# C−H Bond Activation by Dicationic Platinum(II) Complexes

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Double protonolysis of diimine platinum dimethyls [(N-N)PtMe$_2$] (N-N = ArN=C(Me)C(Me)=NAr) generates dicationic Pt(II) complexes that can activate a variety of C−H bonds, liberating 1 equiv of acid and forming organoplatinum species that are moderately stable to the resulting acidic conditions. Ethylbenzenes lead to $\eta^3$-benzyl complexes; mechanistic experiments suggest that $\eta^3$-benzyl product formation proceeds via C−H bond activation at the benzylic methylene position. In some cases $\pi$-arene complexes can be observed, but their role in the C−H activation process is not clear. Cyclohexane and 1-pentene react to give $\eta^3$-allyl complexes; allylbenzene gives a chelated phenyl-$\eta^2$-olefin structure, as determined by X-ray diffraction. No stable C−H activation products are obtained from methylbenzenes, benzene itself, or alkanes.

## Introduction

The area of C−H bond functionalization has generated considerable activity over the last three decades.[1] One of the earliest discoveries—the so-called Shilov system for selective platinum-mediated oxidation of alkanes to alcohols[2]—has continued to stimulate interest, both as a potentially useful methodology and as a topic for mechanistic investigation. The reaction is believed to occur in three stages: (1) reversible electrophilic C−H bond activation to afford a platinum(II) alkyl complex with liberation of a proton,[3] (2) oxidation of R−Pt(II) to R−Pt(IV) by hexachloroplatinate,[4,5] and (3) reductive elimination via $S_N2$ displacement by water (or chloride) to give ROH (or RCl) and regenerate the platinum(II) catalyst.[6,7] Because R−Pt(II) is highly labile with respect to protonolysis, the second step must be at least as fast as the reverse of the first.[8]

Our investigations of the C−H bond activation step have made extensive use of reactions of diimine-ligated platinum methyl complexes **2** (eq 1).[9] In comparison to conditions involving aqueous $HBF_4$,[9g,h] reactivity is enhanced when **2** is generated under anhydrous conditions (by adding $B(C_6F_5)_3$ to trifluoroethanol-$d_3$ (TFE) as shown in eq 1), but the $[(F_6C_5)_3BOCD_2CF_3]^-$ counterion leads to a (competing or consecutive) side reaction—transfer of a pentafluorophenyl group from B to Pt—that in many cases complicates the kinetics and/or product characterization.[9i,j]

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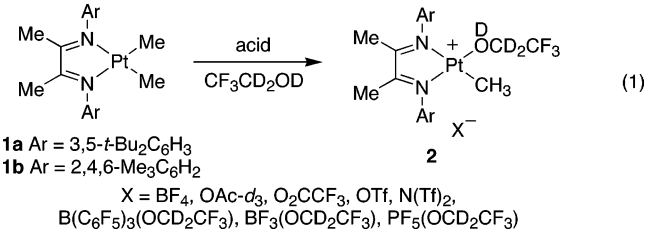



(1)

To circumvent this complication, we have examined alternate methods for generating anhydrous **2**. In the course of this work we discovered that it is possible to *doubly* protonolyze the starting platinum dimethyl complex **1** to generate methyl-free, dicationic Pt(II) complexes.

Note that in the model system **2**, unlike the "real" Shilov system, the H of the activated C−H bond is lost as $CH_4$ rather than as a proton. As a consequence, whether or not the detailed mechanistic information gleaned from the former is applicable to the latter, complexes such as **2** are not directly applicable as catalysts for practical alkane functionalization. In contrast, formation of an organoplatinum complex via C−H activation by a dicationic species *would* generate a proton; hence, whether a particular hydrocarbon leads to an observable organoplatinum product will depend on the issues of thermodynamic stability toward protonolysis and the kinetic reactivity of the C−H bond with the dicationic center. The latter may or may not resemble reactivities toward the monocationic models **2**.

We report here that a platinum dication complex can indeed activate a variety of C−H bonds, that the thermodynamic stability of the resulting product in the presence of liberated proton is strongly dependent upon the specific structure, and that the mechanism for the formation of one class of product is substantially different from that previously established for the corresponding reaction of platinum methyl monocations.

## Results and Discussion

**Protonolysis of 1 by Various Acids.** Generation of the platinum methyl cation **2** by protonolysis of the dimethyl complex **1** in trifluoroethanol-$d_3$ (TFE) is effected by a variety of acids ($HBF_4$·$OEt_2$, DOAc-$d_3$, $DO_2CCF_3$, DOTf, $HN(Tf)_2$) and acid precursors ($B(C_6F_5)_3$, $BF_3$, $PF_5$, $Tf_2O$) (eq 1). In general, more than 1 equiv of acid is required for clean formation of **2**. Both the stability and the reactivity of the resulting cationic species depend on the counteranion as well as the aryl group on the diimine ligand (Ar). In particular, when acetic or trifluoroacetic acid is used, no C−H activation can be observed at all, presumably a consequence of strong coordination of $X^-$ (acetate, trifluoroacetate).

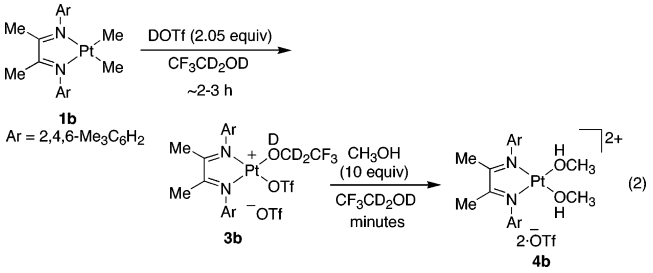
**Table 1. Qualitative Comparison of Platinum Methyl Cation Stability**[a]

| entry | Ar | $X^-$ | [(N-N)Pt-Me(TFE)]$^+$ (mM) | $t_{1/2}$(dec) (22 °C) |
|---|---|---|---|---|
| 1 | 3,5-(*t*-Bu)$_2$C$_6$H$_3$ | $[(F_5C_6)_3BOCD_2CF_3]^-$ | 26 | 8 h |
| 2 | 2,4,6-Me$_3$C$_6$H$_2$ | $[(F_5C_6)_3BOCD_2CF_3]^-$ | 26 | 6 days |
| 3 | 2,4,6-Me$_3$C$_6$H$_2$ | $[OTf]^-$ | 26 | 9 h |
| 4 | 2,4,6-Me$_3$C$_6$H$_2$ | $[OTf]^-$ | 13 | 27 h |
| 5 | 3,5-*t*-Bu$_2$C$_6$H$_3$ | $[F_3BOCD_2CF_3]^-$ | 26 | 60 h |

[a] Abbreviations: N-N = ArN=C(Me)C(Me)=NAr; TFE = 2,2,2-trifluoroethanol-$d_3$.

