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Diiron Complexes with Pendant Phenol Group(s) as Mimics of the Diiron Subunit of [FeFe]-Hydrogenase: Synthesis, Characterisation, and Electrochemical Investigation

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Four diiron hexacarbonyl complexes, $[Fe_2(\mu-SCH_2-o-C_6H_4OMe)_2(CO)_6]$ (4a), $[Fe_2\{\mu-SCH_2-o,m-C_6H_3(OMe)_2\}_2$ -(CO)₆] (4b), $[Fe_2\{\mu-SCH_2-o,o'-C_6H_3(CO_2Me)(OMe)\}_2(CO)_6]$ (4c) and the demethylated form of complex 4a, $[Fe_2(\mu-SCH_2-o-C_6H_4OH)_2(CO)_6]$ (5a), were synthesised and fully characterised. Complexes 4b and 4c were also structurally analysed. Electrochemical investigations revealed that the integrity of the bridging linkages of the examined diiron complexes significantly affect their reduction reversibility and catalysis through a coupled chemical reaction in a unique ECE mechanism, widely adopted by complexes with the core

Introduction

Hydrogen is a potential energy vector, which is clean and carbon-free since its "combustion" produces only energy without by-products but only water. From water hydrogen could be regenerated at the expense of solar energy under the catalysis of hydrogenases as demonstrated by the principle possessed by photosystem II (PSII). This would be an ideal scenario, sustainable, renewable, and environmentally benign, which is undoubtedly what mankind would like to ideally achieve for our future. [FeFe]-hydrogenase is one of the two metalloenzymes existing in nature, capable of reversibly and rapidly catalysing hydrogen evolution and oxidation.^[1] The crystal structures of the metalloenzymes isolated from Desulfovibrio desulfuricans and Clostridium *pasteurianum*, respectively, were revealed a decade ago.^[2,3] The active site, H-cluster, is composed of one {4Fe4S}-cubane and one {2Fe2S}-subunit, Figure 1. The two iron atoms are bridged by a dithiolate ligand, whose true nature is still under debate,^[2–5] and further coordinated by carbonyl and

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{Fe₂(CO)₄₋₆}. Demethylation of complexes **4a** and **1**Me, [Fe₂(μ -SCH₂)₂CMe(CH₂-o-C₆H₄OMe)(CO)₆], by BBr₃ led to complexes (**5a** and **1**H, [Fe₂(μ -SCH₂)₂CMe(CH₂-o-C₆H₄OH)-(CO)₆]) with pendant phenol group(s), a weak acid. Deprotonation of the two complexes produced the pendant phenolate, which instantly intramolecularly substitutes the bound CO to yield species of the coordination form Fe^I–OR (R = phenolic moiety). Electrochemical investigation revealed that the pendant phenol groups in complexes **1**H and **5a** do not seem to improve their catalytic efficiency in proton reduction in the medium acetic acid/dichloromethane.

cyanide ligands. On the distal iron atom is located the binding site for a substrate, occupied by an exogenous ligand, H_2O or OH^- in its resting state, Figure 1.



Figure 1. The H-cluster of [FeFe]-hydrogenase.

Since the revelation of the detailed structural information of the enzyme, mimicking of the diiron centre has attracted tremendous attention because of the relevance of hydrogen to energy, and a good collection of model complexes containing either a {2Fe2S} or {2Fe3S} core have been reported.^[6-15] Some of those reported synthetic analogues duplicated delicately key structural features found in the Hcluster.^[16-18] But attempts of preparing models to mimic the bonding feature Fe-OH₂(OH⁻) had not been successful^[19–23] because such a bond is doomed to be labile as it is necessary for this bond to be readily cleaved for substrate binding in the enzymatic catalysis. Indeed, we recently reported a model complex, [Fe2(µ-SCH2)2CMe(CH2-o-C₆H₄OH)(CO)₆] (1H), which bears a pendant phenol group, Scheme 1.^[24] Deprotonation of the pendant phenol group led to an unstable diiron pentacarbonyl complex





whose identity was established by FTIR, tandem mass spectrometry and DFT calculations. This was the first example of a model possessing a Fe^{I} -OR (R = phenol moiety) bond.



