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Synthesis, kinetic studies, and atom transfer reactivity of [2Fe–2E] model compounds†

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The synthesis of [2Fe–2E] (E = S and Se) complexes supported by an *N*-alkyl, *N'*-aryl-β-diketiminato ligand is described. The [2Fe–2S] model compound has an unusually long Fe...Fe distance, but the equivalent distance in the [2Fe–2Se] compound is comparable to those reported in the literature. These model compounds display varying electron transfer capabilities, which were elucidated through electronic spectroscopy and electrochemical analysis. Kinetic data and activation parameters suggest the formation mechanism of the [2Fe–2S] compound. Additionally, to probe the possible sulfur-transfer mechanism of [2Fe–2S] clusters, atom transfer reactivity was pursued.

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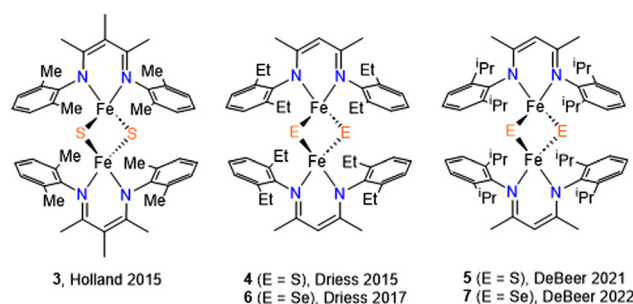
Introduction

Iron-sulfur clusters ([*m*Fe–*n*S], where *m* and *n* = 2–4) form redox active, multiple-metal cofactors in the active sites of many enzymes. These clusters are often viewed as special inorganic cofactors and elicit a variety of biological functions, including electron transfer, sensing, and regulation.^{1–4} A majority of the functions of such clusters stem from their redox reactivity. The electronic structure of iron-sulfur clusters has been widely studied and it was found that the oxidation state of iron centers commonly ranges from +2 to +3,^{1,5} which contrasts with the higher oxidation states found in heme systems. A common structural feature of these clusters is that each iron center is coordinated by four donor atoms (N-donor or S-donor) in a tetrahedral environment.¹

Although many functions of iron-sulfur clusters are considered well-understood, there are two newly emerging interests in this area: (1) the exploration of new biological functions of iron-sulfur clusters, and (2) understanding the electronic origins of the chemistry of iron-sulfur *versus* iron-selenium clusters and how these may influence or determine enzyme function and mechanism. For example, the sulfur-atom transfer involving an iron-sulfur cluster in the last step of the biotin biosynthetic pathway has long been debated.^{6–11} In addition, several studies have shown that sulfur atoms can be substituted by selenium in iron-sulfur clusters while retaining structural integrity.^{12–14} Studying iron-selenium clusters or

related model compounds could yield valuable information as to why S has been universally selected to function in these clusters over Se at the active sites of enzymes.^{15,16}

Researchers have extensively explored structure-function relationships of naturally occurring iron-sulfur clusters. Synthetic model iron sulfur compounds can provide additional insight into the complexity of the natural systems. While continuous efforts have led to the successful synthesis of [3Fe–4S] and [4Fe–4S] model clusters,^{17,18} methods to make and study [2Fe–2E] (where E = S and Se) models are less developed.^{11–14} The production of synthetic [2Fe–2S/Se] clusters with supporting chalcogenide ligand and its effect on spectroscopy and reduction potentials of natural systems has been reported.⁹ Due to the coordination arrangement, some bidentate ligands have been successfully demonstrated to mimic the [2Fe–2S] active site of enzymes.^{19–24} More recently, bidentate β-diketiminates were used to synthesize [2Fe–2S] clusters owing to their high tunability as supporting ligands.^{25–27} [2Fe–2Se] model systems supported by the nitrogen donor ligands are however rather rare (Scheme 1).^{23,28,29}



Scheme 1 [2Fe–2S] and [2Fe–2Se] model compounds supported by β-diketiminato ligands.

