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Heterolytic CH Activation with a Cyclometalated Platinum(II) 6-Phenyl-4,4′-di-*tert*-butyl-2,2-Bipyridine Complex

Kenneth J. H. Young,[†] Steven K. Meier,[†] Jason M. Gonzales,[‡] Jonas Oxgaard,[‡]
William A. Goddard III,[‡] and Roy A. Periana*[,†]

*Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1661, and Materials and Process
Simulation Center, Beckman Institute (139-74) Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, California 91125*

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*Summary: The more electron-rich, thermally, air, and protic stable, cyclometalated Pt(II)(NNC) trifluoroacetate complex (**3**) (NNC = κ^3-6-phenyl-4,4′-di-tert-butyl-2,2′-bipyridine) was synthesized with the expectation that it would be less susceptible to H_2O inhibition than the Pt(bpym)$(TFA)_2$ system (bpym = κ^2-2,2′-bipyrimidine) for the catalytic oxidation of hydrocarbons. Complex **3** was found to catalyze the H/D exchange between benzene and trifluoroacetic acid via CH activation but at a rate slower than the Pt(bpym) complex. Experimental and theoretical studies show that while the use of the more electron-rich NNC ligand motif lowered the ΔH for substrate coordination relative to the Pt(bpym) system, a larger increase in the barrier for CH cleavage led to an increase in the overall barrier for CH activation.*

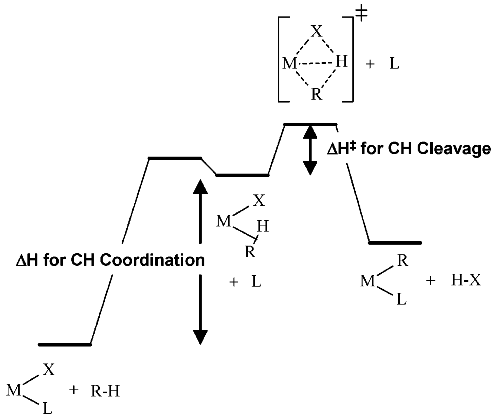

Figure 1. Generalized energy diagram emphasizing the two key steps involved in the CH activation reaction: RH coordination and CH cleavage.

Homogeneous catalysts that operate by the CH activation reaction currently show the greatest potential for the development of new, selective, hydrocarbon oxidation chemistry.[1] Many of the new systems currently being studied utilize neutral bidentate nitrogen ligands with Pt.[2] Recently a monoanionic bidentate nitrogen-ligated Pt system has been reported by Baker and Bercaw and shown to undergo CH activation.[3] Peters et al. have recently reported a monoanionic tridentate amido NNN platinum pincer complex that activates the CH bond of benzene in the presence of a bulky organic base.[4] We previously reported a bidentate, N-ligated, electrophilic platinum(II) bipyrimidine catalyst, Pt(bpym)Cl_2 (bpym = κ^2-2,2′-bipyrimidine), for the direct conversion of methane to methylbisulfate in 70% yield and >90% selectivity in concentrated sulfuric acid.[1a] Studies indicated that this catalyst system operates via a CH activation/functionalization reaction sequence involving a Pt−CH_3 intermediate.[1a,5] The key limitation of this system is inhibition of the catalyst with decreasing acidity of the sulfuric acid solvent as the reaction products, H_2O and CH_3OH, increase beyond ∼1 M.

