C–H Bond Activation of Methane by Pt^{II} N-Heterocyclic Carbene Complexes. The Importance of Having the Ligands in the Right Place at the Right Time

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* Supporting Information

ABSTRACT: A DFT study of methane C–H activation barriers for neutral NHC–Pt^{II} methoxy complexes yielded 22.8 and 26.1 kcal/mol for oxidative addition (OA) and oxidative hydrogen migration (OHM), respectively. Interestingly, this is unlike the case for cationic NHC–Pt^{II} methoxy complexes, whereby OHM entails a calculated barrier of 26.9 kcal/mol but the OA barrier is only 14.4 kcal/mol. Comparing transition state (TS) and ground state (GS) geometries implies an ~10 kcal/mol “penalty” to the barriers arising from positioning the NHC and OMe ligands into a relative orientation that is preferred in the GS to the orientation that is favored in the TS. The results thus imply an intrinsic barrier arising from C–H scission of ~15–2 kcal/mol for NHC–Pt^{II} methoxy complexes. Calculations show the importance of designing C–H activation catalysts where the GS active species is already structurally “prepared” and which either does not need to undergo any geometric perturbations to access the methane C–H activation TS or is not energetically prohibited from such perturbations.

INTRODUCTION

Petroleum-based hydrocarbons (in particular, alkanes) are an important feedstock source for the chemical industry.¹ In recent years, the U.S. has become a leader in the production of natural gas.² However, methane, which is approximately 87% by volume of natural gas,³ is not as easily and economically transported as methanol, which is a liquid at ambient temperatures and pressures. The process currently used to produce methanol from methane entails two stages; the first stage utilizes a high-temperature/high-pressure process to produce syngas, and the second step utilizes the syngas (CO/H₂) that is formed via initial high-temperature/high-pressure steam re-forming to produce methanol. Direct methane-to-methanol (MTM) catalysis, operating at temperatures of <200 °C, via a partial oxidation mechanism has been widely investigated using a variety of transition-metal (M) and ligand sets (L_n),^{1,4–8} the latter including N-heterocyclic carbenes (NHC).^{9,10}

The MTM process is complicated with respect to controlling overoxidation of methanol. Thus, considerable effort has focused on the critical component reactions: activation of the inert methane C–H bond and C–O bond formation (oxy insertion), intramolecular insertion of an oxygen atom into a metal–methyl bond (M–Me → M–OMe) to yield a

methoxide intermediate. If the latter could activate C–H bonds, a reaction for which there is precedent,¹¹ one could generate methanol and regenerate the M–Me metal alkyl species.¹²

We focus our attention in the present research on catalyst models with N-heterocyclic carbene (NHC) supporting ligands. The unexpected stability of NHC ligands in catalysis was pioneered by Herrmann et al. for their potential utility for C–H activation.^{13,14} NHC complexes of the transition metals have been well studied in catalysis over the past 40 years since they were first introduced by Arduengo.^{9,15,16} NHC ligands are of interest as supporting ligands for MTM catalysis, given their ability to be systematically modified in terms of their steric and electronic properties.^{17–30} Also, NHCs have proven less prone to oxidative degradation in an acidic environment than traditional organometallic ligands such as phosphines and bipyrimidine.³¹ This paper focuses on model Pt^{II} NHC complexes and their ability to accomplish C–H activation.³² The cationic NHC model complex studied has an unsaturated C–C spacer (Scheme 1). The nitrogen

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Scheme 1. Binding of Methane to $[(\text{NHC})\text{Pt}(\text{OMe})]^+$ ^a

^aNote that methane preferentially bonds trans to the methoxy ligand and cis to the NHC.

atoms of NHC are decorated with methyl groups to avoid spurious hydrogen-bonding interactions with electro-negative chemical groups while maintaining a reasonable degree of computational tractability. As discussed previously,⁹ NHC ligands display reasonably strong trans influences, which may direct weakly ligated reacting species cis to any open coordination sites.