Several qualitative decomposition rates are shown in Table 1. With $X = [(F_6C_5)_3B(OCD_2CF_3)]^-$ **2a** (Ar = 3,5-(*t*-Bu)$_2$C$_6$H$_3$) decomposes by pentafluorophenyl transfer to platinum with a half-life of about 8 h at 22 °C; increasing the steric crowding around platinum (**2b**; Ar = 2,4,6-Me$_3$C$_6$H$_2$) slows the rate of decomposition (entry 2). When X = triflate, the decomposition rate is comparable (entry 3), although it is significantly slower at lower concentration (entry 4), suggesting a bimolecular pathway. Using $BF_3$ as the Lewis acid for protonolysis affords a substantial increase in the stability of the platinum methyl cation (entry 5).

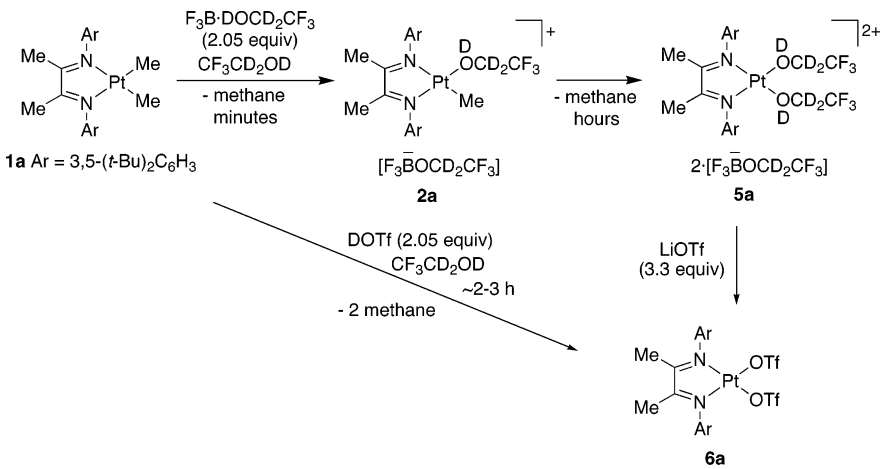
**Diprotonolysis of 1 by Triflic Acid or $BF_3$.** In contrast to the behavior observed with $B(C_6F_5)_3$, reaction of **1a** or **1b** with 2.05 equiv of triflic acid effects protonolysis of *both* methyl groups to liberate 2 equiv of methane and new methyl-free platinum complexes. In the case of **1b**, the $^1$H NMR shows an unsymmetrical environment for the diimine ligand, suggesting structure **3b** (eq 2). Addition of methanol to the solution results




(2)

in the formation of a new symmetrical species, presumably **4b**. Similar protonolysis of **1a** gives a product that is symmetrical, but with broad NMR signals.

**Scheme 1**



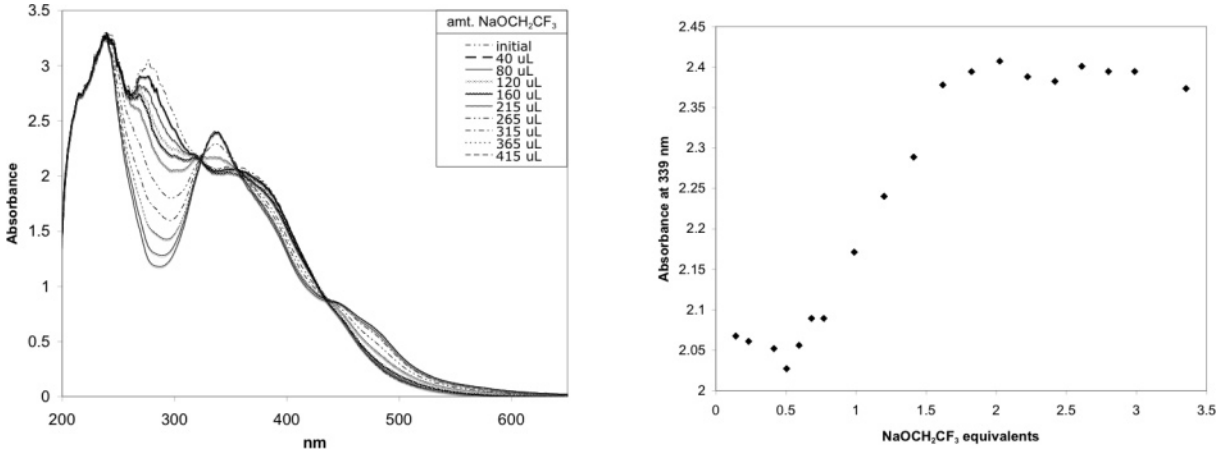
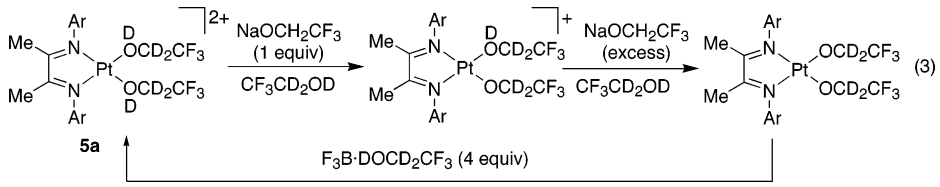



**Figure 1.** UV/visible spectral shanges during titration of **5a** (0.505 mM) with a solution of $NaOCH_2CF_3$ (30 mM).

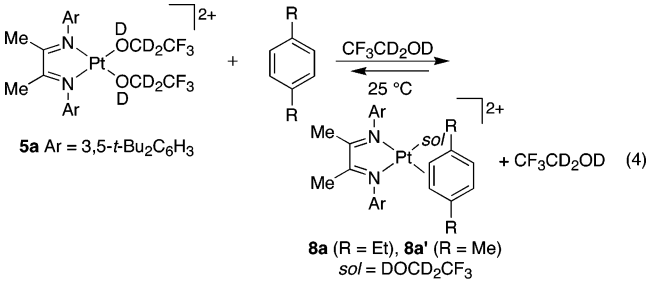



Diprotonolysis can also be achieved with $BF_3$; the detailed behavior is somewhat different. Exposure of **1a** to 2.1 equiv of $BF_3$ (in trifluoroethanol-$d_3$) results in rapid protonolysis of the first methyl group to generate **2a**, followed by slow loss of the second methyl group to produce a new symmetrical product, again exhibiting broad NMR signals. Addition of excess LiOTf to this solution gives the same (symmetrical) NMR spectrum observed when **1a** is treated with excess triflic acid. These findings strongly suggest that the symmetrical species are the bis(solvento) dication **5a** and the bis(triflato) neutral species **6a** (Scheme 1). Addition of acetonitrile to a solution of **5a** gives a new, sharp, symmetrical spectrum, assigned to $[(N\text{-}N)Pt(NCCH_3)_2]^{2+}$ (**7a**). We have not able to cleanly isolate platinum dication **5a**; concentration of a solution of **5a** produces yet another symmetrical species, tentatively assigned as a dimer.[10]

