Graphical Abstract

DFT was utilized to model the reductive functionalization of a bipyridine Co(III)–methyl complex, an integral step in metal-catalyzed hydrocarbon functionalization.

DFT STUDY OF REDUCTIVE FUNCTIONALIZATION IN CIS AND TRANS COBALT-METHYL-BIPYRIDINE COMPLEXES

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Abstract: Density functional theory (DFT) calculations were utilized to study the reductive functionalization (RF) of a bipyridine Co(III)–methyl complex, an integral step in metal-catalyzed hydrocarbon functionalization. In general, for the different X co-ligands modeled, ground and transition states were computed to be cis geometric isomers and singlet spin states, thus implying RF with these 3d metal complexes will proceed without impediment from large amplitude geometric changes or spin forbidden reactions. Barriers for nucleophilic attack (NA) by hydroxide were also compared with Co–Me bond homolysis, and the former revealed to be lower by a substantial free energy margin. Furthermore, the differences between the NA free energy barriers and the bond dissociation free energies (BDFE) varied for each ligand, indicating that the X co-ligands, although cis to the cobalt-methyl-nucleophile active site, can have significant impact in determining which catalysts will prove desirable. Overall, this research suggests that the bipyridine Co(III) complexes studied here are worthy of experimental studies.

1. Introduction

The direct selective partial oxidation of an alkane to an alcohol, especially methane to methanol, is a process of interest for alternative energy production [1, 2]. An abundant source of energy, worldwide natural gas reserves were estimated in 2013 to be around 185.7 trillion cubic meters [3]. Methane comprises the majority of natural gas, but faces limitations as a transportation fuel source due to its limited portability as a gas [4, 5]. In addition, in comparison with methanol, methane is unreactive due to the strength of its C–H bond [bond dissociation enthalpy = 105 kcal/mol], low acidity ($pK_a=48$), high ionization potential (291 kcal/mol), and low proton affinity (130 kcal/mol) [1, 6, 7]. A cost-effective solution to methane's aforementioned disadvantages could be catalytic methane-to-methanol conversion at relatively low pressures and temperatures (*e.g.*, ≤ 500 psi and ≤ 250 °C) [2, 8]. As a liquid, methanol would serve as a much more manageable source of fuel, especially as the U.S. already relies on pipelines to transport liquid materials over long distances [3, 9]. In previous studies, achieved yields for the partial oxidation of methane to methanol were too low and required reaction temperatures (often $T > 400$ °C) that were too high for commercialization [1, 10–12].

One reaction to effect carbon-oxygen bond formation within a catalytic cycle for methane oxidation is nucleophilic attack (NA) on an electrophilic late transition metal, specifically cobalt(III) in this research [1]. In the proposed mechanism, a bipyridyl methyl cobalt complex with supporting ligands undergoes nucleophilic attack by a hydroxide nucleophile, forming methanol and a metal-based leaving group. Because previous organometallic studies provided evidence that gold [13] and rhodium [2, 14] could be effective electrophilic catalysts in the methane to methanol process, the possibility of cobalt as a more inexpensive, yet effective, Earth-abundant transition metal catalyst in this reaction was pursued [2].

The feasibility of the NA reaction depends critically on the Co–CH₃ bond dissociation free energy (BDFE), which must be greater than the NA free energy barrier. A representative transition state is shown in **Scheme 1**. A relatively low Co–CH₃ bond energy would engender Co–methyl homolysis from the cobalt complex, outcompeting the desired nucleophilic attack. The indiscriminately reactive methyl radical resulting from bond homolysis would impede selective partial oxidation of methane to methanol.

Scheme 1. Schematic of a “trans” nucleophilic attack (NA) transition state with OH[−] nucleophile and X co-ligand. N–N denotes the 2,2′-bipyridine (bpy) supporting ligand.

2. Computational Methods

All density functional theory (DFT) calculations were performed with the GAUSSIAN09 package [15] at the B97D/6-31+G(d) level of theory [16]. Additional preliminary calculations were done with the B3LYP functional and the CEP-31G(d) basis set, but little difference in predicted results found. Complexes were optimized in continuum dimethylsulfoxide solvent (DMSO, SMD model [17]), which was deemed to be most experimentally relevant and most appropriate for stabilizing anions and cations [2] in nucleophilic attack reactions. Enthalpies and free energies were calculated at 298.15 K and 1 atm, and were recorded in kcal/mol. Ground states were identified as local minima by zero imaginary frequencies, and transition states were identified as local maxima by one imaginary vibrational frequency.