Five mechanistic C–H bond activation pathways are modeled for Pt^{II} NHC systems (Scheme 2): two via $\{[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})]^+ + (\text{CH}_4)\}$, a mono-methoxy cationic complex, and the remainder by pathways starting from the neutral bis-methoxy complex $\{[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2] + (\text{CH}_4)\}$. The main goals of this research are to (1) compare and contrast the cationic and the neutral species intermediates, transition states (TS), and potential energy surface (PES) pathways, (2) investigate competing pathways such as σ -bond metathesis (σ BM), oxidative hydrogen migration (OHM), oxidative addition/reduction elimination (OA/RE), and base-assisted deprotonation (BAD), and (3) probe the impact of charge and coordination numbers upon C–H activation for low-valent late-transition-metal species.

COMPUTATIONAL METHODS

Density functional theory (DFT) within the Gaussian 09³³ package was used to characterize the structures and energies of stationary points. The hybrid functional combining Becke's three-parameter exchange functional (B3) with the Lee Yang Parr (LYP) correlation functional (B3LYP) was used.³⁴ The basis set was a pseudo-potential valence double- set with d polarization functions added to main-group elements (CEP-31G(d)).^{34,35} All quoted energies are free energies, calculated with THF ($\epsilon = 7.4257$), CH_3CN ($\epsilon = 35.688$), and DMSO ($\epsilon = 46.826$) solvent models (CPCM method)³⁶ at 298.15 K and 1 atm and utilize unscaled B3LYP/CEP-31G(d) vibrational frequencies and gas-phase optimized stationary points. Little difference among these solvents is observed; therefore, the present paper focuses on the THF results. Stationary points are characterized in the gas phase as minima or transition states (TSs) via calculation of the energy Hessian and observation of the correct number of imaginary frequencies: zero (0) and one (1), respectively. Intrinsic reaction coordinates (IRC) are calculated from all TS geometries to authenticate the imaginary modes and confirm that the TS of interest connected the requisite products and reactants.^{37,38} Except for one geometry optimization discussed in the Prospectus, all geometry optimizations were performed without symmetry restraint. All species were closed-shell singlets, unless stated otherwise, for which restricted Kohn–Sham theory was employed.³⁹

Scheme 2. B3LYP/CEP-31G(d) (THF Solvent Corrections Included) Calculated C–H Bond Activation Pathways for Pt^{II} NHC Complexes^a

^aAbbreviations: OHM, oxidative hydrogen migration; OA, oxidative addition; σ BM, σ -bond metathesis; RE, reductive elimination. Free energies are given in kcal/mol. Note that the same color scheme is used throughout.

Scheme 3. B3LYP/CEP-31G(d) Calculated Free Energies for Oxidative Addition/Reductive Elimination (Pink), as well as σ -Bond Metathesis (BM, Higher) and Oxidative Hydrogen Migration (OHM, Lower) (Blue) in kcal/mol^a

^aFree energies are corrected for continuum THF solvent effects.

RESULTS AND DISCUSSION

1. C–H Activation of Methane by a Cationic Pt^{II} NHC Complex. Scheme 3 depicts the calculated free energies for several of the mechanisms investigated for methane carbon hydrogen (C–H) bond activation.^{1,40} The “internal” C–H activation mechanisms studied for a cationic Pt^{II} NHC 5d⁸ complex are oxidative addition, followed by reductive elimination and σ -bond metathesis. Note also that an oxidative hydrogen migration (OHM)^{1,41,42} transition state was also isolated. Oxidative addition is common for low-valent, electron-rich complexes.⁴² The BM (or the related OHM and σ -complex assisted metathesis (σ -CAM) pathways) occur without the formal oxidation state of the metal changing.^{43,44} Metathesis mechanisms are known for both early and late transition metals for C–H bond activation.¹¹

For the reactions involving cationic Pt^{II} complexes shown in Scheme 3, both redox (OA/RE)¹¹ and nonredox (OHM) pathways are calculated to be reasonably facile, while the cationic BM pathway has a much higher barrier. Analysis of pertinent geometries and orbitals suggests that the effect arises from the pyramidalization (or lack thereof) of the methyl group from the methane substrate. To wit, in ⁺BM, the methyl carbon is sp²; hence, the remaining p orbital can overlap with the s orbital of H but less well with the Pt center. However, in ⁺OHM, the methyl carbon is more pyramidalized, and the hybrid sp³ orbital points more or less midway between the H and the Pt centers, thus assisting in stabilizing both groups in the active site and also the methyl from the substrate, which in turn lowers the kinetic barrier for the OHM pathway.

