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Complexes of MN_2S_2 ·Fe(η^5 -C₅R₅)(CO) as platform for exploring cooperative heterobimetallic effects in HER electrocatalysis†

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The control of aggregation at sulfur by metallodithiolates (MN₂S₂) has made them prime candidates as building blocks for the synthesis of biomimetics of various bimetallic enzyme active sites, with reactivity consequences implicating redox control by both metal centers. Recent studies of MN_2S_2 (M = Ni²⁺, $Fe(NO)^{2+}$ bound to $[(\eta^5-C_5H_5)Fe(CO)]^+$ as electrocatalysts for proton reduction, the hydrogen evolution reaction, demonstrated reduction-induced hemi-lability of the bridging *cis*-dithiolates as a key step in the electrochemical proton reduction process (Ding, et al., J. Am. Chem. Soc., 2016, 138, 12920-12927). The MN_2S_2 ·Fe(η^5 -C₅R₅)(CO) platform offers numerous possibilities for tuning the electronic character of the $M(\mu-S_2)$ Fe core. As well as modifying M within the metallodithiolate ligand, replacing H by CH₃ at the η^{5} -C₅R₅ moiety increases the electron density at the Fe center, which might facilitate the reductive Fe-S bond cleavage. Although release of a free thiolate in these hemi-labile ligands creates a needed internal pendant base, this benefit might be countered by the increase in over-potential for addition of the first electron. Herein we report the preparation and characterization of four bimetallic aggregates with the $(\eta^5-C_5R_5)Fe(CO)$ (R = H, CH₃; Fe' or Fe'', respectively) or the dicarbonyl $(\eta^5-C_5R_5)Fe(CO)_2$ scaffold (R = H, CH₃; Fe" or Fe^{*}", respectively) bound to redox active MN₂S₂ ligands (M = Ni²⁺, Co(NO)²⁺; N₂S₂ = bismercaptoethane diazacycloheptane) Co-Fe*', Ni-Fe*', Co-Fe' and Co-Fe*'' complexes. The bidentate complexes were found to be electrocatalysts for proton reduction, although at high over-potential, especially for the derivatives of the electron-rich (η^5 -C₅(CH₃)₅)Fe(CO)⁺. The turnover (TON) and turnover frequencies (TOF) were determined and found to be comparable to the previously reported $MN_2S_2 \cdot Fe(\eta^5 - C_5H_5)$ (CO)⁺ analogues.

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Introduction

Synthetic approaches to small molecule models of the active sites [FeFe]-, [NiFe]-hydrogenases¹ and Acetyl CoA synthase (ACS)^{2,3} and potential heterobimetallic catalysts have exploited the mono/bidentate binding possibilities of metallodithiolates, particularly MN₂S₂, in development of a number of structural and functional analogues.^{4–8} In particular, the π^* interaction resulting from filled Ni_d–S_p orbital contacts in square planar NiN₂S₂ or NiS'₂S₂ (S' = thioether) complexes, promote the nucleophilic reactivity of *cis*-dithiolate sulfurs including specific

metal aggregation via monodentate or bidentate binding.^{9,10} The ability of the N₂S₂ tetradentate ligand to securely bind a variety of metals, including the redox active {Fe(NO)}^{7/8} and ${\rm Co(NO)}^{8/9}$ units (Enemark Feltham notation¹¹), encourages explorations of redox cooperativity between MN₂S₂ donors and receivers. Various receiver units such as ${Fe(NO)_2}^{9/10}$, as well as Fe^{II} or Ru^{II} bound to η^5 -C₅R₅ (where R = H, CH₃) or η^6 -arenes have been used in this rapidly growing area of bioinspired heterobimetallics.12-24 Especially notable are the NiN2S2 derivatives of $(\eta^6$ -arene)Ru^{II} or $[P(OR)_3]_3$ Fe^{II} from the Ogo group which demonstrated impressive heterolytic splitting of H₂ in aqueous or methanol media, generating a bridging hydride.^{25,26} Replacement of the neutral methyl-substituted arenes on such Ni-Ru/Fe complexes with anionic η^5 -C₅Me₅, Cp*, showed oxidative addition of O_2 , resulting in $\eta^2 - O_2^{2-}$ derivatives of Ru^{IV}/Fe^{IV} complexes that were isolated and characterized.14,19,27,28 Thus subtle modulations in the electronic features of the model complexes lead to unique organometallic chemistry that exploits a wide range of electrochemical potentials.



