton, smokin' his stogies while hobbling around the bases; to Tim and EQG, gunning down some unsuspecting base runner at home plate.

And may the "grope meeting" traditions continue on forever! If you can't "fight the power," then just wait till he graduates. It was fun while it lasted. Chris, may you never leave cake or ice cream unfinished.

Although the platinum group has always been somewhat small, I've benefited from interactions with some great postdocs. Gerrit, I think I will always remember your encouraging words (one conversation in particular) when I first started in the lab. They continue to inspire me. Matt and Lin,

thanks for your example—you put your wives and families first, but still produced lab results as if you worked 16 hours a day. And Matt, I'd like to be one of the first to eat from your catfish farm. Jim, while your claim-to-fame lies with your Z-N work, you were a great colleague on the platinum project. Most of what I know about NMR spectroscopy came from you. Bercaw group meetings wouldn't have been the same without you (from the "Pneumatokakis" cartoon, to the infamous chalk-talk, to your conspicuous absence during the first 15 minute of every meeting... "Where's Jim?"). Shilov (a.k.a. Seva), I expect great things from you; may you live up to your name.

The Bercaw group hasn't attracted too many women (this was also the case before I arrived, I think), but those who have joined have been top notch. Eva, I don't know if we ever satisfactorily treated you like a full-fledged member of the group, but your presence sure added a spark. And your graduating in under four years still impresses me. Susan your personality seemed to light up the entire lab (after you'd had your morning coffee!); its a bummer you left so soon. Deanna earns the title of "The Nicest Person I May Ever Meet." There's never any shortage of "things to be happy about" with you around. OH YEAH!! And your constant sensitivity and thoughtfulness truly made an impression on me. I can only hope to have gleaned some of your traits. Annita, if you do as well in graduate school as you did in Chem 154, you've got an incredibly bright future.

Eugene, I actually began to enjoy your blunt, honest, and often confrontational manner, and it was great to have someone in the group with biochemical interests. No Fighting Illini can be all bad. Dario, I always enjoyed your analysis of American personalities and culture (especially over a

homemade spaghetti dinner at your place!). Shige, your periodic "omiyage" treats brought back many fond memories of Japan.

The recent basketball excursions have gone a long way to preserve my sanity—thanks Matt, Koert, Seva, Chris, and others. Koert, thanks for the Baja Fresh trips (one Dos Manos and two fish tacos). Steve, I wish you the best in your race against extraterrestrial competitors, even if you'll never really know whether you've won or lost. Between Jim, Andy, Steve, and K-man, I had plenty of opportunity for stimulating discussions on controversial and/or eccentric topics. They were fun while they lasted. Jeff, I appreciated the few opportunities we had together to "refocus." (OK, and Señor Fish isn't really that bad.) Antek, I'll always remember your car as the quickest way to the sleaziest fast food available. Paul, it's great to see someone else who enjoys thinking about mechanisms. Best of luck.

Long live Dr. Pepper and Baja Fresh!! ('nuf said.)

Abstract: Currently, there is considerable interest in alkane oxidation reactions catalyzed by transition metal complexes. Chapter 1 reviews many of the recent advances in this field involving electrophilic late transition metals. The C–H activation step appears to dictate both the rate and selectivity of these reactions. Unfortunately, however, very little is known about the mechanism of this step.

In chapter 2, mechanistic studies of the protonolysis of several alkylplatinum(II) complexes [(tmeda)PtMeCl, (tmeda)Pt(CH_2Ph)Cl, (tmeda)$PtMe_2$, and *trans*-(PEt_3)$_2$Pt(CH_3)Cl] are described. These reactions model the microscopic reverse of C-H activation by aqueous Pt(II). Kinetics, activation parameters, and isotope effects were determined, and the results support a common mechanistic sequence for all of the reactions: (1) chloride- or solvent-mediated protonation of Pt(II) to generate an alkylhydridoplatinum(IV) intermediate, (2) dissociation of solvent or chloride to generate a cationic, five-coordinate platinum(IV) species, (3) reductive C-H bond formation producing a platinum(II) alkane σ-complex, and (4) loss of alkane either through an associative or dissociative substitution pathway. These studies provide insight into the role of solvent and ancillary ligands in aqueous Pt(II)-mediated C–H activation. The results also support the viability of Pt(II) σ-adducts and alkylhydridoplatinum(IV) intermediates in this reaction.

Chapter 3 describes the preparation and study of Pt(II) H_2-adducts and Pt(IV) dihydride complexes. The species of interest are generated by protonation of hydridoplatinum(II) complexes of the type *trans*-(PCy_3)$_2$Pt(H)X [X = SiH_3, H, CH_3, Ph, Cl, Br, I, CN, CF_3SO_3] and [*trans*-(PCy_3)$_2$Pt(H)L][BAr^f_4] [L = CO, 4-picoline; BAr^f_4 = B(3,5-$C_6H_3(CF_3)_2)_4$]. The proton attacks one of three different sites on these complexes (hydride, platinum, or the *trans* ligand), depending on which ligand is *trans* to hydride. These studies reveal several factors affecting the stability and reactivity of Pt(II) σ-adducts, which thus have implications for C–H activation by Pt(II).

Mechanistic Studies of Alkane Activation by Platinum(II) Complexes

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Chapter 1

Homogeneous Oxidation of Alkanes by Electrophilic Late Transition Metals

INTRODUCTION

The basic chemical feedstock for the industrial synthesis of commodity organic chemicals periodically shifts, driven by economic factors and technological innovations. For years acetylene was the primary starting material for the commercial synthesis of bulk chemicals, including vinyl chloride, acetic acid, and acetaldehyde. Acetylene's high energy content renders virtually any desired commercial synthesis thermodynamically accessible; however, its expense combined with the development of new olefin transformations allowed ethylene, propylene and butadiene to replace acetylene as primary feedstocks for the chemical industry.

Alkanes are even less expensive and more abundant than the olefins listed above, and thus represent an important potential resource for the chemical industry. Unfortunately, very few selective methods are available for converting alkanes into more valuable products. Furthermore, several desirable transformations utilizing alkanes are not thermodynamically favorable. One important process in which alkanes are used is the generation of synthesis gas ($CO + H_2$, abbreviated "syngas") (eq 1) by the "steam reforming" of methane, the primary component of natural gas. Syngas may then be used directly in industrial reactions (e.g., hydroformylation of olefins), but it is often converted to methanol for use as a fuel or as a chemical feedstock (eq 2). The direct oxidation of methane represents a much more efficient pathway for methanol synthesis (eq 3).

Attempts to selectively oxidize alkanes encounter two important problems. First, with respect to *chemoselectivity*, the initial product of alkane oxidation is often more reactive toward the oxidant than the alkane itself. For example, the C–H bond in methanol is 11 kcal/mol weaker than that in

$$CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{[Ni]} CO(g) + 3\,H_2(g) \qquad (1)$$
$$\Delta H° = 49.3 \text{ kcal/mol}$$

$$CO(g) + 2\,H_2(g) \xrightarrow{[Cu/ZnO]} CH_3OH(g) \qquad (2)$$
$$\Delta H° = -21.7 \text{ kcal/mol}$$

$$CH_4(g) + 1/2\,O_2(g) \longrightarrow CH_3OH(l) \qquad (3)$$
$$\Delta H° = -30.7 \text{ kcal/mol}$$

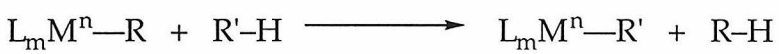
methane (93 versus 104 kcal/mol, respectively). Consequently, if methane oxidation involves a hydrogen-atom abstraction step, overoxidation of methanol (ultimately leading to CO_2) will dramatically reduce the desired product selectivity, unless the reaction is stopped at very low conversion.[1] The *regioselectivity* of alkane oxidation is also problematic. In reactions with alkanes, both radical and electrophilic (i.e., superacid) reagents preferentially attack tertiary over primary and secondary C–H bonds (3° > 2° > 1°).[2,3] However, the selectivity is often not high, and the desired preference is often in the opposite direction.

Homogeneous organometallic systems can potentially overcome these selectivity problems, and considerable effort has been directed toward exploring this possibility.[4-9] Indeed, the many examples of "organometallic"[10] alkane activations suggest that a reversed regioselectivity pattern can be attained (i.e., 1° > 2° > 3°). Further, strong C–H bonds can be activated selectively in the presence of weaker C–H bonds (e.g., aromatic > benzylic activation in toluene).[11] Several approaches to organometallic activation reactions are shown in Figure 1.[4-9] Despite the success in this area, few systems are capable of subsequent substrate functionalization and

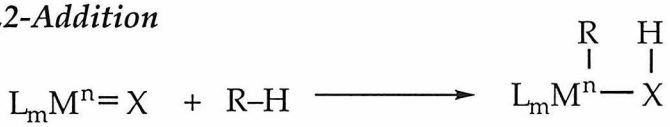
regeneration of the metal fragment as required for catalytic turnover. In most cases the reactive metal species responsible for alkane activation is incompatible with oxidants (O_2, H_2O_2, etc.) required for catalysis.

A) Oxidative Addition

B) Sigma-bond metathesis

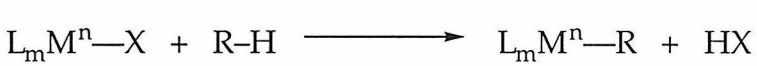


C) 1,2-Addition



X = O, NR, CR_2

D) Electrophilic Activation



X = halide, hydroxide, triflate, etc.

E) Metalloradical Activation

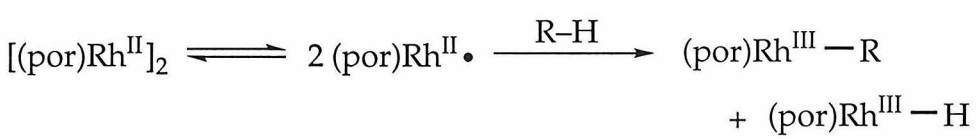


Figure 1: Various pathways discovered for the activation of alkane C–H bonds. (see text for references)

An important exception to this limitation is the reaction of alkanes with chloroplatinum salts in aqueous solution. Ironically, this system is one of the earliest examples of C–H activation. In 1969 Shilov and co-workers observed deuterium incorporation into alkanes in D_2O/acetic acid-d_1 solutions of K_2PtCl_4.[12] Three years later the same group reported that addition of H_2PtCl_6 to the reaction mixture generated oxidized alkane products (i.e., RCl and ROH) (eq 4).[13] This system is remarkably

$$CH_4 + PtCl_6^{2-} + H_2O\,(Cl^-) \xrightarrow[H_2O,\,120^\circ C]{PtCl_4^{2-}} CH_3OH\,(CH_3Cl) + PtCl_4^{2-} + 2\,HCl \qquad (4)$$

robust; unlike most of the reactions in Figure 1 which are extremely air- and moisture-sensitive, this reaction is carried out in aqueous solution and is unaffected by the presence of O_2. The doubly solvated complex, $PtCl_2(H_2O)_2$, has been proposed as the active catalytic species, and the observed selectivity patterns reflect those of other organometallic activation systems, namely 1° > 2° > 3°.[8]

In recent years, several new alkane oxidation reactions have been discovered which utilize electrophilic late transition metals in strongly acidic media (e.g., CF_3CO_2H, H_2SO_4).[14-32] These systems exhibit significant similarities to the platinum chemistry discussed above, and together, they represent an extremely promising approach to alkane functionalization. They not only offer new insights into factors necessary for selective conversion of alkanes into more valuable products, but also have potentially practical utility. This introduction will survey recent studies exploring the scope, selectivity, and detailed mechanism of aqueous platinum(II)-catalyzed

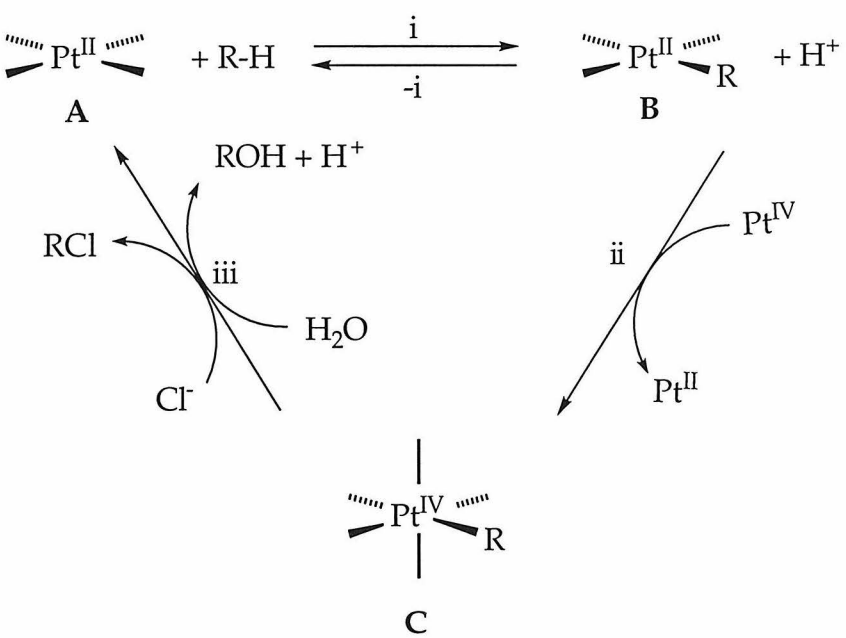
alkane oxidations,[33] and will summarize related homogeneous oxidation reactions involving other late transition metals in strong acid solvents.

ALKANE OXIDATION BY AQUEOUS PLATINUM COMPLEXES

Mechanistic Studies.

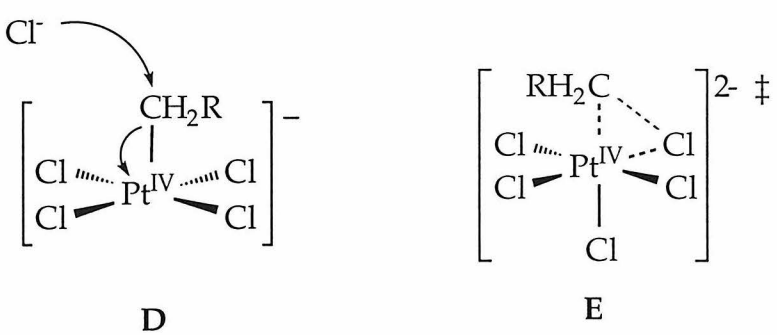
Proposed Mechanism. In 1983, Shilov et al. proposed a mechanism for platinum-catalyzed alkane oxidation consisting of three basic transformations (Scheme I)[34]: (i) electrophilic activation of the alkane by Pt(II) to generate an alkylplatinum(II) intermediate, (ii) two-electron oxidation of alkylplatinum(II) to generate an alkylplatinum(IV) species, and (iii) reductive elimination of R–X (X = Cl or OH) to liberate the oxidized alkane and the Pt(II) catalyst.

Scheme I



This proposal has received considerable mechanistic attention by several research groups. While the general scheme shown above was quickly accepted, many features of the individual steps have only recently been identified. Each of the three steps in Scheme I can potentially proceed by (at least) two different pathways. These possibilities and the experiments used to distinguish between them are discussed below. The steps of the catalytic cycle will be discussed in reverse order, according to the chronology of their elucidation.

Step iii: Reductive Elimination of ROH/RCl from Pt(IV). Alkane functionalization is completed by reductive elimination of R–X from platinum(IV). Two different mechanisms have been postulated for this reaction: a nucleophilic (S_N2) pathway (**D**, Figure 2) versus a concerted, three-center transition state (**E**).



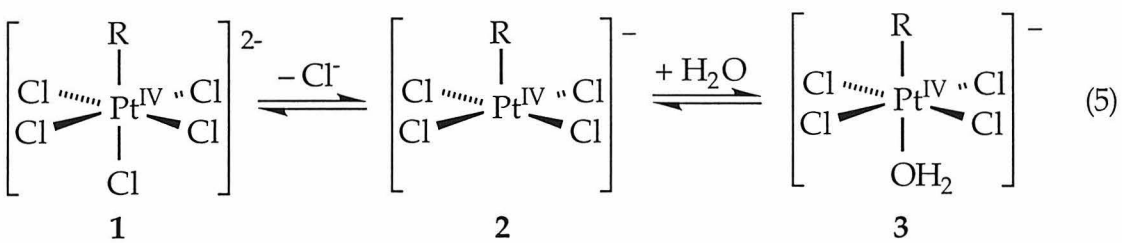
D **E**

Figure 2: Two possible pathways for reductive elimination of RCH_2Cl from Pt(IV): S_N2 (**D**) versus a three-centered concerted mechanism (**E**)

Zamashchikov and co-workers were the first to examine this step directly. They prepared the alkylplatinum(IV) intermediate, $[Pt(R)Cl_5]^{2-}$ (**1**) (R = CH_3,

CH_2CH_3, CH_2COCH_3, etc.) independently and monitored the kinetics of its decomposition in aqueous solutions to form RCl and ROH.[35-42] As described below, these and additional studies by Luinstra et al.,[43,44] definitively establish that R–X bond formation proceeds by an S_N2 mechanism.

Various alkylplatinum(IV) complexes are most readily prepared by oxidative addition of R–I to $PtCl_4^{2-}$, although they also have been observed under certain conditions by oxidation of R–H in aqueous solutions of $PtCl_4^{2-}/PtCl_6^{2-}$ (i. e., undergoing steps i and ii in Scheme I).[34,45] These complexes exist in equilibrium with their monoaquo derivatives (**3**) (eq 5) in



(5)

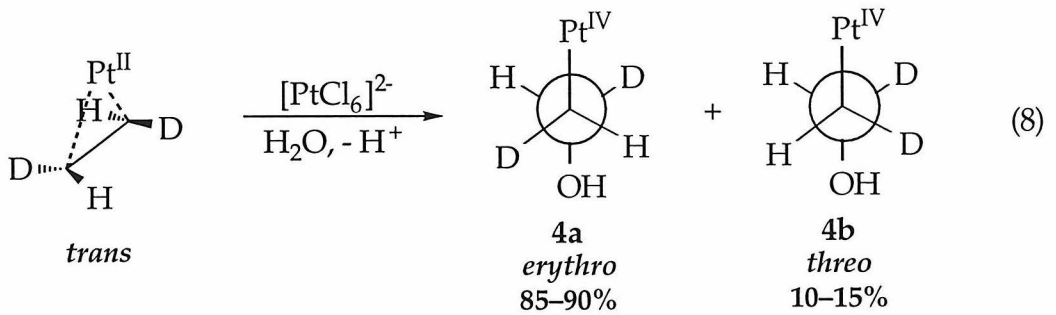
aqueous solution. Complex **2** is presumed to be an intermediate in this equilibrium. The equilibrium constant (K) between **1** and **3** when R = methyl is ≈ 0.8 M (eq 6).[36,43,44] The rate expression for the formation of RCl shown in eq 7 was obtained by monitoring the decay of the alkylplatinum(IV) complexes (**1** + **3**). The kinetics cannot distinguish between nucleophilic attack on the aquo complex (**3**) or the five-coordinate intermediate (**2**); however, the latter has been favored since it represents the microscopic reverse of methyl halide oxidative addition to square planar, d^8 complexes.

$$K = \frac{[\mathbf{3}][Cl^-]}{[\mathbf{1}]} \qquad (6)$$

$$\frac{d[\mathbf{1}+\mathbf{3}]}{dt} = k_{obs}[\mathbf{1}+\mathbf{3}]; \qquad k_{obs} = \frac{k_1[Cl^-] + k_2[H_2O]}{1 + K^{-1}[Cl^-]} \tag{7}$$

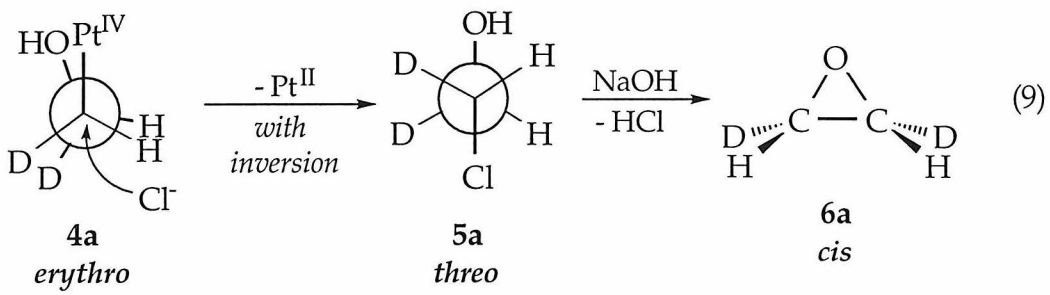
Evidence against a 3-center, concerted pathway was obtained when monitoring the decomposition of **1** + **3** in the presence of other anions such as bromide and iodide. Under reaction conditions where these halides are not incorporated into the platinum coordination sphere *cis* to the alkyl group, formation of R–X (X = Br, I) is observed in large preference to R–Cl.[39,40] This result strongly supports R–X bond formation by external nucleophilic attack.

Perhaps the most definitive evidence favoring the S_N2 pathway for R–X bond formation is inversion of stereochemistry at the platinum-bound carbon center upon reductive elimination.[43,44] (Concerted reductive elimination through a three-centered transition state is expected to result in retention of configuration.) Formation of a platinum(IV) complex bearing a chiral alkyl group is obtained by oxidation of isotopically labeled Zeise's salt by $PtCl_6^{2-}$ (see below for mechanism). For example, oxidation of Zeise's salt bearing *trans*-dideuteroethylene yields predominantly (≈ 85–90%) the *erythro* β-hydroxyethyl product, $[Pt(CHDCHDOH)Cl_5]^{2-}$ (**4a**). Ten to fifteen percent of the *threo* isomer (**4b**) is also formed (eq 8). Decomposition of **4** in the presence of chloride and subsequent conversion of the resulting 2-chloroethanol (**5**) to



(8)

ethylene oxide (**6**) reveals the *cis* isomer in isotopic purity identical to the initial alkylplatinum(IV) complex, **4** (eq 9). This sequence clearly reflects inversion of stereochemistry in the reductive elimination reaction, consistent with an S_N2 mechanism.



4a *erythro* **5a** *threo* **6a** *cis* (9)

Step ii: Oxidation of Pt(II)R to Pt(IV)R. Development of a practical alkane oxidation method requires that the reaction be coupled to consumption of an inexpensive stoichiometric oxidant (preferably O_2). Platinum(IV) is clearly impractical as a stoichiometric oxidant! Two possible mechanisms have been considered for oxidation of the alkylplatinum(II) intermediate by platinum(IV): (1) alkyl transfer from R–Pt(II) to Pt(IV) or (2) inner sphere, two-electron transfer from R–Pt(II) to Pt(IV) (i.e., chloronium ion transfer) (Figure 3). Whereas the former demands the presence of Pt(IV) to produce the alkylplatinum(IV) intermediate, the latter is compatible with the use of less expensive oxidants. Importantly, recent studies support the second pathway, suggesting that practical alternatives to Pt(IV) may be possible.[44,46,47]

Direct study of the oxidation step was delayed for many years because the alkylplatinum(II) intermediate (**B**) could not be prepared. In protic solvents the methyl derivative rapidly undergoes protonolysis to liberate methane,[35,44,48] and in non-protic media it disproportionates to

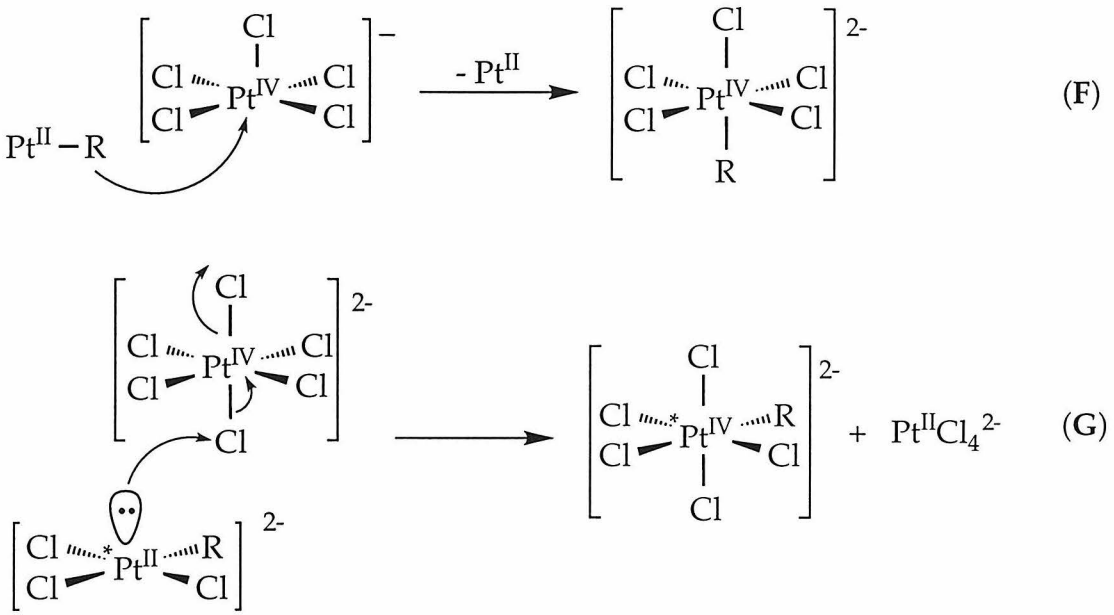
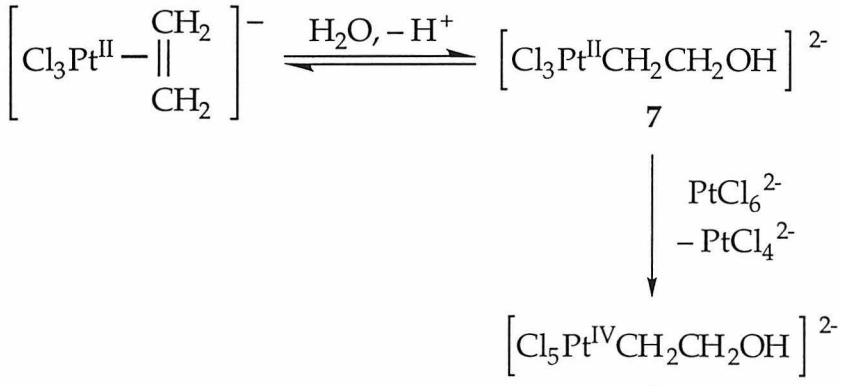


Figure 3: Two possible pathways for oxidation of the alkylplatinum(II) intermediate by $[PtCl_6]^{2-}$: alkyl transfer from Pt(II) to Pt(IV) (**F**) versus inner sphere electron transfer (i.e., "Cl^+" transfer) (**G**). Only pathway X is compatible with replacement of Pt(IV) with a less expensive oxidant.

$[Pt(CH_3)_2Cl_2]^{2-}$ and $[PtCl_4]^{2-}$.[47] Luinstra et al. recently circumvented this problem by examining the oxidation of Zeise's salt by $PtCl_6^{2-}$.[44,46] Kinetic studies reveal that this reaction proceeds through a transient alkylplatinum(II) intermediate, **7** (Scheme II). When isotopically labeled $Na_2{}^{195}PtCl_6$ was used, the ^1H NMR of the product (**4**) revealed ^{195}Pt satellites for the Pt–C*H*$_2$CH$_2$OH peak of *normal* intensity, i.e., 33% of the total peak area (^{195}Pt natural abundance ≈ 33%). Thus, no alkyl transfer occurs in this reaction.

Recently, the methylplatinum(II) complex $[Pt(CH_3)Cl_3]^{2-}$ was prepared by reduction of $[Pt(CH_3)Cl_5]^{2-}$ by cobaltocene in THF.[47] Rapid precipitation of

Scheme II



the product prevents the disproportionation reaction discussed above. Subsequent dissolution of $[Pt(CH_3)Cl_3]^{2-}$ into an aqueous solution containing $^{195}PtCl_6^{2-}$ (eq 10) confirms the result obtained in the oxidation of Zeise's salt: the reaction proceeds by electron transfer *not* alkyl transfer.

$$\left[Cl_3Pt^{II}-CH_3\right]^{2-} + {}^{195}PtCl_6^{2-} \xrightarrow{H_2O} \left[Cl_5Pt^{IV}-CH_3\right]^{2-} + {}^{195}PtCl_4^{2-} \qquad (10)$$

Step i: Electrophilic Activation of Alkanes by Pt(II). The C–H activation step (step i, Scheme I) appears to appears to determine both the rate and selectivity of the alkane oxidation reaction, thus providing significant motivation to understand its detailed mechanism. Unfortunately, this step has proven to be the most difficult to study. As indicated in Scheme I, the reaction stoichiometry involves electrophilic displacement of a proton on the alkane by Pt(II). Once again two different mechanisms have been considered for this reaction[1,8,49-51](Figure 4): (1) oxidative addition of the C–H bond at Pt(II) yielding an alkylhydridoplatinum(IV) species which is subsequently deprotonated, or (2) deprotonation of an intermediate Pt(II)-alkane σ-adduct.

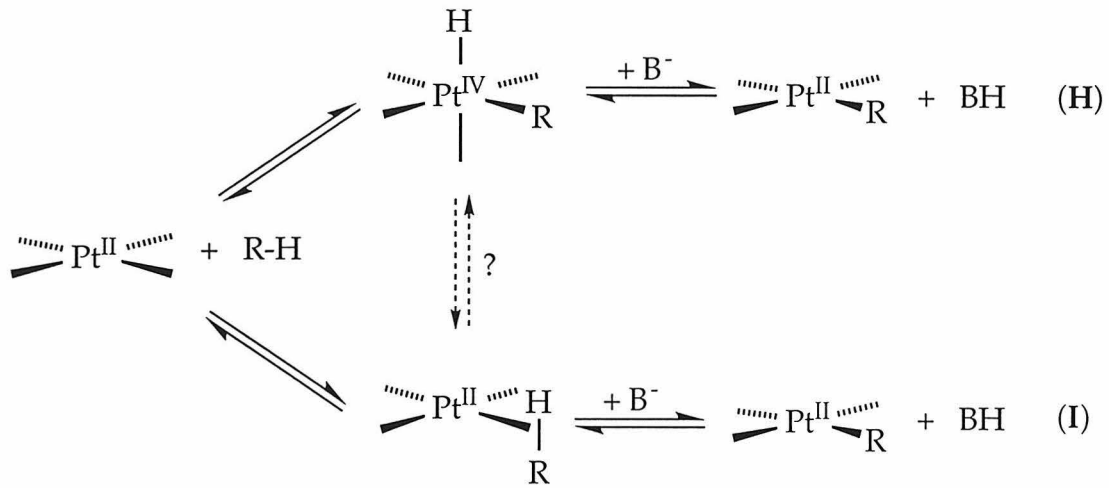


Figure 4: Two possible pathways for alkane C–H activation by Pt(II): C–H oxidative addition and subsequent deprotonation of the Pt(IV) hydride (**H**) versus formation and subsequent deprotonation of an alkane σ-adduct (**I**)

In contrast to steps ii and iii (Scheme I), definitive evidence supporting one of the two proposals for step i has not been obtained.

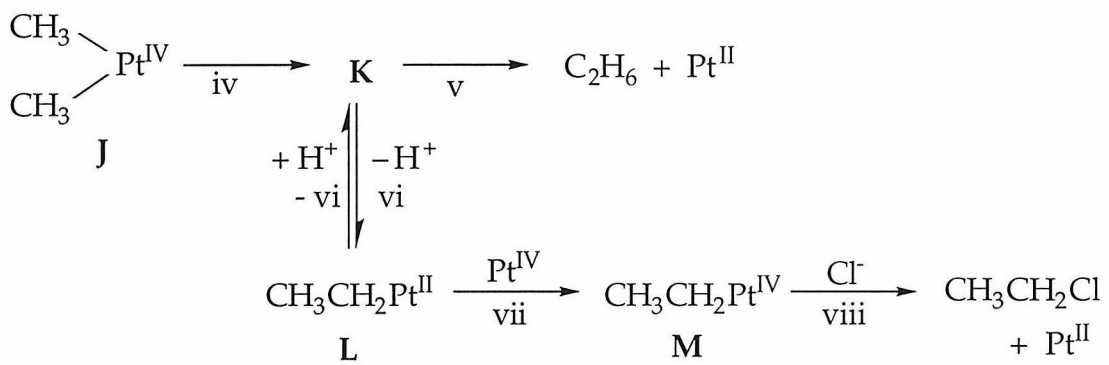
Early studies of C–H activation focused on deuterium incorporation into protio alkanes in D_2O solutions of $PtCl_4^{2-}$.[8] While substantial evidence supports the homogeneity of these reactions, platinum metal deposition often complicates detailed studies. Furthermore, the reaction conditions (> 100 °C) for C–H activation are not expected to allow detection of reactive intermediates.

Under conditions closely resembling those of alkane oxidation (95 °C, aqueous chloride solutions), Zamashchikov et al. recently examined the elimination of ethane from the dimethylplatinum(IV) complex, $Cs_2Pt(CH_3)_2Cl_4$.[52-55] When this reaction is carried out in D_2O, multiple deuteration is observed in the ethane produced. The range of ethane isotopomers observed in this reaction ($C_2H_{6-i}D_i$: 1 : 0.85 : 2.0 : 2.2 : 0.2 : 0.3 : 0.3

for i = 0–6 respectively) indicates that H/D exchange is largely localized on one of the carbon centers. Furthermore, if $PtCl_6^{2-}$ is present in the reaction mixture, ethyl chloride is generated. The H/D exchange result resembles that obtained for an isolable rhodium(III) ethyl hydride complex proposed to undergo isotopic exchange through an ethane σ-adduct.[56]

The proposed mechanism shown in Scheme III accounts for these observations. Formation of intermediate **K** (step iv) can either result in

Scheme III



elimination of ethane (step v) or loss of a proton to generate the ethylplatinum(II) complex (**L**). Compound **L** can then undergo a reversible protonation reaction (step vi/-vi) which leads to multiple deuteration of the ethyl group in the presence of D^+, or reaction with Pt(IV) to produce the ethylplatinum(IV) species (**M**) which decomposes into ethyl chloride and Pt(II). Intermediate **K** may be either an Pt(II)-ethane σ-adduct or an ethyl(hydrido)platinum(IV) species. Zamashchikov et al. have argued for the intermediacy of the latter on the basis of isotope effects,[53] however, their analysis assumes that σ-adduct formation from free Pt(II) and alkane exhibits

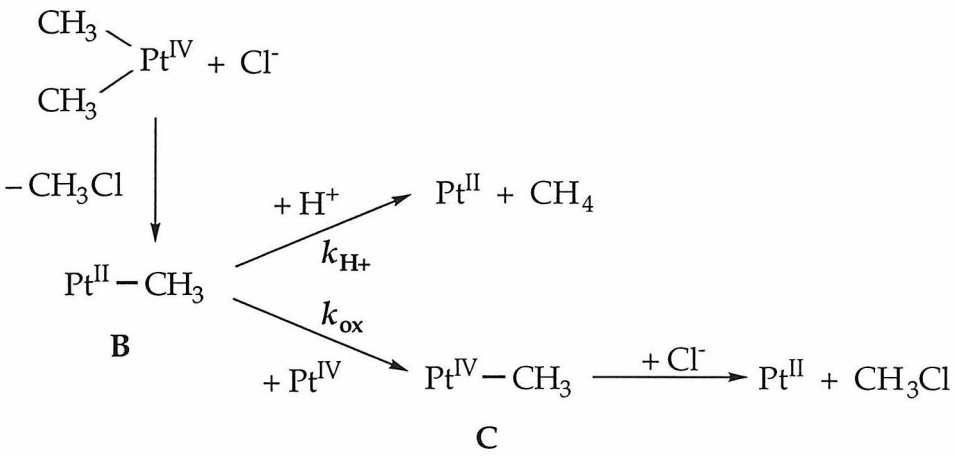
no isotope effect. Recent evidence indicates that this is not a valid assumption.[57-59]

A recent theoretical study by Siegbahn and Crabtree examined the mechanism of C–H activation by Pt(II).[51] The data indicate that the energy barrier for a reaction proceeding through $Pt^{IV}(R)(H)$ is somewhat lower than a single-step, non-redox mechanism. Nevertheless, the authors argued in favor of the single-step mechanism for Pt(II) based on analogy to Pd(II) which can effect similar chemistry. The +4 oxidation level is prohibitively high in energy for Pd. In summary, neither experiments nor theory have been able to distinguish between the mechanistic alternatives shown in Figure 4.

Other Mechanistic Studies: The Fate of Pt^{II}–R Under Catalytic Conditions. As suggested in Scheme I, the alkylplatinum(II) intermediate (**B**) can undergo protonolysis to regenerate the alkane (step -i) or two-electron oxidation to produce the alkylplatinum(IV) intermediate (**C**) (step ii). Because step ii in Scheme I appears irreversible under catalytic conditions, the relative ratio of these reaction rates can have important implications on the reaction selectivity. Two groups have examined this competition directly by the *in situ* generation of **B** in solutions containing varied concentration of H^+ and Pt(IV).[41,47,52] Nucleophilic attack by chloride on $[Pt^{IV}Me_2Cl_4]^{2-}$ at 95 °C in aqueous solutions liberates CH_3Cl and $[Pt^{II}MeCl_3]^{2-}$ (cf. **D**, Figure 2). Zamashchikov and co-workers identified a branching ratio of the secondary rate constants (k_{ox}/k_{H+}) of ~18 (see Scheme IV).[52]

In related experiments, a ratio (k_{ox}/k_{H+}) of ~1 was obtained at room temperature when **B** was prepared by cobaltocene reduction of $[Pt^{IV}MeCl_5]^{2-}$,[47] and a value for k_{ox}/k_{H+} of 70 was found for an ethylplatinum(II) complex at 80 °C.[41] Although the origin of these differences

Scheme IV



is not entirely clear, it appears that the ratio is larger at higher temperatures. Under catalytic conditions (typically 120 °C), the oxidation of **B** by Pt(IV) is likely much faster than the protonolysis reaction. These results explain why no deuterium incorporation was observed in hydrocarbon substrates when the catalytic reaction was carried out in D_2O.[50,60] This confirmation that C–H activation is the rate determining step emphasizes the importance of understanding the detailed mechanism of this reaction.

Recent Advances in Platinum-Catalyzed Alkane Oxidation.

Studies on the Selectivity of C–H Activation. The alkane oxidation system discovered by Shilov is especially attractive because of the unique selectivity patterns observed.[8] The reactivity contrasts with that effected by radical reagents both from the standpoint of regio- and chemoselectivity. With respect to regioselectivity, reactions with linear alkanes often lead to selective chlorination/hydroxylation at the methyl positions rather than at the weaker, secondary C–H bonds. The chemoselectivity of the reaction is reflected by the initial oxidation products being relatively stable to

overoxidation. Several recent studies have examined the scope of this reaction selectivity to identify its potentially practical utility.[45,50,61-66]

Methane is perhaps the most attractive substrate for direct oxidation to its alcohol product, since it is by far the most abundant alkane and represents an enormous natural resource for use as a fuel and as a chemical feedstock.[67] Results published by Sen et al.[65] and Labinger and Bercaw et al.[62] indicate that methane and methanol exhibit similar reactivity with the platinum salts under standard oxidation conditions. Unfortunately, the similarity in rates combined with the greater solubility of methanol in water will limit the practicality of this system. Nevertheless, this selectivity stands in sharp contrast to reactions involving hydrogen atom abstraction, where methanol can be expected to react up to six orders of magnitude faster than methane.

Further support for the unique selectivity patterns was obtained by oxidation of the two-carbon substrates, ethane and ethanol.[45,50,61,65] Here the relative rate of C–H bond activation follows the order $H–CH_2CH_3$ > $H–CH_2CH_2OH$ > $H–CH(OH)CH_3$, opposite to that expected on the basis of bond dissociation energies. Recent mechanistic studies by Sen and co-workers indicate that Zeise's salt, $[PtCl_3(C_2H_4)]^-$, is an intermediate in the oxidation of *both* ethane and ethanol. These results support the viability of direct oxidation of ethane to ethylene glycol! An industrial process based on such technology would be a very attractive alternative to the oxidation of ethylene.

The water soluble substrate, *p*-toluenesulfonic acid, is oxidized at the methyl group 1.5 times faster than at the corresponding hydroxymethyl product.[50] No oxidation of the aldehyde product was observed. Furthermore, use of *p*-ethylbenzenesulfonic acid reveals comparable rates of functionalization at both the methyl and benzylic positions. Sen and co-

workers have also noted the importance of the "chelate effect" in the oxidation of functionalized organic substrates such as aliphatic alcohols, carboxylic acids, sulfonic acids, and phosphonic acids.[63,64,66] In their studies, they observe the following order of reactivity: α-C–H << β-C–H < γ-C–H < δ-C–H for alcohols and α-C–H << β-C–H < γ-C–H ≥ δ-C–H for acid substrates supporting a reaction pathway involving initial substrate coordination to the platinum center followed by substrate activation. Thus, in addition to the inherently unusual selectivity patterns observed in Shilov chemistry, the "chelate effect" can also be employed to enhance selectivity and direct the oxidation chemistry to typically unreactive C–H bonds.