Consistent with the inhibition of the Pt(bpym) system by weaker acid solvents, the related Pt(bpym)$(TFA)_2$ complex shows no H/D exchange reaction with methane in CF_3CO_2D ($H_o = 2.6$). As with most systems examined in detail,[1g,2b,5,6] theoretical and experimental studies show that the overall activation energy for CH activation with the Pt(bpym)Cl_2/H_2SO_4 system results from two key barriers: (A) hydrocarbon (RH) coordination and (B) CH cleavage, defined as shown in Figure 1. Of these two contributions, the ΔH for methane coordination (27 kcal mol^{-1}, L = X = HSO_4^-) far outweighs the $\Delta H^\ddagger$ for CH cleavage (5 kcal mol^{-1}).[5] Further, calculations show that the inhibition by H_2O results from ground state stabilization, L = H_2O in Figure 1, which increases the ΔH for methane coordination by ∼7 kcal mol^{-1}, rather than from destabilization of the transition state (TS) for CH cleavage.[5b]

One strategy that we are exploring to increase the rate of CH activation and overcome water inhibition is to develop more electron-rich Pt catalysts that are sufficiently stable to protic, oxidizing media. Conceptually, increasing electron density at the Pt(II) center could be expected to *reduce* H_2O or CH_3OH binding to the σ-acceptor orbitals on Pt(II) since H_2O and CH_3OH are good σ- or π-donors but not π-acids, thereby minimizing inhibition by *destabilizing* the ground state.[7] Assuming that

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* Corresponding author. E-mail: rperiana@usc.edu.

[†] University of Southern California.

[‡] California Institute of Technology.

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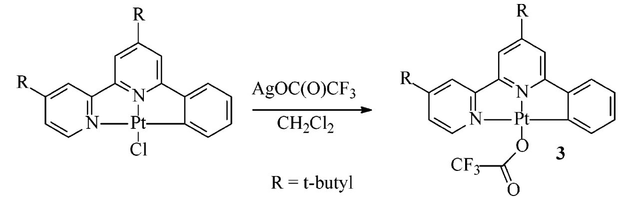
binding of the hydrocarbon, RH, is *not* the rate-determining step, then the activation barrier for the overall CH activation reaction will depend on the energy differences between the ground state, L−M−X, and the CH cleavage transition state (i.e., the energetics for binding RH is not relevant to the overall activation barrier). Under these circumstances, the key to obtaining a net reduction in the overall barrier for CH activation in weakly acidic solvents will be to ensure that the degree of *destabilization* of the ground state brought about by ligand modifications is *greater* than that for the CH cleavage transition state.

Significantly, unlike non-transition metal ions such as Hg(II), Pt(II) can potentially interact in the TS for CH cleavage with both σ-acceptor and π-donor orbitals.[8] In the Pt(bpym)Cl_2/H_2SO_4 system, the CH bond was shown theoretically to be cleaved by an electrophilic substitution (ES) pathway that involves CH donor interactions to σ-acceptor orbitals on Pt(II).[5] Increasing electron density at the metal center in a weaker acid solvent, HX, could be expected to *destabilize* the transition state for this mode of cleavage (either minor or significant changes), assuming that the metal center still behaves as an electrophilie. However, if the dominant pathway for CH cleavage switches to an insertion (so-called oxidative addition (OA)) pathway (by interactions between the CH σ^* antibonding orbitals and π-donor orbitals on Pt(II)), followed by rapid proton loss, then a net decrease in the overall barrier for CH activation could be possible by ligand modifications that increase electron density at the Pt center. Therefore, it should be possible to *stabilize* the CH cleavage by insertion as well as destabilize water coordination by increasing the electron density at Pt(II). Herein, we report on the synthesis of an electron-rich, thermally stable, monoanionic, tridentate, pincer, platinum NNC complex, Pt(NNC)TFA, and experimental and theoretical comparison of the reactivity for CH activation and functionalization relative to the Pt(bpym)$(TFA)_2$ system.