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Paper

Recent studies from our laboratory of MN_2S_2 (M = Ni²⁺, $[Fe(NO)]^{2+}$) bound to $[(\eta^5-C_5H_5)Fe'(CO)]^+$, demonstrated electrocatalytic HER (hydrogen evolution reactivity) in the presence of trifluoroacetic acid (TFA). A computation-based approach for assignment of the electrochemical events suggested that reduction-induced, iron–sulfur bond cleavage, *i.e.*, the hemilability of the N₂S₂ metalloligand,²⁹ should be a key step in the HER mechanism.³⁰ That is, in such complexes that do not have an open site on the metal envisioned as an electron/ proton landing site for conversion to a hydride, nor a pendant base for positioning a proton, the hemi-lability of a metallodithiolate may be invoked to provide both needed components for the heterolytic H⁻/H⁺ coupling to make dihydrogen, Fig. 1.



Fig. 1 Salient features in the computationally proposed mechanistic path for electrocatalytic H₂ production catalyzed by MN_2S_2 ·[Fe(η^5 -C₅H₅) (CO)]⁺ as catalyst.³⁰

The consequence of exchange of η^5 -C₅H₅ with the electron rich η^5 -C₅Me₅ unit, generating the $(\eta^5$ -C₅Me₅)Fe(CO)⁺ receiver group for the bidentate metallodithiolate ligand, might be anticipated as follows: expected for hemi-lability, the $M(\mu$ -SR)₂Fe' ring opening should be enhanced by the additional electron richness, thus more easily generating the open sites on sulfur and on Fe'. The proton affinity of the available thiolate sulfur could be enhanced, although likely not by much. Most debatable is the reduction potential of the Fe', which in the $(\eta^5$ -C₅Me₅) derivative is expected to be more negative and hence increase the overpotential for the overall reaction. However the enhanced proton affinity at the Fe', coupled with the proximal thiolate S-H orientation that yields the optimal H⁺/H⁻ coupling distance might compensate for the overpotential. These are questions to be addressed, beginning with the synthesis of complexes with MN₂S₂ metallodithiolate ligands bound to $[(\eta^5-C_5R_5)Fe(CO)]^+$ (R = H, CH₃; Cp and Cp*, respectively). Herein we report the synthesis and characterization of a set of such bimetallics, emphasizing their structural

and electronic properties for assessing features of significance to electrocatalysis of the hydrogen evolution reaction.

Results and discussion

Synthesis

Similar to published reports,^{8,14,17,18,23,30} the preparation of heterobimetallic complexes, $[MN_2S_2 \cdot FeCp(CO)]^+ [BF_4]^-$ and $[MN_2S_2 \cdot FeCp^*(CO)]^+ [PF_6]^-$, (M = Ni, [Co(NO)]) is readily accomplished by thermal and photochemical displacement of CO as shown in Scheme 1. The receiver units for the bidentate products, FeCp(CO) and FeCp*(CO), are hereafter abbreviated as Fe' and Fe*', respectively; while the monodentate products, $FeCp(CO)_2$ and $FeCp^*(CO)_2$ are abbreviated as Fe'' and $Fe^{*''}$, respectively. Overall, the room temperature reaction of [CpFe $(CO)_2(Solv)$]⁺[BF₄]⁻ or $[Cp*Fe(CO)_3]^+[PF_6]^-$ with MN_2S_2 in CH_2Cl_2 forms the monodentate complexes, $[\kappa^1-MN_2S_2\cdot FeCp]$ $(CO)_2$ ⁺[BF₄]⁻ (Co-Fe'') and $[\kappa^1-MN_2S_2\cdot FeCp^*(CO)_2]^+[PF_6]^-$ (Ni-Fe*" and Co-Fe*"). Although Co-Fe" can be synthesized and isolated as a pure purple solid, the Ni-Fe*" and Co-Fe*" are present as a mixture with the starting material. Positive-ion ESI mass spectrum of Ni-Fe*" and Co-Fe*" displayed prominent signals at the molecular ion masses, m/z 523.05 and m/z554.05, respectively, with characteristic isotopic distribution patterns which closely matched the calculated bundle, Fig. S25 and S26.†

Photolysis of the monodentate (**M-Fe**" or **M-Fe***") complexes resulted in loss of one CO to form air-stable, bidentate complexes, **Co-Fe**' as the BF₄⁻ salt, and **Ni-Fe***'and **Co-Fe***' as PF₆⁻ salts. Additional photolysis of the bidentate complexes led to



Scheme 1 Synthesis of Co-Fe' and Co-Fe' as BF_4^- salts and Co-Fe*' and Ni-Fe*' as PF_6^- salts. The IR frequencies of the complexes in CH_2Cl_2 are shown in the table.