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We recently reported an asymmetric *N*-alkyl,*N'*-aryl- β -diketiminate (**L1**) ligand and its low-valent iron complex³⁰ as a suitable candidate for preparing [2Fe–2E] model compounds. Herein we report the synthesis of [2Fe–2E] model compounds **1** and **2**, which were characterized by X-ray crystallography, ¹H-NMR spectroscopy, and electrochemical studies. In the context of the recent advances in [2Fe–2E] model compounds, our objective was to gain a deeper understanding of their formation from low-valent iron precursors and elemental sulfur. Thus, we conducted kinetic experiments to investigate the kinetic isotopic effect and activation parameters involved in the reaction of an Fe(I) complex with elemental sulfur, resulting in the formation of **1**. Moreover, in light of the unusually long Fe...Fe distance noted in **1**, further investigations were performed to explore the atom transfer reactions.

Experimental section

Materials and methods

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or in an M. Braun UNILab Pro glovebox. Glassware was dried at 150 °C overnight. Diethyl ether, *n*-pentane, tetrahydrofuran, and toluene were purified using a pure process technology solvent purification system. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. All reagents were purchased from commercial vendors and used as received. (L1)Fe(cod) (cod = 1,5-cyclooctadiene) was prepared according to a literature procedure.³⁰ ¹H NMR data were recorded on a Varian Inova 500 MHz spectrometer at 22 °C. Resonances in the ¹H NMR spectra are referenced to residual C₆D₅H at δ = 7.16 ppm. Solution magnetic susceptibilities were determined using the Evans method.³¹ UV-vis spectra were recorded on an Agilent Cary 8454 UV-vis spectrophotometer equipped with a Unisoku Scientific Instruments Cryostat USP-203B for various temperature experiments. An IR spectrum of **1** was recorded on a Jasco FT-IR spectrometer (model 4600) equipped with an ATR diamond probe head. Elemental analysis was conducted by Midwest Microlab, LLC (Indianapolis, IN).

Synthetic procedures

[(L1)Fe(μ -S)]₂ (**1**). To a stirred solution of S₈ (49 mg, 0.19 mmol) in toluene (5 mL) at ambient temperature under N₂ atmosphere was added a solution of LFe^I(cod) (100 mg, 0.19 mmol) in toluene (10 mL) for 24 h. The reaction mixture was filtered twice through Al₂O₃. Volatiles were removed under reduced pressure, and the residue was extracted with *n*-pentane and filtered through Celite. The filtrate was dried *in vacuo* to yield a dark purple solid (42 mg, 49%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in *n*-pentane at –20 °C. ¹H NMR (500 MHz, C₆D₆, δ): 8.57, 8.19, 7.65 (br), 7.29, 7.00, 3.79, 2.02, 1.60, 1.48, 1.41, 1.38, –4.55. UV-vis (toluene at 25 °C) λ_{max} (ϵ [mM^{–1} cm^{–1}]): 306 (21 080), 327 (sh) (19 800), 430 (5900), 448 (sh) (5400), 545

(6440). Anal. Calcd for C₅₀H₆₆Fe₂N₄S₂: C, 66.81; H, 7.40; N, 6.23. Found: C, 66.90; H, 7.24; N, 6.18.

Preparation of Se₈. Red Se₈ was prepared according to a literature procedure.³² To a stirred, heated solution of concentrated sulfuric acid (100 mL, 150 °C) was slowly added grey selenium (1.00 g, 1.27 mol). The reaction mixture was refluxed until it turned to dark green (*ca.* 12 h). Upon cooling, the reaction mixture was filtered and the filtrate was slowly added to ice (250 g). After the ice had completely melted, the red precipitate was collected through vacuum filtration and was washed using deionized water until the filtrate was neutral. Red Se₈ was then washed with ethanol and then with diethyl ether (950 mg, 95%).

Caution: When handling and heating concentrated H₂SO₄, it is imperative to exercise utmost caution given its strong corrosive properties and potential hazards.

[(L1)Fe(μ -Se)]₂ (**2**). To a stirred solution of Se₈ (119 mg, 0.19 mmol) in toluene (5 mL) at ambient temperature under N₂ atmosphere was added 100 mg (0.19 mmol) of LFe^I(cod) in toluene (15 mL). The resulting slurry was stirred for 48 h at ambient temperature. The reaction mixture was filtered twice through Al₂O₃. The filtrate was dried *in vacuo*, and the residue was extracted with *n*-pentane and filtered through Celite. Volatiles were removed under reduced pressure to afford a dark teal solid (57 mg, 60%). Crystals suitable for X-ray diffraction were grown from a concentrated *n*-pentane solution of the complex at –20 °C. ¹H NMR (500 MHz, C₆D₆, δ): 8.75, 8.36, 7.64 (br), 7.28, 6.98, 3.41, 2.28, 2.21, 1.72, 1.61, 1.46, 1.28, 1.16, –6.05. UV-vis (toluene at 25 °C) λ_{max} (ϵ [mM^{–1} cm^{–1}]): 319 (20 560), 434 (2880), 613 (3000). Anal. Calcd for C₅₀H₆₆Fe₂N₄Se₂: C, 60.13; H, 6.59; N, 5.72. Found: C, 60.31; H, 6.44; N, 5.83.