It is now well established that the tridentate pincer ligand motif can impart both thermal stability and reactivity to transition metal complexes.[9] This has been demonstrated with the thermally stable PCP−Ir systems of Kaska, Jensen, and Goldman[10] that catalyze the thermal dehydrogenation of alkanes. The tridentate ligand 6-phenyl-2,2′-bipyridine (NNC−H) and its derivatives have been shown to readily form stable, cyclometalated complexes with platinum, Pt(NNC)X.[11] However, most of the interest in these complexes has been focused on the photoluminescent properties, and to our knowledge no catalysis studies have been reported. The corresponding cyclometalated NNC platinum(II) chloride complex, **1**, Pt(NNC)Cl (NNC = κ^3-6-phenyl-4,4′-di-*tert*-butyl-2,2′-bipyridine), was prepared through a modified procedure reported by Lu et al.,[11c] by heating the NNC−H ligand with K_2PtCl_4 in glacial acetic acid. To create a potentially active catalyst, the chloride was replaced by a more labile leaving group using silver trifluoroacetate to obtain the corresponding trifluoroacetate complex (**3**), Pt(NNC)TFA, in good yields (Scheme 1). Complex **3** is air stable and was fully characterized by ^1H and ^{13}C NMR, as well as mass spectroscopy and elemental analysis. All nine expected aromatic resonances were observed, and platinum satellites (J_{Pt-H} = 33 Hz) were observed for the ortho proton on the metalated phenyl ring of **3**.

Scheme 1. Synthesis of Pt(NNC)X Complex 3



Control studies carried out by heating a trifluoroacetic acid solution of **3** for 11 h at 200 °C under argon confirmed that **3** was thermally stable to acidic solutions. No insoluble Pt metal was visible and analysis by NMR (after workup) showed that no significant decomposition occurred as **3** was recovered with ∼91% mass balance (1,3,5-trimethoxybenzene as an internal standard) with minor amounts of what is believed to be the ion-pair or solvento complex.

Dissolution of **3**, an orange solid, in CH_2Cl_2 results in an orange solution. However, consistent with the hoped-for destabilization of the ground state and lability of the TFA^- by use of the more electron-rich NNC ligand, dissolution in CF_3CO_2H leads to a blue solution, which we believe is due to acid-assisted dissociation of the TFA^- ligand and formation of $[Pt(NNC)]^+TFA^-$ as either a three-coordinate ion-pair or solvento complex. Some evidence for this is that removal of the CF_3CO_2H in vacuo leads to a blue residue that after treatment with a mixture of water and CH_2Cl_2 and subsequent evaporation of the CH_2Cl_2 layer leads to quantitative recovery of **3** as a yellow-orange solid. Additional evidence that the blue solution results from dissociation of the TFA^- ligand is the observation that when orange CD_2Cl_2 solutions of **3** are treated with the poorly coordinating, strong Lewis acid $B(Ph-F_5)_3$, a dark blue-black solid is generated. Consistent with the expected lability of the TFA^-, reaction of the blue solution of **3** in CF_3CO_2H with excess LiCl leads to immediate formation of the yellow-orange chloride derivative Pt(NNC)Cl, **1**. While a three-coordinate ion-pair or solvento complex best fits these observations, another possibility is that the complex becomes protonated in the presence of added CF_3CO_2H to generate a Pt(IV) hydride. However, ^1H NMR studies in which HTFA (3.8 equiv) was added to a solution of **3** in CD_2Cl_2 at −70 °C did not show any evidence of a protonated platinum species.

Having established that **3** was thermally stable under protic conditions and the TFA ligand was labile in CF_3CO_2H solvent, the efficiency for catalyzing the H/D exchange reactions between methane and CF_3CO_2D or D_2SO_4 was investigated and compared to the reference system, Pt(bpym)$(TFA)_2$. As was the case for the Pt(bpym)$(TFA)_2$ system, **3** was also found to be *inactive* for catalyzing the H/D exchange between methane and CF_3CO_2D at temperatures as high as 200 °C. Significantly, however, while solutions of the Pt(bpym)$(TFA)_2$ in CF_3CO_2D are stable in both the presence and absence of methane, **3** decomposed at 200 °C to colloidal platinum in the presence of methane. Since the control studies showed that trifluoroacetic acid solutions of **3** are thermally stable at 200 °C in the *absence* of methane, these results could suggest that reaction with methane occurred with the Pt(NNC)TFA complex in CF_3CO_2D. Given the instability of **3** with methane that precludes rigorous study, this potentially interesting result was not further investigated. Interestingly, catalytic H/D exchange between methane and sulfuric acid could be observed with Pt(NNC)Cl, **1**, without obvious decomposition, but at a factor of ∼10 lower than the Pt(bpym) system. Thus, heating **1** in D_2SO_4 with methane (500 psi) for 10 h at 180 °C