decomposition. The $\nu(CO)$ stretching frequency is an important reporter unit for the electron density at the Fe' or Fe*' centers in accordance with the conventional σ-donor/π-backbonding arguments. Due to the greater electron donor ability of the η^5 -C₅Me₅, the ν (CO) stretching frequency of Ni-Fe^{*'} and Co-Fe*', (1905 and 1907 cm⁻¹ respectively), showed a bathochromic shift of ca. 25 cm⁻¹ compared to the $[\text{NiN}_2\text{S}_2\cdot\text{FeCp(CO)}]^+[\text{BF}_4]^-$ and Co-Fe' congeners.³⁰ The effect on the $\nu(NO)$ stretching frequency was less prominent with an overall lowering of $\nu(NO)$ by 3 cm⁻¹ for Co-Fe^{*/}. Slightly lower ν (CO) stretching frequencies of Ni-Fe*', compared to Co-Fe*', has precedence from previous studies with $(\eta^5-C_5H_5)Fe(CO)$ or W(CO)₄ reporter units, showcasing the higher electron donor ability of NiN2S2 over (NO)CoN2S2 metalloligands.30,31 The monodentate complex, Co-Fe", showed two ν (CO) stretching frequencies at 2045 and 2002 cm⁻¹ and a ν (NO) at 1630 cm⁻¹. All the newly synthesized complexes are diamagnetic and were characterized by ¹H and ¹³C NMR spectroscopies, Fig. S28-S35.†

X-ray diffraction analysis

X-ray quality crystals were obtained by layering a concentrated solution of the complexes in CH_2Cl_2 with hexanes at -28 °C. While the monodentate **Co-Fe**" was obtained as dark needles, the **Co-Fe**' and **Co-Fe***' presented as dark violet blocks, and the **Ni-Fe***' complex crystallized as brown blocks. The molecular structures of the complexes **Co-Fe**", **Co-Fe**', **Ni-Fe***' and **Co-Fe***' are shown in Fig. 2 as ball and stick renditions and selected metric parameters are tabulated in Table 1. Full structural reports are deposited in the Cambridge Crystallographic Data Centre. The structures feature typical piano-stool coordination geometries about the iron in FeCp(CO)⁺ and FeCp*(CO)⁺ units. In **Co-Fe**', **Ni-Fe***' and **Co-Fe***' the convergent lone pairs on the bridging thiolates enforce bidentate binding at the iron (**Fe**' or **Fe**") center leading to a butterfly-like [M(μ -SR)₂Fe] core, con-



Fig. 2 Molecular structures of Co-Fe", Co-Fe', Co-Fe* and Ni-Fe*'. The BF_4^- counter anions of Co-Fe" and Co-Fe' and the PF_6^- counter anions of Co-Fe* and Ni-Fe*' are omitted for clarity.

Table 1 Selected metric parameters of Co-Fe", Co-Fe', Co-Fe*' and Ni-Fe*'

Co-Fe"	Co-Fe'	Co-Fe*'	Ni-Fe*'
3.913 (1)	3.153 (1)	3.136 (2)	3.005 (1)
$4.559(2)^{a}$	3.386 (4)	3.370 (4)	3.096 (5)
3.321 (1)	2.994 (2)	2.977 (1)	2.954 (2)
2.545 (3)	2.598 (5)	2.585(4)	2.571 (9)
124.7 (9)	131.4 (4)	126.6 (3)	_ ``
_ ()	81.9 (2)	80.8 (3)	79.6 (6)
95.9 (3)	85.8 (5)	85.2 (4)	87.1 (7)
80.4 (9)	81.7 (1)	81.7 (1)	83.7 (3)
$118.3(3)^{c}$	126.2	121.9	121.5
0.361	0.432	0.429	0.205
	$\begin{array}{c} \textbf{Co-Fe''} \\ \hline 3.913 (1) \\ 4.559 (2)^a \\ 3.321 (1) \\ 2.545 (3) \\ 124.7 (9) \\ - \\ 95.9 (3) \\ 80.4 (9) \\ 118.3 (3)^c \\ 0.361 \end{array}$	$\begin{array}{c cccc} \textbf{Co-Fe'} & \textbf{Co-Fe'} \\ \hline 3.913 (1) & 3.153 (1) \\ 4.559 (2)^a & 3.386 (4) \\ 3.321 (1) & 2.994 (2) \\ 2.545 (3) & 2.598 (5) \\ 124.7 (9) & 131.4 (4) \\ & 81.9 (2) \\ 95.9 (3) & 85.8 (5) \\ 80.4 (9) & 81.7 (1) \\ 118.3 (3)^c & 126.2 \\ 0.361 & 0.432 \\ \end{array}$	$\begin{array}{c cccc} \textbf{Co-Fe'} & \textbf{Co-Fe'} & \textbf{Co-Fe^{\star\prime}} \\ \hline 3.913 (1) & 3.153 (1) & 3.136 (2) \\ 4.559 (2)^a & 3.386 (4) & 3.370 (4) \\ 3.321 (1) & 2.994 (2) & 2.977 (1) \\ 2.545 (3) & 2.598 (5) & 2.585 (4) \\ 124.7 (9) & 131.4 (4) & 126.6 (3) \\ - & 81.9 (2) & 80.8 (3) \\ 95.9 (3) & 85.8 (5) & 85.2 (4) \\ 80.4 (9) & 81.7 (1) & 81.7 (1) \\ 118.3 (3)^c & 126.2 & 121.9 \\ 0.361 & 0.432 & 0.429 \\ \hline \end{array}$

