UCI University of California, Irvine

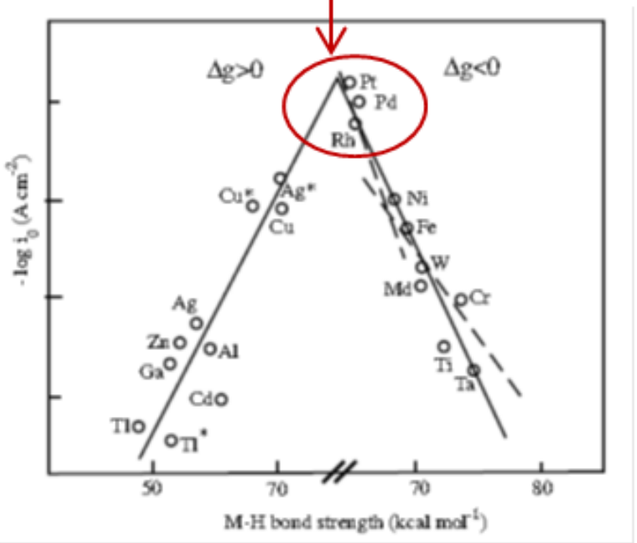
Design of Efficient Molecular Electrocatalysts for Water and Carbon Dioxide Reduction Using Predictive Models of Thermodynamic Properties

Jenny Y. Yang (2014 Early Career Awardee)
University of California, Irvine

Thermodynamic Descriptors for Hydrogen Evolution and Selective CO_2 Reduction

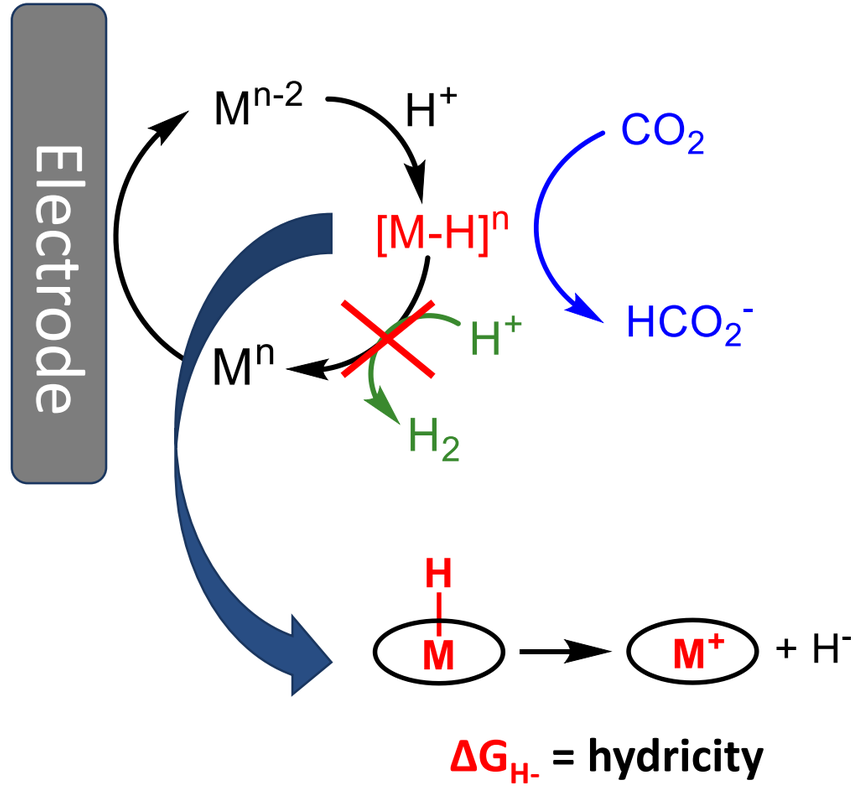
M = abundant metal

*Proposal to design non-noble metal molecular complexes with optimal **M–H** bond strength for H_2 catalysis*



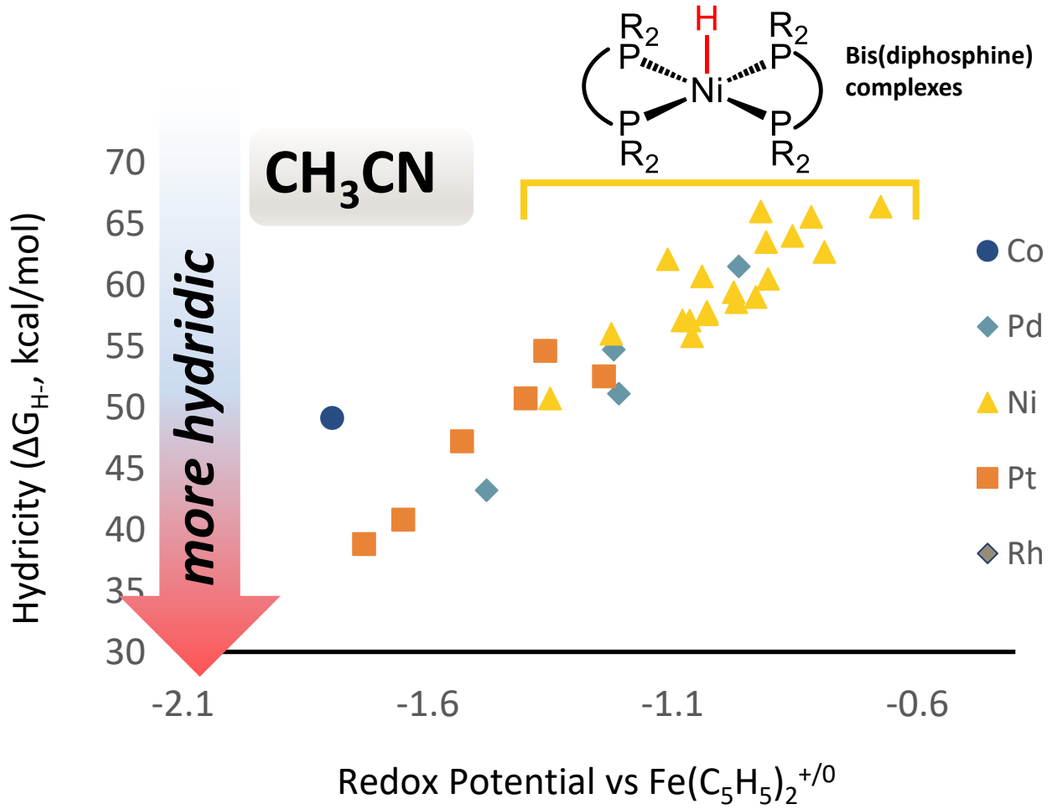
Reactions of Interest

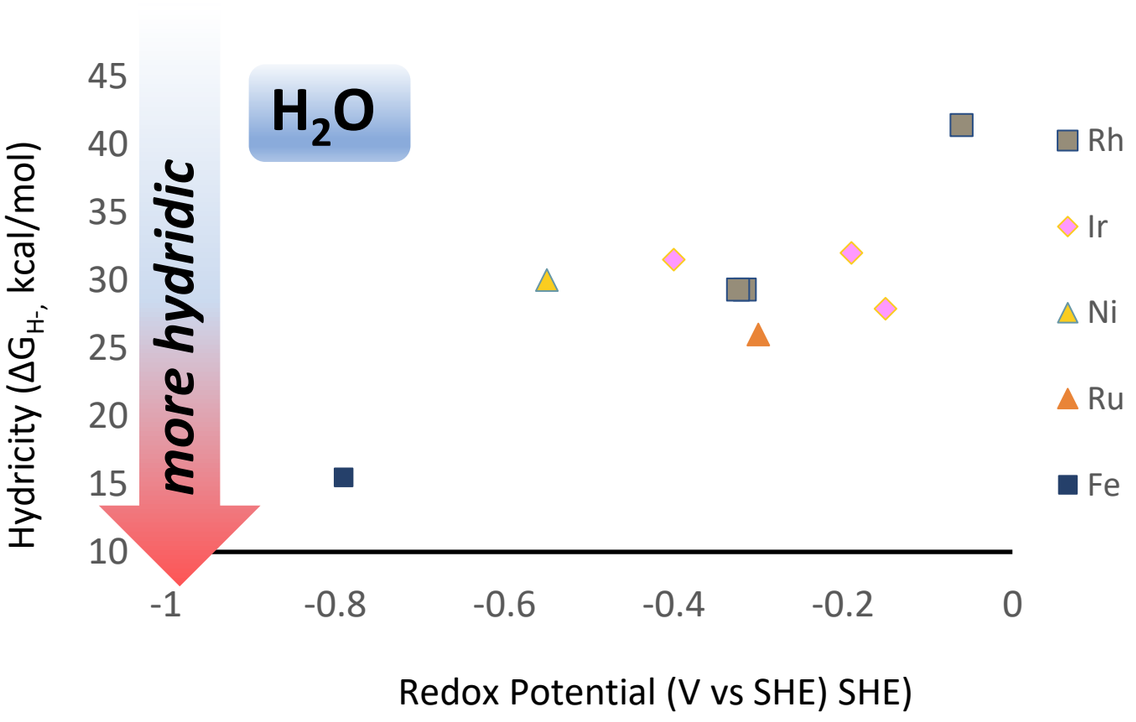
	ΔE vs SHE
$2\ H_2O + 2e^- \rightarrow H_2 + 2OH^-$	ΔE = 0.00 V
$CO_2 + 2e^- + 2H^+ \rightarrow H_2CO_2$	ΔE = −0.12 V