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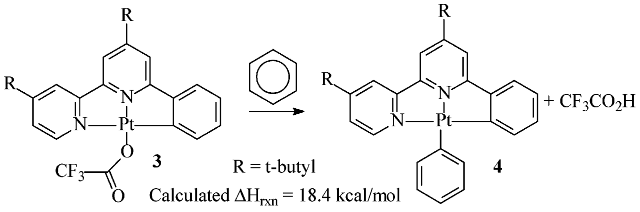
Scheme 2. Stoichiometric CH Activation of Benzene with 3



resulted in ~14% conversion of methane to the deuterated methane isotopologues (CH_3D 5.39%, CH_2D_2 2.53%, CHD_3 2.3%, CD_4 4.2%), with a turnover number (TON) of 61.70 and a turnover frequency (TOF) of ~1.61 × 10^{-3} s^{-1}. However, unlike the Pt(bpym) system, only a small amount of methylbisulfate production (TON of ~2) was observed, suggesting that the Pt(NNC) system may not undergo efficient functionalization of the Pt−CH_3 intermediates in sulfuric acid, an oxidizing acid.

To further investigate the chemistry of this Pt(II)(NNC) system, we turned to benzene as a substrate, as the barriers for CH activation could be expected to be lower and the system more stable and amenable to fundamental study in the weaker, nonoxidizing acid solvent CF_3CO_2H. Complex **3** is soluble[12] in benzene, and we investigated whether the stoichiometric CH activation, Scheme 2, would proceed to generate the phenyl complex Pt(NNC)Ph, **4**. In situ NMR analyses showed that no reaction is observed after heating **3** in C_6D_6 for 12 h at 180 °C. To investigate whether this was due to unfavorable thermodynamic or kinetics, we used DFT to calculate the ΔH_{rxn} for the formation of **4** from reaction of benzene with **3** as shown in Scheme 2. The calculations[20] show that the CH activation reaction, Scheme 2 (assuming trifluoroacetic acid as solvent), is unfavorable by ~18 kcal mol^{-1} (vide infra) and that the equilibrium concentration of the likely CH activation product, Pt(NNC)Ph, **4**, would be too low to observe. In an attempt to drive the formation of the CH activation product, **3** was heated in neat benzene at 160 °C with Hunig's base (diisopropylethylamine) in the hope that this strong base could drive Scheme 2 to completion. However, no phenyl product was observed in this reaction and **3** was recovered.

To examine whether **4** could be reversibly generated by CH activation, we investigated if **3** could catalyze the H/D exchange between benzene and trifluoroacetic acid. When the reaction was carried out at 180 °C with a 1:4 by volume mixture of benzene (C_6H_6) and deuterated trifluoroacetic acid (CF_3CO_2D), respectively, catalytic incorporation of deuterium into benzene was observed to generate C_6H_5D with a TOF of 8.18 × 10^{-3} s^{-1} (TON of 14.7 turnovers after 30 min). Almost *no* other benzene isotopologues, e.g., $C_6H_4D_2$ or higher, are observed at TONs below 60, suggesting that H/D exchange occurs via sequential, as opposed to parallel, formation of the isotopologues $C_6H_5D_1 \rightarrow C_6H_4D_2 \rightarrow$ etc.[1g,2c,21] At these temperatures, control experiments in the absence of **3** show that some H/D exchange occurs between C_6H_6 and CF_3CO_2D, and the reported H/D exchange rates are corrected for this background activity (see Supporting Information).

