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### Introduction

Iron sulfur clusters are prevalent in many metalloproteins, particularly those that perform the activation of small molecules such as  $H_2$ ,  $CO_2$  and  $N_2$ .<sup>1</sup> Among these, the [FeFe]hydrogenase<sup>2-5</sup> and nitrogenase<sup>6-9</sup> have received much attention due to the investigation of synthetic analogues in exploring fundamental processes of electron transfer, cluster reactivity and substrate activation – in addition to possible uses for industrial catalysis. While applications of [2Fe-2S]-type clusters generally pertain to proton reduction,<sup>10–13</sup> they have also been shown to perform additional reactions such as liberation of  $H_2$  from amino-boranes<sup>14</sup> and the reduction of molecular oxygen.<sup>15,16</sup> In related biomimetic work, [2Mo-6Fe-8S] clusters have been shown to form a chalcogel when reacted with [2Sn-6S], generating a system that photo-catalyzes the

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# Synthesis and interconversions of reduced, alkali-metal supported iron-sulfur-carbonyl complexes†

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We report the synthesis, interconversions and X-ray structures of a set of [mFe-nS]-type carbonyl clusters (where S = S<sup>2-</sup>, S<sub>2</sub><sup>2-</sup> or RS<sup>-</sup>; m = 2-3; n = 1-2). All of the clusters have been identified and characterized by single crystal X-ray diffraction, IR and  $^{13}$ C NMR. Reduction of the parent neutral dimer [ $\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1) with KC<sub>8</sub> affords an easily separable  $\sim 1:1$  mixture of the anionic, dimeric thiolate dimer K[Fe<sub>2</sub>(SPh)  $(CO)_6(\mu$ -CO)] (2) and the dianionic, sulfido trimer [K(benzo-15-crown-5)<sub>2</sub>]<sub>2</sub>[Fe<sub>3</sub>( $\mu$ <sub>3</sub>-S)(CO)<sub>9</sub>] (3). Oxidation of **2** with diphenyl-disulfide ( $Ph_2S_2$ ) cleanly returns the starting material **1**. The Ph-S bond in **1** can be cleaved to form sulfide trimer 3. Oxidation of sulfido trimer 3 with  $[Fc](PF_6)$  in the presence of S<sub>8</sub> cleanly affords the all-inorganic persulfide dimer  $[\mu_2-(S)_2Fe_2(CO)_6]$  (4), a thermodynamically stable product. The inverse reactions to form 3 (dianion) from 4 (neutral) were not successful, and other products were obtained. For example, reduction of 4 with KC<sub>8</sub> afforded the mixed valence Fe(I)/Fe(II) species [((Fe<sup>1</sup><sub>2</sub>S<sub>2</sub>)- $(CO)_6)_2 Fe^{II}_2^{2-}$  (5), in which the two  $\{Fe_2S_2(CO)_6\}^{2-}$  units serve as bidendate ligands to a Fe(II) center. Another isolated product (THF insoluble portion) was recrystallized in MeCN to afford [K(benzo-15crown-5)<sub>2</sub>]<sub>2</sub>[((Fe<sub>2</sub>S)(CO)<sub>6</sub>)<sub>2</sub>( $\mu$ -S)<sub>2</sub>] (**6**), in which a persulfide dianion bridges two {2Fe-S} moieties (dimer of dimers). Finally, to close the interconversion loop, we converted the persulfide dimer 4 into the thiolate dimer **1** by reduction with  $KC_8$  followed by reaction with the diphenyl iodonium salt [Ph<sub>2</sub>I](PF<sub>6</sub>), in modest yield. These reactions underscore the thermodynamic stability of the dimers 1 and 4, as well as the synthetic and crystallization versatility of using the crown/ $K^+$  counterion system for obtaining structural information on highly reduced iron-sulfur-carbonyl clusters.

reduction of dinitrogen.<sup>17</sup> In nitrogenase, the biogenesis of the catalytically active M-cluster involves the transformation of cysteinyl sulfur to inorganic sulfide in the form of a [2Fe–2S] cluster, and then later to [4Fe–4S] clusters. Recent work by Wiig *et al.* demonstrated that NifEN catalyzes the transfer of  $CH_3^+$  derived from S-adenosyl methionine to a [4Fe–4S] sulfide by a nucleophilic attack.<sup>18,19</sup> Radical abstraction of protons by the adenosyl radical likely begins the process of forming multiple Fe–C bonds.

In one case closely related to the present work, models of [NiFe]-hydrogenase were prepared by installing a nucleophilic sulfur on an [Fe<sub>2</sub>(SR)] cluster *via* a reaction with carbon disulfide (CS<sub>2</sub>): specifically, reaction of (NEt<sub>3</sub>H)[( $\mu$ -SPh)( $\mu$ -CO) Fe<sub>2</sub>(CO)<sub>6</sub>] with CS<sub>2</sub> afforded (NEt<sub>3</sub>H)[( $\mu$ -SPh)Fe<sub>2</sub>(S==C-S) (CO)<sub>6</sub>].<sup>20,21</sup> Subsequent metalation with nickel-phosphine sources provided the heterobimetallic model complexes. Another report explored the facile modularity of the  $\mu_3$ -S  $\leftrightarrow \mu_2$ -S sulfido motif: Tatsumi and coworkers reported the interconversion of [4Fe-4S]  $\leftrightarrow$  [2Fe-2S] clusters supported by N(Si (CH<sub>3</sub>)<sub>3</sub>) ligands, promoted by the absence or presence (respectively) of pyridine.<sup>22</sup> This same report delineated the redox conversion of the [(py)<sub>2</sub>Fe<sub>2</sub>S<sub>2</sub>]<sup>0</sup> cluster to either the [4Fe-4S]<sup>-</sup> or

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 $[4Fe-4S]^{2-}$  cluster upon reduction with 0.5 or 1 equiv. of  $Na[C_{10}H_8]$ , respectively. Notably, the clusters were isolated and crystallized as stable alkali metal adducts.

