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Pt-Mechanistic Study of the β-Hydrogen Elimination from Organoplatinum(II) Enolate Complexes

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Abstract

A detailed mechanistic investigation of the thermal reactions of a series of bisphosphine alkylplatinum(II) enolate complexes is reported. The reactions of methylplatinum enolate complexes in the presence of added phosphine form methane and either free or coordinated enone, depending on the steric properties of the enone. Kinetic studies were conducted to determine the relationship between the rates and mechanism of β-hydrogen elimination from enolate complexes and the rates and mechanism of β-hydrogen elimination from alkyl complexes. The rates of reactions of the enolates were inversely dependent on the concentration of added phosphine, indicating that β-hydrogen elimination from the enolate complexes occurs after reversible dissociation of a phosphine. A normal, primary kinetic isotope effect was measured, and this effect was consistent with rate-limiting β-hydrogen elimination or C-H bond-forming reductive elimination to form methane. Reactions of substituted enolate complexes were also studied to determine the effect of the steric and electronic properties of the enolate complexes on the rates of β-hydrogen elimination. These studies showed that reactions of the alkylplatinum enolate complexes were retarded by electron-withdrawing substituents on the enolate and that reactions of enolate complexes possessing alkyl substituents at the β-position occurred at rates that were similar to those of complexes lacking alkyl substituents at this position. Despite the trend in electronic effects on the rates of reactions of enolate complexes and the substantial electronic differences between an enolate and an alkyl ligand, the rates of decomposition of the enolate complexes were similar to those of the analogous alkyl complexes. To the extent that the rates of reaction of the two types of complex are different, those involving β-hydrogen elimination from the enolate ligand were faster. A difference between the identity of the rate-determining step for decomposition of the two classes of complexes and an effect of stereochemistry on the selectivity for β-hydrogen elimination are possible origins of the observed phenomena.

Introduction

β-Hydrogen elimination from transition metal alkyl complexes is an important fundamental transformation of organometallic chemistry.[1–3] This process is a common elementary reaction of transition metal alkyl complexes and typically occurs with a low barrier in many catalytic processes. In some cases, it is a productive step in transition metal catalyzed processes, such as Mizoroki-Heck reactions,[4,5] transition metal-catalyzed cycloisomerizations,[6,7] alkane dehydrogenations,[8,9] oxidative heterofunctionalizations of alkenes,[10] alkene isomerizations,[11] and "chain walking" during alkene polymerizations that form highly branched polyolefins,[12] In other cases, β-hydrogen elimination is an unproductive side reaction. For example, β-

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Supporting Information Available. Detailed experimental procedures, spectral data, and X-ray diffraction data for platinum complexes. An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

hydrogen elimination can lead to reduction, rather than C-C bond formation, during cross-couplings involving alkyl nucleophiles[13] or alkyl electrophiles.[14]

Mechanistic studies of β-hydrogen elimination from transition metal alkyl complexes have shown that the process is fastest when the complex possesses an open coordination site for binding of the alkene product and when a *syn*-coplanar arrangement of the metal-carbon bond and the carbon-hydrogen bond at the β-position can be adopted. Some of the first detailed mechanistic studies in this area involved the thermolysis of bisphosphine platinum(II) dialkyl complexes.15,16 These systems yielded alkenes, alkanes, and platinum(0) complexes. Kinetic data implied that these reactions, under most conditions,17 proceed through a pathway involving initial ligand dissociation, followed by β-hydrogen elimination, and eventual C-H bond-forming reductive elimination.

β-Hydrogen elimination is also involved in many catalytic processes that occur through transition metal enolate complexes as either a productive step or a step that can form side products. For example, β-hydrogen elimination from enolate complexes is a productive step of processes such as Saegusa oxidations of silyl enol ethers[18] and Mizoroki-Heck reactions of acrylates,[4,5] whereas it is a possible unproductive side reaction of processes such as transition metal-catalyzed α-arylations[19,20] and conjugate additions of organoboranes to enones.[21,22] Although the mechanisms of the decompositions of metal alkyl complexes have been studied in detail, much less information has been gained on the rates and mechanism of the decomposition of transition metal enolate complexes. With few exceptions,[23,24] published studies on the structure and stability of transition metal enolate complexes have involved those that lack β-hydrogens.[25,26] Such complexes are rarely the types of enolate species involved in the catalytic processes described above.

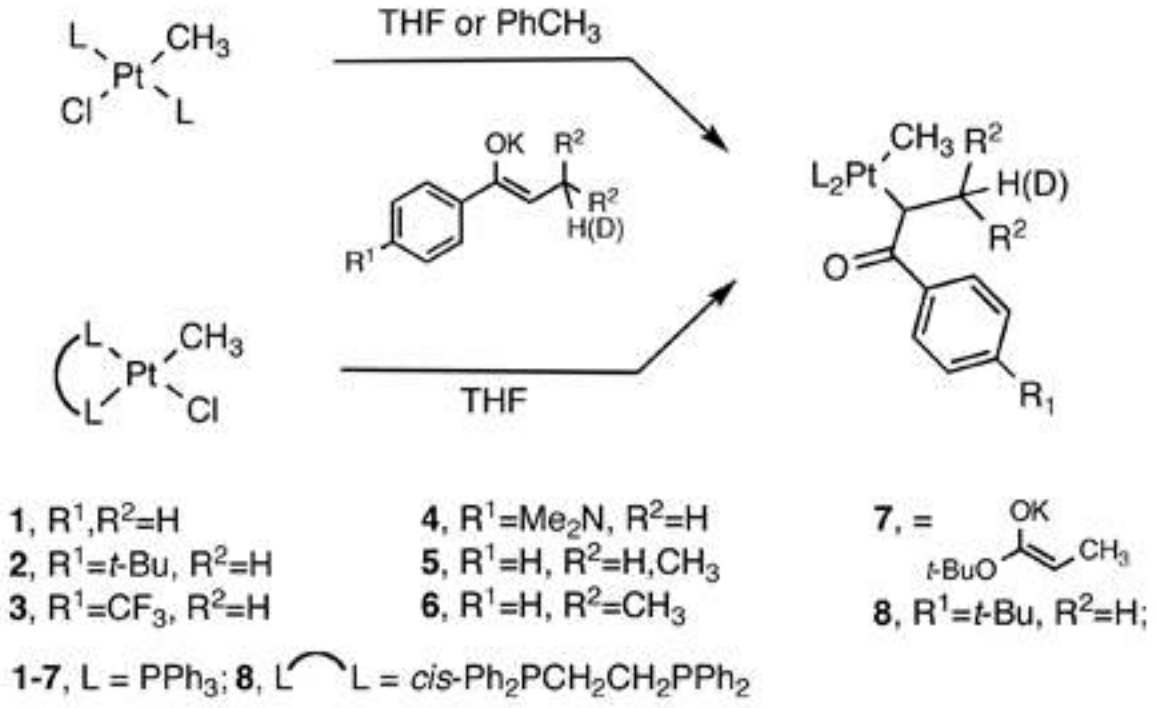
The reactants and products of β-hydride eliminations from transition-metal enolate complexes possess electronic properties that are distinct from the reactants and products of β-hydrogen eliminations from transition-metal alkyl complexes. In contrast to simple alkyl complexes, enolate complexes contain an electron-withdrawing substituent on the α-carbon. In contrast to simple alkenes, which result from β-hydrogen elimination from alkyl complexes, the enone and enoates that result from β-hydrogen elimination from enolate complexes, are conjugated and electron poor. These different properties can affect the thermodynamics and ultimately the rates of β-hydrogen elimination. An electron-withdrawing group on the α-carbon typically stabilizes alkyl complexes, whereas an electron-withdrawing group on an olefin typically stabilizes binding of the olefin to a low-valent metal center. Thus, it is not clear if the electronic differences between enolate and alkyl complexes will make the rates of β-hydride eliminations from enolate complexes faster, slower, or similar to those of analogous eliminations from alkyl complexes.

To address these questions regarding β-hydrogen elimination we have conducted a study of the rates and mechanism of the thermolysis of organoplatinum enolate complexes of the general formula [$Pt(PPh\text{-}_3)_2(CH_3)$(enolate)]. Data from these studies can be compared to those from classic studies on the thermolysis of (bisphosphine)Pt(II) dialkyl complexes. We show that the electronic effects on the rates of β-hydrogen elimination are pronounced, but that several counterbalancing effects lead to a complex relationship between the rates of reaction of platinum(II) enolate and alkyl complexes. Our data demonstrate that electron-withdrawing groups retard the rate of β-hydrogen elimination within a homologous series of compounds, but that the rates of β-hydrogen eliminations from complexes of enolates ligands are similar or even faster than β-hydrogen eliminations from complexes containing more electron-donating alkyl groups.