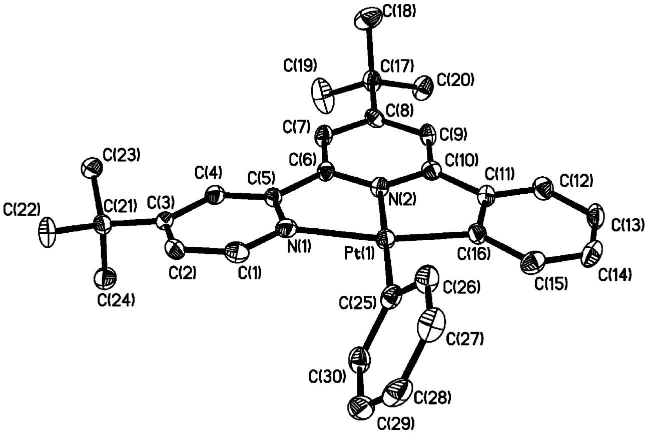


Figure 2. Thermal ellipsoid plot of **4** with 50% probability. Hydrogens and benzene cosolvent were removed for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pt(1)−C(16), 1.990(4); Pt(1)−N(1), 2.116(3); Pt(1)−N(2), 2.006(3); Pt(1)−C(25), 2.014(4); N(2)−Pt(1)−C(25), 179.65(15); C(16)−Pt(1)−N(1), 159.50(13).

The catalytic system is stable, as a plot of TON versus time shows a linear increase (see Supporting Information). Complex **3** could also be isolated from the C_6H_6/CF_3CO_2H reaction mixtures by quenching with water followed by extraction with CH_2Cl_2 and evaporation. Both ^1H and ^{19}F NMR analyses of the solid residue confirmed that **3** could be recovered in 92% yield based on internal standardization with 1,3,5-trimethoxybenzene. Consistent with the theoretical calculations showing that the expected phenyl complex, **4**, is less stable than **3**, no evidence for formation of **4** was found in these isolation experiments. The H/D exchange reactions were carried out at several temperatures between 160 and 190 °C, and the activation barrier was determined to be 32.4 (±2.5) kcal mol^{-1}. Significantly, under similar conditions, the related system Pt(bpym)$(TFA)_2$[7a] was found to be *more* active for H/D exchange between C_6H_6 and CF_3CO_2D with an activation barrier of ~27 kcal mol^{-1}.

Given the central importance of the phenyl complex Pt(NNC)-Ph, **4**, in the expected mechanism for H/D exchange, we synthesized this material for study. The phenyl complex was obtained by heating the chloro complex, **1**, with diphenyl zinc in THF at 80 °C. The compound was fully characterized by ^1H and ^{13}C NMR, as well as mass spectrometry, elemental analysis, and X-ray crystallography. Suitable crystals of **4** were grown by slow vapor diffusion of pentane into a benzene solution.[22] As can be seen in the thermal ellipsoid plot in Figure 2, the ligand binds in a tridentate fashion with the phenyl ring (C26−C25−Pt1−C16) at 60.9° to the plane of the ligand. Consistent with this phenyl complex as an intermediate in the proposed mechanism for H/D exchange, complex **4** was found to catalyze the H/D exchange between benzene and trifluoroacetic acid at 180 °C with an almost identical TOF (9.1 × 10^{-3} s^{-1}) as that of **3**. Also consistent with the proposed intermediacy of **4** in the CH activation reaction with **3** as well as the calculations showing that **4** is unstable with respect to **3**, Scheme 2, treatment of **4** with trifluoroacetic acid (2.5 equiv) resulted in the formation of free benzene and the trifluoroacetate complex **3**. Significantly, when CF_3CO_2D was used for the protonolysis, only C_6H_5D was

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(12) Complex **3** is moderately soluble at room temperature, but very soluble at elevated temperatures.