Generating precursors for these systems can be an arduous task, as the chemistry is highly thermodynamic in nature. Clusters such as  $[Fe_3(\mu_3-S)(CO)_9]^{2-}$  and  $[Fe_2(\mu-SR)(\mu-CO)(CO)_6]^{-}$ are synthesized by "spontaneous self-assembly"<sup>23</sup> of starting materials such as  $[Fe(CO)_5]$  and  $S_8$ , with multiple clusters forming in a single reaction. Often times the desired cluster is not a major product, leading to further complications in purification. To remedy this, in this work we have isolated and characterized two new alkali-supported iron sulfur clusters  $K[Fe_2(\mu-SR)(\mu-CO)(CO)_6]$  (2) and  $K_2[Fe_3(\mu_3-S)(CO)_9]$  (3), which can provide a much more robust starting material for synthetic modeling. These clusters also provide a unique advantage in the characterization of products by X-ray diffraction due to the utility of the alkali cation(s) and associated crown(s) ether in providing convenient separation and multiple avenues of crystallization. Additionally, the alkali counterions are more resilient than their organic counterparts under reductive conditions, enabling broader exploration of reaction pathways. In this work, we have explored the isolation of reduced, anionic iron-sulfur-carbonyl clusters and their reactions with carbonbased electrophiles (CH<sub>2</sub>I<sub>2</sub>, CF<sub>2</sub>Br<sub>2</sub>), as well as sulfur based modifications (alkylation, de-alkylation, S-S bond making/ breaking). Discrete interconversions among species are investigated to understand the reactivity properties of the iron versus sulfur centers in the clusters.

### Experimental

Unless otherwise stated, all reactions were performed void of oxygen with the aid of an argon atmosphere glovebox or  $N_2$  atmosphere Schlenk line. The starting materials Fe(CO)<sub>5</sub>, PhSH, S<sub>8</sub>, Ph<sub>2</sub>IPF<sub>6</sub>, [Fc]PF<sub>6</sub> and benzo-15-crown-5 were purchased from Strem, Aldrich, Acros, or Oakwood Chemicals and used without further purification. KC<sub>8</sub> was prepared from a reported synthesis.<sup>24</sup> Deuterated MeCN was purchased from Cambridge Isotopes and was used as received. HPLC grade solvents were purchased from EMD, Fisher, Macron, or J. T. Baker, and dried with the use of an alumina column system (Pure Process Technology). *Caution:* Reduced iron-carbonyl complexes can be pyrophoric and should only be handled under inert atmosphere.

#### Synthesis of the iron complexes

K[Fe<sub>2</sub>(SPh)(CO)<sub>6</sub>( $\mu$ -CO)] (2) and [K(benzo-15-crown-5)<sub>2</sub>]<sub>2</sub> [Fe<sub>3</sub>( $\mu_3$ -S)(CO)<sub>9</sub>] (3). These two reduced clusters were isolated as separable products resulting from the same reaction. First, 262 mg (0.526 mmol) of [ $\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1) was dissolved in 15 mL of THF and brought to -20 °C. Next, a portion of KC<sub>8</sub> (207 mg, 1.53 mmol) was added, and the mixture was allowed to warm to room temperature. After 2 h the reaction was filtered, and the solvent was removed *in vacuo*, resulting in a black oil.

Workup part A for  $K[Fe_2(SPh)(CO)_6(\mu-CO)]$  (2). The mixture was separated into the two desired components by extracting 2 as a dark brown solution into  $Et_2O$  (10 × 2 mL extractions, until the extractions are colorless); a red powder of complex 3 remained insoluble. The combined Et<sub>2</sub>O extractions were allowed to stand overnight, during which time complex 2 remained soluble; any precipitate (3) was removed by filtration and combined with the original Et<sub>2</sub>O insoluble portion. The brown Et<sub>2</sub>O soluble portion was evaporated in vacuo and washed thoroughly with pentane to afford a brownish golden powder. The product was isolated as golden brown X-ray quality crystals grown by slow diffusion of pentane into an  $Et_2O$  solution of the complex at -20 °C; the product was identified as the thiolate-bridged dimer  $K[Fe_2(SPh)(CO)_6(\mu-CO)]$  (2). Yield: 208 mg (50%). IR ( $\nu_{CO}$  in cm<sup>-1</sup>): 2027, 1970, 1901, 1726. Elem. analysis (%): calcd C 34.34, H 1.11; found C 34.25, H 1.30. <sup>13</sup>C NMR in  $d^3$ -MeCN ( $\delta$  from TMS): 118.3, 127.0, 128.7, 133.1, 143.7, 224.9.

Workup part B for  $[K(benzo-15-crown-5)_2]_2[Fe_3(\mu_3-S)(CO)_9]$  (3). The remaining Et<sub>2</sub>O insoluble portion of K<sub>2</sub>[Fe<sub>3</sub>( $\mu_3$ -S)(CO)<sub>9</sub>] (red material) was dissolved in MeCN containing excess benzo-15-crown-5 ether, and the red crystalline product was obtained *via* slow vapor diffusion of Et<sub>2</sub>O. The product was identified as  $[K(benzo-15-crown-5)_2]_2[Fe_3(\mu_3-S)(CO)_9]$  (3). Yield: 120 mg (43%). IR ( $\nu_{CO}$  in cm<sup>-1</sup>): 1995, 1914, 1892, 1874. Elem. analysis: calcd C 48.70, H 5.03; found C 49.47, H 5.35. <sup>13</sup>C NMR in *d*<sup>3</sup>-MeCN ( $\delta$  from TMS): 15.64, 66.26, 67.71, 68.67, 69.44, 148.5, 223.5.