Results

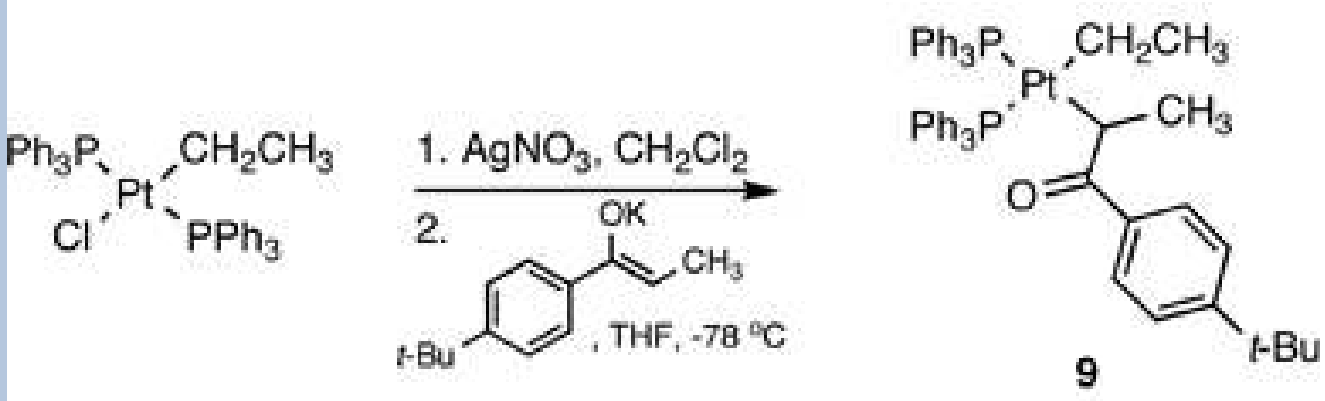
1. Synthesis and Structures of PPh_3-Ligated Alkylplatinum Enolate Complexes

The platinum enolates for this study were synthesized by reaction of $(PPh_3)_2Pt(CH_3)(Cl)$[27] or *cis*-$[Pt(dppe)(CH_3)(Cl)]$[28] (dppe=$Ph_2PCH_2CH_2PPh_2$) with the appropriate potassium enolate in THF or toluene (eq 1). Following aqueous workup, the crude platinum(II) enolate complexes were isolated by trituration with pentane, followed by filtration. In some cases, the products were further purified by silica gel column chromatography. The yields of pure product obtained from these substitution reactions ranged from 33–88%. The lower yield of formation of some of the complexes was due to incomplete conversion of the starting halide, but sufficient material was obtained after purification, even in these cases. Once formed, the complexes were obtained as white powders that could be stored at room temperature without need for an inert atmosphere.



(1)

A platinum enolate complex containing both alkyl and enolate β-hydrogens was also synthesized by a slightly modified protocol (eq 2). $[Pt(PPh_3)_2(Et)(Cl)]$ was treated with $AgNO_3$ in CH_2Cl_2 to abstract the halide, followed by removal of AgCl and addition of the enolate at −78 °C. After isolation, complex **9** was isolated in 40% yield.



(2)

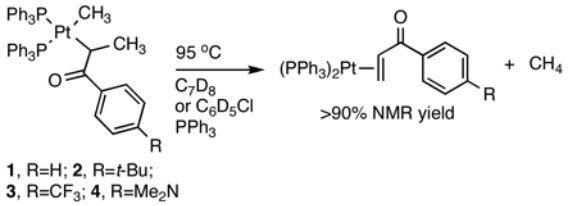
Enolate complexes **1**-**9** existed as the C-bound isomers in solution, as determined by ^{1}H NMR spectroscopy. The methine α-protons were observed between δ2.58 and δ4.23, and these protons in all of the complexes exhibited clear coupling to the platinum nucleus. ^{31}P NMR spectroscopy clearly showed that all complexes were isolated as the *cis* isomers. The ^{31}P NMR spectra consisted of two doublets possessing platinum satellites.

The known bisphosphine-ligated dialkylplatinum(II) complex $(PPh_3)_2Pt(CH_2CH_3)(CH_3)$[16] (**10**) was also prepared to compare the rates of the thermal reactions of the platinum(II) enolate complexes with those of the directly analogous dialkyl complexes. This complex was generated by the reaction of EtMgCl with [Pt(COD)(Cl)(Me)] to form [Pt(COD)(Et)(Me)], followed by addition of PPh3. Attempts to prepare an α-branched alkyl complex, such as [Pt $(PPh_3)_2(CH_3)$(*i*-Pr)], led to formation of linear alkyl complexes. The reaction of [Pt(COD) (CH_3)(Cl)] with *i*-PrMgBr, followed by ligand exchange with PPh_3, led to a compound assigned by ^{1}H NMR spectroscopy to be $[Pt(PPh_3)_2(CH_3)$(*n*-Pr)], instead of the intended isopropyl complex $[Pt(PPh_3)_2(CH_3)$(*i*-Pr)].

The structure of propiophenone enolate **1** was determined by single crystal X-ray diffraction (Figure 1). Enolate complex **1** adopts a slightly distorted cis square-planar geometry containing a C-bound enolate. The sum of the four angles about the platinum center is 361°. The P-Pt-P angle is significantly larger than 90° (97.8°), while the C(1)-Pt-C(2) angle is somewhat smaller than 90° (86.8°), presumably because of the greater steric demands of the phosphine ligand. The carbonyl group of the enolate is oriented away from the metal, indicating the absence of any degree of κ^2 or η^3 structure of the enolate. The structure of **1** allows a direct comparison of the M-C bond lengths to an enolate and a simple alkyl group. The Pt-C(1) bond to the enolate carbon (2.16Å) is slightly longer than that to the methyl group (2.10Å), presumably because of the smaller size of the methyl group.

2. Reactivity of the Alkylplatinum Enolate Complexes

The isolated platinum(II) enolates were heated in toluene-d_8 or chlorobenzene-d_5 at 95 °C in the presence of 7.5–15 mM PPh_3, and the conversions were followed by ^{1}H NMR spectroscopy. These reactions are summarized in eq 3 and eq 4. In general, these reactions generated methane, along with coordinated enone, free enone, or a combination of the two. As described in more detail later, these products would be expected to form from a sequence of β-hydrogen elimination, followed by reductive elimination of methane from the resulting hydrido alkyl olefin complex. Small amounts of free ketone were observed, presumably resulting from some reaction with an adventitious proton source.

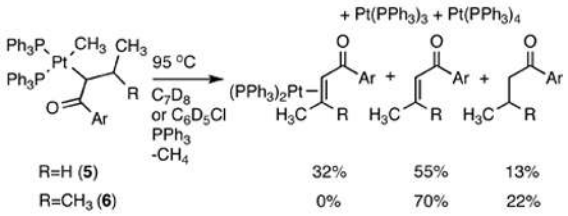


(3)

The products from heating of enolate complexes derived from propiophenone derivatives **1-4** are shown in eq 3. These complexes, as well as the enolate **7** derived from *tert*-butylpropionate, smoothly yielded methane and the η^2-bound, monosubstituted alkene complexes in yields >90%, as determined by ^{1}H NMR spectroscopy.

The products from heating of the enolate complexes containing alkyl substituents on the β carbon are shown in eq 4. These reactions also occurred with high mass balance and high combined yields of the enone. These reactions formed the platinum enone complexes, the combination of free enone and phosphine-ligated Pt(0),[29] and small amounts of free ketone. For example, heating of the butyrophenone complex **5** at 95 °C for 1 h in the presence of 7.5 mM PPh_3 in C_7D_8 formed the corresponding η^2-bound enone complex (32%), along with the combination of free enone (55%) and $Pt(PPh_3)_n$ (n=3 30%, n=4 14%). Free ketone from some type of protonolysis was formed in a small 13% yield. The same reaction at 95 °C in C_6D_5Cl in the absence of added ligand for 30 min provided the η^2-bound enone complex in 50% yield, along with the combination of free enone (43%) and $Pt(PPh_3)_n$. A small amount (ca 5%) of butyrophenone was also formed.

Heating of isovalerophenone enolate complex **6** at 95 °C for 5 h in the presence of 15 mM PPh_3 in C_6D_5Cl formed 70% free enone and $Pt(PPh_3)_n$, with 22% isovalerophenone as side product. The same reaction in the absence of PPh_3 yielded 61% free enone and $Pt(PPh_3)_n$, with only a small amount (8%) of isovalerophenone. Thus, the yields of the products from β-hydrogen elimination are high; the different coordinating abilities of the unsubstituted and substituted enones and different concentrations of phosphine lead to the different distribution of free and coordinated enone.



(4)

In an attempt to identify the source of the hydrogen atom or proton involved in the production of the ketone product, reactions conducted with added labeled ligand and reactions of labeled complexes were performed. Thermolyses of enolate complexes **5** and **6** were conducted in the presence of PPh_3-d_{15}. The starting platinum complex exchanges free and coordinated ligands faster than it undergoes β-hydrogen elimination. Thus, if the hydrogen in the ketone were derived from free or coordinated ligand, some deuterium should be present in this product. However, the ketone product did not contain a measurable amount of deuterium enrichment

as determined by integration of ^{1}H NMR spectra. Enolate complexes **6-*d*$_5$** and **6-*d*$_3$** containing deuterium in the ketone aryl group and platinum methyl group shown in Figure 2 also did not yield isovalerophenone that was enriched in deuterium.

To determine if trace H_2O in the reaction mixture was capable of hydrolyzing the enolate complexes, the thermolysis of isovalerophenone enolate **6** was performed in the presence of 5.0 equiv of D_2O. Upon heating at 95 °C for 45 min in the presence of 15 mM PPh_3, the enolate was completely consumed. Isovalerophenone-α-d_1 and *cis*-$(PPh_3)_2Pt(CH_3)(OD)$.[30] were formed as products. Therefore, hydrolysis of the enolate complexes could be responsible for ketone production, if the small amount of accompanying hydroxo product is either undetected or decomposes to form Pt(0) phosphine products.