Additional support for the proposed identity of dication **5a** was obtained from a titration experiment. Addition of $NaOCH_2CF_3$ to the platinum dication results in a color change of the solution (light orange to blood red) accompanied by an upfield shift of the diimine methyl resonance in the $^1H$ NMR. The peak initially appears at $\delta$ 2.32; after the addition of 1 equiv of $NaOCH_2CF_3$, it shifts to $\delta$ 1.82 and, after 3 equiv, to $\delta$ 1.72. (The peak gradually disappears over time due to base-catalyzed H/D isotope exchange with the solvent.[9e]) Addition of 4 equiv of $F_3B{\cdot}DOCD_2CF_3$ at this point regenerates the original spectrum. Following the same titration by UV/visible spectroscopy reveals only one well-defined transition, corresponding to the addition of 1 equiv of base (Figure 1); the overlaid spectra show a number of apparent isosbestic points, but several are not perfect. These results strongly imply that the three NMR signals above correspond to dicationic, monocationic, and neutral complexes respectively (eq 3), with the UV/visible spectrum differing significantly between the first and second but much less so between the second and third.

The steric and electronic environment around platinum affects the conditions required for diprotonolysis of **1**. All the complexes shown in Table 2 undergo diprotonolysis, but whereas **1c** (like **1a**) gives complete formation of the dication **5c** in a few hours at room temperature, both **1b** and **1d** require more prolonged reaction at elevated temperature. This difference in reactivity presumably reflects inhibition of protonation by steric crowding (**1b**) or reduced electron density (**1d**). The fact that diprotonolysis of **1a** and **1b** with triflic acid gives different products (**5a** and **3b**, respectively) is probably also a steric effect: the larger ligand in **1b** disfavors coordination of two relatively bulky triflate groups.

**Observation of Platinum $\pi$-Arene Complexes.** Addition of 1,4-diethylbenzene or *p*-xylene to a solution of **5a** produces new NMR signals, including sharp singlets at 6.78 and 6.87 ppm, respectively, assigned to arene complexes **8a** and **8a′** (eq 4).




On the basis of literature precedent[3a,b,11] the coordination is expected to be $\eta^2$; if so, the observation of a single peak for the aryl protons requires that the molecules be fluxional.[12] The relative intensities of the NMR signals for **5a** and **8a** vary with the amount of added arene, as expected for an equilibrium situation. Attempts to determine equilibrium constants met with complications, however. Duplicate determinations with different preparations of **5a** gave apparent values of $K_{eq}$ for replacement of TFE by 1,4-diethylbenzene ranging from 45 to 115 at room

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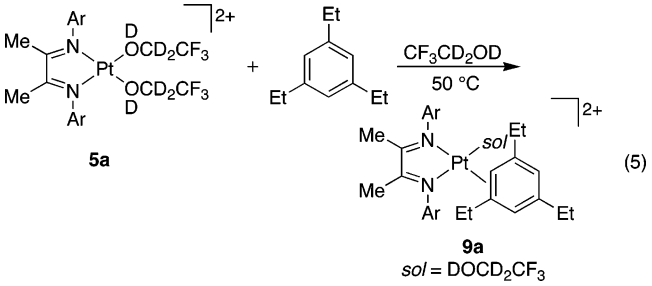
**Table 2. Conditions Required for Complete Diprotonolysis of 1 to 5**

| complex | Ar | time (h) | *T* (°C) |
|---|---|---|---|
| **1a** | 3,5-(*t*-Bu)$_2$C$_6$H$_3$ | 8 | 22 |
| **1b** | 2,4,6-Me$_3$C$_6$H$_2$ | 15 | 60 |
| **1c** | 3,5-Me$_2$C$_6$H$_3$ | 8 | 22 |
| **1d** | 3,5-(CF$_3$)$_2$C$_6$H$_3$ | 36 | 50 |

temperature. Furthermore, the apparent $K_{eq}$ value generally increases as the temperature is raised but does not return to its original value upon recooling. A group of new NMR signals grows in intensity during the latter experiments; similar peaks are observed when **5a** is allowed to decompose by itself at elevated temperature. It is probable that decomposition generates one or more NMR signals that coincide with those used to quantify **8a**. Additionally, the amount of acid used in the protonolysis of **1**—which is difficult to control or determine with high precision—appears to affect both the initial apparent equilibrium constant and the rate of decomposition. Hence, it is not possible to obtain reliable $K_{eq}$ values.

The formation of $\pi$-arene complexes is sensitive to both the steric and electronic environment around platinum. When the steric crowding is increased (**5b**) or the electron density around platinum is reduced (**5d**), no $\pi$-arene complexes are observed. Also, irrespective of the ligand environment around platinum, no $\pi$-arene complex formation is observed for monosubstituted arenes or benzene itself. On the other hand, for the bulkier arene 1,3,5-triethylbenzene a $\pi$-arene complex does form, but more slowly: at room temperature only about 20% of **5a** converts to **9a**, but heating to 50 °C results in complete consumption of the platinum dication and formation of the $\pi$-arene complex (eq 5).



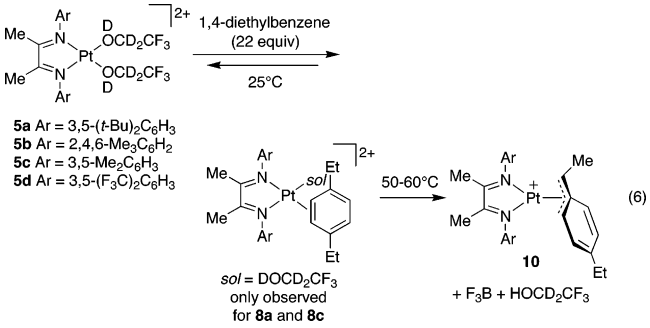

**5a** **9a** $sol$ = $DOCD_2CF_3$ (5)

Coordinated arenes are readily displaced by acetonitrile to afford **7a**, similar to the reactivity reported by related (pyrazolylborate)platinum $\pi$-arene complexes above −30 °C.[13] The addition of less than 2 equiv of acetonitrile to **8a** does not result in a mixed acetonitrile−arene complex but rather a mixture of dinitrile **7a** and $\pi$-arene complex **8a**, indicating that the equilibrium strongly disfavors a mononitrile complex and/or that it undergoes a second ligand substitution much faster than the first.