Reaction of K[Fe<sub>2</sub>(SPh)(CO)<sub>6</sub>( $\mu$ -CO)] (2) with CH<sub>2</sub>I<sub>2</sub> and CF<sub>2</sub>Br<sub>2</sub> to (1). In a typical reaction, 100 mg (0.202 mmol) of 2 was dissolved in 20 mL of Et<sub>2</sub>O and cooled to -20 °C and 2.0 equiv. CH<sub>2</sub>I<sub>2</sub> or CF<sub>2</sub>Br<sub>2</sub> were then dissolved in Et<sub>2</sub>O and added to the chilled solution. As the reaction warmed to room temperature a white precipitate formed (KI or KBr, respectively). After 4 h, the solution was filtered, and the solvent was removed *in vacuo* to afford a bright red oil. The oil was dissolved in pentane, and X-ray quality crystals from both reactions were obtained by prolonged storage of the pentane solution of the products at -80 °C. Both CH<sub>2</sub>I<sub>2</sub> and CF<sub>2</sub>Br<sub>2</sub> reactions afforded crystalline samples of [ $\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1). Yield: 25 mg (25%).

Synthesis of  $[K(benzo-15-crown-5)_2]_2[((Fe_2S_2)(CO)_6)_2Fe]$  (5) and  $[K(benzo-15-crown-5)_2]_2[((Fe_2S)(CO)_6)_2(\mu-S)_2]$  (6) from (4). These two clusters were isolated as the primary products in the reduction of  $[\mu_2-(S)_2Fe_2(CO)_6]$  (4). The starting material for this reaction was synthesized from the reported procedure.<sup>25</sup> A vial was charged with 202 mg  $[\mu_2-(S)_2Fe_2(CO)_6]$  (0.406 mmol) and dissolved in 15 mL of THF. Next, two equiv. of KC<sub>8</sub> (109 mg, 811 mmol) were added to the translucent red solution at room temperature. The slurry was allowed to stir at room temperature, and the reaction quickly changed to a dark opaque green color. After 90 min, the mixture was filtered to remove the graphite byproducts. The solvent was then removed *in vacuo* to afford a brown-green oil. The crude reaction product was washed thoroughly with Et<sub>2</sub>O (20 × 2 mL) until the resulting washes were virtually colorless and a forest green powder remained. Workup part A for  $[K(benzo-15-crown-5)_2]_2[((Fe_2S_2)(CO)_6)_2Fe]$ (5). To obtain  $K_2[((Fe_2S_2)(CO)_6)_2Fe]$  (5), a small amount of THF (5–10 mL) was added to the green powder; the resulting solution was filtered and treated with an excess of benzo-15-crown-5 for crystallization *via* vapor diffusion of Et<sub>2</sub>O. Successive recrystallization of the polycrystalline solid with MeCN and Et<sub>2</sub>O produced X-ray quality crystals. Yield: 53 mg (12%). IR ( $\nu_{CO}$  in cm<sup>-1</sup>): 2018, 1978, 1917. Elem. analysis calcd: C 43.1, H 4.26; found: C 43.46, H 4.65. <sup>13</sup>C NMR in  $d^3$ -MeCN ( $\delta$  from TMS): 26.17, 68.20, 68.67, 69.24, 69.97 148.79, 214.60.

Workup part B for  $[K(benzo-15\text{-}crown-5)_2]_2[((Fe_2S)(CO)_6)_2(\mu-S)_2]$ (6). To obtain 6, the remaining powder (THF insoluble) can be dissolved in 10 mL of MeCN. If MeCN is added to the mixture before extraction into THF, the aforementioned product is somewhat soluble, but will not precipitate out in subsequent recrystallizations. To the MeCN extract, excess benzo-15-crown-5 was added, and the solution was filtered. Vapor diffusion of Et<sub>2</sub>O afforded the desired product 6, which crystallizes in bluegreen rods and needles. Yield: 106 mg (20%). IR ( $\nu_{CO}$  in cm<sup>-1</sup>): 2023, 1992, 1945, 1911. Elem. analysis calcd: C 44.41, H 4.38; found: C 44.77, H 4.71. <sup>13</sup>C NMR in  $d^3$ -MeCN ( $\delta$  from TMS): 67.95, 68.36, 68.86, 69.62, 148.4, 223.2.

Conversion of  $[\mu_2$ -(S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (4) to  $[\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1). A vial was charged with 149.1 mg (0.436 mmol) of complex 4, which was dissolved in 15 mL of THF. Next, 116 mg of KC<sub>8</sub> (2 equiv.) was added to the reaction, and the solution turned green, indicating the reduction of the starting material. After 1 h reaction time, excess graphite was filtered from the reaction, and 368.2 mg (0.873 mmol, 2 equiv.) of  $[Ph_2I]PF_6$  was added to the solution. An immediate color change to red was observed, and after 1 h the solvent was removed under vacuum. Nonpolar products were extracted into pentane (5 × 2 mL) and purified by column chromatography through silica gel with hexanes. The product was confirmed to be complex 1 by IR. Yield: 8.2 mg (4%).

Synthesis of [K(benzo-15-crown-5)<sub>2</sub>]<sub>2</sub>[Fe<sub>3</sub>S(CO)<sub>9</sub>] (3) from  $K_2SO_3$ . The following is a modification of the procedure to isolate the NEt<sub>4</sub> salt of  $[Fe_3(\mu_3-S)(CO)_9]$  first reported by Cherng et al.26 A Schlenk flask was filled with 40 mL MeOH and purged with N2 for 30 min. Next, 1.59 g of KOH and 0.41 g of K<sub>2</sub>SO<sub>3</sub> were added under N<sub>2</sub>. Finally, 1 mL of Fe(CO)<sub>5</sub> (1.45 g, 7.42 mmol) was added and the solution slowly turned red. The reaction heated to reflux under N2 for 4 days. Upon cooling, the insoluble byproducts were removed by filtration using a fritted, airfree filter tube and the MeOH was removed in vacuo. The crude product was dissolved in THF and filtered to remove another crop of insoluble material. Following removal of THF solvent by vacuum, the crude product was washed thoroughly with  $Et_2O(20 \times 2 \text{ mL})$  until the solvent became virtually colorless. (Note: The resulting powder can be used as a starting material as the bare potassium salt.) To obtain crystals for the purpose of analysis, the powder was dissolved in MeCN and an excess amount (about 4.2 equiv.) of benzo-15-crown-5 ether was added. Vapor diffusion of Et2O afforded dark red plates of  $[K(benzo-15-crown-5)_2]_2[Fe_3(\mu_3-S)(CO)_9]$  (3). Yield: 206 mg (5%).

