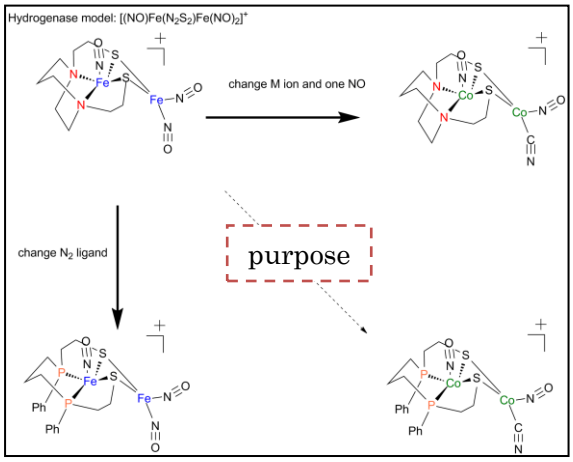
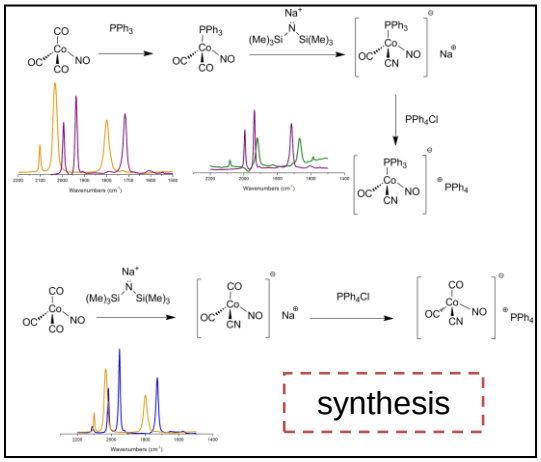
Synthesis of [FeFe]-hydrogenase model complexes with nitrosyl ligand and its cobalt analog for the proton reduction.

Ting-Chun Lin and Chung-Hung Hsieh
Student of Department of Chemistry, Tamkang University (TKU)
151, Yingzhuan, Tamsui, New Taipei 25137, Taiwan (R.O.C.)
E-mail: kkjen1221@gmail.com

The hydrogenases is a redox active enzyme for the interconversion of proton and hydrogen in a biological system.The chemical structure of [FeFe]-hydrogenase contains iron centers, bridging dithiolate and diatomic CO^-/CN^- ligands on the iron centers. [1]In 2014, we reported the cationic complex $[(NO)Fe(\boldsymbol{N_2S_2})Fe(NO)_2]^+$ and neutral $[(NO)Fe(\boldsymbol{N_2S_2})Fe(NO)_2]$ [2] (N_2S_2=N, N-bis(2-mercaptoethyl)-1,4-diazacycloheptane) can be the biomimetic functional model for [FeFe]-hydrogenase.The conversion of strong (HBF_4)and weak(CH_3COOH) acid to the hydrogen can be achieved by one and two electron reduction, respectively.

Our goal is to enhance the ability of proton production.In this study, we will synthesize the cobalt analog and modify the $\boldsymbol{N_2S_2}$ ligand to the $\boldsymbol{P_2S_2}$(meso-1,3Bis[(mercaptoethyl)phenylphosphino]) ligand to compare the efficiency. [3]





Reference:

1. Tard, C. D. & Pickett, C. J. *Chem. Rev.* **2009**, 109 (6), 2245.
2. Hsieh, C. H.; Ding, S.; Erdem, Ö . F.; Crouthers, D. J.; Lubitz, W.; Popescu, C. V.; Reibenspies, J. H.; Hall, M. B.; Darensbourg, M. Y. *Nature Communications*, **2014**, 5, 3684.
3. Champness, N. R.; Frampton, C. S.; Reid, G.; Tocher, D. A.; *J. Chem. Soc. Dalton Trans*, **1994**, 3031.

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Ting-Chun Lin, Chung-Hung Hsieh* E-mail: kkjen1221@gmail.com

Department of Chemistry, Tamkang University, Tamsui, New Taipei City, Taiwan

淡江大學化學系

Abstract:

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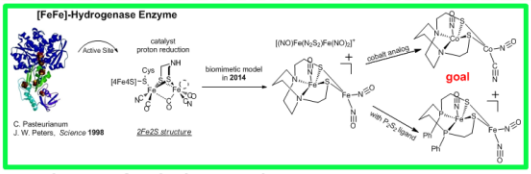
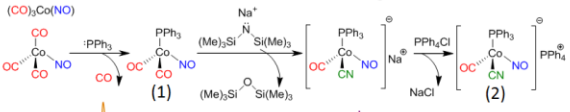
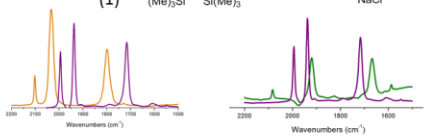
Our goal is to enhance the ability of proton reduction. In this study, we will synthesize the cobalt analog and modify the $\boldsymbol{N_2S_2}$ ligand to the $\boldsymbol{P_2S_2}$(meso-1,3 Bis[(mercaptoethyl)phenylphosphino]) ligand to compare the efficiency. [3]