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(22) Crystal data for **4**: $C_{30}H_{32}N_2Pt$, C_6H_6; monoclinic, space group *P*2-(1)/*c*, $a = 13.002(2)$ Å, $b = 16.534(3)$ Å, $c = 13.345(2)$ Å, $V = 2853(8)$ Å^3, $Z = 4$, final *R* indices ($I > 2\sigma(I)$) R1 = 0.0298, wR2 = 0.0638. Details for the crystal structure can be found in the Supporting Information.

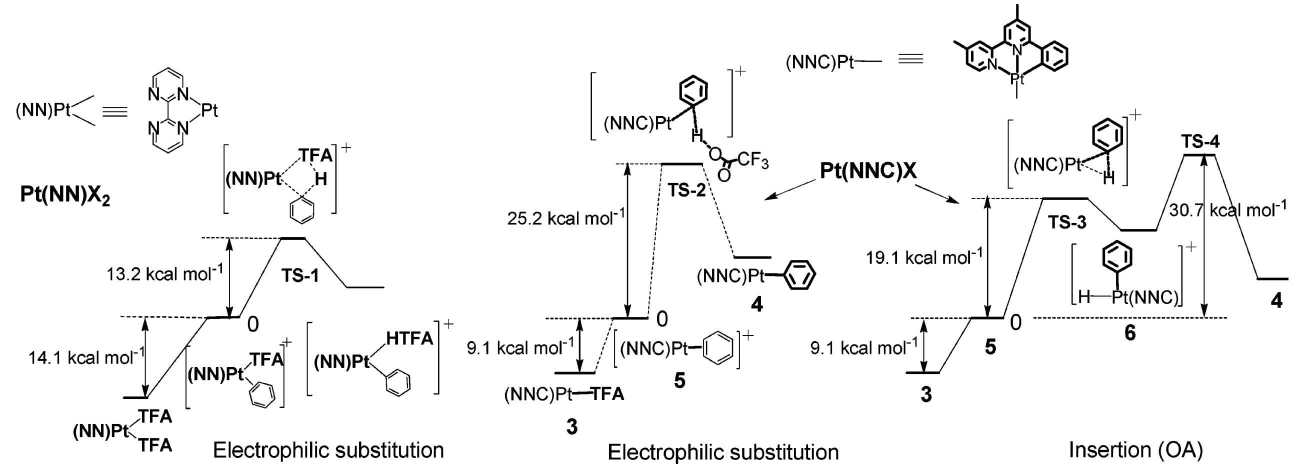

Figure 3. Energy diagram for the Pt(NNC)X and Pt(NN)X_2 systems.

observed; no other isotopologues of benzene were observed. This is consistent with the sequential H/D exchange observed with CF_3CO_2D/C_6H_6 mixtures and the proposed intermediacy of **4** in the catalytic reaction.

To obtain further insight into why the Pt(NNC) system was slower than the Pt(bpym) system for CH activation, DFT calculations were used to compare the systems, Figure 3. Significantly, the calculations show that stabilization of the TFA^- anion with an explicit HTFA solvent molecule, $[TFA-H-TFA]^-$, is required to correlate the theoretical with the experimental data. The calculations show that the global ground state is a solvento species, $[Pt(NNC)(HTFA)]^+[TFA]^-$, **2**, that is ~1.8 kcal mol^{-1} lower in energy than **3**.[23] This is consistent with the experimental observation that upon heating the blue CF_3CO_2H solutions (attributed to TFA^- ionization) of **3** (an orange solid), the color reversibly changes to reddish-orange. As can be seen, in accordance with experimental results, the calculations predict that the Pt(NNC)TFA system has a higher barrier for the overall CH activation reaction.[24] As observed in earlier theoretical studies with methane in sulfuric acid,[5] the lowest energy pathway identified for the Pt(bpym) system[7a] involves benzene coordination ($\Delta H \approx 14$ kcal mol^{-1}) via a dissociative process (that can be considered an upper limit for this step), followed by CH cleavage via electrophilic substitution (ES), **TS1** ($\Delta H^{\ddagger} \approx 13$ kcal mol^{-1}), Figure 3. The predicted value (which is the sum of these two steps) of the overall CH activation barrier, $\Delta H^{\ddagger} = \sim 27$ kcal mol^{-1}, for the Pt(bpym)$(TFA)_2$ system is consistent with the experimental activation barrier of ~27 kcal mol^{-1}.