**C−H Bond Activation of Alkylbenzenes at Dicationic Platinum Centers.** Methyl- and ethyl-substituted benzenes react readily at room temperature with methylplatinum cations **2**, leading to $\eta^3$-benzyl complexes as the final product.[9h,i] Since these C−H activations are formulated as electrophilic reactions, one might expect dicationic species to be even more reactive. On the other hand, all previous mechanistic studies indicate that displacement of coordinated solvent by hydrocarbon is a requisite (often rate-determining) first step, and one might expect that solvent would be more tightly bound to a dicationic center, thus reducing reactivity. On yet another hand, though, equilibrium displacement of TFE by 1,4-diethylbenzene can be observed, even at room temperature (see above). We find that formation of $\eta^3$-benzyl complexes **10** from the reaction of platinum dications **5** with 1,4-diethylbenzene (eq 6) is slower

**Table 3. Formation of $\eta^3$-Benzyl Complexes from Platinum Dications**

| complex | Ar | *T* (°C) | time (h) | yield of **10** (%) |
|---|---|---|---|---|
| **5a** | 3,5-(*t*-Bu)$_2$C$_6$H$_3$ | 50 | 15 | 93 |
| **5b** | 2,4,6-Me$_3$C$_6$H$_2$ | 50 | 20 | 30 |
| **5c** | 3,5-Me$_2$C$_6$H$_3$ | 50 | 15 | 76 |
| **5d** | 3,5-(CF$_3$)$_2$C$_6$H$_3$ | 60 | 15 | 97 |




(6)

than the corresponding reactions of **2** and requires elevated temperature, as shown in Table 3. **10b** is also obtained on starting from triflate complex **3b**, but the reaction requires higher temperatures (95 °C) and gives low yields (around 35%), in part a consequence of product instability: independently synthesized **10b** decomposes in the presence of excess triflic acid at 95 °C with a $t_{1/2}$ value of approximately 6 h. Complexes with more tightly binding ligands, such as platinum ditriflate **6a**, methanol-ligated complex **4b**, and bis(acetonitrile) complex **7a**, all fail to react productively with 1,4-diethylbenzene.

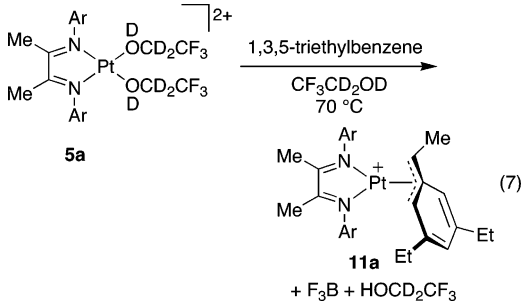
As shown in eq 6, net activation of a benzylic C−H bond would liberate a proton that ends up as $HOCD_2CF_3$ with concomitant formation of $BF_3$/TFE. (Indeed, the $^1$H NMR peak associated with the residual "O*H*" present in solution grows significantly over the course of the reaction, but this is primarily due to acid-catalyzed arene H/D exchange, which takes place under reaction conditions even in the absence of any Pt complex. Demonstration that benzylic C−H activation results in growth of the O*H* peak requires a specifically labeled substrate: see below.) Hence, the $\eta^3$-benzyl complexes **10** must be stable to the presence of 1 equiv of acid. Reactions of **5b** were carried out in the presence of added base ($K_2CO_3$, $CsCO_3$, 2,6-lutidine, 2,6-di-*tert*-butylpyridine, or $NaOCH_2CF_3$) to determine whether the low yields are a consequence of a less favorable equilibrium between C−H activation and protonolysis, but all such additives only inhibited the formation of $\eta^3$-benzyl **10b**. Furthermore, no H/D exchange was observed in the ethyl group of unreacted 1,4-diethylbenzene, arguing against any equilibrium.

Increasing the steric bulk of the substrate from 1,4-diethylbenzene to 1,3,5-triethylbenzene slows the reaction. After 15 h at 50 °C, the $\eta^3$-benzyl species **11a** was observed in only 30% conversion, the balance being $\pi$-arene complex **9a**. After prolonged heating at 70 °C **11a** was obtained in 92% yield (eq 7).

It is notable that both **5b** and **5d** activate 1,4-diethylbenzene, even though no intermediate arene complex is detectable.

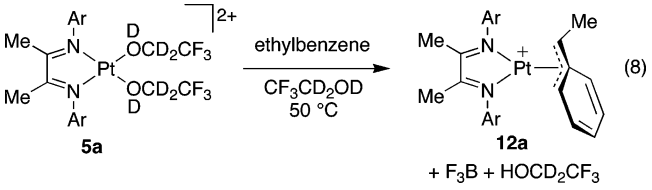
(12) No change was observed in the NMR down to −30 °C. The rotation barrier for a related platinum complex was estimated to be 9.4 kcal mol$^{-1}$ (−90 °C): Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649−5656.

(13) Norris, C. M.; Templeton, J. L. *Organometallics* **2004**, *23*, 3101−3104.




(7)

Similarly, heating **5a** in the presence of excess ethylbenzene (which also forms no observable arene complex) yields $\eta^3$-benzyl **12a** in 91% yield (eq 8). On the other hand, *p*-xylene




(8)

(which *does* form an arene complex) does *not* react with **5a** to give the expected $\eta^3$-benzyl species. This appears to be a consequence of product instability: the complex prepared by reaction of *p*-xylene with **2a** is completely decomposed after 10 h at 50 °C in a solution of $BF_3$/TFE.

**Mechanism of $\eta^3$-Benzyl Formation: Kinetics.** The kinetics of formation of the platinum $\eta^3$-benzyl complex **10a** were determined for 1,4-diethylbenzene concentrations ranging from about 0.2 to 0.6 M; disappearance of the dicationic platinum complex followed good first-order behavior in all cases. Previous studies strongly indicate that benzene C−H activation by **2** proceeds via an intermediate $\eta^2$-arene complex.[9b,e] Although we have been unable to measure a reliable equilibrium constant for formation of the $\eta^2$-diethylbenzene complex **8a** (see above), the qualitative observations indicate that much or most of the dicationic platinum species in solution should be in the form of **8a** over the range of arene concentrations used; hence, we expected the rate to exhibit approximate zero-order dependence on diethylbenzene. In contrast, the reaction was found to be first-order in 1,4-diethylbenzene over the entire range studied (Figure 2), with a second-order rate constant of $5.1 \times 10^{-4}$ $M^{-1}$ $s^{-1}$. (The large *y* intercept undoubtedly reflects the competing decomposition processes discussed above.) Only small kinetic isotope effects (determined from separate kinetics runs) were found using 1,4-diethylbenzene-(aryl)$d_4$ ($k_H/k_D = 1.38$) or 1,4-diethylbenzene-$d_{10}$ ($k_H/k_D = 1.19$).

