

The role of alkane coordination in C–H bond cleavage at a Pt(II) center

George S. Chen, Jay A. Labinger[†], and John E. Bercaw[†]

The Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, 1200 East California Avenue, Mail Code 127-72, Pasadena, CA 91125

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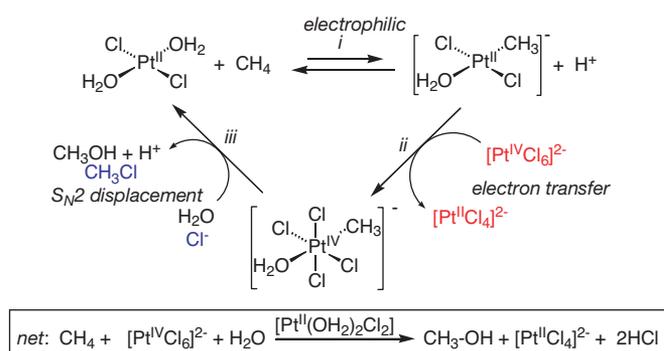
The rates of C–H bond activation for various alkanes by [(N–N)Pt(Me)(TFE-*d*₃)]⁺ (N–N = Ar–N=C(Me)–C(Me)=N–Ar; Ar = 3,5-di-*tert*-butylphenyl; TFE-*d*₃ = CF₃CD₂OD) were studied. Both linear and cyclic alkanes give the corresponding alkene-hydride cation [(N–N)Pt(H)(alkene)]⁺ via (i) rate determining alkane coordination to form a C–H σ complex, (ii) oxidative cleavage of the coordinated C–H bond to give a platinum(IV) alkyl-methyl-hydride intermediate, (iii) reductive coupling to generate a methane σ complex, (iv) dissociation of methane, and (v) β -H elimination to form the observed product. Second-order rate constants for cycloalkane activation (C_nH_{2n}), are proportional to the size of the ring ($k \sim n$). For cyclohexane, the deuterium kinetic isotope effect (k_H/k_D) of 1.28 (5) is consistent with the proposed rate determining alkane coordination to form a C–H σ complex. Statistical scrambling of the five hydrogens of the Pt-methyl and the coordinated methylene unit, via rapid, reversible steps ii and iii, and interchange of geminal C–H bonds of the methane and cyclohexane C–H σ adducts, is observed before loss of methane.

alkane functionalization | C–H activation | catalysis | organometallic chemistry

The selective activation and functionalization of saturated alkane C–H bonds represent important areas of research (1–5). Alkanes are the main constituents of oil and natural gas; hence the ability to efficiently transform alkanes to more valuable products is highly desirable (1, 2). Unfortunately, alkanes are relatively inert at ambient temperatures and pressures, due to their high homolytic bond strengths and very low acidity and basicity (1, 5). Partial oxidations of alkanes (hydroxylation, oxidative coupling, and oxidative dehydrogenation) are among the few processes that could, in principle, provide valuable products (alcohols, higher alkanes, and alkenes, respectively) in thermodynamically favorable transformations, but such reactions are difficult to carry out with high selectivity at high conversion (1, 2, 4). More traditional high-temperature routes often proceed by free radical mechanisms, for which the products derived from alkanes are virtually guaranteed to be more reactive than the alkane itself, placing an inherent constraint on selectivity (2–4).

In contrast, low-temperature homogeneous activations of C–H bonds need not, and often do not, involve radicals, and may lead to more selective reactions than those promoted by heterogeneous catalysts operating at high temperatures. Although many transition metal complexes have been shown to activate C–H bonds, the development of a practical catalyst to transform alkanes to value-added products remains elusive (1, 2). The key problem lies in finding a catalyst system that has both adequate reactivity and selectivity while tolerating oxidizing and protic conditions (4, 5).

In recent years, several oxidation catalysts based on platinum(II), palladium(II), and mercury(II) salts have been shown to functionalize C–H bonds, leading to good yields of partially oxidized products (4, 6–8). For example, [(2,2'-bipyrimidine)PtCl₂] catalyzes the selective oxidation of methane in fuming sulfuric acid to give methyl bisulfate in 72% one-pass yield at 81% selectivity based on methane (8). This system, although not yet practical, does demon-

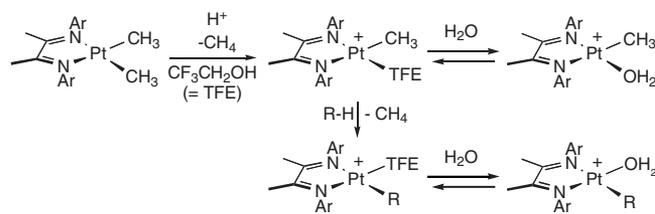


Scheme 1.

strate the potential promise of homogeneous catalytic alkane conversion.