IR ( $\nu_{CO}$  in cm<sup>-1</sup>): 1995, 1914, 1892, 1874. Elem. analysis calcd: C 48.70, H 5.03; found: C 49.47, H 5.35.

**Conversion of** [Fe<sub>3</sub>( $\mu_3$ -S)(CO)<sub>9</sub>] (3) **to** [ $\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1). A vial was charged with 197 mg (0.372 mmol) of the bare potassium starting material [Fe<sub>3</sub>( $\mu_3$ -S)(CO)<sub>9</sub>], and dissolved in ~15 mL THF. Once the solution was homogeneous, 125 mg S<sub>2</sub>Ph<sub>2</sub> (1.5 equiv., 0.562 mmol) was added, followed by 249 mg (0.752 mmol) [Fc]PF<sub>6</sub> at room temperature. The reaction was allowed to proceed for 2 h before solvent was removed by vacuum. The desired product was extracted into pentane, and was purified by column chromatography (silica gel) with hexanes as eluent. The first purple band was identified as [Fe<sub>3</sub>S<sub>2</sub>(CO)<sub>9</sub>], a common byproduct in the synthesis of [ $\mu_2$ -(S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (4); the subsequent yellow band that followed was not collected (ferrocene byproduct of the oxidant). The last red band was collected and identified as [ $\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] by TLC and IR. Yield: 20 mg (7%).

Conversion of  $[Fe_3(\mu_3-S)(CO)_9]$  (3) to  $[\mu_2-(S)_2Fe_2(CO)_6]$  (4). This reaction proceeded in analogous fashion to the previous conversion to  $[\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1). A vial was charged with 152 mg K<sub>2</sub>[Fe<sub>3</sub>(µ<sub>3</sub>-S)(CO)<sub>9</sub>] (0.287 mmol) and dissolved in ~15 mL THF. Once the solution was homogeneous, 21.1 mg S<sub>8</sub> (0.658 mmol) was added to the reaction, and a slight darkening of the solution to red-brown was observed. After 15 minutes, 190 mg [Fc]PF<sub>6</sub> (0.574 mmol) was added to the solution, and the reaction was allowed to proceed for 2 h. After removing all solvent by vacuum, the product was extracted into hexanes, and the nonpolar products were purified by column chromatography (silica gel) using hexanes as eluent. Again, a purple band was present in the crude mixture, and was identified as  $[Fe_3S_2(CO)_9]$ ; the red band prior to the purple band was collected and identified by IR and TLC to be the desired product  $[\mu_2$ -(S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>]. Yield: 15 mg (11%).

#### Physical methods

The <sup>13</sup>C NMR spectra were obtained on an Agilent MR 400 MHz spectrometer, and chemical shifts are reported in ppm referenced to TMS. Infrared spectra were recorded by using a Bruker Alpha spectrometer with the use of a diamond ATR crystal. Elemental analyses were performed by Midwest Microlab. Details regarding X-ray data collection and analysis are located in the ESI.<sup>†</sup>

### Results and discussion

#### Synthesis and interconversions

Generally, iron–sulfur clusters generated by spontaneous selfassembly are not isolated as 'bare' alkali-supported salts due to their tendency to form viscous oils. Instead, they are precipitated out of solution *via* the introduction of organic salts such as NEt<sub>4</sub>Cl or PPh<sub>4</sub>Br.<sup>20,23,27–31</sup> While this is sufficient for isolation of the complexes, the utility of these formulations are limited when harsh reductions are required to generate or isolate further reduced species. In this same vein, many of the anionic iron–sulfur complexes are quite reducing, causing

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instability on an intramolecular basis as well. Our original goal was to synthesize a reduced [2Fe-2S] cluster that was compatible with both strong reductants and electrophiles. The known diiron dithiolate dimer  $[\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1) was chosen as a starting material, as the two singly valent iron centers were deemed to be susceptible to reduction. Initial attempts to reduce the cluster with Na/Hg amalgam afforded an intractable black oil containing multiple products that were inseparable by differential solvent extraction or crystal growth. The reductant KC<sub>8</sub> proved more effective, as the potassium counterion allowed for the separation of the two major products by their respective solubility in Et<sub>2</sub>O. Another advantage of KC<sub>8</sub> lies in its modularity, considering the wide variety of crowns and clathrates available for K<sup>+</sup> sequestration, most of which retain high solubility in organic solvents. Interestingly, we found the 'bare' mono-potassium salt  $K[Fe_2(\mu-RS)(\mu-CO)(CO)_6]$  (2) was soluble in Et<sub>2</sub>O, providing a facile means of obtaining pure samples of the cluster for crystallization. However, after extraction into Et<sub>2</sub>O as the 'bare' potassium salt, subsequent addition of benzo-15-crown-5-ether did not afford the crown-K<sup>+</sup> supported cluster of formulation [K(benzo-15-crown-5)][Fe<sub>2</sub>(µ-SR)  $(\mu$ -CO)(CO)<sub>6</sub>]. This could be due to the unique position of the K in the crystal lattice, forming a network of bonds with neighboring COs, thiolates and phenyl carbons (vide supra, Fig. 1). The Et<sub>2</sub>O insoluble portion from the extraction process described above was then extracted with MeCN containing excess benzo-15-crown-5-ether afforded the (crown)alkali-supported trimeric species  $[K(benzo-15-crown-5)_2]_2[Fe_3(\mu_3-S)(CO)_9]$  (3).