To determine if free enone is generated reversibly during the overall process, we conducted reactions in the presence of an enone that is different from the one formed by β-hydrogen elimination. More specifically, thermolysis of ester enolate complex **7** in the presence of 5 equiv of phenyl vinyl ketone proceeded without the accumulation of detectable amounts (by ^{1}H NMR spectroscopy) of a propiophenone enolate complex. Thus, any free enone must be generated irreversibly in the overall reaction sequence.

3. Kinetic Studies

Initial kinetic studies were performed to determine if the pathway for reaction of the methylplatinum enolate complexes paralleled that for reaction of the related alkyl complexes. If so, then the differences in rates of reaction of alkyl and enolate complexes can be explained with a single reaction manifold. To determine if the β-hydrogen elimination process occurs after formation of an open coordination site, we measured the effect of added ligand on the rate of the reaction, and to determine if a step involving C-H bond cleavage is rate limiting, we measured a deuterium kinetic isotope effect.

The rate constants for reactions of the methylplatinum enolatecomplexes were measured by ^{1}H NMR spectroscopy on samples containing 1,3,5-trimethoxybenzene as standard. Solutions of complexes **1-10** (15 mM) were heated in toluene-d_8 or chlorobenzene-d_5 at 95 °C in the spectrometer probe, and spectra were accumulated using an automated data acquisition program every 2–3 min for at least 3 half-lives. A clear exponential decay of the platinum complex was observed, indicating that the reactions were first-order in the platinum complexes. A representative plot of this decay is provided as Figure SI in the supporting information.

The dependence of $1/k_{obs}$ on added PPh_3 is shown in Figure 3. These data indicate that the reaction is inverse first order in phosphine. This order in added ligand demonstrates that reversible dissociation of ligand occurs before the rate-limiting step, and this order of events is consistent with a standard pathway for β-hydrogen elimination involving C-H bond cleavage after generation of an open coordination site.

Studies of a complex containing the chelating phosphine DPPE further support a mechanism involving dissociation of ligand prior to β-hydrogen elimination. No conversion of DPPE-ligated methylplatinum enolate **8** was observed after heating at 95 °C for 15 min. Under these conditions in the absence of added PPh_3, the analogous complex **2** containing monodentate ligands underwent full conversion to the elimination products.

The effect of phosphine on the thermolysis of methyl ethyl complex **10** was investigated qualitatively. The decomposition of **10** in the presence of 15 and 150 mM added PPh_3 was conducted side by side. The reaction in the presence of the higher concentration occurred much more slowly than that in the presence of the lower concentration of phosphine. These data

indicate that complex **10** reacts by a mechanism similar to that of $[Pt(PPh_3)_2Bu^n_2]$ in previous work[31] and the PPh_3-ligated enolate complexes **1-7** in the current work.

Kinetic isotope effects were obtained by examining the thermolysis of a deuterated enolate complex (**2-*d*$_3$**) containing a fully deuterated methyl group in the β-position. A primary isotope effect of $k_H/k_D = 3.2 \pm 0.1$ was deduced by comparison of the rate constant for reaction of **2-*d*$_3$** with that for thermolysis of **2**. The kinetic isotope effect on the thermolysis of the alkyl complex **10** was also obtained using complex **10**-d_5 containing a fully deuterated ethyl group. A primary isotope effect of $k_H/k_D = 2.5 \pm 0.1$ was obtained from the rate constant for reaction of **10**-d_5 and for reaction of **10**.

4. Electronic and Steric Effects on the Reaction Rates of Enolate Complexes

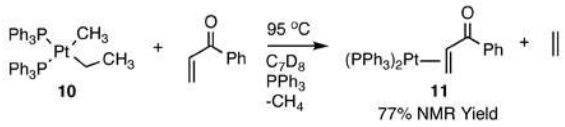
Studies on the series of alkylplatinum enolate and dialkylplatinum complexes allowed an assessment of the effect of the enolate electronic and steric properties on the rate of the thermolysis. To reveal this effect, we measured the rate constants for the thermolysis of the series of methylplatinum enolate complexes in the presence of PPh_3. These data are summarized in Table 1. These rate data demonstrate that the electronic properties of the enolate ligands significantly affect the observed reaction rate.

To study the electronic effects of substituents on the rates of reactions of the enolate complexes, the rates of reaction of *p*-*t*-Bu propiophenone enolate **2**, *p*-CF_3 propiophenone enolate **3** and ester enolate **7** were measured first in C_7D_8 solvent. Comparison with the unsubstituted enolate **1** was not possible due to its lack of solubility in C_7D_8. The reactions of the enolates at 95 °C in C_7D_8 in the presence of 7.5 mM PPh_3 were followed by ^{1}H NMR spectroscopy (Table 1). In general, complexes containing less electron-donating enolate ligands underwent β-hydrogen elimination more slowly than those containing more electron-donating enolate ligands. In more quantitative terms, enolate complex **3** containing an electron-withdrawing CF_3 group in the *para* position of the aryl ring of the enolate reacted about 5 times more slowly than enolate complex **2** containing a *t*-Bu group at this position. Likewise, complex **7** containing a less σ-donating enolate derived from an ester (higher Taft σ-parameter32·33) reacted about 3-times more slowly than did **2**.

The effects of additional substituents were measured by comparing the rate constants for reactions of unsubstituted enolate **1** with those for reactions of *p*-*t*-Bu complex **2** and *p*-Me_2N complex **4** in chlorobenzene solvent. This comparison was conducted on reactions in chlorobenzene to the lack of solubilities of **1** and **4** in toluene. The enolate complex **2** containing the electron-donating *p*-*t*-Bu reacted two times faster than the unsubstituted enolate complex **1**. In addition, *p*-Me_2N complex **4** reacted 2.5-times faster than complex **1**.

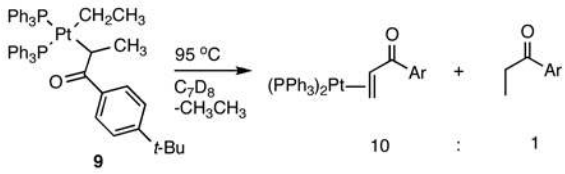
The effect of substitution on the β-carbon was revealed by comparing the rates of reaction of enolate complexes **1** and **2** that lack a substituent on the β carbon with enolate complexes **5** and **6** that contain one and two substituents on the β-carbon, respectively (Table 1). The rates of reaction of complexes **1** and **6** were compared because they were both soluble in C_6D_5Cl, while the rates of reaction of complex **2** and **5** were compared because they are both soluble in C_7D_8. The rates of the reactions of complex **1** and **6** at 95 °C in C_6D_5Cl were similar to each other, even though complex **6** contains two methyl substituents at the β-carbon. Additionally, the rates of the reactions of complexes **2** and **5** in C_7D_8 were similar to each other, even though complex **5** contains a methyl substituent on the β carbon. Thus, the effect of substitution at the β-carbon on the rates of β-hydrogen elimination was small; the reactions of enolates containing methyl, methylene, and methine hydrogens occurred at similar rates when other substituents were constant.

To compare the rates of the thermal reactions of alkylplatinum enolate complexes to those of directly analogous dialkyl complexes, we studied the thermal reaction of the methylplatinum ethyl complex $(PPh_3)_2Pt(CH_3)(CH_2CH_3)$[16] **10** (eq 5). This reaction was performed in C_7H_8 containing 15 mM PPh_3 and 75 mM phenyl vinyl ketone to trap the initial Pt(0) product. Previous studies examining the thermal reactions of bisphosphine platinum dialkyl complexes have shown that the addition of electron poor alkenes to the reaction has a negligible effect on the reaction rate at concentrations below 100 mM.[16] The products of the reaction were the $(PPh_3)_2Pt$ complex of phenyl vinyl ketone (77%), ethylene, and methane (eq 5). Dialkyl complex **10** reacted with a rate constant ($k_{obs} = 2.5 \times 10^{-4}$ s^{-1}, C_7D_8) that was approximately one-third of that of the reaction of the simple propiophenone-derived platinum enolate **2**.



(5)

Finally, we examined the thermal reaction of enolate **9** containing both alkyl and enolate β-hydrogens (eq 6) and a deuterium-labeled version of **9**. The thermolysis of complex **9** led to the formation of the η^2-bound enone complex and ethane as the major products in approximately 65% yield after 15 min. A small amount of free ketone was also produced, but no ethylene complex was observed in parallel with this free ketone. The ratio of the enone complex to the free ketone was about 10:1. The thermal reaction of complex **9**-d_3 (Figure 4) containing an ethyl group deuterated at the β-position was also performed to probe for scrambling of the α and β positions of the ethyl group that could occur by reversible β-hydrogen elimination from the ethyl group. Monitoring of the reaction of this complex by ^1H NMR spectroscopy at 60 °C in C_6D_5Cl in the presence of 15 mM PPh_3 did not lead to the growth of ^1H NMR signals corresponding to the β-position of the ethyl group after approximately one half-life of the reaction ($t_{1/2}$ ~ 8 hr). Thus, scrambling of the α and β positions of the ethyl group does not appear to occur on the timescale of the β-hydrogen elimination process.