The single-step electrophilic BM pathway [(NHC)-Pt^{II}(OMe)]⁺ CH₄ $\rightarrow$ ⁺BM [(NHC)Pt^{II}(CH₃)(MeOH)]⁺

is exergonic by 23.9 kcal/mol, while the free energy of methane C–H bond activation is $G = 49.7$ kcal/mol. Pertinent bond distances for the cationic BM transition state (⁺BM) within the active site are 2.09, 2.54, and 2.24 Å for Pt–O_{CH₃}, Pt–H, and Pt–CH₃, respectively. However, a lower energy cationic transition state oxidative hydrogen migration (⁺OHM), whose geometry is more reminiscent of those coined oxidative hydrogen migration (OHM) by Goddard et al.,⁴¹ has a calculated barrier of only $G = 26.9$ kcal/mol relative to the methane adduct depicted in Scheme 3. Metal ligand bond lengths in the active site of ⁺OHM are 2.04, 1.84, and 2.34 Å for Pt–O_{CH₃}, Pt–H, and Pt–CH₃, respectively. It is notable that the Pt–H bond lengths in ⁺OHM and ⁺BM differ by 0.70 Å, with the former being much shorter: hence, our designation of it as an oxidative hydrogen migration TS. Calculation of the intrinsic reaction coordinates (IRCs) from ⁺OHM and ⁺BM reveal that they connect the same reactants and products (Scheme 3). For the latter, [(NHC)Pt^{II}(CH₃)(MeOH)]⁺, the strong trans-influencing methyl ligand is trans to an open coordination site.⁴⁵

Scheme 3 also summarizes the energetics of a two-step MTM mechanism (oxidative addition followed by reductive elimination) starting from the cationic methane adduct. The first step from [(NHC)Pt^{II}(OMe)]⁺ CH₄ $\rightarrow$ ⁺OA [(NHC)Pt^{IV}(CH₃)(MeO)(H)]⁺ is mildly endergonic (+3.7 kcal/mol), leading to a Pt^{IV}-metal-hydride intermediate. The oxidative addition proceeds with a calculated free energy barrier of $G = 14.4$ kcal/mol. The second step, [(NHC)Pt^{IV}(CH₃)(MeO)(H)]⁺ $\rightarrow$ ⁺RE [(NHC)-Pt^{II}(CH₃)(MeOH)]⁺, reductive elimination has an activation barrier of $G = 9.5$ kcal/mol from the Pt^{IV} hydride. The G value for the reductive elimination TS is thus 13.2 kcal/mol uphill versus the methane adduct. Of course, the overall thermodynamics for OA/RE is the same as the one-step processes, $G = 23.9$ kcal/mol. Taken as a whole, the calculations predict for the cationic Pt^{II} NHC model complex (Scheme 3) that a two-step, OA/RE process is preferred over one-step, nonredox pathways. Additionally, the calculations indicate that the initial methane C–H oxidative addition would be the rate-determining step.

2. Base Assisted Deprotonation (BAD) of Methane. Scheme 4 represents a fourth (C–H) calculated bond activation mechanistic pathway investigated by Macgregor and

Scheme 4. B3LYP/CEP-31G(d) Calculated Free Energies (kcal/mol) for Base-Assisted Deprotonation (BAD) of Methane by External Base (Methoxide)^a

^aFree energies are corrected for continuum THF solvent using the CPCM method.

co-workers:^{46,47} base-assisted deprotonation.^{40,48,49} Deprotonation of coordinated methane by methoxide anion was investigated: $\{[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})]^+ \text{CH}_4 + \text{OMe}\} \rightarrow \{[(\text{NHC})\text{Pt}^{\text{II}}(\text{Me})(\text{OMe})]^+ \text{MeOH}\}$. The TS identified is only 7.7 kcal/mol above the cationic methane adduct. However, an IRC calculation indicates that the base-assisted transition state connects to a neutral bis-methoxy Pt^{II} methane adduct reactant (see section 3). From this mechanism, the minimum is exergonic by 5.7 kcal/mol (Scheme 4). However, the calculated activation barrier is very high ($G = 63.8$ kcal/mol) relative to the neutral methane adduct [*trans*-Pt^{II}(OMe)₂(NHC)(CH₄)].