Further indication that C−H activation is not a simple intramolecular reaction of coordinated arene was obtained from a competition experiment. A solution of $\pi$-arene complex **8a**, generated by adding 1,4-diethylbenzene (8.4 equiv, 0.183 M) to platinum dication **5a**, was treated with ethylbenzene addition (53 equiv, 0.9 M). No change in platinum speciation was observed, consistent with the failure to observe any $\pi$-arene complex of ethylbenzene (see above). After the temperature was raised to 50 °C, the resulting product consisted of a 44:56 mixture of $\eta^3$-benzyls **10a** (from 1,4-diethylbenzene) and **12a** (from ethylbenzene). The ratio of the products reflects neither the initial ratio of substrates (1:6) nor the preferential coordination to platinum.

One possible interpretation of these findings is shown in eq 9. The rate-determining step is substitution of trifluoroethanol by 1,4-diethylbenzene in **8a**. Formation of the bis(arene)

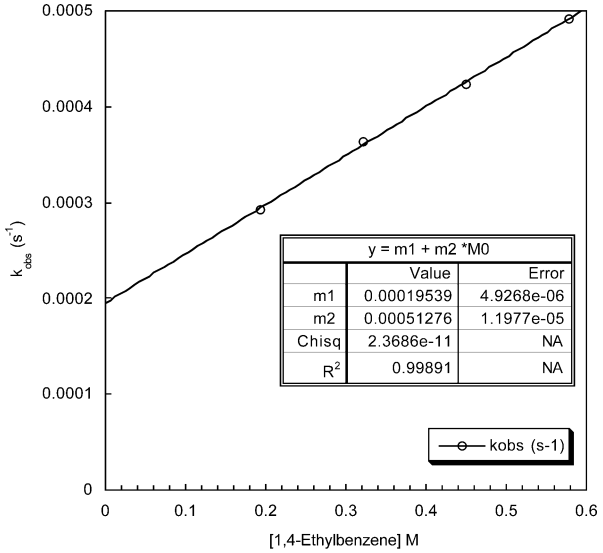
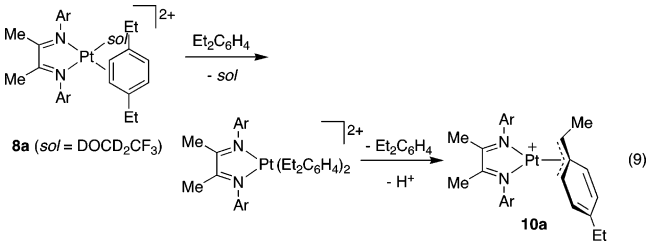


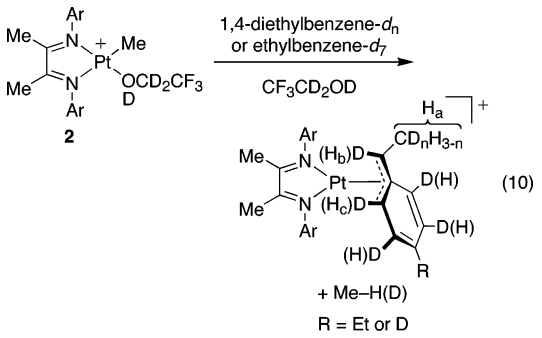

**Figure 2.** Dependence of rate of reaction of **5a** to **10a** on [1,4-diethylbenzene].




(9)

intermediate might involve coordination of a second $\pi$ bond or a C−H bond generating a $\sigma$ complex. The low KIE values could be consistent with either; they do appear to rule out the possibility that actual C−H activation is rate determining. However, since the NMR observations indicate that not *all* of the platinum is in the form of **8a** under these conditions, that mechanism would not be expected to give such clean first-order dependence on arene concentration. At present we do not have a fully satisfying explanation of this finding.

**Mechanism of $\eta^3$-Benzyl Formation: Isotopic Labeling.** Isotopic labeling experiments were previously used to elucidate the mechanism of formation of $\eta^3$-benzyl products from the reactions of ethyl- and 1,4-diethylbenzene isotopologues with platinum methyl cations **2** (eq 10).[9i] Information was obtained




(10)

from both the C/H distribution of the liberated methane and from the observation of isotope exchange between the various positions of $\eta^3$-benzyl groups derived from regiospecifically labeled substrates. We concluded that initial attack occurs exclusively at aryl positions (in contrast to the analogous reactions of methylbenzenes, where initial attack at aryl and methyl positions compete), followed by a complex pathway

**Scheme 2**

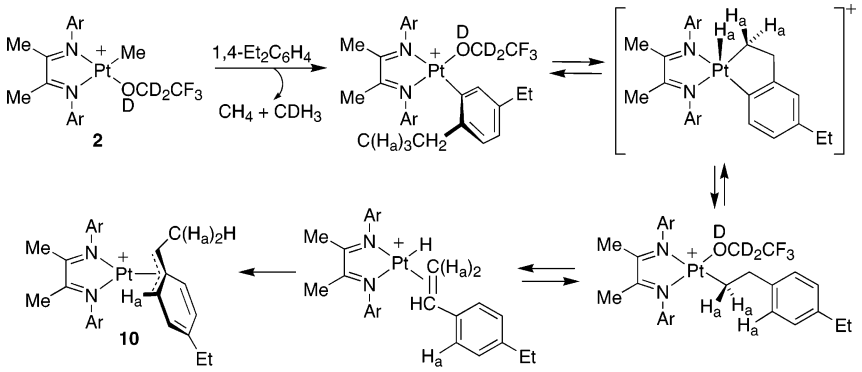


**Table 4. Isotope Exchange in $\eta^3$-Benzyl Products from Two Routes[a]**

| | | D in **10a** from **2a** (%) | | | D in **10a** from **5a** (%) | | |
|---|---|---|---|---|---|---|---|
| entry | substrate | $H_a$ | $H_b$ | $H_c$ | $H_a$ | $H_b$ | $H_c$ |
| 1 | 1,4-$(CH_3CH_2)_2C_6H_4$ | 16 | 0 | 12 | 21 | *b* | 65 |
| 2 | 1,4-$(CD_3CD_2)_2C_6H_4$ | 87 | 100 | 84 | 96 | 100 | 82 |
| 3 | 1,4-$(CH_3CH_2)_2C_6D_4$ | 73 | 0 | 27 | 20 | *b* | 87 |
| 4 | $CH_3CH_2C_6H_5$ | 18 | 0 | 0 | 12 | *b* | 20 |
| 5 | $CH_3CD_2C_6D_5$ | 30 | 100 | 34 | 18 | 100 | 94 |