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Discussion

1. Mechanism of Thermal Reactions of the Alkylplatinum Enolates

The thermal reactions of bisphosphine dialkylplatinum(II) complexes had previously been shown to occur by multiple reaction pathways depending on the concentration of added phosphine. Whitesides[15] and Yamamoto16 reported that the reactions conducted in the absence of added phosphine proceed by rate-limiting dissociation of phosphine, followed by β-hydrogen elimination. Whitesides reported that reactions in the presence of low concentrations of excess phosphine occurr by reversible dissociation of ligand to yield a three-coordinate species that undergoes β-hydrogen elimination, followed by rate-limiting reductive

elimination. Both authors reported that the β-hydrogen elimination occurs in the presence of a high concentration of excess phosphine from the four-coordinate dialkyl complex. In this case the reaction was proposed to form a five-coordinate η^2-bound alkene intermediate that undergoes rate-limiting dissociation of alkene or rate-limiting reductive elimination of alkane. Our qualitative kinetic data on the reaction of the methyl ethyl complex **10** are consistent with these data. At the modest concentrations of added phosphine used in our study, the reactions of complex **10** are inhibited by added phosphine, and these data indicate that the reaction occurs by reversible dissociation of ligand, followed by β-hydrogen elimination and C-H bond-forming reductive elimination.

Five potential pathways for thermal reactions of the alkylplatinum enolate complexes in the current study are shown in Scheme 1. Path A depicts reaction without dissociation of phosphine to form a five-coordinate olefin hydride complex. Path B shows initial, irreversible dissociation of phosphine. Paths C–E show initial reversible dissociation of phosphine prior to β-hydride elimination, but they differ in the identity of the rate-determining step that follows reversible dissociation of phosphine. Path C involves irreversible rate-determining β-hydride elimination, followed by reductive elimination, Path D involves reversible β-hydride elimination, followed by rate-limiting dissociation of alkene, and Path E involves reversible β-hydrogen elimination, followed by rate-determining reductive elimination.

Reaction by Path A would be independent of the concentration of added phosphine and would occur with a primary isotope effect. Reaction by Path B would also be independent of the concentration of added phosphine, but would occur without a primary isotope effect. Reaction by Path C would occur with a primary isotope effect and would be expected to occur more slowly or at a similar rate with increased alkyl substitution at the enolate β-carbon. Reaction by Path D should occur without a primary isotope effect and should occur faster from complexes containing a greater degree of alkyl substitution at the enolate β-carbon (a more substituted alkene should dissociate faster than a less substituted alkene). Reaction by Path E should occur with a primary isotope effect and should occur faster from complexes containing alkyl substitution at the enolate β-carbon because the rate-determining reductive elimination of methane would involve a more sterically congested platinum(II) complex. Reaction by a modified path E involving a reversible dissociation of alkene prior to the rate-determining reductive elimination of methane would also occur faster from complexes containing alkyl substitution at the enolate β-carbon and would lead to a new enolate complex when the reaction is run in the presence of a labeled enone.

Our data are inconsistent with reaction by Paths A, B, D, and the modified path E. The dependence of the reaction rate on the concentration of added phosphine is inconsistent with Paths A or B. The observation of a primary isotope effect and the similar rate of reaction of the β-substituted and unsubstituted enolate complexes are inconsistent with reaction by Path D, The lack of formation of a new platinum enolate complex when the reaction is run in the presence of an added enone is inconsistent with the modified path E.

Instead, the inverse dependence of the rate on the concentration of phosphine and the primary isotope effect are consistent with reaction by Path C or E. The observation of a primary kinetic isotope effect is consistent with rate-determining β-hydrogen elimination (Path C) or reductive elimination (Path E). In contrast to many small or inverse isotope effects on reductive elimination to form C-H bonds,[34] the kinetic isotope effect on the rate of reductive elimination from $[Pt(PPh_3)_2(Me)(H)]$ was shown previously to be a substantial 3.3.[35] Nevertheless, we favor reaction by Path C for two reasons. First, the complexes containing electron-withdrawing *p*-substituents on the aromatic ring of the enolate complexes reacted more slowly than those containing electron-donating *p*-substituents. Because electron-poor alkene ligands facilitate reductive eliminations from group 10 d^8 metal complexes,36 electron-withdrawing

substituents would more likely accelerate, rather than decelerate, reactions occurring by rate-limiting reductive elimination. Second, the rates of reaction of the β-substituted and unsubstituted enolate complexes were similar, and increased substitution on the alkene ligand would be expected to increase steric congestion and increase the rate of reductive elimination.[37] Thus, the decrease in rate of reactions of complexes containing less electron-donating enolate ligands and the similar rates of reaction of β-substituted and unsubstituted enolate complexes are more consistent with reaction by Path C involving rate-determining β-hydrogen elimination than they are with reaction by Path E involving rate-determining reductive elimination of alkane from an enone-bound hydridoplatinum(II) methyl complex.

2. Electronic Effects on β-Hydride Eliminations Involving Transition Metal Enolates

Electronic properties of reactive and ancillary ligands have been shown to have a large effect on the rates of many fundamental organometallic reactions, including oxidative additions, reductive eliminations, migratory insertions, nucleophilic attack onto π-systems, and α-eliminations.[38] Less precise information has been reported on the effect of the electronic properties of alkyl ligands on the rate of β-hydrogen elimination, but a few pieces of data imply that the electronic properties of substituents on an alkyl group can influence the rate of β-hydrogen elimination. For instance, fluoroalkyl complexes of late transition metals tend to be stable, despite possessing β-hydrogens.[39,40] In these cases, the rate of β-hydride elimination is thought to decrease due to an increase in the strength of the metal alkyl bond.[41]

As noted in the introduction, different predictions for the rates of reactions of the enolate complexes in the current work could be made based on the electronic properties of the starting enolates and the initial or final enone complex products. First, polarization of the metal-carbon bond by the carbonyl group would be expected to strengthen the metal-carbon bond of the enolate complexes,[42] and this factor would be expected to increase the barrier to β-elimination from enolate complexes, relative to the barrier for β-hydrogen elimination from simple alkyl complexes. Second, η^2-bound complexes formed between electron-poor alkenes and π-basic metals can be particularly stable due to π-backbonding.[43] However, the initial product of β-hydrogen elimination from an alkylplatinum enolate complex is a platinum(II) complex, not the final platinum(0) complex. Previous studies of the electronic effects on binding of olefins to [Pt(pyridine)Cl_2] showed that electron-rich olefins bind more strongly to this neutral Pt(II) species than electron-poor olefins.[44] Although the ligands in this complex are different from those in the current work, this previous study does suggest that binding of a simple alkene to neutral platinum(II) fragments, such as [Pt(PPh_3)(Me)H], are preferred over binding of an electron-poor enone or acrylate. Thus, the effect of the carbonyl group could lead to several different effects on the rate of the reaction, and it was not clear which effect would be most important.

Potential effects of these properties on the energetics of the reaction coordinate for β-hydrogen elimination from platinum alkyl and enolate complexes are shown in Figure 5. These reaction coordinates can be used to represent either the energetic difference between platinum complexes containing a more electron-donating alkyl ligand (Pt-R) and less electron-donating enolate ligand (Pt-R′), or the difference between platinum complexes containing more electron-donating (Pt-R) and less electron-donating (Pt-R′) enolate ligands. Reaction profile A depicts a larger effect of the electron-withdrawing group on the stability of the starting platinum(II) complexes than on the stability of the initially formed, platinum(II) alkene complex. Profiles B and C depict smaller effects of the electron-withdrawing group on the stability of the starting complex than on the initially formed alkene complex. In profile B the complex of the electron-poor alkene is more stable than the complex of the electron-rich alkene, whereas in profile C, the complex of the electron-rich alkene is more stable than the complex of the electron-poor alkene. The relative stabilities in profile B are typically observed when back-donation into the

alkene dominates electron donation from the alkene to the metal, whereas the relative stabilities in profile C are typically observed when donation from the alkene to the metal dominates over back-donation into the alkene. Profile D depicts a similar electronic effect on the starting platinum complexes and the alkene-bound products. In profile A and C, the rate of β-hydrogen elimination from the Pt-R complex would be faster than from the Pt-R′ complex in which R′ is less electron donating than R. In profile B, the rate of β-hydrogen elimination from the Pt-R complex would be slower than from the Pt-R′ complex. In profile D, β-hydrogen elimination would occur with similar rates from both complexes, despite the difference in properties of the starting complexes.

Our kinetic data on the reactions of the propiophenone-derived enolates **1-4** substituted with *p*-H, *p*-*t*-Bu, *p*-NMe_2, and *p*-CF_3 substituents, as well as the ester enolate **7** are most consistent with differences in rates that result from a combination of the energetic changes depicted in profiles A and C in Figure 5. Electron-withdrawing groups are known to strengthen M-C bonds,[42] and electron-poor alkenes typically bind more weakly to Pt(II) complexes. These effects would both contribute to slower rates of β-hydrogen elimination from the complexes containing the more electron-poor enolates.