With the novel alkali-supported iron–sulfur–carbonyl clusters in hand, we investigated their propensity to react with  $C_1$ electrophiles (Scheme 1, top). Due to the reported examples for reactions of carbonyl-containing FeS clusters with electrophilic carbon sources,<sup>22,23,30</sup> CH<sub>2</sub>I<sub>2</sub> and CF<sub>2</sub>Br<sub>2</sub> were chosen as



Fig. 1 ORTEP diagram (50% thermal ellipsoids) of  $K[Fe_2(\mu-SPh)(\mu-CO)(CO)_6]$  (2) at 100 K. Two molecules are shown to highlight the unique bonding motif of the K-counterion.



Scheme 1 Synthetic scheme detailing syntheses and interconversions arising from compound 1 as reported in this work.

initial reactants. Our first attempt involved the chargebalanced reaction of two equiv. of  $K[Fe_2(\mu-SPh)(\mu-CO)(CO)_6]$ with the dihalo  $C_1$  sources, aiming to achieve 2 × KX elimination and isolation of a corresponding neutral complex containing a  $CH_2^{2+}$  or  $CF_2^{2+}$  fragment within cluster. Indeed, precipitation of KX from Et<sub>2</sub>O was observed, and a pentane soluble red material was isolated as the product. However, subsequent crystallization from pentane at -80 °C revealed the product as the original neutral dimer,  $[\mu_2-(SPh)_2Fe_2(CO)_6]$  (1). Our tentative explanation for this behavior is that the electrophilic carbon units accepted four electrons from two Fe<sup>0</sup>-Fe<sup>0</sup> clusters to regenerate two Fe<sup>I</sup>-Fe<sup>I</sup> dimers, with concomitant generation of  $C_2X_4$ , (X = H, F). Based on the stoichiometry required to produce complex 1, it can be deduced that some  $Fe_x(CO)_y$  byproduct is also formed, but evidence of such clusters after chromatography of the crude product mixture was not conclusive.

To deconvolute these results, a more straightforward set of reaction conditions were chosen to investigate the reproducibility of this process (Scheme 1). Reactions containing 0.5 equiv. of diphenyl-disulfide  $(Ph_2S_2)$  by itself did not regenerate the [2Fe<sup>I</sup>-2(SPh)] starting material 1. However, the combination of 0.5 equiv. of Ph<sub>2</sub>S<sub>2</sub> plus 1.0 equiv. of [Fc]PF<sub>6</sub> did lead to quantitative conversion of anionic 2 to neutral 1. This is likely due to the need for redox-driven elimination of potassium (as  $KPF_6$ ) before the ensuing coordination chemistry can occur at the iron centers. This suggests that the coordination environment of the iron centers is controlled by the oxidation state of the iron complex, and not the available ligand reagents in solution. Indeed, this was further substantiated by the generation of the dianion  $K_2[Fe_3(\mu_3-S)(CO)_9]$  (3) from the reduction of  $[\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (2) with KC<sub>8</sub> (Scheme 1). Simply reducing the [Fe<sup>I</sup>Fe<sup>I</sup>] dimer leads to cleavage of an S–C bond to generate a new bridging sulfide species, despite phenyl thiolate being present in solution.

During the conversion of 1 to 3, we observed that free phenyl thiolate (PhSK) is formed as a byproduct (observed by XRD in subsequent reactions as  $C(SPh)_4$ ). The anionic PhS<sup>-</sup> (as K<sup>+</sup> salt) has quite similar solubility properties to the dianion 3, render-

ing solvent separation unviable. While 3 can be purified by the addition of crowns and subsequent recrystallization, we were unable to isolate the bare potassium complex from the reduction of 1. This limited the utility of 3 as a starting material, as the synthetic versatility derives comes from the ability to use multiple crown ethers in subsequent crystallization attempts.

Thus, another more direct route was devised. The known persulfide iron carbonyl dimer  $[Fe_2(\mu-S_2)(CO)_6]$  (4) was selected due to the hypothesized 'redox-only' ease of converting the  $\mu_2$ -(S<sub>2</sub>)<sup>2-</sup> ligand in 4 to the  $\mu_3$ -(S)<sup>2-</sup> moiety found in 3. Surprisingly, reduction of 4 (red) in THF with  $KC_8$  in an attempt to generate 3 (also red) instead generated a green solution,<sup>32,33</sup> ultimately affording THF soluble and insoluble portions. Treatment of the THF soluble portion with dibenzo-15crown-5 in THF afforded a sparing quantity of red polycrystalline material (not suitable for single crystal XRD). Recrystallization of this material from MeCN afforded single crystals of the novel dianionic complex [K(dibenzo-15-crown- $5_{2}$ [Fe(Fe<sub>2</sub>( $\mu$ -S)<sub>2</sub>(CO)<sub>6</sub>)<sub>2</sub>] (5), in which the sulfide moieties of two  $[Fe_2S_2(CO)_6]^{2-}$  units serve as two sets of bidentate ligands, coordinating a central Fe(II) ion (Scheme 2). There is precedence for the starting material 4 serving as a bidentate sulfur chelate following reduction of the persulfide bridge to inorganic sulfides, as evident in the complexes reported by Song, namely  $[Fe_2(CO)_6(\mu-S_2)GeCl_2]$  and  $[Fe_4(CO)_{12}(\mu-S_4)Ge]$ .<sup>34</sup>

The THF *insoluble green* portion from the above reaction was re-crystallized from MeCN to afford dark *red* single crystals. However, instead of the expected outcome of the reduction of the persulfide bridge into two bridging sulfides, the product was identified as  $[K(benzo-15-crown-5)_2]_2[((Fe_2S) (CO)_6)_2(\mu-S)_2]$  (6), containing a 'dimer of dimers' vis a vis a persulfide bridge between di-iron units. This result is evidently not a direct conversion from the starting material. The starting material 4 was treated with two equiv. of KC<sub>8</sub>, likely generating the doubly-reduced species (green solution) *in situ*.<sup>35</sup> However, during isolation and crystallization, the complex auto-oxidized (perhaps *via* reduction of MeCN) to generate the more stable persulfide bridge between the diiron units. As of yet, crystals of the green material have not been obtained. However, this reduction can be used to afford a transformation from

(CO)<sub>3</sub>

(CO)<sub>3</sub>

(CO)

5

ק [K(b-15-c-5)₂]₂



(OC)3

(OC)3

THF/Et<sub>2</sub>O

extraction

MeCN/Et<sub>2</sub>O

extraction

(CO)3

complex 4 to complex 1. By adding a source of  $Ph^+$ , namely  $[Ph_2I]PF_6$ , the nucleophilic sulfides can be arylated. This conversion is low-yielding, likely due to the formation of 5 and 6 as side products, thus preventing a clean transformation. Using PhI as a reagent to perform this conversion was unsuccessful (no reaction with the reduced species), demonstrating the need for a more labile Ph–I bond.