Substitution of Pt(IV) with Less Expensive Oxidants. One of the most formidable challenges facing the Shilov system is replacing Pt(IV) with an economically viable oxidant. Although numerous high-potential oxidants will convert the alkylplatinum(II) intermediate (**B**) to alkylplatinum(IV) (**C**), the challenge lies in identifying a reagent which will not irreversibly oxidize the Pt(II) catalyst as well. Pt(IV) does not encounter this dilemma since the reduced product of catalyst oxidation is the catalyst itself (eq 11).

$$Pt^{II} + {}^{*}Pt^{IV} \rightleftharpoons Pt^{IV} + {}^{*}Pt^{II} \qquad (11)$$

Despite several attempts to address this issue, success has been quite limited.[60,62,68-70] Shortly after their initial discovery of platinum-mediated alkane oxidation, Shilov et al. reported that addition of quinones or Cu(II) to a reaction mixture of $H_2PtCl_6/PtCl_4^{2-}$ under air led to oxidation of acetic acid to chloroacetic acid, catalytic in both Pt(IV) and Pt(II).[68] However, only five turnovers were achieved.

Heteropolyacids (also known as polyoxometallates) have also been employed to alleviate the need for stoichiometric Pt(IV).[69,70] $Na_8HPMo_6V_6O_{40}$ (HPA-6) was added to the standard reaction mixture in order to couple alkane oxidation to O_2; the reduced form of HPA-6 can be reoxidized by O_2. Although up to two turnovers were observed, the methanol generated in the reaction was typically overoxidized.[69] Another heteropolyacid, $H_3PMo_{12}O_{40}$ (phosphomolybdic acid), was successfully employed as a redox mediator for the electrocatalytic oxidation of p-toluenesulfonic acid under bulk electrolysis conditions (+0.7 V vs. Ag/AgCl at 120 °C).[70] In this case, no Pt(IV) was added to the initial reaction mixture. Nevertheless, after ~6 turnovers (with respect to Pt(II)) overoxidation of the alcohol product was observed, likely due to deposition of Pt^0 which was observed at longer reaction times.

Recently, Horvath and co-workers have reported the oxidation of methane by Cl_2, mediated by platinum salts in aqueous solution.[60] While no deposition of metallic platinum is observed in this reaction, overoxidation products are still observed after several hours at 125 °C. Thus, despite several attempts to circumvent the requirement for Pt(IV) using a variety of stoichiometric oxidants and/or redox mediators, success remains elusive.

Future Challenges.

The platinum-mediated chemistry described above has been a fruitful system to explore a range of mechanistic and selectivity issues related to alkane oxidation by homogeneous transition-metal complexes. Unfortunately, several features render it impractical in large scale reactions. The previous section outlined some of the difficulties involved in replacing Pt(IV) as the stoichiometric oxidant. Practical applications will clearly require

the use of a less expensive reagent, preferably O_2. The selectivity of these reactions also does not appear sufficiently high for large scale implementation. Deposition of platinum metal further erodes the characteristic selectivities of the homogeneous reaction, and unlike palladium(0) which is often reoxidized in catalytic reactions, reduction to platinum(0) appears much less reversible. These issues must be addressed in order to develop a useful platinum-mediated alkane oxidation system. The next section will demonstrate that many of these problems can been circumvented by using different transition and main group metals and alternative solvents.

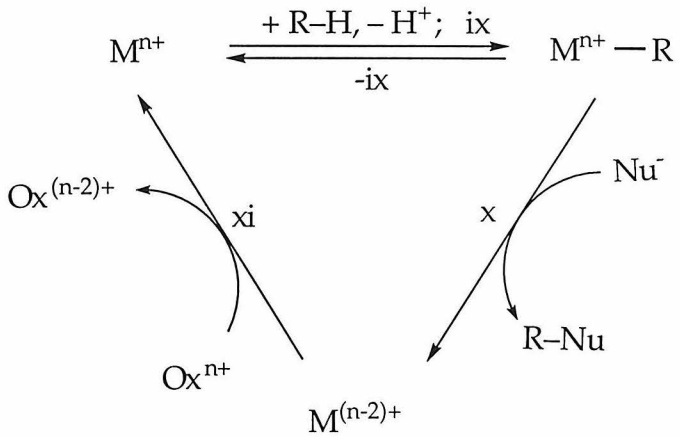
ALKANE OXIDATION BY ELECTROPHILIC METAL IONS IN STRONG ACID MEDIA

Overview.

Considerable attention has recently been directed toward the oxidation of alkanes by electrophilic metal ions in strong acid media. At first glance, these systems seem quite similar to the aqueous platinum chemistry discussed above. For example, the overall reaction appears consistent with an electrophilic C–H activation mechanism followed by subsequent oxidation/functionalization steps. However, many of the metals are in their highest stable oxidation state (e.g., Hg^{2+}, Co^{3+}, etc.) suggesting that an alternative mechanism may be operating. One possible alternative, shown in Scheme V, has the functionalization step *preceding* the oxidation step, thereby avoiding the unstable $M^{(n+2)+}$ oxidation level. Curiously, this mechanism suggests the organometallic intermediate, M^{n+}—R, is susceptible to both electrophilic (step -ix) and nucleophilic attack (step x). Other

mechanisms (e.g., outer sphere electron transfer) have also been proposed, and these studies remain the subject of current research efforts.

Scheme V



Catalytic Systems.

Mercury-Catalyzed Functionalization of Methane. By far, the most successful system for the direct, two-electron oxidation of methane is the mercury(II)-mediated system discovered by Periana and co-workers at Catalytica, Inc.[21,22] This reaction, shown in eq 12, can be carried out in a variety of strong acid solvents; it is unsuccessful in weaker acids such as acetic acid.

$$CH_4 + HgX_2 \xrightarrow{HX} CH_3X + HX + Hg_2X_2 \qquad (12)$$

$$X = CF_3SO_3, HSO_4, \text{ or } CF_3CO_2$$

Most importantly, in 100% sulfuric acid the reaction becomes catalytic in Hg(II) (eq 13), generating methyl bisulfate (CH_3OSO_3H) in 43% yield (85%

$$CH_4 + 2\,H_2SO_4 \xrightarrow[180\ ^\circ C]{Hg(II)} CH_3OSO_3H + 2\,H_2O + SO_2 \qquad (13)$$

selectivity at 50% conversion. The high selectivity suggests that CH_4 is ~100-fold more reactive than CH_3OSO_3H. Similar reactivity was observed in triflic and sulfuric acids in the presence of thallium(III), gold(I), palladium(II), and platinum(II/IV), however, no efficient catalysis was observed. A potentially viable approach for the direct conversion of methane to methanol using dioxygen as the stoichiometric oxidant is shown in Figure 5.

Step 1: $CH_4 + 2\,H_2SO_4 \longrightarrow CH_3OSO_3H + 2\,H_2O + SO_2$

Step 2: $CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4$

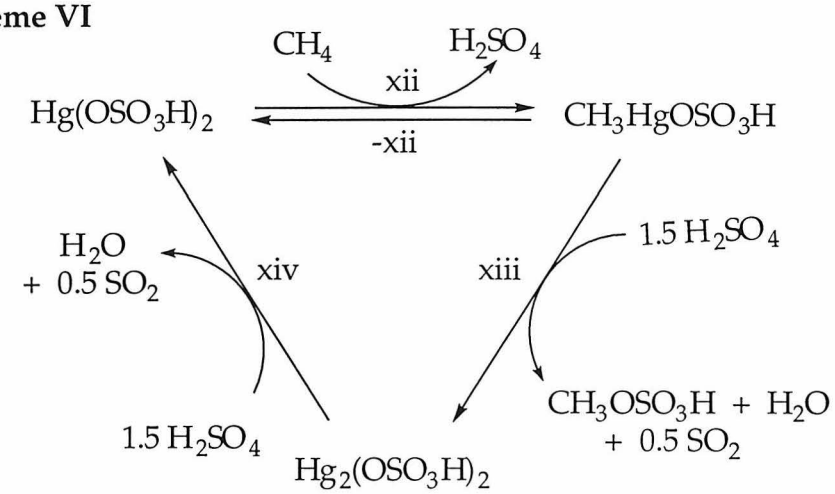
Step 3: $SO_2 + 1/2\,O_2 + H_2O \longrightarrow H_2SO_4$

Net Rxn: $CH_4 + 1/2\,O_2 \longrightarrow CH_3OH$

Figure 5: Possible reaction sequence allowing the direct oxidation of methane to methanol by O_2

Based on a series of observations, the Catalytica group proposed the following catalytic cycle (Scheme VI): (1) electrophilic activation of methane to generate a methylmercury(II) intermediate (step xii), (2) reductive elimination of methyl bisulfate (step xiii), and (3) subsequent oxidation of mercurous bisulfate to regenerate the catalyst (step xiv). As discussed above, the functionalization and oxidation steps have reversed their order relative to the Shilov system (Scheme I) due to the inaccessibility of Hg(IV).

Scheme VI

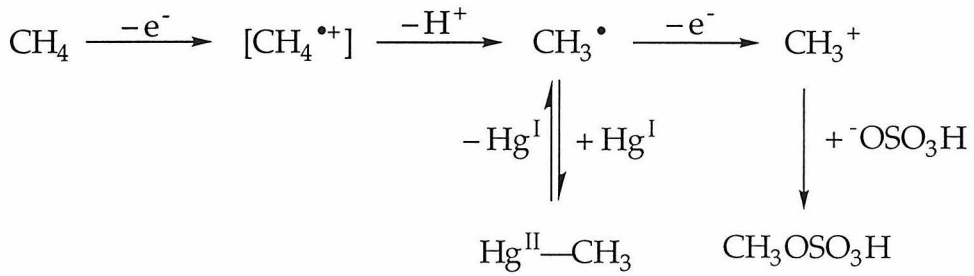


In support of this mechanism, low steady-state concentrations of the methylmercury(II) intermediate are observed under the reaction conditions. When this species is independently prepared, it undergoes competitive reductive elimination of methyl bisulfate (step xiii) and protonolysis (step -xii) in H_2SO_4 at 180 °C with approximately equal rates.[22] When the catalytic reaction is carried out in D_2SO_4, deuterium incorporation into the methane is observed, reflecting the reversibility of the C–H activation step.

The precise mechanism of C–H activation by Hg(II) remains the subject of some debate. While many of the features of this reaction are consistent with a simple electrophilic substitution mechanism (i.e., deprotonation of a transient Hg(II) methane σ-adduct), Sen and co-workers have recently suggested that an outer-sphere electron-transfer pathway may also account for many of the observations.[65,71] For example, comparison of the reaction between methane and a series of one and two electron oxidants (including Hg(II)) in sulfuric acid led the authors to propose that Hg(II) was acting as a one-electron outer-sphere oxidant.[65,71] Formation of methyl bisulfate in the

catalytic oxidation reaction can arise by combination of methyl radicals with Hg(I) in solution (Scheme VII).

Scheme VII



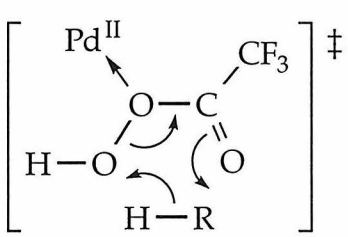
The stability of CH_3OSO_3H under the reaction conditions is consistent with both mechanistic proposals: the electron withdrawing $-OSO_3H$ group will not only deactivate CH_3OSO_3H toward electrophilic attack but also toward H-atom abstraction. Moreover, increasing the solvent acidity is expected to increase the reaction rate for both and electrophilic an electron transfer pathway. Strong acids enhance the electrophilicity of the metal center because their conjugate bases are weaker ligands. A similar explanation accounts for the higher redox potential of metal ions in strong acids: less-donating ligands are available to stabilize the higher oxidation state. Furthermore, the redox potential of alkanes has been shown to decrease dramatically in strong acid media.[2] Thus, while the outer-sphere oxidation of alkanes by Hg(II) does not initially appear plausible, the reaction conditions may, in fact, promote such a pathway.

Oxidation of Alkanes by Other Late Transition Metals. The Catalytica system was preceded by closely related chemistry involving other late transition metals. Strong acid solvents are also used in these

transformations, with trifluoroacetic and sulfuric acids being the most popular.[25] Oxidation of hydrocarbons by metal ions in strong acids has been known for more than two decades,[72,73] with much of the early work summarized in previous reviews.[25,74] In 1987, Sen and co-workers extended this chemistry to methane when they reported its palladium(II) acetate-mediated oxidation to $CF_3CO_2CH_3$ in trifluoroacetic acid (eq 14).[14-16]

$$CH_4 + Pd(O_2CMe)_2 \xrightarrow[80\ ^\circ C]{CF_3CO_2H} CF_3CO_2CH_3 + Pd(0) \qquad (14)$$

Subsequently, a catalytic version of this reaction was accomplished in trifluoroacetic anhydride using H_2O_2 as the stoichiometric oxidant.[17] The authors suggested that the mechanism may involve electrophilic cleavage of the C–H bond by palladium (Scheme V, step ix), or alternatively, Pd(II)-activation of *in situ* generated peroxyacid leading to methane oxidation through a cyclic transition state (**N**). Unfortunately, several attempts to expand the scope of this chemistry have been complicated by difficulties in reproducing these results.[19,21,24,75]



N

Another system utilizes cobalt(III) ions in trifluoroacetic acid to successfully oxidize methane to $CF_3CO_2CH_3$ (90% yield at 180 °C).[19]

Importantly, the methyl ester product is stable to further oxidation under the reaction conditions. Addition of O_2 to the reaction results in a 400% yield of $CF_3CO_2CH_3$ based on the Co(III) oxidizing equivalents available, presumably reflecting reoxidation of Co(II) by O_2. Examination of the oxidation of ethane and propane by Co(III) reveals that C–C bond cleavage products are observed in addition to the expected alkyl trifluoroacetates.[20] The authors proposed a mechanism involving outer-sphere electron transfer to produce an alkyl radical cation in the first step. This intermediate subsequently undergoes competitive C–H or C–C bond cleavage leading to the observed products. Similarly, rhodium(III) salts also catalyze the oxidation of higher alkanes in trifluoroacetic acid to the corresponding alkyl trifluoroacetates using H_2O_2 as the stoichiometric oxidant.[76]

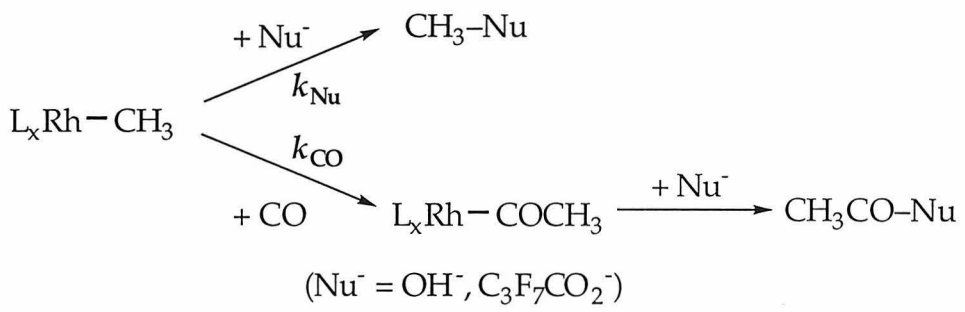
Direct Carboxylation of Alkanes Mediated by Late Transition Metals. In an exciting series of recent papers, Sen[23,77] and Fujiwara[32] have demonstrated the direct carboxylation of alkanes (including methane) catalyzed by rhodium and palladium complexes (eq 15). These systems not only effect the catalytic functionalization of C–H bonds, but also utilize O_2 as the stoichiometric oxidant!

$$\text{R—H} + \text{CO} + 1/2\,\text{O}_2 \xrightarrow{\text{M}^{n+}} \text{RCOOH} \qquad (15)$$

The rhodium-catalyzed reaction, which is carried out in a mixture of perfluorobutyric acid and water, generates both methanol and acetic acid from methane, carbon monoxide, and dioxygen at 80 °C.[23,77] Addition of several equivalents of Cl^- and I^- to the reaction mixture dramatically improves the

reaction yields, however, the reason for this effect is currently not fully understood. While the detailed mechanism of this reaction has not yet been determined, the origin of *both* methanol and acetic acid can be explained by competitive nucleophilic attack (k_{Nu}) versus CO insertion (k_{CO}) into a rhodium methyl bond possibly generated by electrophilic C–H activation of methane (Scheme VIII). The ratio of methanol to acetic acid can be altered by changing the solvent composition. Studies of higher alkanes revealed that

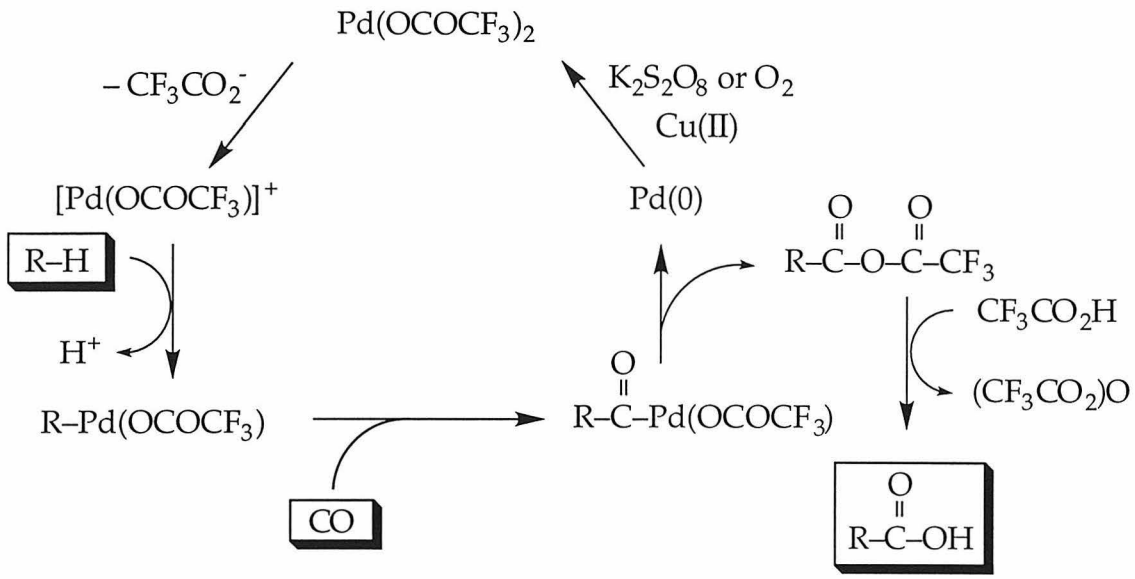
Scheme VIII



C–C bond cleavage is competitive with (and in many cases more favorable than) C–H cleavage! This reaction is effectively a "one pot" catalytic system capable of both cracking and selectively oxidizing simple alkanes. The authors argue against a radical mechanism that might account for cleavage of the weaker C–C bonds.

The catalytic carboxylation of alkanes such as methane, ethane, propane and cyclohexane has also been observed using palladium and/or copper salts in trifluoroacetic acid.[26-32] A possible catalytic cycle is shown in Scheme IX. $K_2S_2O_8$ is the oxidant in most of these reactions conforming to the overall stoichiometry shown in eq 16. A recent report[31] suggests that O_2

Scheme IX



$$R\text{—}H + CO + K_2S_2O_8 + 2\,CF_3CO_2H \xrightarrow{M^{n+}} RCOOH + 2\,KHSO_4 + (CF_3CO)_2O \qquad (16)$$

can also be used. Mixtures of palladium(II) and copper(II) salts are more effective than either of the metals used alone, except for the oxidation of methane where Cu(II) alone is most efficient. Again, the detailed mechanism of these reactions is not entirely known, however kinetic deuterium isotope effects (3.0-3.2) in the reaction of cyclohexane with Pd(II)/Cu(II) or Pd(II) alone suggest that C–H bond cleavage is involved in the rate determining step.[28] In contrast, the reactions using Cu(II) alone do not exhibit a kinetic deuterium isotope effect, leading the authors to propose a radical mechanism.[28]

Unfortunately, the complexity of the above systems has hindered elucidation of the detailed mechanisms. While direct electrophilic alkane

activation is an attractive proposal, other possibilities such as radical and/or electron transfer pathways are difficult to rule out.

CONCLUSION & FOCUS OF THIS THESIS

The above reactions involving electrophilic late transition metals offer a promising and potentially practical approach to alkane oxidation. Importantly, the selectivities commonly associated with organometallic C–H activation reactions (e.g., 1° > 2° > 3°) appear attainable in catalytic oxidation reactions as well.

A rather clear mechanistic picture has emerged for the final two steps (oxidation and functionalization) of the Shilov system. However, many open questions remain regarding the mechanism of C–H activation for both the Shilov and other systems. Because this step often dictates both the rate and selectivity of the overall reactions, further mechanistic studies appear crucial to the advancement of this chemistry. While oxidative addition of the C–H bond may be possible in the Pt(II)-mediated reaction, this is not a viable pathway for many of the other systems (e.g., with Hg(II) or Pd(II)). It is possible, perhaps likely, that a universal mechanism does not exist for all of the systems.

What role, if any, does the solvent play in these systems? In all the examples discussed, the solvent is highly polar and in many cases a strong acid such as sulfuric or trifluoroacetic acid. Do such solvents merely provide a polar, weakly-coordinating medium to enhance an electrophilic C–H activation pathway (e.g., involving deprotonation of an alkane σ-adduct), or are such solvents are necessary to alter the metal and alkane redox potentials to facilitate an electron transfer pathway?

Strong acid solvents also appear to play another role in these reactions, namely esterification of the alcohols produced in the reaction. By doing so, the acids deactivate the products toward further oxidation. For instance, the strong electron withdrawing groups in $CH_3O_2CCF_3$ and CH_3OSO_3H render them much less reactive toward both electrophilic *and* radical reagents. Thus, even in cases where one-electron redox/radical chemistry is operating, the selectivity of the reaction can still be quite high, especially in reactions with methane.[71] Clearly, the role of solvent cannot be ignored in these reactions.

The numerable recent advances in this field hold great promise for the future discovery and development of new, practical approaches to selective, high yield alkane functionalization reactions. A more thorough understanding of the C–H activation reaction will almost certainly facilitate such progress. The work described in this thesis will address some of the unanswered questions in this area, specifically relating to the mechanism of C–H activation by Pt(II).

REFERENCES AND NOTES

1) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987-1007.

2) Olah, G. A.; Farooq, O.; Prakash, G. K. S. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed. John Wiley & Sons, Inc.: New York, 1989; pp 27-78.

3) Field, L. D. In *Selective Hydrocarbon Activation*; Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A., Eds.; VCH Publishers, Inc.: New York, 1990; pp 241-264.

4) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245-269.

5) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154-162.

6) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed. John Wiley & Sons, Inc.: New York, 1989.

7) *Selective Hydrocarbon Activation*; Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A., Eds.; VCH Publishers, Inc.: New York, 1990.

8) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984.

9) Labinger, J. A. *Fuel Process. Technol.* **1995**, *42*, 325-338.

10) The term "organometallic alkane activation" refers to the formation of a metal-carbon bond in the C–H activation step. The reactive metal fragment is not necessarily an "organometallic" complex (e.g., $[(por)Rh]_2$). (Figure 1).

11) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

12) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174.

13) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1972**, *46*, 1353.

14) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109-8111.

15) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421-428.

16) Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755-760.

17) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700-701.

18) Sen, A. *Platinum Metals Rev.* **1991**, *35*, 126-132.

19) Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1049-1050.

20) Stolarov, I. P.; Vargaftik, M. N.; Shishkin, D. I.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1991**, 938-939.

21) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340-343.

22) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. In *Natural Gas Conversion II*; Curry-Hyde, H. E.; Howe, R. F., Eds.; Elsevier: New York, 1994; pp 533-544.

23) Lin, M.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 4574-4580.

24) Gol'dshleger, N. F.; Kresova, E. I.; Moravskii, A. P. *Kinet. Katal.* **1991**, *32*, 1023.

25) Gol'dshleger, N. F.; Moravskii, A. P. *Usp. Khim.* **1994**, *63*, 130-143.

26) Fujiwara, Y.; Jintoku, T.; Uchida, Y. *New J. Chem.* **1989**, *13*, 649-650.

27) Fujiwara, Y.; Takaki, K.; Watanabe, J.; Uchida, Y.; Taniguchi, H. *Chem. Lett.* **1989**, 1687-1688.

28) Nakata, K.; Miyata, T.; Jintoku, T.; Kitani, A.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3755-3759.

29) Nakata, K.; Yamaoka, Y.; Miyata, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *J. Organomet. Chem.* **1994**, *473*, 329-334.

30) Nakata, K.; Miyata, T.; Yamaoka, Y.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. In *Natural Gas Conversion II*; Curry-Hyde, H. E.; Howe, R. F., Eds.; Elsevier: New York, 1994; pp 521-526.

31) Kurioka, M.; Nakata, K.; Jintoku, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Chem. Lett.* **1995**, 244.

32) Fujiwara, Y.; Takaki, K.; Taniguchi, Y. *Synlett* **1996**, 591-599.

33) Much of the early work in this area has been reviewed in a monograph by Shilov. (ref. 8).

34) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729.

35) Zamashchikov, V. V.; Rudakov, E. S.; Mitchenko, S. A.; Litvinenko, S. L. *Teor. Eksper. Khim.* **1982**, *18*, 510-512.

36) Zamashchikov, V. V.; Mitchenko, S. A. *Kinet. Katal.* **1983**, *24*, 254-255.

37) Zamashchikov, V. V.; Kitaigorodskii, A. N.; Litvinenko, S. L.; Rudakov, E. S.; Uzhik, O. N.; Shilov, A. E. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1985**, 1730-1733.

38) Zamashchikov, V. V.; Rudakov, E. S.; Garkusha-Bozhko, V. S.; Mitchenko, S. A.; Litvinenko, S. L.; Chuprina, V. S. *Koord. Khim.* **1986**, *12*, 822-826.

39) Zamashchikov, V. V.; Litvinenko, S. L.; Uzhik, O. N.; Galat, V. F. *Zh. Obs. Khim.* **1986**, *56*, 2417.

40) Zamashchikov, V. V.; Litvinenko, S. L.; Shologon, V. I. *Kinet. Katal.* **1987**, *28*, 1059-1063.

41) Mitchenko, S. A.; Zamashchikov, V. V. *Kinet. Katal.* **1989**, *30*, 297-302.

42) Zamashchikov, V. V.; Mitchenko, S. A.; Shubin, A. A.; Kostenko, E. L. *Kinet. Katal.* **1992**, *33*, 498-502.

43) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004.

44) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75.

45) Hutson, A. C.; Lin, M.; Basickes, N.; Sen, A. *J. Organomet. Chem.* **1995**, *504*, 69.

46) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1994**, *13*, 755.

47) Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Catal. A* **1997**, *116*, 269-275.

48) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961-5976.

49) Shilov, A. E. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed. John Wiley & Sons: New York, 1989; p 1.

50) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horvath, I. T.; Eller, K. *Organometallics* **1993**, *12*, 895.

51) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442-4450.

52) Zamashchikov, V. V.; Popov, V. G.; Litvinenko, S. L. *Izv. Akad. Nauk., Ser. Khim.* **1993**, *42*, 389-395.

53) Zamashchikov, V. V.; Popov, V. G.; Rudakov, E. S.; Mitchenko, S. A. *Dokl. Akad. Nauk SSSR* **1993**, *333*, 34-36.

54) Zamashchikov, V. V.; Popov, V. G.; Rudakov, E. S.; Mitchenko, S. A. *Izv. Akad. Nauk., Ser. Khim.* **1993**, *42*, 2142-2143.

55) Zamashchikov, V. V.; Popov, V. G.; Rudakov, E. S. *Kinet. Katal.* **1994**, *35*, 436-442.

56) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

57) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585.

58) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281.

59) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.

60) Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8.

61) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5628.

62) Labinger, J. A.; Bercaw, J. E.; Luinstra, G. A. L., D. K.; Herring, A. M. In *Natural Gas Conversion II*; Curry-Hyde, H. E.; Howe, R. F., Eds.; Elsevier: New York, 1994; pp 515-520.

63) Kao, L.-C.; Sen, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1242.

64) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

65) Sen, A.; Benvenuto, M. A.; Lin, M.; Hutson, A. C.; Basickes, N. *J. Am. Chem. Soc.* **1994**, *116*, 998.

66) Basickes, N.; Sen, A. *Polyhedron* **1995**, *14*, 197-202.

67) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987.

68) Gol'dshleger, N. F.; Lavrushko, V. V.; Khrushch, A. P.; Shteinman, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2174.

69) Geletii, Y. V.; Shilov, A. E. *Kinet. Katal.* **1983**, *24*, 486-489.

70) Freund, M. S.; Labinger, J. A.; Lewis, N. S.; Bercaw, J. E. *J. Mol. Catal.* **1994**, *87*, L11-L15.

71) Basickes, N.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1996**, *118*, 13111-13112.

72) Rudakov, E. S.; Zamashchikov, V. V.; Belyaeva, N. P.; Rudakova, R. I. *Zh. Fiz. Khim.* **1973**, *47*, 2732.

73) Gol'dshleger, N. F.; Khidekel', M. L.; Shilov, A. E.; Shteinman, A. A. *Kinet. Katal.* **1974**, *15*, 261.

74) See pp 67-73 in ref. 8.

75) Nelson, K. T.; Foger, K. In *Natural Gas Conversion II*; Curry-Hyde, H. E.; Howe, R. F., Eds.; Elsevier: New York, 1994; pp 545-550.

76) Nomura, S.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, 129-130.

77) Lin, M.; Sen, A. *Nature* **1994**, *368*, 613-615.

Chapter 2

Exploring the Mechanism of Aqueous C-H Activation by Pt(II) through Model Chemistry: Evidence for the Intermediacy of Alkylhydridoplatinum(IV) and Alkane σ-Adducts

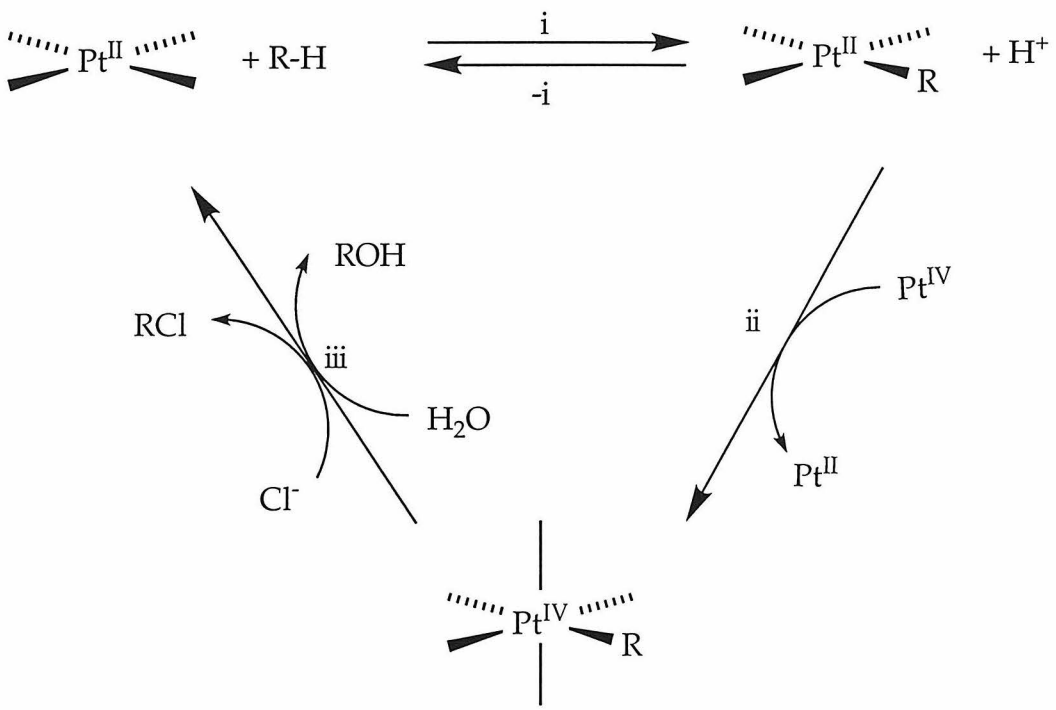
INTRODUCTION

Although many organometallic systems have now been identified which selectively *activate* C-H bonds,[1-4] most rely on the generation of a high-energy, reactive intermediate which decomposes rapidly if exposed to oxidants necessary for catalytic turnover. Recently, several promising, rather robust systems have been developed based on late transition metals (e.g., Pd, Pt, and Hg).[5-8] These metal complexes undergo electrophilic activation and subsequent oxidation of alkanes. The first such homogeneous alkane oxidation system was discovered by Shilov and co-workers more than twenty years ago;[9] it utilized a mixture of Pt(II) and Pt(IV) salts in aqueous solution to convert methane to mixtures of methanol and methyl chloride. Although various features have thus far prevented its practical utility, this system remains one of few examples of catalytic (in Pt(II)) routes to alkane functionalization. Recently, we[10-13] and others[14-21] have been exploring some of the mechanistic features of this system in order to better understand this remarkable reactivity.

In agreement with Shilov's original proposal,[14] we believe the catalytic mechanism consists of three primary transformations (Scheme 1): (i) electrophilic activation of the alkane by Pt(II) to generate an alkylplatinum(II) intermediate, (ii) two-electron oxidation of alkylplatinum(II) to generate an alkylplatinum(IV) species, and (iii) reductive elimination of R-X (X = Cl or OH for example) to liberate the functionalized alkane and Pt(II) catalyst.

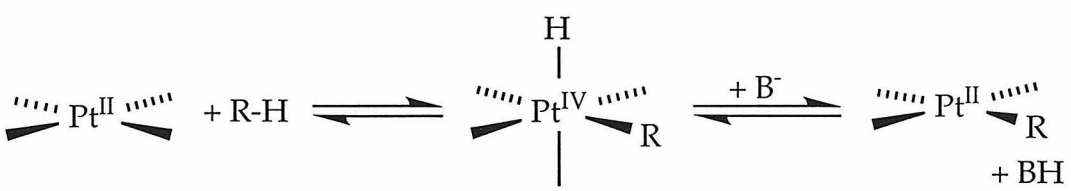
In recent years, we have elucidated several details related to the final two steps of the mechanism.[10-13,22] Unfortunately, very little is known about the nature of C-H activation, the step which appears to govern the overall

Scheme 1

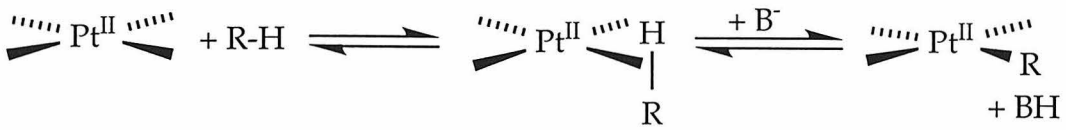


rate as well as the selectivity of the catalytic cycle. Recently we have been attempting to delineate some of the mechanistic features of this reaction.

Two possible pathways have been proposed for C-H activation leading to an alkylplatinum(II) intermediate:[10,23-25] (1) oxidative addition of the C-H bond at Pt(II) yielding an alkylhydridoplatinum(IV) species which is subsequently deprotonated (eq 1), or (2) deprotonation of an intermediate Pt(II)-alkane σ-complex (eq 2). Neither intermediate has been observed directly.



(1)



(2)

In the course of our investigations, we have encountered difficulties exploring direct reactions of aqueous Pt(II) salts with alkanes. Even in the absence of Pt(IV), oxidation products are generated with immediate precipitation of platinum metal, accompanied by extensive H/D exchange between alkanes and deuterated solvent. Unlike previous reports,[23,26] we have *not* observed H/D exchange prior to formation of Pt(0).

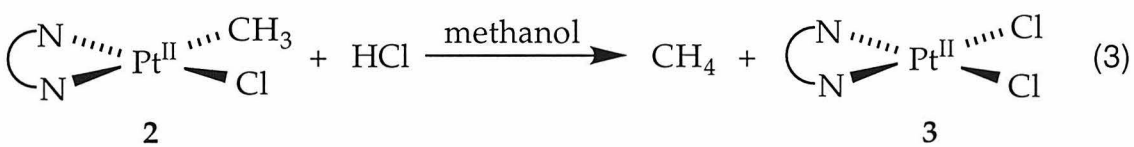
We subsequently began investigating the microscopic reverse of the C-H activation step, namely protonolysis of alkylplatinum(II) species. The catalytic intermediate, $[Cl_3Pt^{II}CH_3]^{2-}$ (**1**), is presumed to be generated upon $2e^-$ reduction of $[Pt^{IV}MeCl_5]^{2-}$, however **1** immediately liberates methane when the reaction is carried out in a protic solvent (i.e., CH_3OH and H_2O) Furthermore, in aprotic media we found that **1** is unstable with respect to disproportionation into $[PtCl_4]^{2-}$ and $[Cl_2Pt^{II}(CH_3)_2]^{2-}$.[13,27]

Related alkylplatinum(II) model complexes containing stabilizing donor ligands (e.g., amines or phosphines) proved more amenable to study. Protonolysis studies of such complexes have been conducted by other groups in the past; however, several different mechanisms have been proposed.[28-32] Furthermore, when we began our work, no intermediates had been identified in such reactions, and thus mechanistic proposals were based on less direct evidence such as rate laws, isotope effects, or competition studies. Recently, however, three groups have independently identified the presence of alkylhydridoplatinum(IV) intermediates in the protonolysis of

alkylplatinum(II) species in organic solvents.[22,33-39] Reported here are studies of the protonolysis reaction intended to examine the viability of alkane adducts (σ-complexes) and/or alkylhydridoplatinum(IV) species as intermediates in alkane activation by Pt(II) in aqueous solution.

RESULTS

Protonolysis of (tmeda)Pt(CH_3)Cl (2) (tmeda = *N, N, N′, N′*-tetramethylethylenediamine) in methanol. The protonolysis of (tmeda)Pt(CH_3)Cl (**2**) with HCl in methanol proceeds cleanly to generate (tmeda)$PtCl_2$ and methane (eq 3).



2 **3** (3)

Monitoring the reaction at low temperature (-50 to -25 °C) in CD_3OD by ^1H NMR spectroscopy reveals pseudo-first order kinetics for the conversion of **2** to (tmeda)$PtCl_2$ (**3**); *no intermediates are observed*.[40] The rate is first order in both hydrogen ion and chloride concentration (Figures 1 and 2, respectively) at constant ionic strength (μ = 1.0 M = [HOTf] + [$LiClO_4$] + [LiCl]) over the concentration ranges [HOTf] = 0 to 0.38 M and [Cl^-] = 0.13 M to 0.66 M. Significantly, the dependence on chloride exhibits a non-zero intercept (Figure 2). Activation parameters were determined from an Eyring plot: $\Delta H^{\ddagger}$ = 19.4 ± 1.5 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = 14 ± 5 e. u..[41]

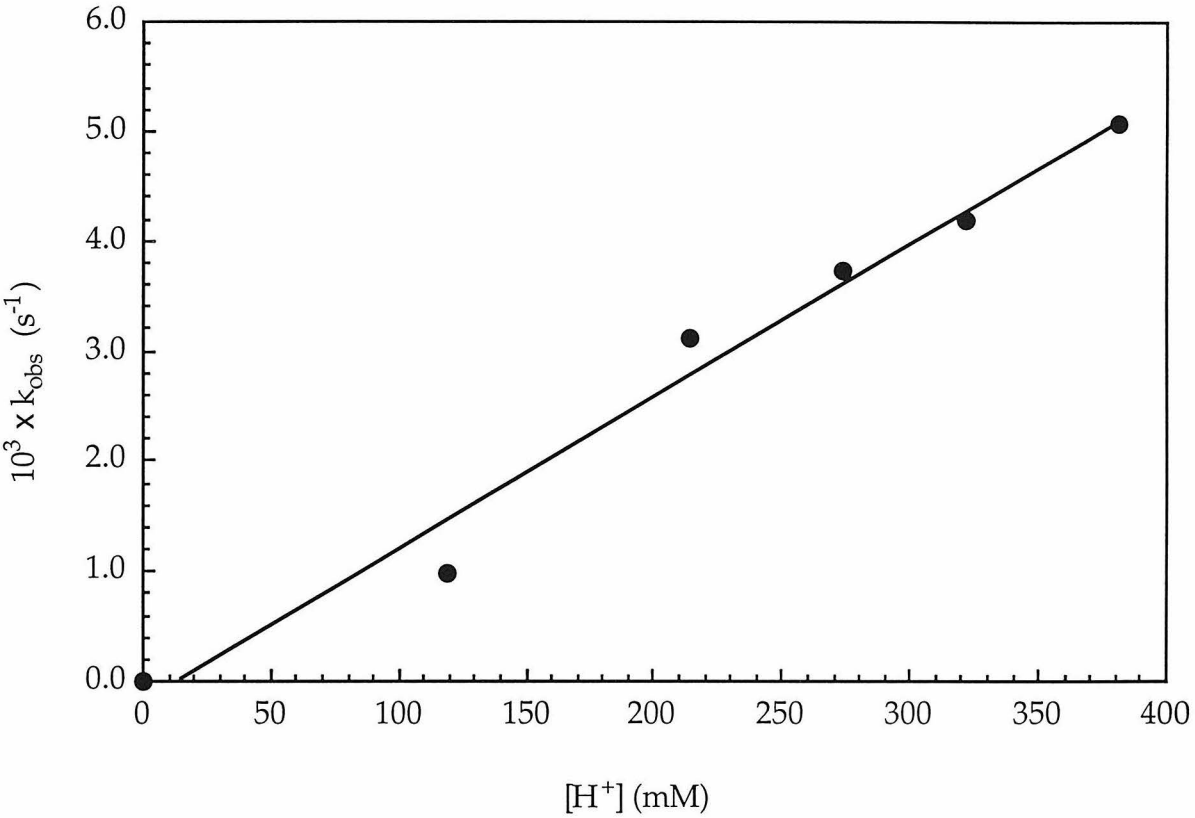


Figure 1. Plot of the [H^+] dependence of the rate of protonolysis of **2** in CD_3OD. [H^+] = 0 - 32 equivalents.; [**2**] = 11.9 mM; [Cl^-] = 0 M; μ = 1.0 M; Temperature = -35 °C.