Work in our group has been centered on the Shilov system for selective hydroxylation of alkanes (1, 2, 4). Detailed studies established the three-step mechanism and overall stoichiometry shown in Scheme 1, in which platinum(II) catalyzes the oxidation of alkanes to alcohols by platinum(IV) at 120°C (9–12). Although it is currently impractical because of low reaction rates, expensive oxidant, and catalyst instability, the system does exhibit useful regioselectivity (1° > 2° > 3°) and chemoselectivity.

The C–H activation step (step i in Scheme 1) is responsible for determining both activity and selectivity; however, direct detailed study of its mechanism is not possible in the “real” Shilov system because of its complexity and interfering side reactions. Accordingly, we turned to model systems, generalized in Scheme 2. The platinum methyl cations



Scheme 2.

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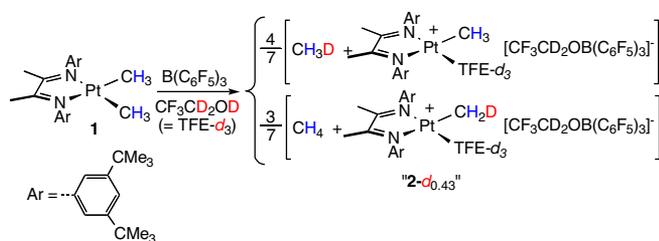
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[†]To whom correspondence may be addressed. E-mail: jal@caltech.edu or bercaw@caltech.edu.

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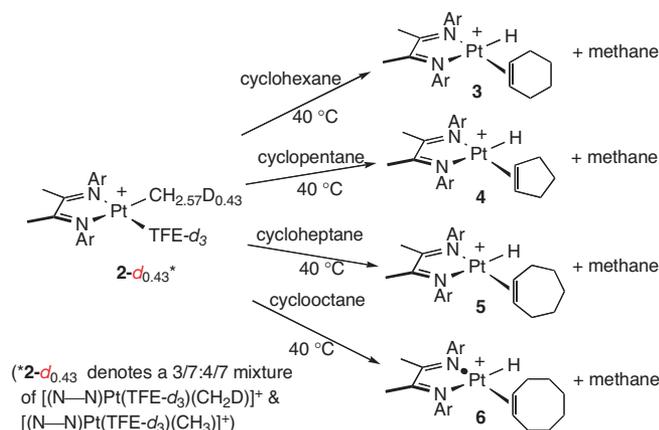
Scheme 3.

$[(N-N)Pt(Me)(solv)]^+$ ($N-N=Ar-N=C(Me)=C(Me)=N-Ar$; $solv = TFE = 2,2,2$ -trifluoroethanol) react with a variety of R-H groups (Ar-H, benzyl-H, indenyl-H, Me_3SiCH_2 -H, etc.) to afford the corresponding organoplatinum products, and have proved to be particularly well suited for mechanistic investigations (13–18). The relative reactivities of chemically differing C—H bonds are of particular importance for determining selectivity. We report herein on an investigation of the rate and selectivity of C—H bond activation for various linear and cyclic alkanes.

Results

Preparation of $[(N-N)Pt(Me)(TFE-d_3)]^+$ (2**) and Reactions with Cyclic Alkanes.** Protonolysis of **1** with $B(C_6F_5)_3$ in anhydrous $TFE-d_3$ gives platinum(II) monomethyl cation **2**, trifluoroethoxytris(pentafluorophenyl)borate, and methane (Scheme 3). Although only 1 equivalent of $B(C_6F_5)_3$ is required by the stoichiometry of the protonation, 2 equivalents are needed to cleanly generate **2**. Both **2** ($2-CH_3$ and $2-CH_2D$) and the released methane (CH_3D and CH_4) are obtained as a statistical mixture of isotopologs, the result of fast H/D scrambling among the seven positions of the $[(N-N)Pt(D)(CH_3)_2]^+$ intermediate before methane dissociation (18).