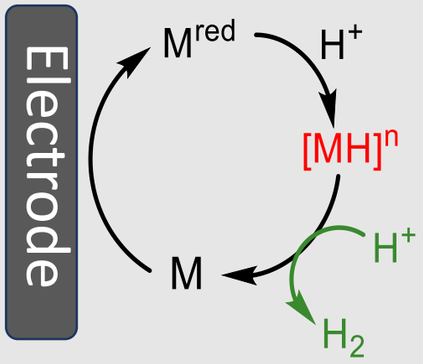
ΔG_{H^-} = hydricity

Hydricity as Thermodynamic Descriptor





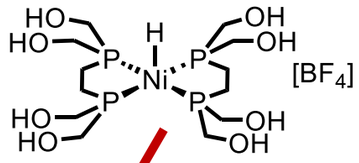
Chem. Rev. **2016**, 116, 8655



Heterolytic Hydrogen Bond Formation

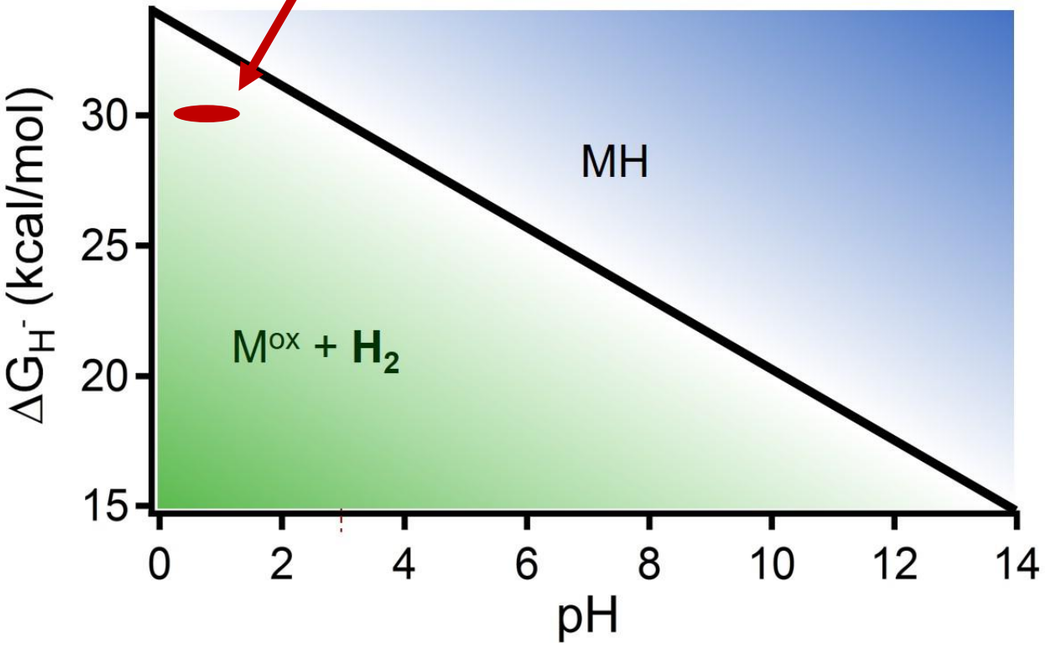
$$[LMH]^n + HB \longrightarrow [LM]^{n+1} + H_2 + B^-$$

$$\Delta G = \Delta G_{H^-} + 1.37*pH - \Delta G_{H2}$$



$[HNi(dhmpe)_2]^+$ ΔG_{H^-} = 30 kcal/mol hydrogen evolution catalyst between pH 1-3

H_2O

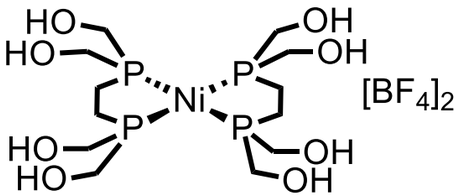


Dr. Charlene Tsay
(Vertex)

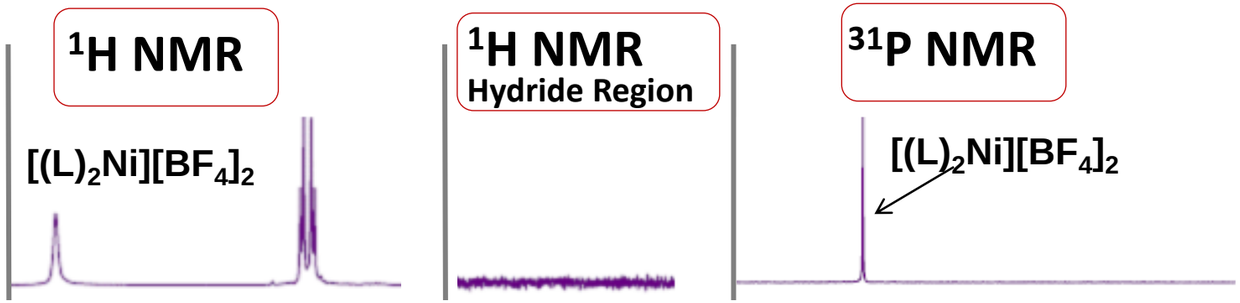
- Ni complex stable at pH 1 (0.1 M H_2SO_4)
- Electrolysis at pH 1: H_2 > 98% F.E.
- Electrocatalytic HER rate (k_{obs}) ~1850 s^{-1}
- ^{31}P NMR: complete retention of catalyst after ~18 h electrolysis

Tsay, C.; Livesay, B.; Ruelas, S. Yang, J. Y. *J. Am. Chem. Soc.* **2015**, *137*, 14114 • Tsay, C.; Yang J. Y., *J. Am. Chem. Soc.*, **2016**, *138*, 14174 • Ceballos, B. M.; Tsay, C. T.; Yang, J. Y., *Chem. Commun*, **2017**, *53*, 7405 • Tsay, C.; Ceballos, B. M.; Yang, J. Y. *Organometallics,* **2019**, *38, 1286* • Ceballos, B.; Yang, J. Y. *Proc. Natl. Acad. Sci.*, **2018**, *115(50)*, 12686.

Catalytic Cycle for Hydrogen Evolution

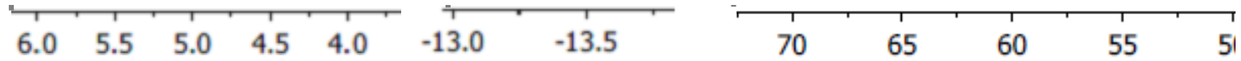


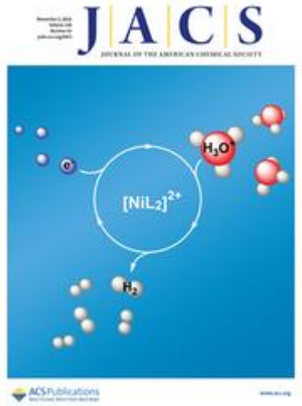
[(DHMPE)$_2$Ni][BF$_4$]$_2$



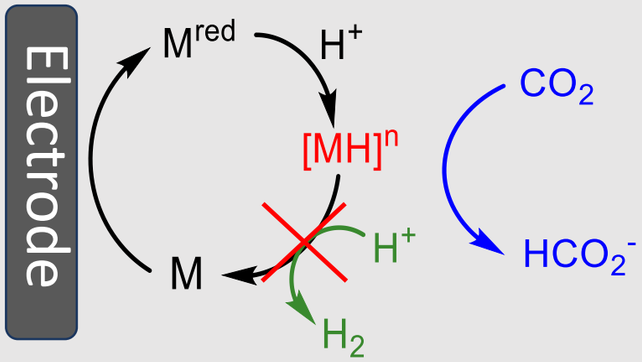
(in DMSO)