While both 4 and 3 contain only iron, sulfide and carbonyl moieties, introduction of 2–4 equivalents of KC<sub>8</sub> to 4 paradoxically does not generate 3. This is somewhat counterintuitive, as the conversion of persulfide to sulfide appears facile, whereas de-arylation of phenyl thiolate to sulfide appears difficult. Further attempts to perform the  $4 \rightarrow 3$  conversion using balanced stoichiometry *via* addition of  $^{2}/_{3}$  equiv. [Fe<sub>3</sub>(CO)<sub>12</sub>] led only to elimination of sulfur and isolation (and crystallization) of other known reduced iron clusters, such as [K<sub>2</sub>(benzo-15-c-5)<sub>4</sub>][Fe<sub>2</sub>(CO)<sub>8</sub>] and [K(benzo-15-c-5)<sub>2</sub>]<sub>2</sub>[Fe(CN)<sub>4</sub>].

Relatedly, a synthesis by Cherng et al.<sup>26</sup> demonstrated that  $[NEt_4][Fe_3(\mu_3-S)(CO)_9]$  can be generated by refluxing KOH and  $Fe(CO)_5$  in methanol with  $Na_2SO_3$  as the sulfur source. Modification of this procedure finally allowed for 3 to be isolated as the bare potassium salt (a versatile synthon), or crystallized in the form  $[K_2(benzo-15-c-5)_4]_2[Fe_3(\mu_3-S)(CO)_9]$ . In the isolation of this complex, various crown ethers were employed to aid in the solvent separation and subsequent crystallization of the complex. Crown ethers offer the unique ability to modify the solubility of charged alkali metal complexes, as well as lowering the solvent effects of Lewis basic solvents such as THF by encapsulating the potassium ion in a saturated oxygen coordination sphere<sup>36</sup> (Fig. 5). Generally, an increase in the number of benzo groups on the crown ether correlates with lower solubility. For instance, the application of a the alkyl-only 15-crown-5 often results in K[FeSCO] complexes that are too soluble to crystallize from MeCN/Et2O mixtures. However, use of benzo-15-crown-5 imparts a more ideal solubility that facilitates crystallization in standard solvents. Furthermore, the addition of dibenzo-15-crown-5 rendered the K[FeSCO] clusters much less soluble, and all crystallization attempts resulted in only powder products.

Following the eventual isolation of pure 3 from the K<sub>2</sub>SO<sub>3</sub> route, interconversions involving oxidations of  $K_2[Fe_3(\mu_3-S)]$  $(CO)_9$  proceeded in a straightforward manner (Scheme 1). Addition of 1.5 equiv. of  $S_2Ph_2$  followed by 2 equiv. of  $[Fc]PF_6$ afforded  $[\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (1) as a product. Substitution of  $SPh_2$  for  $S_2Ph_2$  resulted in no conversion to 1. While the atom identity of SPh2 would indicate a more straightforward conversion, the greater stability of the S-C bond compared to the S-S bond precluded the desired conversion. The analogous conversion of 3 to 4 using  $[Fc]PF_6$  and  $S_8$  was also viable, albeit in low yield (10%). We report this reaction not as a method to efficiently generate 4, but rather as a proof of concept for this type of interconversion. A common byproduct that was, in fact, separated the mixture via chromatography was the known violet iron cluster [Fe<sub>3</sub>S<sub>2</sub>(CO)<sub>9</sub>]; this cluster is also formed during the synthesis of 4 and is easily recognized by its bright color, IR spectrum and distinct  $R_f$  value (Fig. 1–4).



Fig. 2 ORTEP diagram (50% thermal ellipsoids) of  $[K_2(benzo-15-c-5)_4]_2[Fe_3(\mu_3-S)(CO)_9]$  (3) at 100 K.



Fig. 3 ORTEP diagram (50% thermal ellipsoids) of [K(dibenzo-15-crown-5)<sub>2</sub>]<sub>2</sub>[Fe(Fe<sub>2</sub>( $\mu$ -S)<sub>2</sub>(CO)<sub>6</sub>)<sub>2</sub>] (5) at 100 K.



Fig. 4 ORTEP diagram (50% thermal ellipsoids) of [K(benzo-15-crown- $5)_2$ ]<sub>2</sub>(((Fe<sub>2</sub>S)(CO)<sub>6</sub>)<sub>2</sub>( $\mu$ -S)<sub>2</sub>] (6) at 100 K.