Cyclohexane, cyclopentane, cycloheptane, and cyclooctane react cleanly with the platinum methyl cation **2** at $40^\circ C$, as shown in Scheme 4. Addition of cyclohexane to a solution of $2-d_{0.43}$ in $TFE-d_3$ produces a single species **3** over the course of several



Scheme 4.

hours. No intermediate platinum species are observed. 1H NMR spectra for **3** support the proposed cyclohexene-hydride formulation,[‡] exhibiting in particular a platinum-coordinated olefin

[‡]We have not yet succeeded in isolating any of these products in pure form: they decompose on concentration, or more slowly on just standing in $TFE-d_3$ solution.

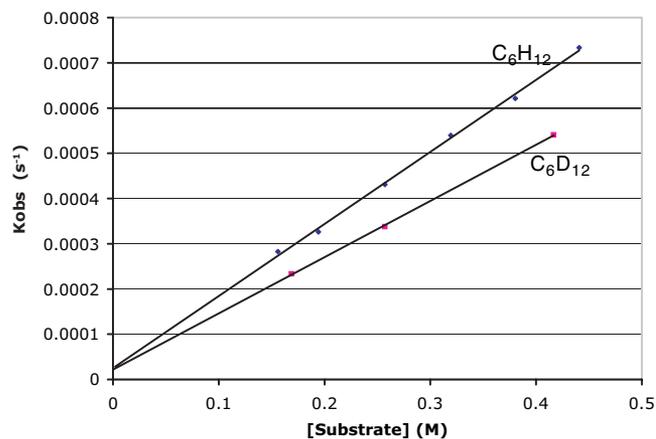


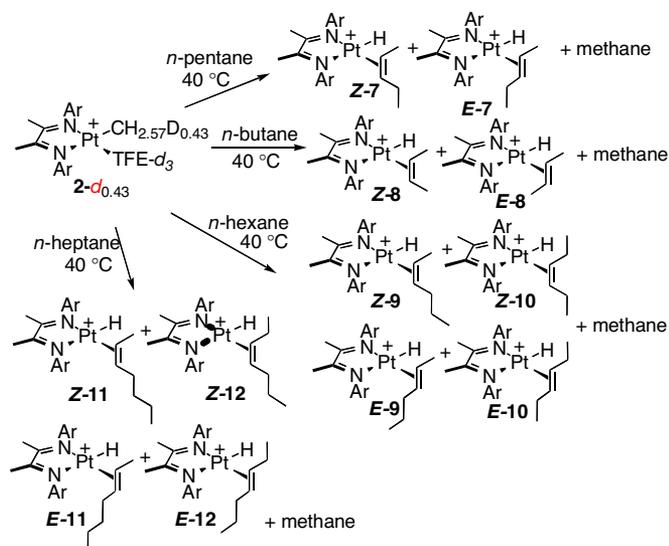
Fig. 1. Plot of k_{obs} vs. [hydrocarbon] for C_6H_{12} (diamonds) and C_6D_{12} (squares) at $40^\circ C$.

peak at $\delta = 4.9$ and a distinctive platinum hydride peak at $\delta = -22.2$ with ^{195}Pt satellites ($J_{Pt-H} = 1,320$ Hz). Cyclopentane, cycloheptane, and cyclooctane all react similarly with **2** to generate the corresponding species **4**, **5**, and **6** (Scheme 4).

Kinetics of Cycloalkane C-H Activation by **2.** The kinetics for reactions of $2-d_{0.43}$ with C_6H_{12} or C_6D_{12} at $40^\circ C$ were examined by following the disappearance of $2-d_{0.43}$ (methyl backbone signal at $\delta = 2.0$) and appearance of **3** by 1H NMR. Reactions displayed clean first-order kinetics for the disappearance of [**2**] and first-order dependence on $[C_6H_{12}]$ (Fig. 1), with $k_2 = 1.59(4) \times 10^{-3} M^{-1} s^{-1}$. The methane isotopologs CH_3D and CH_4 were generated in the ratio of $\approx 1:2$. Formation of **3** was accompanied by a much slower background decomposition reaction (18), indicated by both the appearance of additional new 1H NMR signals and the nonzero intercept of Fig. 1 [$k_{decomp} = 2.52(5) \times 10^{-5} s^{-1}$]. The rate constant for the reaction of $2-d_{0.43}$ with C_6D_{12} at $40^\circ C$ (Fig. 1) was found to be $k_2 = 1.24(4) \times 10^{-3} M^{-1} s^{-1}$ [with a similar nonzero intercept, $k_{decomp} = 2.14(8) \times 10^{-5} s^{-1}$], corresponding to a kinetic deuterium isotope effect of $k_H/k_D = 1.28(5)$. Methane isotopologs (CH_4 , CH_3D , CH_2D_2 , CHD_3) were observed by 1H NMR in the latter reaction.