Electrochemistry

Cyclic voltammetry was conducted using a CH-Instruments electrochemical analyzer (model 620E), employing a 3 mm glassy carbon working electrode, a silver wire pseudo-reference electrode, and a platinum coiled wire counter electrode. All measurements were performed using THF solutions, containing 1 mM analyte and 0.1 M N(Bu)₄PF₆ as the supporting electrolyte. The potentials were referenced to a ferrocene/ferrocenium redox couple.

Crystallography

Data were collected using a Rigaku Rapid II curved image plate diffractometer with Cu-K α radiation (λ = 1.54178 Å). Single crystals were mounted on a Mitegen micromesh mount using a trace of Fomblin oil and cooled *in situ* to at 100 K. Data were processed using HKL3000 and the data were corrected for absorption and scaled using Scalepack.³³ The space groups were assigned using XPREP within the SHELXTL suite of programs,^{34,35} were solved by direct methods using ShelXS and refined by full matrix least squares against F^2 with all reflections using ShelXL2018 using the graphical interface ShelXle.³⁶ H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for alkene and

aromatic C–H, 1.00 and 0.98 Å for aliphatic C–H and CH₃, respectively. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C})$ with 1.5 for CH₃ and 1.2 for C–H groups respectively.

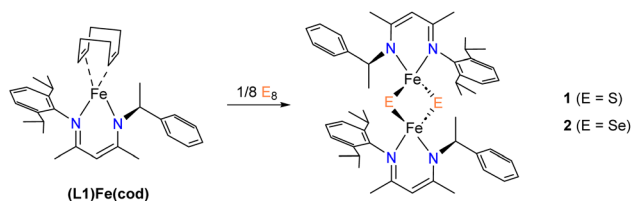
Kinetic measurements

Pseudo-first-order reaction conditions were employed for all kinetic studies, using 20-fold and greater excesses of ³²S₈ or ³⁴S₈. Reactions were monitored by UV-Vis spectroscopy. Due to the low solubility of S₈, low concentrations of (L1)Fe(cod) were used in kinetic experiments. Typically, 3 mL of a toluene solution containing the (L1)Fe(cod) complex (0.3 μmol) in a sealable cuvette under N₂ was placed in a temperature-controlled cryostat. Upon temperature equilibration, a toluene solution of ³²S₈ or ³⁴S₈ was added rapidly *via* syringe. Spectra were taken at 30 s to 45 min intervals. The reaction was followed by monitoring the increase in one of the ligand-to-metal charge transfer (LMCT) absorption bands used to indicate the formation of **1**. Nonlinear least-squares fitting of the absorbance at 545 nm using a first-order model yielded the pseudo-first-order rate constants, k_{obs} . The transition state parameters were determined over a temperature range of –40 to –70 °C and *via* an Eyring plot, which shows a linear relationship. S/Se atom transfer reactions were performed by mixing (L1)Fe(cod) complex (9.5 μmol) with an excess of S₈ or Se₈ and PPh₃ in C₆D₆ at 40 °C and monitored by ¹H NMR spectroscopy. The formation of S=PPh₃ and Se=PPh₃ were quantified with respect to hexamethylbenzene (internal standard). Each parameter reported represents the average value of duplicate or triplicate determinations.

Results and discussion

Syntheses

1 was synthesized by the reaction of S₈ with (L1)Fe(cod) at room temperature (Scheme 2). Immediately a color change of the solution from green to dark purple was observed. However, when treating Se₈ with (L1)Fe(cod) to yield **2**, the reaction occurred at a much slower rate with a gradual color change to teal over the course of several hours. Note that reactions run at lower temperature did not produce significantly improved yields. At room temperature, the ¹H NMR spectra of compounds **1** and **2** display characteristics of paramagnetism, manifesting as broadening and up-field shifted peaks (–4.5 and –6.0 ppm for **1** and **2**, respectively), despite most of the resonances lying within the diamagnetic region. The β-methyl