3. Results and Discussion

a. Systems and Reactions Under Investigation

On the basis of previous research by our group, the impact of the co-ligand X upon the barriers to nucleophilic attack, **Scheme 1**, by hydroxide on the Co(III)–methyl bond was investigated for a series of co-ligands [2]. To facilitate comparison among the modeled complexes, the ligands were fixed at 2,2′-bipyridine, a common experimentally relevant supporting ligand for this chemistry [2]. Both cis and trans isomers of [(bpy)₂Co^{III}(Me)X]⁺ were considered. Representative ground and transition states for cis and trans complexes (X = CO) are shown in **Figure 1** and **Figure 2**, respectively.

Figure 1. Example of a B3LYP/6-31+G(d)/SMD-DMSO optimized singlet cis-[(bpy)₂Co^{III}(Me)X]⁺ ground state (left) and transition state (right) complex with X = CO. The Co–Me bond length, Co–X bond length, and Me–Co–X angle are shown. Bond lengths are in Å, and angles are in °.

Figure 2. Example of a B3LYP/6-31+G(d)/SMD-DMSO optimized singlet trans-[(bpy)₂Co^{III}(Me)X]⁺ ground state (left) and transition state (right) complex with X = CO. The Co–Me bond length, Co–X bond length, and Me–Co–X angle are shown. Bond lengths are in Å, and angles are in °.

b. Geometries and spin states of reactant and transition states

The reaction was modeled with the OH nucleophile (leading to the desired methanol product) and various X co-ligands to determine whether the latter would positively or negatively influence the nucleophilic attack energy barrier when interacting with the cis and trans geometric isomers of [(bpy)₂Co^{III}(Me)X]⁺. The co-ligands (X) modeled in this research included H⁺, H₃C⁺, CO, Cl[−], HO[−], and Py to mimic prototypical σ-donor, π-donor/acceptor, hard/soft ligand types. Due to the d⁶ electronic configuration of the cis and trans [(bpy)₂Co^{III}(Me)X]⁺ complexes, singlet, triplet and quintet spin states were considered. As a result of consistently high free energies in comparison to their singlet and triplet counterparts for agiven co-ligand, quintet states were eliminated from further analysis in this research. Therefore, free energy barriers were calculated for the complex in the singlet and triplet spin states.

Free energies for cis-[(bpy)₂Co^{III}(Me)X]⁺ complexes were consistently calculated to be lower than free energies for the trans isomers (Table 1). For example, for X = H⁺, the cis singlet was determined to be 23.8 kcal/mol lower in free energy than the trans singlet, which was the highest cis-trans free energy difference (ΔG_{cis-trans}) computed in this research. The lowest ΔG_{cis-trans} was 7.5 kcal/mol, again in favor of a cis disposition between the methyl ligand and the chloride co-ligand. A similar preference for the cis isomer over the trans isomer was observed for the rhodium analogues of this system and a similar rationale can be applied to understand this preference. When compared to Me and most of the X ligands studied, bipyridine is a weaker trans influence ligand. The trans isomer places, in most cases, the two strongest trans influencing ligands in a trans orientation. In comparison the cis isomer, which places both of these stronger trans influence ligands trans to a weaker trans influence

ligand is expected and calculated to be the more stable isomer. Also, the trans isomer has negative steric interactions at the 6 and 6' positions of the bipyridine rings which are not present in the cis isomer. Pyridine complexes were studied to minimize the effect of the trans influence in order to quantify this steric interaction which accounts for the 11.5 kcal/mol preference for the cis isomer of the pyridine complex. This steric interaction is stronger for cobalt complexes than the analogous rhodium complexes for which this interaction was 9.4 kcal/mol, which would be expected given the smaller radius of the cobalt ion.

Table 1. Relative free energies for cis and trans, singlet and triplet, ground and transition states in kcal/mol.