The kinetics of the reactions of the other cyclic alkanes with $2-d_{0.43}$ showed similar behavior (background decomposition rates were somewhat higher) releasing CH_3D and CH_4 in $\approx 1:2$ ratio, with second-order rate constants $k_2 = 1.34(20) \times 10^{-3} M^{-1} s^{-1}$ and $1.86(12) \times 10^{-3} M^{-1} s^{-1}$ for cyclopentane and cycloheptane, respectively. The solubility of cyclooctane in TFE is too low to attain pseudo-first-order conditions, precluding a comparably precise determination; an approximate value of $k_2 = 2.1(5) \times 10^{-3} M^{-1} s^{-1}$ was estimated. In contrast, cyclopropane undergoes rapid C—C bond cleavage under these conditions, presumably promoted by the strong Brønsted acidity resulting from the excess of $B(C_6F_5)_3$ in CF_3CD_2OD required for clean generation of $2-d_{0.43}$ (19).

Reactions of Linear Alkanes with **2.** The reaction of n -pentane with $2-d_{0.43}$ in $TFE-d_3$ proceeds similarly to those described above: new 1H NMR signals attributable to platinum-olefin-hydride complexes along with CH_3D and CH_4 (again in a ratio of $\approx 1:2$) grow over several hours at $40^\circ C$. However, in this case, the NMR shows clear evidence for two products: platinum hydride signals at $\delta = -22.2$ and -23.3 in an $\approx 2:1$ ratio, respectively, along with two distinct sets of platinum-coordinated olefin peaks. As before, isolation of products was not achieved, and conclusive identification by NMR was not possible; however, addition of excess PMe_3 to the reaction mixture after completion displaced coordinated olefins. These were extracted and shown to consist



Scheme 5.

of *E*-2-pentene and *Z*-2-pentene in $\approx 2:1$ ratio (gc); no 1-pentene was detected. We conclude therefore that the products of the reaction of *n*-pentane with **2-d_{0.43}** are the *E* and *Z* internal olefin adducts (**7-E** and **7-Z**) formed in a 2:1 ratio (Scheme 5). In a much slower secondary reaction, the mixture of **7-E** and **7-Z** converts at room temperature over several weeks essentially completely to the *Z*-2-pentene adduct **7-Z**.

The reactions of **2-d_{0.43}** with *n*-butane, *n*-hexane, and *n*-heptane proceed similarly but with several additional features. With *n*-butane, three different Pt-H signals are initially observed, at $\delta = -22.2$, -22.1 , and -23.1 ; the first of these is much weaker than the other two and disappears completely by the time reaction is complete. We ascribe these signals to platinum complexes of 1-butene, *E*-2-butene, and *Z*-2-butene, respectively; at the end of the reaction, only the *E*- and *Z*-2-butene complexes are present in a 2.5:1 ratio. With both *n*-hexane and *n*-heptane, four different platinum hydride signals are observed by ^1H NMR. Displacement with PMe_3 and gc/ms analysis of the liberated olefins reveals the presence of the four possible internal olefins (*E*- and *Z*-2- and 3-enes in each case), indicating that the multiple signals correspond to the four isomeric platinum complexes as shown in Scheme 5. No hydride signal attributable to a 1-alkene adduct was observed with *n*-pentane, *n*-hexane, or *n*-heptane.

