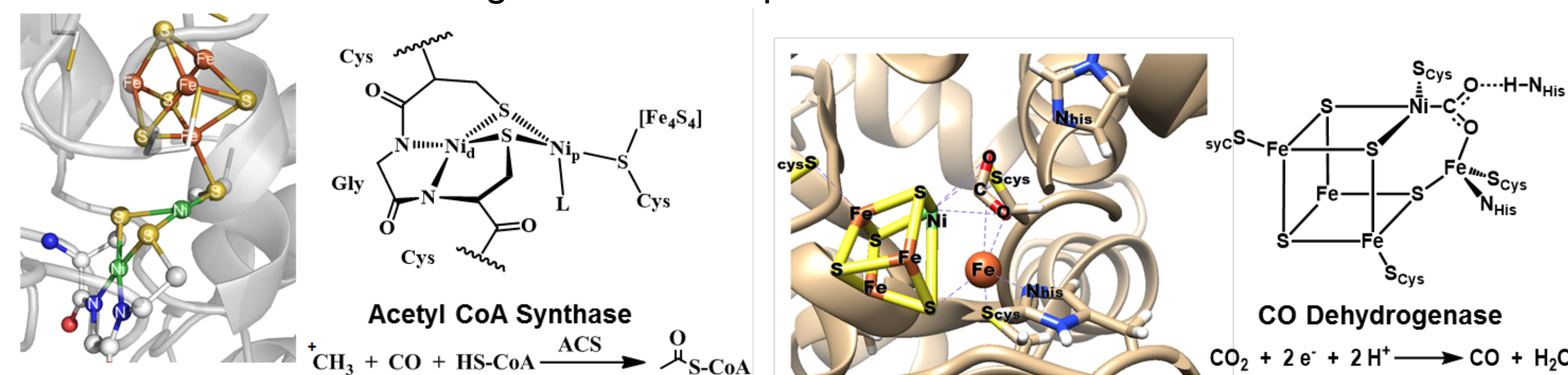


Comparisons of MN_2S_2 vs. Bipyridine as Redox-Active Ligands to Manganese and Rhenium in $(L-L)M'(CO)_3Cl$ Complexes

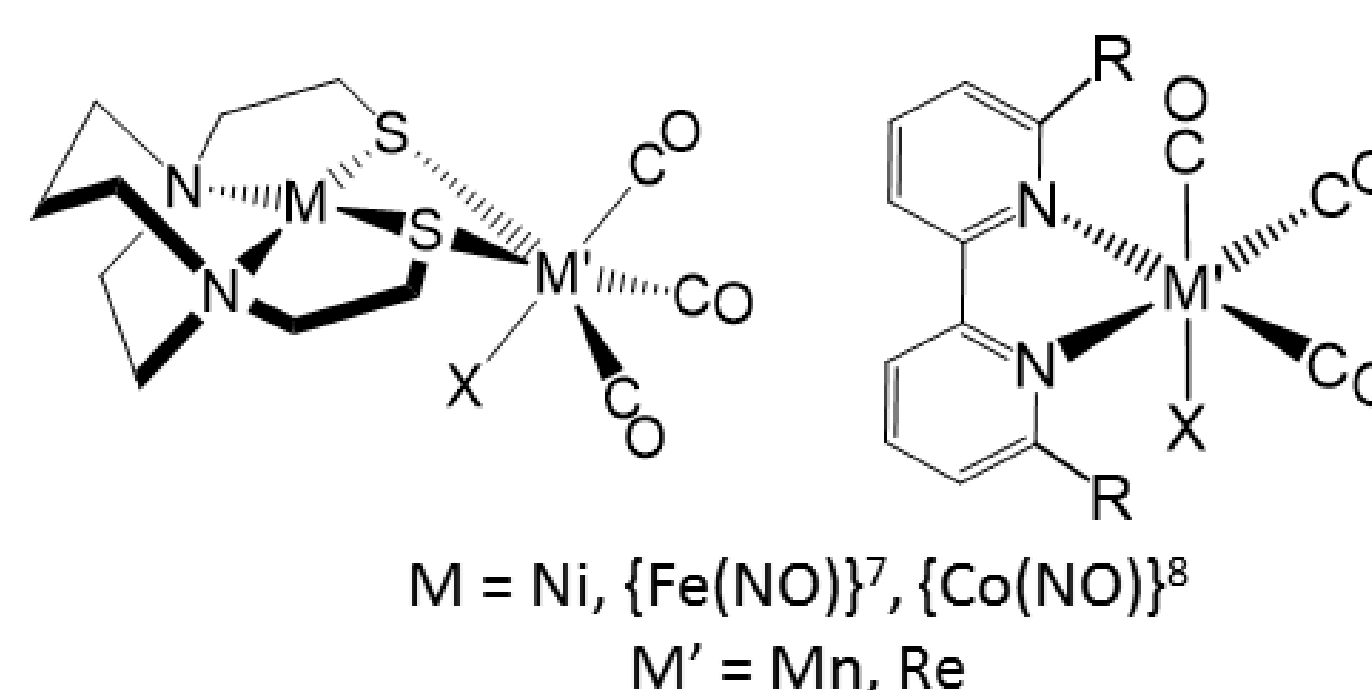
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Introduction