	¹ cis	¹ cis [‡]	³ cis	³ cis [‡]	¹ trans	¹ trans [‡]	³ trans	³ trans [‡]
CO	0.0	5.2	25.4	n/c	15.7	20.3	34.9	22.7
Py	0.0	13.6	20.4	17.4	11.5	21.9	24.6	28.5
Cl [−]	0.0	16.4	14.0	16.5	7.5	19.1	23.7	25.2
HO [−]	0.0	23.5	13.7	26.5	17.0	36.3	24.4	33.6
H ⁺	0.0	25.3	25.2	35.6	23.8	41.0	35.7	47.8
H ₃ C ⁺	0.0	25.9	21.4	36.9	20.3	37.8	33.4	46.1

n/c – This transition state could not be located with the basis sets and density functionals investigated in this research.

Free energy differences among competing spin states were calculated to be sensitive to the nature of X. However, it was computed that singlet spin states were generally significantly lower (Table 1) than the corresponding triplet spin states for all X co-ligands studied, for both cis and Trans geometric isomers. A similar energetic preference for the low spin d⁶ configuration was seen in the NA transition states. Only for the transition state of trans-[(bpy)₂Co^{III}(Me)(OH)]⁺ was there a calculated a free energy preference for the triplet (intermediate spin) state by ca. 3 kcal/mol, Table 1; all other transition states isolated were computed to be lower in free energy as singlets. Thus, for the majority of X co-ligands studied, the ground and transition states are copacetic both in geometry (cis) and multiplicity (singlet). This implies that for these cobalt complexes, there is no decrease expected in the rate of nucleophilic attack due to spin flips.

The computed Co–C bond lengths in the transition states (relative to their values in the ground state) as a function of X were of particular interest in terms of describing the nucleophilic attack reaction (Table 2). The Co–C bond lengths increased, as expected, during nucleophilic attack as the bond neared dissociation (Table 2). Additionally, it is seen that there is little variation in Co–C bond lengths in the ground state, ave. Co–C = 2.01 ± 0.02 Å (relative standard deviation ~ 1 %). However, the X co-ligand had a more demonstrable effect on the Co–C distance in the TS, ave. Co–C = 2.36 ± 0.09 Å (relative standard deviation ~ 4%). These averages imply that the Co–C bond lengthens by ~ 16% on average in the nucleophilic attack transition state, relative to the ground state, suggestive of an early TS. The foregoing also implies that the X group can appreciably modify the position of the NA transition state along the reaction coordinate, making it earlier (i.e., shorter Co–C distance) or later (i.e., longer Co–C distance).

Table 2. Optimized Co–C and C–O bond lengths in the lowest energy ground and transition states (i.e., cis geometric isomer) and singlet spin states. Bond lengths are in Å.

	Co–C Bond Length		C–O Bond Length
	¹ cis	¹ cis [‡]	¹ cis [‡]
CO	2.04	2.20	2.16
Py	2.00	2.35	2.12
Cl [−]	2.00	2.36	2.13
HO [−]	1.99	2.37	2.09
H ⁺	2.00	2.45	2.09
H ₃ C ⁺	2.00	2.45	2.08

Figure 3. Correlation between free energy barriers (kcal/mol) and Co–C and C–O bond lengths (Å) in the transition states for nucleophilic attack of hydroxide on the cobalt–methyl bond of $^1\text{cis}[(\text{bpy})_2\text{Co}^{\text{III}}(\text{Me})\text{X}]^+$.

The C–O bond being formed during the transition state is also of interest, and like the Co–C bond length, is strongly dependent on the identity of the X-group (**Figure 3**). There is a strong linear correlation between the C–O and the Co–C bond lengths and the free energy barrier (**Figure 3**) for nucleophilic attack. These linear correlations suggest longer C–O and shorter Co–C bond lengths in the NA transition states yield lower free energy barriers. Looking at the slopes for the best fit lines, suggests the C–O bond lengths in the nucleophilic attack transition states are more sensitive to the X group.