[NiL$_2$]$^{2+}$





J. Am. Chem. Soc., **2016**, *138*, 14174



Heterolytic Hydrogen Bond Formation

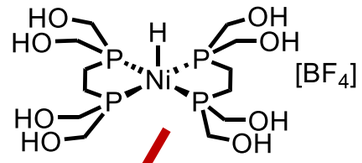
$[LMH]^n + HB \longrightarrow [LM]^{n+1} + H_2 + B^-$

$\Delta G = \Delta G_{H^-} + 1.37*pH - \Delta G_{H2}$

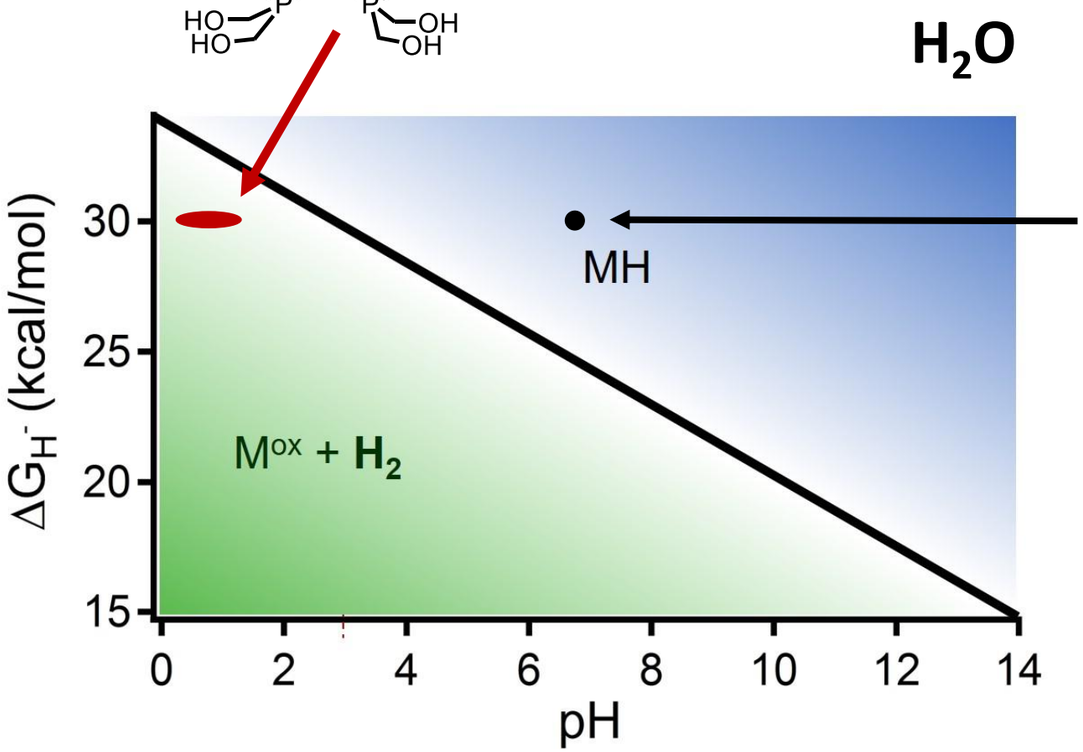
Hydride Transfer to CO_2

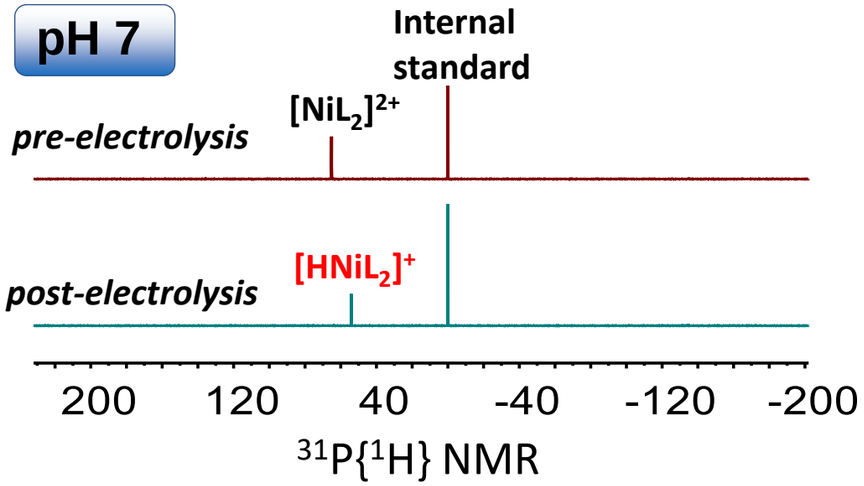
$[LMH]^n + CO_2 \longrightarrow [LM]^{n+1} + HCO_2^-$

$\Delta G = \Delta G_{H^-} - \Delta G_{(HCO2-)}$

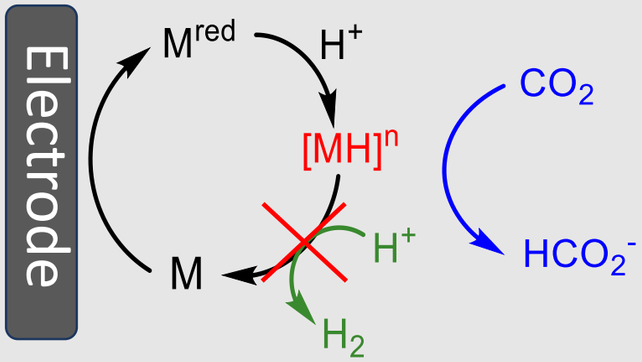


$[HNi(dhmpe)_2]^+$ ΔG_{H^-} = 30 kcal/mol
HER catalyst between pH 1-3





Tsay, C.; Livesay, B.; Ruelas, S. Yang, J. Y. *J. Am. Chem. Soc.* **2015**, *137*, 14114 • Tsay, C.; Yang J. Y., *J. Am. Chem. Soc.*, **2016**, *138*, 14174 • Ceballos, B. M.; Tsay, C. T.; Yang, J. Y., *Chem. Commun*, **2017**, *53*, 7405 • Tsay, C.; Ceballos, B. M.; Yang, J. Y. *Organometallics,* **2019**, *38,* 1286 • Ceballos, B.; Yang, J. Y. *Proc. Natl. Acad. Sci.*, **2018**, *115(50)*, 12686.



Heterolytic Hydrogen Bond Formation

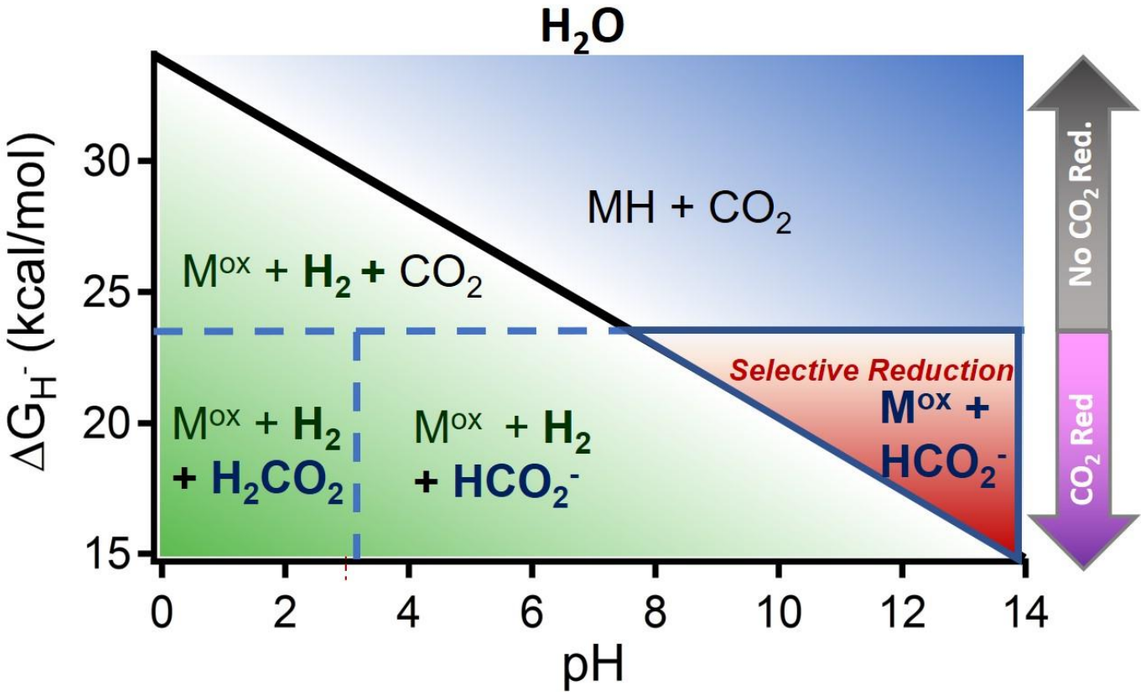
$[LMH]^n + HB \longrightarrow [LM]^{n+1} + H_2 + B^-$