3. C–H Activation of Methane by a Neutral Pt^{II} NHC Complex. The most stable coordination isomer of $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2\text{CH}_4]$ found is that in which the NHC ligand is trans to methane, and hence the methoxy ligands are mutually trans. This places both OMe ligands cis to the methane substrate for -BM/OHM C–H activation by the Pt^{II} complex. The isomer of $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2(\text{CH}_4)]$ where the methoxy ligands are cis and the NHC is now trans to a methoxy ligand is 10.3 kcal/mol higher in free energy than the trans coordination isomer.

For neutral Pt^{II} species (Scheme 5) nonredox (BM/OHM) and redox (OA/RE) pathways are computed to be competitive.

Scheme 5. B3LYP/CEP-31G(d) Calculated Free Energies for Oxidative Addition/Reductive Elimination (Red) and Bond Metathesis (Brown) in kcal/mol from a Neutral Pt^{II} NHC Complex^a

^aFree energies are corrected for continuum THF solvent effects using the CPCM method.

The calculated free energy for *trans*- $[(\text{NHC})\text{Pt}(\text{OMe})_2(\text{CH}_4)]$ OHM $[(\text{NHC})\text{Pt}(\text{OMe})(\text{CH}_3)(\text{HOCH}_3)]$ is 1.8 kcal/mol relative to the bis-methoxy methane adduct, while the barrier for C–H bond activation is $G = 26.1$ kcal/mol. The IRC from OHM connects to the product $[(\text{NHC})\text{Pt}^{\text{II}}(\text{CH}_3)(\text{OMe})(\text{MeOH})]$ with the strongly trans influencing methyl ligand cis to methanol.⁴⁵ Calculations suggest that this intermediate at $G_{\text{rel}} = 57.9$ kcal/mol converts to the minimum at $G_{\text{rel}} = 66.6$ kcal/mol (Scheme 5) via methanol dissociation, rearrangement of the three-coordinate complex formed, and reassociation of methanol. The Pt–H bond length in the OHM (1.95 Å) more closely resembles the value calculated for the cationic OHM TS (⁺OHM), suggesting oxidative hydrogen migration as a more apt description of this TS than σ -bond metathesis.⁴¹

An oxidative addition/reductive elimination (OA/RE) pathway starting from the neutral methane adduct is given in Scheme 5. The insertion of Pt^{II} into the C–H bond of methane *trans*- $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2(\text{CH}_4)]$ OA $[(\text{NHC})\text{Pt}^{\text{IV}}(\text{OMe})_2(\text{CH}_3)(\text{H})]$ to produce the metal hydride Pt^{IV} intermediate is calculated to be endergonic by +23.3 kcal/mol relative to the neutral methane adduct. The oxidative addition barrier (OA) is calculated to have $G = 22.8$ kcal/mol. Notably, the calculated TSs for OHM and OA for the neutral Pt^{II} NHC model are energetically competitive ($G = 3.3$ kcal/mol), unlike the cationic Pt^{II} models, which show a marked preference for the oxidative addition pathway.

The reductive elimination step, $[(\text{NHC})\text{Pt}^{\text{IV}}(\text{CH}_3)(\text{MeO})_2(\text{H})]$ RE $[(\text{NHC})\text{Pt}^{\text{II}}(\text{CH}_3)(\text{OMe})(\text{MeOH})]$, has a calculated $G = 6.6$ kcal/mol from the neutral Pt^{IV} hydride intermediate. The G value for the neutral reductive elimination TS is thus +29.9 kcal/mol in relation to the neutral methane adduct *trans*- $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2(\text{CH}_4)]$. On the basis of the present calculations, the neutral OHM is favored over the neutral OA pathway due to the RE step showing a higher barrier than the OHM pathway. It should be noted that the stepwise OA/RE pathway (Scheme 5) is overall exergonic

from the neutral bis complex by 10.5 kcal/mol, which is much less than the OA/RE pathway for the cationic model (see Scheme 3).

