Tuning Ligand Properties in Cyclopentadienyl Cobalt Complexes for the Electrocatalytic Oxidation of Formate

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Introduction

In trying to address the intermittency of renewable energy sources like solar and wind power, we can store energy generated from these resources during periods of peak production in chemical fuels, which can be released later on-demand. Direct Liquid Fuel Cells (DLFCs) allow for the harvest of electrical energy via electrochemical oxidation of liquid fuels such as formate, but they require efficient inexpensive catalysts for the oxidation reaction for implementation on a global scale. Existing catalysts utilize expensive precious metals[1] or do not exhibit high enough selectivity and/or reaction rate to be considered effective.[2] In order to understand how to design optimized first-row transition metal catalysts for formate oxidation, we are exploring the incorporation of different ligands in molecular cobalt catalysts and their effects on the accessibility and energetic favorability for the electrochemical oxidation of formate.
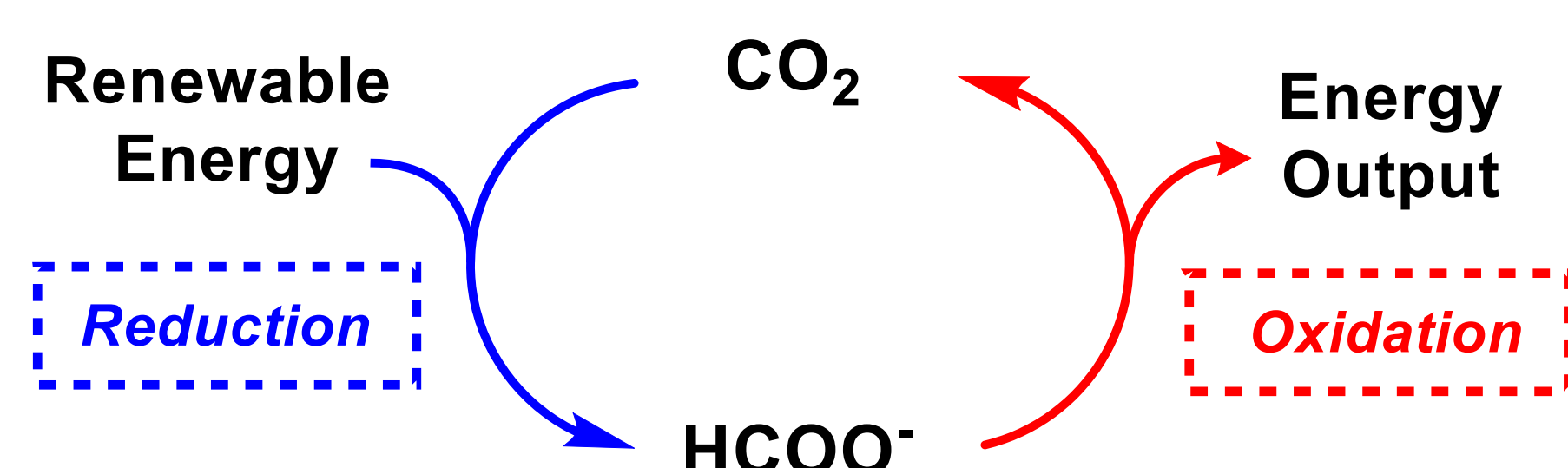

Approach

- A crucial step in the oxidation process is the ability of the catalyst complex to accept a hydride from formate and form a metal hydride intermediate.
- The hydricity of formate (44 kcal/mol in acetonitrile) acts as a benchmark value and dictates the thermodynamically favored direction of hydride transfer.[3]
- Using the hydricity ($\Delta G°_{H^-}$) of a metal complex, we can predict which direction of hydride transfer will be favorable.