Kinetics of C—H Activation for Linear Alkanes. Reactions of **2-d_{0.43}** at 40°C were examined as before, by following the disappearance

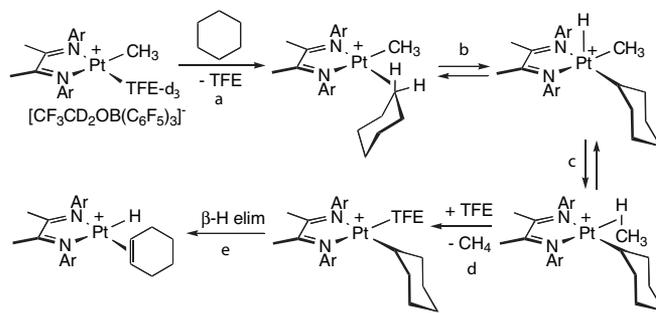
Table 1. Rate constants for reactions of alkanes with **2**

Substrate	k_2^* ($\text{M}^{-1} \text{s}^{-1}$)	k_{norm}^\dagger
Cyclopentane	$1.34(20) \times 10^{-3}$	1.34×10^{-4}
Cyclohexane	$1.59(4) \times 10^{-3}$	1.33×10^{-4}
Cycloheptane	$1.86(12) \times 10^{-3}$	1.33×10^{-4}
Cyclooctane	$2.1(5) \times 10^{-3}$	1.31×10^{-4}
<i>n</i> -butane	$1.33(4) \times 10^{-3}$	1.33×10^{-4}
<i>n</i> -pentane	$1.02(3) \times 10^{-3}$	0.85×10^{-4}
<i>n</i> -hexane	$1.06(4) \times 10^{-3}$	0.76×10^{-4}
<i>n</i> -heptane	$9.5(18) \times 10^{-4}$	0.59×10^{-4}
Methane [‡]	$2.7(2) \times 10^{-4}$	0.68×10^{-4}

*Second-order rate constant at 40°C.

[†]Normalized rate per C—H bond.

[‡]Data from ref. 18.



Scheme 6.

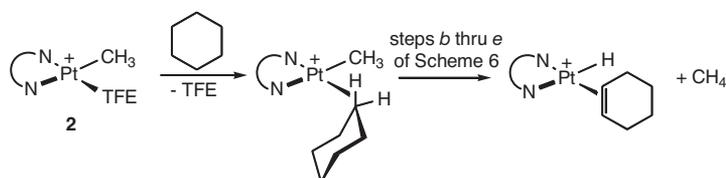
of **2-d_{0.43}** by ^1H NMR at varying excess concentrations of *n*-alkanes. In all cases pseudo-first-order behavior is observed, rates are first order in alkane concentration, and the ratio of isomers remains relatively constant throughout the course of the reaction. Rate constants at 40°C are given in Table 1.

Discussion

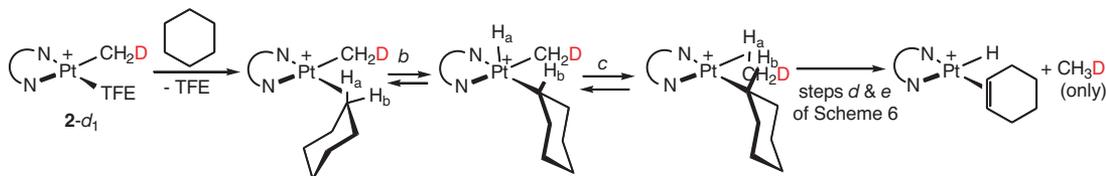
The reactions of linear and cyclic alkane substrates with **2** afford alkene-hydride cations $[(\text{N}-\text{N})\text{Pt}(\text{H})(\text{alkene})]^+$. The most likely mechanism, based on previous work (ref. 20 and H.A. Zhong, J.A.L., and J.E.B., unpublished) as well as present findings (see below), is shown (for cyclohexane) in Scheme 6. It involves (i) displacement of trifluoroethanol (TFE) by alkane to give a C—H σ complex, (ii) oxidative cleavage to a 5-coordinate $[\text{Pt}^{\text{IV}}(\text{methyl})(\text{alkyl})(\text{hydride})]$ intermediate, (iii) reductive coupling to afford a methane C—H σ complex, (iv) displacement of methane by TFE, and (v) β -H elimination. Questions of interest include: which step is rate-determining, what is the role and behavior of the proposed C—H σ complex intermediate, and how does reactivity vary with structure?