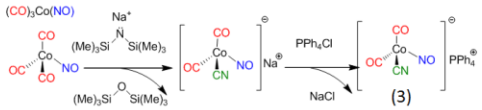
• Synthesis of cobalt complexes with diatomic $CO^-/CN^-/NO^-$ ligands

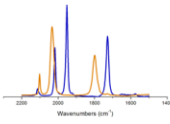




IR spectra

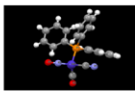
Overlaid IR spectra **precursor** , **1** and **2** in THF.
[yellow : ν(CO): 2101(m), 2033(vs), ν(NO): 1798(s) cm^{-1}]
[(1)purple : ν(CO): 2032(m), 1976(vs), ν(NO): 1754(s) cm^{-1}]
[(2)green : ν(CN): 2083(w), ν(CO): 1919(vs), ν(NO): 1667(s) cm^{-1}]





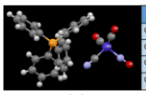
Overlaid IR spectra **precursor** and **3** in THF.
[yellow : ν(CO): 2101(m), 2033(vs), ν(NO): 1798(s) cm^{-1}]
[(3)blue : ν(CN): 2113(w), ν(CO): 2017(m), 1951(vs), ν(NO): 1728(s) cm^{-1}]

X-ray structure



Bond distance(Å)			
Co-P_1	2.209(1)	-	-
Co-N2O1	1.671(4)	N1O	1.166(5)
Co-C2O2	1.707(4)	C2O	1.141(6)
Co-C1N1	1.930(5)	C1N	1.150(6)

Complex(2)
$[Co(PPh_3)(NO)(CO)(CN)]$ PPh_4



Bond distance(Å)			
Co-N1O1	1.894(5)	N1O	1.187(7)
Co-C2O2	1.661(5)	C1O	1.129(7)
Co-C1O3	1.651(4)	C2O	1.139(6)
Co-C3N2	1.928(5)	C1N	1.150(7)

Complex(3)
$[Co(NO)(CO)_2(CN)]$ PPh_4

Referance

Chung-Hung Hsieh Research Group

1. Tard, C. D. & Pickett, C. J. *Chem. Rev.*, **2009**, 109 (6), 2245.
2. Hsieh, C. H.; Ding, S.; Erdem, Ö. F.; Crouthers, D. J.; Lubitz, W.; Popescu, C. V.; Reibenspies, J. H.; Hall, M. B.; Darensbourg, M. Y. *Nat. Commun.*, **2014**, 5, 3684.
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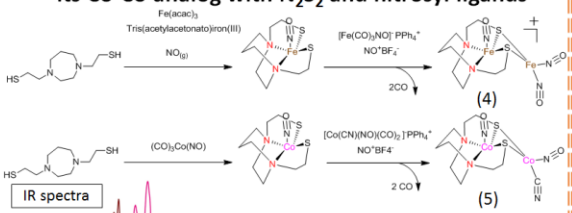
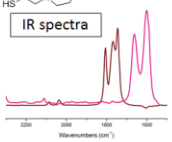
• Synthesis of [FeFe]-hydrogenase model complex and its Co-Co analog with N_2S_2 and nitrosyl ligands

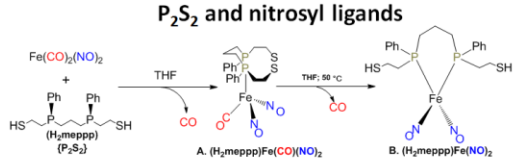


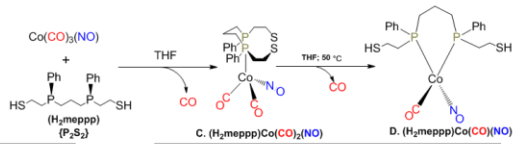
IR spectra



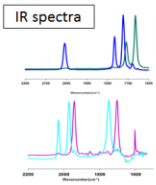
Overlaid IR spectra of **4** and **5** in DCM.
[**4 brown** : ν(NO): 1806(m), 1768(s) , 1745(vs) cm^{-1}]
[**5 pink** : ν(CN): 2111(w), ν(NO): 1662(s) , 1602(vs) cm^{-1}]

• Synthesis of iron and cobalt complexes with P_2S_2 and nitrosyl ligands





IR spectra



Overlaid IR spectra of **A** and **B** in THF.
[**A. blue** : ν (CO): 2008(s)cm^{-1},
ν(NO): 1765(s) , 1724(vs) cm^{-1}]
[**B. green** : ν(NO): 1708(s) , 1664(vs) cm^{-1}]

Overlaid IR spectra of **C** and **D** in THF.
[**C. Light blue** : ν (CO): 2033 (m), 1977 (s),
ν(NO): 1761 (s) cm^{-1}]
[**D. purple** : ν (CO): 1943(vs),
ν(NO): 1704 (vs) cm^{-1}]

• Enhanced catalystic ability with graphene oxide(GO)