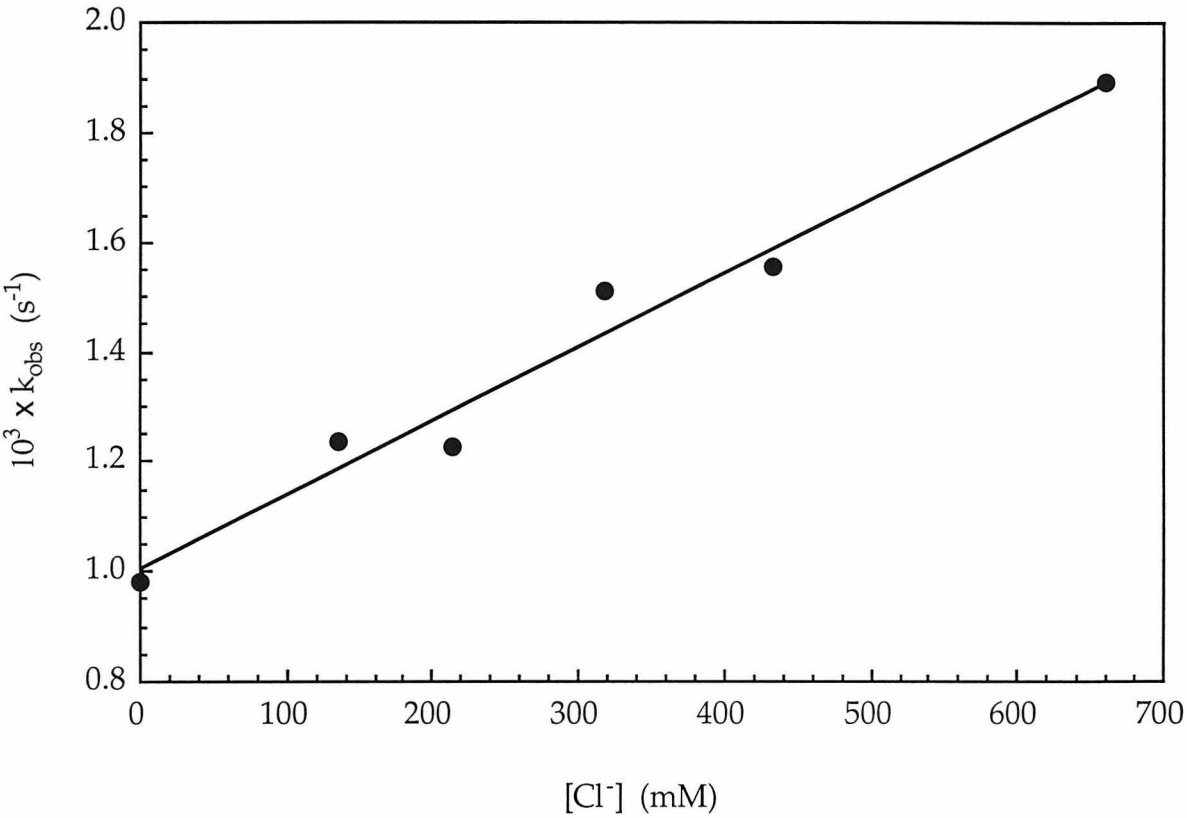
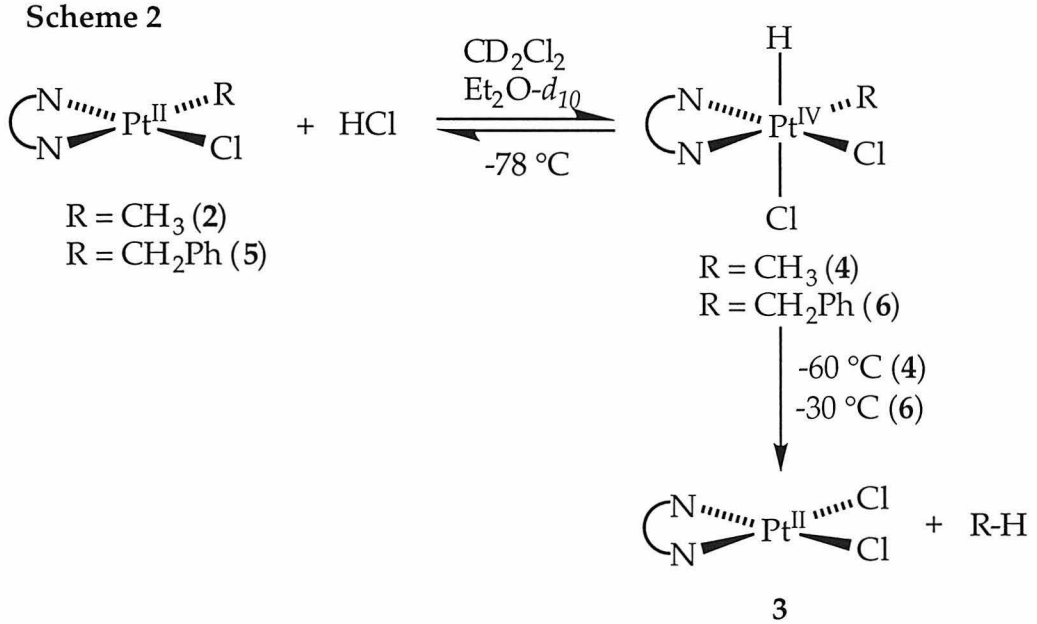


Figure 2. Plot of k_{obs} versus [Cl^-] for the protonolysis of **2** in CD_3OD. [Cl^-] = 0 - 55.4 equivalents; [**2**] = 11.9 mM; [H^+] = 0.12 M; μ = 1.0 M; Temperature = -35 °C.

Protonolysis of **2** with LOTf (L = H, D) in a 19.3 : 1 mixture of CD_3OD:CD_3OH at 0 °C generates a mixture of methane isotopomers, CH_4:CH_3D = 1 : 2.1, leading to a kinetic deuterium isotope effect of 9.1 (± 0.5). Comparing the pseudo-first order rate constant for protonolysis of **2** in CD_3OH with HOTf ($k_{obs} = 1.8 \times 10^{-3}$ s^{-1}) versus CD_3OD with DOTf ($k_{obs} = 0.77 \times 10^{-3}$ s^{-1}) at -40 °C leads to a different isotope effect: k_H/k_D = 2.3 (± 0.5).

Protonolysis of (tmeda)Pt(R)Cl (R = CH_3, CH_2Ph) in methylene chloride. Protonolysis of **2** also proceeds rapidly in dichloromethane at room temperature, releasing methane and also generating **3**. In contrast to reaction with HCl in methanol, addition of excess HCl (dissolved in diethyl ether-d_{10}) at -78 °C to a CD_2Cl_2 solution of **2** first results in oxidative addition to generate (tmeda)Pt(CH_3)(H)Cl_2 (**4**). Upon warming this solution to -60 °C, the reductive elimination of methane ensues along with formation of (tmeda)$PtCl_2$ (Scheme 2).

Scheme 2



Although **4** is not sufficiently stable to isolate at room temperature, it has been characterized by ^{1}H NMR spectroscopy at low temperature (Table 1). The most distinctive characteristic is the platinum(IV) hydride resonance which appears far upfield (δ -23.6 ppm) with corresponding platinum satellites ($^1J_{^{195}Pt\text{-}H}$ = 1290 Hz, ^{195}Pt 33.8% natural abundance, S = 1/2). These data are consistent with other Pt(IV) hydrides containing nitrogen ligands.[33,34,42] The methyl resonance of **4** appears as a singlet (δ 1.6 ppm) with $^2J_{^{195}Pt\text{-}H}$ = 66.5 Hz.

The benzyl analog of **2**, (tmeda)Pt(CH_2Ph)Cl (**5**), reacts similarly with HCl, except the benzylhydridoplatinum(IV) complex (**6**) (Table 1) is more stable than **4** — toluene reductive elimination proceeds at -30 °C (Scheme 2). Consequently, this species was used to evaluate further mechanistic details. Oxidative addition of HCl to **5** is rapid and reversible: addition of DCl (as a diethyl ether-d_{10} solution) to **5** in CD_2Cl_2 at -78 °C produces **6**-d_1. Subsequent addition of a large excess of HCl results in the immediate appearance of the hydride resonance for **6** with no other spectroscopic changes.

Reductive elimination of toluene follows a first order dependence on [**6**]. The temperature dependence of the reductive elimination rates allowed determination of activation parameters: $\Delta H^{\ddagger}$ = 14.0 ± 2.5 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = -18.5 ± 7.0 e.u.[43] (Figure 3). The rate of toluene formation from **6** is substantially increased by addition of Bronsted or Lewis acids (HCl, HOTf, $SnCl_4$), and in the case of triflic acid, the rate of reductive elimination of toluene is first order with respect to [HOTf] (0 - 263 mM; 0 - 20 equivalents) (Figure 4). Moreover, direct protonation of **5** with HOTf (i.e., rather than addition of HOTf to a solution of **6**) at -80 °C proceeds immediately to toluene without evidence of (tmeda)Pt(CH_2Ph)(H)(Cl)(OTf). A series of experiments

Table 1. Selected ^{1}H NMR spectroscopic data for compounds discussed in text.

Compound	Solvent	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz
(tmeda)Pt(CH_3)Cl (**2**)	CD_2Cl_2	25	Pt-CH_3	0.434 (s); $^2J_{Pt-H}$ = 78.9
			Pt-N-CH_3	2.84 (s); $^3J_{Pt-H}$ = 51
				2.70 (s); $^3J_{Pt-H}$ = <10
			Pt-N-CH_2-	2.77 (m)
				2.54 (m)
(tmeda)Pt(CH_3)(H)Cl_2 (**4**)	CD_2Cl_2/	-70	Pt-CH_3	1.57 (s); $^2J_{Pt-H}$ = 66.5
	Et_2O-d_{10}		Pt-*H*	-23.6 (s); $^1J_{Pt-H}$ = 1292
	(10:1)		Pt-N-CH_3	3.02; $^3J_{Pt-H}$ ~ 57
				2.89; $^3J_{Pt-H}$ = <10
				2.89; $^3J_{Pt-H}$ = <10
				2.86; $^3J_{Pt-H}$ ~ 33
(tmeda)Pt(CH_2Ph)Cl (**5**)	CD_2Cl_2	25	Pt-CH_2Ph	2.96 (s); $^2J_{Pt-H}$ = 109.8
	(300 MHz)		Pt-N-CH_3	2.76 (s); $^3J_{Pt-H}$ = 83
				2.70 (s); $^3J_{Pt-H}$ = <10
			Pt-N-CH_2-	2.47 (m)
				second multiplet obscured by
				peaks at 2.76 and 2.70

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Table 1 (cont'd). Selected ^{1}H NMR spectroscopic data for compounds discussed in text.

Compound	Solvent	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz
(tmeda)Pt(CH_2Ph)(H)Cl_2 (**6**)	CD_2Cl_2	-60	Pt-CH_aH$_b$Ph	4.8 (d); $^2J_{Pt-H}$ = 107, $^2J_{Ha-Hb}$ = 10
			Pt-CH$_a$$H_b$Ph	3.2 (d); $^2J_{Pt-H}$ = 92
			Pt-H	-23.9 (s); $^1J_{Pt-H}$ = 1230
			Pt-N-CH_3	3.0; $^3J_{Pt-H}$ ~ 32
				2.9; $^3J_{Pt-H}$ = <10
				2.8; $^3J_{Pt-H}$ = <10
				2.7; $^3J_{Pt-H}$ ~ 56
(tmeda)Pt(CH_2Ph)$_2$ (**7**)	CD_2Cl_2	25	Pt-CH_2Ph	2.71 (s), $^2J_{Pt-H}$ = 122
			Pt-N-CH_3	2.56 (s); $^3J_{Pt-H}$ = 20
			Pt-N-CH_2-	2.54 (s); $^3J_{Pt-H}$ = <10
(tmeda)Pt(CH_2Ph)$_2$(H)Cl (**8**)	CD_2Cl_2/	-20	Pt-CH_aH$_b$Ph	3.44 (d); $^2J_{Pt-H}$ = 95, $^2J_{Ha-Hb}$ = 10
	Et_2O-d_{10}		Pt-CH$_a$$H_b$Ph	3.31 (d); $^2J_{Pt-H}$ = 117
	(10:1)		Pt-H	-23.1 (s); $^1J_{Pt-H}$ = 1630
			Pt-N-CH_3	2.76 (s), $^3J_{Pt-H}$ = <15
				2.51 (s), $^3J_{Pt-H}$ = 27
			Pt-N-CH_2-	2.63 (br. s)
				2.91 (br. s)

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Table 1 (cont'd). Selected ^{1}H NMR spectroscopic data for compounds discussed in text.

Compound	Solvent	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz
(4,4'-dimethyl-2,2'-bipyridyl)Pt(CH_3)$_2$ (**9**)	CD_2Cl_2	25	Pt-C***H***$_3$	0.90 (s); $^2J_{Pt-H}$ = 85
			Pt-(py-C***H***$_3$)	2.36 (s)
(4,4'-dimethyl-2,2'-bipyridyl)Pt(CH_3)$_2$(H)Cl (**10**)	CD_2Cl_2/	-65	Pt-C***H***$_3$	1.25 (s); $^2J_{Pt-H}$ = 66
	Et_2O-d_{10}		Pt-***H***	-22.1 (s); $^1J_{Pt-H}$ = 1610
	(10:1)		Pt-(py-C***H***$_3$)	2.44 (s)
(tmeda)Pt(CH_3)$_2$(H)Cl (**12**)	CD_3OD	-50	Pt-C***H***$_3$	0.87 (s, 3 H); $^2J_{Pt-H}$ = 66
			Pt-***H***	-23.1(s); $^1J_{Pt-H}$ = 1726
			Pt-N-C***H***$_3$	2.78 (s); $^3J_{Pt-H}$ = 24
				2.72 (s); $^3J_{Pt-H}$ = 10
			Pt-N-C***H***$_2$-	2.91 (br.s)
[(tmeda)Pt(CH_3)$_2$(H)(CD_3OH)](OTf) (**13**)	CD_3OD	-55	Pt-C***H***$_3$	0.84 (s); $^2J_{Pt-H}$ = 66
			Pt-***H***	-23.1 (s); $^1J_{Pt-H}$ = 1721
			Pt-N-C***H***$_3$	2.79 (s); $^3J_{Pt-H}$ = 27
				2.70 (s); $^3J_{Pt-H}$ = <10
			Pt-N-C***H***$_2$-	2.91 (br. s)

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Table 1 (cont'd). Selected ^{1}H NMR spectroscopic data for compounds discussed in text.

Compound	Solvent	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz
trans-$(PEt_3)_2Pt(CH_3)Cl$ (**15**)	$CDCl_3$	25	Pt-CH_3	0.325 (t); $^3J_{P\text{-}H} = 6$; $^2J_{Pt\text{-}H} = 84$
$(PEt_3)_2Pt(CH_3)(H)Cl_2$ (**16**)	CD_2Cl_2/ Et_2O-d_{10} (10:1)	-65	Pt-CH_3	0.935 (t); $^3J_{P\text{-}H} = 5$; $^2J_{Pt\text{-}H} = 65$
			Pt-***H***	-18.8 (t); $^2J_{P\text{-}H} = 6$; $^1J_{Pt\text{-}H} = 1223$

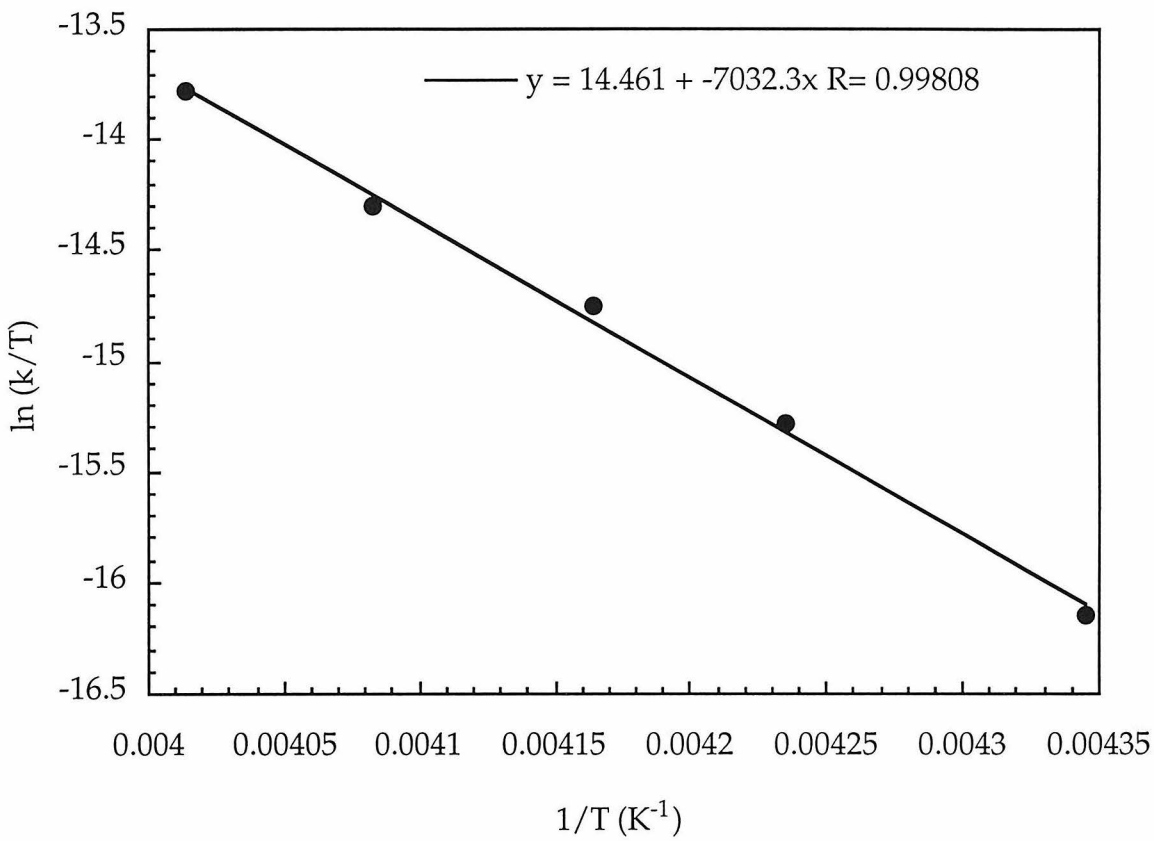


Figure 3. Eyring plot for the reductive elimination of toluene from **6** in CD_2Cl_2. Calculated activation parameters: $\Delta H^{\ddagger}$ = -14.0 ± 2.5 kcal/mol, $\Delta S^{\ddagger}$ = -18.5 ± 7.0 e.u.. [**6**] = 13 mM; [HCl] = 65 mM; Temperature range: -24 – -43 °C.

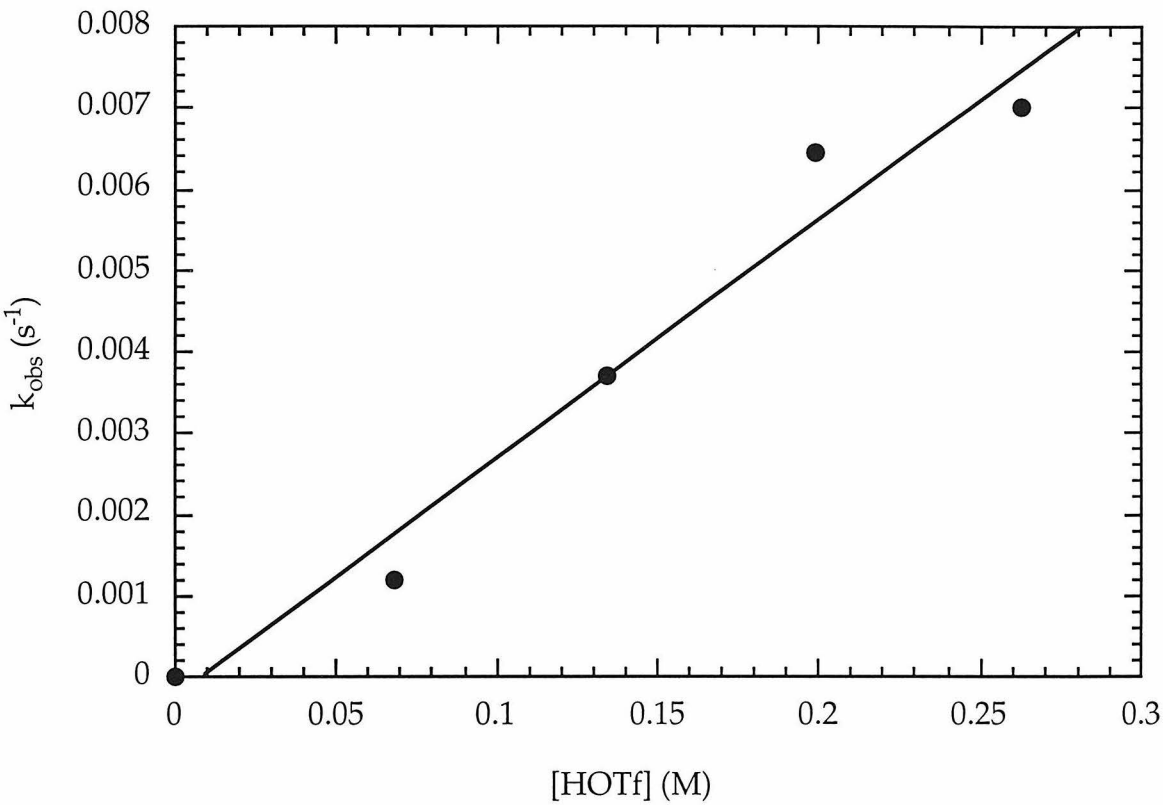
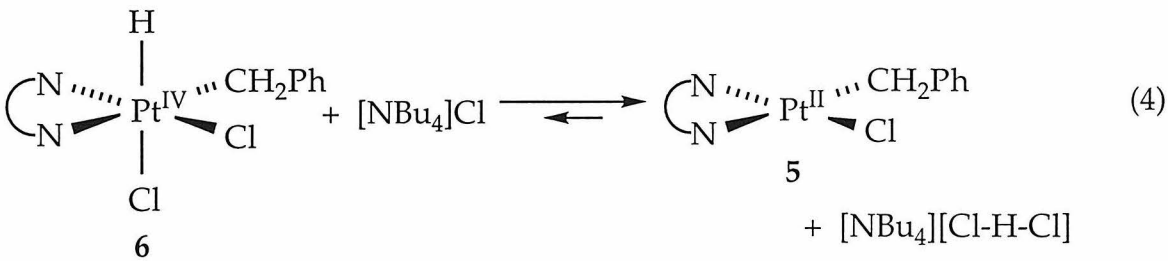


Figure 4. [HOTf] dependence of the rate of reductive elimination of toluene from **5** in CD_2Cl_2. [HOTf] = 0 - 20 equivalents (relative to [**6**]); [**6**] = 13 mM; [HCl] = 65 mM; Temperature = -61 °C.

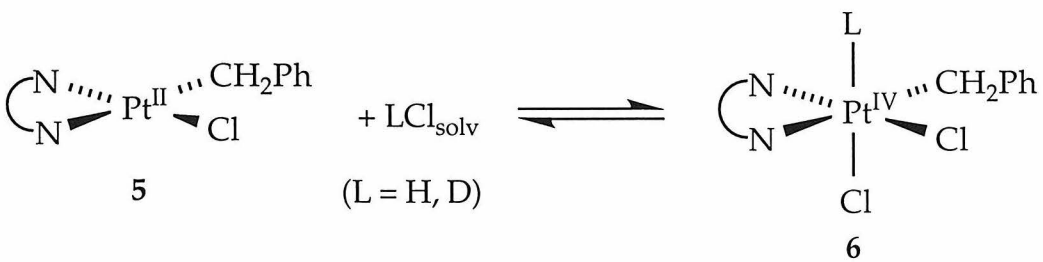
were carried out in which the [HOTf] was held constant (5 equivalents relative to [**6**]) and the HCl concentration was varied between 0.11 - 0.62 M (9.4 - 51 equivalents). As is apparent from Figure 5, toluene elimination is inhibited by added HCl. The dependence of the rate on chloride alone was also examined; however, surprisingly, the addition of tetrabutylammonium chloride to the reaction mixture results in immediate deprotonation of **6** and formation of **5** and tetrabutylammonium bichloride (eq 4).



(4)

The presence of $[NBu_4][Cl\text{-}H\text{-}Cl]$ was verified by comparing a solution FTIR spectrum of the reaction mixture to a solid-state infrared spectrum reported for $[NMe_4][Cl\text{-}H\text{-}Cl]$.[44]

Integration of the Pt^{IV}-*H* peak relative to one of the benzyl protons for **6** obtained by addition of a mixture of HCl and DCl to **5** reveals an *inverse* equilibrium deuterium isotope effect, $(K_H/K_D) = 0.51 \pm 0.05$ (-28° C), for equilibrium 5.



(5)

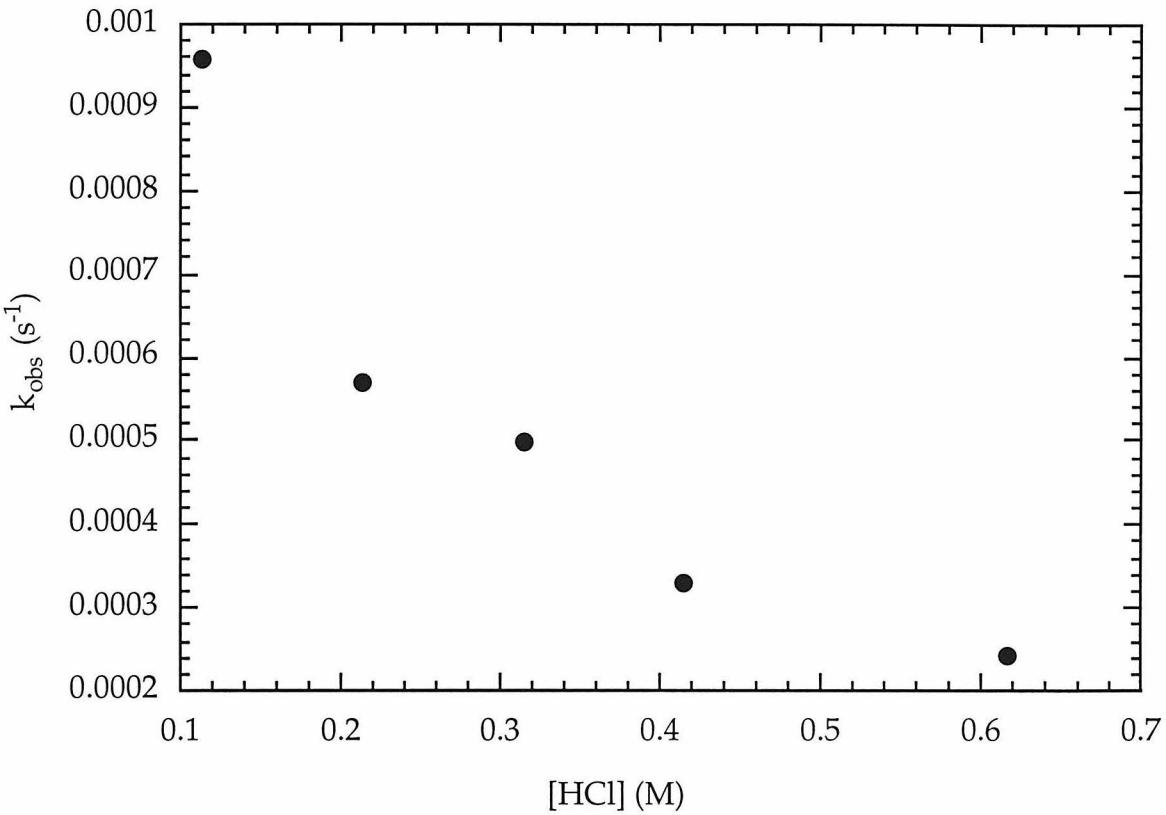


Figure 5. Plot of k_{obs} versus [HCl] revealing that HCl inhibits the reductive elimination of toluene from **6** in CD_2Cl_2 when [HOTf] is present. [HCl] = 9.4 - 51 equivalents (relative to [**6**]); [**6**] = 12 mM; [HOTf] = 61 mM; Temperature = -62 °C.

Comparison of the resulting concentrations of $PhCH_3$ versus $PhCH_2D$ generated upon decomposition of this mixture of isotopomers indicates a kinetic deuterium isotope effect for reductive elimination $k_H/k_D = 1.55 \pm 0.10$ at both -28 and 0 °C.

Protonolysis of (tmeda)Pt(CH_2Ph)$_2$, (4,4'-dimethyl-2,2'-bipyridyl)Pt(CH_3)$_2$, and (tmeda)Pt(CH_3)$_2$ in methylene chloride. Since the Pt(IV) complexes described above were not characterized by X-ray crystallography, we were unable to unambiguously establish the stereochemistry of HCl addition to **2** or **5**. We gained further insight by investigating the reaction of HCl with dialkylplatinum(II) species, since the products exhibit greater symmetry. Protonation of (tmeda)Pt(CH_2Ph)$_2$ (**7**) produces (tmeda)Pt(CH_2Ph)$_2$(H)Cl (**8**) which exhibits two inequivalent resonances for its tmeda methyl protons in the ^{1}H NMR spectrum at -45 °C (Table 1). Furthermore, addition of HCl to (4,4'-dimethyl-2,2'-bipyridyl)Pt(CH_3)$_2$ (**9**) leads to a dialkylhydridoplatinum(IV) complex (**10**) with only a single resonance in the ^{1}H NMR spectrum corresponding to the methyls on the bipyridyl ligand (see Table 1). These results indicate *trans* addition of HCl to **7** and **9**, and thus, by extension, to **2** and **5** as well (see Discussion section).

During this study, we discovered that dialkylhydridoplatinum(IV) complexes are more stable than the corresponding monoalkylhydridoplatinum(IV) species with respect to alkane loss. Whereas (tmeda)Pt(CH_2Ph)(H)Cl$_2$ (**6**) eliminates toluene at approximately -30 °C, a comparable rate for reductive elimination from (tmeda)Pt(CH_2Ph)$_2$(H)Cl (**8**) does not occur until -5 °C. The methyl derivatives, (tmeda)Pt(CH_3)(H)Cl$_2$ (**4**)

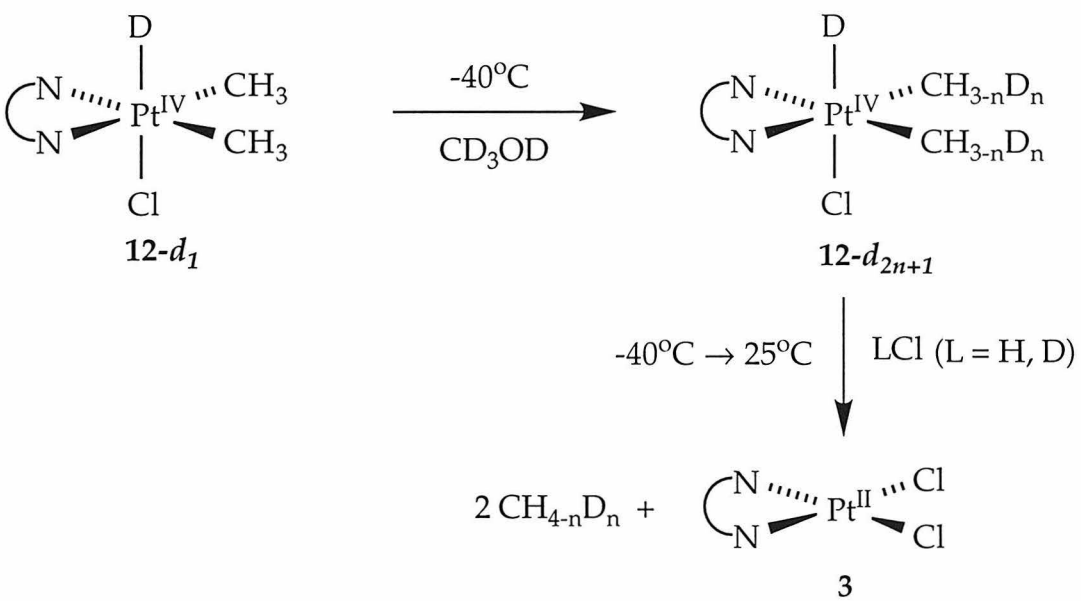
and (tmeda)Pt(CH_3)$_2$(H)Cl (**12**) show a more pronounced effect — methane loss from **4** occurs rapidly at -60 °C, but not until *+10 °C* from **12**.

Protonolysis of (tmeda)Pt(CH_3)$_2$ (11) in CD_3OD. Upon observing the higher stability of dialkylhydridoplatinum(IV) species, we investigated the protonolysis of (tmeda)Pt(CH_3)$_2$ (**11**) in methanol. Since **11** appears to decompose in methanol even in the absence of acid at room temperature,[45] the following procedure was adopted: **11** was dissolved in a minimal amount of CD_2Cl_2 and then cooled to -78 °C before adding methanol-d_3 (CD_3OH:CD_2Cl_2 = 13:1). Subsequent addition of excess HCl to this solution at -78 °C leads to formation of the oxidative addition product, (tmeda)Pt(CH_3)$_2$(H)Cl (**12**) (Table 1). Addition of HOTf also leads to a stable alkylhydridoplatinum(IV) complex, presumably the methanol coordinated product, [(tmeda)Pt(CH_3)$_2$(H)(CD_3OH)](OTf) (**13**) (Table 1). Significantly, monitoring the ^{1}H NMR spectrum of **12-*d*$_1$** in CD_3OD as it is warmed to -40° C revealed deuterium incorporation into the methyl positions (Scheme 3, Figure 6). When warmed to room temperature to allow methane loss prior to complete deuterium exchange, the full range of methane isotopomers is observed (Figure 7).

H/D exchange rates were obtained by monitoring the decrease in total integration of ^{1}H NMR signals corresponding to Pt-C*L*$_3$ (L = H, D) for a solution of **12** in CD_3OD. The activation parameters for H/D exchange were derived from an Eyring plot: $\Delta H^{\ddagger}$ = 15.8 (± 1.8) kcal/ mol and $\Delta S^{\ddagger}$ = -4.7 (± 7.5) e.u.[46] At constant ionic strength, added chloride inhibits H/D exchange, and the rate was found to depend on the inverse of [Cl^-] (see Figure 8).

By monitoring the ^1H NMR resonance of methylplatinum(IV) in CD_3OH (*i.e.*, a solvent in which no H/D exchange occurs), **12** was found to lose methane cleanly at approximately -25 °C exhibiting first order kinetics with activation parameters: $\Delta H^{\ddagger}$ = 19.1 (± 0.6) kcal/ mol and $\Delta S^{\ddagger}$ = 4.1 (± 2.2) e.u..[47] The rate of methane elimination from **12** is also inversely proportional to the chloride concentration (Figure 9).

Scheme 3



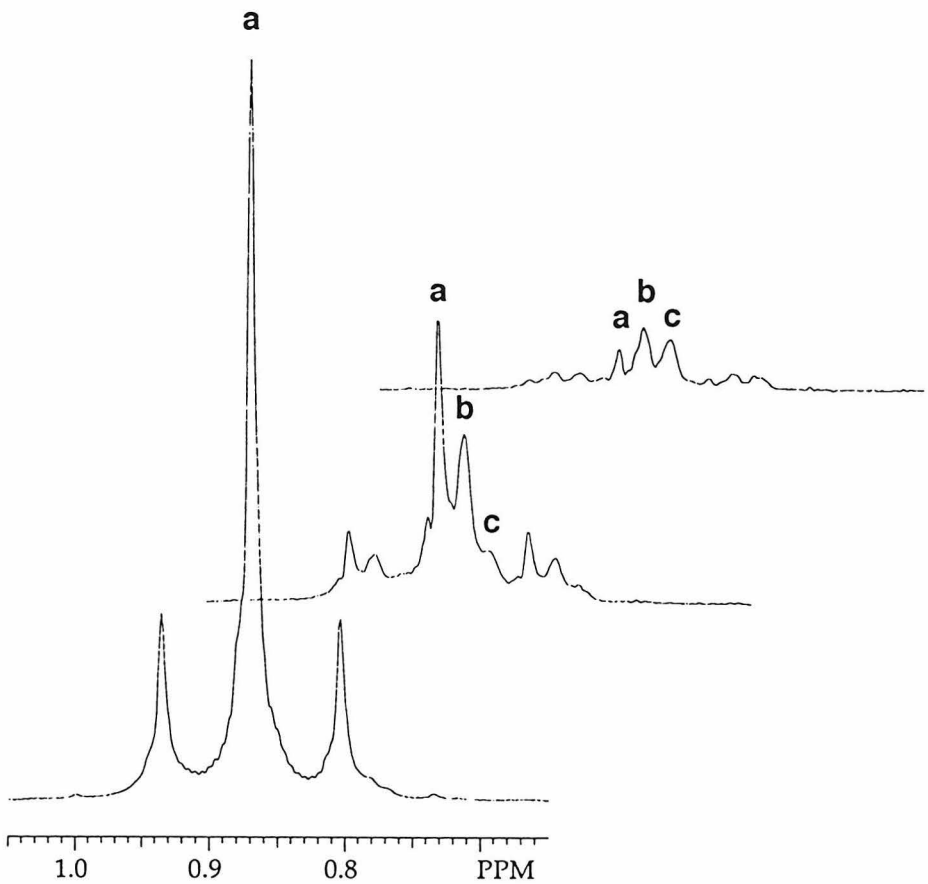


Figure 6. Sequence of ^{1}H NMR spectra demonstrating the appearance of shoulders upfield of the original Pt(IV)-CH_3 resonance from **12** in CD_3OD along with an overall decrease in the peak integration. The upfield shoulders are assigned as the sequentially deuterated methyl groups: **a** = Pt-CH_3, **b** = Pt-CH_2D, and **c** = Pt-CHD_2.

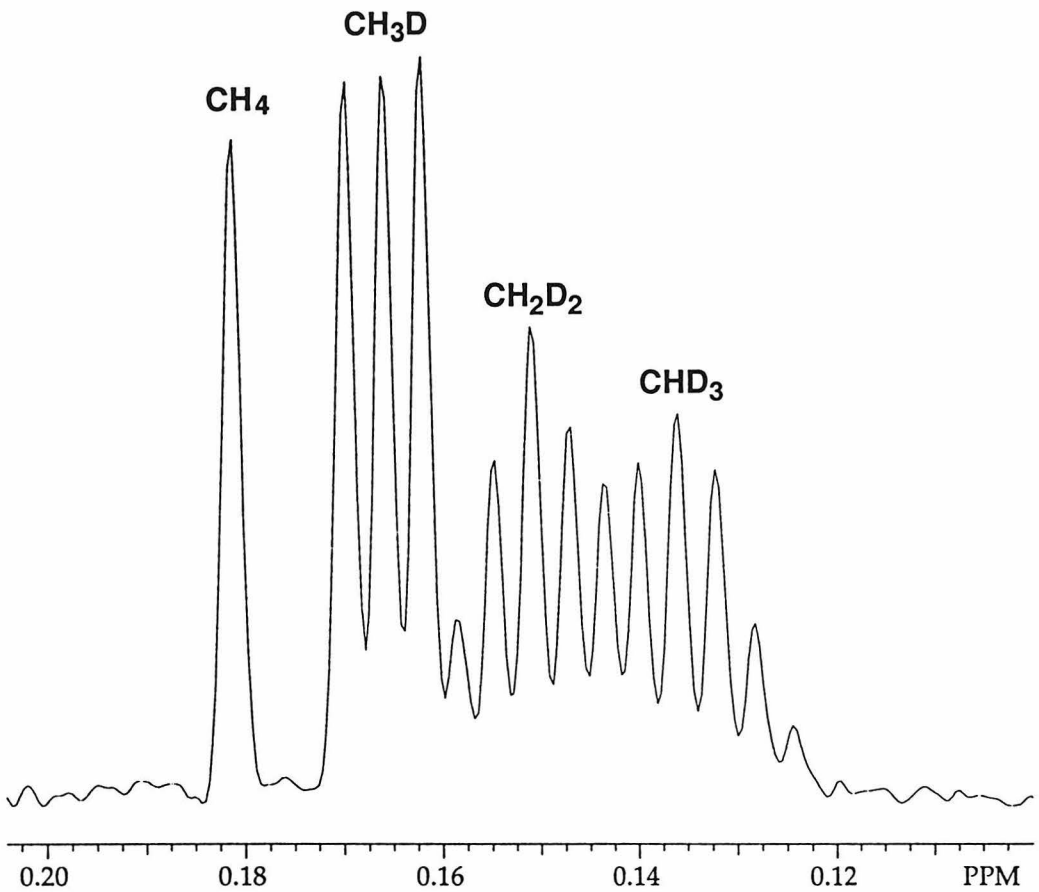


Figure 7. Full range of methane isotopomers that arise upon warming a reaction mixture containing **12** in CD_3OD prior to complete deuterium incorporation into the platinum-methyl groups.