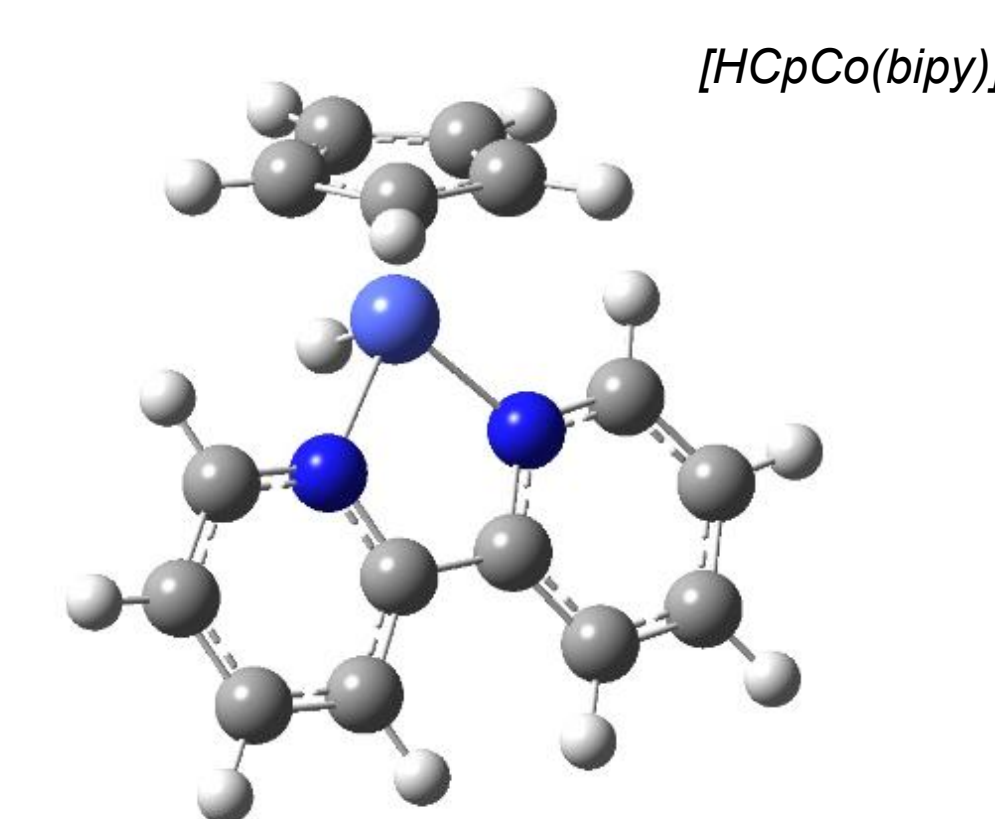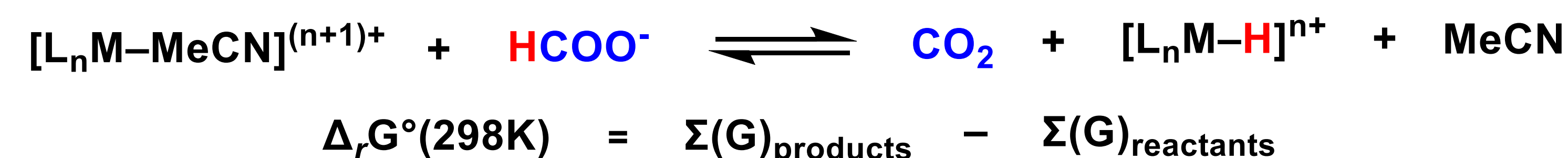$$[L_nM-H]^{(n-1)+} \rightleftharpoons H^- + [L_nM]^{n+} \qquad \Delta G°_{H^-}$$
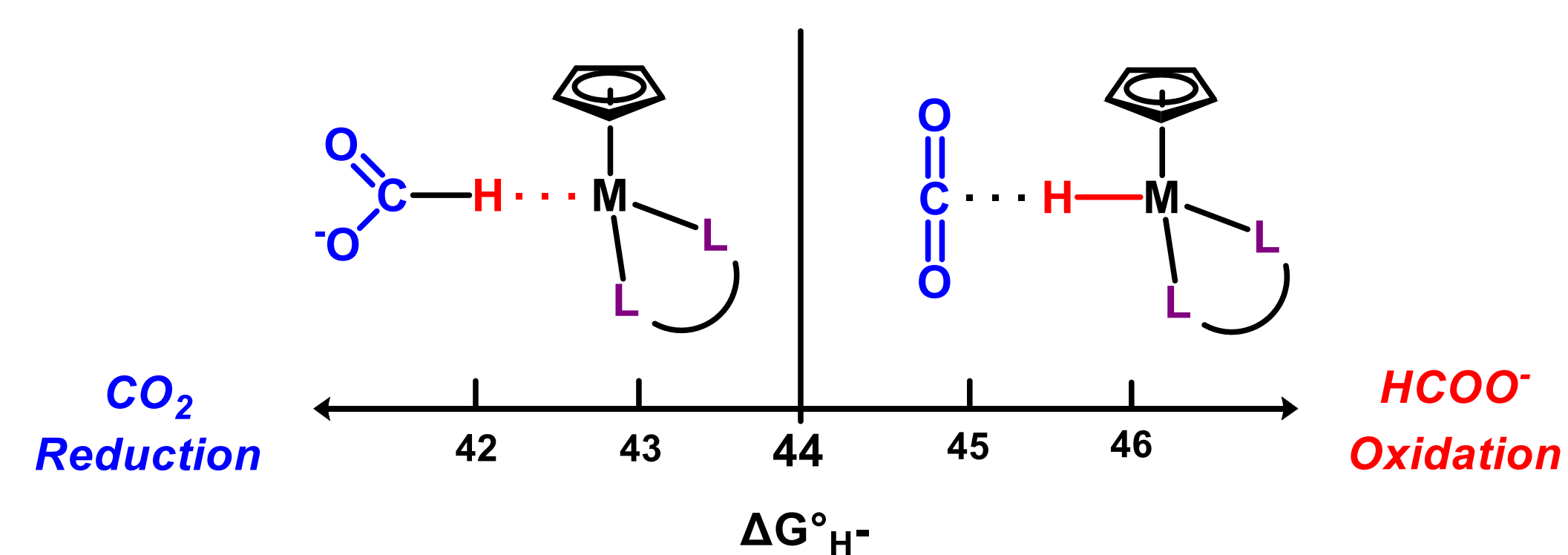
- Co^{III}-hydride complexes typically have hydricities above 44 kcal/mol.
- The cyclopentadienyl (Cp) ligand binds securely to cobalt in multiple oxidation states (Co^{III}, Co^{II}, Co^I).
- Our objective is to explore how varying the bidentate ligand system (L–L) in [CpCo] complexes changes the reactivity at the open coordination site (X) while keeping the hydricity above 44 kcal/mol.