$\Delta G = \Delta G_{H^-} + 1.37*pH - \Delta G_{H2}$

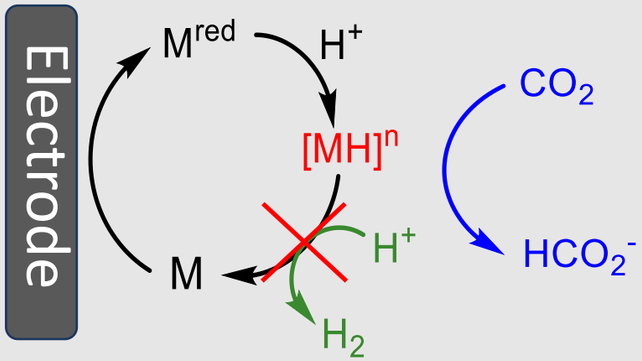
Hydride Transfer to CO_2

$[LMH]^n + CO_2 \longrightarrow [LM]^{n+1} + HCO_2^-$

$\Delta G = \Delta G_{H^-} - \Delta G_{(HCO2-)}$



Tsay, C.; Livesay, B.; Ruelas, S. Yang, J. Y. *J. Am. Chem. Soc.* **2015**, *137*, 14114 • Tsay, C.; Yang J. Y., *J. Am. Chem. Soc.*, **2016**, *138*, 14174 • Ceballos, B. M.; Tsay, C. T.; Yang, J. Y., *Chem. Commun*, **2017**, *53*, 7405 • Tsay, C.; Ceballos, B. M.; Yang, J. Y. *Organometallics,* **2019**, *38, 1286* • Ceballos, B.; Yang, J. Y. *Proc. Natl. Acad. Sci.*, **2018**, *115(50)*, 12686.



Heterolytic Hydrogen Bond Formation

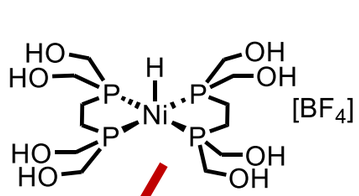
$[LMH]^n + HB \longrightarrow [LM]^{n+1} + H_2 + B^-$

$\Delta G = \Delta G_{H^-} + 1.37*pH - \Delta G_{H2}$

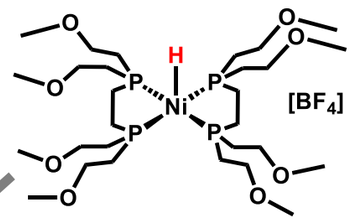
Hydride Transfer to CO_2

$[LMH]^n + CO_2 \longrightarrow [LM]^{n+1} + HCO_2^-$

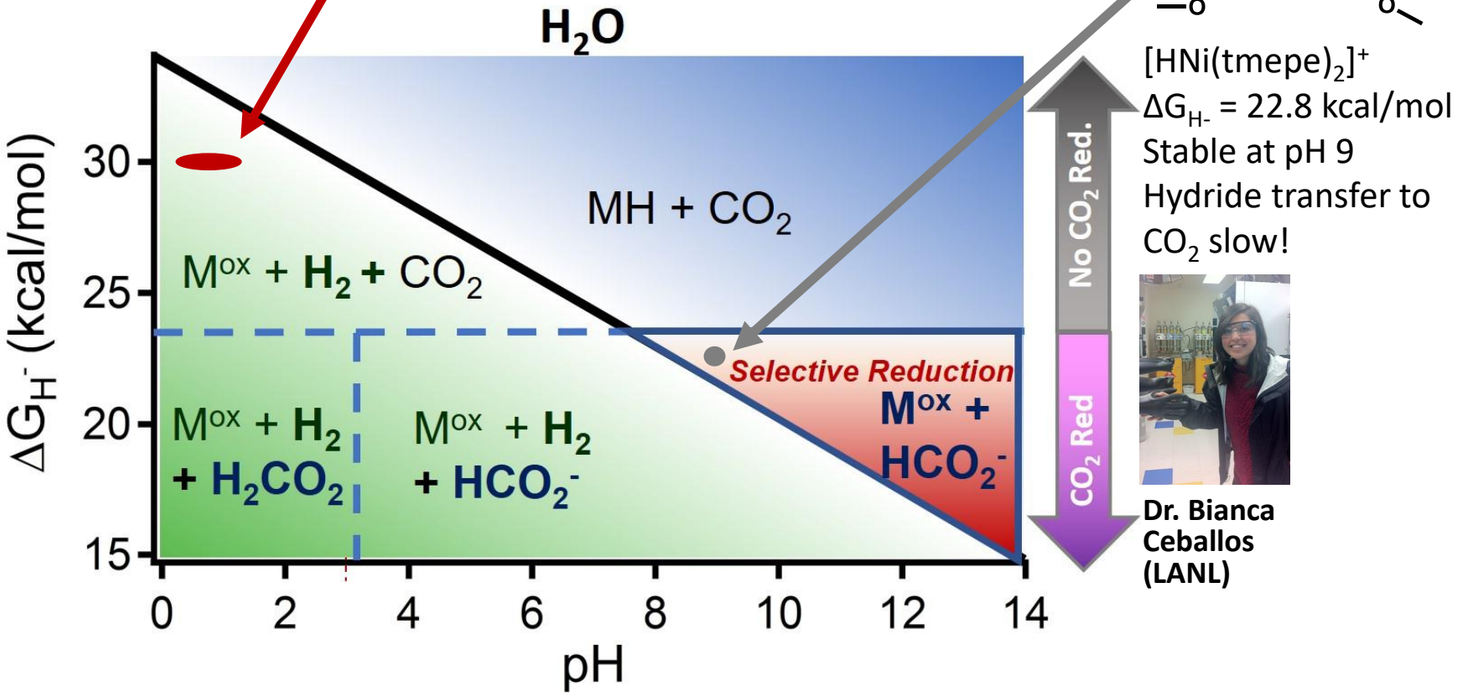
$\Delta G = \Delta G_{H^-} - \Delta G_{(HCO2-)}$



$[HNi(dhmpe)_2]^+$ ΔG_{H^-} = 30 kcal/mol
hydrogen evolution catalyst
between pH 1-3

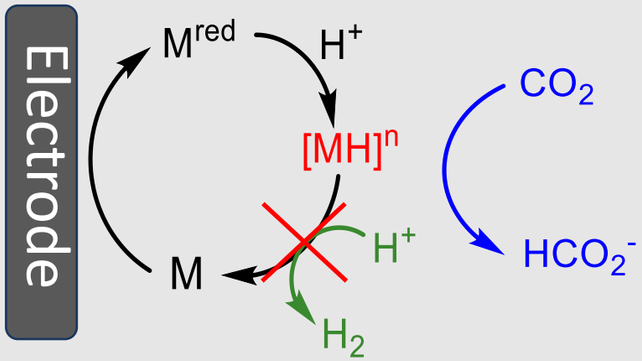


$[HNi(tmepe)_2]^+$
ΔG_{H^-} = 22.8 kcal/mol
Stable at pH 9
Hydride transfer to CO_2 slow!



Dr. Bianca Ceballos (LANL)

Tsay, C.; Livesay, B.; Ruelas, S. Yang, J. Y. *J. Am. Chem. Soc.* **2015**, *137*, 14114 • Tsay, C.; Yang J. Y., *J. Am. Chem. Soc.*, **2016**, *138*, 14174 • Ceballos, B. M.; Tsay, C. T.; Yang, J. Y., *Chem. Commun*, **2017**, *53*, 7405 • Tsay, C.; Ceballos, B. M.; Yang, J. Y. *Organometallics,* **2019**, *38, 1286* • Ceballos, B.; Yang, J. Y. *Proc. Natl. Acad. Sci.*, **2018**, *115(50)*, 12686.