^{*a*} Average value. ^{*b*} The angle between N_2S_2 and S_2Fe' best planes. ^{*c*} The \angle Co–S–Fe is given in lieu of the hinge angle. ^{*d*} Displacement of M from N_2S_2 best plane.

straining the \angle S–M–S by *ca*. 7–9° compared to the free metallodithiolate ligands.¹⁰ The hinge angle (the intersection of the N_2S_2 best plane with the S_2Fe' or $S_2Fe^{*'}$ best plane) is *ca.* 126° for Co-Fe' which constricts by ca. 4° in Ni-Fe*' and Co-Fe*'. This might be related to the added electron density and steric encumbrance in the Ni-Fe^{*'} and Co-Fe^{*'} due to the $(\eta^5$ -C₅Me₅) compared to the $(\eta^5-C_5H_5)$. The Co-Fe' and Co-Fe*' derivatives find the NO positioned transoid to the CO on the FeCp and FeCp* units. Furthermore, in the bidentate complexes, Co-Fe' and Co-Fe*', the NO is on the side of the N₂S₂ ligand that has the 3-carbon chain between the two N atoms, whereas in the monodentate complex, Co-Fe", the NO resides on the side of the 2-carbon chain. In all three bidentate complexes, the N to S linkers are eclipsed and the bridging dithiolate hinge positions the downward oriented methylene groups, α to S, so as to cradle the Fe–CO moiety, resulting in C_{CO} to $H_{\alpha-CH_2}$ distances of ca. 2.7-2.8 Å. Space-filling models highlight the close encounter of the hydrocarbon linkers on the CO, Fig. 3, and the minimal space taken up by the folded structure. Nevertheless, the M…Fe' and M…Fe*' distances of 3.0–3.2 Å in our complexes are too long to implicate a bonding interaction. The report of Kure, Tanase, et al., of analogous MP₂S₂·M'Cp* structures (M = Ni^{II}, Pd^{II}, Pt^{II}; M' = Rh^{III}, Ir^{III}) that find a μ -H between M and M' describe this pocket as a nest, and the bridging hydride as a "nesting" hydride.²⁴

The bridging thiolate (μ -SR) of the monodentate complex, uses one of its divergent lone pairs to bind FeCp(CO)₂⁺, allowing the latter to be oriented away from the free thiolate. The \angle Co–S–Fe' opens up by *ca*. 30° compared to the bidentate complexes. A similar phenomenon was observed for $[\kappa^1$ -NiN₂S₂·FeCp(CO)₂]⁺[BF₄]⁻³⁰

Electrochemistry

Cyclic voltammetry

Cyclic voltammograms (CV) of **Co-Fe**' as BF_4^- salt and **Co-Fe***' and **Ni-Fe***' as PF_6^- salts were recorded at room temperature under argon in CH_3CN solutions containing 0.1 M [^tBu₄N][PF₆]



Fig. 3 Space filling models of, **Co-Fe**^{*} and **Co-Fe**['] shown in two orientations; (B) is rotated by 90° from (A).

as supporting electrolyte using a glassy carbon working electrode. The scans at 200 mV s⁻¹ are shown in Fig. 4 with assignments listed therein. Scan rate overlays to determine reversibility or quasi-reversibility are given in Fig. S15–S19.†



Fig. 4 Cyclic voltammograms of Co-Fe', Co-Fe*' and Ni-Fe*' as 2 mM CH_3CN solutions containing 0.1 M [$^{t}Bu_4N$][PF₆].