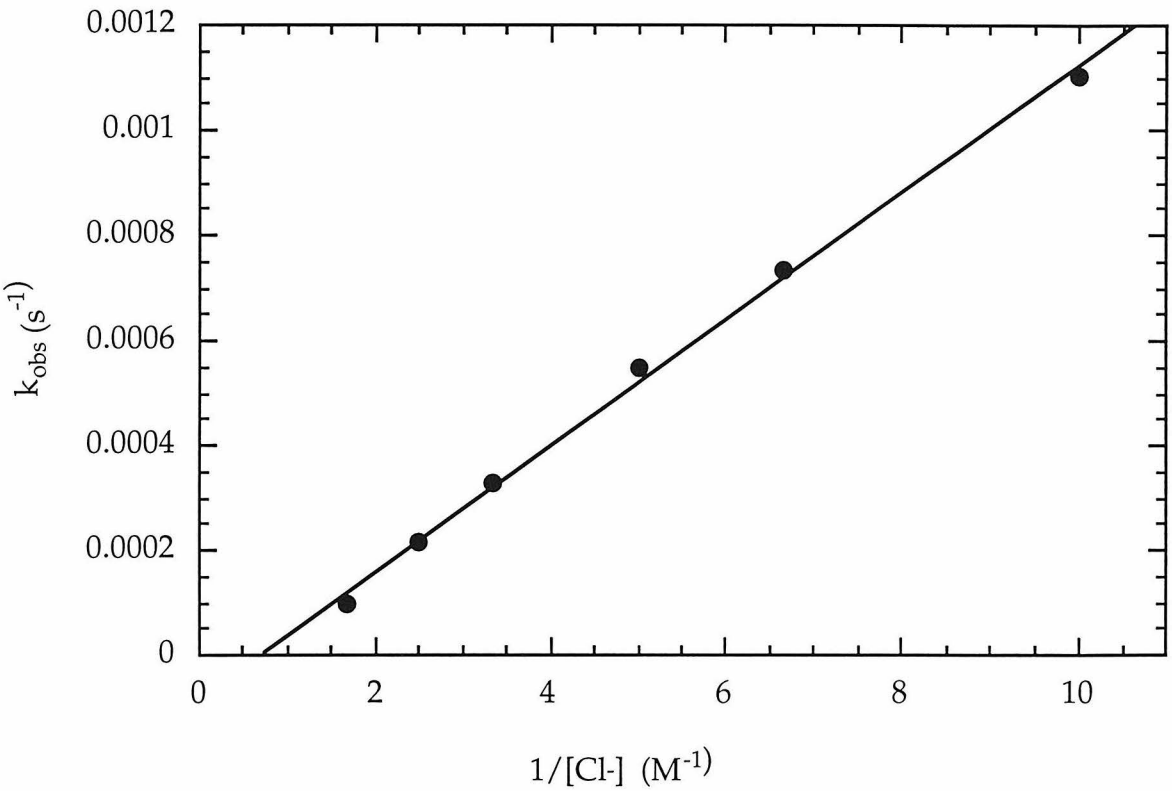


Figure 8. Plot of k_{obs} versus 1/[Cl^-] for deuterium incorporation into **12** in CD_3OD:CD_2Cl_2 (13:1). [Cl^-] = 0.10 – 0.60 M; [**12**] = 21 mM; [H^+] = 0.21 M; μ = 1.21 M; Temperature = -43 °C.

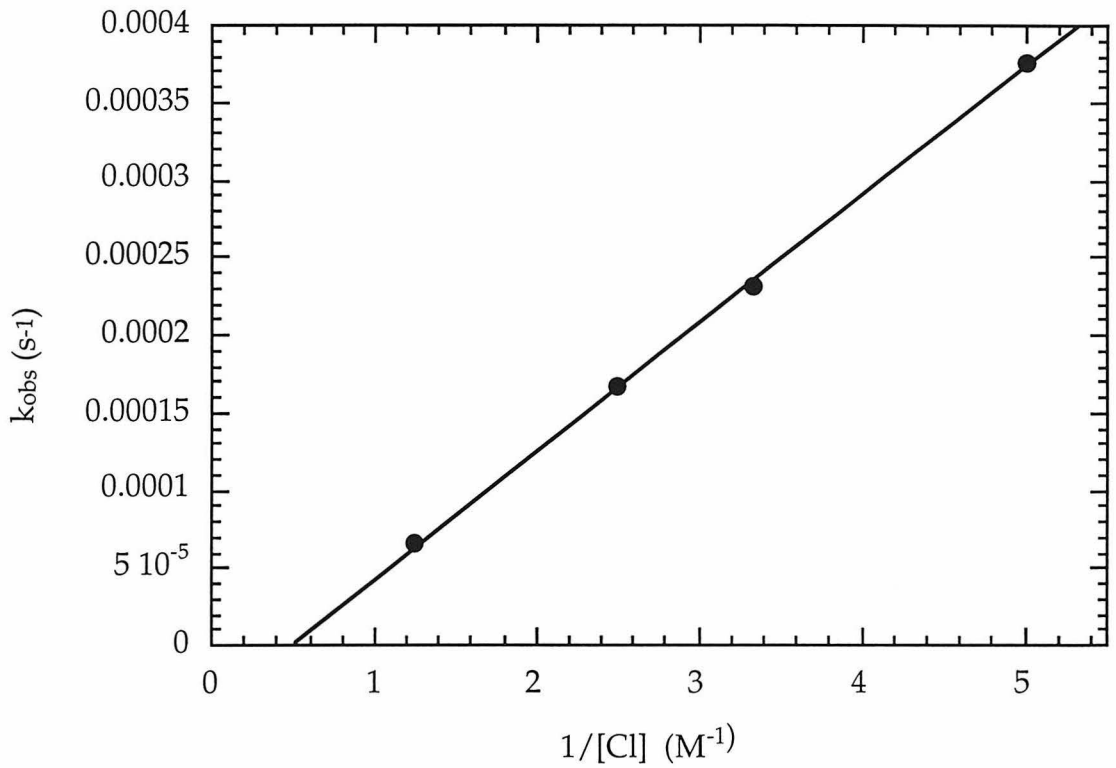
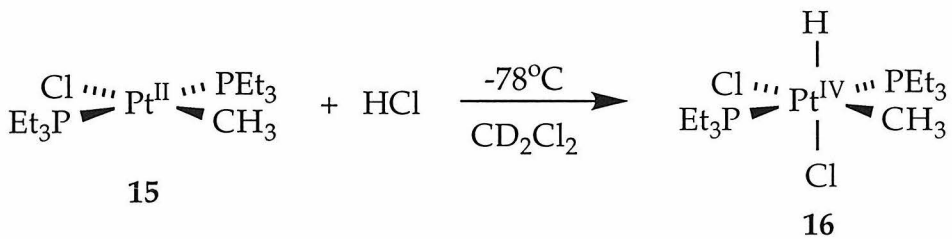


Figure 9. Plot of k_{obs} versus $1/[Cl^-]$ for methane elimination from **12** in $CD_3OH:CD_2Cl_2$ (13:1). $[Cl^-] = 0 - 0.80$ M; [**12**] = 21 mM; $[H^+] = 0.21$ M; $\mu = 1.21$ M; Temperature = -28 °C.

As expected (tmeda)Pt(CH_3)Cl (**2**) is not observed during the conversion of **12** to **3**; **2** decomposes rapidly under these conditions (see above). However, a different methylplatinum(II) intermediate (**14**) does appear as the reaction proceeds. The amount of **14** observed in solution decreases as the initial chloride concentration is increased; furthermore, loss of methane from **14** does not take place until approximately +15 °C — well above the temperature for methane loss from **12** or **2**. **14** was identified as $[(tmeda)Pt(CH_3)(methanol)]^+$ by independent synthesis (from treating **2** with AgOTf) and comparison of ^1H NMR parameters and protonolysis behavior. Fortunately, formation of **14** does not interfere with the kinetics for conversion of **12** to methane and **3**.

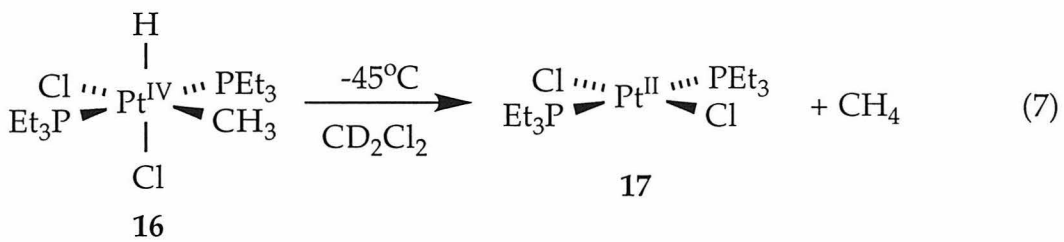
Proton incorporation into the platinum-methyl positions of (tmeda)Pt(CD_3)$_2$(H)Cl (**12-*d*$_6$**) in CD_3OH and CD_4 loss from **12-*d*$_7$** in CH_3OD, were monitored by ^2D NMR. Kinetic isotope effects were calculated by comparing these rates with those for deuterium incorporation and CH_4 loss from **12**: k_H/k_D = 1.9 (± 0.2) at -47.6 °C for H/D incorporation into Pt-CL_3; k_H/k_D = 0.29 (± 0.05) at - 26.8 °C for methane loss.

Protonolysis of *trans*-(PEt_3)$_2$Pt(CH_3)Cl (15) in methylene chloride and methanol. Addition of HCl (as a Et_2O-d_{10} solution) to a CD_2Cl_2 solution of *trans*-(PEt_3)$_2$Pt(CH_3)Cl (**15**) at -78 °C generates (PEt_3)$_2$Pt(CH_3)(H)Cl_2 (**16**) (eq 6).



(6)

The ^{1}H NMR spectrum for **16** clearly reveals the hydride resonance at δ -18.8 ppm with coupling to both platinum and phosphorus (Table 1). Consistent with the formation of a platinum(IV) complex, the resonances associated with the methyl group shift downfield and the two-bond platinum-hydrogen coupling constant decreases relative to **15**. As the solution is warmed to approximately -45 °C loss of methane is observed along with formation of $(PEt_3)_2PtCl_2$ (**17**) (eq 7).

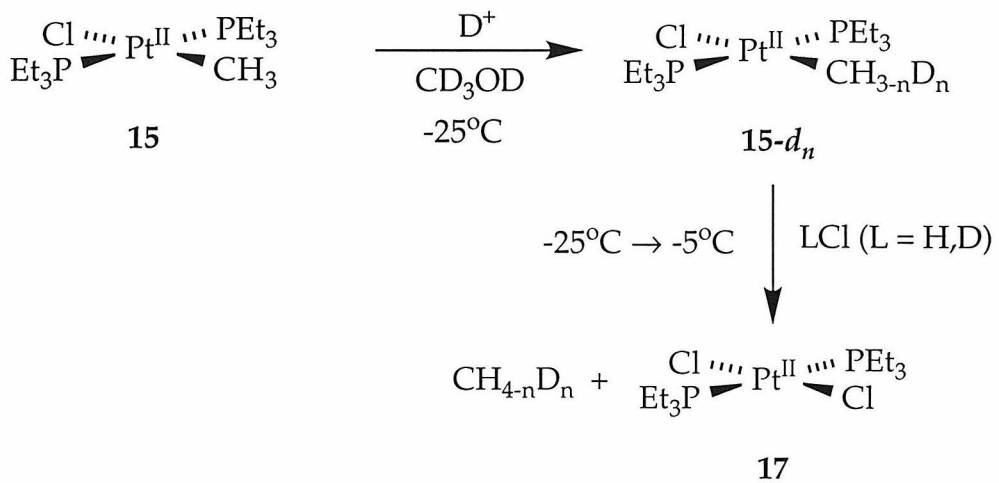


(7)

Protonolysis of **15** in CD_3OH revealed yet another reaction pattern. Addition of DOTf to **15** in CD_3OD at -78 °C (μ = 1M) produces no reaction, *i.e.*, neither an alkylhydridoplatinum(IV) intermediate nor methane is generated. But as the solution is warmed to -25 °C, deuterium incorporation into the Pt-CH_3 sites takes place with *no* Pt(IV) intermediate observed (Scheme 4); only **15** and its isotopomers are detected in solution by ^{1}H NMR spectroscopy prior to methane loss. The kinetics were monitored by integrating the total Pt-C$H_{3-n}D_n$ ^{1}H NMR signal over time (Figure 10).

In the presence of DOTf, with no excess chloride added to the reaction mixture, full deuterium incorporation takes place with no competition from methane loss. As the chloride concentration is increased, methane loss begins to compete with H/D exchange. Rate data for the loss of methane from **15** was obtained by monitoring the protonolysis reaction in CD_3OH (i.e., in the absence of H/D exchange) at -5 °C in the presence of 0.14 M chloride.[48]

Scheme 4



The rate of H/D exchange exhibits a first order dependence on [Cl^-] (Figure 11). Loss of methane from **15** in CD_3OH is also dependent on chloride concentration (approximately first order) (Figure 11). In contrast to the chloride dependence for H/D exchange, methane loss exhibits no measurable rate when [Cl^-] = 0 (Figure 11).

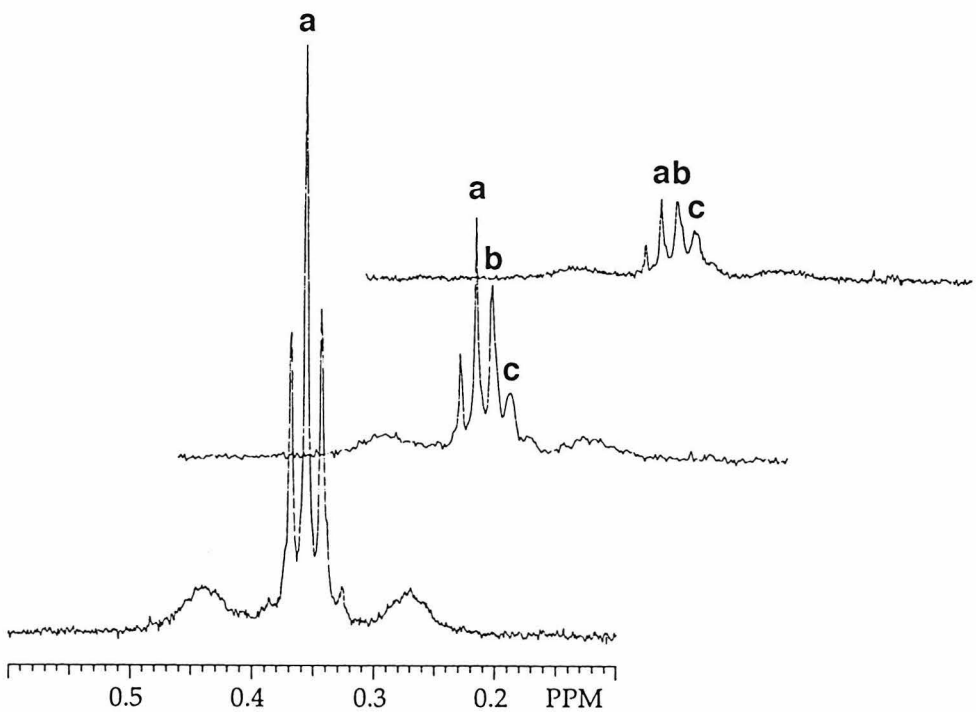


Figure 10. Sequence of ^{1}H NMR spectra demonstrating the appearance of new resonances upfield of the original Pt(II)-CH_3 resonance from **15** along with an overall decrease in the peak integration. The upfield resonances are assigned as the sequentially deuterated methyl groups: **a** = Pt-CH_3, **b** = Pt-CH_2D, and **c** = Pt-CHD_2.

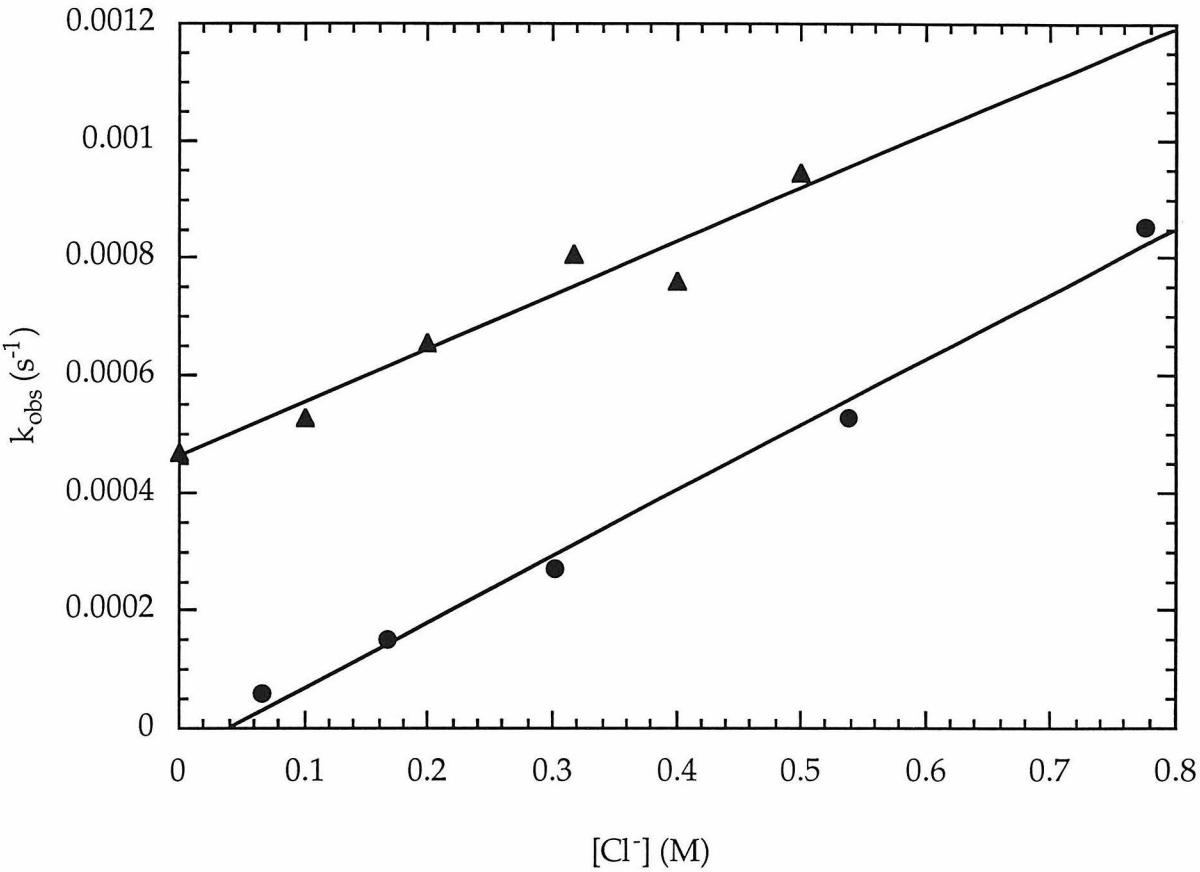


Figure 11. Plot of k_{obs} versus [Cl^-] for deuterium incorporation into **15** in CD_3OD (▲) and for the protonolysis of **15** in CD_3OH (●). Conditions for H/D exchange: [Cl^-] = 0.10 – 0.50 M; [**15**] = 15 mM; [H^+] = 0.15 M; μ = 1.15 M; Temperature = -23 °C. Conditions for protonolysis: [Cl^-] = 0.067 – 0.78 M; [**15**] = 15 mM; [H^+] = 0.15 M; μ = 1.15 M; Temperature = -10 °C.

Activation parameters were determined for both reactions: for H/D exchange, $\Delta H^{\ddagger}$ = 14.5 (± 1.5) kcal/ mol and $\Delta S^{\ddagger}$ = -14.8 (± 4.5) e.u.,[49] and for loss of methane, $\Delta H^{\ddagger}$ = 16.8 (± 0.8) kcal/ mol and $\Delta S^{\ddagger}$ = -12.5 (± 2.6) e.u..

Preparation of *trans*-$(PEt_3)_2Pt(CD_3)Cl$ (**15-d_3**) allowed the determination of kinetic isotope effects for both H/D exchange and loss of methane. Both isotope effects obtained for this system are *inverse*: k_H/k_D = 0.80 (± 0.05) at -26.8 °C for H/D exchange, and k_H/k_D = 0.11 (± 0.02) at -12.0 °C for methane loss.

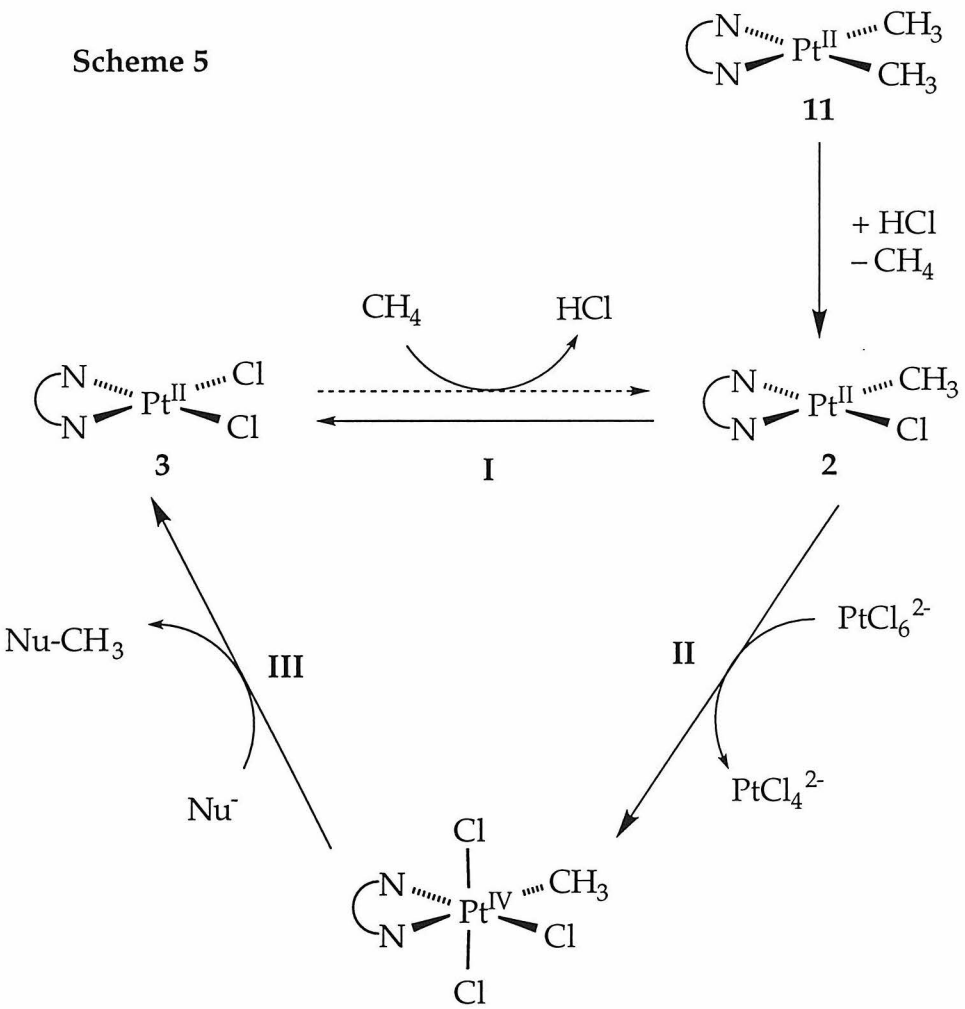
Reduction of $[Pt^{IV}MeCl_5]^{2-}$ in methanol-$d_{3,4}$ and water-$d_{0,2}$. Reduction of $[Pt^{IV}MeCl_5]^{2-}$ (**19**) with two equivalents of $CrCl_2$ in a 10:1 mixture of D_2O:H_2O at 0 °C generates CH_4 and CH_3D (3.2:3.6), from which a kinetic deuterium isotope effect is calculated: k_H/k_D = 8.8 (± 0.5). Upon warming a heterogeneous mixture of $[Pt^{IV}MeCl_5]^{2-}$ and $CrCl_2$ in CD_3OD:CD_3OH (4:1) from -78 °C to 0 °C, the reagents dissolve and methane evolution is observed. The methane generated is composed of a mixture of CH_4, CH_3D, and CH_2D_2 (~ 2.6 : 2.2 : 1).[50] Small amounts of CHD_3 and CD_4 are also presumably present, but they were not quantified.

DISCUSSION

Relevance of Model Complexes. Based on the principle of microscopic reversibility, a mechanistic study of the protonolysis of alkylplatinum(II) could provide insight into C-H activation by Pt(II). Although we had originally hoped to conduct our mechanistic studies on the catalytic intermediate $[Cl_3Pt^{II}CH_3]^{2-}$ (**1**), we encountered a series of complications while studying this species (see Introduction).[13,27] We therefore chose to

investigate the protonolysis of (tmeda)Pt(CH_3)Cl (**2**). The relevance of this model is supported by the ability of tmeda-ligated platinum species to undergo reactions directly analogous to those proposed for catalytic alkane oxidation (steps -I, II, and III in Scheme 5).[13] Further support derives from the observation of isotopic exchange prior to liberation of methane when **1** is generated by reduction of **19** in CD_3OD, behavior closely resembling that of several of the model systems.

Scheme 5



Nevertheless, whenever one investigates model chemistry, there always exists a certain degree of ambiguity with respect to its relevance to the "real" system.

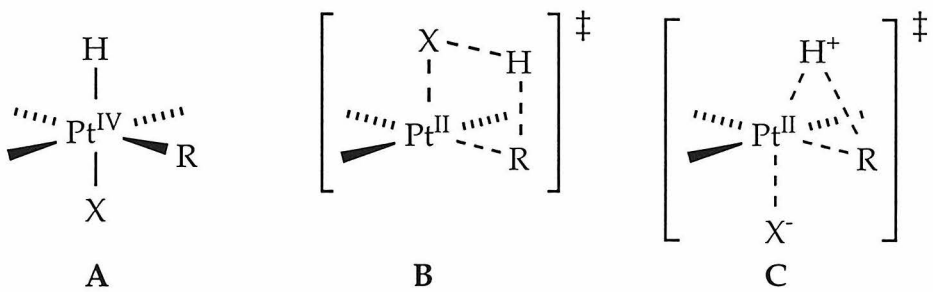
Protonolysis of (tmeda)Pt(CH_3)Cl (2) in CD_3OD. Although the protonolysis of alkylplatinum(II) species has been investigated previously by a variety of other groups, no consensus has been reached on the detailed mechanism of the reaction. Only indirect evidence such as kinetic analysis, isotope effects, and competition experiments was available in these studies until recently. Protonolysis of **2** in CD_3OD is no exception.

This reaction's first order dependence on chloride and proton concentration (Figures 1 and 2) combined with the non-zero intercept in Figure 2 supports a two-term rate law (eq 8), namely one term independent of [Cl^-] and the other with a first-order dependence on [Cl-]. Various rate laws

$$\text{rate} = k_2[\mathbf{2}][H^+] + k_3[\mathbf{2}][H^+][Cl^-] \qquad (8)$$

have been obtained in related studies, and that shown in eq 8 is not without precedent. This rate law can be interpreted in several different ways, however. Initially, this rate law was invoked to support the intermediacy of an alkylhydridoplatinum(IV) species (intermediate **A**) which subsequently reductively eliminates alkane.[28] According to this mechanism, the chloride dependent term in the rate law reflects stabilization of the Pt(IV) intermediate by chloride coordination. The chloride independent term, then, implies a parallel, solvent-stabilized version of intermediate **A** (which is kinetically invisible).

It has been recognized, however, that this rate law is also consistent with chloride-assisted, direct electrophilic attack at the Pt-C bond (transition states **B** or **C**).[29] The four-centered "σ-bond metathesis"-style mechanism (**B**) has been commonly invoked in electrophilic attack of alkylmercury(II) and other species which do not have an accessible higher oxidation state,[51-53] and a recent theoretical study has analyzed this pathway for C-H activation by platinum(II).[32] Transition state **C** was proposed by Alibrandi, et al., following an extensive kinetic study of alkylplatinum(II) species.[29]



A **B** **C**

X^- = halide, solvent, etc.

With respect to the activation of alkanes to generate the alkylplatinum(II) intermediate, structure **A** reflects a mechanism involving alkane oxidative addition/alkylhydridoplatinum(IV) deprotonation (eq 1), whereas **B** and **C** are transition states along reaction profiles for non-redox processes as in the alternative (eq 2).

The activation parameters are of little value for mechanistic interpretation because of the significant role of ion solvation/desolvation in the entropy of activation. The isotope effects are also ambiguous. Isotope effects obtained from a competition experiment in protic solvents are well known to be strongly affected by fractionation factors.[54,55] This consideration accounts for the discrepancy between the isotope effects obtained under

competitive (i.e., comparing the ratio of methane isotopomers generated in a mixture of CD_3OH and CD_3OD -- k_H/k_D = 9.1) versus non-competitive conditions (i.e., comparing the ratio of protonolysis rate constants measured for the two separate solvents -- k_H/k_D = 2.3). Due in part to this complication, these values do not distinguish between the possible mechanisms.

Protonolysis of alkylplatinum(II) species in CD_2Cl_2. Simply changing the reaction solvent from CD_3OD to CD_2Cl_2 led to an important result: the identification of an alkylhydridoplatinum(IV) complex when tmeda was incorporated as a stabilizing ligand. Such intermediates had not been observed in alkylplatinum(II) protonolysis studies when we began our work. Since then, two other groups have identified similar species by hydrolyzing trialkylsilylhalides (to generate HX *in situ*; X = Cl, Br, I) in solutions of dialkylplatinum(II) complexes at low temperature. These reports also involved nitrogen-donor ligands (bipyridyl or phenanthroline ligands) to stabilize the platinum(IV) species. HCl addition to *trans*-$(PEt_3)_2Pt(CH_3)Cl$ (**15**) (i.e., a complex containing soft ligands) in CD_2Cl_2 (eq 6) also yields the platinum(IV) product at low temperature. These observations appear to refute earlier proposals, based on an extensive study of phosphine-ligated complexes (including **15**), that protonolysis of alkylplatinum(II) always proceeds via a concerted mechanism (specifically, transition state **C**).[29]

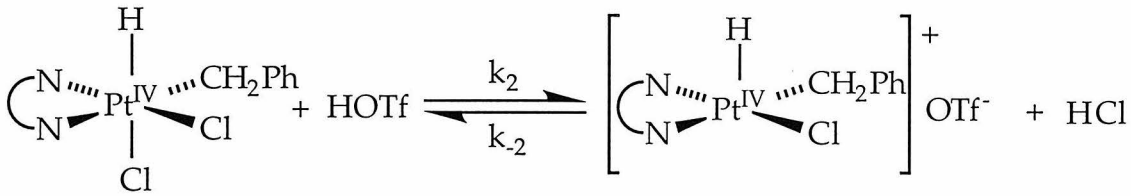
We next considered the detailed mechanism of alkane reductive elimination. Nearly all of our mechanistic work focused on loss of toluene from (tmeda)$Pt(CH_2Ph)(H)Cl_2$ (**6**). It was straightforward to demonstrate that oxidative addition of HCl to alkylplatinum(II) was rapid and reversible on the time scale of hydrocarbon elimination. The negative entropy of activation

($\Delta S^{\ddagger}$ = -18.5 ± 7.0 e.u.) obtained for this reaction suggests a mechanism other than simple reductive elimination from 6-coordinate Pt(IV). Reductive elimination reactions often exhibit near-zero or positive entropies of activation due to the formation of two products from one reactant. However, formation of an ionic intermediate can lead to a negative entropy of activation due to significant ordering of the solvent molecules;[56] in our system, chloride dissociation could lead to such an intermediate. Our first attempt to verify such a mechanism by checking for chloride inhibition was thwarted, however, because excess chloride deprotonates **6** to regenerate **5** (eq 4). We did obtain support for this mechanism by adding HOTf or $SnCl_4$ to solution of **6**; addition of either reagent greatly accelerates the rate of toluene elimination.

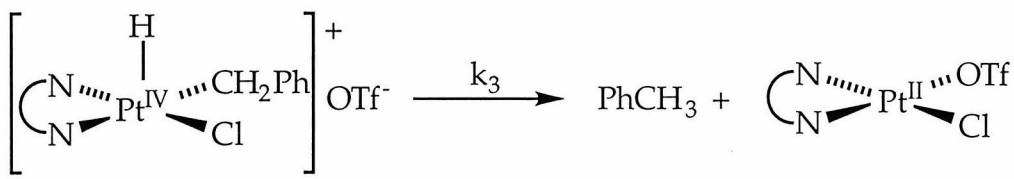
A possible mechanism for the reductive elimination of toluene from **6** in the presence of HOTf is shown in Scheme 6. This mechanism suggests that chloride must dissociate from **6** to generate a five-coordinate cationic intermediate **20** prior to reductive elimination. Triflic acid facilitates loss of chloride; Lewis acids such as $SnCl_4$ function similarly. Prerequisite ligand dissociation has been identified in previous studies of alkyl-hydride reductive elimination,[57-59] although this mechanistic feature is by no means universal.[60-63]

An alternative mechanism that might also be considered is shown in Scheme 7. Here **6** is merely generated in an unproductive side reaction, while alkane formation requires reductive elimination of HCl from **6** followed by direct electrophilic attack by H^+ at the platinum alkyl bond of **5**. Indeed, both schemes look very similar kinetically, and the derived rate expressions have been outlined in Table 2.

Scheme 6

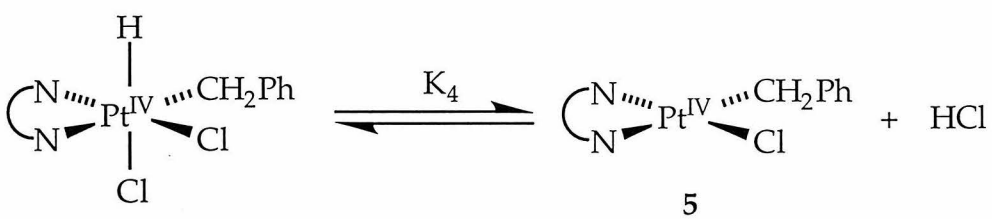


6 20

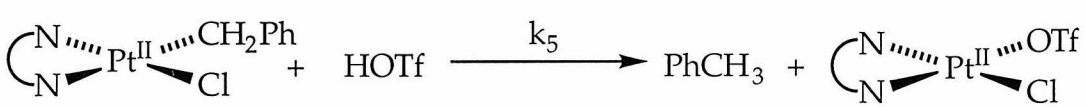


20

Scheme 7



6 5



5

Table 2. Predicted Rate Expressions for Mechanisms Proposed in Schemes 6 and 7.

	Scheme 6	Scheme 7
Pre-equilibrium First Step	$\frac{k_3K_2[HOTf][6]}{[HCl]}$	$\frac{k_5K_4[HOTf][6]}{[HCl]}$
Steady State	$\frac{k_2k_3[HOTf][6]}{k_3 + k_{-2}[HCl]}$	$\frac{k_4k_5[HOTf][6]}{k_{-4}[HCl] + k_5[HOTf]}$

Both pre-equilibrium and steady-state situations have been considered. Because full equilibration between **6** and **5** was demonstrated by isotopic labeling (Scheme 2), the "steady-state" option for Scheme 7 is eliminated. The other three mechanistic possibilities were distinguished kinetically by evaluating the effect of [HCl] on the reaction rate with [HOTf] held constant. As demonstrated in Figure 5, the reaction is inhibited by HCl. Figure 12 shows the same data, presented as $1/k_{obs}$ vs. [HCl]. The non-zero intercept in this plot supports the mechanism in Scheme 6 with steady-state kinetic behavior. Both pre-equilibrium rate laws predict that a plot of $1/k_{obs}$ vs. 1/[HCl] would go through the origin. According to this mechanism, the negative entropy of activation would likely arise from ion solvation effects.

Isotope effects determined for this system (using calibrated mixtures of HCl and DCl) also support the mechanism in Scheme 6. Based on the isotope effects that were determined in this system (K_H/K_D = 0.51 for pre-equilibrium oxidative addition of LCl to **5**, and k_H/k_D = 1.55 for overall toluene formation from **5** + LCl (L = H, D)), other isotope effects for Scheme 6 and 7 can be calculated. If Scheme 6 is the correct mechanism, a kinetic deuterium isotope

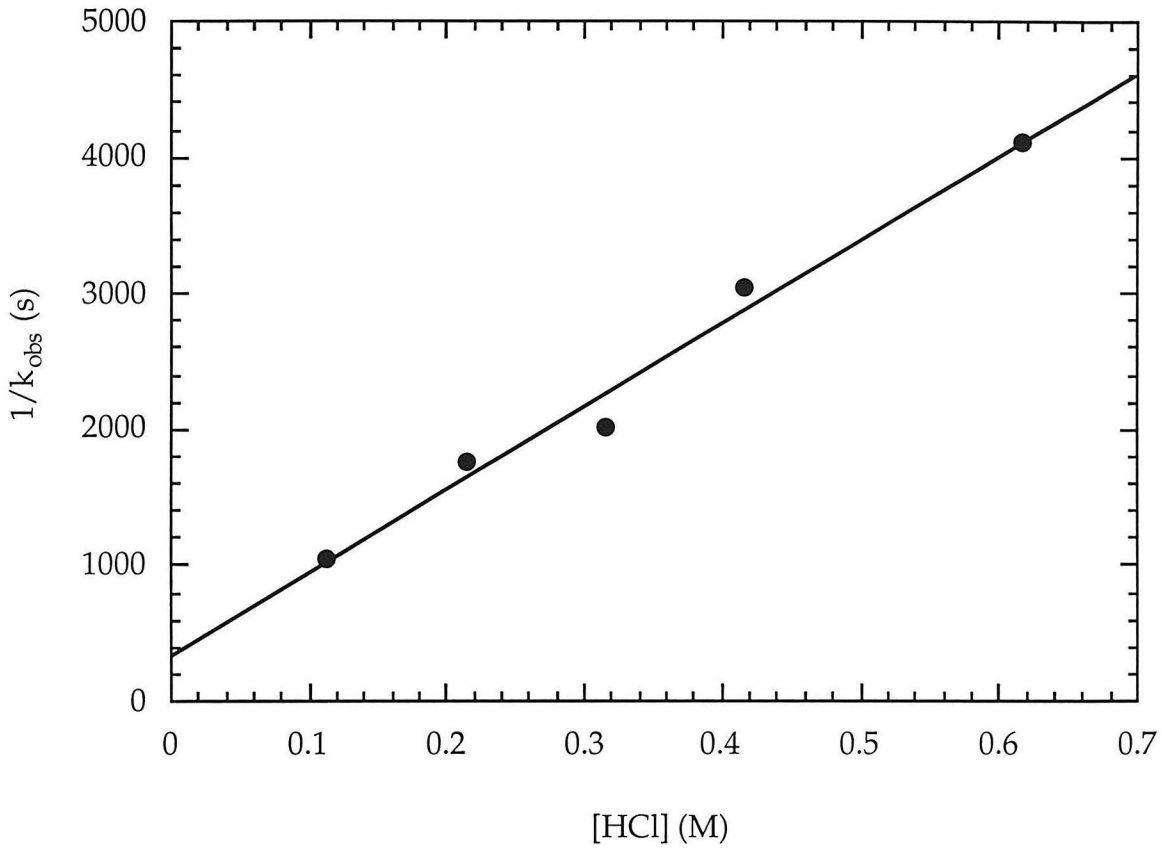
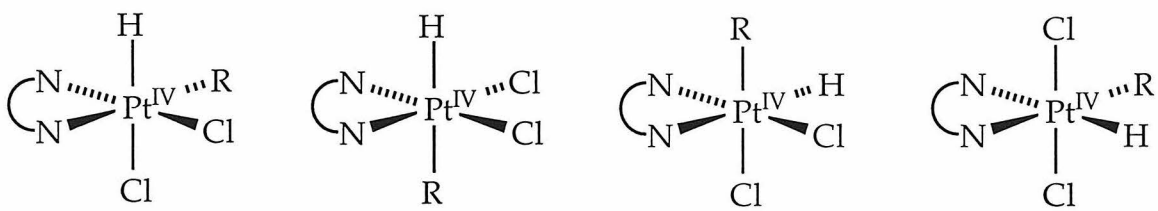


Figure 12. $1/k_{obs}$ vs. [HCl] for reductive elimination of toluene from **6** in the presence of varying [HCl] and constant [HOTf]. For reaction conditions see Figure 5.