Heterolytic Hydrogen Bond Formation

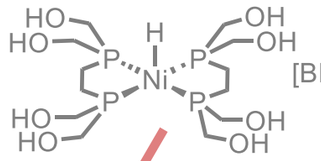
$[LMH]^n + HB \longrightarrow [LM]^{n+1} + H_2 + B^-$

$\Delta G = \Delta G_{H^-} + 1.37*pH - \Delta G_{H2}$

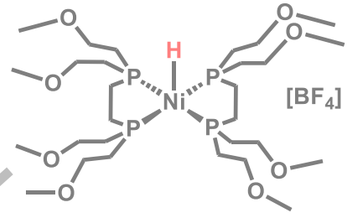
Hydride Transfer to CO_2

$[LMH]^n + CO_2 \longrightarrow [LM]^{n+1} + HCO_2^-$

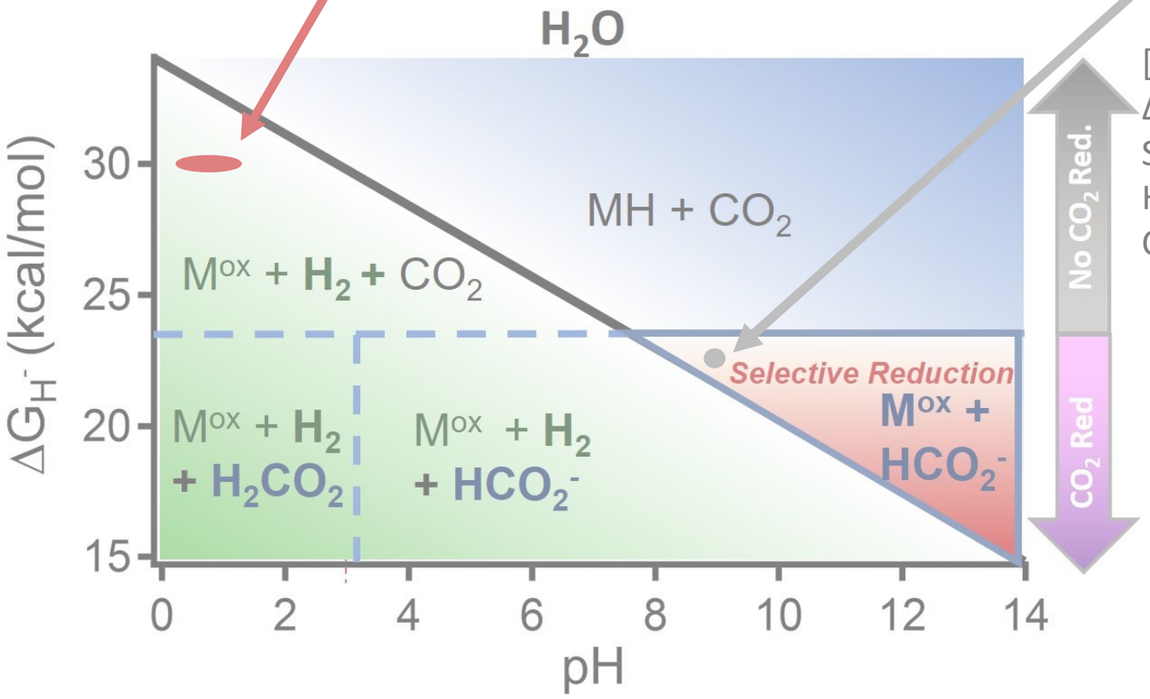
$\Delta G = \Delta G_{H^-} - \Delta G_{(HCO2-)}$



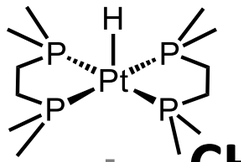
$[HNi(dhmpe)_2]^+$ ΔG_{H^-} = 30 kcal/mol
hydrogen evolution catalyst
between pH 1-3



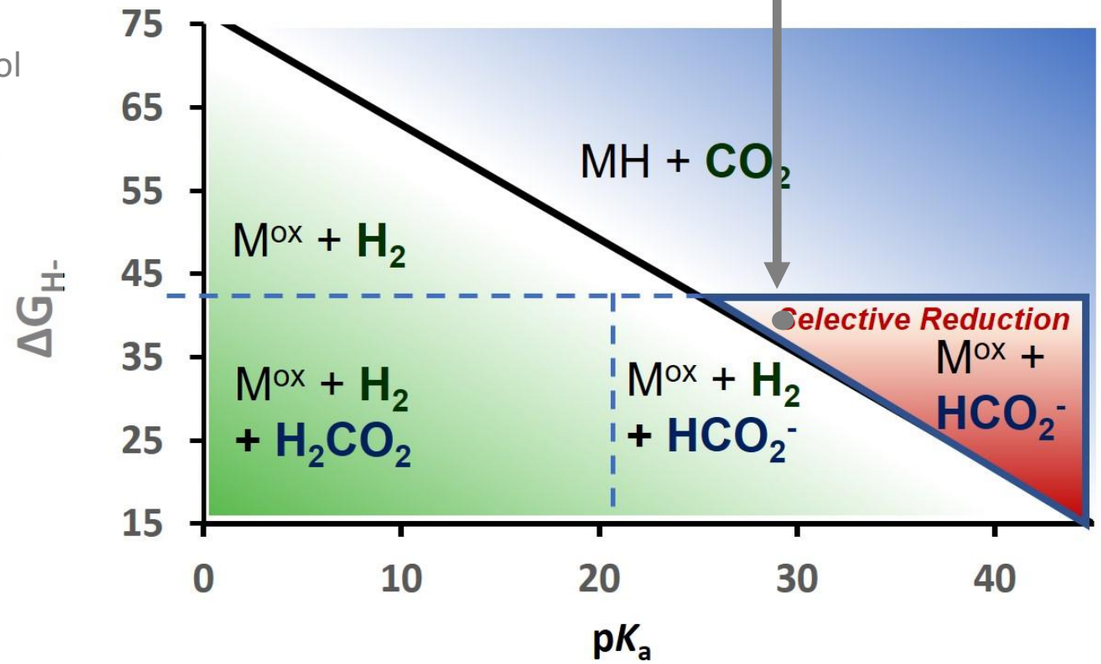
$[HNi(tmepe)_2]^+$
ΔG_{H^-} = 22.8 kcal/mol
Stable at pH 9
Hydride transfer to
CO_2 slow!



$[HPt(dmpe)_2]^+$, ΔG_{H^-} = 41 kcal/mol
Selective CO_2 to HCO_2^- reduction
using phenol (pK_a = 30)



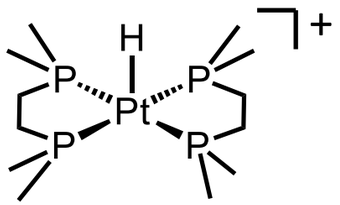
CH_3CN



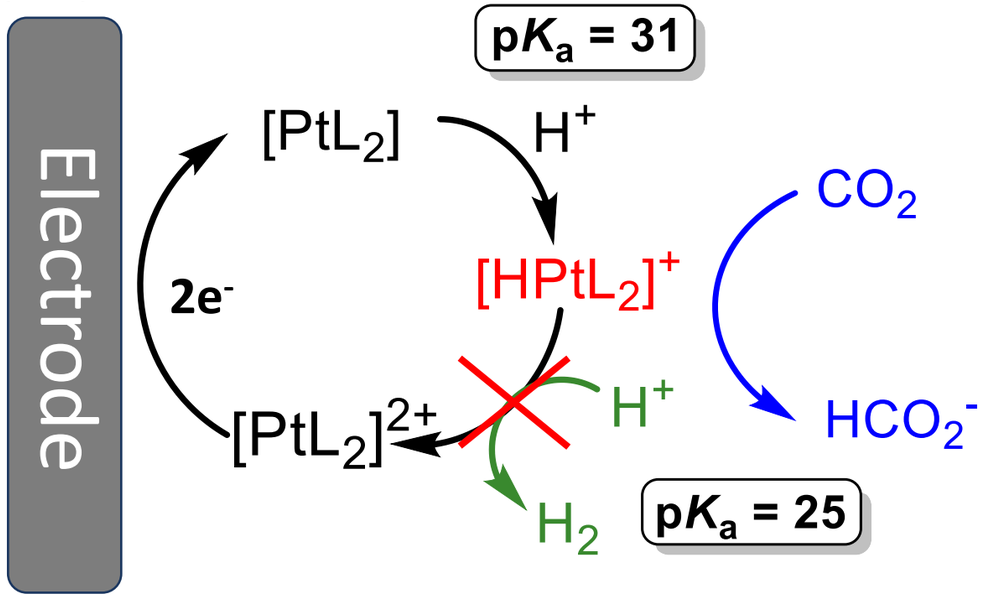
Tsay, C.; Livesay, B.; Ruelas, S. Yang, J. Y. *J. Am. Chem. Soc.* **2015**, *137*, 14114 • Tsay, C.; Yang J. Y., *J. Am. Chem. Soc.*, **2016**, *138*, 14174 • Ceballos, B. M.; Tsay, C. T.; Yang, J. Y., *Chem. Commun*, **2017**, *53*, 7405 • Tsay, C.; Ceballos, B. M.; Yang, J. Y. *Organometallics,* **2019**, *38, 1286* • Ceballos, B.; Yang, J. Y. *Proc. Natl. Acad. Sci.*, **2018**, *115(50)*, 12686.