c. Comparison of Nucleophilic Attack Barriers with Co–Methyl Bond Homolysis

The research presented above shows reasonable hydroxide nucleophilic attack barriers ranging from 5.2 (X = CO) to 25.9 (X = methyl) kcal/mol, ave. = 18.3 ± 8.1 kcal/mol (relative standard deviation ~ 44%) for the six co-ligands studied. It is expected that metal–carbon bond homolysis, leading to methyl radicals (and Co^{II} complexes), is problematic for many 3d metal catalysts as methyl radicals tend to compete with non-radical pathways, such as the nucleophilic attack mechanism that is the focus of this research. To this end, the Co–methyl bond dissociation free energies (BDFEs) were computed as depicted in **Scheme 2**. These BDFE data are tabulated in **Table 3**. The relative sensitivity of the Co–methyl BDFEs to change in X is less than the barriers (ave. = 25.7 ± 4.1 kcal/mol, relative standard deviation ~ 16%) by a factor of three. Moreover, the computed BDFE are higher by 7 kcal/mol than the NA free energy barriers, ranging from 1 kcal/mol higher for X = hydroxide to 21 kcal/mol higher for X = carbon monoxide. *Thus, the present simulations suggest that nucleophilic attack by hydroxide will outcompete cobalt–methyl bond homolysis.* Only for the hydroxide co-ligand are the barriers competitive, and for this small difference, 0.8 kcal/mol, a Boltzmann distribution would suggest a roughly 4-to-1 partitioning in favor of the nucleophilic attack pathway. Inspection of the data in **Table 3**, reveals no obvious correlation between the Co–C homolytic bond strengths and their respective energy barriers.

Scheme 2. Schematic showing the reaction used to calculate the Co–CH₃ bond dissociation free energy (BDFE) for $[(\text{bpy})_2\text{Co}^{\text{III}}(\text{Me})\text{X}]^+$. The different X groups modeled are shown in **Scheme 1**.

Table 3. Comparison between NA free energy barriers and cobalt–methyl bond dissociation free energy (BDFE) as a function of co-ligand X for $\text{cis}[(\text{bpy})_2\text{Co}^{\text{III}}(\text{Me})\text{X}]^+$ reactant complexes, measured in kcal/mol.

X	$\Delta G_{\text{NA}}^\ddagger$	BDFE
CO	5.2	26.2
Py	13.6	21.9
Cl [−]	16.4	21.0
HO [−]	23.5	24.3
H [−]	25.3	31.0
H ₃ C [−]	25.9	29.7

4. Summary and Conclusion

For all X groups studied *cis* ground states for $[(\text{bpy})_2\text{Co}^{\text{III}}(\text{Me})\text{X}]$ and their corresponding *cis* transition states for nucleophilic attack on the Co–CH₃ bond (to yield methanol) are lower in free energy as compared to their respective *trans* geometric isomers, **Table 1**. Likewise, calculations suggest that the reductive functionalization of cobalt–methyl bonds by hydroxide will remain on the singlet potential energy surface with the lone exception of X = HO[−], for which a triplet TS was computed to be more stable than the corresponding singlet for the *trans* isomer. Hence, kinetic impediments from spin-crossover or geometric reorganization, which can be problematic for Earth-abundant 3d metals as compared to their previous metal (4d, 5d) counterparts, are not predicted to retard the formation of methanol via RF for these Co(III) complexes.

Previous work by Pahls *et al.* [2] suggests that the ligand *trans* to the Nuc–CH₃–M has an important impact on the barriers for nucleophilic attack. Indeed, this proposal was borne out in subsequent experimental studies of terpyridine complexes [19] which led to successful experimental demonstration of nucleophilic attack on Rh(III)–methyl complexes to form Me–X. The present research suggests that even *cis* X groups, if chosen judiciously, can also significantly modulate the free energy barrier to C–X formation via nucleophilic attack.

Competing radical pathways can be a challenge in designing catalytic cycles for 3d metals, given their greater propensity to engage in 1-electron chemistry versus the heavier 4d and 5d metals. Co(III)–alkyl complexes are well known to be relevant in bioinorganic chemistry and so competition of the nucleophilic attack pathway of interest in this research with those that entail Co–CH₃ homolysis are of interest. With the exception of X = OH[−], the computed bond dissociation free energies are significantly higher than the free energy barriers for nucleophilic attack. Hence, the calculations predict that competing radical pathways – at least at T = 298.15 K as assumed in this work – should not significantly deteriorate selectivity for these and related Co(III) reactions.

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