The complexes in general showed two distinct redox events. The quasi-reversible event at slightly positive potential was assigned to the $Fe'^{II/III}$ or $Fe^{*II/III}$ redox couple, and the one at negative potential was assigned to the $M^{II/I}N_2S_2$ reduction. The oxidation event at 0.32 V assigned to the Fe'^{II/III} couple for the Co-Fe' complex showed a positive shift of ca. 200 mV with respect to the Fe^{*/II/III} couple of **Co-Fe***' implying a greater ease of oxidation at the Fe center electron-enriched by the η^5 -C₅Me₅ unit. Consistently, the $\{Co(NO)\}^{8/9}$ reduction event of **Co-Fe**^{*} at -1.19 V differs by 70 mV as compared to the Co-Fe' indicating the greater stabilization of the oxidized $\{Co(NO)\}^8$ state in the **Co-Fe**^{*'} complex. The Fe^{*'II/III} couple of the **Ni-Fe**^{*'} complex showed a quasi-reversible oxidation event at 0.07 V, which is ca. 220 mV less positive than the Fe'^{II/III} couple of the $[NiN_2S_2 \cdot FeCp(CO)]^+ [BF_4]^-$ complex, for similar reasons.³⁰ Likewise a negative shift of the Ni^{II/I} couple by 280 mV was observed for the Ni-Fe*' complex relative to the [NiN2S2·FeCp (CO)]⁺[BF₄]⁻ complex.³⁰ All complexes showed an irreversible oxidation event at greater than 1.00 V, possibly due to dithiolate-based oxidation. Overall, the effect of greater electron donor ability of η^5 -C₅Me₅ over the η^5 -C₅H₅ unit was manifested in a more energetically demanding reduction couple and, consistently, more facile oxidation events.

Electrocatalysis

Electrochemical studies of **Co-Fe'**, **Co-Fe*'** and **Ni-Fe*'** were carried out in the presence of trifluoroacetic acid (TFA) and are shown in Fig. 5. The increase in the cathodic current that was observed at the $\{Co(NO)\}^{8/9}$ reduction event for **Co-Fe*'** (-1.19 V) and **Co-Fe'** (-1.12 V), was saturated after addition of 8 equivalents of TFA. An additional event at -1.75 V appeared for the **Co-Fe*'** on addition of first equivalent of acid and further acid additions showed a steady increase in this current response. A new major current event appeared at -1.56 V, for complex **Co-Fe'**, with TFA > 6 equivalents. A similar pre-peak phenomenon was observed for $[(NO)FeN_2S_2 \cdot FeCp(CO)]^+[BF_4]^-$ complex at -1.66 V.³⁰ Similarly, addition of TFA to the **Ni-Fe*'** complex showed the formation of a pre-peak at -1.74 V that increased in current intensity along with the major Ni^{II/I} reduction event at -1.91 V.

The attribution of the reduction-induced cathodic current enhancement upon addition of TFA to electrocatalytic H₂ production was verified by gas chromatography and quantified by an average of two consistent bulk electrolysis experiments. A constant potential at -1.80 V (dotted line in Fig. 5D), for 30 min, was applied in a CH₃CN solution containing 2 mM of catalyst and 50 equivalents of TFA. Since the background H₂ evolved from TFA itself at this potential overlaps the response from the electrocatalyst, the former was subtracted to obtain corrected values of the catalytic response, Fig. S1.† The turnover numbers (TON) for Ni-Fe*', Co-Fe*' and Co-Fe' were found to be 0.32 ± 0.05 , 0.15 ± 0.01 and 0.35 ± 0.05 , respectively, with Faradaic efficiencies of $88 \pm 4\%$, $99 \pm 0.2\%$ and $92 \pm 1\%$, respectively, for H₂ production. Following the approach of Wiese³² and Helm and Appel,³³ turnover frequencies (TOF), derived from the cyclic voltammetry studies, were determined



Fig. 5 Cyclic voltammograms of (A) Co-Fe', (B) Co-Fe' and (C) Ni-Fe*' as 2 mM CH₃CN solutions containing 0.1 M [^tBu₄N][PF₆] as supporting electrolyte with added equivalents of TFA. (D) Overlay of catalytic current responses of Co-Fe', Co-Fe*' and Ni-Fe*' in presence of 50 equivalents of TFA and 50 equivalents of TFA in absence of catalyst. The dotted line indicates the constant potential applied for bulk electrolysis, –1.80 V.