Selective CO_2 Reduction to HCO_2^-

Dr. Bianca Ceballos (LANL)

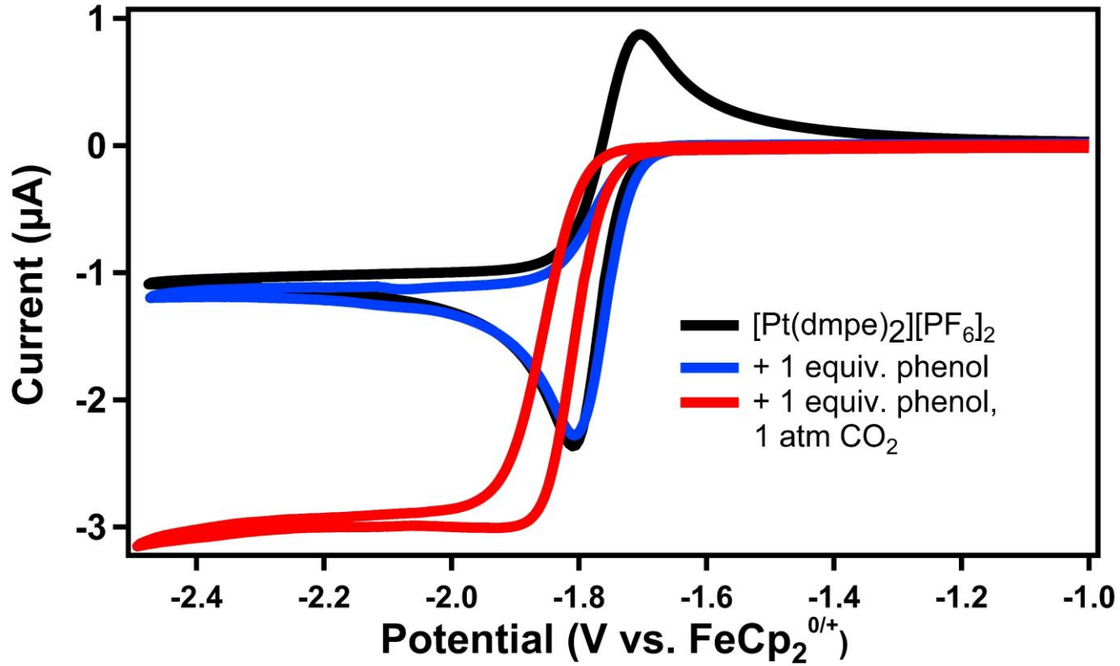


$[HPt(dmpe)_2]^+$
ΔG_{H^-} = 41 kcal/mol



E = −1.73 V vs $[Fe(C_5H_5)_2]^{+/0}$

❖ Use of Et_3NHBF_4 (pK_a = 18.8) results in electrocatalytic H_2 evolution



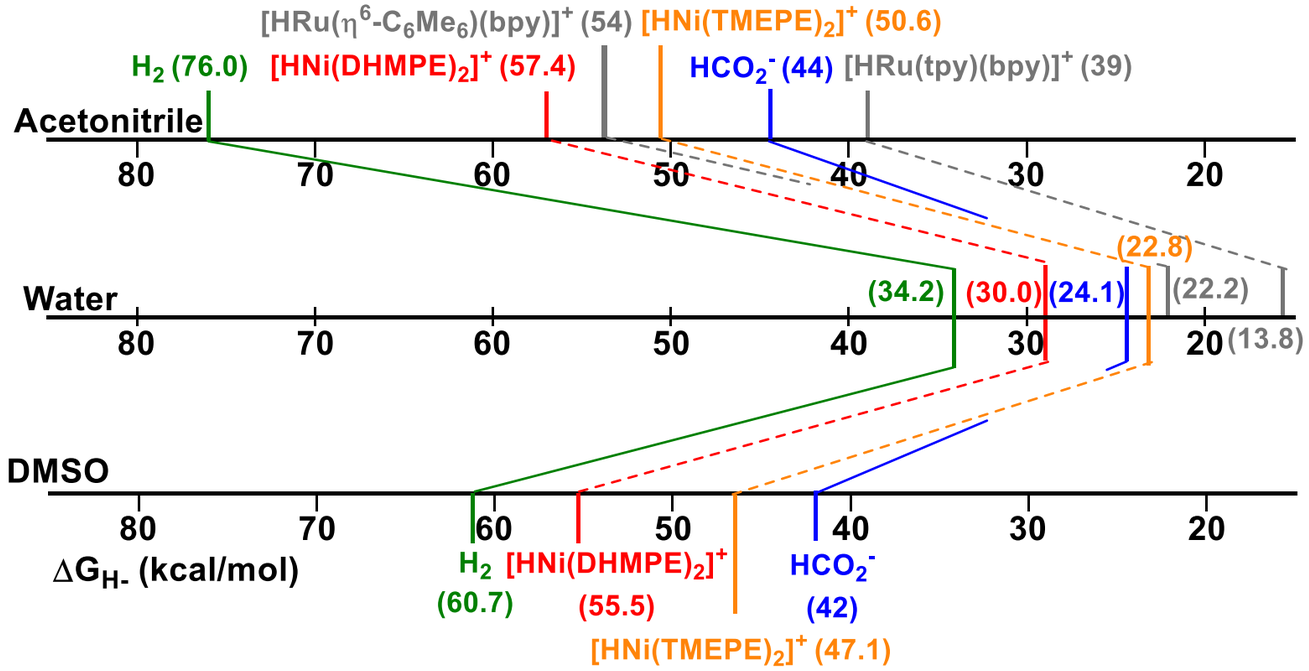
❖ **Selective electrolytic generation of $[HPt(dmpe)_2]^+$ with phenol (pK_a=30) under N_2**

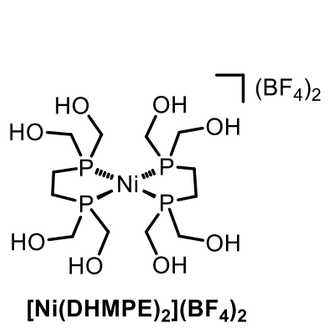
❖ **Electrocatalytic CO_2 reduction to HCO_2^-, Faradaic efficiency > 90% and η < 200 mV**

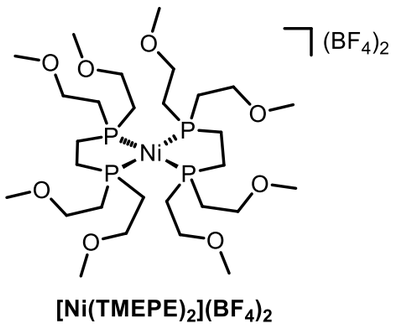
Understanding thermodynamics taught us how to 'turn off' H_2 evolution from a Pt complex

Ceballos, B.; Yang, J. Y. *Proc. Natl. Acad. Sci.*, **2018**, *115(50)*, 12686.