Scheme 2 Synthesis of **1** and **2**.

protons are responsible for the paramagnetic chemical shifts, which can also be observed in other [2Fe–2S] model compounds containing β-diketiminato ligands (–0.4 ppm for **3** and –8.1 ppm for **4**).^{26,27} The magnetic properties of synthetic [2Fe–2E] model compounds are primarily determined by strong antiferromagnetic coupling between the two high-spin $S = 5/2$ Fe³⁺ ions.^{19–21,23,24} The presence of an antiferromagnetic coupled dimer was evident by measuring the magnetic moment of **1** and **2** in C₆D₆ which were found to be by Evan's method 1.2 and 1.3 μ_B, respectively. The values agree with those of other reported [LFe(μ-E)]₂ complexes.

Crystal structures of **1** and **2**

Single crystals suitable for X-ray structure determination were obtained for complex **1** and **2**. The ORTEP diagrams of **1** and **2** are given in Fig. 1 and selected bond lengths and angles are summarized in Table 1 and Table S1.† The solid-state structures confirm complexes **1** and **2** as binuclear iron complexes, where each iron center is coordinated by two N atoms from a β-diketiminato ligands and two bridged S atoms (**1**) or Se atoms (**2**) (Fig. 1). The molecular geometry of the metal ion in **1** ($\tau_4 = 0.847$) and **2** ($\tau_4 = 0.932$) is best described as distorted tetrahedral. For **1**, the average Fe–N distances of 1.989(7) Å agrees with those of other β-diketiminato supported complexes of [2Fe–2S] clusters bearing high-spin Fe(III) centers.^{26,27} However, the average bond distances of Fe–S (2.377(3) Å) and inter-atomic distance of Fe...Fe (3.360(2) Å) are much longer than any of the reported values for other synthetic [2Fe–2S] model compounds. On the other hand, the average bond distance of Fe–Se (2.317(7) Å) and inter-atomic distance of Fe...Fe (2.750(3) Å) in **2** are only slightly longer than those in [(Pipiso)Fe(μ-Se)]₂ (Pipiso = [(DipN)₂C(cis-2,6-Me₂NC₅H₈)][–], (Dip = 2,6-C₆H₃iPr₂). Interestingly, the Fe...Fe distance in [(Pipiso)Fe(μ-E)]₂ (E = O, S, Se) reflects the size of bridging chalcogenide ligands, but the opposite trend was found for **1** and **2**.²³ Therefore, by comparing the crystal structures of **1** and **2** the unusual Fe...Fe distance found in **1** can be attributed to the steric effect of methyl groups pointing toward the aryl ring.

The Fe...Fe distance for most [2Fe–2S] model complexes are typically in a small range of 2.69–2.82 Å, which are smaller

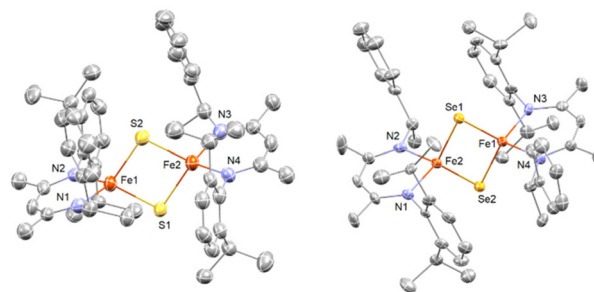


Fig. 1 X-ray crystal structures of **1** (left) and **2** (right). Thermal ellipsoids shown at 50% probability, hydrogen atoms and solvate molecules (toluene, pentane) omitted for clarity. Color key: orange = Fe, blue = N, gray = C, yellow = S, gold = Se.

Table 1 Selected averaged bond distances (Å) and angles (°) for **1–6**^a

	1 (E = S)	3 ²⁶	4 ²⁷	5 ²⁵	2 (E = Se)	6 ²⁹
Fe–N	1.989(7)	1.973(5)	2.004(1)	2.028(2)	1.983(5)	1.996(2)
Fe–E	2.377(3)	2.204(2)	2.194(1)	2.210(1)	2.317(1)	2.318(1)
∠N–Fe–N	94.6(3)	97.7(2)	93.23(6)	91.64(8)	96.1(3)	92.6(1)
∠E–Fe–E	90.07(9)	105.49(7)	104.72(2)	100.82(3)	107.23(8)	107.46(2)
∠Fe–E–Fe	89.83(9)	74.51(6)	75.28(2)	79.18(2)	72.77(7)	72.55(2)
Fe...Fe	3.360(2)	2.669(1)	2.679(1)	2.816(1)	2.750(3)	2.743(1)
N–Fe–Fe–N ^b	11.17	2.44	8.43	1.93	1.92	5.66
τ ₄	0.816	0.910	0.891	0.895	0.932	0.913