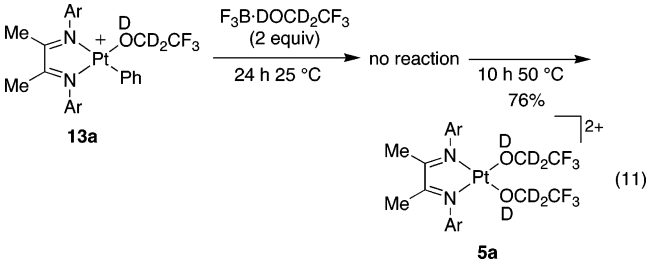
[a] See eq 10 for position labels. [b] Could not resolve necessary peaks,

(Scheme 2) that eventually leads to cleavage of the benzylic C−H bond, effecting substantial isotope exchange between the aryl $H_c$ and methyl $H_a$ positions whenever these two positions contain different labels in the starting 1,4-diethyl- or ethylbenzene isotopologue (Table 4).

For C−H activation at a dicationic platinum center, we no longer have liberated methane to look at, but we can examine the liberated proton. Unfortunately, as noted above, the acidic conditions effect facile H/D exchange between solvent OH and aryl positions; thus, evidence for initial attack at an aryl position cannot be obtained in this way. However, when **5a** is allowed to react with 1,4-$C_6D_4(CH_2CH_3)_2$, the NMR signal for the hydroxylic proton increases by almost exactly the amount expected for liberation of one proton per Pt. A corresponding experiment with $C_6D_5CD_2CH_3$ results in a negligible increase in the OH signal. Taken together, these results imply that **2** and **5** follow different mechanisms for C−H activation of ethylbenzenes: the former reacts at an aryl position and the latter at a benzylic methylene.

As a further test, the isotope scrambling patterns for the two routes to $\eta^3$-benzyls are compared in Table 4. Although the pattern for activation by **5a** is complicated by the substantial acid-catalyzed H/D exchange between solvent and aryl C−H bonds, comparison of entries 1 and 3 seems definitive. There is some exchange of D into the methyl $C_a$ position in both cases; this was previously shown to take place after formation of the product. However, entry 3 for reaction of **2a** shows much more extensive deuteration of $H_a$ by transfer from the original aryl positions; no such increase is observed for the reaction of **5a**. Hence, in this case net benzylic C−H activation *does* result from direct attack at the benzylic position, unlike the previous case of activation by **2**. The activation is irreversible: analysis of unreacted diethyl- and ethylbenzene isotopologues by GC/MS shows no H/D exchange in the alkyl groups.

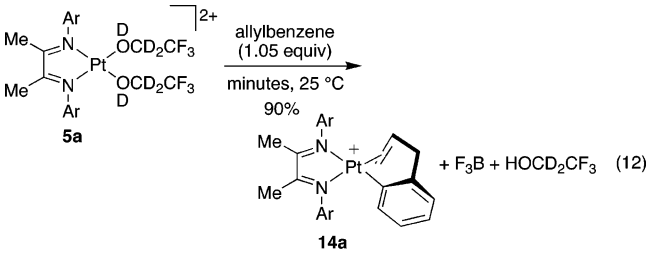
**Other C−H Bond Activations at Dicationic Platinum Centers.** Addition of benzene to the platinum dication **5a** results in neither arene complex formation nor C−H activation; no new products are formed, even after heating. There is no decomposition under these conditions: after the reaction mixture is heated for 24 h, addition of an excess of 1,4-diethylbenzene still gives $\eta^3$-benzyl product **10a** in 98% yield. The possibility that reversible aryl C−H bond activation takes place but the resulting phenyl product is unstable to the liberated acid cannot be tested by isotope exchange, as that process occurs in the acidic medium even in the absence of platinum complex. Evidence in support of platinum-catalyzed reversible exchange was obtained by exposing platinum phenyl cation **13a** (prepared from **2a** and benzene) to the reaction conditions (eq 11). While **13a** is stable



(11)

to the acidic reaction environment at room temperature, warming the reaction mixture to 50 °C results in complete dephenylation to give the solvated platinum complex **5a** in 76% yield. Addition of 1,4-diethylbenzene to the resulting solution again gives $\eta^3$-benzyl **10a**.

In striking contrast, **5a** reacts rapidly with 1 equiv of allylbenzene at room temperature to cleanly afford the ortho-metalated product **14a** (eq 12); the structure was confirmed crystallographically.[14] If more than 1 equiv of allylbenzene is



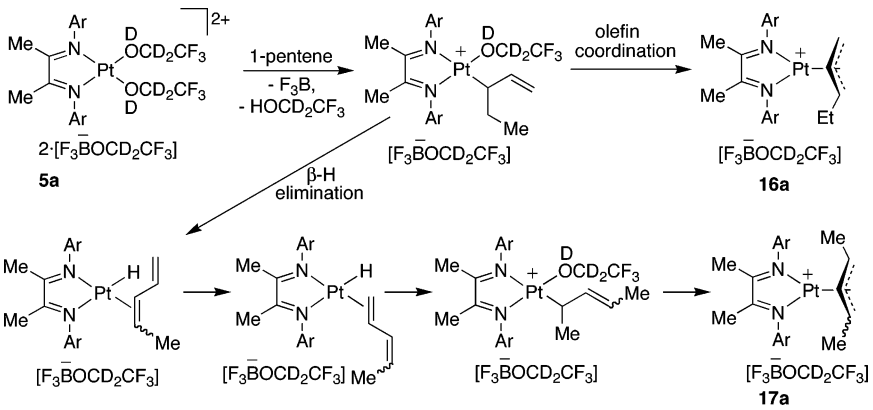
(12)

used, the excess substrate is all consumed and the product—apparently an oligomeric species—oils out of solution. No oligomerization of allylbenzene takes place in $BF_3$/TFE in the absence of platinum.

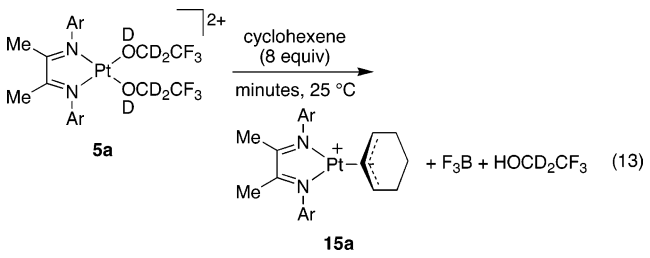
Compounds with allylic C−H bonds also react rapidly at room temperature. Reaction of cyclohexene with the platinum

(14) See the Supporting Information for details. Full crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 614486.