$$\left[\begin{array}{c} \text{Co} \\ L \quad L \\ X \end{array} \right]^{n+}$$

X = H⁻, n = 1
X = CH₃CN, n = 2
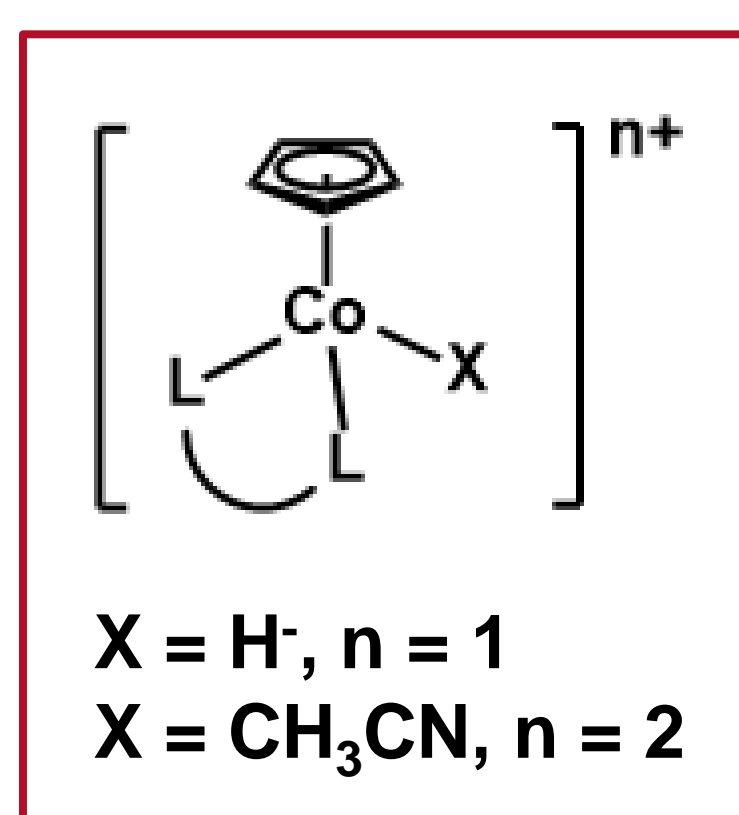
Methods

- The free energy of several $[CpCo(L-L)X]^{n+}$ complexes (X = CH_3CN, H^-) were calculated using DFT, where L-L was various phosphine or pyridine-derived ligands with different steric and electronic properties.
- **Functional:** wb97xd
  Basis set: 6-31++g(d,p)
- The free energy of formate, CO_2, and acetonitrile were also calculated.
- The reaction free energy for hydride transfer from formate to cobalt was then calculated using this equation:

$$[L_nM-MeCN]^{(n+1)+} + HCOO^- \rightleftharpoons CO_2 + [L_nM-H]^{n+} + MeCN$$

$$\Delta_r G°(298K) = \Sigma(G)_{products} - \Sigma(G)_{reactants}$$
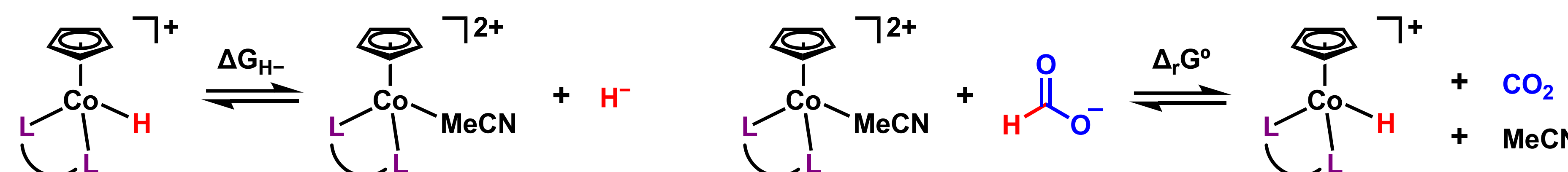
[HCpCo(bipy)]⁻

Density Functional Theory (DFT) Calculation

Proposed structure is built in Gaussian 16

↓
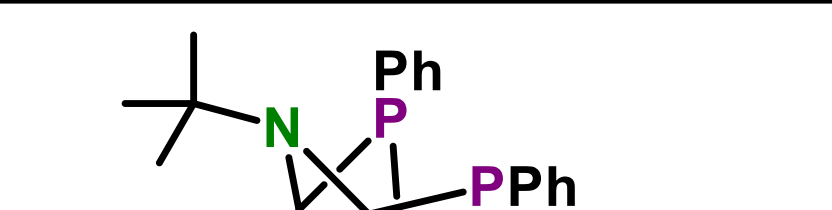
Optimization + Frequency calculations performed

↓

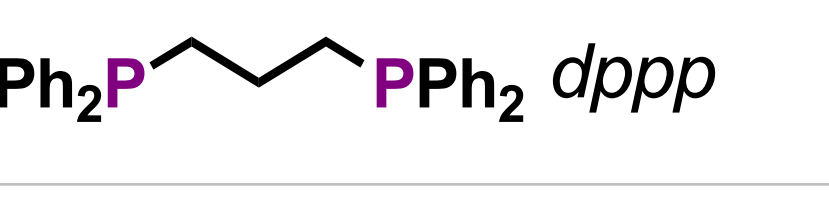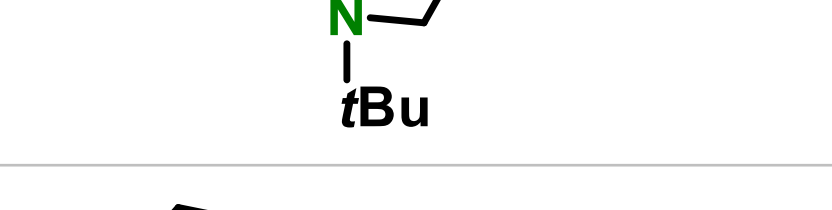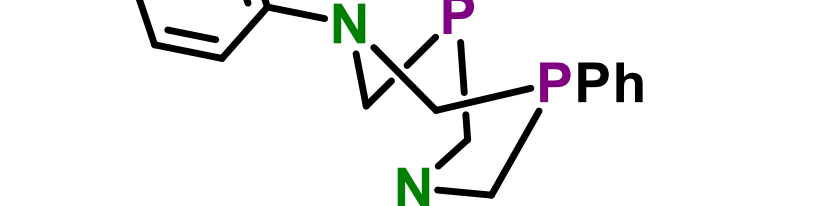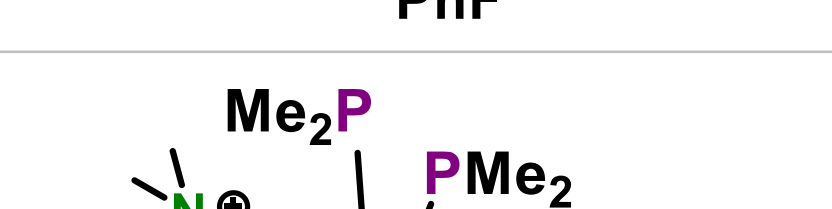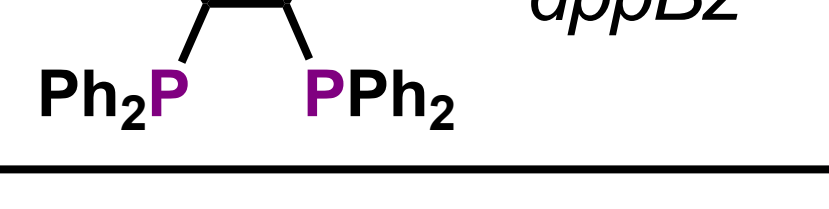Gaussian output details free energy of complex