^a Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Fig. 1. ^b Torsion angle is defined by a dihedral angle between two N–Fe–N planes.

than protein [2Fe–2S] clusters.^{19–24,26,27,37,38} It is known that a short Fe...Fe distance is one of the contributions for strong antiferromagnetic coupling between two Fe(III) centers.³⁹ However, diamagnetism of complex **1** suggests antiferromagnetic coupling occurring in solution although the Fe...Fe distance is rather long in solid state. In comparison of [2Fe^{III}–2S] with the super-reduced cluster, [2Fe^{II}–2S], the difference of their Fe...Fe distances is <0.1 Å.^{21,24} Furthermore, long Fe...Fe distances (3.2 to 3.4 Å) are often observed in thiolate-bridged complexes [2Fe^{II}–2SR],^{40–42} which may imply that complex **1** is a [2Fe^{II}–2SH] cluster compound and the hydrogen atoms were not resolved by X-ray crystallography. However, this possibility can be ruled out since no characteristic S–H stretching vibrations were observed in **1**.

In addition, although some monosulfido-bridged Fe(II) complexes are diamagnetic,^{43,44} most [2Fe^{II}–2SR] complexes are paramagnetic with large magnetic moments.^{40–42} Hence, **1** is most likely a [2Fe^{III}–2S] model compounds with an unusual long Fe–Fe distance resulting from the steric repulsion between the two β-diketiminato ligands. The steric profiles were also suggested by the τ₄ values among all [2Fe–2S] model complexes supported by β-diketiminato ligands (Table 1). In addition, as the steric bulkiness increases, the torsion angle between the two chelated faces (N–Fe–N) increases (Table 1 and Fig. S1†).

Electrochemical and UV-vis studies of complex **3** and **4**

Cyclic voltammetry of complex **1** (Fig. 2) suggests there are two quasi-reversible events occurring, while there is only one quasi-reversible event observed for complex **2** (Fig. S2†). These events indicate the electron transfer is a diffusion controlled process which was confirmed by the linear relationship in the plot of peak current vs. square root of the scan rate (Fig. 2 inset). The first quasi-reversible event of **1** appears at –1.68 V and the second is at –2.13 V. However, the peak height of the first event is twice as large as the second event. This suggests the first event may involve two times the number of electrons with respect to the second event. To understand the number of electrons transferred based on the voltammograms, titration of complex **1** with a chemical reductant, bis-pentamethylcyclopentadienylcobalt(II) (CoCp*₂) was monitored using UV-vis spectroscopy. Since the second quasi-reversible event of **1** is

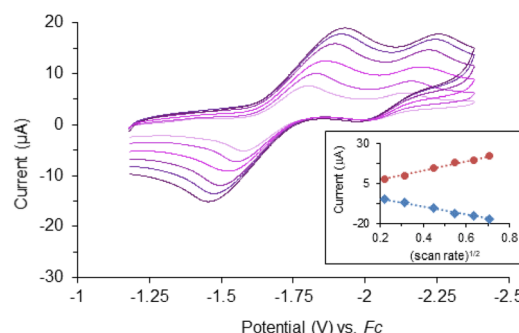


Fig. 2 Overlaid cyclic voltammograms of **1** (1 mM) in THF with 0.1 M N(Bu)₄PF₆. Scan rates = 50, 100, 200, 300, 400, 500 mV s^{–1} referenced to a ferrocene/ferrocenium redox couple (Fc). Inset: plot of cathodic peak current (●, R² = 0.9953) and anodic peak current (◆, R² = 0.9962) versus square root of scan rate.

at –2.13 V, we can use this chemical reductant, whose redox potential is –1.94 V, to investigate only the first electron transfer process at –1.61 V.