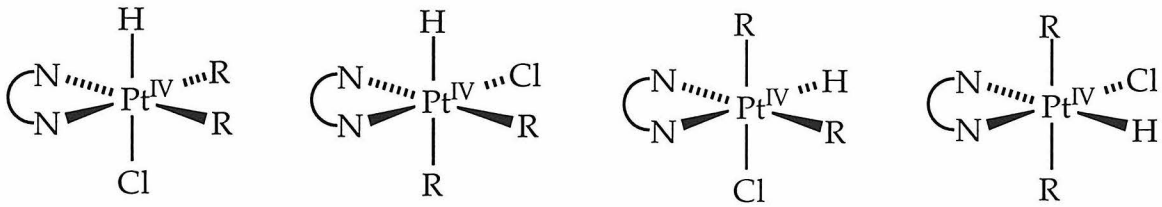
effect for the reductive elimination of toluene from **6** is k_H/k_D = 3.1 (± 0.6) ($KIE_{overall}$ = $EIE_{HCl\ ox.addn.}$ x KIE_{k_3}). This value is similar to those observed in alkane reductive elimination of platinum(II) alkyl hydrides.[60,61,64] On the other hand, if Scheme 7 is the operating mechanism, the isotope effect for k_5 is simply the observed overall isotope effect, k_H/k_D = 1.55. This value appears rather low for a single step mechanism involving direct proton transfer.[65] Therefore, based on the kinetic argument described above and these isotope effect calculations, we favor the mechanism proposed in Scheme 6.

Stereochemistry of HCl Addition. The spectroscopic data obtained for **4** and **6** (Table 1) are unable to distinguish between *trans* versus *cis* addition of HCl to **2** and **5**, respectively. In theory, four possible stereoisomers could arise from this reaction (Structures **D** - **G**). *Trans* addition of HCl would lead to



structure **D**, whereas *cis* addition could produce any of the structures **D** - **G**. Of course, any of the structures are also accessible via isomerization during or after the addition of HCl. Compound **6** contains four spectroscopically distinct methyl groups on the tmeda ligand (Table 1), consistent with structures **D** and **F**.

Evaluating HCl addition to related *dialkyl*platinum(II) species provided further insight. There are still four possible products however (Structures **H** - **K**). In the absence of isomerization, structure **H** results from *trans* addition



H **I** **J** **K**

of HCl, **I** and **J** from *cis* addition. The remaining stereoisomer, **K**, can only arise from isomerization following HCl addition. The ^{1}H NMR spectrum of (tmeda)Pt(CH_2Ph)$_2$(H)Cl (**7**) exhibits two inequivalent resonances for its tmeda methyl protons (Table 1). This spectrum is consistent with either structure **H** or **K**. Protonation of (4,4'-dimethyl-2,2'-bipyridyl)Pt(CH_3)$_2$ (**9**) leads to a dialkylhydridoplatinum(IV) complex (**10**) with only a single resonance in the ^{1}H NMR spectrum corresponding to the methyls on the bipyridyl ligand (Table 1). This result is only consistent with the *trans* HCl addition product **H**, a conclusion also reached by Puddephatt and co-workers in an identical reaction between HCl and (4,4'-di-*tert*-butyl-2,2'-bipyridyl)Pt(CH_3)$_2$.[34] By contrast, Panunzi and co-workers have identified structure **J** as the product arising from HX (X = Cl, Br) addition to (dmphen)Pt(CH_3)$_2$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) in acetone/diethyl ether solution.[33] As noted by both groups, this product geometry is likely due to the steric constraints of the dmphen ligand used in this reaction. Nevertheless, by analogy to the products of HCl addition to dialkylplatinum(II) species, **7** and **9**, we believe the addition proceeds with

trans stereochemistry. The spectroscopic data for $(PEt_3)_2Pt(CH_3)(H)Cl_2$ (**16**) is also consistent with *trans* HCl addition to **15**, although this has not been verified by experiments with related dialkyl complexes.

Stability of dialkylhydridoplatinum(IV) versus monoalkylhydridoplatinum(IV): A digressionary anomaly. We have previously reported that preparation of (tmeda)$Pt(CH_3)Cl$ (**2**) is readily accomplished in high yield by addition of one equivalent of HCl to (tmeda)$Pt(CH_3)_2$ (**11**) in CH_2Cl_2 (Scheme 3).[13] Based on the decreased stability of (tmeda)$Pt(CH_3)(H)Cl_2$ (**4**) relative to (tmeda)$Pt(CH_3)_2(H)Cl$ (**12**), we might have expected that once **2** begins forming in solution, it would be consumed more rapidly than **11**, leaving a 1:1 mixture of **11** and (tmeda)$PtCl_2$. Because mixing equal amounts of **11** and (tmeda)$PtCl_2$ in CD_2Cl_2 revealed only a minor amount of comproportionation after 24 hours,[66] this is not a kinetically competent mechanism to account for the clean formation of **2** under preparative conditions.

This apparently anomalous result is perhaps best explained by the energy diagram in Figure 13. We demonstrated above that protonation of the alkylplatinum(II) complexes is rapid and reversible. In other words, a mixture of (tmeda)$Pt(CH_3)Cl$, (tmeda)$Pt(CH_3)_2$, and HCl in CH_2Cl_2 will rapidly equilibrate between both alkylhydridoplatinum(IV) species, (tmeda)$Pt(CH_3)(H)Cl_2$ (**4**) and (tmeda)$Pt(CH_3)_2(H)Cl$ (**12**), prior to reductive elimination. The relative stabilities of **4** and **12** with respect to reductive elimination indicate that $\Delta G_{12}^{\ddagger} > \Delta G_4^{\ddagger}$. However as long as the transition state for reductive elimination from **12** is lower in energy than the transition state for elimination from **4**, the reaction will selectively generate (tmeda)$Pt(CH_3)Cl$ until either HCl or (tmeda)$Pt(CH_3)_2$ is consumed.

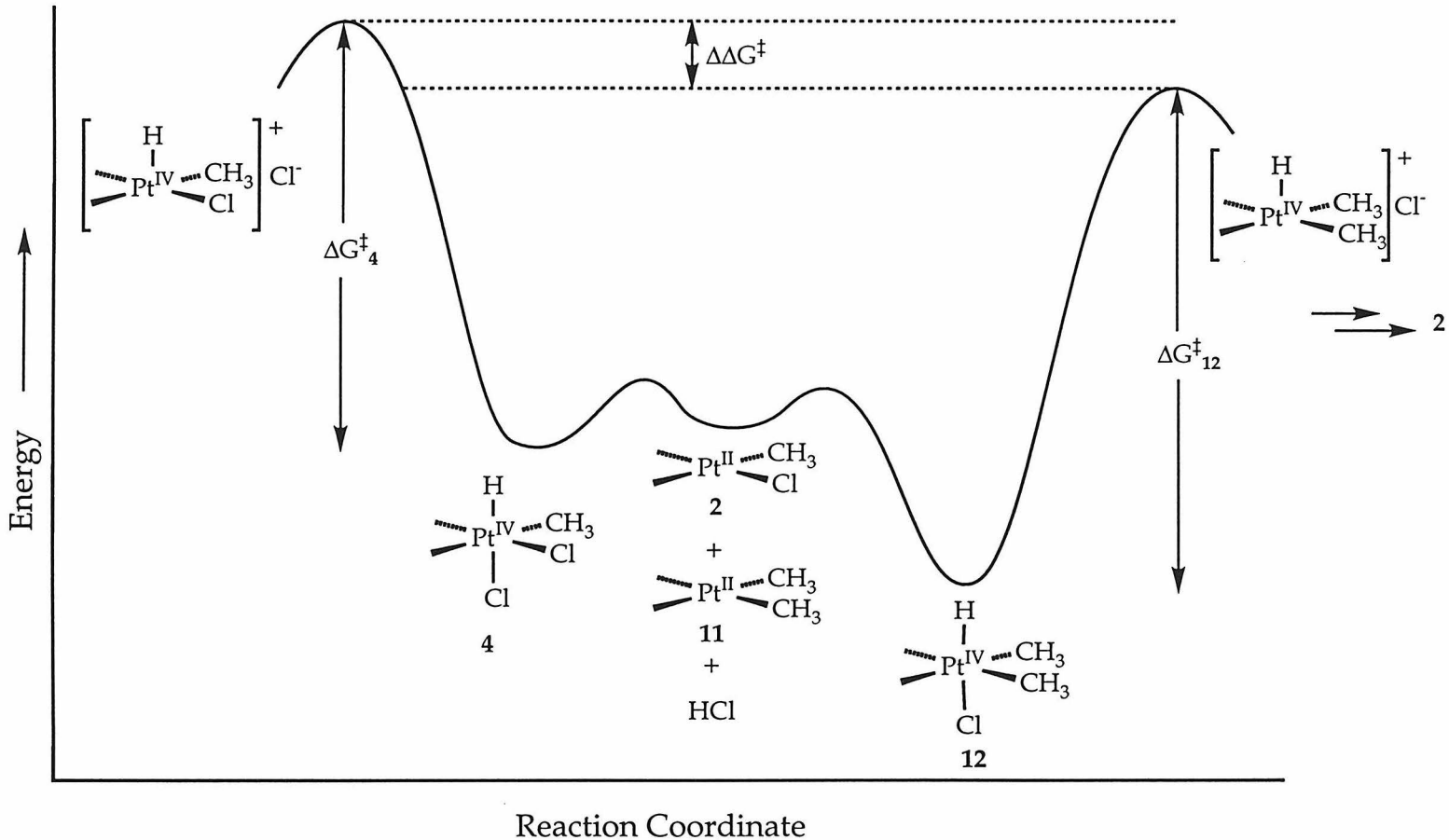


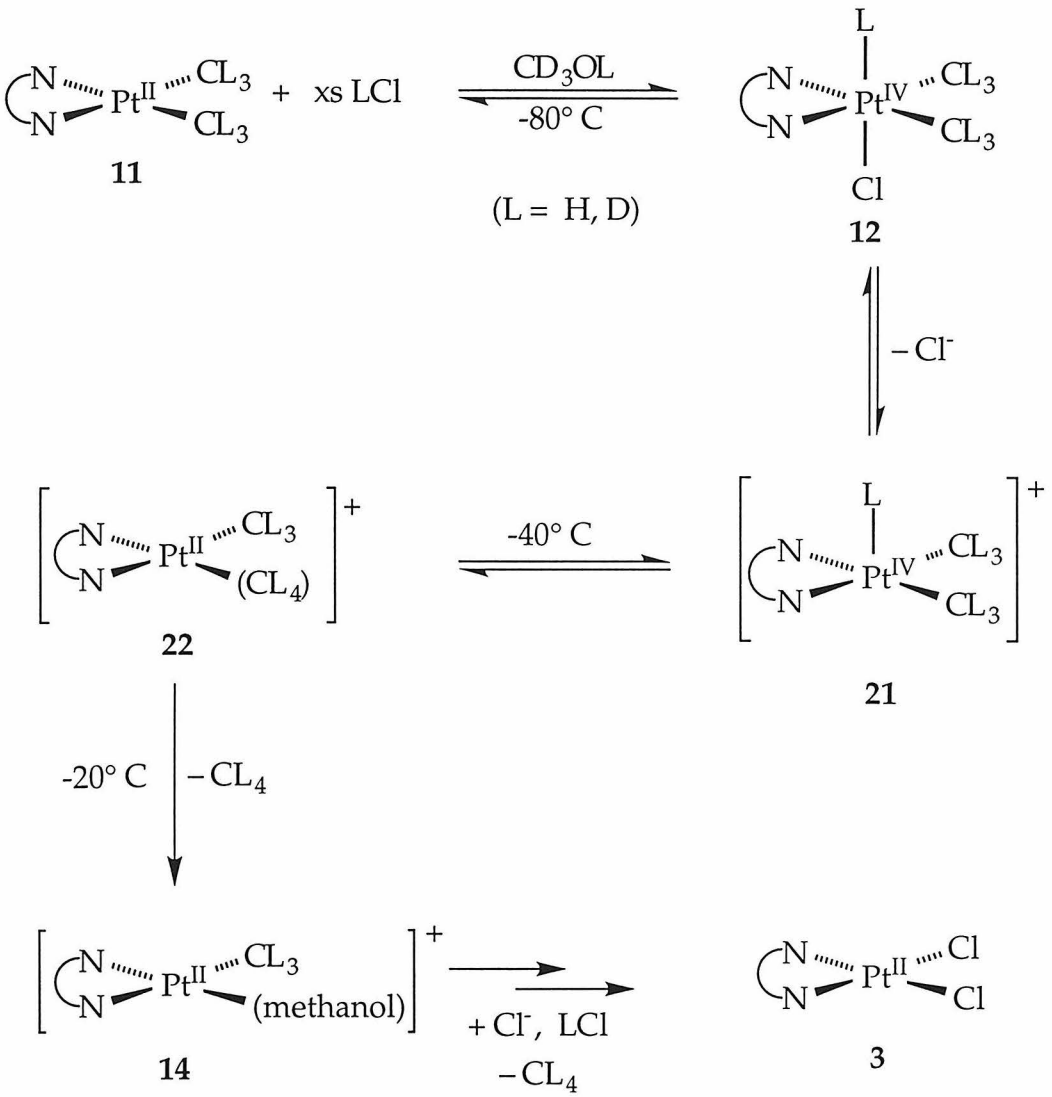
Figure 13. Qualitative reaction coordinate diagram for the reaction of HCl with **2** and **11**. While the barrier to reductive elimination from **12** ($\Delta G_{12}^{\ddagger}$) is greater than from **4** ($\Delta G_{4}^{\ddagger}$), the overall barrier to the reaction of HCl with **11** is lower than with **2** ($\Delta\Delta G^{\ddagger}$).

Protonolysis of (tmeda)Pt(CH_3)$_2$ (11) in CD_3OD. Because the protonolysis of (tmeda)Pt(CH_3)Cl (**2**) in methanol reveals no intermediate prior to loss of methane, whereas an alkylhydridoplatinum(IV) intermediate is observed in CD_2Cl_2, we must consider whether changing the solvent changes the protonolysis mechanism. However, observation of the dialkylhydridoplatinum(IV) species (tmeda)Pt(CH_3)$_2$(H)Cl (**12**) upon treating (tmeda)Pt(CH_3)$_2$ (**11**) with HCl in methanol verifies the viability of Pt(IV) intermediates in polar/protic solvent. Not only is a platinum(IV) intermediate observed, but deuterium from CD_3OD is incorporated into the platinum-bound methyl groups prior to reductive elimination of methane, implicating the potential involvement of an alkane σ-complex.

We propose the mechanism shown in Scheme 8 for protonolysis of **11** in methanol. The fundamental steps involve (1) pre-equilibrium oxidative addition of HCl to generate **12**, (2) dissociation of chloride to produce a cationic, five-coordinate intermediate (**21**), (3) reductive C-H bond formation leading to the Pt(II) methane σ-complex (**22**) (the nature of this interaction will be discussed below), and finally, (4) unimolecular dissociation of alkane resulting in the cationic methylplatinum(II) species (**14**). Trapping of **14** by chloride to form **2** results in the immediate liberation of the second equivalent of methane. (**2** has already been shown to be unstable under these reaction conditions.) Small to significant concentrations of **14** can be observed by ^{1}H NMR, depending on the initial chloride concentration.

According to this proposal, methane dissociation is the rate determining step; all preceding steps can fully equilibrate prior to loss of methane. In order for H/D exchange to take place, the σ-complex (**22**) must rearrange to coordinate a different C-H(D) bond prior to reversion to **21**.

Scheme 8



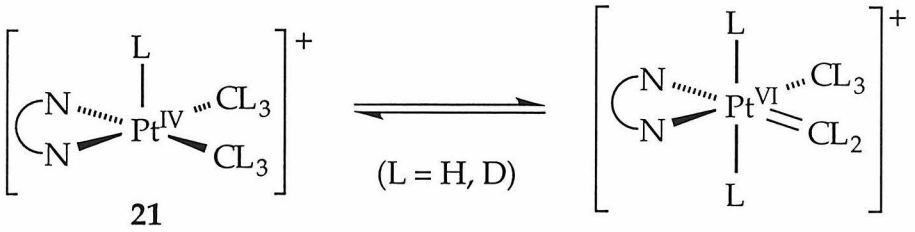
Recently, significant evidence has been provided for alkane σ-complexes mediating the solution-phase reductive elimination and oxidative addition of alkanes at transition metal centers.[67-80] For example, Bergman, Moore and co-workers have obtained transient IR spectroscopic data directly supporting such an intermediate in the oxidative addition of alkanes at a Cp*Rh(CO) fragment.[67-69] The viability of alkane adducts has received

additional support from a variety of other sources: theory,[81-85] and gas phase,[86-91] condensed phase,[92-96] and low-temperature matrix studies.[97,98] Furthermore, analogous η^2-dihydrogen and silane complexes along with 3-center-2-electron agostic C-H-M interactions[99] are now well known and many have been structurally characterized.

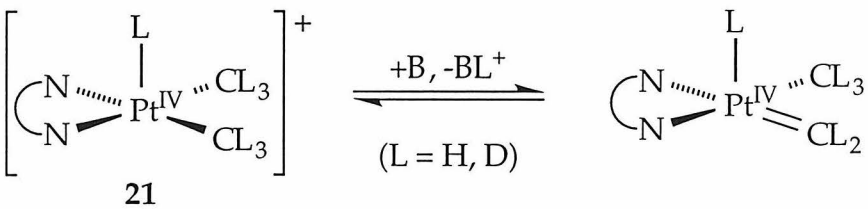
Deuterium scrambling between hydride and alkyl positions prior to alkane elimination has been observed previously in other transition metal complexes.[70,71,73,75-77,79] In some cases the exchange proceeds rapidly enough to allow full equilibration of a single deuterium atom between the two different sites prior to methane loss. Equilibrium isotope effects determined in such cases reveal a preference for deuterium to reside in the alkyl site, as expected.[71,73,75,77] In our case, such equilibration leads to complete isotopic exchange because the platinum hydride also exchanges with the large excess of deuterium in the solvent. Complete proton incorporation into **12-d_6** is also observed when the reaction is carried out in CD_3OH. That H/D exchange takes place *intra*molecularly was verified by monitoring deuterium incorporation into **12** under approximately 15 atmospheres of CH_4. No evidence for incorporation of CH_4 was obtained; loss of CL_4 in Scheme 8 is irreversible.

Although such isotopic exchange has been invoked to support the intermediacy of σ-complexes in the reductive elimination of alkanes, it is often difficult to definitively exclude alternative mechanistic possibilities. Such is the case here, too. The mechanism for H/D exchange need not lie on the reaction coordinate for reductive elimination. For example, it might proceed by formation of a carbene intermediate generated via α elimination or via deprotonation by an external base (e.g., solvent) (eqs 9 and 10,

respectively). Reversal of either reaction could account for H/D exchange: in the former case, exchange of either platinum hydride with solvent deuterons followed by carbene insertion, or in the later case, deuteration of the platinum carbene by solvent deuterons.



21 (9)



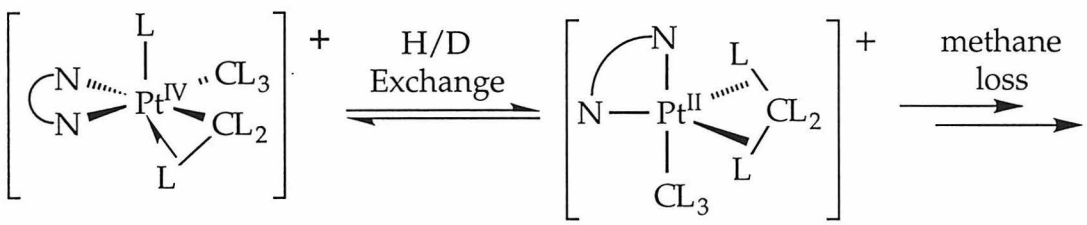
21 (10)

The magnitude of the normal isotope effect that we obtained for H/D exchange (k_H/k_D = 1.9 (± 0.2)) appears unable to accommodate either carbene mechanism which should lead to *inverse* isotope effects. (The predicted inverse nature of these isotope effects arises solely from our definition of k_H and k_D. Both eqs 9 and 10 for H/D exchange involving a carbene intermediate should lead to faster rates for deuterium incorporation into $-CH_3$ (k_H)versus proton incorporation into $-CD_3$ (k_D).)

The inverse dependence of the rates of H/D exchange *and* methane elimination on chloride concentration (Figures 8 and 9) implies that chloride must dissociate from **12** prior to further reaction. A similar observation (involving iodide dissociation) has been made by Canty and Puddephatt, et

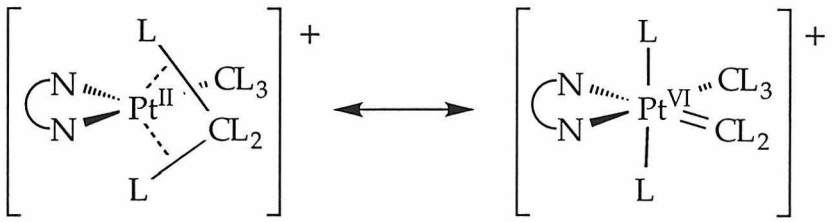
al., and Goldberg, et al., when investigating the reductive elimination of ethane from trimethyl palladium(IV) and platinum(IV) species, respectively.[56,100-103] Canty and Puddephatt suggest that upon iodide dissociation, an agostic interaction might develop between one of the methyl C-H bonds and the coordinatively unsaturated palladium center. This interaction could stabilize the redirection of a carbon sp^3 orbital away from the metal center and toward the second methyl group, ultimately leading to C-C bond formation. In our case, an agostic interaction could stabilize the *C-H* bond formation. The intermediate alkane σ-complex then might involve an η^3 (H-C-H) interaction with the metal center (**25**$_\sigma$). (Scheme 9) Such an alkane binding mode was evaluated in theoretical work by Low and Goddard as an intermediate in the reductive elimination of methane from Pt(II).[83]

Scheme 9



24 **25$_s$**

With such an intermediate, H/D exchange does not require that the bound alkane rearrange to coordinate a different C-H(D) bond as the oxidative C-H bond cleavage (**25**$_\sigma$ → **24**) may select either coordinated bond. It should perhaps be noted that **25**$_\sigma$ can be considered a resonance structure of a carbene complex (**25**$_c$). Unfortunately, we have no direct data that allows us to evaluate the nature of this intermediate further.



25_s 25_c

The isotope effect for methane loss from (tmeda)Pt$(CH_3)_2$(H)Cl (**12**) is substantially inverse (k_H/k_D = 0.29 (± 0.05)). Inverse isotope effects have been reported by a number of groups who investigated the reductive elimination of alkanes from transition-metal centers; however, this is the smallest value obtained so far.[70,71,73,75-77] As has been discussed thoroughly in several of these references, inverse isotope effects often suggest the presence of an unobserved equilibrium preceding the rate-determining step. A single-step mechanism may also produce an inverse isotope effect;[104,105] however, one would expect such a value to arise only from a highly endothermic reaction in which the transition state is very "product-like," namely, one in which a considerable amount of C-H bond formation has already taken place.

Several instances of *normal* isotope effects (including the one discussed above: (tmeda)Pt$(CH_2Ph)(H)Cl_2$ (**5**) in CD_2Cl_2, k_H/k_D = 3.1) for C-H reductive elimination have also been reported.[57,60,61,64] The data in Table 3 compare all the isotope effects that we have found for C-H reductive elimination; the table is arranged in the order of decreasing isotope effect. Not only do the values vary widely (some of this variation is of course due to differences in temperature), but they do not appear to correlate directly with the relative exothermicity of the reaction. The lack of correlation between these values

suggests that reaction exothermicity alone cannot explain the discrepancy in isotope effects. Interestingly, for *all reported cases* of inverse isotope effects

Table 3. Deuterium kinetic isotope effects measured for the reductive elimination of alkanes from various alkylhydrido transition metal complexes

Entry	Compound	Temp. (°C)	Isotope Effect	Reference
1	*cis*-$(PPh_3)_2Pt(Me)(H)$	-25	3.3	60
2	$(tmeda)Pt(CH_2Ph)(H)Cl_2$	-28	3.1	this work
3	*cis*-$(PPh_3)_2Pt(CH_2CF_3)(H)$	40	2.2	61
4	(P–P)$Pt(CH_2CMe_3)(H)$ P–P = bis(dicyclohexylphosphino)ethane	69	1.5	64
5	*mer*-$(PMe_3)_3Rh(CH_2COCH_3)(H)Cl$	31	1.3	57
	Normal Isotope Effects			
	Inverse Isotope Effects			
6	$[Cp_2Re(CH_3)(H)]^+ Cl^-$	9	0.8	73
7	$(Cn)Rh(PMe_3)(CH_3)(H)$	75	0.74	77
8	$Cp^*Ir(PMe_3)(Cy)(H)$	130	0.7	70
9	$Cp_2W(CH_3)(H)$	73	0.7	74, 75
10	$Cp^*_2W(CH_3)(H)$	100	0.7	76
11	$Cp^*Rh(PMe_3)(3,5\text{-}C_6H_3Me_2)(H)$	51	0.51	72
12	$Cp^*Rh(PMe_3)(Et)(H)$	-30	0.5	71
13	$(tmeda)Pt(CH_3)_2(H)Cl$	-27	0.29	this work

(entries 6 - 13), H/D exchange is observed between the alkyl (aryl) and hydride positions, constituting independent evidence for the presence of an intermediate preceding alkane loss. Thus, while H/D exchange does not *necessarily* lie on the reaction coordinate for reductive elimination, the data in Table 3 provides substantial support for such a link. It is still possible that σ-complexes mediate the reductive elimination of reactions which reveal normal isotope effects, but in these cases, the rate-determining step would involve formation of the σ-complex rather than dissociation of alkane from the metal center. That is, the transition state would lie much earlier along the reaction coordinate for C-H bond formation.

Finally, based on the difference between the enthalpies of activation ($\Delta\Delta H^{\ddagger}$) for H/D exchange and methane elimination, we can set a lower limit on the strength of the Pt–(CH_4) bond in **22** of ~ 3 kcal/mol. This value is well below that proposed for the strength of a metal-alkane interaction (~ 5–10 kcal/mol),[80] thus with such an interaction leading to H/D exchange. (A value above 5–10 kcal/mol would suggest a σ-adduct is not a legitimate intermediate.)

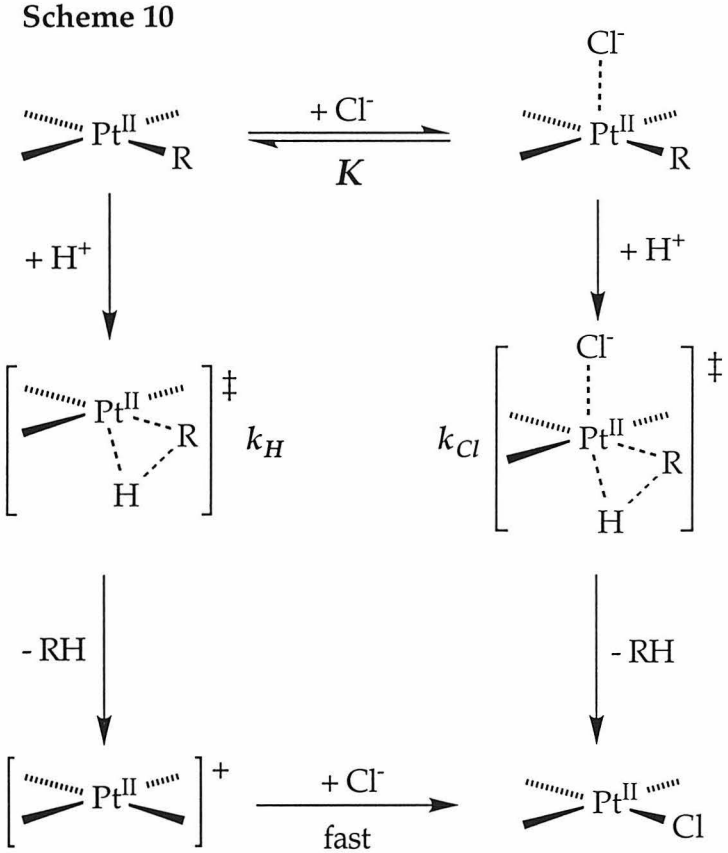
We therefore believe that H/D exchange in (tmeda)Pt(CH_3)$_2$(H)Cl (**12**) supports the presence of a methane σ-complex that lies on the reaction coordinate for reductive elimination. Without an intermediate in this reaction, the inverse isotope effect would be very difficult to explain. The isotope effect for methane loss, then, is a composite value arising from an equilibrium isotope effect (reversible σ-complex formation) and a kinetic isotope effect (dissociation of alkane). Lack of direct observation of the σ-complex prevents us from deconvoluting this value.

Protonolysis of *trans*-$(PEt_3)_2Pt(CH_3)Cl$ (15) in CD_3OD. We initially chose to evaluate the protonolysis of *trans*-$(PEt_3)_2Pt(CH_3)Cl$ (**15**) because of the inverse isotope effect reported by Romeo, et al..[106] Furthermore, **15** has been the subject of several protonolysis studies in the past,[28,29,106] and we wanted to compare its reactivity directly with our tmeda-ligated platinum complexes. Previous investigations utilized UV-visible spectroscopy to monitor the reaction, and clean isosbestic points suggested no intermediates were present in the reaction. However, upon investigating the protonolysis of **15** in CD_3OD by ^1H NMR, we observed deuterium incorporation into the methyl sites prior to methane loss (Scheme 4). Since there is no buildup of the intermediate responsible for this exchange, it would be invisible in the electronic spectrum. In contrast to the protonolysis of (tmeda)$Pt(CH_3)_2$ (**11**), no platinum(IV) intermediate is observed; **15** and its isotopomers are the only species observed prior to elimination. We propose that deuterium incorporation results from the formation of an alkane σ-complex prior to methane dissociation.

Protonolysis of **15** might proceed via direct protonation at the platinum-carbon bond (see structures **B** and **C** above), or alternatively, it may proceed through a mechanism analogous to Scheme 8. In the latter case, the platinum(IV) intermediate would not be observed if it is less stable than the starting alkyl platinum(II) complex **15**. The former conclusion was favored by Alibrandi, et al., in their extensive study of a series of alkylplatinum(II) species.[29] They propose a mechanism involving direct protonolysis of **15** through transition state **B** involving both chloride-dependent (k_{Cl}) and chloride-independent (k_H) pathways (Scheme 10). Nevertheless, we believe that a mechanism similar to Scheme 8, involving a phosphine-ligated

alkylhydridoplatinum(IV) intermediate (**16**), is at least as consistent with the data, and also contributes to a more unified picture for the protonolysis of alkylplatinum(II) species (see below). Indeed, such a mechanism was proposed by Belluco and co-workers in their first study of the protonolysis of **15**.[28]

Scheme 10



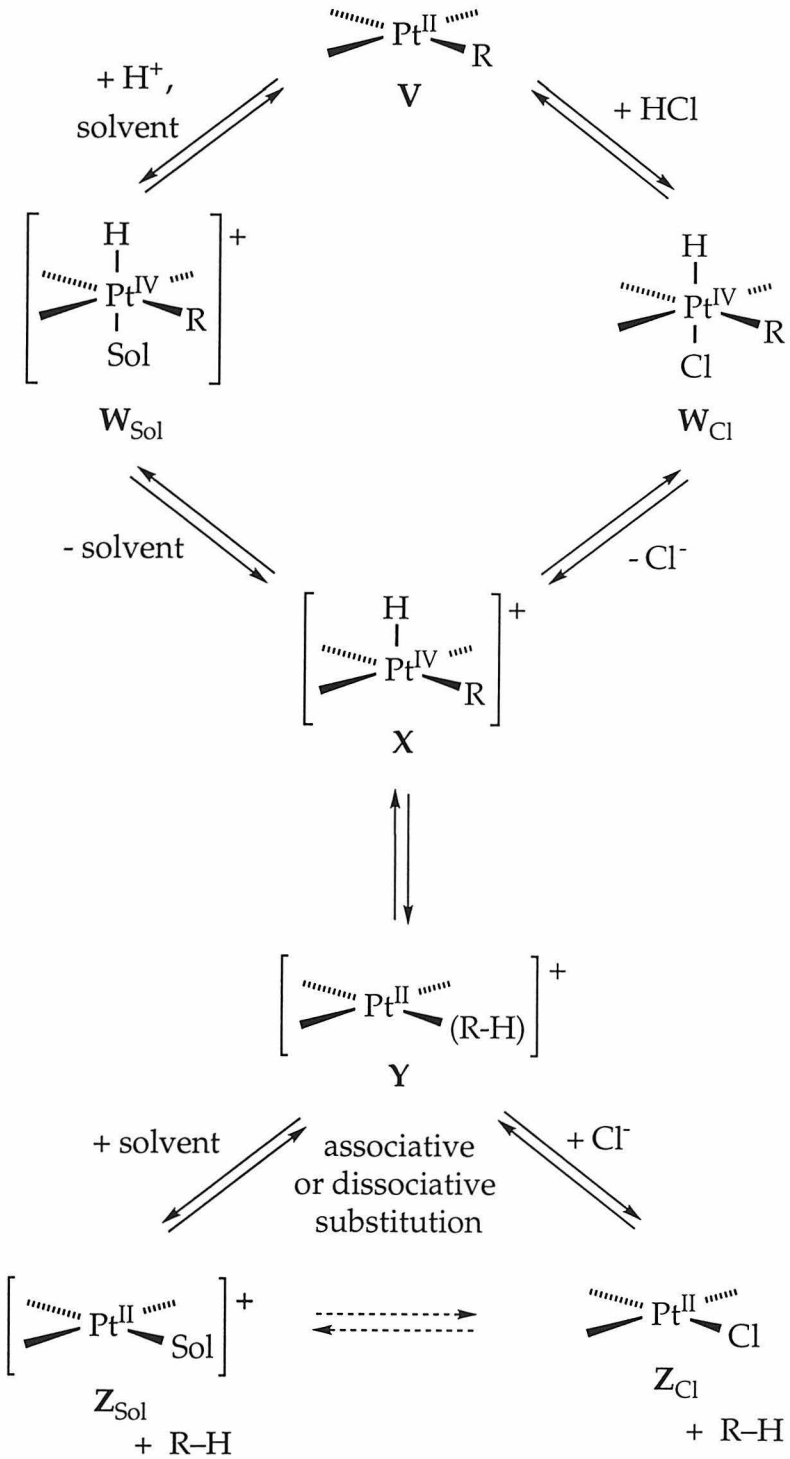
The proposed platinum(IV) intermediate, $(PEt_3)_2Pt(CH_3)(H)Cl_2$ (**16**), can in fact be observed in CD_2Cl_2. Although **16** appears to be less stable than $(tmeda)Pt(CH_3)_2(H)Cl$ (**12**) (eliminating methane at -45 °C versus +10 °C, respectively, in CD_2Cl_2), its formation suggests that it might be an energetically viable (albeit unobserved) intermediate in methanol.

Unfortunately, the kinetic isotope effects are of little utility in identifying the correct mechanism. Because the reagents and the transition state leading to H/D exchange are virtually identical for the two possible mechanisms (i.e., reductive elimination forming a σ-complex versus direct electrophilic attack at the Pt-C bond), the isotope effect for H/D exchange (k_H/k_D = 0.80) is unable to distinguish between them. The isotope effect for methane loss is even more inverse (k_H/k_D = 0.11); this result merely suggests that formation of a strong C-H bond is nearly complete in this transition state.

Analysis: Common Mechanism? In this work we have evaluated the reactivity of four different systems: [1] (tmeda)Pt(CH_3)Cl (**2**) in methanol, [2] (tmeda)PtRCl (R = CH_3, CH_2Ph (**5**)) in dichloromethane, [3] (tmeda)Pt(CH_3)$_2$ (**11**) in methanol, and [4] *trans*-(PEt_3)$_2$Pt(CH_3)Cl (**15**) in methanol. Despite the significant differences among the systems, we believe all of the data supports a common mechanism (Scheme 11): (1) chloride- or solvent-mediated protonation of Pt(II) (**V**) to generate an alkylhydridoplatinum(IV) intermediate (**W**), (2) dissociation of solvent or chloride to generate a cationic, five-coordinate platinum(IV) species (**X**), (3) reductive C-H bond formation producing an alkane σ-complex (**Y**), and (4) loss of alkane either through an associative or dissociative substitution pathway.

Based on this proposal, the origin of the differences between the four systems lies in the fact that changing the solvent or the initial Pt(II) species alters the relative energy of the reagents, intermediates and transition states, thereby changing the rate-determining step and/or dictating which intermediates may be observed.

Scheme 11


Pt^II
R
V
+ H+,
solvent
+ HCl
H
Pt^IV
R
Sol
W_Sol
H
Pt^IV
R
Cl
W_Cl
- solvent
- Cl-
H
Pt^IV
R
X
Pt^II
(R-H)
Y
+ solvent
associative
or dissociative
substitution
+ Cl-
Pt^II
Sol
Z_Sol
+ R–H
Pt^II
Cl
Z_Cl
+ R–H

This proposal also accounts for the differences in the chloride dependency of the reactions. Both the protonolysis of **2** in methanol and H/D exchange in **15** show positive dependence of the reaction rates on [Cl^-] (see Figures 2 and 11), however, the reactions still proceed with measurable rate in the absence of chloride. These results reflect the fact that formation of **W**, **X**, and **Y** may be mediated by either solvent or chloride, with chloride being a more effective mediator for these reactions than solvent.

On the other hand, *loss of methane* from intermediate **Y** in the protonolysis of **15** exhibits no measurable rate in the absence of chloride (Figure 11). This result suggests that alkane loss occurs via an *associative* chloride substitution pathway.

The reactions starting from an alkylhydridoplatinum(IV) intermediate (**6** in CD_2Cl_2 and **12** in methanol) exhibit an *inverse* dependence of the reaction rates on [Cl^-]. This result is most easily explained by pre-equilibrium chloride dissociation from $\mathbf{W_{Cl}}$ preceding the rate determining step (see above). Because both H/D exchange and methane loss from **12** exhibit this inverse chloride dependence, we believe this reflects a *dissociative* substitution pathway, since an associative pathway, as observed for **15**, should cancel the chloride dependence.

Shown in Figures 14a-d are qualitative reaction coordinate diagrams for each of the four systems analyzed. The diagrams, based on Scheme 11, account for the different observations made in each case. For the protonolysis of **2** in methanol, we obtain no direct evidence for intermediates in the reaction. Nevertheless, the data is still consistent with the mechanism proposed in Scheme 11 (Figure 14a). Although many specific features of the diagram remain speculative, the important details are the following: (1) the

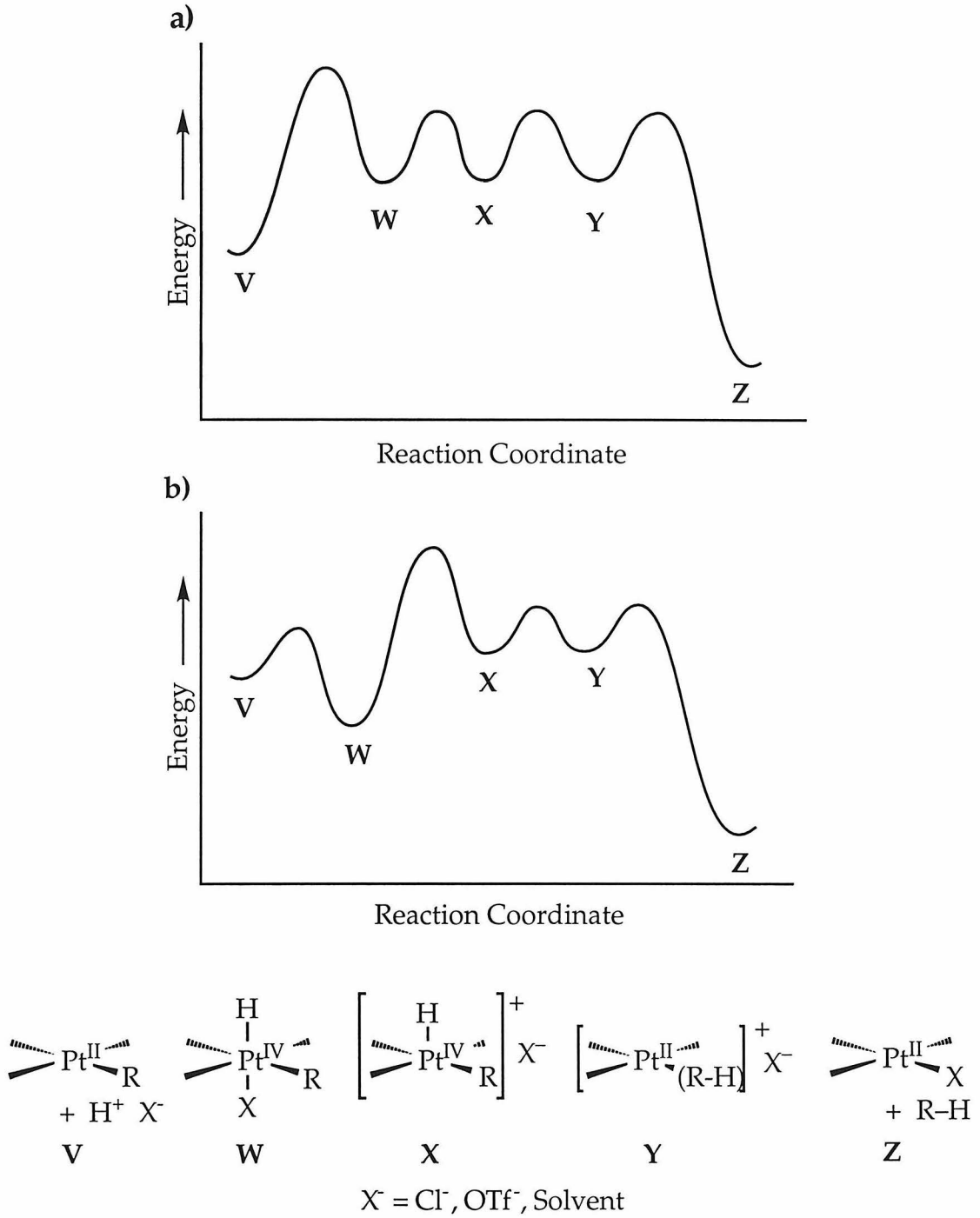


Figure 14. Qualitative reaction coordinate diagrams (based on Scheme 11) for the protonolysis reactions of **a)** (tmeda)PtMeCl (**2**) in methanol, **b)** (tmeda)PtMeCl (**2**) in dichloromethane, **c)** (tmeda)$PtMe_2$ (**11**) in methanol, and **d)** *trans*-$(PEt_3)_2$PtMeCl (**15**) in methanol. (See discussion in text.)