Although electron-withdrawing groups were clearly shown to retard the rate of β-hydrogen elimination from alkylplatinum enolate complexes when studied in a systematic fashion, the rates of β-hydrogen elimination from dialkylplatinum complexes, such as complex **10,** were slower than those from the simple propiophenone-derived enolate complex **2**. These relative rates for reactions of alkyl and enolate complexes that appear to override the electronic properties of alkyl and enolate ligands could result from compensating steric and electronic effects or by a change in the rate-determining step between the overall sequence for decomposition of the enolate and alkyl complexes. The greater steric properties of the enolate complex could increase the equilibrium for dissociation of phosphine and could provide a greater driving force for conversion of the enolate ligand to a hydride ligand and bound enone. At the same time, the electronic properties of the enolate ligand should make the thermodynamics for the elementary β-hydrogen elimination from the enolate complex less favorable than from the alkyl complex. The electron-withdrawing group on the alkyl ligand of the starting material strengthens the M-C bond and the electron-withdrawing group on the alkene in the initial product weakens binding of the alkene to platinum(II). These compensating steric and electronic effects could then lead to similar rates of reaction of the alkylplatinum enolate and dialkylplatinum complexes.

Alternatively, the relative rates of reaction of the enolate and alkyl ligands can be rationalized by a change in rate-determining step (Figure 6). We have provided evidence that the rate-determining step of the reaction of platinum enolates to form alkane and free enone is β-hydrogen elimination. However, kinetic data reported previously on the reactions of dialkylplatinum complexes in the presence of added phosphine have indicated that β-hydrogen elimination is reversible and subsequent reductive elimination or dissociation of alkene is rate limiting.[15,16] We observed a primary kinetic isotope effect in our studies of the reaction of dialkylplatinum complex **10** in the presence of PPh_3 ($k_H/k_D = 2.5 \pm 0.1$). This value is similar to the value reported by Whitesides ($k_H/k_D \approx 3$) for the reaction of $(Et_3P)_2PtEt_2$ in the presence of PEt_3 for which reductive elimination was proposed to be the rate-determining step and is similar to the kinetic isotope effect of 3.3 ± 0.3 reported by Halpern for the reductive elimination from $[Pt(PPh_3)_2(Me)(H)]$.[35]

The scenario in Figure 6 involving two reaction profiles possessing two different rate-determining steps shows graphically how a change in rate-determining step can account for the similar rates for the reactions of the dialkylplatinum complexes and the alkylplatinum enolate complexes. The alkyl hydride complex resulting from β-hydrogen elimination from

the enolate group of the alkylplatinum enolate complex contains an electron-withdrawing enone ligand, whereas the alkyl hydride complex resulting from β-hydrogen elimination from the dialkyl complex contains a more electron-donating alkene ligand. Because reductive elimination tends to be faster from complexes containing less electron-donating ligands,[36] reductive elimination from the complex containing the enone as ligand should be faster than from the complex containing the alkene as ligand. This difference in the identity of the alkene would favor a pathway involving *reversible* β-hydrogen elimination from a dialkylplatinum complex to form an alkene-ligated hydridoplatinum alkyl complex and a pathway involving *irreversible* β-hydrogen elimination from an alkylplatinum enolate complex to form an enone-ligated hydridoplatinum alkyl complex.

Consistent with reversible β-hydrogen elimination from the dialkyl complex, attempts to prepare a triphenylphosphine-ligated methylplatinum isopropyl complex [$Pt(PPh_3)_2(Me)(i\text{-}Pr)$] led to formation of the *n*-propyl complex. The *n*-propyl complex presumably forms in this reaction by rapid β-hydrogen elimination from the less stable *iso*-propyl complex to form the linear alkyl analog. A similar isomerization was reported by Yamamoto in attempts to synthesize [$Pt(PPh_3)_2(Et)(i\text{-}Pr)$] through the reaction of $(PPh_3)_2Pt(Et)(Cl)$ with *i*-PrLi.[16] Regardless of the origin of the similar rates of reaction of the alkylplatinum enolate and dialkylplatinum complexes, the electronic effect on the rate of the elementary β-hydrogen elimination reaction does not directly translate into a difference in rate for the overall process.

Intermolecular vs Intramolecular Comparisons of the Rates of β-Hydrogen Elimination—Although the rate of reaction of methylplatinum enolate and methylplatinum alkyl complexes were similar, reaction of an ethylplatinum enolate complex greatly favored formation of products resulting from β-hydrogen elimination from the enolate ligand. The reaction of complex **9** containing an ethyl and an enolate ligand formed almost exclusively alkane and the corresponding enone complex.

We considered that the high selectivity for the formation of products from β-hydrogen elimination of the enolate ligand in the ethylplatinum enolate complex could again result from differences in rate-determining step. In this case, β-hydrogen elimination involving the alkyl ligand would be reversible and β-hydrogen elimination from the enolate ligand would be irreversible. To test this hypothesis, we prepared the partially deuterated ethylplatinum enolate complex in which the methyl hydrogens of the alkyl ligand contained deuterium. If β-hydrogen elimination from the ethyl ligand were reversible, then the hydrogens in the α-position would exchange into the β position. This scrambling was not observed, and the absence of this scrambling is inconsistent with this explanation for the predominant formation of products by β-hydrogen elimination from the enolate ligand.

Instead, this selectivity can be explained by the stereochemistry of the unsaturated intermediate that undergoes β-hydrogen elimination. As shown in Scheme 2, dissociation of phosphine from the enolate complex should favor formation of the unsaturated intermediate **14**, due to the larger trans effect of the stronger σ-donating ethyl group and the greater steric effect of the larger enolate group. Because the open coordination site in this intermediate would be located *cis* to the enolate ligand, β-hydrogen elimination of the enolate ligand would occur, and the η^2-bound enone complex would predominate. Again, this result most generally indicates that the rates of β-hydrogen elimination are similar enough that separate factors, such as relative rates of ligand dissociation, can control the rates of β-hydrogen elimination from two different types of alkyl ligands.

Conclusion

We report a set of compounds that has allowed a particularly detailed analysis of the electronic effects on the reactions of alkyl and enolate complexes by the common sequence of β-hydrogen elimination followed by reductive elimination. The mechanism of the reactions of the alkylplatinum enolate complexes involves initial ligand dissociation, followed by rate-determining β-hydride elimination. Because the pathways involving initial dissociation of ligand parallel those for β-hydrogen elimination from dialkylplatinum complexes, one can directly compare the relative rates for reactions of these two classes of compounds. Our data show that the rate of β-hydrogen elimination was measurably retarded by the presence of electron-withdrawing groups on the enolate. These data were obtained on systems in which β-hydrogen elimination was the rate-limiting step. This electronic effect can be attributed to both increased stabilization of the enolate complex and decreased stabilization of the η^2-bound alkene products due to the electron-withdrawing group attached to the α-carbon in the starting complex. At the same time, we showed that methylplatinum enolate complexes and methylplatinum ethyl complexes react with similar rates, and to the extent that the rates of their reactions differ, the methylplatinum enolate complex reacts faster. This seemingly contradictory result can be explained by a difference in rate-determining step for reaction of the enolate and alkyl complexes as a result of the identity of the olefin bound to the alkylplatinum hydride intermediate. We also determined that the product from heating an alkylplatinum enolate complex resulted from β-hydrogen elimination from the enolate ligand, rather than from the alkyl ligand. This observation can be rationalized by the preferred stereochemistry of the unsaturated intermediate prior to β-elimination. In the most general sense, our data show that the electronic effects on β-hydrogen elimination from substituted alkyl complexes are measurable within a homologous series of complexes, but that these effects can be overridden by the relative rates of reactions occurring before and after the elementary β-hydrogen elimination process.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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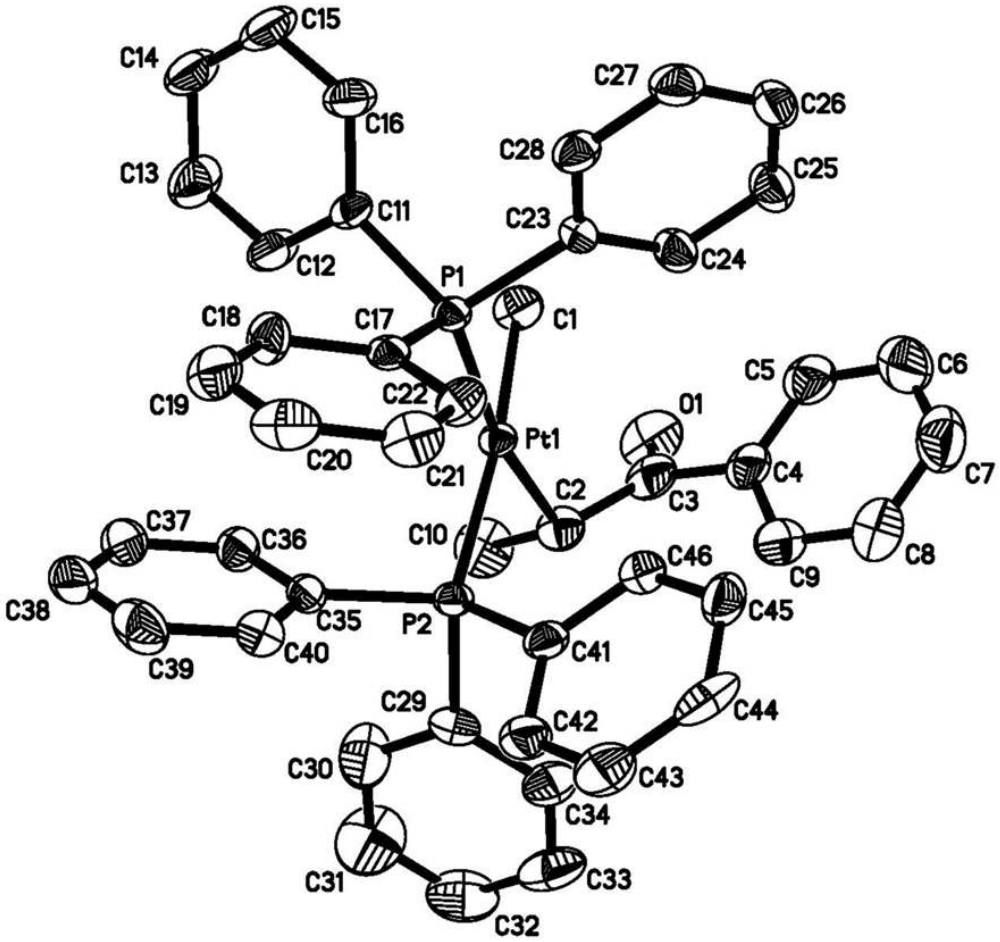
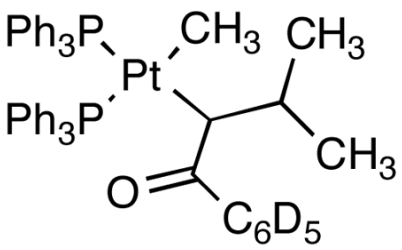
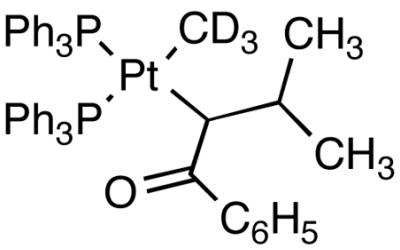