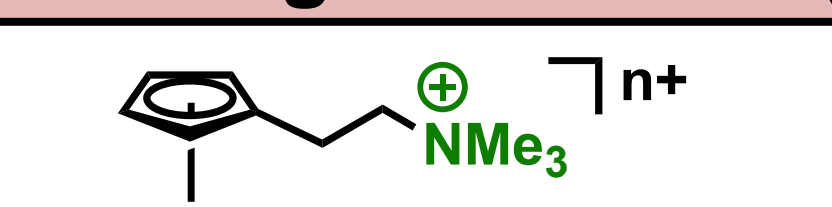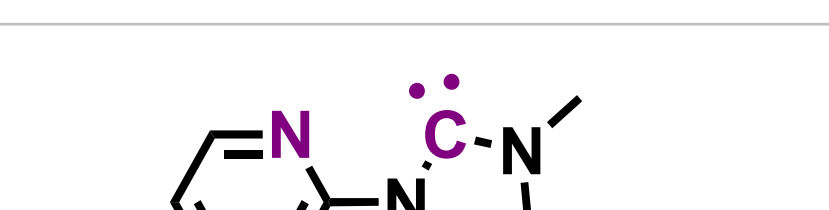|		
EE + Zero-point Energy	-834.777143	Hartree
EE + Thermal Energy Correction	-834.762989	Hartree
EE + Thermal Enthalpy Correction	-834.762045	Hartree
EE + Thermal Free Energy Correction	-834.819222	Hartree
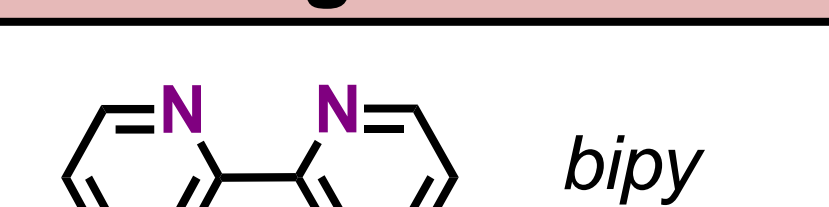
Results

DFT-calculated hydricities ($\Delta G°_{H^-}$) and reaction free energies ($\Delta_r G°_{298K}$) for the ligand systems investigated here are tabulated below:

Phosphine Ligand		$\Delta G°_{H^-}$ (kcal/mol)	$\Delta_r G°_{298K}$ (kcal/mol)
Ph₂P—PPh₂	dppe	70.6 *	-26.6 *
Ph₂P—PPh₂	dppp	*In progress*	
Et₂P—PEt₂	depe	64.8 *	-20.8 *
Py₂P—PPy₂	dpype	72.5 *	-28.5 *
Ph₂P—PPh₂	dppBz	65.4	-21.4

Phosphine Ligand	$\Delta G°_{H^-}$ (kcal/mol)	$\Delta_r G°_{298K}$ (kcal/mol)
(tBu/Ph PNP)	59.8	-15.8
(PhF PNP)	*In progress*	
(Me₂P PNP)	63.1	-19.1