Figure continued on next page.

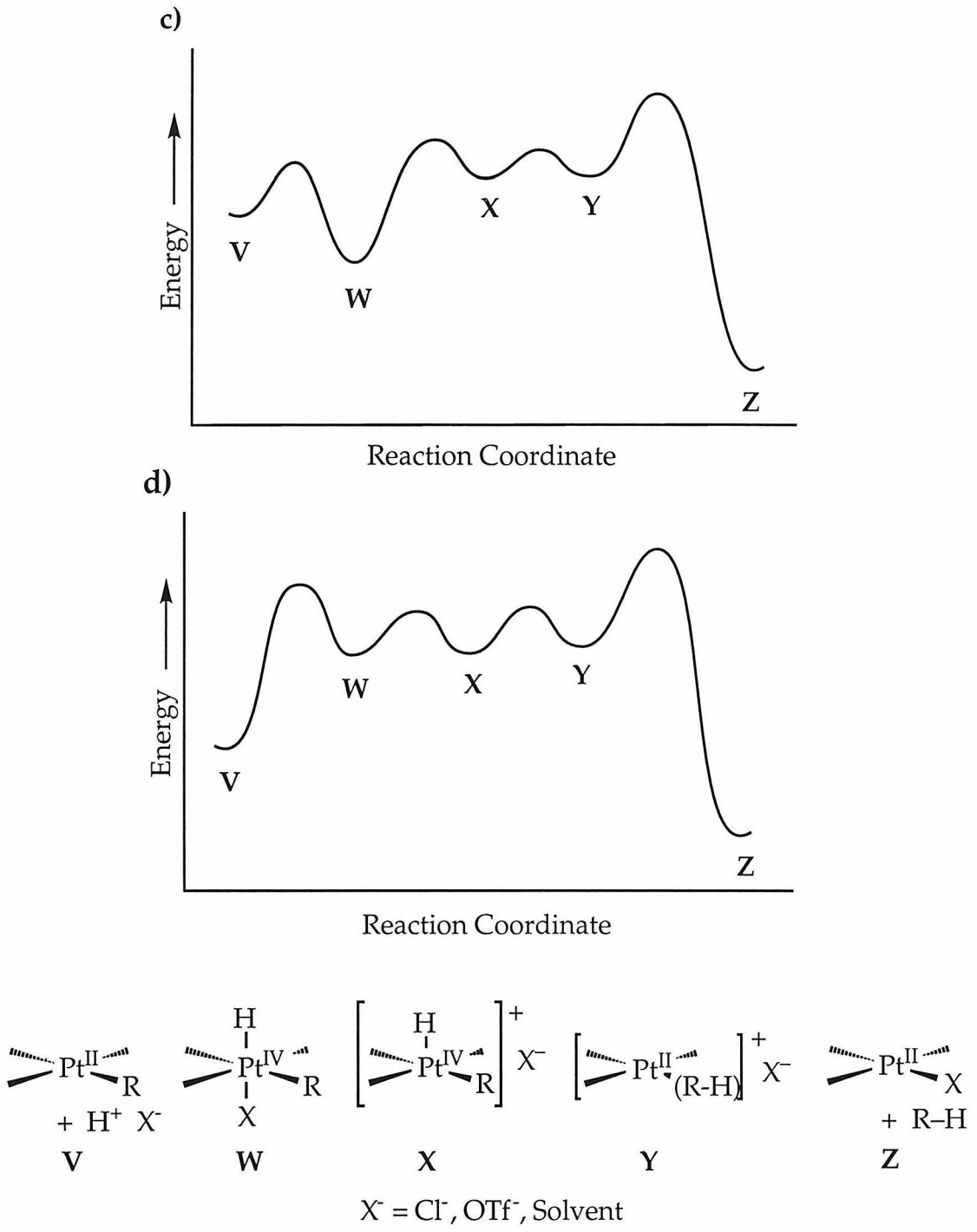


Figure 14 (cont'd). Qualitative reaction coordinate diagrams (based on Scheme 11) for the protonolysis reactions of **a)** (tmeda)PtMeCl (**2**) in methanol, **b)** (tmeda)PtMeCl (**2**) in dichloromethane, **c)** (tmeda)$PtMe_2$ (**11**) in methanol, and **d)** *trans*-$(PEt_3)_2$PtMeCl (**15**) in methanol. (See discussion in text.)

reagents are significantly more stable than any other species preceding the rate determining step (i.e., only **2** is observed prior to product formation) and (2) the rate determining step lies *before* dissociation of alkane from **Y**. Based on the [Cl^-] dependence of the reaction, we assign formation of **W** as the rate-determining step; such an energy profile reveals why no intermediates can be observed. It is also consistent with the observation that **14** is less susceptible to protonolysis than **2**, as generation of **W** from a cationic **V** should be more difficult.

Upon carrying out the same reaction in dichloromethane (rather than methanol), significant differences are observed. In this case alkylhydridoplatinum(IV) (**W**) is the most stable species under the reaction conditions. Although **W** is in rapid equilibrium with **V** prior to loss of alkane, it is the only species observed aside from the products (**Z**); Figure 14b reflects this change. The differences between Figures 14a and 14b can be accounted for by the change in solvent polarity, i.e., methanol is better able to stabilize the charged reagents and intermediates. Consequently, upon shifting to dichloromethane, the charged intermediate (**X**) and the preceding transition state become much less stable, thus making its formation the rate determining step.

Protonolysis of (tmeda)Pt(CH_3)$_2$ (**11**) in methanol differs significantly from that of (tmeda)Pt(CH_3)Cl (**2**). Although the only difference is replacement of chloride with a more electron-donating methyl group in the platinum coordination sphere, this change is apparently sufficient to stabilize Pt(IV) (**W**) relative to Pt(II) (**V**), because **W** becomes the species observed by ^1H NMR at low temperature. The other significant feature of this reaction is that alkane dissociation from the σ-complex (**Y**) is now the rate determining step.

Although **Y** is never seen directly, its existence is supported by deuterium incorporation into the methyl groups and the inverse isotope effect for methane loss (see above). These results are shown schematically in Figure 14c.

The protonolysis of $(PEt_3)_2Pt(CH_3)Cl$ (**15**) also exhibits some unique features. Again we believe the data is consistent with the mechanism proposed in Scheme 11 with the differences arising from the relative energy of the reagents, intermediates, and transition states (Figure 14d). As with the protonolysis of **11**, the rate determining step is loss of alkane from the σ-complex (**Y**). In this case, however, no Pt(IV) intermediate (**W**) is observed; **15** is the species observed under the reaction conditions. This feature likely arises from the substitution of relatively "hard" amine donors (i.e., tmeda) with "soft" phosphine ligands. Soft ligands are commonly used to stabilize lower oxidation states. The relative energies of intermediates **W**, **X**, and **Y** remain unknown.

Despite the data that we have obtained for the four different systems, several detailed features of this mechanism remain uncertain. For example, although chloride loss precedes alkane reductive elimination, our kinetic data cannot distinguish between elimination from solvated six-coordinate and five-coordinate cationic intermediates. Furthermore, many aspects of the HCl oxidative addition mechanism remain unanswered. Although the reaction appears to proceed with *trans* stereochemistry (suggesting a heterolytic mechanism), it is not known whether the mechanism involves initial proton attack at Pt(II) followed by chloride association or the reverse order of addition. In the latter case, chloride or solvent are in fact necessary in order to generate the reactive five-coordinate intermediate (**X**). In the former

case, however, **X** is rapidly trapped in a non-productive equilibrium by chloride or solvent. It must then be regenerated in a subsequent step prior to alkane elimination. Another area of uncertainty concerns the nature of the alkane σ-complex, because of our inability to observe this intermediate.

CONCLUSION: Implications for Alkane Activation by Pt(II)

We began this study hoping to gain insights into the mechanism of aqueous C-H activation by Pt(II), the microscopic reverse of the reactions discussed here. Based on our results, we believe we can now speculate further on some of the detailed aspects of this reaction. The mechanism for protonolysis of alkylplatinum(II) complexes involves a significant number of ligand association, dissociation, and substitution steps, and furthermore, the reaction proceeds through both ionic and neutral intermediates (Scheme 11). These features suggest an important role for the solvent (water) in Shilov's alkane oxidation system: it must be able to accommodate both neutral and/or ionic intermediates in order to facilitate the various mechanistic steps. Significant stabilization *or* destabilization of any of the reaction intermediates relative to the others could dramatically decrease the rate of C-H activation. Interestingly, nearly all of the "electrophilic" alkane oxidation systems utilize highly polar solvents (H_2O, H_2SO_4, CF_3COOH).[5-8] This may be rationalized at least in part by comparing Figures 14a and 14b reading right-to-left — destabilization of ionic species in nonpolar solvent (Figure 14b) translates to a higher barrier for C-H activation.

The nature of the platinum ligands also appears crucial; they must be sufficiently labile to allow the various ligand exchange reactions to proceed at rapid rates. The initial interaction between the alkane and Pt(II) involves a

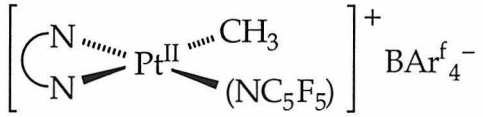
ligand substitution reaction (alkane for chloride or solvent). Although we cannot address whether the substitution takes place via an associative or dissociative mechanism, this step is likely the origin of chloride inhibition of alkane oxidation. In other words, chloride competes favorably with alkane for a coordination site on Pt(II); that alkane can compete at all still seems quite remarkable. We cannot exclude the possibility that chloride plays a more intimate role in these processes as well, perhaps along the lines of structure **B** above as suggested by theoretical studies.[32]

Our results implicate the presence of *both* alkane σ-complexes and alkylhydridoplatinum(IV) as intermediates in the C-H activation reaction.[107] Contrary to our previous suggestion,[10] it appears that the alkylplatinum(II) species is generated by deprotonation of alkylhydridoplatinum(IV) (eq 1), *not* the σ-complex (eq 2). According to this proposal, the σ-adduct is an intermediate preceding the oxidative addition of the C-H bond. Such a mechanism is presumably facilitated by the accessibility of the Pt(IV) oxidation state. The other electrophilic alkane oxidation systems (such as those involving palladium or mercury) likely operate through a different pathway considering the significant instability of their M(IV) oxidation states.

Clearly these systems are highly complex, involving a number of intermediates. To date we have significant, but incomplete, understanding of how their relative stabilities and reactivities depend upon structure and reaction conditions. Studies continue towards the long-range goal: to exploit detailed understanding of the mechanism and energetics of electrophilic alkane oxidation for the rational design of improved catalysts.

Note Added in Proof.

As stated above, we were unable to achieve *inter*molecular C–H activation with any of our model complexes, even in cases where reversible H/D exchange is observed. However, subsequent to these studies, Dr. Matt Holtcamp in our group prepared the cationic Pt(II) complex, $[(tmeda)Pt(CH_3)(PFP)]^+BAr^f_4^-$ (**26**), where PFP is the weakly coordinating



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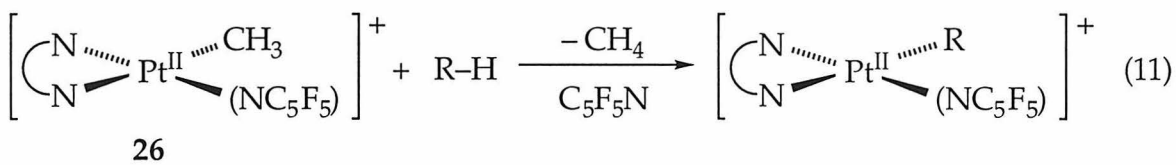
ligand, pentafluoropyridine, and BAr^f_4 is the non-coordinating anion, $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]^-$. This complex *is* able to effect the *inter*molecular C–H activation of numerous hydrocarbons (including methane!) in pentafluoropyridine (eq 11).[108,109] Upon activation of deuterated



(11)

R = $^{13}CH_3$, cyclohexyl, phenyl, tolyl

hydrocarbons (e.g., CD_4, C_6D_6, C_6D_{12}), multiply deuterated methane is liberated, consistent with the mechanistic proposal in Scheme 8 involving a reversible equilibrium between σ-adduct and Pt(IV) dialkyl hydride intermediates. These results further support the relevance of the model chemistry discussed above and furnish the only remaining step in the "model catalytic cycle" shown in Scheme 5.

EXPERIMENTAL

General considerations. Protonolysis reactions involving **5** and **11** were carried out under an inert atmosphere using standard Schlenk techniques or in a glovebox, but for other reactions, this was unnecessary. ^{1}H and ^{2}H NMR spectra were obtained using General Electric QE300 and Bruker AM500 spectrometers. Low temperature kinetics were obtained on the AM500 spectrometer using an automated sequence to record sequential spectra; the microprograms used have been included in the supplementary material. NMR kinetics were all carried out in NMR tubes equipped with a screw cap and silicone/PTFE septum available from Wilmad Glass Company. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Solvents were dried prior to use: Et_2O-d_{10} over Na/benzophenone, CD_2Cl_2 over CaH_2 followed by 4 Å molecular sieves, and CD_3OD (and other isotopomers) over 4 Å molecular sieves. The following compounds were prepared according to literature procedures or analogous methods: (tmeda)$PtMe_2$ (**11**), (tmeda)PtMeCl (**2**), (tmeda)$Pt(CH_2Ph)Cl$ (**5**), and *trans*-$(PEt_3)_2Pt(CH_3)Cl$ (**15**), (4,4'-dimethyl-2,2'-bipyridyl)$Pt(CH_3)_2$ (**9**).[110,111]

^{1}H NMR kinetics for the protonolysis of (tmeda)PtMeCl (2) in CD_3OD. **2** (3 mg, 0.0083 mmol) and various amounts of LiCl and $LiClO_4$ were added to a series of NMR tubes according to the amounts determined for the particular experiment. For [Cl^-] dependence experiments, the [LiCl] was varied between 0 and 0.66 M. For [H^+] dependence experiments, [HOTf] was varied between 0 and 0.38 M. $LiClO_4$ was always added such that the ionic strength (μ = [HOTf] + [LiCl] + [$LiClO_4$]) equaled 1 M. This was followed by addition of the solvent (CD_3OD) containing a known amount of tBuOH as an integration standard. In order to monitor the kinetics at low temperature, the individual tubes

were cooled to -78 °C prior to the addition of HOTf. After HOTf addition (total volume of reaction mixture = 700 μL.), the contents of the tube were mixed thoroughly (while keeping the tube as cold as possible), and the tube was then placed in the pre-cooled NMR probe. After adjusting the necessary shims, a microprogram was initiated to automatically acquire spectra at regular time intervals. Spectra were then processed and integrated using WIN-NMR™ software; the Pt-Me peak was integrated relative to the *tBu*OH resonance. Data analysis was carried out using KaleidaGraph™.

Kinetic isotope effects for the protonolysis of (tmeda)PtMeCl (2) in CD_3OD. See previous section for reaction details. The competitive isotope effect was measured by comparing the integration of CH_3D to CH_4 generated from the reaction carried out in a mixture of CD_3OD and CD_3OH. The non-competitive isotope effect was determined by comparing the rates of the reaction carried out in CD_3OH and CD_3OD.

Preparation of alkylhydridoplatinum(IV) species (4, 6, 8, 10, 12, 16) in CD_2Cl_2. HCl(g) was dissolved in Et_2O-d_{10} (using a gas bulb containing a known amount of HCl) and the solution was then titrated to determine the HCl concentration. (An aliquot of the solution was added to a few mL of water containing phenolphthalein, and then titrated against a 0.100 N solution of NaOH.) Approximately 10 equivalents of the HCl solution were added via syringe to a 5mm NMR tube containing the appropriate alkylPt(II) reagent dissolved in CD_2Cl_2 at -78 °C. After mixing the contents while keeping the tube as cold as possible, the tube was placed in the pre-cooled NMR probe. Relevant ^1H NMR data is recorded in Table 1.

^1H NMR kinetics for the reductive elimination of toluene from 6 in CD_2Cl_2. HCl/Et_2O-d_{10} (60 μL, 0.76 M) was added to a solution of **5** (4 mg,

0.0091 mmol) in CD_2Cl_2 at -78 °C. Pentachloroethane (4 μL) was also added as an integration standard. Sequential ^1H NMR spectra for the reductive elimination of toluene were obtained using the pre-programmed subroutine discussed above for the protonolysis of **2** in CD_3OD. The furthest downfield aromatic protons of **6** (δ 7.42 ppm , br. s., 2 H) were integrated to obtain the kinetics data. A solution of HOTf was also prepared in Et_2O-d_{10} in order to monitor the [HOTf] dependence of the reaction, however, this solution had to be kept cold and used shortly after preparation to avoid its rapid decomposition at room temperature. An typical kinetics run involved adding HCl/Et_2O-d_{10} (25 μL, 1.88 M) to **5** (4 mg, 0.0091 mmol) dissolved in CD_2Cl_2 (0.5 mL) at -78 °C. After thoroughly mixing the solution at low temperature, HOTf/Et_2O-d_{10} (43 μL, 1.07 M) was added. The solution was again thoroughly mixed prior to placement in the precooled probe. To check the effect of a non-protic, Lewis acid, a solution of $SnCl_4$ in CD_2Cl_2 was prepared and was similarly added to a pre-formed solution of **6**.

Determination of isotope effects involving 6 in CD_2Cl_2. Solutions containing DCl and mixed HCl/DCl solutions were prepared in a manner analogous to that described for HCl above. To obtain the equilibrium and overall kinetic isotope effects, the mixed HCl/DCl solution (130 μL, 2.09 M) was added to a solution of **5** (4 mg, 0.0091 mmol) in rigorously dried CD_2Cl_2 (0.5 mL), and the ratio of CH_4 and CH_3D was obtained by integrating the corresponding peaks in the resulting ^1H NMR spectrum. The syringe used to dispense the HCl/DCl solution was rinsed several times with approximately 100 μL of the solution to avoid complications arising from H/D exchange with the protic sites on the glass syringe. The ratio of HCl to DCl was calibrated by adding the solution (using the same pre-rinsed syringe) to an

excess of $CH_3Li \bullet LiBr$ (relative to $[H^+] + [D^+]$) dissolved in THF-d_8. Integration of the CH_4 and CH_3D gave the HCl/DCl ratio, and this ratio was used to determine the equilibrium and kinetic isotope effects. Isotope effect and calibration experiments were typically done in triplicate.

^{1}H NMR kinetics for H/D exchange and methane elimination in 12 in CD_3OD. In an inert atmosphere glovebox, **11** (5 mg, 0.015 mmol) was loaded into an 5mm NMR tube and then removed from the glovebox. CD_2Cl_2 (50 μL) was added to dissolve **11**, and the solution was then cooled to -78 °C. LiCl and $LiClO_4$ (of varying ratios depending on the experiment) were then dissolved in methanol (total solvent volume for reaction = 0.7 mL), and the solution was added to the cooled NMR tube. For $[Cl^-]$ dependence experiments, the [LiCl] was varied between 0.10 and 0.60 M for H/D exchange, and between 0 and 0.80 for methane elimination. The ionic strength was held constant ($[HOTf] + [LiCl] + [LiClO_4] = 1.21$ M) for all the reactions. After thoroughly mixing the solution at low temperature, a triflic acid solution (in methanol) was added to the NMR tube. The solution was again mixed thoroughly before placing in the precooled NMR probe to monitor the kinetics. The kinetics were monitored for both the H/D exchange reaction and methane loss by integrating the Pt(IV)-Me resonance from **12** relative to an internal standard (pentachloroethane). The H/D exchange reactions were carried out in CD_3OD, while reactions involving methane loss were done in CD_3OH. Again preprogrammed subroutines were used to record the spectra; the program for monitoring methane loss included a solvent presaturation sequence to delete the -OH resonance.

^{1}H NMR kinetics for H/D exchange and methane loss from 15 in CD_3OD. In an NMR tube, **15** (5 mg, 0.010 mmol) was combined with the

appropriate amount of LiCl and $LiClO_4$ (ratio varied depending on the experiment). The ionic strength was held constant ([HOTf] + [LiCl] + [$LiClO_4$] = 1.15 M) for all experiments. In order to determine the [Cl^-] dependence of the reactions, [LiCl] was varied between 0.10 and 0.50 M for H/D exchange, and between 0.067 and 0.78 M for methane elimination. The reagents were dissolved in methanol (CD_3OD for monitoring H/D exchange and CD_3OH for methane loss) and then cooled to -78 °C. After addition of a methanol solution of triflic acid (DOTf/CD_3OD for H/D exchange and HOTf/CD_3OH for methane loss), the reaction was mixed thoroughly and then place in the NMR probe. Kinetics data was obtained by monitoring the loss in the integration intensity of the Pt-Me resonance relative to an internal standard (pentachloroethane). Again preprogrammed subroutines were used to record the spectra; the program for monitoring methane loss included a solvent presaturation sequence to delete the -OH resonance.

Kinetic isotope effects for H/D exchange and methane elimination from 12 and 15 in methanol. Kinetic isotope effects for H/D exchange and methane elimination from **12** in CD_3OD were obtained by comparing these rates with those of analogous reactions of **12-d_6** in CH_3OH and CH_3OD respectively. Standardized solutions of HOTf in CH_3OH and DOTf in CH_3OD were prepared for these reactions. Reaction conditions were identical to the reactions carried out in CD_3OD. Reactions involving **12-d_6** were monitored by ^2D NMR, and again spectra were accumulated automatically. Kinetic data was obtained by monitoring the loss in the integration intensity of the Pt-CD_3 resonance relative to an internal standard (toluene-d_8). When monitoring elimination of CD_4 in CH_3OD, the solvent resonance was suppressed using the "1-3-3-1" pulse sequence developed by Hore.[112,113]

Isotope effect for protonolysis of "$[PtMeCl_3]^{2-}$" in water and methanol. The dry reagents, $[NMe_4]_2[PtMeCl_5]$ (100 mg, 0.19 mmol) and $CrCl_2$ (46 mg, 0.37 mmol) were combined and thoroughly mixed in a small flask equipped with a stir bar. The flask was placed on the high vacuum line, evacuated and cooled to liquid N_2 temperature. A 10:1 mixture of degassed D_2O:H_2O was then condensed into the flask and allowed to warm. Upon thawing, the solution turned dark green (reaction with Cr(II)) and gas evolution was immediately apparent along with formation of a black precipitate. The gas was collected and quantified using a Toepler pump, and the CH_4/CH_3D mixture was characterized and their ratio determined using ^1H NMR spectroscopy. Alternatively, the dry reagents were loaded into an NMR tube equipped with a J. Young valve (Wilmad Glass Company) under inert atmosphere. Methanol was then vacuum transferred into an NMR tube at -78 °C. The heterogeneous mixture was mixed while warming to 0 °C. Methane evolution was again immediately apparent along with formation of black precipitate. The methane generated was analyzed by vacuum transfer of all volatiles into a separate NMR tube.

REFERENCES AND NOTES

1) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

2) *Selective Hydrocarbon Activation*; VCH: New York, 1990.

3) *Activation and Functionalization of Alkanes*; John Wiley & Sons: New York, 1989.

4) Labinger, J. A. *Fuel Process. Technol.* **1995**, *42*, 325-338.

5) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109.

6) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700.

7) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5628.

8) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340.

9) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1972**, *46*, 1353.

10) Labinger, J. A.; Herring, A. M.; Lyon, D. K.; Luinstra, G. A.; Bercaw, J. E.; Horvath, I. T.; Eller, K. *Organometallics* **1993**, *12*, 895.

11) Luinstra, G. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 3004.

12) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **1994**, *13*, 755.

13) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75.

14) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729.

15) Horvath, I. T.; Cook, R. A.; Millar, J. M.; Kiss, G. *Organometallics* **1993**, *12*, 8.

16) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385.

17) Sen, A.; Benvenuto, M. A.; Lin, M.; Hutson, A. C.; Basickes, N. *J. Am. Chem. Soc.* **1994**, *116*, 998.

18) Hutson, A. C.; Lin, M.; Basickes, N.; Sen, A. *J. Organomet. Chem.* **1995**, *504*, 69.

19) Zamashchikov, V. V.; Litvinenko, S. L.; Uzhik, O. N.; Galat, V. F. *Zh. Obs. Khim.* **1986**, *56*, 2417.

20) Zamashchikov, V. V.; Popov, V. G.; Litvinenko, S. L. *Izv. Akad. Nauk., Ser. Khim.* **1993**, *42*, 389-395.

21) Zamashchikov, V. V.; Popov, V. G.; Rudakov, E. S.; Mitchenko, S. A. *Dokl. Akad. Nauk SSSR* **1993**, *333*, 34.

22) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.

23) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984.

24) Shilov, A. E. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed. John Wiley & Sons: New York, 1989; p 1.

25) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987.

26) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174.

27) Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Catal. A* **1997**, *116*, 269-275.

28) Belluco, U.; Giustiniani, M.; Graziani, M. *J. Am. Chem. Soc.* **1967**, *89*, 6494.

29) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim. Acta* **1985**, *100*, 107.

30) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U. *Inorg. Chim. Acta* **1986**, *112*, L15.

31) Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332.

32) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442-4450.

33) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13.

34) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

35) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745-8746.

36) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209-1217.

37) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684-5689.

38) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845-2847.

39) Arylhydridoplatinum(IV) species have been identified previously: (a) Arnold, D. P.; Bennett, M. A. *Inorg. Chem.* **1984**, *23*, 2110. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484.

40) Monitoring the reaction by UV-visible spectroscopy was attempted, but the product, (tmeda)$PtCl_2$, is insoluble and precludes the acquisition of reproducible data.

41) Reaction conditions (Eyring plot for protonolysis of **2** in CD_3OD): [**2**] = 11.9 mM; $[Cl^-]$ = 0 M; $[H^+]$ = 0.18 M; μ = 1.18 M; Temperature range: -25 – -49 °C.

42) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484.

43) Reaction conditions (Eyring plot for reductive elimination of toluene from **6** in CD_2Cl_2): [**6**] = 13 mM; [HCl] = 65 mM; Temperature range: -24 – -43 °C.

44) Waddington, T. C. *J. Chem. Soc.* **1958**, 1708.

45) No methane is generated in this side reaction. The reactivity is likely related to that previously observed for similar compounds dissolved in protic solvents (alcohols and water): (a) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444. (b) Holtcamp, M. W., Labinger, J. A., Bercaw, J.E., unpublished results.

46) Reaction conditions (Eyring plot for deuterium incorporation into **12** in CD_3OD:CD_2Cl_2 (13:1)): [**12**] = 21 mM; $[H^+]$ = 0.21 M; $[Cl^-]$ = 0.20 M; μ = 1.21 M; Temperature range: -31 – -55 °C.

47) Reaction conditions (Eyring plot for methane elimination from **12** in CD_3OH:CD_2Cl_2 (13:1)): [**12**] = 21 mM; $[H^+]$ = 0.21 M; $[Cl^-]$ = 0.20 M; μ = 1.21 M; Temperature range: -15 – -35 °C.

48) In the absence of added chloride ($[Cl^-] < 0.14$ M), side reactions complicate the kinetics. Upon methane loss from **15**, the product $(PEt_3)_2Pt(Cl)(OTf)$ can abstract chloride from **15** to generate a new phosphine-ligated methylplatinum(II) species, $(PEt_3)_2Pt(CH_3)(OTf)$ (**18**) which is much less reactive toward protonolysis. Small amounts of **18** can be identified in these reaction mixtures by ^1H NMR spectroscopy, and the spectroscopic data is consistent with independently prepared samples of **18**. These results will be discussed in further detail in a future paper: Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* Submitted for publication.

49) Reaction conditions (Eyring plot for deuterium incorporation into **15** in CD_3OD): [**15**] = 15 mM; $[H^+]$ = 0.15 M; $[Cl^-]$ = 0.14 M; μ = 1.15 M; Temperature range: -13 – -40 °C.

50) Along with formation of methane, another methylplatinum species is produced in the reaction mixture as observed by ^1H NMR spectroscopy. This product appears consistent with $[PtMe_2Cl_4]^{2-}$, formed by nucleophilic attack by Pt(II) (from $[PtMeCl_3]^{2-}$, **1**) at carbon in $[PtMeCl_5]^{2-}$ displacing $[PtCl_4]^{2-}$. (see ref. 27) This reaction competes with the protonolysis of **1**.

51) *Mechanisms of Electrophilic Substitution at Saturated Carbon*; Abraham, M. H., Ed. Elsevier: Amsterdam, 1973; Vol. 12, p 10-21.

52) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978, p 292-340.

53) Nugent, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5979.

54) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1973.

55) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Krieger: Malabar, FL, 1987, p 202.

56) A very large negative entropy of activation (-39 ± 4 e.u.) has been obtained for ethane elimination from dimethylPd(IV) in which iodide dissociation has been shown to precede alkane loss: Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363.

57) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227.

58) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649.

59) Basato, M.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972.

60) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

61) Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831.

62) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

63) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

64) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436.

65) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism;* 3rd ed.; John Wiley & Sons: New York, 1981, p 367.

66) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. unpublished results.

67) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369.

68) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585.

69) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281.

70) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

71) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

72) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

73) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502.

74) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727.

75) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897.

76) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

77) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647.

78) Mobley, T. A.; Schade, C.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 7822.

79) Green, M. L. H. personal communication.

80) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125-3146.

81) Cundari, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10557.

82) Cundari, T. R. *J. Am. Chem. Soc.* **1994**, *116*, 340.

83) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609.

84) Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118.

85) Ziegler, T.; Tschinke, V.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177.

86) Brown, C. E.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 2530.

87) Carroll, J. J.; Weisshaar, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 800.

88) Hop, C. E. C. A.; McMahon, T. B. *J. Am. Chem. Soc.* **1991**, *113*, 355.

89) Ishikawa, Y.; Brown, C. E.; Hackett, P. A.; Rayner, D. M. *Chem. Phys. Lett.* **1988**, *150*, 506.

90) Schroder, D.; Fiedler, A.; Hrusak, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215.

91) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315.

92) Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M.; Turner, J. J.; Firth, S.; Asali, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218.

93) Dobson, G. R.; Asali, K. J.; Cate, C. D.; Cate, C. W. *Inorg. Chem.* **1991**, *30*, 4471.

94) Klassen, J. K.; Selke, M.; Sorensen, A. A. *J. Am. Chem. Soc.* **1990**, *112*, 1267.

95) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1989**, *93*, 291.

96) Yang, C. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett.* **1986**, *125*, 566.

97) Billups, W. E.; Chang, S.-C.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 2039.

98) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

99) Crabtree, R. H. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

100) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363.

101) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83.

102) Goldberg, K. I.; Yan, J. Y.; Winter, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 1573.

103) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

104) Bigeleisen, J. *Pure Appl. Chem.* **1964**, *8*, 217.

105) Melander, L. *Acta Chem. Scand.* **1971**, *25*, 3821.

106) Romeo, R.; Minniti, D.; Lanza, S.; Uguagliati, P.; Belluco, U. *Inorg. Chem.* **1978**, *17*, 2813.

107) Independent work by Zamashchikov *et. al.*, (ref. 21) also supports the intermediacy of alkylhydridoplatinum(IV) in C-H activation, however their argument is based on isotope effects and relies on the assumption that σ-complex formation would have no isotope effect. In light of strong evidence to the contrary (see refs. 67 - 69), their conclusions appear open to question.

108) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *119*, 848-849.

109) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* Submitted for publication.

110) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

111) Appleton, T. G.; Hall, J. R.; Williams, M. A. *J. Organomet. Chem.* **1986**, *303*, 139.

112) Hore, P. J. *J. Magn. Reson.* **1983**, *54*, 539.

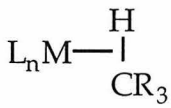
113) Hore, P. J. *J. Magn. Reson.* **1983**, *55*, 283.

Chapter 3

Systematic Investigation of Factors Affecting the Stability of Dihydrogen Adducts of Platinum(II)

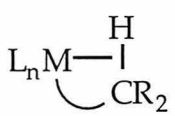
INTRODUCTION

Over the past 15 years, several successful approaches have been identified for alkane activation by transition metal complexes .[1-3] Considerable evidence from numerous laboratories supports the intermediacy of alkane σ-adducts (**A**) in the C–H activation step.[4]

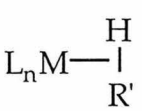


A

However, because such complexes have eluded isolation and structural characterization (and typically are not even detected spectroscopically[5]), several approaches have been used to examine their reactivity, including the study of *agostic* complexes (**B**) (i.e., intramolecular alkane adducts)[6-8] and intermolecular σ-adducts of other R'–H bonds such as silanes (**C**) or dihydrogen (**D**).[7-13]



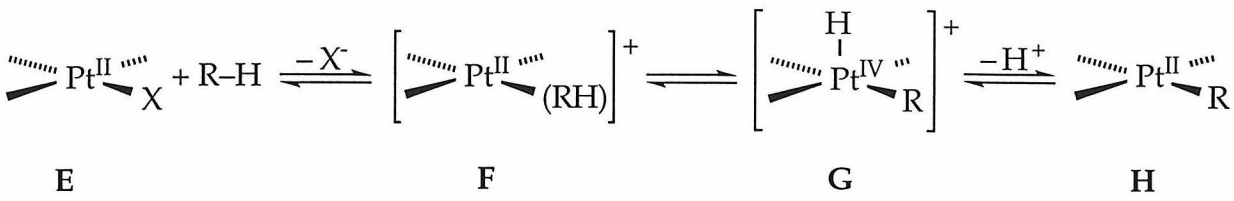
B



C (R' = SiR''_3)
D (R' = H)

We have been interested in studying the mechanism of C–H activation by Pt(II) complexes in aqueous solution, the first step in the homogeneous alkane oxidation system discovered by Shilov and co-workers.[14] A recent mechanistic study of the microscopic reverse of this reaction (i.e., the protonolysis of alkylplatinum(II) species) implicates the intermediacy of both alkylhydridoplatinum(IV) and alkane σ-adducts (Scheme I; the reactions are shown in the direction of C–H activation).[15,16] Unlike the alkylhydridoplatinum(IV) intermediate, the σ-adduct (**F**) was not detected

Scheme I



E **F** **G** **H**

directly at low temperatures. Consequently, our ability to explore the mechanism of its formation, its stability and reactivity was limited. For example, is the σ-adduct generated through an associative or dissociative mechanism? Also, what factors affect the equilibrium between the alkane adduct (**F**) and the alkylhydridoplatinum(IV) intermediate (**G**)? We chose to investigate these issues by examining related, more stable σ-adducts of Pt(II), namely dihydrogen complexes prepared by the protonation of platinum(II) hydrides. Despite numerous examples of transition metal–H_2 complexes,[7-11,13] the vast majority are d^6 octahedral complexes. Examples of square planar d^8 complexes analogous to **F** are quite rare and have been identified only recently.[17-19] The studies reported here represent the first systematic investigation of such complexes.

RESULTS

Preparation of hydridoplatinum(II) complexes. The complexes examined in this study include those of the type *trans*-$(PCy_3)_2Pt(H)X$ [X = SiH_3 (**1**), H (**2**), CH_3 (**3**), Ph (**4**), Cl (**5**), Br (**6**), I (**7**), CN (**8**), CF_3SO_3 (**9**)] and [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO (**10**), 4-picoline (**11**)]; BAr^f_4 = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$]. Only **4** and **6–8** have not been reported previously; however, all were readily prepared according to literature methods or analogous procedures.[20-27] Relevant NMR spectral data is provided in Table 1 for these and other compounds discussed below.

Table 1. Selected NMR spectroscopic data.

Compound	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz	T_1 (msec) (500 MHz)
trans-$(PCy_3)_2Pt(SiH_3)(H)$ (**1**)	22	Pt-*H*	-0.97 (t) $^1J_{Pt\text{-}H} = 760$, $^2J_{P\text{-}H} = 11$	
		Pt-Si*H*$_3$	3.13 (s)	
trans-$(PCy_3)_2Pt(H)_2$ (**2**)	22	Pt-*H*	-3.97 (t) $^1J_{Pt\text{-}H} = 796$, $^2J_{P\text{-}H} = 17$	
trans-$(PCy_3)_2Pt(CH_3)(H)$ (**3**)	-85	Pt-*H*	-6.47 (t) $^1J_{Pt\text{-}H} = 660$, $^2J_{P\text{-}H} = 17$	
		Pt-C*H*$_3$	-0.31 (s), $^2J_{Pt\text{-}H} = 44$	
trans-$(PCy_3)_2Pt(Ph)(H)$ (**4**)	22	Pt-*H*	-8.01 (t), $^1J_{Pt\text{-}H} = 595$, $^2J_{P\text{-}H} = 17$	
		Pt-C$_6$*H*$_5$	7.44 (2H, d), $^3J_{Pt\text{-}H} = 42$	
			6.84 (2H, t)	
			6.62 (1H, t)	
trans-$(PCy_3)_2Pt(H)Cl$ (**5**)	-85	Pt-*H*	-18.86 (t), $^1J_{Pt\text{-}H} = 1300$, $^2J_{P\text{-}H} = 12$	$T_{1(min)}$= ~480 (-55°C)
	-95	Pt-*P*Cy$_3$	38.6, $^1J_{Pt\text{-}P} = 2755$	

(continued on next page)

Table 1. (cont'd) Selected ^{1}H and ^{31}P NMR spectroscopic data.

Compound	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz	T_1 (msec) (500 MHz)
trans-$(PCy_3)_2Pt(H)Br$ (**6**)	-85	Pt-*H*	-17.58, $^{1}J_{Pt\text{-}H} = 1365$, $^{2}J_{P\text{-}H} = 12$	
		Pt-*P*Cy_3	37.75, $^{1}J_{Pt\text{-}P} = 2735$	
trans-$(PCy_3)_2Pt(H)I$ (**7**)	-85	Pt-*H*	-14.65, $^{1}J_{Pt\text{-}H} = 1390$, $^{2}J_{P\text{-}H} = 11$	
	-65	Pt-*P*Cy_3	36.5, $^{1}J_{Pt\text{-}P} = 2714$	
trans-$(PCy_3)_2Pt(H)CN$ (**8**)	22	Pt-*H*	-8.82, $^{1}J_{Pt\text{-}H} = 775$	
trans-$(PCy_3)_2Pt(H)(OTf)$ (**9**)	22	Pt-*H*	-27.6 (t), $^{1}J_{Pt\text{-}H} = 1585$, $^{2}J_{P\text{-}H} = 14$	
[*trans*-$(PCy_3)_2Pt(H)(CO)]BAr^{f}_4$ (**10**)	22	Pt-*H*	-4.63 (t), $^{1}J_{Pt\text{-}H} = 920$, $^{2}J_{P\text{-}H} = 12$	
[*trans*-$(PCy_3)_2Pt(H)$(4-picoline)]BAr^{f}_4 (**11**)	22	Pt-*H*	-19.60 (t), $^{1}J_{Pt\text{-}H} = 1070$, $^{2}J_{P\text{-}H} = 13.5$	

(continued on next page)

Table 1. (cont'd) Selected ^{1}H and ^{31}P NMR spectroscopic data.

Compound	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz	T_1 (msec) (500 MHz)
[*trans*-$(PCy_3)_2Pt(H)(H_2)]BAr^f_4$ (**12**)	-65	Pt-*H*	-10.43 (m) $^{1}J_{Pt\text{-}H}$ = 1445	606 (-85° C)
		Pt-(H_2)	-0.28, $^{1}J_{Pt\text{-}H}$ = 295	36 (-85° C)
		Pt-*H* (arising from loss of H_2)	-26.71, $^{1}J_{Pt\text{-}H}$ = 1525, $^{2}J_{P\text{-}H}$ = 12	
[*trans*-$(PCy_3)_2Pt(CH_3)(H_2)]BAr^f_4$ (**14**)	-85	Pt-(H_2)	-2.35, $^{1}J_{Pt\text{-}H}$ = ~ 300	26 (-95° C)
		Pt-CH_3	0.87(s), $^{2}J_{Pt\text{-}H}$ = 83	
		Pt-*H* (arising from loss of H_2)	-26.3, $^{1}J_{Pt\text{-}H}$ = 1480	
[*trans*-$(PCy_3)_2Pt(Ph)(H_2)]BAr^f_4$ (**15**)	-80	Pt-(H_2)	-1.9, $^{1}J_{Pt\text{-}H}$ = 255	20 (-65° C)
trans-$(PCy_3)_2Pt(H)_2Cl_2$ (**16**)	-85	Pt-*H*	-18.76 (s), $^{1}J_{Pt\text{-}H}$ = 1125, $^{2}J_{P\text{-}H}$ = 6	
trans-$(PCy_3)_2Pt(H)_2I_2$ (**17**)	-45	Pt-*H*	-15.79, $^{1}J_{Pt\text{-}H}$ = 1115	
$(PCy_3)_2Pt(H)_2(Cl)I$ (**18**)	-45	Pt-*H*	-15.60, $^{1}J_{Pt\text{-}H}$ = 1165 -18.88, $^{1}J_{Pt\text{-}H}$ = 1075	

(continued on next page)

Table 1. (cont'd) Selected ^{1}H and ^{31}P NMR spectroscopic data.