Nature provides convincing evidence that molecular catalysts for the redox-based activation of small molecules under ambient conditions requires intricate arrangements of at least two first row transition metals, typically bridged by sulfides or thiolate sulfurs.^{1,2} In this way, two metal centers obviate the necessity of two-electron redox processes at a single metal, but rather are positioned to share the burden of binding substrates as well as electronic stresses during sequential one-electron redox level changes. Two examples from nature are shown below.



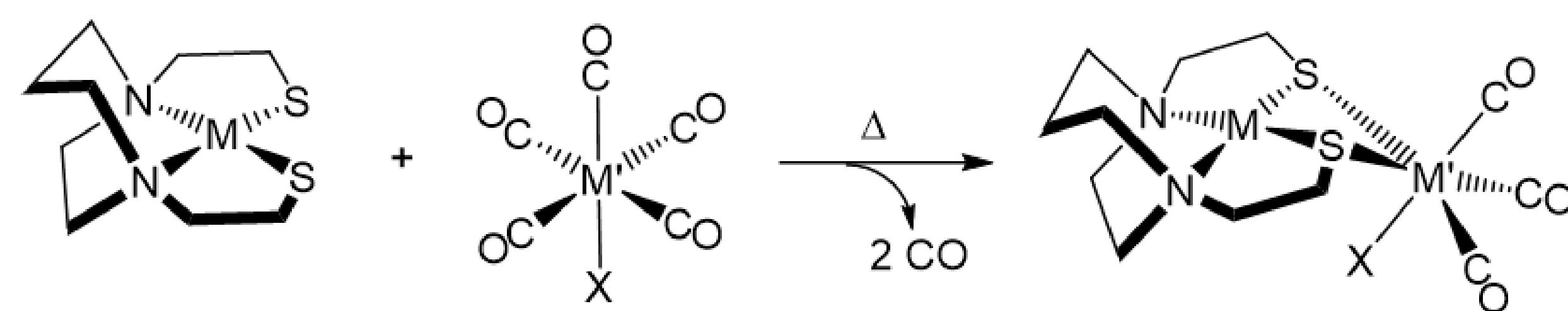
While redox-active organic-based ligands such as bipyridine and derivatives may fulfill the electronic buffering needed to soften electron uptake in mono-metallic systems, the delocalization of electron density on such ligands does not provide landing sites for the substrates, or orient Lewis acid/base pairs, as would a second metal.³ Our approach to this area has been to develop the chemistry of MN_2S_2 complexes as S-donor, metallodithiolate ligands.⁴ Herein we report the MN_2S_2 -as-bidentate ligand approach to metal fragments which are known to take up CO_2 , namely the $Mn/Re(CO)_3X$ unit, however with bipyridine as ligand.



Questions

- Can a bidentate, redox-active MN_2S_2 metallodithiolate ligand in heterobimetallic complexes of Mn and Re might serve as a receptor and conduit of electrons as does bipyridine?
- Does the hemi-lability of the cis-dithiolates play a role in the redox activity or catalytic activity of these complexes?
- Is electronic communication between the two metal centers facilitated by the bridging dithiolates?