Interestingly, despite our expectations that CH cleavage by $[Pt(NNC)X]^+$ could proceed by a lower energy pathway involving an insertion (as opposed to ES) pathway followed by rapid proton loss, the pathway that best fits the experimental activation energy of ~32 kcal mol^{-1} is one involving CH activation via benzene coordination, **5** ($\Delta H \approx 9$ kcal mol^{-1} via an upper limit dissociative process), and cleavage via electrophilic substitution (ES), **TS2** ($\Delta H^{\ddagger} \approx 25$ kcal mol^{-1}), for an overall barrier of ~34 kcal mol^{-1}. The calculations do show, as expected, that CH cleavage by insertion (**TS3**, $\Delta H^{\ddagger} \approx 19$ kcal mol^{-1}) is lower than the ES pathway, **TS2**. However, the calculations show that reversible proton loss from the product of CH cleavage by insertion, $[Pt(NNC)(Ph)(H)]^+$, **6**, is a higher energy pathway, **TS4**, than the ES, **TS2**, pathway. Thus, the calculations and experiment show that our expectations were met that the Pt(NNC) would be (A) thermally stable to protic media, (B) able to catalyze the CH activation reaction, and (C) able to reduce the ΔH for substrate coordination from ~14 for the Pt(bpym) system to ~9 kcal mol^{-1} for the Pt(NNC) system. However, the expected reduction in the $\Delta H^{\ddagger}$ for CH cleavage with the Pt(NNC) system (~25 and ~19 kcal mol^{-1} via the ES and insertion pathways, respectively) relative to the Pt(bpym) system (~13 kcal mol^{-1} via a ES pathway) was *not* realized, and this accounts for the lower overall CH activation rates of the Pt(NNC) system.

In conclusion we report the synthesis of a new, acid and thermally stable cyclometalated 6-phenyl-4,4′-di-*tert*-butyl-2,2′-bipyridine Pt(II) trifluoroacetate complex (**3**) that is more electron-rich than the Pt(bpym) system. The results suggest that this complex, unlike Pt(bpym)$(TFA)_2$, reacts with methane in trifluoroacetic acid but decomposes. The complex catalyzes H/D exchange with methane in sulfuric acid at a lower activity than the Pt(bpym)Cl_2 system, and only low levels of methylbisulfate are generated. In a comparison to the bpym system for H/D exchange between C_6H_6 and CF_3CO_2D we find that the bpym system is faster. Thus, our expectations that the more electron-rich Pt(NNC) system would minimize inhibition by H_2O by ground state destabilization did not lead to a more effective catalyst. Theoretical studies show that while we were successfully able to lower the energetics for substrate coordination, the concomitant increase in CH cleavage barrier was greater, therefore leading to an overall increase in the barrier for CH activation. These results show that modifying the bpym system to increase the overall activity for methanol generation in the presence of water will require a more detailed understanding and greater predictability of the various structure–function relationships for coordination, CH cleavage, and oxidative functionalization.

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Supporting Information Available: Details of the synthesis of complexes **1**–**4**, H/D exchange experiments, deconvolution tables for benzene and methane, crystallographic data in cif format for **4**, and the Cartesian coordinates and enthalpies (in kcal mol^{-1}) of all structures in Figure 3 are available free of charge via the Internet at http://pubs.acs.org.

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[23] The −1.8 kcal/mol value listed for the solvento complex is the relative energy with respect to the reference reactant computed using solvent-optimized structures and energetics. All other values are enthalpies using gas-phase structures with single-point solvation corrections. A full energy diagram can be found in the Supporting Information.

[24] We define the CH activation reaction as a two-step process—hydrocarbon coordination and CH cleavage—and the barrier for this process is the sum of these two steps.