to be 32 s⁻¹, 65 s⁻¹, 79 s⁻¹ for Ni-Fe*', Co-Fe*' and Co-Fe', respectively. The high overpotentials for Ni-Fe*' and Co-Fe*' complexes, 1.31 V and 1.27 V, respectively, are consistent with the electron rich η^5 -C₅Me₅ unit present in these complexes while the moderately lower overpotential for Co-Fe', 1.06 V, with the η^5 -C₅H₅ unit, is comparable to those reported for the $[(NO)FeN_2S_2 \cdot FeCp(CO)]^+ [BF_4]^-$ and $[NiN_2S_2 \cdot FeCp(CO)]^+ [BF_4]^$ complexes.³⁰ Table 2 shows a comparative listing of overpotential, turnover number (TON) and turnover frequency (TOF) of the different complexes used in this study. The data obtained for calculating such values are given in Tables S1-S7.† The complexes, $[(NO)FeN_2S_2 \cdot FeCp(CO)]^+[BF_4]^-$ and $[NiN_2S_2 \cdot FeCp(CO)]^+[BF_4]^-$ (CO)]⁺[BF₄]⁻, showed H/D kinetic isotope effects on TOF and the $(k_{\rm H}/k_{\rm D})$ were determined to be *ca*. 1.5.³⁰ The consistency in the TOF values for M-Fe*' and M-Fe' complexes leads to the overall assumption that the reaction path for the catalytic process is similar and involves a metal-hydride species as an intermediate in the catalytic cycle.

Table 2Overpotential, turnover number (TON) and turnover frequency(TOF) of Ni-Fe*', Co-Fe*', Ni-Fe', ³⁰ Fe-Fe'³⁰ and Co-Fe'

	Overpotential (V)	Turnover number (TON)	Turnover freq. (TOF) (s ⁻¹)
Ni-Fe*'	1.31	0.32 ± 0.05	32
Co-Fe*'	1.27	0.15 ± 0.01	65
Ni-Fe' ³⁰	0.94	0.26 ± 0.01	52
Fe-Fe' ³⁰	0.94	0.33 ± 0.02	69
Co-Fe'	1.06	0.35 ± 0.05	79

Conclusions

In summary, the proficiencies of three $MN_2S_2 \cdot Fe(\eta^5 - C_5R_5)(CO)^+$ complexes $(R = H \text{ or } CH_3)$ for catalysis of the HER were determined by standard electrochemical analyses and structure/ function comparisons are made. The Co-Fe' complex relates to **M-Fe'** complexes, $M = Ni^{2+}$ and $[Fe(NO)]^{2+}$ reported earlier.³⁰ Its properties are by and large precise analogues of the Fe(NO) derivative, Fe-Fe', and can be used as a reference to connect the two studies.³⁰ The CO and NO ligands that report via vibrational spectroscopy on electronic results from aggregating the individual components of the bimetallics are entirely consistent with the shifts in redox potentials of the Fe' and Fe*' units and the metallodithiolate ligands. The overall conclusion must be that the Cp* enriches the electron density mainly at the Fe center, and has an effect, however less prominent, at the metallodithiolate ligand. At this point, we have not attempted an extensive computational study of the mechanism as was done for the prior study.³⁰ We assume that the reaction path is similar (or identical) and the energy requirement for the ring opening process that creates the needed Lewis pair for $H^+ \cdots H^-$ coupling is a dominant factor for determining overpotential but has less significance for other electrochemical features such as turnover number and turnover frequency. Our working hypothesis continues to focus on the bimetallic mechanism, assuming that the bimetallic remains intact via a single thiolate bridge. Clearly it would be reassuring to obtain experimental evidence for the presumed iron-hydride/protonated thiolate sulfur intermediate.³⁰ At this point we still

search for these illusive species, and other mechanistic possibilities cannot be ruled out. Concomitant with the more negative reduction event is a more accessible, reversible oxidation event. Hence the catalytic propensities of these Cp* complexes might be more advantageously applied to oxidation catalysis.^{19,27}

Experimental section

Methods and materials

The MBraun Manual Solvent Purification System with Alcoa F200 activated alumina desiccant was used to purify acetonitrile (CH₃CN), benzene, dichloromethane (CH₂Cl₂), hexane and diethylether. Reactions were carried out using standard Schlenk conditions under N₂ atmosphere. All reagents were used as received from standard vendors unless otherwise stated. Published procedures were followed to synthesize the known complexes (NO)Co(bme-dach) (bme-dach = *N*,*N*-bis (2-mercaptoethyl)-1,5-diazacycloheptane),³⁴ Ni(bme-dach),³⁵ (η^5 -C₅H₅)Fe(CO)₂I,³⁶ and [(η^5 -C₅Me₅)Fe(CO)₃][PF₆].³⁷ HPLCgrade acetonitrile, [*n*-Bu₄N][PF₆], and AgBF₄ were reagent grade and purchased from Sigma-Aldrich.