#### **X-Ray structures**

 $K^+$  counterion in 2. Due to the redox active nature of ironsulfur-carbonyl complexes and the nucleophilic character of the reduced iron carbonyl species, characterization of clusters by X-ray diffraction can be difficult due to their instability. For example, in 2013 Song and coworkers reported a synthesis of the anion of complex 2, crystallized with various organic

cations. They were unable to crystallize the complex  $[NEt_3H]$   $[Fe_2(SPh)(\mu-CO)(CO)_6]$ , instead growing crystals of  $[PPh_4][Fe_2(SPh)(\mu-CO)(CO)_6]$ . Although this complex was stable for characterization, it may not be a suitable precursor for further reductive or reactivity studies. Song et al. were, however, able to crystalize  $[NEt_3H]$   $[Fe_2S(p-MeC_6H_4)(\mu-CO)]$  $(CO)_6$ ], demonstrating the importance of both cation selection and the electronics of the sulfur ligand. In our work, cluster 2 appears to be stable due to the position adopted by the 'free' (*i.e.* no crown) potassium cation. The K<sup>+</sup> ion is 'sandwiched' among a thiolate, a phenyl unit and the O atom of several CO ligands. The Lewis acidity and (relatively) small size of the potassium ion allows it to reside much closer to the atoms on the cluster than organic cations would allow. This likely allows a direct mode of stabilization of the complex by delocalizing some of the electron density localized on the sulfur and CO moieties. In cluster 2, the closest atom to the K is the oxygen from the single bridging CO at 2.608(4) Å, followed by the terminal CO ligands at 2.890(3) Å. Meanwhile, the thiolato sulfur participates in a long-range contact with the potassium ion  $[S \cdots K = 3.1760(19) \text{ Å}]$  (Table 1).

Fe-S bonds. The wide range of sulfur-based donors in this set of clusters results in an overall dataset that is not amenable to predicting (or rationalizing) any systematic trend between iron oxidation state and Fe-S bond distance. Complex 2 shows a high extent of uniformity in the bond lengths of atoms that are interchangeable through chemical symmetry operations (but not crystallographic symmetry). Both of the Fe-S distances are experimentally identical at 2.2676(13) Å. This is not present in any of the other clusters, even if they contain higher symmetries in the FeS cluster. For example, complex 3 exhibits a 3-fold rotational axis, and yet all of Fe-S bonds are dissimilar (2.1878(8), 2.1933(8), 2.1932(8) Å). This is likely due to the steric bulk and asymmetric location of the potassium crown complexes in the crystal structure, affording a lower symmetry space group. In the sulfide-trimer cluster 3, the two faces of the pyramid closest to the cation exhibit slightly longer bond lengths for the metal-sulfide bonds (2.1933(8), 2.1932(8) Å vs. 2.1878(8) Å). Also, complex 3 contains the shortest Fe-S bonds, as would be expected due to the high level of covalency between the diffuse  $S^{2-}$  and Fe(0) orbitals, with lengths ranging from 2.1878(8) Å to 2.1933(8) Å. This trimeric structure also contains the most Fe-S bonds to a single sulfur (three); the higher extent of bonding presumably results in the shorter bond distances.

Complex 5 exhibits a notable variation in its Fe–S bond lengths, ranging from 2.2917(14)-2.3289(15) Å. Complex 6 (bearing the persulfide bridge between {Fe<sub>2</sub>S} units) exhibits only a very slight variation in bond lengths: the distance from each set of iron atoms to the bridging persulfide are 2.2574(11) Å and 2.2644(11) Å (0.007 Å difference). The bonds from the irons to the sulfides lie in a larger range from 2.2875(10) Å and 2.3028(11) Å (0.0153 Å difference). Both variations are due to the steric bulk and asymmetric placement of the potassium crown complexes. The disulfide bond [S–S = 2.1657(17) Å] is quite similar to the previously reported value of 2.164(2) Å (as AsPh<sub>4</sub> salt).<sup>39</sup>



**Fig. 5** ORTEP diagram (50% thermal ellipsoids) of a typical [K(benzo-15-crown 5)<sub>2</sub>] complex (in this case, derived from **3**). Two perspectives are shown to demonstrate the 'sandwich-style' bonding motif. The saturated coordination sphere prevents interactions between the potassium ion and Lewis basic solvents.

**Fe–Fe bonds.** Despite the fact that Fe(I)-Fe(I) distances are generally shorter than Fe(0)-Fe(0) distances, we found no reliable correlation between oxidation state and Fe–Fe bond distance. For example, while the shortest Fe–Fe bond length is the Fe(I)-Fe(I) bond in the persulfide dimer (5) at 2.4885(11) Å, the next shortest is the Fe(0)-Fe(0) bond in complex 2 at 2.5006(11) Å. The longest Fe–Fe bonds by far among the three Fe(0) atoms in the sulfide trimer 3, with lengths ranging from 2.5864(6) Å to 2.5940(5) Å. Notably, these distances can be considered as 'outliers', due to the trimer structure *versus* the diiron core in all of the other clusters. Thus, within the set of dimer-based clusters, the longest Fe–Fe distance is found in the previously reported structure of 4 (Fe<sub>2</sub>S<sub>2</sub> dimer, where S<sub>2</sub> =

persulfide), where the Fe(1)–Fe(1) distance is 2.555 Å. As a result, Fe(1)–Fe(1) distances 'bookend' the range of Fe–Fe bonds, with the remaining Fe(1)–Fe(1) and Fe(0)–Fe(0) distances in the intermediate range.

**Fe-C(O) bonds.** Contrary to Fe–Fe bond lengths, the C $\equiv$ O bonds across all complexes follow a distinct trend correlated to the oxidation state of the iron centers present in each cluster, as well as the overall charge of the complex. The neutral Fe(I) complexes  $[\mu_2$ -(SPh)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] and  $[\mu_2$ -(S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] have the shortest C $\equiv$ O bonds (1.132 Å and 1.135 Å respectively) as expected due to their low back-bonding capabilities. Meanwhile, the reduced thiolate cluster 2 contains only Fe(0), the C $\equiv$ O bond lengths are shorter (1.145(4) Å) than the mixed

