Formation and Reductive Elimination of a Hydridoalkylplatinum(IV) Intermediate upon Protonolysis of an Alkylplatinum(II) Complex

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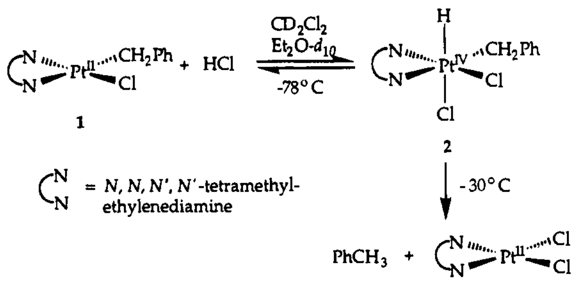
More than 20 years ago, Shilov et al. discovered the remarkably selective oxidation of alkanes by aqueous platinum salts.[1] We[2] (and others[3-6]) have elucidated some of the mechanistic features of this process. However, the details of the first step—electrophilic activation of the alkane by platinum(II) to generate an alkylplatinum(II) intermediate—remain unclear.

We chose to examine the microscopic reverse of this activation process by investigating the protonolysis of an alkylplatinum(II) complex, (tmeda)Pt(CH$_2$Ph)Cl (**1**) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine). Two limiting mechanisms can be considered for this reaction: protonation at platinum, generating a Pt^{IV}(R)(H) intermediate which reductively eliminates R−H, and protonation at the platinum alkyl bond, leading to direct liberation of R−H. Intermediate mechanisms (e.g., anion-assisted electrophilic attack) are also possible.[7,8] Previous studies of such reactions have led to several (sometimes contradictory) mechanistic proposals.[9-11] Unfortunately, only indirect evidence (such as kinetic analysis, isotope effects, and competition experiments) was available in those studies. We report here the direct observation of a Pt^{IV}(R)(H) species which subsequently reductively eliminates R−H.[12]

Addition of excess HCl (as a Et$_2$O-d_{10} solution) to a solution of **1** in CD$_2$Cl$_2$ at −78 °C results in complete conversion to the oxidative addition product, (tmeda)Pt(CH$_2$Ph)(H)Cl$_2$ (**2**), as identified by ^{1}H NMR spectroscopy. Upon warming the reaction to −30 °C, the reductive elimination of toluene from **2** proceeds rapidly and is accompanied by precipitation of (tmeda)PtCl$_2$ (Scheme 1). The most distinctive characteristic of **2** is its platinum(IV) hydride resonance in the ^{1}H NMR spectrum that appears at −24 ppm (CD$_2$Cl$_2$) with its associated ^{195}Pt satellites ($^1J_{Pt-H}$ = 1230 Hz; ^{195}Pt 33.8% natural abundance).[13] Concomitantly, the resonances corresponding to the diastereotopic benzyl protons in **2** shift downfield and split into two doublets.[14]

Scheme 1



Oxidative addition of HCl is rapid and reversible, as shown by isotopic substitution. Protonation of **1** with DCl results in a ^{1}H NMR spectrum identical to that of **2** except for a greatly diminished hydride resonance.[15] Subsequent addition of a large excess of HCl results in the immediate growth of this peak.

As anticipated, toluene reductive elimination proceeds with a first-order dependence on [**2**]; however, the temperature dependence of the reaction revealed an unexpected negative entropy of activation,[16] suggesting that the reaction might not proceed via direct elimination from the six-coordinate alkyl hydride species. To examine the possibility of a five-coordinate intermediate arising from chloride dissociation, tetrabutylammonium chloride was added to the reaction mixture. Surprisingly, chloride is found to deprotonate **2** to generate starting material **1** and tetrabutylammonium bichloride (eq 1). The presence of the latter was supported by IR spectroscopy.[17]

$$\mathbf{2} + [NBu_4]Cl \rightleftharpoons \mathbf{1} + [NBu_4][Cl{-}H{-}Cl] \qquad (1)$$