Compound	Temp. (°C)	Peak Assignment	Chemical Shift/ppm (multiplicity); Coupling /Hz	T_1 (msec) (500 MHz)
trans-$(PCy_3)_2Pt(H)_2Br_2$ (**19**)	-55	Pt-*H*	-17.58, $^{1}J_{Pt\text{-}H}$ = 1145	
$[(PCy_3)_2Pt(H)]Cl$ (**20**)	-60	Pt-*H*	-23.11, $^{1}J_{Pt\text{-}H}$ = 1559	
	-55	Pt-*P*Cy_3	42.9, $^{1}J_{Pt\text{-}P}$ = 2716	
$[(PCy_3)_2Pt(H)]Br$ (**21**)	-55	Pt-*H*	-17.76, $^{1}J_{Pt\text{-}H}$ = 1655, $^{2}J_{P\text{-}H}$ = 11	
	-85	Pt-*P*Cy_3	43.08, $^{1}J_{Pt\text{-}P}$ = 2715	
$[(PCy_3)_2Pt(H)]I$ (**22**)	-75	Pt-*H*	-18.07, $^{1}J_{Pt\text{-}H}$ = 1640	
	-60	Pt-*P*Cy_3	40.7, $^{1}J_{Pt\text{-}P}$ = 2670	
trans-$(PBu^t_3)_2Pt(H)Cl$ (**23**)	22	$C(CH_3)_3$	1.55, $^{3}J_{P\text{-}H}$ = 6	
		Pt-*H*	-19.9, $^{1}J_{Pt\text{-}H}$ = 1110, $^{2}J_{P\text{-}H}$ = 12	
[*trans*-$(PBu^t_3)_2Pt(H)(CD_2Cl_2)]BAr^f_4$ (**24**)	-30	$C(CH_3)_3$	1.48, $^{3}J_{P\text{-}H}$ = 5	
		Pt-*H*	-36.3, $^{1}J_{Pt\text{-}H}$ = 2600	

Protonation of 1–4 at low temperature: Complexes containing σ-donor ligands *trans* to hydride. Addition of $[H(Et_2O)_2]^+BAr^f{}_4^-$ (abbreviated $HBAr^f{}_4$) to a CD_2Cl_2 solution of *trans*-$(PCy_3)_2Pt(H)_2$ (**2**) at -95 °C leads to formation of the dihydrogen adduct, [*trans*-$(PCy_3)_2Pt(H_2)H]BAr^f{}_4$ (**12**) analogous to those recently reported with $PBu^t{}_3$ and $PPr^i{}_3$ ligands.[17,18] The dihydrogen resonance in the ^1H NMR spectrum (Table 1) is characteristically broadened and exhibits a short T_1 (36 ms, 500 MHz) at -85 °C. In contrast, the hydride *trans* to the H_2 ligand has a long T_1 (606 ms, -85 °C, 500 MHz). A short H–H bond in this H_2 adduct is implicated from the large H–D coupling constant observed upon protonation of *trans*-$(PCy_3)_2Pt(D)_2$ with $HBAr^f{}_4$ ($^1J_{H\text{-}D}$ = 31 Hz). The solvent-coordinated complex [*trans*-$(PCy_3)_2PtH(CD_2Cl_2)]BAr^f{}_4$ (**13**) is in equilibrium with $[(PCy_3)_2Pt(H_2)H]BAr^f{}_4$ (**12**) under 1 atm of hydrogen.

In contrast to the reactions with $HBAr^f{}_4$, the dihydrogen complex formed upon protonation of $(PCy_3)_2Pt(H)_2$ (**2**) with HOTf (OTf = O_3SCF_3) irreversibly loses H_2 after a few minutes at -95 °C along with formation of *trans*-$(PCy_3)_2Pt(H)(OTf)$ (**9**) (see Table 1). Protonation of **2** with HCl leads directly to *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) and H_2 at -95 °C, i. e., no intermediate H_2 adduct is observed.

Treatment of *trans*-$(PCy_3)_2Pt(SiH_3)H$ (**1**) with $HBAr^f{}_4$ at -95 °C in CD_2Cl_2 leads to immediate liberation of H_2. In contrast, dihydrogen adducts *are* observed upon carrying out the same reaction with *trans*-$(PCy_3)_2Pt(CH_3)H$ (**3**) and *trans*-$(PCy_3)_2Pt(Ph)H$ (**4**) (Figure 1). The dihydrogen resonance for these complexes are shifted upfield relative to those for $[(PCy_3)_2Pt(H_2)H]BAr^f{}_4$ (**12**) (Table 1): [*trans*-$(PCy_3)_2Pt(H_2)CH_3]BAr^f{}_4$ (**14**) (δ -2.35 ppm, -85 °C) and [*trans*-$(PCy_3)_2Pt(H_2)Ph]BAr^f{}_4$ (**15**) (δ -1.9 ppm, -80 °C). While at -95 °C, **14** slowly and irreversibly eliminates CH_4; small amounts of free H_2 are also

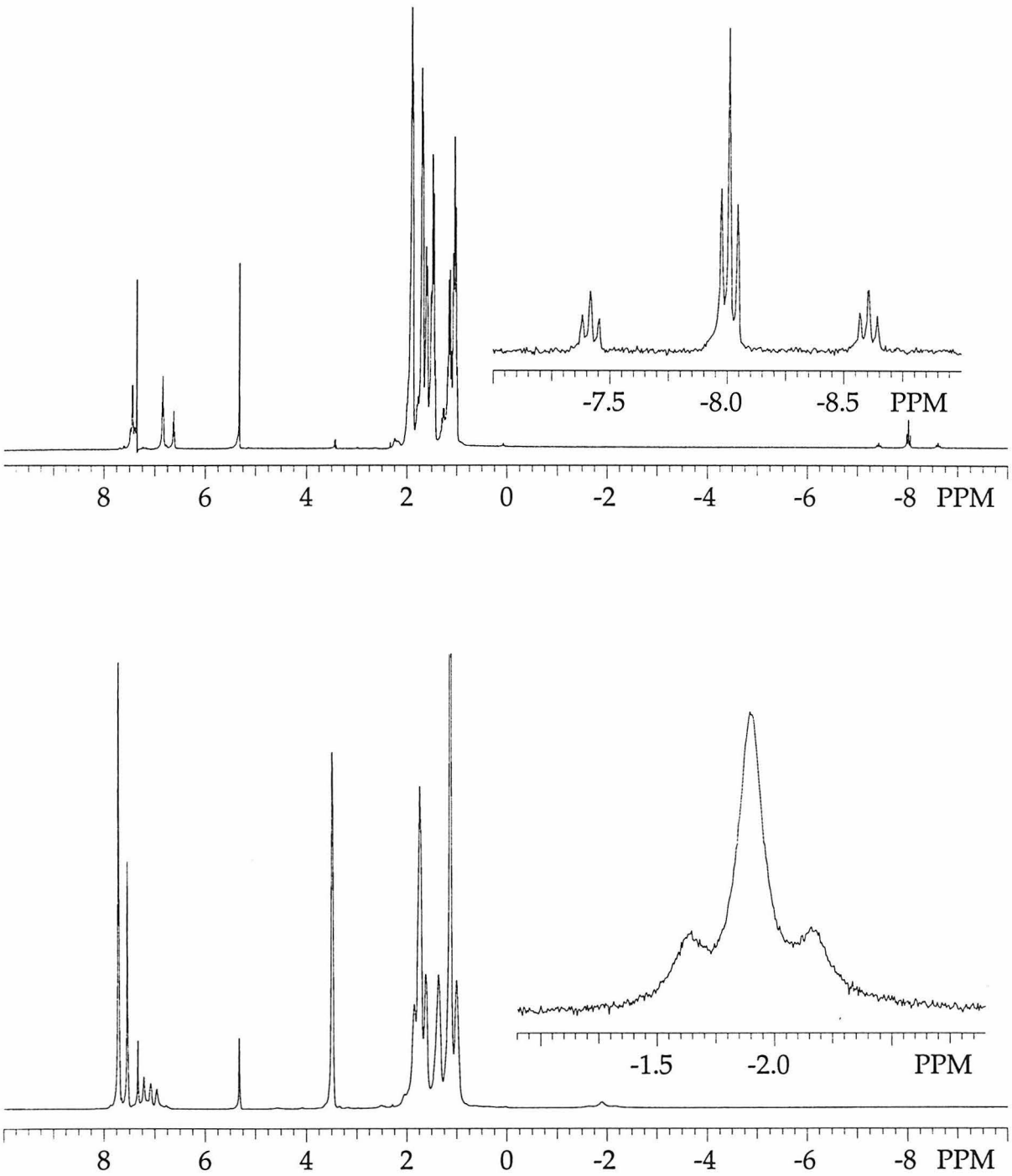
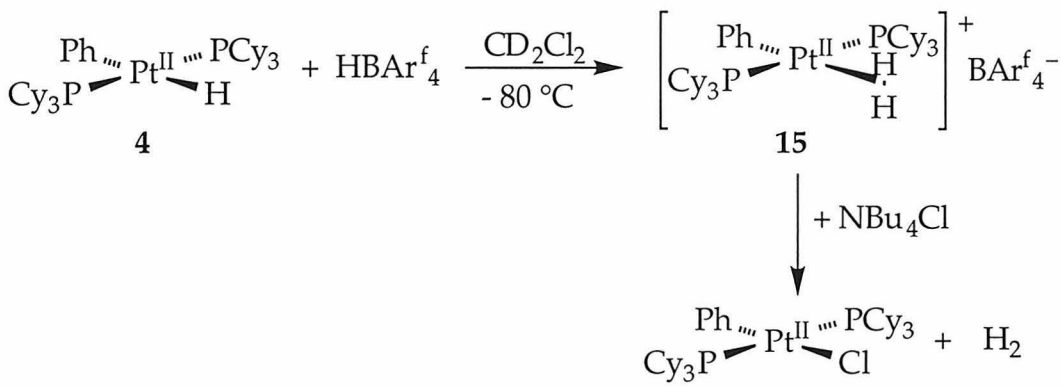


Figure 1: ^{1}H NMR spectra of *trans*-$(PCy_3)_2Pt(Ph)H$ (**4**) (top spectrum) and the H_2-adduct $(PCy_3)_2Pt(H_2)Ph]BAr^f{}_4$ (**15**) generated upon protonation of **4** with $HBAr^f{}_4$.

observed in this reaction. The phenyl complex **15** is considerably more stable, however, liberating benzene only upon warming to -50 °C. Free H_2 is never observed in this case.

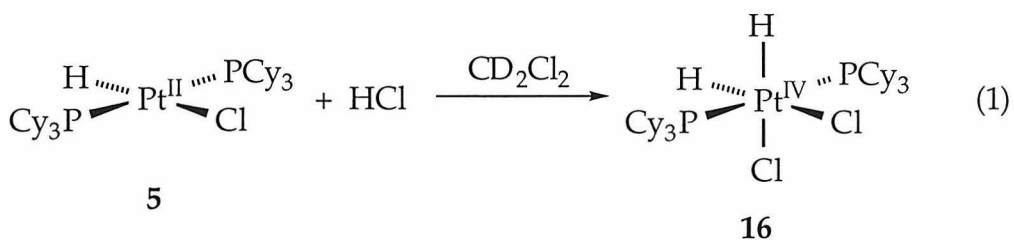
Both $[(PCy_3)_2Pt(H_2)CH_3]BAr^f_4$ (**14**) and $[(PCy_3)_2Pt(H_2)Ph]BAr^f_4$ (**15**) exhibit characteristically short T_1 values (**14**: 26 ms, -95° C; **15**: 20 ms, -65° C).[28] Protonation of $(PCy_3)_2Pt(CH_3)H$ (**3**) and $(PCy_3)_2Pt(Ph)H$ (**4**) with $DBAr^f_4$ generates the HD adducts, **14**-d_1 and **15**-d_1, which exhibit large H–D coupling constants of 30.5 Hz and 33.6 Hz, respectively. Addition of HCl to **4** at -80 °C immediately liberates H_2 along with formation *trans*-$(PCy_3)_2Pt(Ph)Cl$ (no benzene is observed). Correspondingly, addition of chloride to the H_2 adduct, **15**, at -80 °C results in rapid substitution of H_2 by chloride (Scheme II).

Scheme II



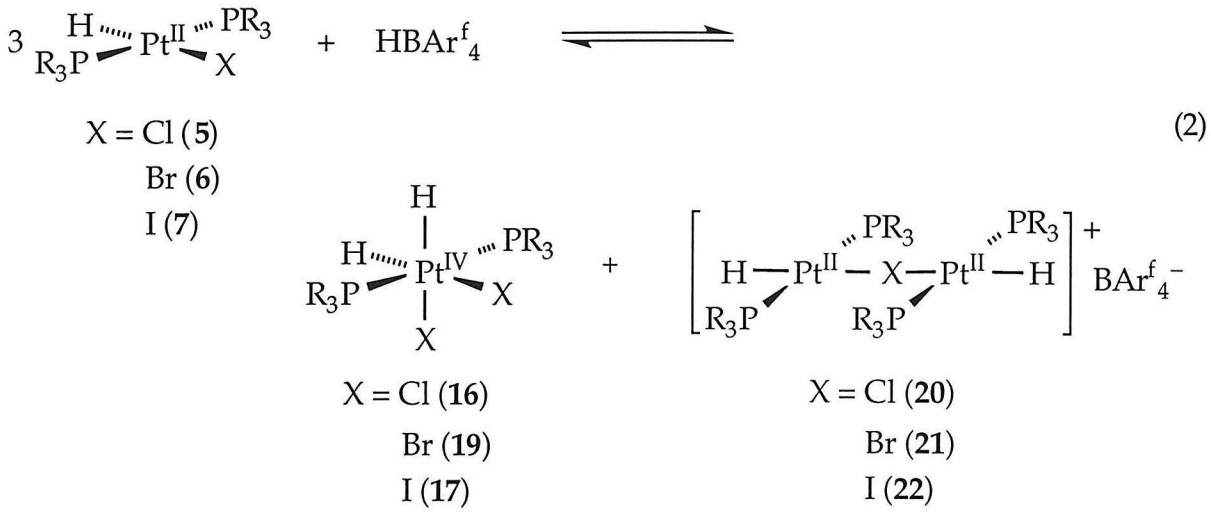
No multiple deuterium incorporation is observed in the methane liberated from the reaction between *trans*-$(PCy_3)_2Pt(CH_3)D$ and ten equivalents of $DBAr^f_4$ at -80 °C. In the presence of a large excess of $HBAr^f_4$ and $DBAr^f_4$, a deuterium kinetic isotope effect of 2.5 (±0.4) was determined for protonolysis of the Pt–CH_3 bond based on the ratio of CH_4/CH_3D generated.

Protonation of 5–7 at low temperature: Complexes containing σ- and π-donor ligands *trans* to hydride. Protonation of *trans*-$(PCy_3)_2Pt(H)Cl$[27] (**5**) with HCl at -80 °C slowly forms the oxidative addition product *trans*-$(PCy_3)_2Pt(H)_2Cl_2$ (**16**) (eq 1, Table 1). Adding HCl to a CD_2Cl_2 solution of *trans*-$(PCy_3)_2Pt(H)I$ (**7**) leads to three Pt(IV) products reflecting facile halide exchange between the complexes: *trans*-$(PCy_3)_2Pt(H)_2Cl_2$ (**16**), *trans*-$(PCy_3)_2Pt(H)_2I_2$ (**17**), *trans*-$(PCy_3)_2Pt(H)_2(Cl)I$ (**18**). (Table 1) While **16** and **17** were prepared independently to verify this assignment, formation of **18** is inferred from the mass balance of the reaction and chemical shifts of the hydride resonances consistent with such an assignment.



5 **16**

Protonation of *trans*-$(PCy_3)_2Pt(H)X$ [X = Cl (**5**), Br (**6**), I (**7**)] with $HBAr^f_4$ rather than HCl leads to different products. In each case, three separate platinum-hydride resonances are observed in the ^1H NMR spectrum of the reaction mixture. These peaks correspond to the three platinum complexes shown in eq 2. For example, upon addition of $HBAr^f_4$ to **7** at -80 °C, resonances appear at δ -14.65 ppm ($^1J_{Pt\text{-}H}$ = 1390) (**7**), -15.79 ppm ($^1J_{Pt\text{-}H}$ = 1115 Hz) (**17**), and -18.07 ppm ($^1J_{Pt\text{-}H}$ = 1655 Hz) (**22**). The peaks associated with **17** and **22** are of equal intensity (Figure 2).



X = Cl (**5**)
Br (**6**)
I (**7**)

X = Cl (**16**)
Br (**19**)
I (**17**)

X = Cl (**20**)
Br (**21**)
I (**22**)

(2)

The chloride-bridged dimer **20** was prepared independently by mixing one equivalent of $(PCy_3)_2Pt(H)Cl$ (**5**) and $(PCy_3)_2PtH(solvent)]BAr^f_4$ in CH_2Cl_2. The reversibility of the equilibrium in eq 2 was qualitatively verified by warming and re-cooling the reaction mixture between -95 and -45 °C, and observing that the relative concentrations of [**17**] + [**22**] versus [**7**] change, depending on the temperature with the left side of the equilibrium being favored at lower temperatures. Upon warming the reaction mixture above ~ -40 °C, irreversible protonation of the phosphine ligands causes decomposition of the products. Addition of NBu_4Cl to the reaction mixture containing **5**, **16**, and **20**, or addition of NBu_4I to the mixture of **7**, **17**, and **22** results in complete formation of the Pt(IV) dihydride products **16** and **17**, respectively.

The reaction between $HBAr^f_4$ and $(PCy_3)_2Pt(H)Cl$ (**5**) is, in fact, more complex than indicated by eq 2. At -95 °C, the Pt–*H* ^{1}H NMR resonance

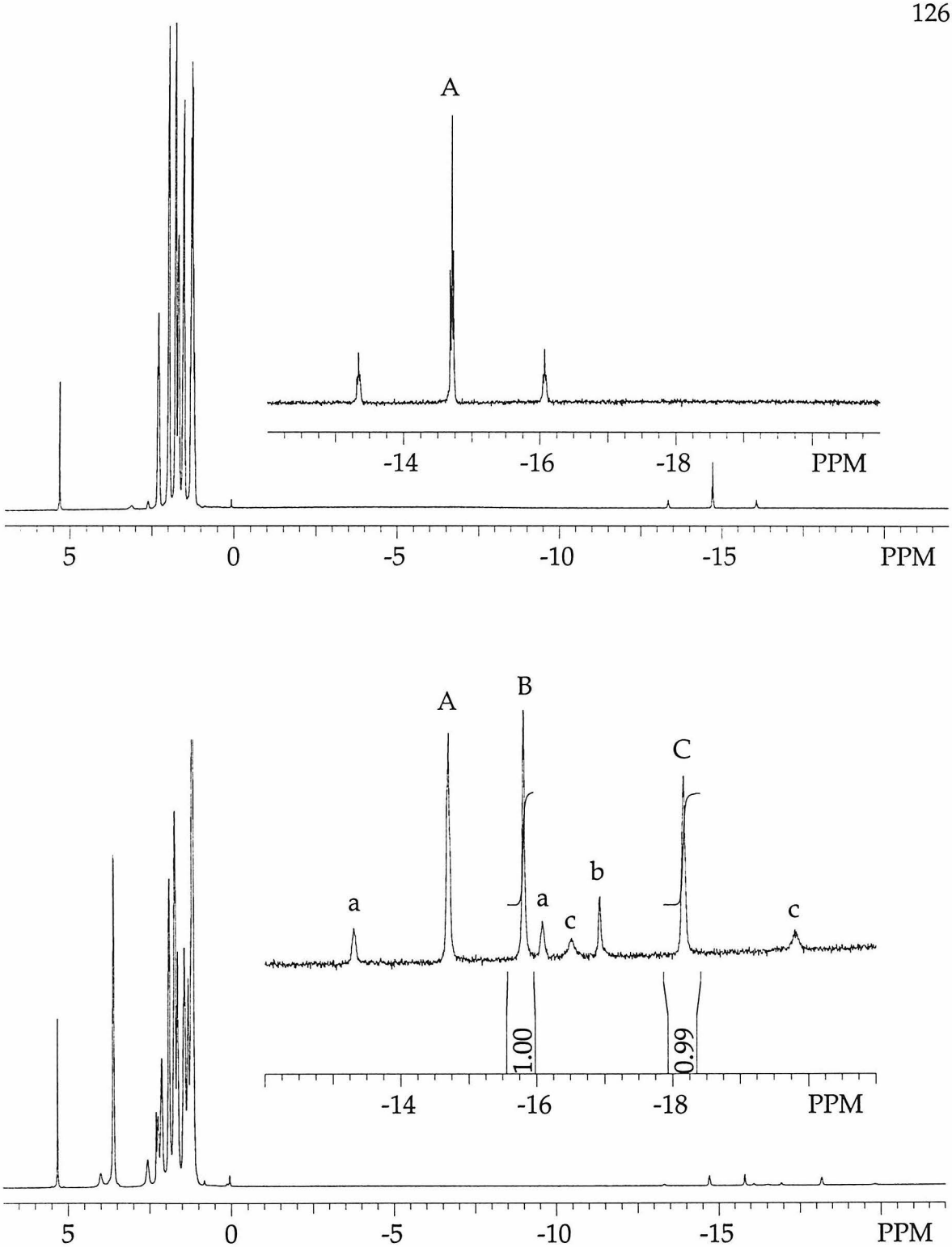


Figure 2: ^{1}H NMR spectra of *trans*-$(PCy_3)_2Pt(H)I$ (**7**) (top spectrum) and of the products generated upon addition of $HBAr^f_4$ to **7** in CD_2Cl_2. The labeled peaks correspond to the following compounds. **A**: *trans*-$(PCy_3)_2Pt(H)I$ (**7**); **B**: $(PCy_3)_2Pt(H)_2I_2$ (**17**); and **C**: $[(PCy_3)_2Pt(H)]_2I$ (**23**). The lowercase letters correspond to platinum satellites of the peaks labeled with uppercase letters.

corresponding to **5** broadens significantly and shifts upfield slightly upon addition of $HBAr^f_4$. This peak is assigned to a new species (or mixture of species), **5**•$HBAr^f_4$. Upon slight warming of the reaction mixture (e.g., at -80 °C), the products **16** and **20** arise in an equilibrium with **5**•$HBAr^f_4$, in accord with eq 2 (Figure 3).

The upfield shift of **5**•$HBAr^f_4$ (peak A' in Figure 3) relative to **5** is dependent on the H^+ concentration, with higher $[H^+]$ leading to a greater upfield shift. The origin of this behavior is not entirely clear, but possibly originates from equilibrium protonation of either the chloride or hydride in **5** (see discussion below). The ^1H NMR resonance associated with **5**•$HBAr^f_4$ exhibits a significantly reduced $T_{1(min)}$ relative to **5** (**5**: $T_{1(min)}$ = 480 ms at -55 °C; **5**•$HBAr^f_4$: $T_{1(min)}$ = 80 ms at -32 °C). Furthermore, addition of $DBAr^f_4$ to **5** results in rapid H/D exchange between D^+ and the platinum hydride.

The same behavior does not appear to be present for the bromide and iodide complexes, **6** and **7**. Addition of $HBAr^f_4$ to **6** or **7** has virtually no effect on their respective ^1H NMR signals (cf. Figure 2). Verification of this observation is the relatively long T_1 observed for **6** in the presence of $HBAr^f_4$: $T_{1(min)}$ = ~ 350 ms at -40 °C.

Treating the PBu^t_3-ligated complex, *trans*-$(PBu^t_3)_2Pt(H)Cl$ (**23**),[23,25] with $HBAr^f_4$ generates the solvated hydridoplatinum(II) complex (**24**) at -30 °C reflecting electrophilic attack at the chloride (eq 3).[29] We obtain no definitive evidence for intermediates prior to HCl elimination such as formation of a Pt(IV) dihydride or an H_2 or HCl adduct.

$$\underset{\textbf{23}}{\mathrm{Bu^t_3P}(\mathrm{H})\mathrm{Pt^{II}Cl}(\mathrm{PBu^t_3})} + \mathrm{HBAr^f_4} \xrightarrow[-30\ ^\circ\mathrm{C}]{\mathrm{CD_2Cl_2}} \underset{\textbf{24}}{\left[\mathrm{Bu^t_3P}(\mathrm{H})\mathrm{Pt^{II}(Sol)}(\mathrm{PBu^t_3})\right]^+ \mathrm{BAr^f_4}^-} + \mathrm{HCl} \quad (3)$$

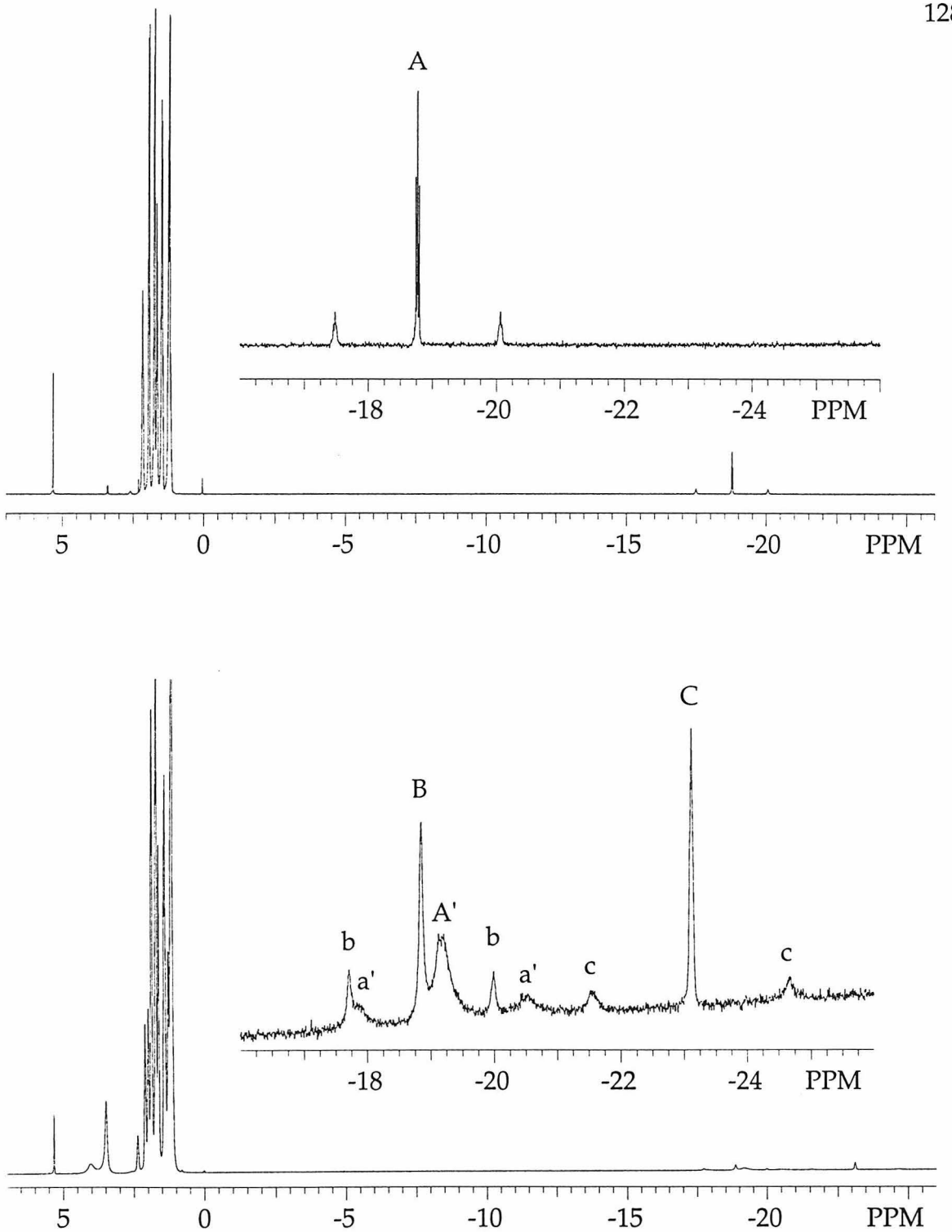
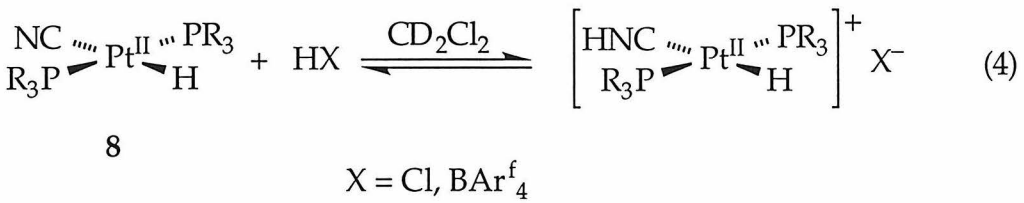


Figure 3: ^{1}H NMR spectra of *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) (top spectrum) and of the products generated upon addition of $HBAr^f_4$ to **5** in CD_2Cl_2. The labeled peaks correspond to the following compounds. **A**: *trans*-$(PCy_3)_2Pt(H)Cl$ (**7**); **A'**: "$(PCy_3)_2Pt(H)Cl \bullet HBAr^f_4$" **B**: $(PCy_3)_2Pt(H)_2Cl_2$ (**16**); and **C**: $[(PCy_3)_2Pt(H)]_2Cl$ (**20**). The lowercase letters correspond to platinum satellites of the peaks labeled with uppercase letters.

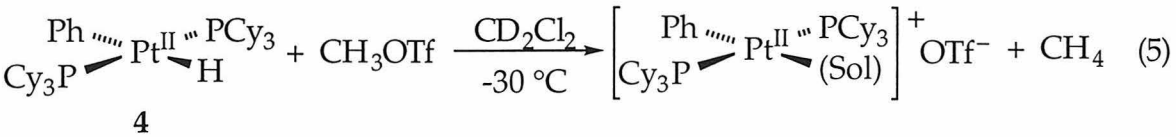
Protonation of 8, 10, and 11: Complexes containing a cationic charge and/or a π-acid ligand *trans* to hydride. No reaction is observed between $HBAr^f_4$ and the cationic complexes, [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO (**10**), 4-picoline (**11**)], in CD_2Cl_2, even after two days at room temperature. In contrast, formation of a dihydrido Pt(IV) product is observed upon addition of HCl to **11**. No reaction is observed with **10**, even in the presence of 15 equivalents of HCl.

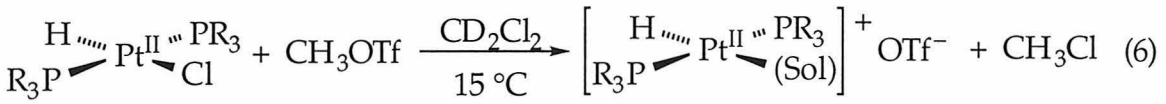
Protonation of the neutral cyanide complex (**8**) with one equivalent of $HBAr^f_4$ at room temperature results in a downfield shift of the Pt–*H* ^{1}H NMR resonance (**8**: δ -8.82 ppm, $^1J_{Pt\text{-}H}$ = 775 Hz; **8** + $HBAr^f_4$: -7.24 ppm, $^1J_{Pt\text{-}H}$ = 835 Hz). Upon cooling the reaction mixture to ~ -120 °C a new "H^+" peak is observed at 13.3 ppm. If, instead, three equivalents of HCl are added to **8** in CD_2Cl_2 two "H^+" peaks are observed at -115 °C in a 2:1 ratio at 12.9 and 14.4 ppm, respectively. Since 12.9 ppm is identical to the chemical shift of HCl in a CD_2Cl_2 solution not containing **8** at -115 °C, the peak at 14.4 is assigned to the hydrogen isocyanide (HNC) ligand (eq 4). No evidence for formation of a dihydrogen adduct or Pt(IV) dihydride intermediate was obtained.



Reactions between CH_3OTf and hydridoplatinum(II) complexes. Electrophilic attack by CH_3OTf on hydridoplatinum(II) complexes was also briefly examined. Whereas methane is liberated at -45 °C in the reaction between CH_3OTf and *trans*-$(PCy_3)_2Pt(H)Ph$ (**4**) (eq 5), electrophilic attack at

chloride is observed in the CH_3OTf reaction with *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) and *trans*-$(PBu^t_3)_2Pt(H)Cl$ (**23**) at +15 °C (eq 6), leading to formation of CH_3Cl and the corresponding solvated cationic hydridoplatinum(II) complexes (**9** and **24**).





R = Cy (**5**)
Bu^t (**23**)

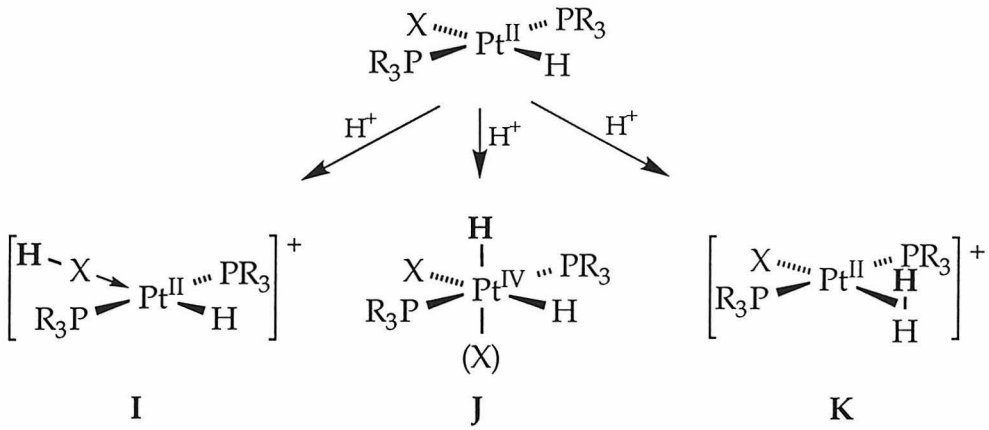
R = Cy (**9**)
Bu^t (**24**)

DISCUSSION

Sites of electrophilic attack: Evidence for protonation at all three possible sites. In 1994, Gusev et al. reported the first example of a platinum(II) dihydrogen complex, [*trans*-$(PBu^t_3)_2Pt(H_2)H]OTf$.[17] Because platinum(IV) dihydrides are also known,[30-32] we decided to undertake a systematic investigation of related hydridoplatinum(II) complexes to examine the factors which dictate the site of electrophilic attack in protonation reactions. Despite the steric stabilization provided by the PBu^t_3 ligand, its extreme bulk (cone angle > 180°[33]) limits the range of complexes that can be readily prepared. Consequently, we chose to investigate complexes containing the PCy_3 ligand. Tricyclohexylphosphine also exhibits a very large cone angle (170°), and its electronic effects are very similar to PBu^t_3.[33]

Protonation of the hydridoplatinum(II) complexes discussed above reveals electrophilic attack at all three possible sites (Scheme III): hydride (**1–4**), platinum (**5–7**), and the *trans* ligand (e.g., cyanide) (**8** and **23**). We know of

Scheme III



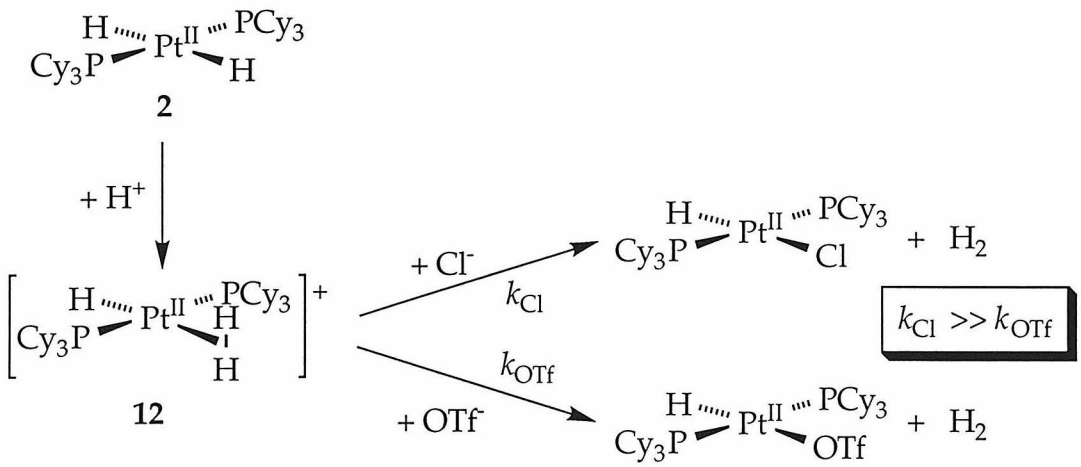
I **J** **K**

no other class of complexes where protonation at *all three* sites has been observed. In addition, irreversible protonation of the phosphine ligands is also observed for the halide complexes **5–7** at higher temperatures. It should be noted that protonation at platinum (**J**) has only been observed in the presence of a sixth ligand to stabilize the d^6, octahedral metal center. We do not observe interconversion between any of our products with the other possible "tautomers",[34] except possibly in the protonation of $(PCy_3)_2Pt(H)Cl$ as discussed below.

Mechanism of H_2 ligand substitution. Our investigation of the protonolysis of various alkylplatinum(II) complexes[16] provided evidence for methane σ-adducts as intermediates in the reaction. Methane displacement from these intermediates appears to follow both an associative (for [*trans*-$(PEt_3)_2Pt(CH_4)Cl]^+$) and a dissociative pathway (for $[(tmeda)Pt(CH_4)Cl]^+$, tmeda = tetramethylethylenediamine) based on kinetics of the protonolysis reaction. However, because the intermediate σ-adducts are not observed, these

conclusions remain somewhat tentative. We can confidently conclude that H_2 displacement from [*trans*-$(PCy_3)_2Pt(H_2)H]^+$ (**12**) proceeds through an *associative* pathway, because a dissociative pathway (i. e., rate-determining ligand dissociation) would exhibit no dependence of the substitution rate on the incoming ligand. Liberation of H_2 from **12** proceeds considerably faster in the presence of chloride (k_{Cl}) than triflate (k_{OTf}) (Scheme IV), as determined by comparing the reaction of **2** with HCl versus HOTf.

Scheme IV

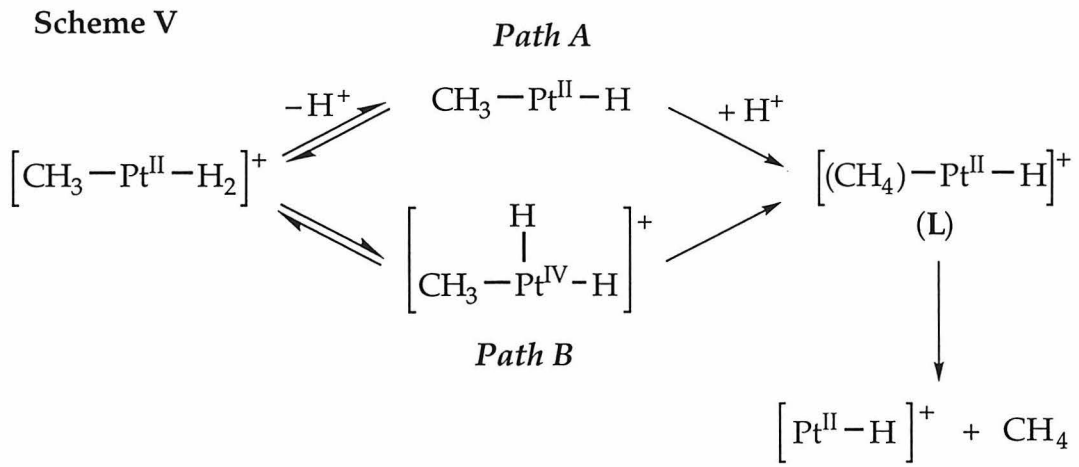


Pt(II)–Dihydrogen complexes: Effect of *trans* ligands and the reversibility of protonation. All of the complexes which lead to formation of an H_2-adduct (**2–4**) bear a strong σ-donor ligand *trans* to the hydride. Presumably the strong donating ability of these ligands enhances the basicity of the *trans* hydride, making it more susceptible to protonation (relative to platinum). This protonation is reversible, however, since the H_2 adducts, **14** and **15**, eventually decompose by irreversible protonolysis of the Pt–C bonds.