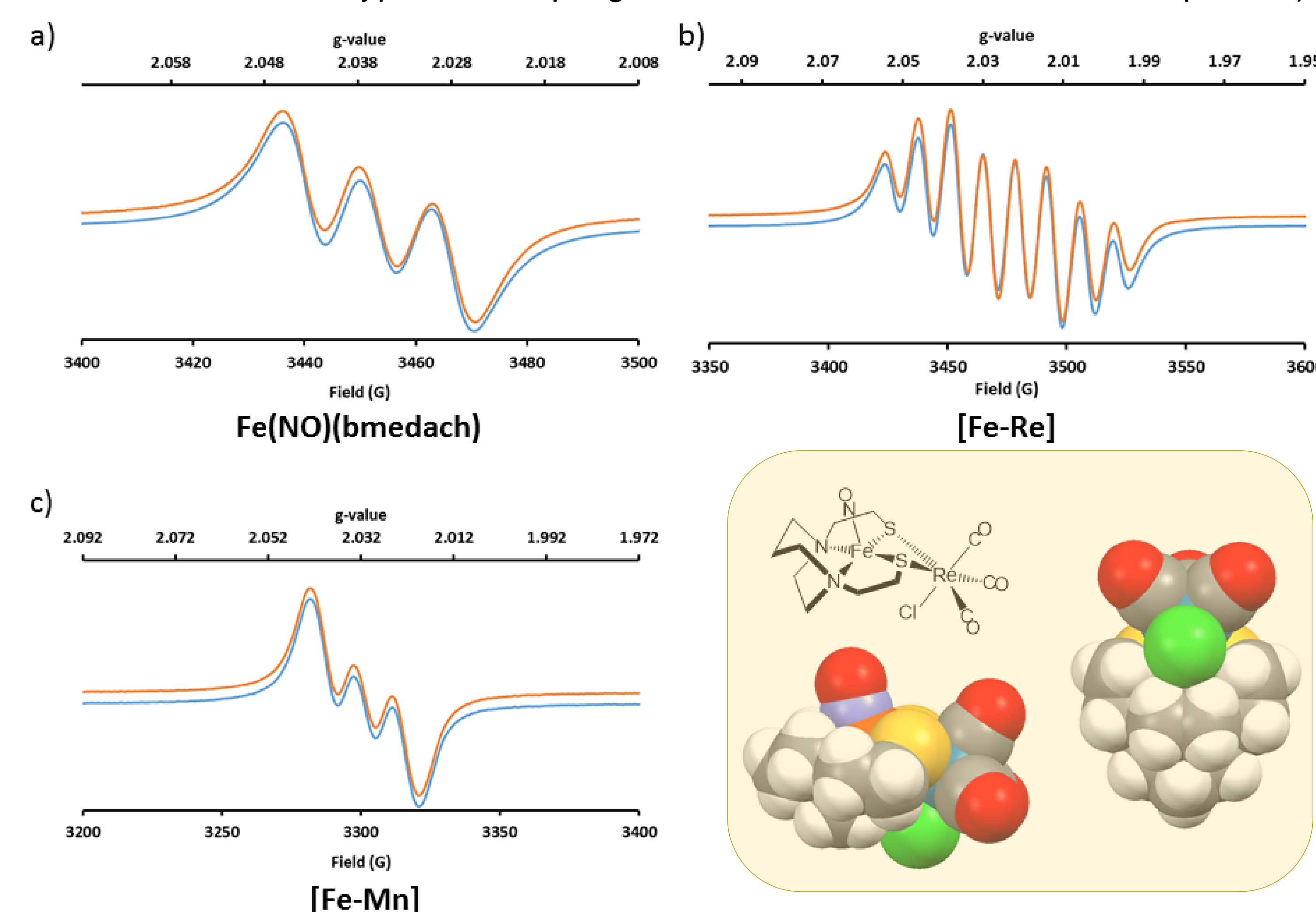
Synthesis of MN_2S_2 Containing Complexes



On refluxing the metallodithiolates with the appropriate $M'(CO)_5X$ compound overnight in MeOH or CH_2Cl_2 (DCM) solvent, two CO molecules are displaced from the Mn/Re, resulting in the binding of the dithiolates. All diatomic ligand absorptions of the heterobimetallics are shifted to lower wavenumbers compared to the $M'(bipy)_2(CO)_3X$ due to greater donating ability of the metallodithiolate ligands resulting in greater back-donation from the Mn/Re centers to the CO ligands.