Figure 1.

ORTEP diagram of unsubstituted propiophenone-derived platinum enolate complex **1** with 35% ellipsoids. Selected distances (Å) and angles (°): Pt1 C1 2.101(8), Pt1 C2 2.156(8), Pt1 P1 2.2997(18), Pt1 P2 2.3112(19), C2 C3 1.464(13), C2 C10 1.498(13), C3 C4 1.508(12), O1 C3 1.236(11), C1 Pt1 C2 86.8(4), C1 Pt1 P1 85.4(3), C2 Pt1 P1 169.2(2), C1 Pt1 P2 171.9(3), C2 Pt1 P2 90.9(3), P1 Pt1 P2 97.79(7), C3 C2 C10 113.0(8), O1 C3 C2 122.2(10), O1 C3 C4 117.9(9).



6-*d*$_5$



6-*d*$_3$

Figure 2.
Deuterium-labeled platinum(II) enolates used to study the source of ketone products.

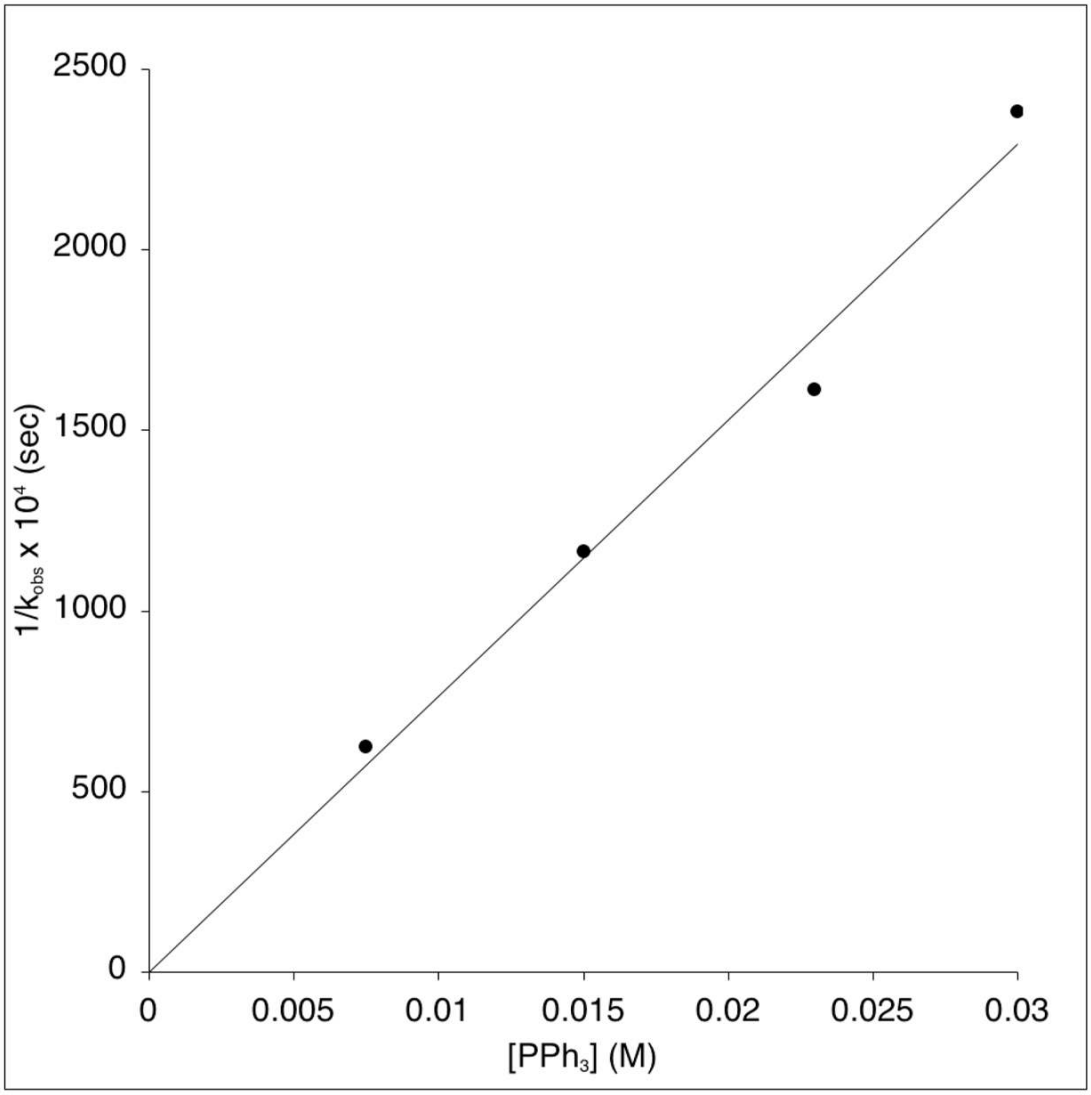


Figure 3.
Plot of $1/k_{obs}$ vs [PPh_3] for the thermolysis of *p*-*t*-Bu propiophenone-derived enolate **2** in toluene-d_8 at 95 °C.

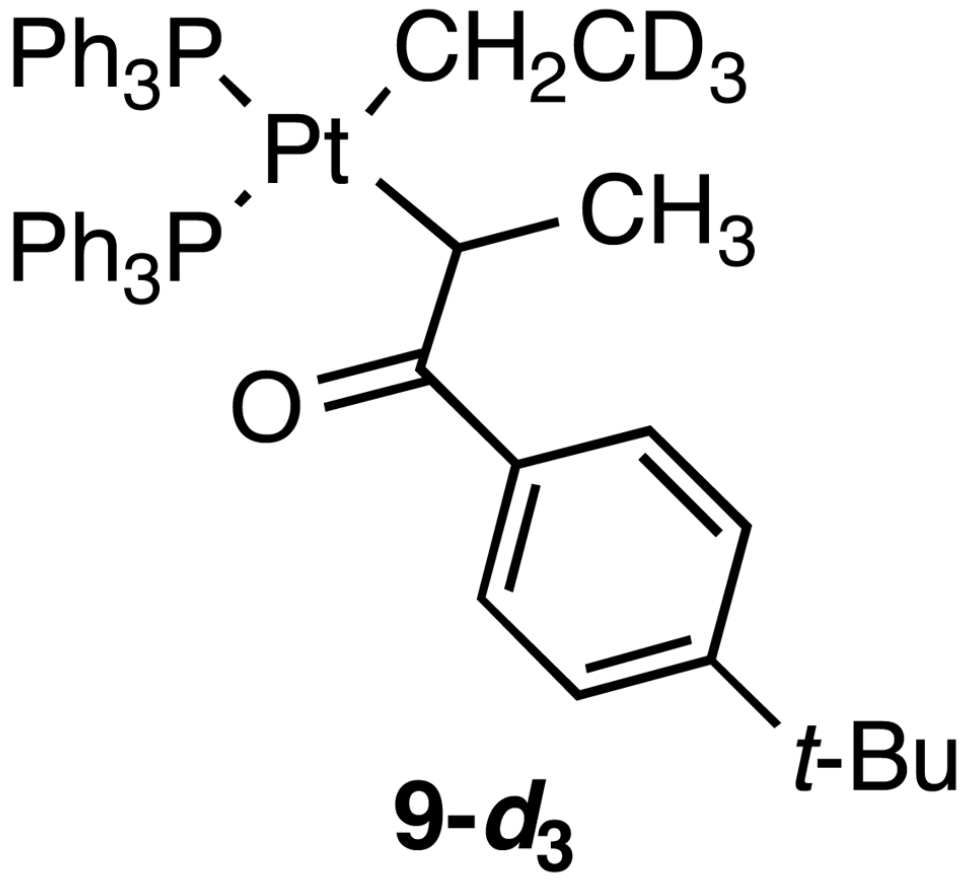


Figure 4.
Partially deuterated ethylplatinum enolate complex **9-d$_3$**.