Protonation of **1** with triflic acid in an attempt to directly prepare the five-coordinate [(tmeda)Pt(CH$_2$Ph)(H)Cl]$^+$ (**3**) results in the immediate formation of toluene with no observed intermediate at −80 °C. Furthermore, addition of triflic acid to a solution containing preformed **2** significantly decreases the thermal stability of the platinum(IV) complex: reductive elimination proceeds rapidly under these conditions, even at −60 °C. The reductive elimination rate exhibits a first-order dependence on [HOTf] (68−265 mM). A mechanism consistent with these results is shown in Scheme 2, the main implication being prerequisite dissociation of chloride to yield a labile five-coordinate platinum(IV) intermediate (**3**), which rapidly eliminates toluene.[18]

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(12) While we were preparing this manuscript, two other groups reported the preparation of similar species by treating platinum(II) dialkyl complexes with halotrimethylsilanes in wet organic solvent. Their resulting platinum(IV) dialkyl hydride species exhibit similar reactivity: (a) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J., personal communication.

(13) Other known platinum(IV) hydrides exhibit similar ^{1}H NMR features. See, for example: Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 854.

(14) ^{1}H NMR (CD$_2$Cl$_2$, −60 °C): δ 7.4 (m, 2 H, C$_6$H$_5$), 7.1 (m, 3 H, C$_6$H$_5$), 4.8 (d, 1 H, −CH$_a$H$_b$Ph, $^2J_{H_a-H_b}$ = 10 Hz, $^2J_{Pt-H}$ = 107 Hz), 3.2 (d, 1 H, −CH$_a$$H_b$Ph, $^2J_{Pt-H}$ = 92 Hz), 3.0 (s, 3 H, −NCH_3, $^3J_{Pt-H}$ = ~32 Hz), 2.9 (s, 3 H, −NCH_3, $^3J_{Pt-H}$ < 10 Hz), 2.8 (s, 3 H, −NCH_3, $^3J_{Pt-H}$ < 10 Hz), 2.7 (s, 3 H, −NCH_3, $^3J_{Pt-H}$ = ~56 Hz), −23.9 (s, 1 H, Pt−H, $^1J_{Pt-H}$ = 1230 Hz). (Resonances for the tmeda ethylene protons are obscured by the much larger methyl resonances in the same region.)

(15) The residual Pt^{IV}−H resonance likely arises from H/D exchange with protic sites on the glass surfaces, i.e., syringe, NMR tube, etc.

(16) The reductive elimination reactions follow first-order kinetics: [**2**] = 13 mM, [HCl] = 65 mM; temperature range, −43 to −24 °C; $\Delta H^\ddagger$ = 14.0 ± 2.5 kcal/mol; $\Delta S^\ddagger$ = −18.5 ± 7.0 eu.

(17) The solution FTIR spectrum was compared with a solid state IR spectrum of [NMe$_4$][Cl−H−Cl]: Waddington, T. C. *J. Chem. Soc.* **1958**, 1708.

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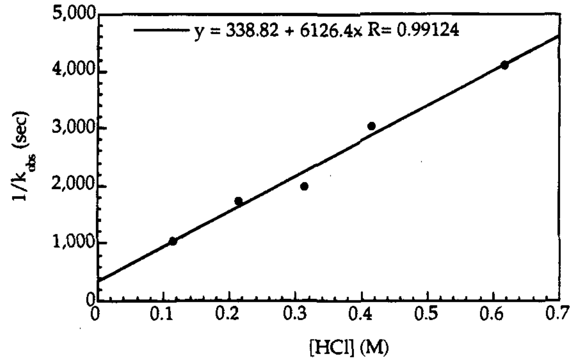
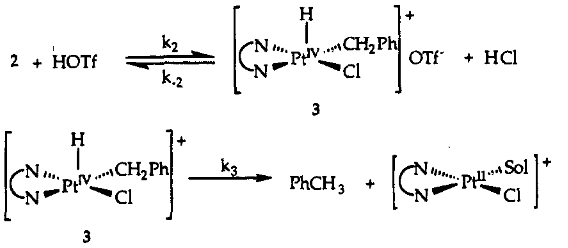


Figure 1. $1/k_{obs}$ vs [HCl] for reductive elimination of toluene from **2** in the presence of varying [HCl] and constant [HOTf] (a double-reciprocal plot of eq 2).