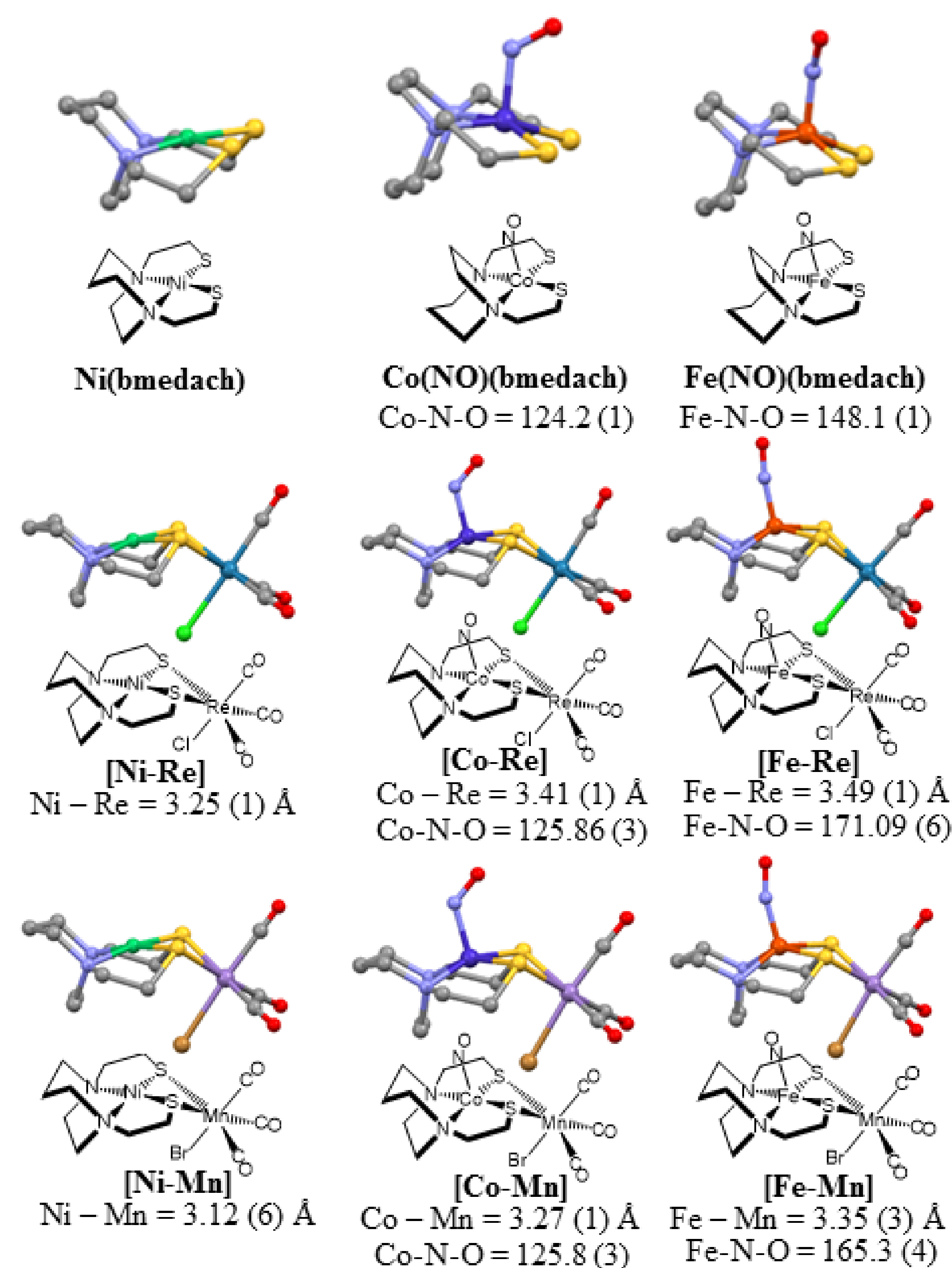
EPR Spectroscopy

Panel a) the EPR spectrum of $Fe(NO)(bmedach)$, $\{Fe(NO)\}^7$: an isotropic triplet centered at $g = 2.03$ and hyperfine coupling constant (A_{iso}) of 37 MHz assigned to the coupling of the unpaired electron to the $I = 1$ nuclear spin of ^{14}N in the nitrosyl ligand. On binding of the metallodithiolate to $Re(CO)_3Cl$ the EPR spectrum changes dramatically at room temperature, see b). Now an eight-line pattern centered at $g = 2.02$ is present which can be simulated with hyperfine coupling to one $I = 1$, the ^{14}N nucleus, as well as one $I = 5/2$, the $^{185/187}Re$. In contrast, the $[Fe-Mn]$ derivative shows no observable hyperfine coupling from the $I = 5/2$, ^{55}Mn nucleus, see panel c).