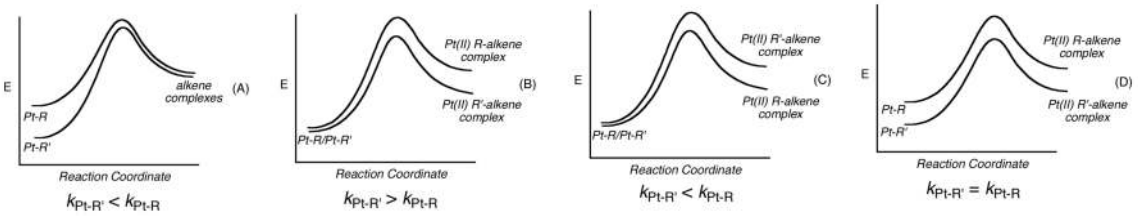


Figure 5.

Four energy profiles for the effect of electronics on the β-hydride elimination from enolates and alkyl complexes to form intermediate olefin complexes. R = more electron-donating X-type ligand, R′ = less electron-donating X-type ligand.

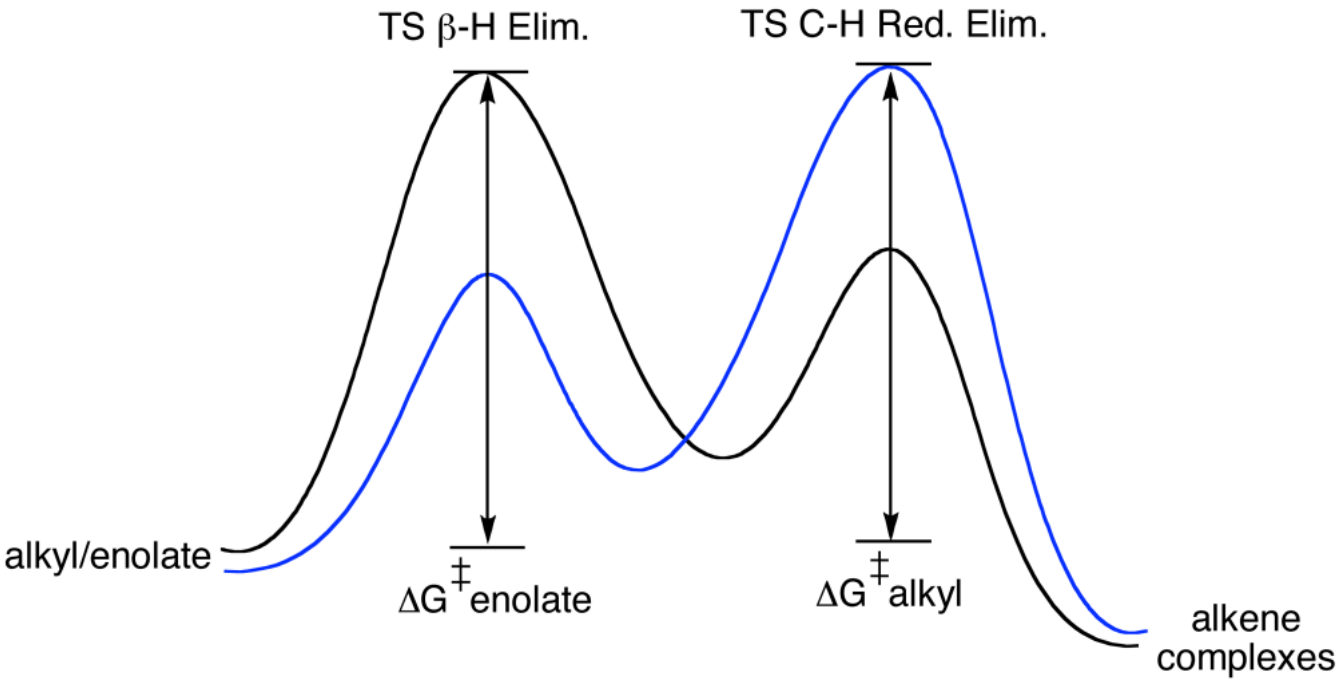
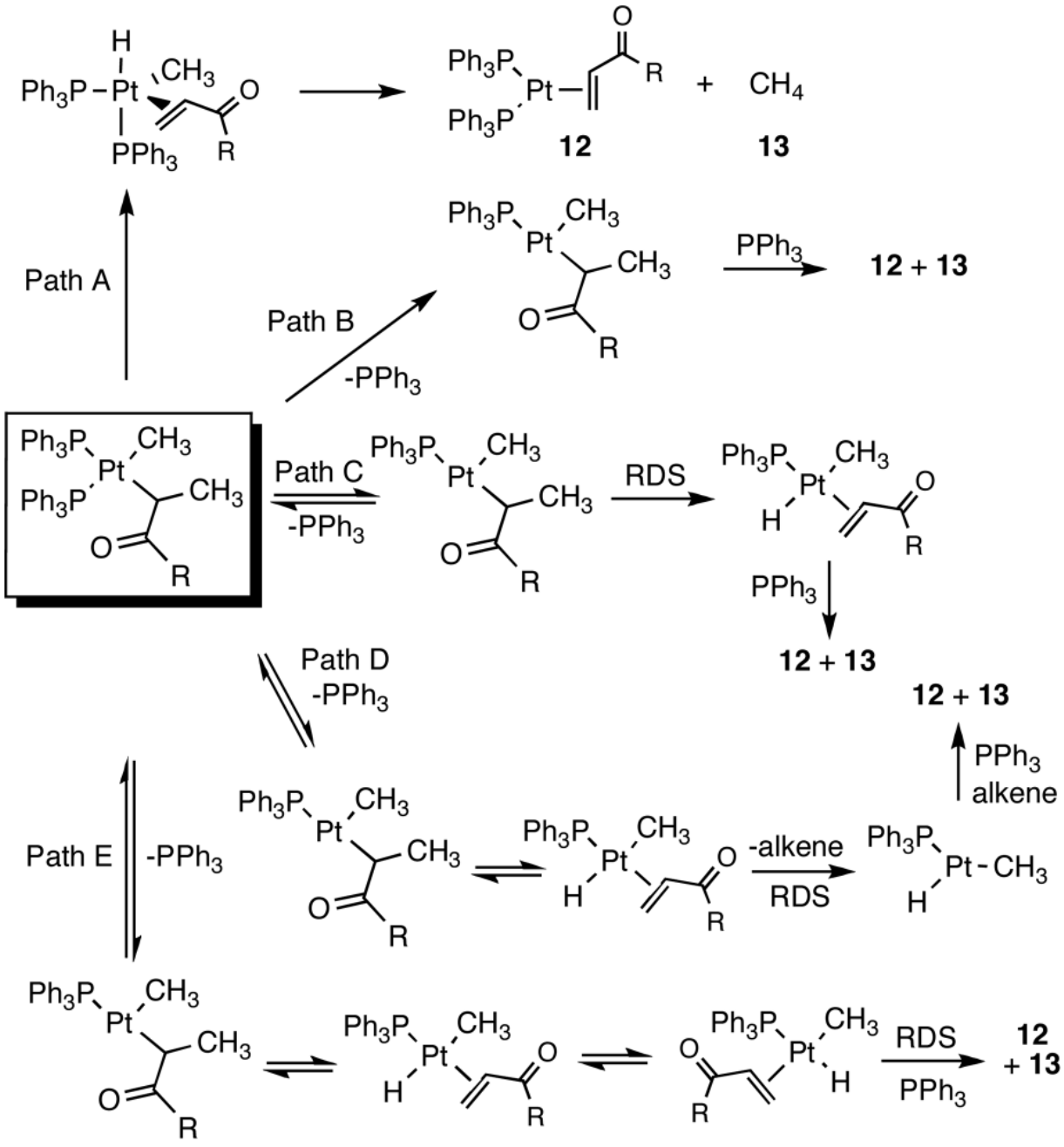
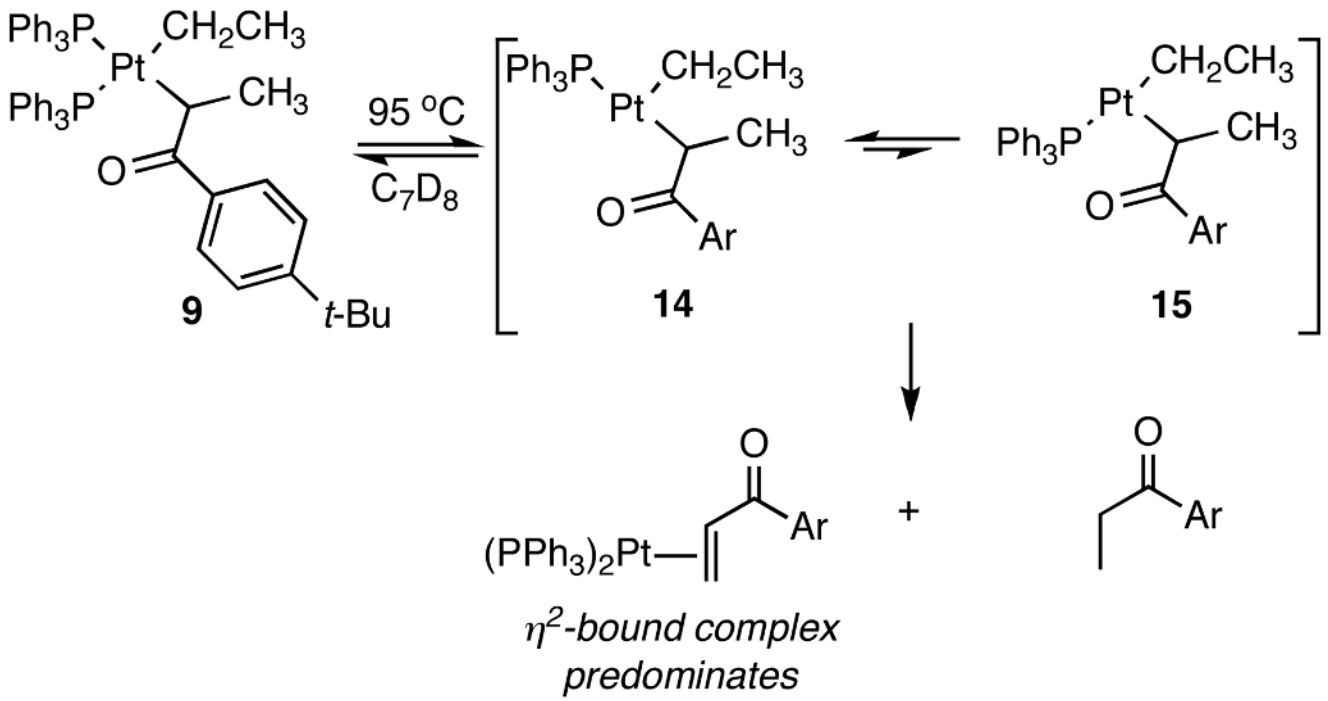