4. Replacing a Small NHC with a Larger Model. Scheme 6 depicts the PES for the calculated lowest barrier model reaction, oxidative addition/reductive elimination of methane to $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})]^+$, where NHC denotes either the smaller model discussed above or a much larger model, depicted by IPr^* . Recently, Marko et al. reported the synthesis of 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazo-2-ylidene (IPr^*).⁵⁰ Among several notable studies,^{51–54} Hillhouse et al. used IPr^* to stabilize a remarkable two-coordinate Ni nitrene complex.⁵⁴

The bulky IPr^* raises the stationary points by an average free energy of 13 kcal/mol along the reaction coordinates. Given that the calculations indicate that IPr^* binds slightly more strongly ($\Delta G = -3.5$ kcal/mol) than the less bulky NHC for the two-coordinate $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})]^+$, this suggests that the calculated free energy differences between NHC and IPr^* for the other stationary points are primarily steric in origin.

SUMMARY AND CONCLUSIONS

A comprehensive DFT study of five specific pathways for C–H activation of methane by cationic and neutral Pt^{II} NHC

complexes has been presented. The study aims to evaluate different C–H bond activation mechanisms vis-a-vis metal coordination number, metal formal oxidation state, and overall charge on the complex. Some important observations have resulted from this study, which should inform experimental efforts to identify novel low-valent, electron-rich late-transition-metal catalysts for methane partial oxidation.

Density functional theory suggests that methane C–H activation by cationic NHC Pt^{II} methoxy complexes is exergonic ($\Delta G = -23.9$ kcal/mol). However, the nonredox, σ -bond metathesis TS (^+BM) has a ΔG of 35.3 kcal/mol relative to the two-step oxidative addition/reductive elimination (OA/RE) pathway, which has a barrier of only 14.4 kcal/mol. Interestingly, an isomeric oxidative hydrogen migration TS (^+OHM), with a calculated free energy barrier of 26.9 kcal/mol for methane C–H activation is much favored versus the σ -bond metathesis TS. The transition state for OHM has a much shorter (0.7 Å) Pt–H distance in the TS than the corresponding σ -bond metathesis TS, pointing to the importance of this transannular interaction in stabilizing nonredox C–H activation transition states.

Therefore, on the basis of the calculations for the cationic Pt NHC model system, the transformation from methane adduct $\{[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})(\text{H}-\text{CH}_3)]^+\}$ to methanol-bound product is predicted to proceed via a two-step OA/RE pathway, with a barrier for the rate-determining step (the initial oxidative addition to form a Pt^{IV} hydrido/methyl intermediate) of only 14.4 kcal/mol.

Base-assisted deprotonation (BAD) using a methoxide as the base was also modeled. However, the kinetic barrier is very large. Calculation of the intrinsic reaction coordinate connects this BAD transition state to the neutral bis-methoxy methane adduct *trans*- $[\text{Pt}^{\text{II}}(\text{OMe})_2(\text{NHC})(\text{CH}_4)]$ by a free energy barrier of >60 kcal/mol.

The neutral bis-methoxy methane adduct *trans*- $[\text{Pt}^{\text{II}}(\text{OMe})_2(\text{NHC})(\text{CH}_4)]$ is favored over the isomer where the OMe ligands are *cis* by 10.3 kcal/mol in free energy. The lower energy isomer places the more strongly trans influencing NHC *trans* to the weakly bound methane ligand, thus allowing for a facile C–H bond activation by the Pt–OMe bonds. For neutral Pt^{II} NHC methoxy models, OHM and oxidative addition transition states are calculated to be competitive ($\Delta G = 3.3$ kcal/mol in favor of the OA/RE pathway), much less than the $\Delta G = 12.5$ kcal/mol for the related TSs for the cationic model complexes.