Table 1 Selected bond lengths and  $\nu$ (CO) values (highest energy feature only) for complexes 2, 3, 5, and 6 from this work, as well as the metrics for 1 and 4 as described elsewhere

| Oxidation state                | $\frac{\operatorname{Fe}_{2}(\operatorname{SPh})_{2}{}^{a}(1)}{\operatorname{Fe}(\operatorname{I})}$ | K[Fe <sub>2</sub> S] (2)<br>Fe(0)  | $K_{2}[Fe_{3}S](3)$<br>Fe(0)        | $\operatorname{Fe}_{2}\operatorname{S}_{2}^{b}(4)$ $\operatorname{Fe}(\mathrm{I})$ | K <sub>2</sub> [(Fe <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> Fe] (5)<br>Two Fe(1)<br>One Fe(1) | $K_2[(Fe_2S)_2(\mu_2-S)]$ (6)<br>Fe(1) |
|--------------------------------|--|------------------------------------|-------------------------------------|--|--|--|
|                                |  |                                    |                                     |  |  |  |
| Fe–S                           | 2.262<br>2.287   | 2.2676(13)                         | 2.1878(8)<br>2.1933(8)<br>2.1932(8) | 2.227<br>2.245   | 2.2917(14)<br>2.3053(16)<br>2.3289(15)   | 2.2875(10)<br>2.3028(11)               |
| S–S<br>Fe–µS                   | _  | _                                  |                                     | 2.026  |  | 2.1657(17)<br>2.2574(11)<br>2.2644(11) |
| μCO–K<br><i>t</i> -CO–K<br>S–K | _  | 2.608(4)<br>2.890(3)<br>3.1760(19) | _                                   |  | _  |  |
| C-O<br>μC-O<br>Έε-CO           | 1.132<br>—<br>1.786  | 1.145(4)<br>1.187(6)<br>1.791(4)   | 1.171(3)                            | 1.135<br>—<br>1.793  | 1.152(6)<br>   | 1.156(5)<br>                           |
| $\nu$ (CO) in cm <sup>-1</sup> | 2072   | 2027                               | 1995                                | 2085   | 2018   | 2023                                   |

Values derived from structures previously reported by <sup>a</sup> Adeleke et al.<sup>37</sup> <sup>b</sup> Farrugia et al.<sup>38</sup>

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Fe(I)/Fe(II) complex 5 (1.152(6) Å) and the all Fe(I) complex 6 (1.156(5) Å). Due to the charge of 2 being only 1<sup>-</sup>, while 5 and 6 are both  $2^-$  charge. More importantly however, the K<sup>+</sup> in 2 is not encapsulated by a crown complex, instead forming an extended lattice with contacts to several CO ligands, allowing for the donation of some electron density away from the CO  $\pi^*$ orbitals. In fact, compared to the same anion balanced by tetraphenylphosphonium \_ namely,  $(PPh_4)[(\mu-SPh)(\mu-CO)]$  $Fe_2(CO)_6$  – reported by Song *et al.*, cluster 2 has drastically shorter terminal and bridging CO ligands (complex 2: 1.145(4) Å and 1.187(6) Å vs. PPh<sub>4</sub> salt: 1.174 Å and 1.221 Å). As  $K_2[Fe_3(\mu_3-S)(CO)_9]$  has the shared effects of an overall 2<sup>-</sup> charge on the FeS cluster, an all Fe(0) network, and the most negative sulfur donor in the series  $(S^{2-})$ , the CO bond lengths are the longest at 1.171(3) Å.

Notably, the IR data corroborates the conclusions derived from comparing the C=O bond metrics. The two neutral [2Fe-2S] clusters 1 and 4 both exhibit their highest energy CO stretching frequencies at 2072 and 2085 cm<sup>-1</sup> (respectively), which are the highest energy values overall in this set of clusters. Interestingly, the stretching frequencies of the corresponding PPh<sub>4</sub><sup>+</sup> and K<sup>+</sup> supported  $[(\mu-SPh)(\mu-CO)Fe_2(CO)_6]$  are quite similar.<sup>20</sup> However, the K<sup>+</sup>-supported cluster reported herein exhibits shorter CO bond lengths, thus indicating comparatively lower electron density in the CO  $\pi^*$  orbitals. Interestingly, the IR stretches of the bridging carbonyl ligands do not reflect this trend ( $\nu_{C=0}$  PPh<sub>4</sub><sup>+</sup>: 1727 cm<sup>-1</sup>, versus K<sup>+</sup>: 1726 cm<sup>-1</sup>). This discrepancy is possibly due to the differences for complex 2 in the crystalline state with a rigorously encapsulated K<sup>+</sup> ion, whereas the powder sample (ATR-IR) may exhibit a less ordered clathrate; this would decrease the electron density transferred from CO to K<sup>+</sup>. This deviation notwithstanding, the comparative electron density at each metal center can be reasonably inferred from either the crystal structure data or IR data. Complexes 5 and 6 exhibit an intermediate extent of back-bonding, with their highest energy CO stretches at 2018 cm<sup>-1</sup> and 2023 cm<sup>-1</sup>, respectively. Following this, the trimeric, dianionic cluster 3 exhibits highest extent of back-bonding (1995  $\text{cm}^{-1}$ ).

### Summary and conclusions

In closing, we have performed a closed loop of interconversions on a series of reduced, alkali-metal supported ironsulfur-carbonyl clusters. The main conclusions are as follows:

(1) The thermodynamically stable thiolate dimer **1** and persulfide dimer **4** are dominant products in this series of transformations, owing to the stability of the diamagnetic Fe(i)–Fe(i)bonding system and their inability to serve as bidentate ligands to other adventitious iron centers.

(2) The crown/ $K^+$  counterion system is superior in isolating reduced clusters to organic counterions like NEt<sub>4</sub> or PPh<sub>4</sub>, due to both the reductive stability of the  $K^+$  ion and the diverse assortment of commercially available 18-crown-6 and 15-crown-5 reagents.

(3) A number of interconversions between iron–sulfur–carbonyl clusters are possible, including reductive de-alklyation, as well as re-alkylation. The diphenyl iodonium salt  $[Ph_2I]PF_6$ is a particularly useful reagent for mild arylation of ironbound sulfides.

(4) The iron oxidation states and extent of negative charge of the complexes has a predictable effect on the C–O bond lengths in the supporting carbonyl ligands. Alternately, the type of sulfur donor (thiolate, sulfide), nuclearity, and the position and identity of the 'bare'  $K^+$  or  $K^+$ -crown counterion(s) exhibit the dominant effect(s) on the Fe–Fe and Fe–S bond distances.

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