Solvation Effects







- Hydride transfer to CO_2 is more favorable in H_2O
- Other products that can hydrogen-bond to H_2O will have similar effect
- Experimental energies are benchmarks for computational calculations

Solvent-dependent free energies

$[HNi(TMEPE)_2]^+$

ΔG = ΔGH⁻ - ΔG(HCO_2^-)

ΔG (CH_3CN) = 6.6

ΔG (H_2O) = -1.3 *(change in favorability)*

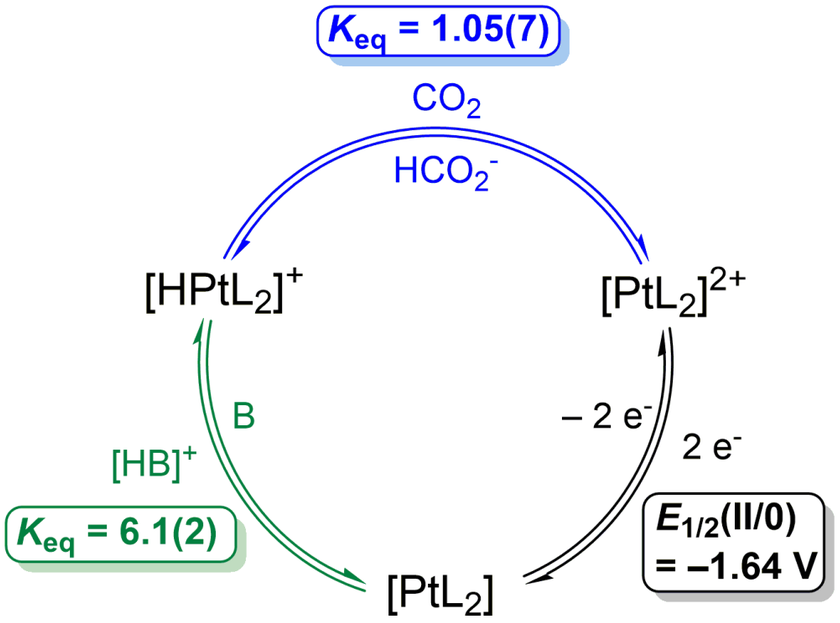
ΔG (DMSO) = 5.1

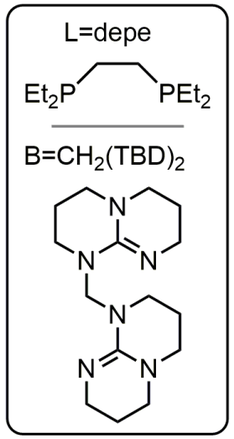
J. Am. Chem. Soc. **2015**, *137*, 14114 • *Chem. Commun.* **2017**, *53*, 7405

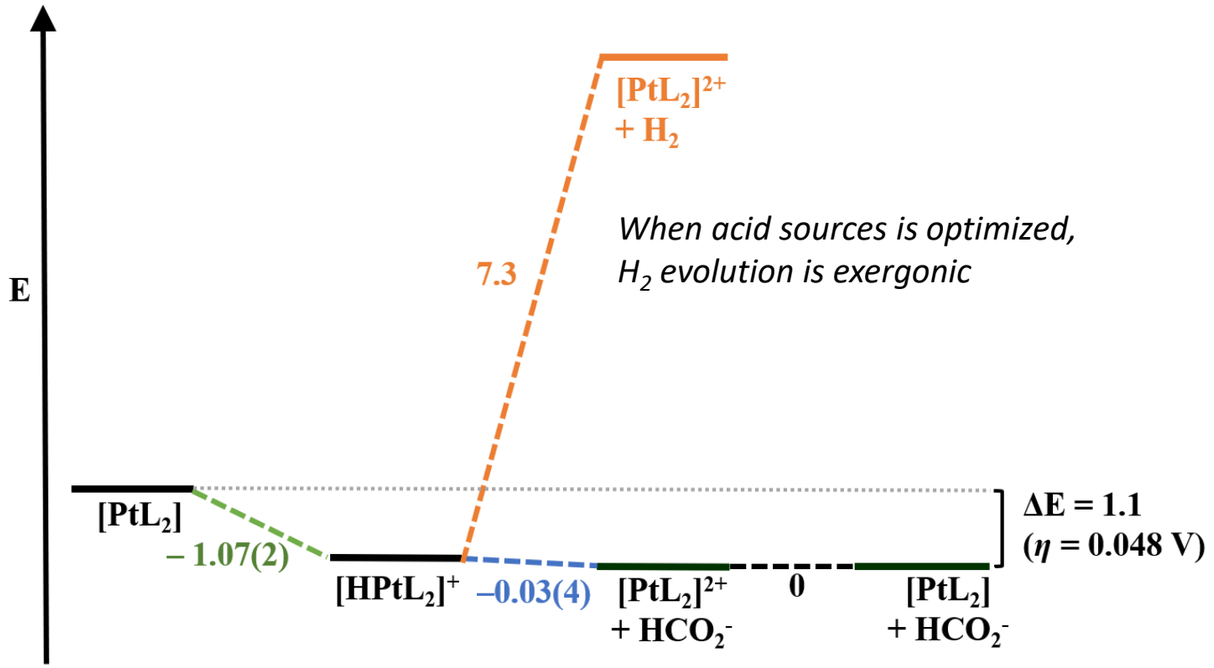
Ru complexes: Creutz, Chou, *J. Am. Chem. Soc.*, **2009**, *131*, 2794 • Matsubara, Fujita, Doherty, Muckerman, Creutz, *J. Am. Chem. Soc.*, **2012**, *134*, 15743

Reversible CO_2/HCO_2^- Catalysis

Reversibility is the hallmark of low overpotential catalysis (i.e. $2H^+/H_2$: Pt, hydrogenase enzymes)
For CO_2/HCO_2^-, was only known for the formate dehydrogenase enzyme & PtPd nanoparticles



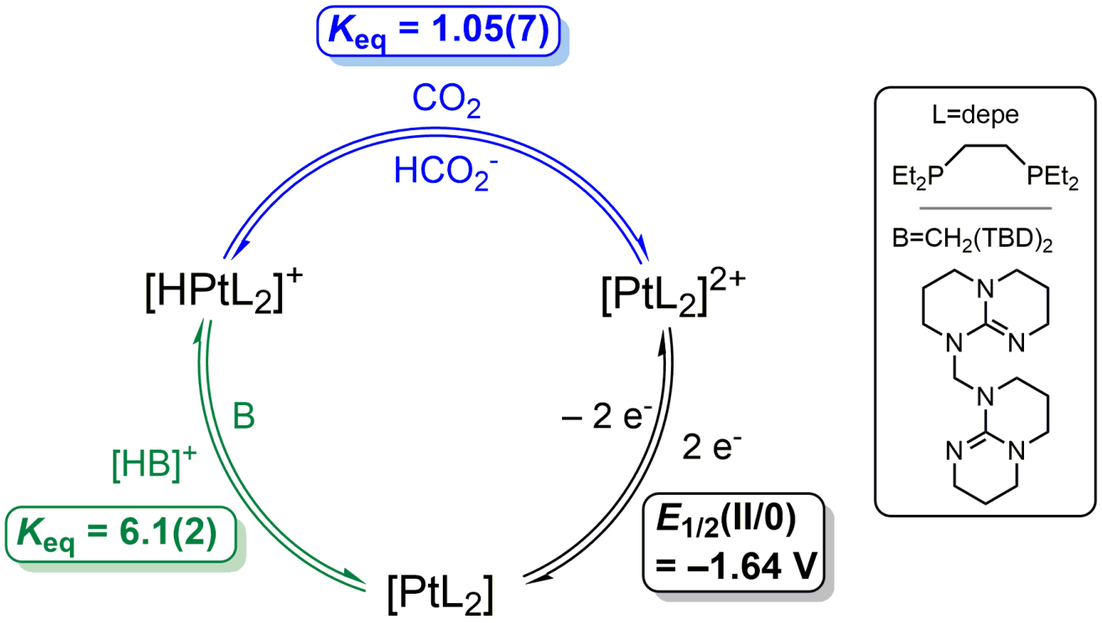




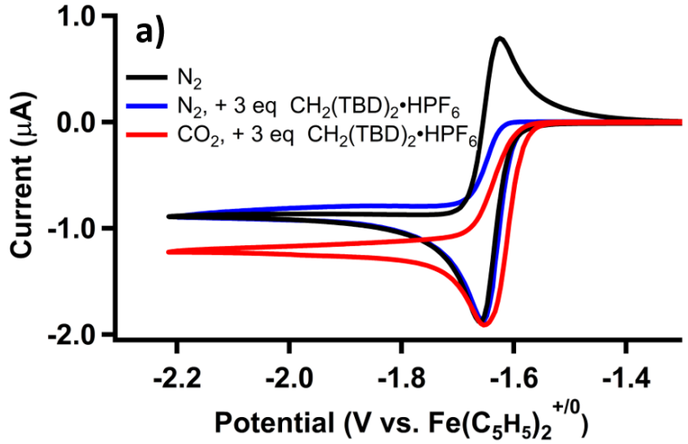
Experimentally measured energy landscape under catalytic conditions (pK_a of 29.0, 1 atm CO_2) at –1.64 V vs $Fe(C_5H_5)_2^{+/0}$ in CH_3CN. Energetic values in kcal/mol unless otherwise indicated.