Complex **1** shows three major LMCT bands (300, 431, and 545 nm) which are consistent with those observed in other model compounds and Rieske-type proteins with the oxidation state of both iron ions being 3⁺.^{23,29,45,46} Complex **2**, on the other hand, exhibits two charge-transfer bands that are bathochromically shifted compared to **1** (Fig. S3†). The red-shift of the LMCT bands is consistent with the trend of ligand field transition energy of the bridging atoms. These features diminished upon titration with reductant, CoCp*₂ (Fig. 3). Further addition of the chemical reductant past two equivalents did not show any additional change. Therefore, the 2 : 1 (CoCp*₂ : **1**) molar ratio suggests the first quasi-reversible event of **1** involves two electrons and implies the second event is a one-electron process. The single quasi-reversible event of complex **2** is at –1.91 V and could represent the transfer of one or two electrons. Similarly, titration of **2** with CoCp*₂ was monitored by using UV-vis spectroscopy at λ_{max} = 614 nm, which diminished and did not show any change after addition of 1 equiv. of CoCp*₂ (Fig. S4†). Therefore, this 1 : 1 (CoCp*₂ : **2**) molar ratio suggests that the single quasi-reversible event of **2** involves one electron. Attempts to reduce **1** were encouraged by the quasi-reversible redox events and relatively stable in

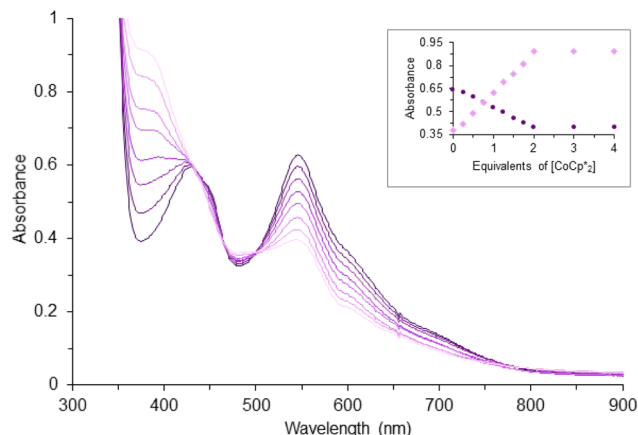


Fig. 3 Reduction of 0.1 mM **1** in THF by addition of CoCp^*_2 in increments of 0.25 equiv. as monitored by UV-vis spectroscopy (path length, 1.0 cm). Inset: corresponding changes of the absorbance at 389 (◆) and 545 (●) nm.

THF solution upon reduction. However, the reactions led to intractable products through many trials under different conditions (e.g. variety of reductants, solvents, and temperatures). Although several reduced species supported by other bidentate nitrogen-donor ligands were successfully synthesized and reported,^{21,24,26,27} the futile attempts for isolating the reduction products of **1** could be due to the unusually long $\text{Fe}\cdots\text{Fe}$ distance.

Kinetic studies of the formation of **1**

Since the synthesis of $[\text{2Fe-2S}]$ model compounds are not always straightforward, with attempts often yielding homoleptic complexes, L_2Fe (L = bidentate ligands), an alternative procedure was discovered by the oxidation of elemental sulfur with mono- or di-nuclear $\text{Fe}(\text{i})$ precursors.^{23,24,26} Therefore, to gain insights into the formation of **1**, we carried out kinetic studies for the activation of elemental sulfur with the low-valent Fe complex, $(\text{L1})\text{Fe}(\text{cod})$. When the observed rate constants k_{obs} are plotted as a function of the concentration of S_8 , a linear dependence that, within error, passes through the origin is observed (Fig. S5 and S6†). These data indicate a bimolecular reaction between $(\text{L1})\text{Fe}(\text{cod})$ and S_8 . When comparing the rates for reactions conducted under the same conditions with $^{34}\text{S}_8$, the kinetic isotopic effect (KIE) of $k^{32}\text{S}_8/k^{34}\text{S}_8 = 1.02$. The normal KIE value suggests that the rate-determining step is likely the cleavage of the S–S bond, but we cannot completely rule out the possibility of experimental errors based on this value. More insights into the formation mechanism of **1** from $(\text{L1})\text{Fe}(\text{cod})$ and $^{32}\text{S}_8$ was gained from temperature-dependence kinetic experiments. An Eyring analysis over a temperature range of -40 to -70 °C gave the activation parameters $\Delta^\ddagger H = 17.0 \pm 0.6$ kJ mol $^{-1}$ and $\Delta^\ddagger S = -155 \pm 8$ J mol $^{-1}$ K $^{-1}$ which correspond to an associated $\Delta^\ddagger G_{298\text{ K}} = 63.2 \pm 0.8$ kJ mol $^{-1}$ (Fig. S7†). The positive enthalpy of activation presumably implies cleavage of the S–S bond in the transition state. The large negative entropy of activation suggests the reaction pro-

ceeds *via* an associative mechanism and could be due to the formation of a highly ordered transition state where a partially broken S–S bond of the S_8 molecule chelates the Fe center.