Scheme 2



Triflic acid, therefore, promotes chloride dissociation. Similarly, the nonprotic Lewis acid $SnCl_4$ also dramatically enhances the rate of reductive elimination from **2**. According to Scheme 2, HCl should inhibit formation of toluene in the presence of HOTf, and this effect was in fact observed, as shown by the "double-reciprocal" plot (Figure 1). Furthermore, the non-zero intercept suggests steady state (eq 2) rather than pre-equilibrium (eq 3) formation of **3**; i.e., k_3 is competitive with k_{-2}[HCl].

$$k_{obs}(\text{steady state}) = \frac{k_2k_3[\text{HOTf}]}{k_3 + k_{-2}[\text{HCl}]} \qquad (2)$$

$$k_{obs}(\text{pre-equilibrium}) = \frac{k_3K_2[\text{HOTf}]}{[\text{HCl}]} \qquad (3)$$

Isotope effects have been determined for this system using calibrated mixtures of HCl and DCl. The equilibrium deuterium isotope effect for the formation of **2** in CD_2Cl_2/Et_2O-d_{10} can be measured directly by integrating the Pt^{IV}-*H* peak relative to one of the benzyl protons; an *inverse* effect is obtained: $K_H/K_D = 0.51 \pm 0.05$ (−28 °C). The overall kinetic deuterium isotope effect can be determined by comparing the resulting concentrations of $PhCH_3$ versus $PhCH_2D$: $k_H/k_D = 1.55 \pm 0.10$ (0 and −28 °C).[19] Based on these values, a kinetic isotope effect for the reductive elimination of toluene from **2** can be calculated: $k_H/k_D = 3.1 \pm 0.6$. This value is similar to those found for the reductive elimination of platinum(II) alkyl hydrides.[20,21]

Thus, contrary to a previous proposal which suggested that proton attack at the platinum−carbon bond leads directly to a σ-complex intermediate/transition state,[11] we have established that hydridoalkylplatinum(IV) species can indeed mediate the protonolysis reaction. In a closely related system, we have recently observed isotopic exchange in $Pt^{IV}(CH_3)(D)$ prior to reductive elimination, demonstrating that σ-complexes do in fact mediate loss of R−H from Pt(II).[22] The above studies have further revealed that formation of a cationic platinum(IV) species via chloride dissociation greatly enhances the rate of reductive elimination. Although not unprecedented,[23] this result was somewhat unexpected, based on the variety of systems that do not exhibit this mechanistic feature.[20,24] Exploring the generality of this reactivity, particularly with respect to its implications for alkane activation by Pt(II), is the subject of ongoing studies in our laboratories.

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(18) As two reviewers pointed out, an alternative mechanism might involve "nonproductive" formation of **2** in solution; that is, the formation of hydrocarbon might arise from reversible dissociation of **2** into **1** and HCl, followed by direct attack by H^+ at the platinum−carbon bond. However, such a mechanism is inconsistent with both our kinetics and isotope effects. An expanded analysis will be presented in a forthcoming full paper.

(19) The isotope effect's lack of temperature dependence is consistent with a two-step mechanism in which the two steps have opposite temperature-dependent trends.

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(21) Whitesides and co-workers have observed similar isotope effects in the thermal decomposition of dialkylplatinum species which likely proceed through alkylhydridoplatinum intermediates. These isotope effects ($k_H/k_D \cong 3$), however, involve not only the effect arising from alkane reductive elimination but also from preliminary steps (e.g., oxidative addition). See: (a) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (b) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713. (c) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948. (d) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396.

(22) Treatment of $(tmeda)Pt(CH_3)_2$ with DCl in CD_3OD leads to formation of $(tmeda)Pt(CH_3)_2(D)Cl$ at −80 °C. Upon warming to −35 °C, deuterium is incorporated into the methyl positions without formation of methane. Methane is liberated only upon further warming. This result is consistent with an intermediate σ-complex lying lower in energy than the activation barrier for dissociation of methane. The details and implications of these results will be addressed in a forthcoming full paper.

(23) A few systems exhibiting alkyl hydride reductive elimination from an intermediate five-coordinate species have been observed previously: (a) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 649. (b) Basato, M.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972. (c) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227.

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