There is precedent for either C—H coordination or oxidative C—H cleavage being rate-determining in alkane activation; a recent theoretical study supports the former (i) as rate-determining in the “real” Shilov system (21). For the reactions of linear and cyclic alkanes with **2**, the same conclusion appears to hold. The extensive isotopic scrambling observed for the reaction of **2-d_{0.43}** with C_6D_{12} , giving CH_2D_2 and CHD_3 (CD_4 is presumably also formed, but not detected by ^1H NMR) in addition to the CH_3D , and CH_4 obtained from reactions of all-protio substrates, indicates that reversible steps iii and iv along with C—H bond interchange in cyclohexane and methane C—H σ complexes (see below) are all fast relative to loss of methane, consistent with rate-determining C—H coordination. This conclusion is further supported by the small KIE [$(k_{\text{H}}/k_{\text{D}}) = 1.28(5)$], which is similar to values measured for iridium- and rhodium-based C—H activation systems where C—H coordination is rate-determining ($k_{\text{H}}/k_{\text{D}} \approx 1.1$ – 1.4) (22–24), but considerably smaller than values for rate-determining oxidative cleavage of an alkane C—H bond by d^8 metal centers ($k_{\text{H}}/k_{\text{D}} \approx 2.5$ – 5) (25, 26).

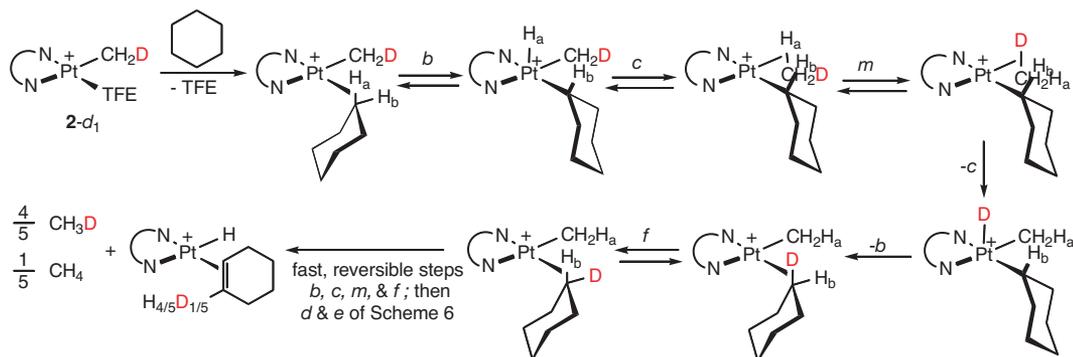
It is also notable, and consistent with rate-determining C—H coordination, that the second-order rate constants for reactions of **2** with cyclic hydrocarbons are roughly proportional to the number of C—H bonds (Table 1). Bergman and coworkers found that rate constants for the activation of *n*-alkanes by $[\text{Cp}^*(\text{PMe}_3)\text{Rh}]$ ($\text{Cp}^* = (\eta^5\text{-C}_5\text{Me}_5)$) are proportional to the number of secondary ($-\text{CH}_2-$) hydrogens in the *n*-alkane (23). In that system, linear alkanes are more reactive than cycloalkanes (on a per C—H bond basis). In contrast, for the present system, linear alkanes are less reactive, and the reactivity per C—H bond decreases for longer alkanes. We do not at present have a satisfying explanation for this trend. One possibility is that steric crowding inhibits C—H coordination in many of the possible conformations accessible to a linear alkane, a problem that should become more severe with increasing chain



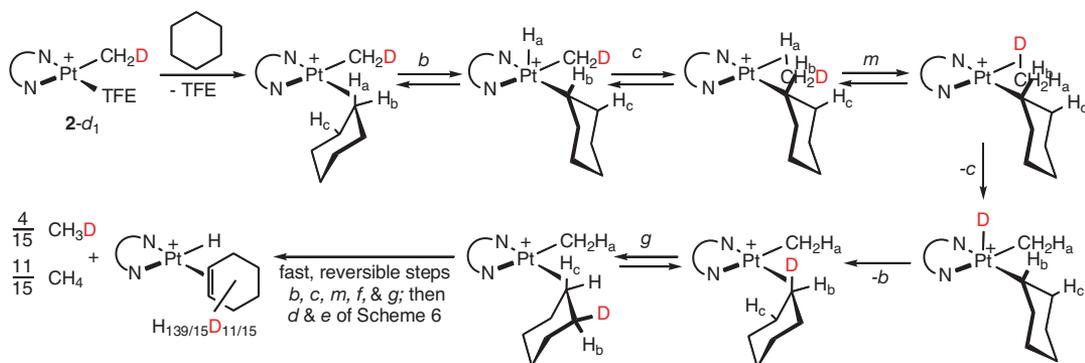
case 1: **no** scrambling of geminal or vicinal cyclohexane C-H bond(s) for cyclohexyl intermediate.



case 2: scrambling of geminal cyclohexane C-H bond for cyclohexyl intermediate (f); no vicinal scrambling.



case 3: scrambling of geminal (f) and vicinal (g) cyclohexane C-H bonds for cyclohexyl intermediate.