As expected, the stability/lability of the Pt–(H_2) bond tracks with the *trans* influence/effect of this ligand: -SiH_3 > -H ~ -CH_3 > -Ph. Competitive formation of methane from [*trans*-$(PCy_3)_2Pt(H_2)CH_3]BAr^f_4$ (**14**) even at -95 °C limits our ability to directly compare this complex with [*trans*-$(PCy_3)_2Pt(H_2)H]BAr^f_4$ (**12**) more closely. The large $^1J_{H\text{-}D}$ values observed for the deuterated analogs of **12**, **14** and **15** indicate they have a rather short, "unactivated" H–H bond (i. e., ~ 0.8–0.9 Å)based on the correlation between $^1J_{H\text{-}D}$ and the H–H bond distances noted in other H_2 complexes.[13,35]

In principle, protonation at platinum may be the kinetic site of protonation followed by formation of the thermodynamically favored H_2 adduct, however we obtain no evidence for such behavior. The deuterium kinetic isotope effect for loss of methane from **14** (k_H/k_D = 2.5) cannot distinguish between a sequence involving pre-equilibrium deprotonation of **14** followed by direct attack of the Pt–C bond (Path A, Scheme V) versus pre-equilibrium formation of a five-coordinate methyldihydridoplatinum(IV) complex which reductively eliminates methane (Path B, Scheme V). A theoretical study of $PtH_3(PH_3)_2^+$ indicated that the Pt(IV)trihydride tautomer is much higher in energy (18 kcal/mol) than the Pt(II)monohydride/dihydrogen-adduct formulation.[17]

Scheme V



Lack of deuterium incorporation into the methyl group in the presence of excess $DBAr^f_4$ indicates that if a methane σ-adduct (**L**), is on the reaction path, the transition state for reactivation is substantially higher in energy than that for dissociation from platinum. In contrast, protonation at hydride is reversible. Two factors likely contribute to this result: (1) a larger barrier for displacement of H_2 versus methane (probably due to a stronger Pt–H_2 bond) and (2) a higher *kinetic* acidity of coordinated H_2 versus coordinated methane.

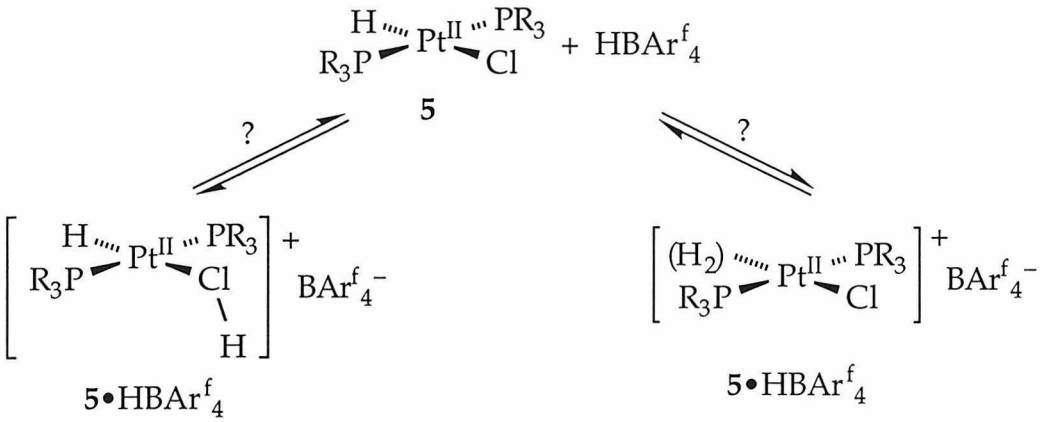
The reaction between "CH_3^+" (as CH_3OTf) and three different platinum(II) hydrides also failed to provide evidence for a methane σ-adduct. In fact, for the complexes *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) and *trans*-$(PBu^t_3)_2Pt(H)Cl$ (**23**), CH_3^+ attacks chloride rather than hydride, generating CH_3Cl. The chloride in **23** is also attacked when H^+ is the electrophile.[29] These results likely arise from the steric effects in the transition state for electrophilic attack. For example, the extreme steric bulk of PBu^t_3 effectively prevents formation of a six coordinate Pt(IV) product. The transition state for attack at the Pt–H bond in **23** would also be extremely sterically congested, thus leaving the chloride lone pairs as the only accessible site for electrophilic attack. Steric effects may also play a role in the electrophilic attack on **5**, with H^+ preferring attack at platinum and CH_3^+ at chloride.

Protonation of halide complexes 5–7: Observation of Pt(IV) dihydride complexes. Substitution of a halide for the strong σ-donor ligand appears to dramatically reduce the basicity of the *trans* hydride; a dihydrogen adduct is no longer observed as the thermodynamic product. Instead, protonation at platinum results, possibly favored by donation of electron density from halide lone pairs which should enhance the basicity of the metal center.

Importantly, the Pt(IV) dihydride product observed upon protonation of all three halide complexes (**5–7**) is *six*-coordinate. When $HBAr^f_4$ is the proton source, the sixth ligand is acquired by halide abstraction from the starting material. We obtain no evidence for a five-coordinate, Pt(IV) dihydride product in any of our reactions.

The Pt(II) chloride complex (**5**), appears to exhibit some interaction with $HBAr^f_4$. At this point we cannot definitively identify the nature of this interaction, however, the ^1H NMR behavior seems consistent with rapid, reversible protonation of either the hydride or chloride ligands.

Scheme VI



Although rapid H/D exchange between $DBAr^f_4$ and the platinum hydride supports protonation at the hydride, the chloride–H^+ interaction still may be thermodynamically favored. Similar observations, namely (1) a reduced T_1 relaxation time and (2) an upfield shift in the hydride resonance, were recently reported for a series of tungsten hydride complexes in the presence of acidic alcohols.[36] These data were interpreted as *inter*molecular hydrogen bonding between the alcohols and the tungsten hydride. Several

other examples of hydrogen bonding to transition metal hydrides have been reported recently,[37] although most are *intra*molecular interactions. In our case, such interaction leads to a "stretched" H_2 adduct. The origin of the *upfield* shift is currently unexplained; formation of dihydrogen adducts **12**, **14**, and **15** results in a downfield shift (see Table 1), approaching the value of free H_2 (δ 4.55 ppm). Direct determination of the pK_a value for an osmium H_2 adduct *trans* to chloride and bromide revealed that the bromide complex is in fact more acidic.[38] This result is consistent with our results, since no interaction is observed between H^+ and the bromide and iodide complexes **6** and **7**.

An alternative explanation for our observations is protonation at chloride. The proposal is consistent with protonation of chloride in the PBu^t_3 complex **23**. Furthermore, formation of an HCl adduct nicely accounts for an upfield shift in the Pt–*H* ^{1}H NMR resonance relative to **5** since HCl is a weaker ligand than Cl^-. Furthermore, the greater basicity of chloride relative to bromide and iodide consistently predicts that **6** and **7** should exhibit a weaker interaction with H^+. However, this proposal does not explain the reduced $T_{1(min)}$ value. At this point, we cannot definitively identify the nature of this interaction.

Protonation of complexes containing a cationic charge and/or a π-acid ligand *trans* to hydride. The CO complex **10** exhibits no affinity for H^+. Presumably the cationic charge of this complex combined with the strong π-acidity of the CO ligand dramatically reduces its basicity. The other cationic complex examined here has picoline, a relatively weak σ-donor, *trans* to the hydride. In this case, a Pt(IV) dihydride product can be observed, but again,

only in the presence of a sixth ligand (chloride) to stabilize the d^6 product. No reaction is observed in the absence of chloride (i.e., upon addition of $HBAr^f_4$).

An isocyanide ligand is formed upon protonation of the cyanide complex, **8**. This is the only example where we directly observe H^+ interaction with the ligand *trans* to hydride. Morris and co-workers recently observed a similar reaction with *trans*-$[FeH(CN)L_2]$ (L = a diphosphine ligand). In their case, however, protonation at either hydride or the cyanide nitrogen is observed depending on the phosphine ligand used.[39]

Contrast between square planar-d^8 and octahedral-d^6 dihydrogen adducts. Because of the rarity of d^8 dihydrogen complexes, it may be valuable to compare our results with those of better known octahedral d^6 complexes. Homolytic cleavage (i. e., oxidative addition) of a dihydrogen ligand appears more facile in the d^6 complexes, as suggested by several examples of reversible dihydride/dihydrogen-adduct equilibria that have been reported for such complexes.[11,13] In these cases, the equilibrium exists between six-coordinate d^6 (H_2 adduct) and seven-coordinate d^4 (dihydride) structures. In our case, the corresponding equilibrium between four-coordinate, d^8 and five-coordinate, d^6 structures appears energetically prohibitive. In fact, the dihydride "tautomer"[34] is only observed in the presence of a sixth ligand. We never observe interconversion between an H_2 adduct and a Pt(IV) dihydride complex. Notably, addition of chloride to the dihydrogen complexes **12**, **14**, and **15** promotes ligand substitution rather than conversion to the dihydride structure. There is evidence for such interconversion between the corresponding tautomers in alkane interactions with platinum (although the alkane adduct is not observed directly).[16,40]

Other features, however, demonstrate the qualitative similarities between octahedral, d^6 and square planar, d^8 dihydrogen complexes. Several studies have examined the impact of the ligand *trans* to H_2 in octahedral ruthenium and osmium complexes.[35,38,41-44] Greater homolytic activation of dihydrogen (i.e., longer *d*(H–H)) is observed in complexes having halides (σ *and* π donors) *trans* to H_2 versus hydride (σ-only donor). Our studies reveal similar behavior. Dihydrogen complexes are observed with *trans* σ-donor ligands (CH_3, Ph, H), whereas the Pt(IV) dihydride structure (i.e., the limit of homolytic activation) is stabilized by halide ligands. This trend is typically attributed to a "π-effect" in which π-symmetry electron density from the halide leads to more back-bonding into the σ^* orbital of bound H_2.

Relative to a hydride ligand, halides enhance the acidity of coordinated dihydrogen. Use of neutral *trans* ligands, which increase the positive charge on the complex, lowers the pK_a even further.[35,38,41,42] Although the pK_a of our complexes has not yet been determined, this qualitative trend is born out. Protonation of the hydride ligand occurs readily when it is *trans* to a strong σ-donor (i.e., **2**, **3**, **4**). Although there may be some affinity between protons and the hydride ligand in the chloride complex (**5**), this interaction appears quite weak. Furthermore, no direct proton-hydride interaction is ever observed for the bromide and iodide complexes (**6** and **7**) or the cationic complexes (**10** and **11**). Such observations are intuitively reasonable: a strong σ-donor should enhance the basicity of the *trans* hydride, and further, cationic hydride complexes should be less basic than related neutral species.

CONCLUSION: Implications for C–H activation by Pt(II)

This study has allowed us to address several questions regarding Pt(II) σ-adducts. As expected the strength and lability of the interaction depends directly on the nature of the *trans* ligand. Also, substitution of coordinated H_2 from the complexes examined here proceeds through an associative mechanism. This result may not be general for other Pt(II) σ-adducts, however, since the mechanism is likely influenced by the ancillary ligands and the strength of the Pt(II)–σ-adduct bond.

The dependence of the electrophilic attack site on the ligand trans to hydride seems particularly relevant to alkane activation. C–H activation by Pt(II) appears to proceed through *both* an alkane σ-adduct and a Pt(IV) alkyl hydride intermediate; however, deprotonation only occurs from the Pt(IV) hydride.[16] Shilov chemistry takes place in the presence of good ligands for Pt(IV), (i. e., Cl^- and H_2O), the same types of ligands that promote electrophilic attack at platinum in the hydride complexes discussed above. Thus, the success of the Shilov system may, in part, depend on appropriate ligands to access the *kinetically* more acidic Pt(IV) alkyl hydride intermediate. Such considerations suggest that an extremely electrophilic platinum(II) complex (i.e., one which strongly destabilizes Pt(IV)) may not be the best candidate for C–H activation.

For systems in which C–H oxidative addition is not a viable option (e.g., with Pd(II)[45] and Hg(II)[46]),[47] alkane activation has only been observed in strong acid solvents which dramatically enhance the electrophilicity of the metal ions. Deprotonation of a coordinated alkane may be the most plausible mechanism in these reactions.

EXPERIMENTAL

General Considerations. All syntheses and reactions were carried out under air-free conditions using standard Schlenk, inert-atmosphere glove box, or high-vacuum techniques. NMR spectral data was obtained using a Bruker AM500 NMR spectrometer. All solvents used were dried prior to use: CD_2Cl_2, distilled from fresh CaH_2 and stored over 4Å molecular sieves; CH_2Cl_2, distilled from P_2O_5; toluene, pre-dried over 4Å molecular sieves and then distilled from sodium. Preparation of the following compounds was carried out according to literature procedures or slight modifications thereof: $[H(Et_2O)_2][BAr^f_4]$ [BAr^f_4 = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$],[48] *trans*-$(PCy_3)_2Pt(H)X$ [X = SiH_3 (**1**),[22] H (**2**),[24] CH_3 (**3**),[27] Cl (**5**),[27] CF_3SO_3 (**9**)[20]], [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO (**10**),[20] 4-picoline (**11**)[20]], and *trans*-$(PBu^t_3)_2Pt(H)Cl$ (**23**).[25] Warning: SiH_4 used in the preparation of **1** is explosive on contact with air. Thus, minimal excess gas should be used is this reaction.

Preparation of *trans*-$(PCy_3)_2Pt(Ph)H$ (4). $(PCy_3)_2Pt(H)Cl$ (200 mg, 0.25 mmol) was dissolved in dry toluene in a Schlenk flask. After cooling the solution to 0 °C, PhMgBr (210 μL, 3.0 M solution, 0.63 mmol) was added via syringe. The reaction mixture was then stirred for several hours while slowly warming to room temperature. The reaction was then quenched with water. The organic layer was then separated, filtered through celite, and dried with $MgSO_4$. Removal of the solvent afforded the product in moderate yield (~60%). The solid was purified by washing with diethyl ether. See Table 1 for NMR data.

Preparation of *trans*-$(PCy_3)_2Pt(H)X$, X = Br (6), I (7). $(PCy_3)_2Pt(H)Cl$ (60 mg, 0.076 mmol) was added to a pear-shaped flask containing a stir bar and suspended in acetone (3-5 mL) under argon. Lithium bromide (66 mg, 0.76

mmol) or LiI (100 mg, 0.75 mmol) was then added to the flask, and the reaction mixture was stirred for two days (this duration is likely not necessary to complete the reaction). The acetone was removed under vacuum and the product was extracted from the resulting solid with toluene. Subsequent evaporation of the toluene afforded the analytically pure products in high (80-90%) yield. See Table 1 for NMR data.

Preparation of *trans*-$(PCy_3)_2Pt(H)CN$ (8). $(PCy_3)_2Pt(H)Cl$ (100 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (5 mL) in a Schlenk flask under argon, and a solution of AgOTf (32.4 mg, 0.13 mmol) in methanol (3 mL) was added via syringe. The mixture was stirred for 80 minutes, and the solvent was then removed under vacuum. A dichloromethane extract of the resulting solid was filtered through celite to remove suspended AgCl. The CH_2Cl_2 was removed under vacuum, and the residue was dissolved in methanol (5 mL). Sodium cyanide (6.2 mg, 0.13 mmol) was added to this solution, and the reaction mixture was stirred for 15 minutes. Solvent was removed and the solid was partitioned between water and CH_2Cl_2. The CH_2Cl_2 fraction was dried over $MgSO_4$. Removal of CH_2Cl_2 led to an oily product which solidified upon washing with pentane. See Table 1 for NMR data.

General Procedure for Low Temperature Protonation Experiments. Except where indicated otherwise, reaction mixtures for low temperature NMR experiments were prepared by loading the solid starting material into a 5mm NMR tube equipped with a screw cap and silicone/PTFE septum (available from Wilmad Glass Company). The reagent was then dissolved in CD_2Cl_2 (~ 450 μL) and cooled to -95 °C. The $HBAr^f_4$ was loaded into a vial in the glovebox and sealed with a rubber septum. It too was dissolved in CD_2Cl_2 (~ 200 μL) and added to the pre-cooled NMR tube via syringe. Alternatively,

for reactions with HCl, a solution of HCl in diethyl ether-d_{10} (1.8 M) was added to the pre-cooled NMR tube via syringe. The combined reagents were vigorously shaken while at -95 °C prior to inserting the tube into a pre-cooled NMR probe. An identical procedure was used for the reaction of **4**, **5**, and **23** with CH_3OTf.

Preparation and Characterization of [*trans*-$(PCy_3)_2Pt(H_2)R]BAr^f_4$, R = H (12), CH_3 (14), Ph (15). The H_2 adducts **12**, **14**, and **15** were prepared by addition of $HBAr^f_4$ to the hydride complexes **2–4** according to the general procedures outlined above. T_1 measurements for these compounds were obtained at 500 MHz at various temperatures using the inversion recovery method. The $^1J_{HD}$ values for **14**-d_1 and **15**-d_1 were obtained by addition of $DBAr^f_4$ to the corresponding hydrides (**3** and **4**). The $^1J_{HD}$ value for **12**-d_2 was obtained by addition of $HBAr^f_4$ to the dideuteride *trans*-$(PCy_3)_2Pt(D)_2$ (**2**-d_2). Compound **2**-d_2 was prepared in identical manner to **2**,[24] except using $NaBD_4$ instead of $NaBH_4$ in the reaction.

Determination of isotope effect for protonolysis of methane from *trans*-$(PCy_3)_2Pt(CH_3)D$ (3-d_1). Compound **3**-d_1 was prepared from $LiCH_3$ and **5**-d_1 according the methods used for **3**.[27] Figure 4 shows a diagram of the glassware used in this experiment. Solid $HBAr^f_4$ (216 mg, 0.21 mmol) and $DBAr^f_4$ (500 mg, 0.49 mmol) were combined in flask A, and $(PCy_3)_2Pt(CH_3)D$ (27.3 mg, 0.035 mmol) was added to flask B. After sealing the ball joint using grease and a joint clamp, the apparatus was evacuated on a high vacuum line connected to Toepler pump. Dichloromethane (degassed and dried) was then vacuum transferred into both flasks (~10 mL into flask A and 5 mL into flask B) and the apparatus was then sealed using the Kontes PTFE valve. After dissolving both solids, the solutions were cooled to -60 °C. Rapid rotation of

flask B around the ball joint allowed the contents of both flasks to be mixed at low temperature. The mixtures was allowed to stir for approximately two hours, after which the gas evolved in the reaction was collected using a Toepler pump and transferred into an NMR tube containing CD_2Cl_2. The relative quantity of CH_4 and CH_3D generated in the reaction was determined by integrating their respective ^1H NMR resonances. The reaction was carried out twice, and identical results were obtained. A control experiment was

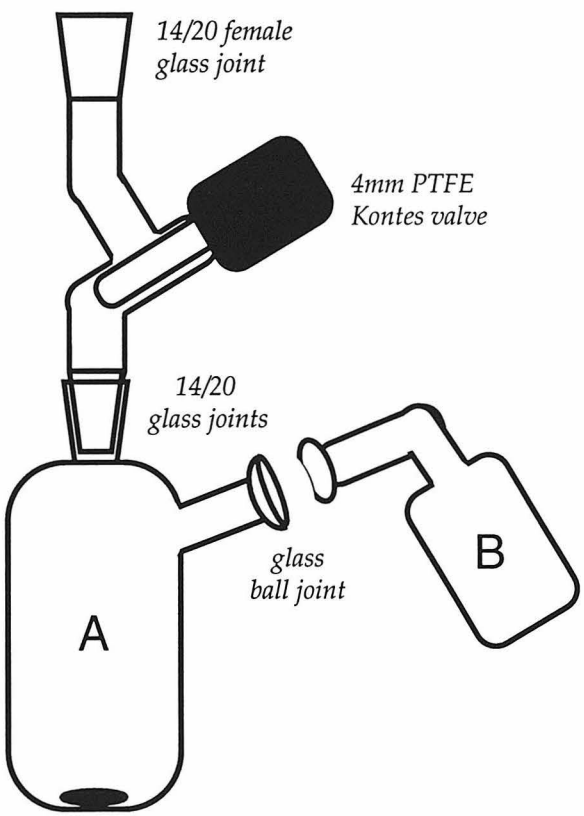


Figure 4: Drawing of apparatus used in determination of the kinetic deuterium isotope effect for protonolysis of Pt–CH_3 in **3**-d_1.

carried out to determine the level of H/D exchange between $DBAr^f_4$ and the glass surface. In this experiment (tmeda)$Zn(CH_3)_2$ (150 mg, 0.71 mmol) was

added to flask B (Figure 3) and $DBAr^f_4$ (500 mg, 0.49 mmol) was added to flask A. Sufficient (tmeda)$Zn(CH_3)_2$ was used to ensure consumption of all the H^+/D^+ in the reaction mixture. After dissolving the reagents in CH_2Cl_2 (added by vacuum transfer), the solutions were mixed, and the gas produced in the reaction was collected. A subsequent ^1H NMR spectrum of the methane generated revealed CH_4 (28.3%) and CH_3D (71.7%) (these percentages are the average of two successive experiments). This ratio was used in calculating the isotope effect for the reaction with **3**-d_1.

REFERENCES AND NOTES

1) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed. John Wiley & Sons, Inc.: New York, 1989.

2) *Selective Hydrocarbon Activation*; Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A., Eds.; VCH Publishers, Inc.: New York, 1990.

3) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154-162.

4) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125-3146.

5) Important exceptions are the following studies carried out in liquid noble gases: (a) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369. (b) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585. (c) Bengali, A. A.; Arndtsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281.

6) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

7) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

8) Crabtree, R. H. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

9) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120-128.

10) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95-101.

11) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155-284.

12) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151-187.

13) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913-.

14) Gol'dshleger, N. F.; Es'kova, V. V.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1972**, *46*, 1353.

15) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.

16) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961-5976.

17) Gusev, D. G.; Notheis, J. U.; Rambo, J. R.; Hauger, B. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 7409-7410.

18) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831-11843.

19) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839-1844.

20) Attig, T. G.; Clark, H. C. *Can. J. Chem.* **1975**, *53*, 3466-3470.

21) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271-277.

22) Ebsworth, E. A. V.; Marganian, V. M.; Reed, F. J. S.; Gould, R. O. *J. Chem. Soc., Dalton Trans.* **1978**, 1167-1170.

23) Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *J. Organomet. Chem.* **1981**, *214*, 405-417.

24) Goel, A. B.; Goel, S. *Inorg. Chim. Acta* **1982**, *65*, L77-L78.

25) Goel, R. G.; Ogini, W. O.; Srivastava, R. C. *Organometallics* **1982**, *1*, 819-824.

26) Goel, R. G.; Srivastava, R. C. *Can. J. Chem.* **1983**, *61*, 1352-1359.

27) Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263-267.

28) Elimination of methane and benzene from **14** and **15**, respectively, did not allow determination of the minimum T_1 values.

29) Caulton and co-workers recently reported work examining the protonation of this complex: Caulton, K. G., personal communication.

30) Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D..W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 854.

31) Blacklaws, I. M.; Brown, L. C.; Ebsworth, E. A. V.; Reed, R. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 877-879.

32) Blacklaws, I. M.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1978**, 753-758.

33) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348.

34) The products shown in Scheme III are not rigorously "tautomers" (which differ only in the position of the proton), because the Pt(IV) dihydride product contains an extra ligand.

35) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396-5407.

36) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105-1112.

37) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348-354.

38) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270-2278.

39) Amrhein, P. I.; Drouin, S. D.; Forde, C. E.; Lough, A. J.; Morris, R. H. *Chem. Commun.* **1996**, 1665-1666.

40) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *119*, 848-849.

41) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278-6288.

42) Rocchini, E.; Mezzetti, A.; R¨uegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711-720.

43) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946-8947.

44) Bacskay, G. B.; Bytheway, I.; Hush, N. S. **1996**,

45) Kao, L.-C.; Sen, A. *New J. Chem.* **1991**, *15*, 575-578.

46) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340-343.

47) Attempts to reproduce the recently reported oxidative addition C-H bonds by Pd(II) [Vedernikov, A. N.; Kuramshin, A. I.; Solomonov, B. N. *J. Chem. Soc., Chem. Commun.* **1994**, 121-122.] were unsuccessful in our laboratories: see Stahl, S. S. Ph.D. Thesis, California Institute of Technology, 1997.

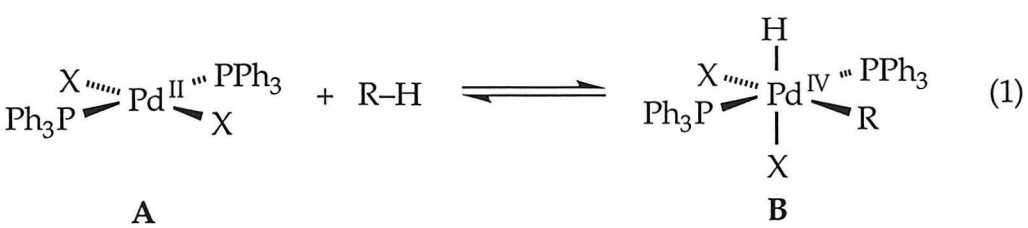
48) Brookhart, M. S.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920-3922.

APPENDIX

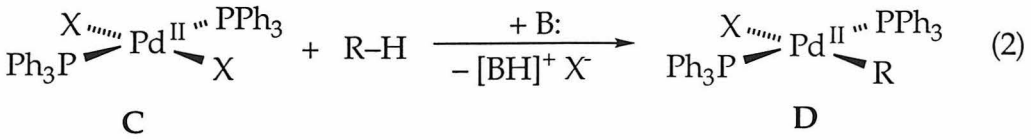
A Reinvestigation of "Reversible Thermal Carbon–Hydrogen Bond Cleavage in Alkanes and Arenes with Dihalogenobis(triphenylphosphine)palladium(II) Complexes"

Introduction

In recent years, considerable effort has been directed toward identifying new catalysts for alkane oxidation. Despite the success of the Shilov system utilizing aqueous platinum salts,[1] it is impractical for several reasons (see discussion in Chapter 1). Perhaps the most crippling drawback is the difficulty in replacing Pt(IV) with a less expensive oxidant, preferably O_2. In contrast, palladium catalyzes numerous hydrocarbon oxidation reactions, many of which use O_2 as the stoichiometric oxidant.[2] Thus, devising a palladium-catalyzed alkane oxidation reaction seems ideal. A few reports have, in fact, appeared[3-5] describing palladium-mediated alkane activation in strong acid solvents. Unfortunately, several research groups have been unable to reproduce these results.[6-9] In 1994, Vedernikov et al. published a remarkable paper reporting that the complexes, $(PPh_3)_2PdX_2$ (X = Cl, Br, I) (**A**), can effect reversible oxidative addition of alkane and arene C–H bonds (eq 1).[10] They also suggest that carrying out the reaction in the presence of a base (e.g., K_2CO_3) generates a alkylpalladium(II) product (eq 2). If Pd(II)–R bonds are susceptible to nucleophilic cleavage as has been suggested[4], such reactions suggest the viability of a catalytic cycle for alkane oxidation (Scheme I). Consequently, an attempt was made to reproduce this chemistry to explore such possibilities.

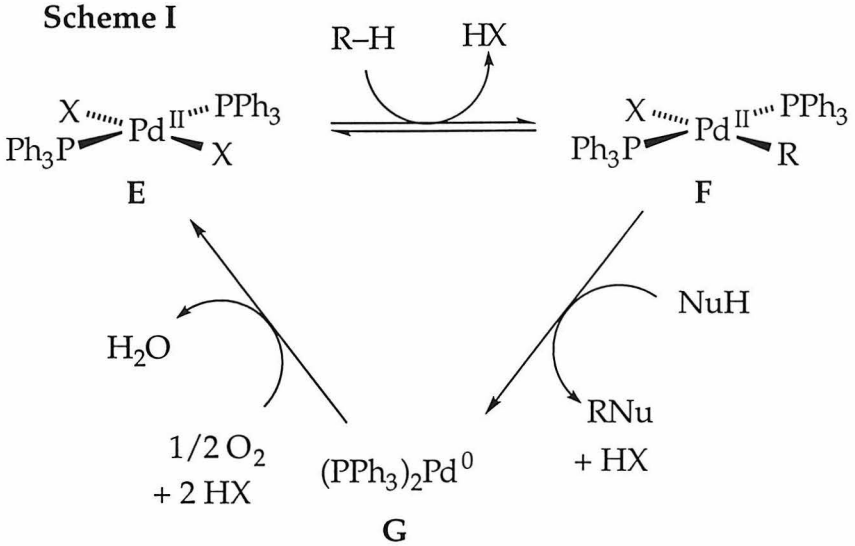


A **B** (1)



C D (2)

Scheme I



Summary and Analysis of Reported Results

Vedernikov et al. reported that dissolution (or suspension) of $(PPh_3)_2PdX_2$ in various hydrocarbon solvents including xylene, toluene, benzene, *n*-hexane, and cyclohexane and heating at moderate temperatures (70-130 °C) led to formation of the $Pd^{IV}(R)(H)$ products (**B**). The extent of the reaction (eq 1) was determined by addition of Br_2 or I_2 to the cooled mixture, followed by GLC determination of the quantity of RBr or RI generated. Yields as high as 36% were reported. The formation of Pd(II) alkyl products (eq 2) were determined by the same method. Other chemical tests for the formation of $Pd^{IV}(R)(H)$ included reactions with carbon tetrachloride, acetyl chloride, and sodium acetate to produce chloroform, methyl ketones, and alkyl (or aryl)

acetates respectively. Isolation of the Pd(IV) products was not possible, leading only to reformation of the hydrocarbon and Pd(II) starting material. However, the authors provide IR and ^{1}H NMR data to suggest the presence of the palladium(IV) cyclohexyl hydride product in a mixture with the Pd(II) starting material.

Several aspects of this report force its data and conclusions to be viewed with skepticism. The initial surprise in this report is the stability of a Pd(IV) alkyl hydride. Pd(IV) is considerably less stable than Pt(IV) as suggested by the nominal M(II/IV) redox couples for the chloride salts: 1.29 versus 0.68 V, respectively. Recently, Pt(IV) alkyl hydride complexes[11] were found to be stable only at low temperatures (e.g., -80 °C). That related Pd(IV) complexes would be stable at room temperature (as reported) is quite remarkable.

The alkyl group in **B** is apparently susceptible to both nucleophilic *and* electrophilic cleavage based on its reaction with acetyl chloride and sodium acetate. Again, this is rather surprising considering alkyl groups on platinum(IV) are remarkably resistant to attack by electrophiles, and a Pd(IV) complex should be even less reactive.[12] One further unexpected result is the reactivity order of various C–H bonds, with weaker bonds activated preferentially to stronger ones. Other studies of C–H oxidative addition identify the opposite trend,[13] which arises from cleavage of stronger C–H bonds being more than compensated by comparatively stronger M–C bonds. There does not appear to be any reason for palladium(II) to violate this behavior.

Finally, the spectroscopic evidence for the Pd(IV) alkyl hydride seems rather dubious. Only scant ^{1}H NMR data is reported for the palladium(IV) cyclohexyl hydride product: no data is included for the cyclohexyl group

bound to palladium, while the reported hydride peaks are 800 Hz wide! No ^{31}P NMR data is provided for the new complex (**B**) despite being provided for the Pd(II) starting material. Furthermore, the IR absorption band reported for the Pd–H stretch should have been verified by identifying the corresponding Pd–D band produced upon activation of deuterated alkanes.

In short, their data does not appear to overwhelmingly support their conclusion. Nevertheless, because of the potential impact of this chemistry, it was decided to re-examine this work. Below a series of experiments are described which suggest (not unexpectedly) that C–H oxidative addition by the reported Pd(II) complexes (**A**) does not occur. Instead, the results appear to be an artifact of the product identification methods.

Results Obtained upon Reinvestigation

Several experiments published by Vedernikov et al. were carried out to confirm or refute the reported C–H activation of alkanes by $(PPh_3)_2PdX_2$ complexes. These studies permitted re-evaluation of both the direct (spectroscopic) and indirect (reactivity) evidence for Pd(IV) hydride products in the reaction mixture.

In the first experiment, an attempt was made identify Pd(IV) hydrides by ^1H NMR spectroscopy. Heating $(PPh_3)_2PdBr_2$ in cyclohexane at 100 °C for one hour is supposed to yield the Pd(IV) product in 26% yield. Despite following the published procedures, no evidence for a Pd–H species was obtained based on a ^1H NMR spectrum of the reaction products in C_6D_6. No resonances were observed in the upfield region (-20 – 0 ppm) where palladium hydrides typically appear. Infrared spectroscopic data was not examined.

Despite this negative evidence, the potential formation of a palladium hydride product was examined chemically. Carbon tetrachloride often reacts with transition metal hydride to generate chloroform and the corresponding metal chloride. Vedernikov et al. used this reaction to confirm formation of a palladium hydride in their reactions. Consequently, $(PPh_3)_2PdBr_2$ was heated in toluene under conditions reported to produce the Pd(IV) hydride in 26% yield. CCl_4 was added to the cooled reaction mixture, and the resulting solution was examined by gas chromatography for the formation of chloroform. None was observed. An identical experiment using cyclohexane rather than toluene also revealed no formation of chloroform.

The reaction between toluene and $(PPh_3)_2PdBr_2$ in the presence of K_2CO_3 was reported to proceed in 80% yield, producing $(PPh_3)_2Pd(CH_2Ph)Br$ (**1**) according to eq 2. This product was synthesized independently[14] in order to compare its spectroscopic data with any products generated in the C–H activation reaction. However, attempts to reproduce this reaction were unsuccessful; no formation of a benzylpalladium(II) product was observed.

As stated earlier, Pt(IV) alkyl hydrides *are* known and are often generated by protonation of the corresponding alkylplatinum(II) complexes.[11,15-22] Based on the apparent stability of the Pd(IV) complexes described by Vedernikov et al., it should be possible to prepare them by addition of HX to alkylpalladium(II) complexes. In our studies of platinum complexes, (tmeda)$Pt(CH_3)_2(H)Cl$ was found to be much more stable than phosphine-ligated complexes.[11] Consequently, protonation of both $(PPh_3)_2Pd(CH_2Ph)Cl$ (**1**) and (tmeda)$Pd(CH_3)_2$ (**2**) was examined at low temperatures. Whereas protonation of **1** should lead to a $Pd^{IV}(R)(H)$ product that was reported in the paper, addition of HX to **2** might be expected to

generate a more stable product. Upon addition of HCl to a solution of **1** in toluene-d_8, formation toluene is observed at -30 °C. There is no evidence for an intermediate in this reaction. Methane is immediately generated upon addition of HCl to a CD_2Cl_2 solution of **2** at -80 °C. Such results argue strongly against the reported stability of $Pd^{IV}(R)(H)$ complexes. None of the data acquired thus far supports the viability of reversible C–H activation by Pd(II) (eq 1). Nevertheless, the results provide only negative evidence, making it difficult to draw definitive conclusions.

Most of the reported data supporting C–H activation is derived from halogenolysis of various reaction mixtures.[10] Consequently some of these experiments were re-examined. Addition of Br_2 or I_2 to the product mixtures upon completion of the reaction (eq 1) generates R–Br or R–I products. Because Br_2 and I_2 are known to cleave palladium–carbon bonds,[23,24] the authors suggest the quantity of R–Br or R–I produced reflects the yield of C–H oxidative addition. Formation of R–Br was, in fact, confirmed. Heating $(PPh_3)_2PdBr_2$ in toluene followed by addition of Br_2 to the cooled reaction mixture leads to formation of benzylbromide, based on GC analysis. Formation of cyclohexyl bromide was observed when an identical sequence was followed, using cyclohexane instead of toluene. Subsequent control experiments revealed that identical (or even greater) quantities of the R–Br product can be generated by addition of Br_2 directly into the alkane in the absence of the palladium! Free radical halogenation of alkanes is, of course, well known.[25] Importantly, radical reagents selectively attack weaker C–H bonds, consistent with the selectivity patterns reported in this paper.

Conclusion

The above experiments suggest that the reported C–H activation by $(PPh_3)_2PdX_2$ complexes is erroneous. All attempts to verify the formation of $Pd^{IV}(R)(H)$ through spectroscopic and chemical means were unsuccessful. Furthermore, the anomalous selectivity pattern for the reactivity of C–H bonds is an artifact arising from free radical halogenation of the hydrocarbons when attempting chemical detection of alkylpalladium species. Thus, the initial skepticism facing this report, unfortunately, appears justified.

Experimental

General Considerations. The experimental procedures provided in the original report were followed as closely as possible when attempting to reproduce published results. All solvents were dried prior to use: toluene was pre-dried over 4Å molecular sieves and then distilled from sodium; cyclohexane was distilled from Na/benzophenone; CD_2Cl_2 was distilled from fresh CaH_2 and stored over 4Å molecular sieves. NMR spectra were obtained using a Bruker AM500 NMR spectrometer. Gas chromatograms were obtained using an Perkin-Elmer 8410 gas chromatograph equipped with a 15 m SE-30 capillary column. $(PPh_3)_2Pd(CH_2Ph)Cl$ (**1**)[14] and $(tmeda)Pd(CH_3)_2$ (**2**)[26] were prepared according to methods described in the literature.

Low temperature protonation of reactions $(PPh_3)_2Pd(CH_2Ph)Cl$ (1) and $(tmeda)Pd(CH_3)_2$ (2). Compound **1** (6 mg, 0.008 mmol) was added to an NMR tube equipped with a J. Young valve (Wilmad Glass Company) and dissolved in toluene-d_8. Upon degassing the solution and freezing it in liquid nitrogen, HCl (5 equivalents) was condensed into the tube using a gas bulb. The solution was then warmed to -78 °C and dropped in a pre-cooled NMR probe

to monitor the reaction. For the other reaction, (tmeda)Pd(CH_3)$_2$ (**2**) (0.031mmol, 8 mg) was added to an NMR tube equipped with a screw cap and silicone/PTFE septum (Wilmad Glass Company). After dissolving **2** in CD_2Cl_2, the solution was cooled to -78 °C. HCl (175 mL, 1.8 M in Et_2O-d_{10}, 0.31 mmol) was then added via syringe. The NMR tube was placed into a pre-cooled probe to monitor the reaction.

Halogenolysis experiments: In order to verify the production of alkyl bromides upon addition of Br_2 to the C–H activation reaction mixtures, the following experiments were performed. (PPh_3)$_2$$PdBr_2$ (8 mg, 0.01 mmol) was suspended/dissolved in 1 mL of the hydrocarbon (cyclohexane or toluene) and sealed (using a Kontes 4mm PTFE valve) in a glass "bomb." The mixture was then heated to 100 °C in an oil bath for one (cyclohexane) or three hours (toluene). After cooling the reaction mixture, a solution of Br_2 in CCl_4 was added and mixed thoroughly with the contents in the "bomb." The mixture was filtered through alumina to remove palladium compounds and then were shaken with an aqueous solution of NaS_2O_3 to remove excess Br_2. The organic layer was tested for the presence of alkyl bromides by gas chromatography. Because the corresponding alkyl bromides were, in fact, observed, the following control experiments were carried out. First, the identical reaction sequence was followed except the reaction mixtures were not heated. And second, the Br_2 solution was added directly to the hydrocarbon solvents in the absence of palladium complexes. In both cases the alkyl bromide products were observed.

Attempted C–H activation in the presence of K_2CO_3. (PPh_3)$_2$$PdBr_2$ (16 mg, 0.02 mmol) was dissolved in toluene (2 mL), and K_2CO_3 (28 mg, 0.2 mmol) was added to the solution. This mixture was heated at 130 °C for 8

min during which time the color changes from light to deep yellow and the K_2CO_3 turns black. Upon cooling to room temperature and filtering the mixture through celite, the toluene was removed under vacuum. A subsequent ^1H NMR spectrum of the resulting solid reveal no formation of $(PPh_3)_2Pd(CH_2Ph)Br$. The reaction was also attempted with 500 mg of K_2CO_3 (3.6 mmol) since the original report does not specify how this reaction was carried out. In this case, the reaction mixture turns dark brown upon heating. However, after work-up no $(PPh_3)_2Pd(CH_2Ph)Br$ is observed in the ^1H NMR spectrum.

References

1) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984.

2) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: New York, 1995.

3) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109-8111.

4) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421-428.

5) Sen, A.; Gretz, E.; Oliver, T. F.; Jiang, Z. *New J. Chem.* **1989**, *13*, 755-760.

6) Periana, R. A.; Taube, D. J.; Evitt, E. R.; Loffler, D. G.; Wentrcek, P. R.; Voss, G.; Masuda, T. *Science* **1993**, *259*, 340-343.

7) Gol'dshleger, N. F.; Kresova, E. I.; Moravskii, A. P. *Kinet. Katal.* **1991**, *32*, 1023.

8) Nelson, K. T.; Foger, K. In *Natural Gas Conversion II*; Curry-Hyde, H. E.; Howe, R. F., Eds.; Elsevier: New York, 1994; pp 545-550.

9) Vargaftik, M. N.; Stolarov, I. P.; Moiseev, I. I. *J. Chem. Soc., Chem. Commun.* **1990**, 1049-1050.

10) Vedernikov, A. N.; Kuramshin, A. I.; Solomonov, B. N. *J. Chem. Soc., Chem. Commun.* **1994**, 121-122.

11) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961-5976.

12) Luinstra, G. A.; Wang, L.; Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Organomet. Chem.* **1995**, *504*, 75.

13) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

14) Ros, R.; Lenarda, M.; Boschi, T.; Roulet, R. *Inorg. Chim. Acta* **1977**, *25*, 61-64.

15) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.

16) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* Submitted for publication.

17) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13.

18) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

19) Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745-8746.

20) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209-1217.

21) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845-2847.

22) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684-5689.

23) Coulson, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 200–202.

24) Wong, P. K.; Stille, J. K. *J. Organomet. Chem.* **1974**, *70*, 121–132.

25) March, J. *Advanced Organic Chemistry;* 3rd ed.; John Wiley & Sons: New York, 1985.

26) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907-2917.