* *Calculations performed by Sriram Katipamula.*

Pyridine Ligand		$\Delta G°_{H^-}$ (kcal/mol)	$\Delta_r G°_{298K}$ (kcal/mol)
	bipy	59.5	-15.5
		59.5	-15.5
	(with Cp*)	*In progress*	

Cp Modified Ligand	$\Delta G°_{H^-}$ (kcal/mol)	$\Delta_r G°_{298K}$ (kcal/mol)
(NMe₃⁺)	63.0	-19.0
(Cp* Ph₂P PPh₂)	*In progress*	

Conclusions

- All phosphine and pyridine ligands examined here are predicted to favor hydride transfer from formate.
- P_2N_2 or PNP complexes appear to have hydricities closer to that of formate compared to the hydrocarbon phosphines, which may enable more energy-efficient catalysis similar to previous literature.[4] Other R and R' groups in these systems will be investigated in future studies.
- The predicted reaction free energy for the pyridine ligands are comparable to those of the P_2N_2 ligands and may be interesting non-phosphine catalyst candidates.
- Complexes with outer sphere pendant groups or pyridine ligands have the closest-to-ergoneutral predicted reactivity in this series. To test their catalytic ability, these complexes should be synthesized and tested experimentally.

Future Considerations:

- Further DFT studies will explore mapping of possible transition states for hydride transfer, especially for the complexes bearing positively-charged pendant groups that may stabilize the transition state by electrostatic effects:
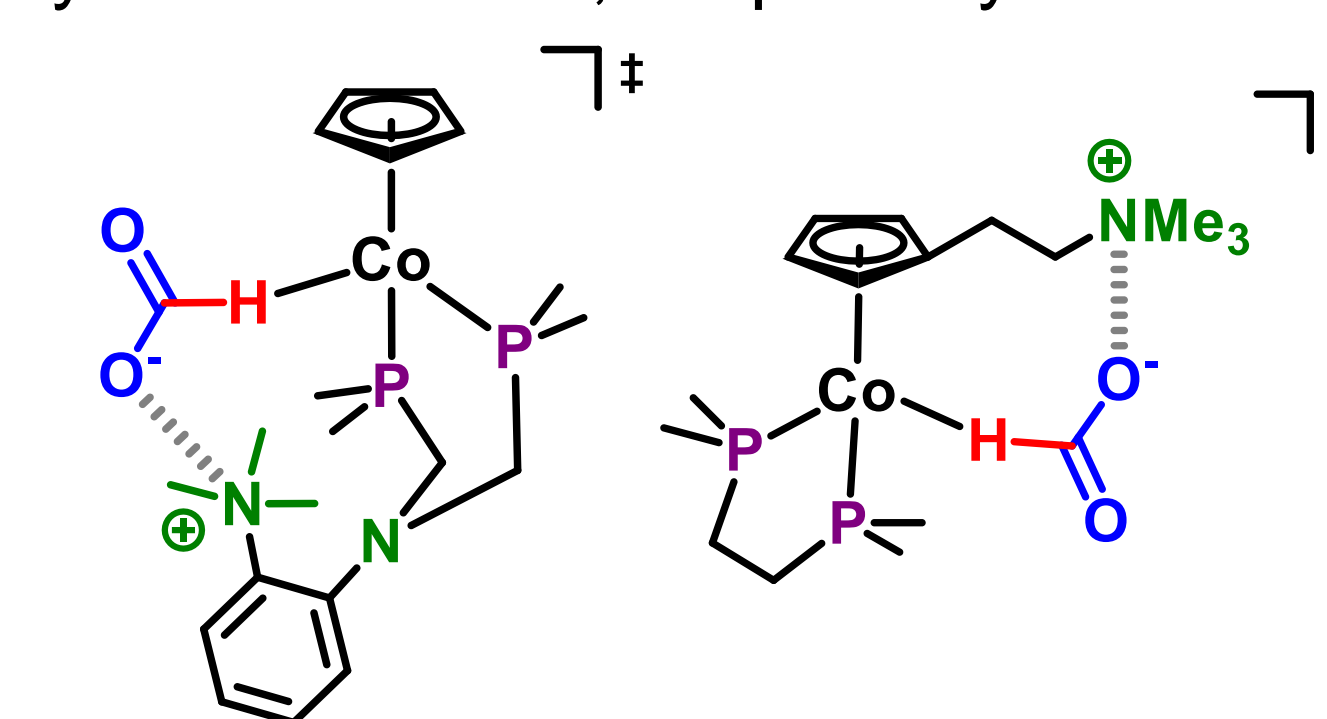
- The inclusion of pendant phenol or amine/ammonium groups on the pyridine-based ligands will also be explored:
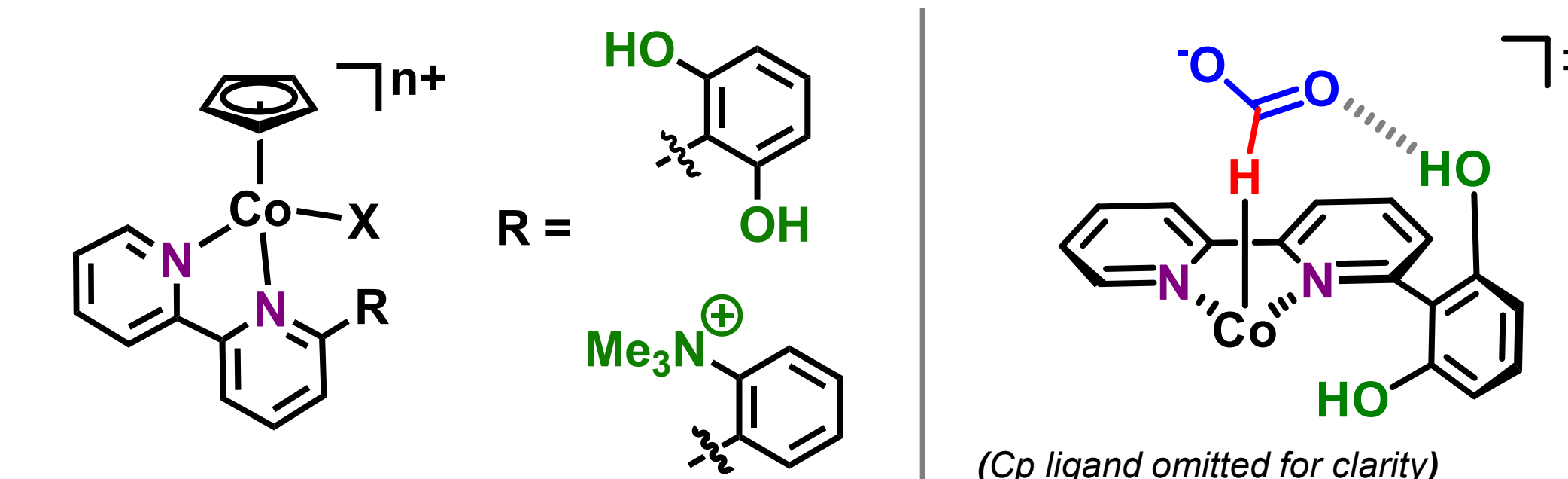
(Cp ligand omitted for clarity)

Acknowledgements

References

1. da Silva, S.; Silva, J.; Buzzo, G.; Neto, A.; Assumpção, M. Use of PtAu/C electrocatalysts toward formate oxidation: electrochemical and fuel cell considerations. *Mater. Renewable Sustainable Energy* **2016**, *5*, 1–8.
2. Roy, S.; Sharma, B.; Pécaut, J.; Simon, P.; Fontecave, M.; Tran, P.; Derat, E.; Artero, V. Molecular Cobalt Complexes with Pendant Amines for Selective Electrocatalytic Reduction of Carbon Dioxide to Formic Acid. *J. Am. Chem. Soc.* **2017**, *139*, 3685–3696.
3. Waldie, K.; Brunner, F.; Kubiak, C. Transition Metal Hydride Catalysts for Sustainable Interconversion of CO_2 and Formate: Thermodynamic and Mechanistic Considerations. *ACS Sustainable Chem. Eng.* **2018**, *6*, 6841–6848.
4. Xue, L.; Ahlquist, M. S. A DFT study: why do [Ni(P(R)(2)N(R')2)2]2+ complexes facilitate the electrocatalytic oxidation of formate? *Inorg. Chem.* **2014**, *53*, 3281-3289.