Physical measurements

The Bruker Tensor 37 Fourier transform IR (FTIR) spectrometer was used to record solution infrared spectra, using CaF_2 cell with 0.2 mm path length. The laboratory for Biological Mass Spectrometry at Texas A&M University performed and provided all mass spectrometry (ESI-MS). The Atlantic Microlab Inc., located in Norcross, Ga, performed all elemental analyses. ¹H NMR and ¹³C NMR spectra were recorded on the Inova 500 MHz superconducting NMR instrument.

X-ray diffraction analyses

The crystal structures of Co-Fe", Co-Fe' were measured at low temperatures (150 and 110 K, respectively) by BRUKER APEX 2 X-ray (three-circle) diffractometer with Mo sealed X-ray tube ($K_{\alpha} = 0.70173$ Å). The single crystals of **Co-Fe**^{*} and **Ni-Fe**^{*} were measured using BRUKER Quest X-ray (fixed-Chi geometry) diffractometer with Mo-Iµs X-ray tube ($K_{\alpha} = 0.71073$ Å) and BRUKER Venture X-ray (kappa geometry) diffractometer with Cu-Iµs X-ray tube (K_{α} = 1.5418 Å), respectively, at 100 K. The structures were refined by weighted least squares refinement on F^2 . At idealized positions, hydrogen atoms were placed and fixed isotropic displacement parameters were used to refine them. For all non-hydrogen atoms, anisotropic displacement parameters were employed. The following programs were used: data collection, APEX3;³⁸ data reduction, SAINT;³⁹ absorption correction, SADABS;40 cell refinement and structure solutions, SHELXS/XT;⁴⁰ The final data presentation and structure plots were generated in Olex2.41 Crystallographic data for the complexes Co-Fe", Co-Fe', Co-Fe*' and Ni-Fe*' are deposited in the Cambridge Crystallographic Data Centre; their numbers are: CCDC 1521064 (Co-Fe"), 1521078 (Co-Fe'), 1521063 (Co-Fe*') and 1521062 (Ni-Fe*'). For convenience pertinent crystal data

and structure refinement parameters are summarized in Tables S8-S11.[†]

Electrochemistry

A three-electrode cell was use to record Cyclic voltammograms (CVs) on the CHI600E electrochemical analyzer (HCH instruments, Inc.). The counter electrode was a platinum wire, the reference electrode was a CH₃CN solution of Ag/AgNO₃ in a Vycor-tipped glass tube, and the working electrode was a 0.071 cm² glassy carbon dish electrode. Diamond paste (3 μ m) was used to polish the glassy carbon working electrode as needed throughout the CV experiment. A blanket of Ar was kept over the solution during the experiments following an Ar purge for 5 min. All solutions were in CH₃CN and the measurements were done at room temperature using 0.1 M [*n*-Bu₄N][PF₆] as the electrolyte and 2.0 mM in analyte. All potentials were shown relative to the Fc/Fc⁺ couple at 0.00 V.

A custom made three-necked truncated conical shaped flask with an outlet port/gas inlet was the apparatus used for bulk electrolysis experiments. A Ni-Cr-coiled wire counter electrode, a Ag/AgNO₃ reference electrode, and a 3 mm glassy carbon working electrode were placed in the necks of the cell. The Ni-Cr-coiled wire placed in a glass tube with a medium glass frit served as the counter electrode. A glass tube containing a Ag wire immersed in a 1 mM solutions of AgNO₃ in MeCN separated from the main solution by a Vycor frit was the make-up of the reference electrode. To the electrochemical cell 10 mL of 0.1 M [n-Bu₄N][PF₆] in CH₃CN was added and then purged with Ar to deplete O_2 . To the cell 2×10^{-5} mol of the appropriate catalyst and 50 equivalents of trifluoroacetic acid were added. To ensure that the experiment was under catalytic conditions, a cyclic voltammogram was recorded. After 30 minutes of bulk electrolysis performed at -1.80 V vs. Fc/Fc⁺, 1 mL of methane was added as the internal standard. Detection of H₂ gas using GC is discussed in the ESI.[†]