PROSPECTUS

The calculated methane C–H activation barriers for the neutral NHC Pt^{II} methoxy complexes are 22.8 and 26.1 kcal/mol for oxidative addition and σ -bond metathesis, respectively. Interestingly, this is unlike the case for cationic Pt^{II} complexes. Specifically, oxidative hydrogen migration (OHM) has a calculated free energy barrier of 26.9 kcal/mol, commensurate with the aforementioned neutral methane activation barrier. However, oxidative addition to the cationic NHC Pt^{II} complex is only 14.4 kcal/mol. Comparing the lowest energy geometries obtained for these four calculated transition states (^+OHM , ^+OA , OHM, and OA) from the same visual perspective (i.e., NHC to the “left” and methane “up”), is instructive (Figure 1). For both neutral TSs, the $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2]$ fragment is in a *cis* conformation, which has a ΔG value ca. 10 kcal/mol higher than for the *trans* isomer (cf. *trans*- and *cis*- $[(\text{NHC})\text{Pt}^{\text{II}}(\text{OMe})_2(\text{CH}_4)]$). Subtracting this 10 kcal/mol “penalty”

Scheme 6. B3LYP/CEP-31G(d) Calculated Free Energies for Oxidative Addition/Reductive Elimination (Pink), Where the Green Reaction Coordinate Depicts a Large NHC (IPr*) Complex^a

^aFree energies are corrected for continuum THF solvent effects.

Figure 1. Lowest energy transition states for methane C–H activation with calculated free energy barriers.

implies intrinsic barriers arising from C–H scission in the range of 13–16 kcal/mol for both neutral Pt^{II} complexes. For the cationic TSs, the OHM transition state has a trans disposition of NHC and OMe (placing the NHC cis to methoxy yields TSs that revert to the trans arrangement upon geometry optimization), but for the cationic OA transition state, NHC and OMe are in the preferred cis arrangement. Constrained geometry optimizations on $[(\text{NHC})\text{Pt}(\text{OMe})]^+$ indicate a free energy penalty of 10 kcal/mol to go from the fully optimized NHC–Pt–OMe angle of 112.5° (Scheme 1) to a linear (NHC–Pt–OMe = 180°) arrangement. Assuming this 10 kcal/mol cis/trans “penalty” is additive in the overall free energy barrier suggests an intrinsic methane C–H scission barrier of 17 kcal/mol, commensurate with what is calculated for the other three TSs (Figure 1). Thus, one may argue that the cationic oxidative addition TS has the lowest calculated barrier because the ground-state active species is already structurally prepared and need not undergo any geometric perturbations to achieve the preferred ligand orientation in the transition state for activation of the methane substrate.

The foregoing analysis highlights the obvious importance of having the ground state (GS) active species in the correct conformation for C–H bond scission in the subsequent transition state. One may reasonably assume that any energetic investment to distort the ligands, putting the active species in an appropriate arrangement for C–H activation, will result in higher free energy barriers. In this regard, three comments seem germane vis-a-vis the continued search for more potent catalysts for hydrocarbon functionalization. First, one might assume that lower coordinate complexes, in addition to being sterically and electronically more potent, would have negligible reorganization free energies. The present results suggest that this may not always be so. Second, a priori, one may further assume that lighter, more earth abundant (3d) metals may have an advantage over heavier, precious (4d, 5d) metal catalysts in terms of the energetic investment needed to position the ligands upon transforming from GS to TS, given that ligand metal ligand bending potentials are expected to be softer for 3d metals. Finally, calculations argue for the importance of designing C–H activation catalysts where the GS active species is already structurally “prepared” and which either does not need to undergo any geometric perturbations to access the methane C–H activation TS, or is not energetically prohibited from such perturbations. Among the important ligand-based design properties impacting this consideration, trans influence comes most immediately to mind.

■ ASSOCIATED CONTENT

★ Supporting Information

Tables giving Cartesian coordinates of all calculated species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ ACKNOWLEDGMENTS

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