**Scheme 3**

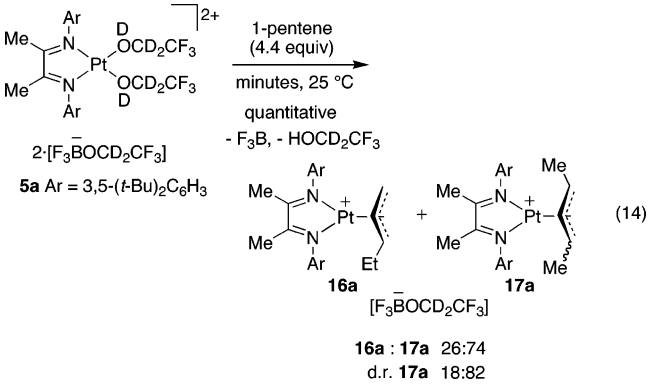



dication **5a** at 25 °C gives the $\eta^3$-allyl complex **15a** in 94% yield (eq 13). In contrast to the case for allylbenzene, excess




substrate could be employed without oligomerization. The addition of cyclohexene to a solution of **5a** at −20 °C did not result in the observation of a discernible $\pi$ complex using $^1$H NMR spectroscopy.

1-Pentene reacts similarly to give a mixture of isomeric allyls, **16a** and **17a**, in a 26:74 ratio (eq 14). The ratio of diastereomers

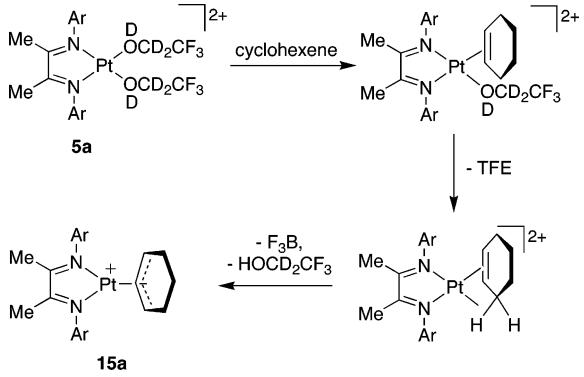



of **17a** was estimated to be approximately 18:82. These product ratios did not change upon warming the reaction mixture to 50 °C for several days. A plausible mechanism for the formation of $\eta^3$-allyl isomers is shown in Scheme 3.

In contrast to olefin or arene substrates, no C−H bond activation products were observed when the solvated platinum dication **5a** was exposed to methane, *n*-pentane, or cyclohexane. No reaction was observed until 90 °C, at which point the starting material slowly decomposed (in the presence or absence of alkane) to give Pt(0) along with the same symmetrical product observed by $^1$H NMR on concentration of **5a** (see above). No H/D exchange of unreacted alkane was observed in any case.

The plausible inference (from kinetics) that activation of a benzylic C−H bond requires prior coordination of a $\pi$-arene ligand raises the possibility that the same might be true for alkane C−H bond activation. To test that, a small amount of

**Scheme 4**




*p*-xylene (2.5 equiv) was added to **5a**, giving the platinum $\pi$-arene complex **8a′** (eq 4). The reaction mixture was then saturated with cyclohexane (94 equiv) and heated. As before, alkane C−H bond activation did not occur.

## Conclusions

We have demonstrated that a platinum dication can activate C−H bonds to afford organoplatinum complexes that are stable to acid. The ultimate goal of this program is the development of catalysts, based on the Shilov system, that can selectively oxidize or otherwise functionalize hydrocarbons, especially alkanes. Major challenges clearly remain—the range of hydrocarbons that can be activated by the complexes studied here is rather limited and methods are needed for completing the functionalization sequence that will not interfere with C−H bond activation, as well as others.

These dicationic platinum complexes (**5**) exhibit complicated behavior, most notably sensitivity to subtle changes in hydrocarbon reagent, major differences of reactivity and mechanism as compared to those of the corresponding methylplatinum monocations (**2**). Much of this can be understood by recognizing the central role of ligand replacement in C−H activation chemistry. It is generally accepted that a C−H $\sigma$ complex is the immediate precursor to C−H activation and that a C−H $\sigma$ bond is a relatively weak ligand, so that a readily displaceable ligand is a requisite component of any C−H activator, hence the role of TFE as solvent/ligand in these model systems.[3c]

The presence of a "soft" electron-releasing methyl group should weaken the bonding of TFE to the monocationic platinum center in **2**, relative to that in the dicationic **5**. Accordingly, activation of diethylbenzene by **5** not only is slower but also (according to one interpretation of the kinetics) requires prior replacement of one TFE by a $\pi$-arene before a second arene

molecule undergoes C−H activation. We suggest, then, that the (unspecified) intermediate shown in eq 9 above is in fact a $\sigma$ complex of a benzylic C−H bond, which is not capable of displacing TFE directly from **5a** but can do so from **8a**. Labeling experiments indicate that the benzylic position is the site of initial C−H bond activation by **8a**, whereas it is an aryl position for **2**; the reasons for this difference are not clear.

The facile C−H activations of allylbenzene and of allylic positions on olefins are consistent with this picture. Initial coordination of the olefinic $\pi$ bond, a considerably better ligand than an $\eta^2$-arene, generates a species electronically similar to **8a**, which furthermore has an aryl or allylic C−H bond appropriately placed for intramolecular activation, as illustrated for cyclohexene in Scheme 4. We cannot determine whether benzene itself undergoes C−H activation by **5**; the expected product (**13**) would not be stable, and background acid-catalyzed H/D exchange obviates that test for reversible activation. It is also not clear why methylbenzenes do not react with **5** to give $\eta^3$-benzyls, in contrast to reactions of **2**, where methyl- and ethylbenzenes react similarly (although by different mechanisms).[9i] We believe this probably reflects product stability rather than inherent reactivity, as decomposition products are observed. A similar situation is found in the formation of $\pi$-arene complexes, where *p*-dialkylbenzenes readily displace a TFE ligand whereas monoalkylbenzenes (and benzene itself) show no observable complexation at all. Presumably this represents a delicate balance between the bonding abilities of the arene vs those of TFE, which is just tipped by the additional electron donation conferred by two alkyl substituents.[15]

The failure of alkanes to react at dicationic platinum may be a consequence of kinetics and/or thermodynamics. A simple alkyl product, $[(N\text{-}N)PtR(TFE)]^+$, is not be expected to be stable to the proton generated in its formation, since the corresponding methyl compound **2** is not. The lack of any observable alkyl H/D exchange, however, suggests that there is a kinetic barrier as well. Previous studies have shown that methane is considerably less reactive than benzenes or alkylbenzenes toward **2**;[9e,h,j] also, there is no ligand available to generate an intermediate (like **8**) that may be more prone to undergo TFE replacement by a C−H bond. An attempt to provide the latter, in the form of *p*-xylene, had no effect. As shown above, a C−H bond at a saturated carbon *can* be activated intramolecularly, at least in a case where a relatively stable product such as an $\eta^3$-allyl group can be reached. It remains to be seen whether a suitable combination of reagents and reaction conditions will make it possible to access a much wider range of C−H bonds for functionalization by this route. Progress toward this end is ongoing in our laboratories.