Angew. Chemie. Int. Ed., **2020**, *59*, 4443, *VIP article* • US Patent #11990658B2

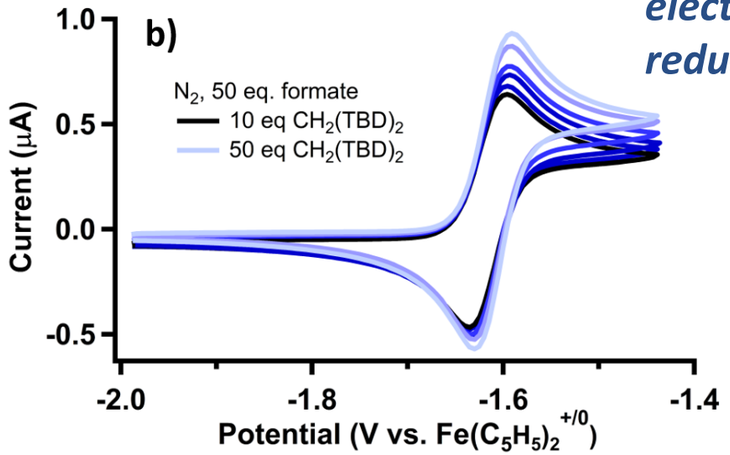
Reversible CO_2/HCO_2^- Catalysis



CO_2 reduction to formate, > 95% F.E. (no H_2 detected)



Formate oxidation, > 95% F.E.

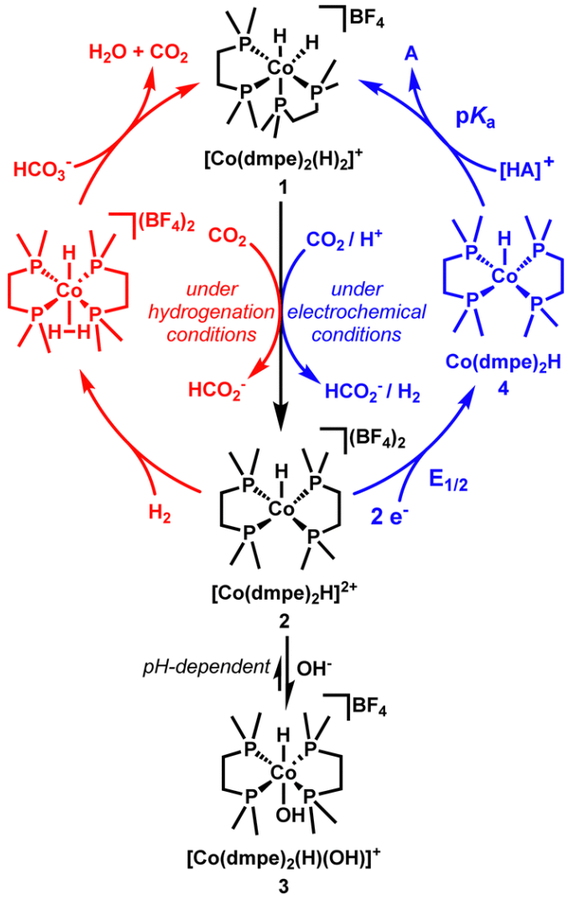


First example of molecular electrocatalyst for CO_2 reduction/HCO_2^- oxidation

Angew. Chemie. Int. Ed., **2020**, *59*, 4443, *VIP article* • US Patent #11990658B2

Beyond the Early Career – Bridging Hydrogenation & Electrocatalysis

Translating hydrogenation activity to electrocatalytic activity

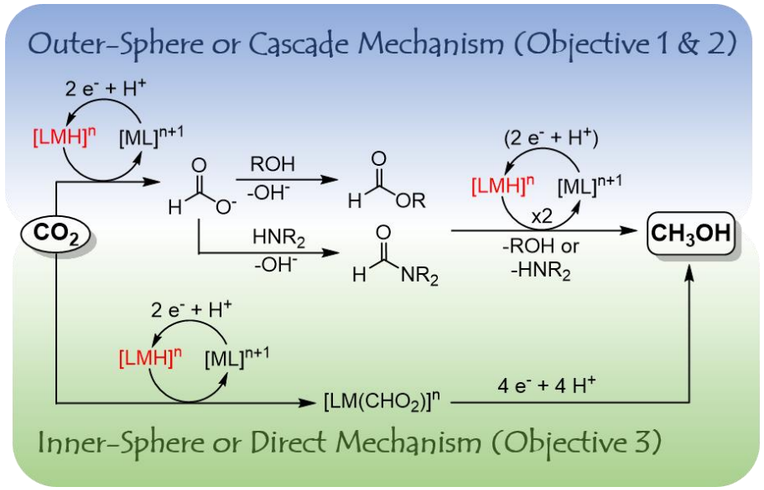


Chem. Commun., **2023**, *59*, 338

Early Career Award Enabling New Diections

- ***5 yrs focused study on electrocatalytic hydride transfer reactions***
- ***Scientific discussions with community & leaders in the field***

- There is minimal overlap between catalyst discovery for homogeneous CO_2 hydrogenation catalysts & CO_2 Reduction (CO2R) electrocatalysts though they share mechanistic similarities
- Hydricity is not commonly measured/considered for hydrogenation catalysts although it is an important thermodynamic descriptor



- There are several examples of homogeneous CO_2 hydrogenation catalysts to CH_3OH – but few for electrocatalytic systems
- Investigating translation of CO_2 to CH_3OH hydrogenation activity to electrocatalytic systems

Early Career Researcher Training & Acknowledgements

Postdoctoral Associates

Charlene Tsay
(*Vertex*)

Janice Wong
(*Cumulus Energy Storage*)

20 publications
> 700 citations
2 patents

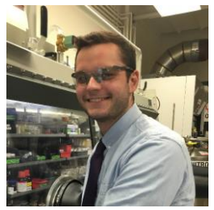
Graduate Students

Juliet Kotyk
(*Fuji Electronic Materials*)

Zachary Thammavongsy
(*Santiago Canyon College*)

Sarah Wang (*Rocky Mountain Institute*)

Bianca Ceballos
(*LANL*)



Drew Cunningham*
(*Cormetech*)

Tyler Kerr
(*UCLA*)

Caitlin Hanna*
(Waters Corp)

Brian Lydon
(Intel)

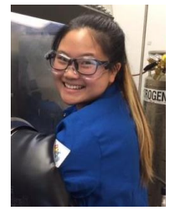
Undergraduate Students (co-authored publication)

Brooke Livesay
(*CSU - LANL*)

Samantha Ruelas
(*Oregon - LLNL*)

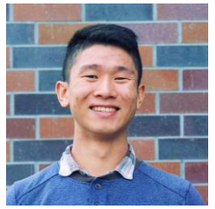
Ivy Kha
(*Optometrist*)

Nehal Idris
(*UC Irvine*)



Natwara Sutthirat
(Med School)

Han Le (*UC Berkeley*)



Andrew Luu
(*Northeastern*)

Zaira Barrera
(*UCLA*)

Stephen Denghausen (*ASP*)

Jessica Mendoza
(HS Teacher)

Rebecca Combs
(*U of Minnesota*)

*DOE SCGSR Recipient

Early Career Impact

Director, Center for Closing the Carbon Cycle EFRC (https://carbonsolution.uci.edu/)
Committee Member, National Academies of Science & Engineering Report: Carbon Utilization Infrastructure, Markets, Research and Development
Associate Editor, *Journal of the American Chemical Society*
2022 Chair, Energy and Environment Subdivision of the Division of Inorganic Chemistry
Editorial Advisory Board, *Chem, Progress in Inorganic Chemistry, Organic and Inorganic Chemistry Au , Accounts of Chemical Research, Chem Catalysis, ACS Energy Letters, Inorganic Chemistry, ACS Sustainable Chemistry and Engineering*

2024	**Fellow of the American Association for the Advancement of Science (AAAS)**
2021	**Inorganic Chemistry Lectureship**
2020	**Research Corporation Scialog Fellow for Negative Emissions Science**
2019	**UC Irvine Academic Senate Early Career Research Award**
2019	**Camille Dreyfus Teacher-Scholar Award**
2019	**Chancellor's Award for Excellence in Fostering Undergraduate Research**
2018	**CIFAR Azrieli Global Scholar**
2018	**Sloan Foundation Fellow**
2017	**Presidential Early Career Award in Science and Engineering (PECASE)**
2017	**Research Corporation Scialog Fellow for Advanced Energy Storage**
2017	**Kavli Frontiers of Science Fellow**
2016	**National Science Foundation CAREER Award**
2015	**Camille and Henry Dreyfus Environmental Postdoctoral Mentor**
2015	**ACS Catalysis Lectureship** (member of team award from work at PNNL)
2015	**Hellman Faculty Fellow**