Predictions of net isotopologs of methane:

case 1: CH₄:CH₃D = 1.33

case 2: CH₄:CH₃D = 1.92

case 3: CH₄:CH₃D = 7.75

Observed: CH₄:CH₃D = 1.97(16)

Scheme 7.

length but that would not apply to cycloalkanes. However, such reasoning would not explain the low reactivity of methane (Table 1).

Additional information about the proposed mechanism can be deduced from quantitative details of isotopic scrambling in the methane liberated during reaction with hydrocarbon. Recall that some deuterium is introduced into **2** during the deuterolysis of **1** by (C₆F₅)₃BODCD₂CF₃ (Scheme 3). When the resulting 4:3 mixture of **2** and **2-d**₁ reacts with a perprotio substrate, **2** liberates only CH₄, whereas **2-d**₁ releases a mixture of CH₃D and CH₄. For the latter there are three possible scenarios, illustrated (for the

example of cyclohexane) in Scheme 7. In case 1, step *b* is effectively irreversible; only a single C—H bond participates in the reaction, so only CH₃D will be generated from **2-d**₁, and the final ratio of CH₄ to CH₃D will be 4:3 = 1.33.

In contrast, if steps *ii* and *iii* as well as the interchange of coordinated C—H bonds are reversible and fast, there are two possible cases, depending on how many C—H bonds of cyclohexane are sampled before dissociation of methane from the methane σ adduct (step *d*, Scheme 6). In case 2, there is fast exchange between geminal positions (H_a and H_b of cyclohexane, as well as all positions of coordinated methane); CH₃D and CH₄

will be generated in a 4:1 statistical ratio with deuterium being retained in the coordinated cyclohexene one-fifth of the time. Summing the methane generated from **2** and **2-d₁**, the expected ratio of [CH₄]:[CH₃D] for case 2 is 23:12 = 1.92. For case 3, both geminal and vicinal exchange are fast, so all 12 of the C—H bonds of cyclohexane participate in H/D exchange, giving an expected ratio of [CH₄]:[CH₃D] of 31:4 = 7.75.

The experimentally observed ratio [CH₄]:[CH₃D] from the reaction of C₆H₁₂ with **2-d_{0.43}** is 1.97(16) for cyclohexane, and approximately the same for all of the other alkanes and cycloalkanes examined. This finding is only consistent with case 2: fast geminal but slow vicinal C—H interchange. By way of comparison, in a metastable rhenium–pentane complex (observed at low temperature by NMR) geminal exchange is fast on the NMR time scale, whereas vicinal exchange takes place much more slowly (rates on the order of 1–10 s⁻¹ at 173 K) (27).

For linear alkanes, we have the additional option of coordinating/reacting at either terminal (methyl) or internal (methylene) positions. Jones and coworkers have shown that in a rhodium system (Tp⁺LRh with L = CNCH₂CMe₃), coordination of secondary C—H bonds is preferred over primary C—H bonds by a factor of 1.5 (27); for the rhenium system cited above, coordination of pentane at the 2- and 3-positions is (very slightly) favored over statistical values (27). We observed a [CH₄]:[CH₃D] ratio of ≈2:1 for all four linear alkanes, which at first glance seems consistent with statistical scrambling involving only one methylene (-CH₂-) group, as with cycloalkanes. However, the predicted [CH₄]:[CH₃D] ratio for participation of a single terminal methyl (-CH₃) group is 15:6 = 2.50; if both primary and secondary C—H activations occur, the [CH₄]:[CH₃D] ratio would be between 1.92 and 2.50, well within the uncertainty of this experimental determination.

In an attempt to gain further information on this question, we examined the methane produced by reaction of partially deuterated propanes[§] (CD₃CH₂CD₃ and CH₃CD₂CH₃) with **2**. The former gives CH₄ (10%), CH₃D (26%), CH₂D₂ (29%), and CHD₃ (35%); exclusive reaction of secondary [C—H] bonds would give only CH₄ and CH₃D, whereas exclusive reaction of primary [C—H] bonds would give no CH₄. Similarly, the latter isotopolog gives CH₄ (63%), CH₃D (32%), and CH₂D₂ (5%). These results are approximately consistent with statistical expectations; i.e., no preference between terminal and internal positions.