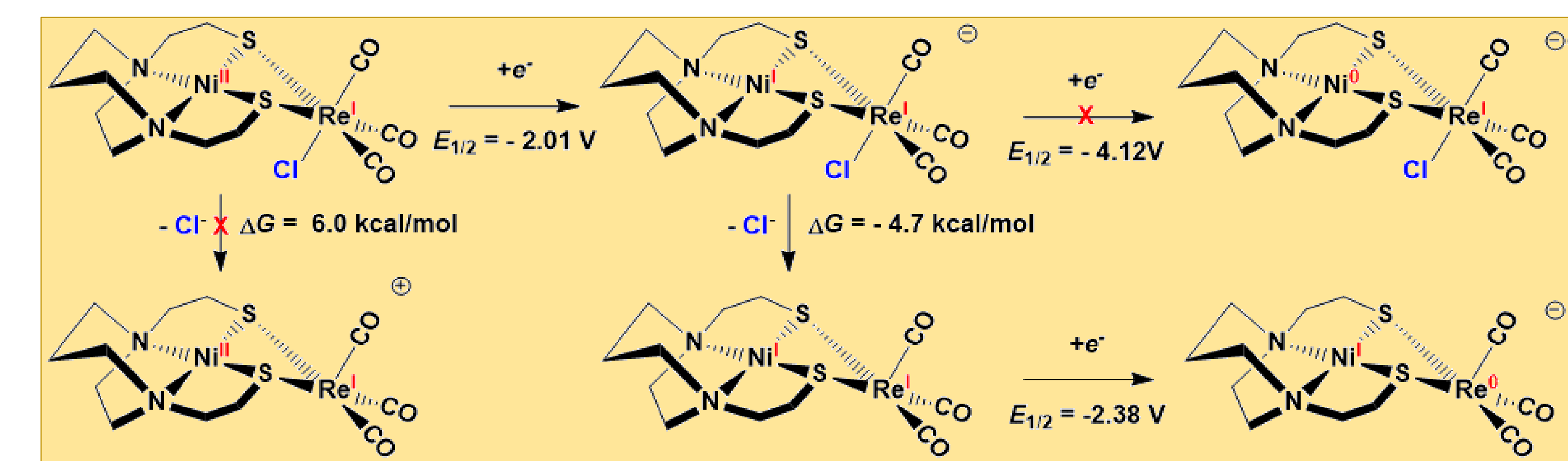
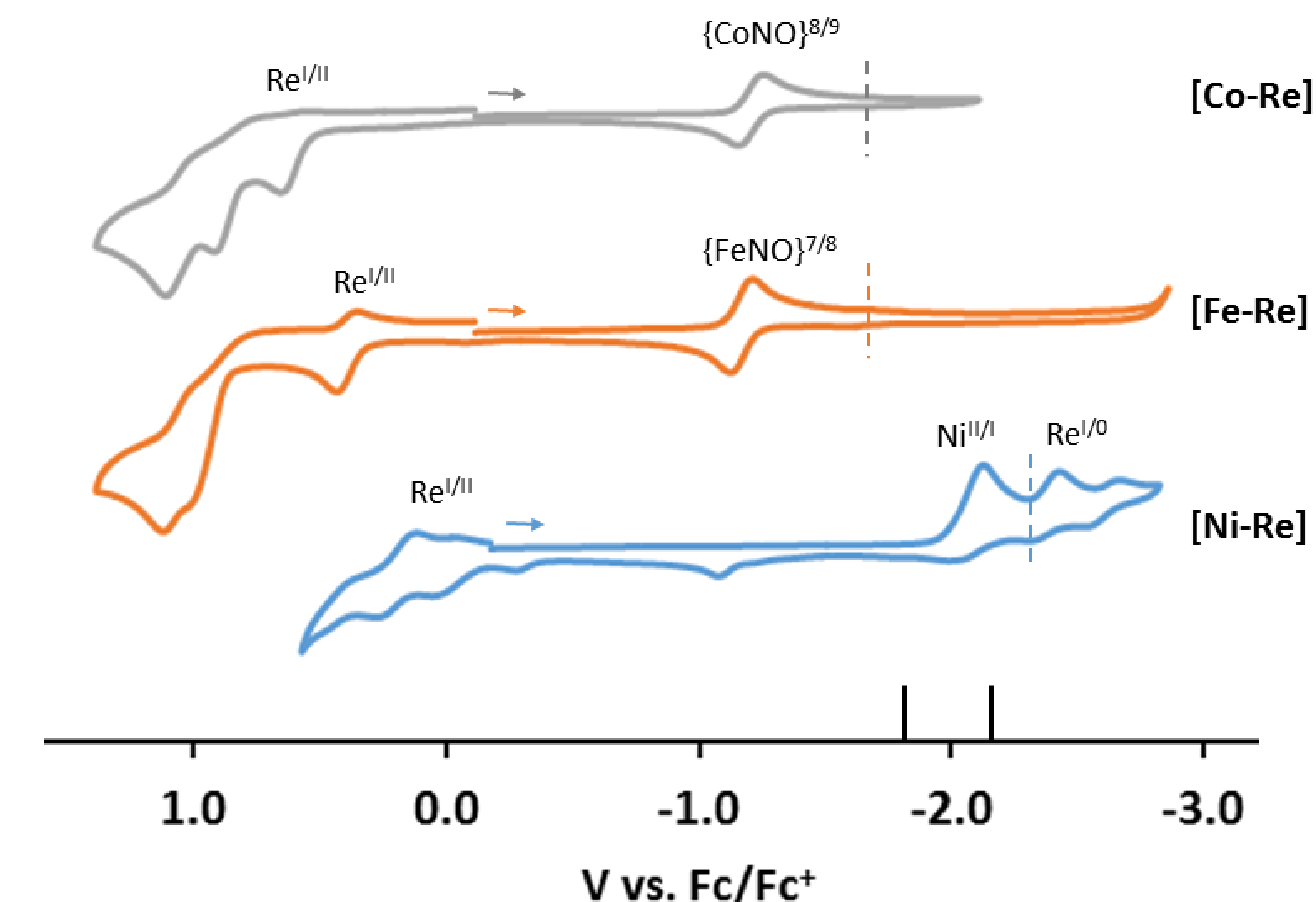


Crystallographic Characterization

Butterfly-like structures result from the orientation of the lone pairs on the sulfur atoms in the $M(\mu-S_2)M'$ core. The $M'-C$ and $M'-X$ bond distances and the $M'-C-O$ angles are substantially the same as in the Re/Mn-bipyridine analogues.



Cyclic Voltammetry and DFT Assignment



Conclusions

- Heterobimetallic complexes featuring a MN_2S_2 unit bound to a second metal center has been expanded to contain manganese and rhenium, group VII metals.
- Electronic communication between metallodithiolate donors and transition metal Lewis acid receivers is evident, in this case, by EPR and electrochemistry.
- The MN_2S_2 metalloligand reduction may or may not induce the chloride loss from Re that permits addition of a second electron.
- Halide loss is shut down in the complexes with $M = Fe(NO)$ and $Co(NO)$ units and is evident in the electrochemical silence at $Re(I)$. Halide loss is allowed in the Ni containing complex which is evident by the $Re(I)$ based reduction. This species is expected to develop as a CO_2 reduction electrocatalyst.

References

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- Carter, E. A.; *J. Am. Chem. Soc.*, **2013**, *135*, 15823–15829.
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