Figure 6.
Reaction profiles leading to similar relative rates of elimination from alkylplatinum enolate and alkyl complexes due to a change in the rate-determining step.



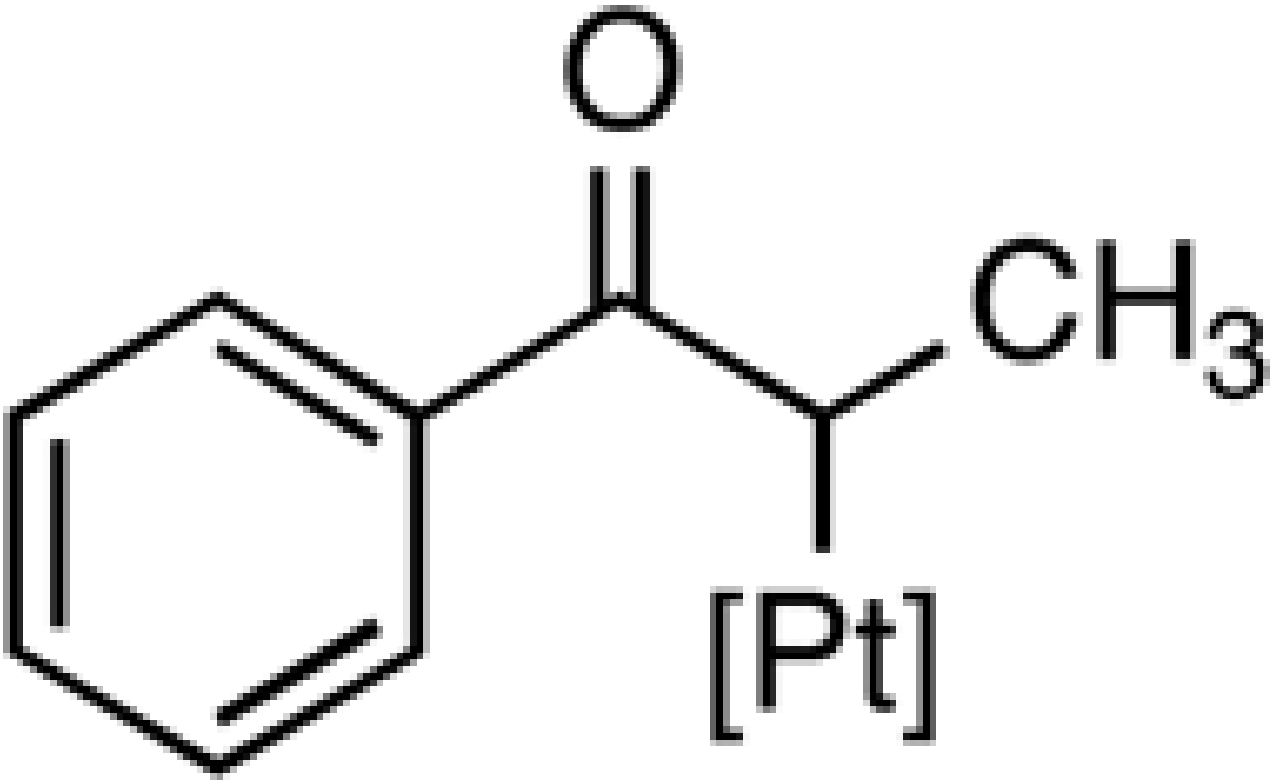
Scheme 1.



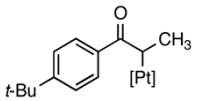
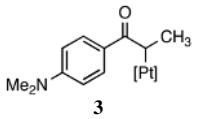
Scheme 2.

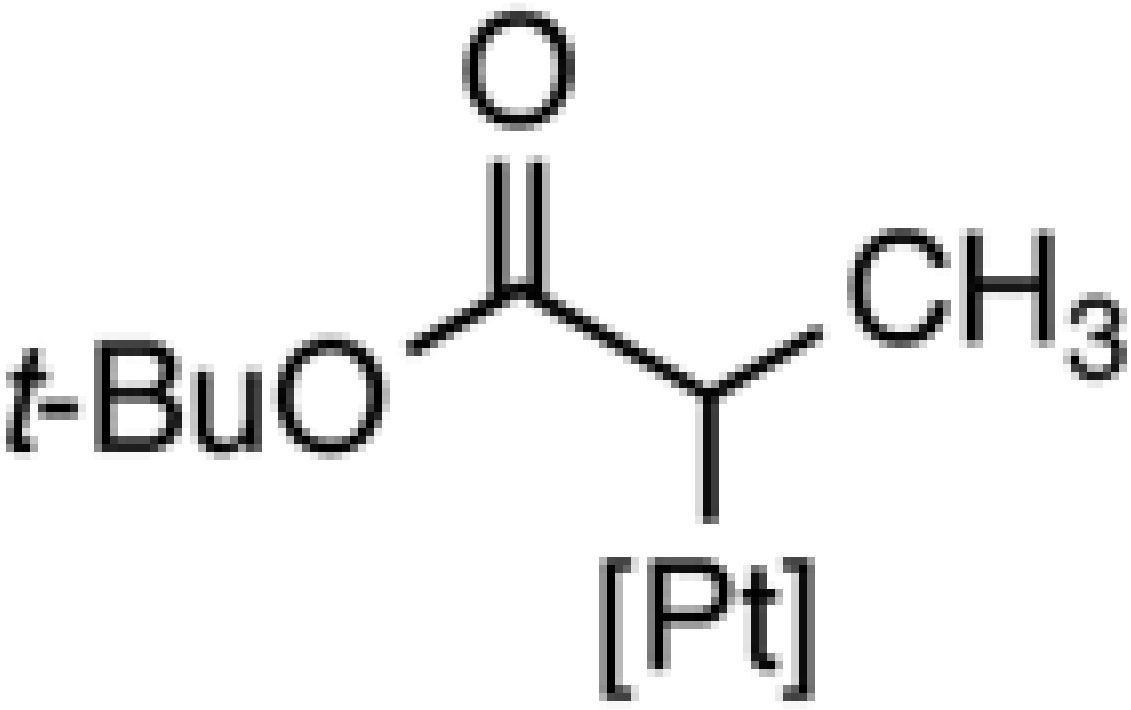
Table 1

Structural Effects on the Rate Constants of Reaction of Pt(II) Enolate Complexes at 95 °C in Toluene-d_8.[a]

Complex	k_{obs} ×
	2.3 (C

1

Complex	k_{obs} ×
 **2**	16 (C 8.6 (C 4.6 (C
 **3**	3

Complex	k_{obs} ×
 **4**	5.8 (C

[a] [Pt] = $(PPh_3)_2Pt(CH_3)$, k_{obs} ± 5–10%

[b] $[PPh_3]$ = 7.5 mM

[c] $[PPh_3]$ = 15 mM