The failure to observe any evidence for terminal olefin adducts in the reactions of *n*-pentane, *n*-hexane, and *n*-heptane with **2-d_{0.43}** might also be taken to suggest a preference for internal reaction. However, it seems more likely that the terminal olefin complex is rapidly isomerized to the internal isomers via the olefin insertion/β-H elimination sequence. Such a process has been shown to operate at -78°C on the order of hours in a related [Tp⁺Pt] system (20), where the initially formed 1-pentene adduct isomerizes to 2-pentene adducts. Our observation of a low transient amount of a terminal alkene adduct only in the case of *n*-butane (which has a small statistical advantage, relative to higher alkanes, for initial coordination and cleavage of primary C—H bonds) is consistent with this interpretation.[¶]

[§]It should be noted, however, that the reactions of propane (and ethane) with **2** do not give olefin-hydride products analogous to those found for higher linear alkanes; these reactions do appear to involve initial C—H activation, but the final products exhibit more complex NMR spectra and have not yet been fully identified. Nonetheless, we believe that the inferences from these selective labeling experiments are probably valid.

Conclusions

We have demonstrated C—H bond activation of various alkanes by [(N–N)Pt(Me)(TFE-*d*₃)]⁺ system to generate [(N–N)Pt(H)(alkene)]⁺ cations. The small KIE (*k*_H/*k*_D = 1.3) for cyclohexane together with statistical isotopic scrambling in the methane released suggests that C—H bond coordination is rate determining. Comparing the relative rates of cyclic and linear alkanes indicates that the platinum center is relatively unselective with respect to different C—H bonds: the rate constants (per C—H bond) for the substrates examined all fall into a narrow range, and there does not appear to be any significant preference for either primary or secondary C—H bonds. Further experimental and computational studies on this point are ongoing.

Materials and Methods

All air- and/or moisture-sensitive compounds were manipulated by using standard high-vacuum line, Schlenk, or cannula techniques, or in a glove box under a nitrogen atmosphere. B(C₆F₅)₃ was purchased from Aldrich (St. Louis, MO) and sublimed at 90°C at full vacuum. Trifluoroethanol-*d*₃ was purchased from Cambridge Isotope Laboratories (Andover, MA) and dried over 3-Å molecular sieves for at least 5 days, then vacuum distilled onto B(C₆F₅)₃, and shortly thereafter distilled into a Strauss flask. All gasses were purchased from Matheson (Joliet, IL) and dried using standard high-vacuum line techniques over 4-Å molecular sieves. CD₃CH₂CD₃ and CH₃CD₂CH₃ were purchased from CND Isotopes (Pointe-Claire, Quebec, Canada) and dried using standard high-vacuum line techniques. The alkanes were all purchased from Aldrich and dried over calcium hydride. NMR spectra were recorded on a Varian Mercury 300 spectrometer at 40°C.

For kinetic experiments, stock solutions of **2** were prepared by weighing out 40 mg of **1** and 60 mg of B(C₆F₅)₃. Five milliliters of trifluoroethanol-*d*₃ was then added, and the solution turned light yellow after a few minutes. A total of 0.7 ml of this solution was added to a J-Young NMR tube. The NMR tube was degassed on a high-vacuum line, and an initial ¹H NMR spectrum was acquired to confirm complete and clean formation of **2**. Alkanes that are liquid at room temperature were then added by syringe and shaken briefly, and the tube was then inserted into an NMR spectrometer that had been preheated to 40°C. Alkanes that are gas at room temperature were vacuum transferred into the NMR tube using standard high-vacuum line techniques. After allowing a few minutes for the NMR tube to reach equilibrium, an array of 40–50 spectra was acquired. Kinetics was monitored by following the disappearance of either one of the backbone methyl peaks or one of the aryl peaks over time. Pseudo first-order rate constants (*k*_{obs}) were then obtained by fitting the data to a first-order exponential function. Second-order rate constants were then obtained from a plot of *k*_{obs} vs. [alkane].

[¶]There may well be a connection between this behavior and the failure to observe stable olefin-hydride products from propane and ethane (see §), which can give only terminal olefin complexes.

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