Sulfur atom transfer studies

Albeit still under debate, sulfur atom transfer reactions in enzymes with $[\text{2Fe-2S}]$ clusters may play an important role in metabolic reactions e.g. biotin synthase transforms dethiobiotin to biotin. Considering the long Fe–S bond length, **1** could be a suitable candidate for an S-atom transfer reaction. When treating **1** with PPh_3 at 40 °C, the formation of $\text{S}=\text{PPh}_3$ was observed by ^1H NMR spectroscopy. This result has encouraged us to further study the potential catalytic S-atom transfer reaction. However, due to the limited solubility of S_8 , it was not possible to obtain consistent kinetic data when using excess (10-fold) amounts of S_8 . Thus, the only viable approach to determine whether the iron complex catalyzes the S-atom transfer reaction is to obtain the overall yields of $\text{S}=\text{PPh}_3$ from reaction of **1** with triphenyl phosphine. Direct reaction of S_8 with PPh_3 was expected to be a much slower process. Since $\text{Fe}(\text{i})$ species are considered to be generated after transferring an S atom from **1**, we tested if catalytic atom transfer is possible by mixing an $\text{Fe}(\text{i})$ precursor, $(\text{L1})\text{Fe}(\text{cod})$, with excess S_8 and PPh_3 . The mixture was maintained at 40 °C for one hour and the formation of $\text{S}=\text{PPh}_3$ was confirmed and quantified (yield = 70%) by ^{31}P and ^1H NMR spectroscopy.⁴⁷ Conversely, in the absence of $(\text{L1})\text{Fe}(\text{cod})$, only 11% conversion was observed. Scheme S1† presented the proposed reaction mechanism, whereby mixing $(\text{L1})\text{Fe}(\text{cod})$ with S_8 resulted in the immediate formation of **1**, which subsequently reacted with PPh_3 to generate $\text{S}=\text{PPh}_3$. The residual two-coordinate $\text{Fe}(\text{i})$ species could form species **A** through binding with an excess amount of triphenylphosphine ligand(s). Note that the two-coordinate $\text{Fe}(\text{i})$ species or **A** may act as an active catalyst, or alternatively, the regeneration of $(\text{L1})\text{Fe}(\text{cod})$ could occur through ligand substitution of free cyclooctadiene and triphenylphosphine ligand (s). The Se atom transfer reaction, under the same conditions, was slower, regardless of the presence (12%) or absence (5%) of $(\text{L1})\text{Fe}(\text{cod})$.

Conclusions

This study reports two $[\text{2Fe-2E}]$ model compounds, $[(\text{L1})\text{Fe}(\mu\text{-S})_2]$ (**1**) and $[(\text{L1})\text{Fe}(\mu\text{-Se})_2]$ (**2**), supported by a chiral diketiminate ligand. The presence of steric hindrance in **1** is believed to be the cause of its remarkably elongated $\text{Fe}\cdots\text{Fe}$ distance, which is thought to have played a role in the failure to synthesize reduced $[\text{2Fe-2S}]$ compounds. **1** is capable of transferring three electrons whereas a single electron redox event is observed in **2**. For the formation of **1**, kinetic analysis suggests that the cleavage of the S–S bond is the rate-determining step and the reaction proceeds *via* an associative mechanism. The highly efficient S-atom transfer reaction could be attributed to the unusually long Fe–S bond length in **1**, and these results imply that S-atom transfer reactions may occur in biological

relevant [2Fe–2S] clusters. The ongoing research is to gain further insight into the reaction mechanism of E-atom transfer reactions with the goal of facilitating the efficient synthesis of chiral E-containing compounds by utilizing these [2Fe–2E] model complexes as catalysts.

Author contributions

Erwin A. Weerawardhana: writing original draft, synthesis and characterization of compounds. Matthias Zeller: crystallography. Wei-Tsung Lee: experimental design, supervision, data validation, manuscript review, and editing. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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