## Experimental Section

**General Considerations.** $^1$H NMR and $^{13}$C NMR spectra were recorded at ambient temperature using Varian 600 or 300 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the $\delta$ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were acquired on a Finnigan LCQ ion trap or Agilent 5973 *Network* mass selective detector and were obtained by peak matching. All reactions were carried out under an atmosphere of nitrogen in glassware which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was purified by sublimation (90 °C, 0.5 mmHg). Trifluoroborane was purified by following the procedure of Brown and co-workers:[16] the borane was condensed into benzonitrile and evacuated. The borane−nitrile complex was decomposed by mild heating to 60 °C. The borane was passed through two −78 °C traps and condensed at −196 °C. It was then vacuum-distilled by warming to −78 °C. A known volume of $BF_3$ was then condensed into trifluoroethanol to form a 0.4776 M solution. Trifluoroethanol-$d_3$ was dried over 3 Å molecular sieves for at least 5 days and then was vacuum-distilled onto $B(C_6F_5)_3$. After 6 h, the trifluoroethanol-$d_3$ was vacuum-distilled to and stored in a valved reaction vessel. The platinum dimethyl complexes were synthesized by following earlier reported procedures.[9g] Trifluoroethanol-$d_3$, $B(C_6F_5)_3$, and platinum dimethyl complexes were stored in a Vacuum Atmospheres nitrogen atmosphere drybox.

**Representative Formation of $[(N\text{-}N)Pt(TFE\text{-}d_3)_2]^{2+}$ (5a) from $[(N\text{-}N)PtMe_2]$ (1a) (N-N = ArN=C(Me)C(Me)=NAr).** To a suspension of the platinum dimethyl complex **1a** (0.010 g, 0.015 mmol) in 0.700 mL of trifluoroethanol-$d_3$ was added 0.070 mL of a 0.455 M solution of $F_3B$ in trifluoroethanol-$d_3$. The reaction progress was analyzed periodically using $^1$H NMR spectroscopy. After 15 h, analysis revealed complete consumption of **1a** and formation of **5a** (in situ characterization): $^1$H NMR (300 MHz, $CF_3CD_2OD$) $\delta$ 7.84 (br s, 2H), 7.35 (br s, 4H), 2.32 (br s, 6H), 1.38 (br s, 36H); $^{13}$C NMR (125 MHz, $CF_3CD_2OD$) $\delta$ 189.8, 157.9, 144.6, 127.8, 117.9, 37.0, 31.8, 20.6; $^{19}$F NMR (282 MHz, $CF_3CD_2OD$) $\delta$ −77.3, −150.5 (br s).

**Representative Formation of the $\eta^3$-Benzyl Complex 10a from $[(N\text{-}N)Pt(TFE\text{-}d_3)_2]^{2+}$ (5a).** To 0.700 mL of a 0.014 M solution of the platinum dication **5a** in trifluoroethanol-$d_3$ was added 0.050 mL of 1,4-diethylbenzene (0.321 mmol). Analysis of the resulting mixture using $^1$H NMR spectroscopy revealed partial formation of the $\pi$-arene complex **8a** (R = Et): $^1$H NMR (300 MHz, $CF_3CD_2OD$) $\delta$ 7.73 (t, $J$ = 1.8 Hz, 2H), 7.22 (d, $J$ = 1.5 Hz, 4H), 6.77 (s, 4H), 2.41 (s, 6H), 1.88 (q, $J$ = 7.5 Hz, 4H), 1.43 (s, 36H), 1.12 (t, $J$ = 7.5 Hz, 6H); $^{13}$C NMR (125 MHz, $CF_3CD_2OD$) $\delta$ 181.3, 157.1, 150.4, 143.5, 132.4, 117.0, 113.6; 36.7, 31.9, 27.2, 20.0, 13.0; $^{19}$F NMR (282 MHz, $CF_3CD_2OD$) $\delta$ −77.2, −81.8, −150.9. The reaction mixture was heated to 50 °C. After 13 h, $^1$H NMR analysis revealed formation of the $\eta^3$-benzyl complex **10a** in 98% yield: $^1$H NMR (600 MHz, $CF_3CD_2OD$) $\delta$ 7.61 (s, 1H), 7.59 (s, 1H), 7.24 (br s, 1H), 7.45 (s, 1H), 6.96 (br s, 2H), 6.80 (br s, 1H), 6.47 (s, 1H), 6.39 (s, 1H), 5.88 (d, $J$ = 6.6 Hz, 1H), 2.82 (q, $J$ = 6.6 Hz, 1H), 2.08 (dd, $J$ = 14.7, 7.5 Hz, 1H), 2.02 (s, 3H), 2.00 (dd, $J$ = 14.7, 7.5 Hz, 1H), 1.93 (s, 3H), 1.44 (s, 9H), 1.39 (br s, 9H), 1.36 (br s, 9H), 1.30 (s, 9H), 0.93 (t, $J$ = 7.5 Hz, 3H), 0.29 (d, $J$ = 6.6 Hz, 3H). The $^1$H NMR data matched those previously reported.[9i]

**Acknowledgment.** Funding for this work was provided by the bp MC2 program and the NIH in the form of NRSA fellowships to T.G.D. (Grant No. GM070272) and T.J.W. (Grant No. GM075691). We thank Tom Dunn for assistance with NMR spectrometry, Dr. Mona Shahgholi for mass spectrometry data, and Mr. Larry M. Henling for crystallographic analysis.

**Supporting Information Available:** Text, tables, and figures giving detailed experimental procedures, characterization data, and integrated rate laws and a CIF file giving X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060792R

(15) Displacement of TFE by ethylbenzene and (to a lesser extent) benzene can be observed at low TFE concentrations by using the weaker ligand hexafluoroisopropyl alcohol as solvent: Driver, T. G. Unpublished results.

(16) Brown, H. C.; Johannesen, R. B. *J. Am. Chem. Soc.* **1953**, *75*, 16−20.