Synthesis

 $[(\eta^5-C_5H_5)Fe(CO)_2(bme-dach)Co(NO)][BF_4]$, Co-Fe". A solution of CpFe(CO)_2I (256 mg, 1.00 mmol) and AgBF₄ (195 mg 1.00 mmol) in CH₂Cl₂ (20 mL) was stirred for 30 min in the dark at room temperature and then filtered through celite. The filtrate was added to a solution of (NO)Co(bme-dach) (307 mg, 1.00 mmol) in CH₂Cl₂ (20 mL) and stirred in the dark for 3 h. The resulting solution was then redissolved in CH₂Cl₂ after it was dried under vacuum and washed with 20 mL (×3) diethyl ether. The solution was filtered through celite to filter any unreacted starting material and X-ray quality crystals for complex Co-Fe" were obtained by layering a CH₂Cl₂ solution of the product with hexanes. IR (CH₂Cl₂, cm⁻¹): ν (CO) 2045, 2001; ν (NO) 1632; ESI-MS⁺: m/z 483.95 (Calc. for [M]⁺, 483.96).

 $[(\eta^5-C_5H_5)Fe(CO)(bme-dach)Co(NO)][BF_4]$, Co-Fe'. A solution of CpFe(CO)₂I (256 mg, 1.00 mmol) and AgBF₄ (195 mg 1.00 mmol) in CH₂Cl₂ (20 mL) was stirred for 30 min in the dark at room temperature and then filtered through celite. The filtrate was added to a solution of (NO)Co(bme-dach) (307 mg, 1.00 mmol) in CH₂Cl₂ (20 mL) and the solution was stirred under UV lamp irradiation. IR spectrum was used to monitor the reaction. Upon completion of the reaction, the product was purified through a silica column with CH₂Cl₂/CH₃OH (20:1, v/v) as the eluent. X-ray quality crystals for complex **Co-Fe'** were also obtained by layering a CH₂Cl₂ solution of the product with hexanes. IR (CH₂Cl₂, cm⁻¹): ν (CO) 1934; ν (NO) 1650; ESI-MS⁺: *m*/z 455.99 (Calc. for [M]⁺, 455.99). Elem. Anal. Calc'd (found) for C₁₅H₂₃BCoFeF₄N₃O₂S₂ (MW = 543 g mol⁻¹): C, 33.17 (33.25); H, 4.27 (4.29); N, 7.74 (7.65).

 $[(\eta^5-C_5Me_5)Fe(CO)(bme-dach)Co(NO)][PF_6], Co-Fe*'. A solution of (NO)Co(bme-dach) (307 mg, 1.00 mmol) and [Fe(Cp*) (CO)_3]PF_6 (419 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) were stirred under UV lamp irradiation. The dark purple reaction mixture was monitored by IR spectroscopy. Once the reaction was completed, the dark purple product was purified by passing through a silica gel column with CH_2Cl_2/CH_3OH (10:1, v/v) as the eluent. X-ray quality crystals for complex Co-Fe*' were obtained by layering a CH_2Cl_2 solution of the product with hexanes. IR (CH_2Cl_2, cm⁻¹): <math>\nu$ (CO) 1907; ν (NO) 1647; ESI-MS⁺: m/z 526.13 (Calc. for [M]⁺, 526.07). Anal. Calc'd (found) for C₂₀H₃₃CoF₆FeN₃O₂PS₂ (MW = 671 g mol⁻¹): C, 35.78 (36.31); H, 4.95 (5.16); N, 6.26 (5.83).

[(η^5 -C₅Me₅)Fe(CO)(bme-dach)Ni][PF₆], Ni-Fe^{*/}. In a similar manner to that of complex Co-Fe^{*/}, complex Ni-Fe^{*/} was prepared by using Ni(bme-dach) (276 mg, 1.00 mmol) and [Fe(Cp^{*})(CO)₃]PF₆ (419 mg, 1.00 mmol) in CH₂Cl₂ (25 mL) which was stirred under UV lamp irradiation. The tan reaction mixture was monitored by changes in the IR spectrum and X-ray quality crystals were obtained by layering a CH₂Cl₂ solution of the product with hexanes. IR (CH₂Cl₂, cm⁻¹): ν (CO) 1905; ESI-MS⁺: *m*/*z* 495.06 (Calc. for [M]⁺, 495.07). Anal. Calc'd (found) for C₂₀H₃₃F₆FeN₂NiOPS₂ (MW = 640 g mol⁻¹): C, 37.47 (36.99); H, 5.19 (5.38); N, 4.37 (4.31).

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