Scheme 1. Deprotonation of complex 1H and the formation of complex $1\mathrm{H}^{-,[^{24}]}$

Herein, we report four diiron model complexes, $[Fe_2(\mu-SCH_2-o-C_6H_4OMe)_2(CO)_6]$ (4a), $[Fe_2\{\mu-SCH_2-o,m-C_6H_3-(OMe)_2\}_2(CO)_6]$ (4b), $[Fe_2\{\mu-SCH_2-o,o'-C_6H_3(CO_2Me)-(OMe)\}_2(CO)_6]$ (4c) and $[Fe_2(\mu-SCH_2-o-C_6H_4OH)_2(CO)_6]$ (5a), of which the last complex also possesses two pendant phenol groups. All the complexes were fully characterised

and complexes **4b**, **4c** and **5a** were also crystallographically analysed. Deprotonation of complex **5a** produced a species that may have the two phenolate groups coordinated to the two iron atoms, $[Fe_2(\mu-SCH_2-o-C_6H_4O)_2(CO)_4]^{2-}$ (**6a**), as suggested by its infrared spectrum. These complexes in addition to two complexes (1Me and 1H) reported previously^[24] were further electrochemically investigated to probe how the bridging linkage affects the ECE mechanism adopted widely by complexes with a core ({Fe_2(CO)_{4-6}}) in their electron transfer and whether a pendant phenol, a weak acid, would exert any influence on the catalytic reduction of a proton.

Results and Discussion

Synthesis

Complexes **4a–c** were prepared from the reaction of $[Fe_2(\mu-S)_2(CO)_6]$, which was prepared following the literature procedure,^[25] with organic bromides (Schemes 2 and



Scheme 2. Synthesis of the bromides bearing methoxy groups.



Scheme 3. Synthesis of complexes 4a-c and 5a.

3). As show in Scheme 2, the three aromatic bromides were prepared by bromination of derivatives of methylanisol. In these complexes, the phenyl moiety is linked to the dimetallic centre with a methylenethiolate. All the diiron complexes possess six carbon monoxide ligands and show characteristic spectral absorption bands of diiron hexacarbonyl complexes, Table 1. Unlike complex 1H in which the bridging linkage is a dithiolate,^[24] the diiron centre in complexes 4a-c is bridged by two identical monothiolates. Therefore, the organic moieties of the two thiolates can take three possible conformations, syn, syn', and anti, as observed widely in their analogues.^[26-29] In the first conformation, both phenyl rings point away from the diiron centre. The opposite conformation is the syn' form, but it is thermodynamically unfavoured and hardly observed. The most thermodynamically stable form is the anti conformation. The distribution of the two conformations depends on the nature of the organic moiety. The ¹H NMR signals of the methylene groups in the spectra of these complexes can be used to determine the ratio of the two forms (antilsyn). For complexes 4a, 4b and 4c, the ratios are approximately 8:1, 6:1 and 2:1, respectively. Apparently, the *anti* form in complex 4c is more stable relative to those in the other two complexes. This can probably be attributed to the bulkiness of the bridging linkage contributed by the acylmethyl ester as shown in Scheme 2.

Table 1. Infrared absorption bands $[{\rm cm}^{-1}]$ of complexes $4a{\rm -c},~5a$ and 6a.

| Complex | ν _{CO} |
|--------------------------|--------------------------------|
| 4a | 2069.2, 2033.5, 1991.8 |
| 4b | 2069.8, 2033.9, 1993.3 |
| 4c | 2068.6, 2032.9, 1990.8 |
| 5a | 2070.9, 2035.9, 1994.6 |
| 1Me ^[a] | 2072.9, 2032.5, 1999.7, 1990.2 |
| 1H ^[a] | 2073.4, 2032.9, 2000.2, 1990.7 |
| 6a ^[b] | 2020.8, 1993.4, 1944.0, 1909.7 |

[a] Adopted from ref.^[24] [b] In acetonitrile.

By employing the same strategy as we described previously, we used BBr_3 to demethylate complexes 4a-c, but only complex 5a was obtained in a moderate yield.



Figure 2. Infrared spectra of complex 4a (solid line) and its demethylated product 5a (dashed line).

Attempts to prepare complexes **5b** and **5c** were unsuccessful because of the difficulty in purifying the demethylated products. Complexes **4a** and **5a** show the same spectral envelope with a 2 cm⁻¹ "blue" shift after demethylation (Figure 2). This small shift in the infrared absorption bands results from the replacement of the methoxy group by a hydroxy group in the conversion from complexes **4a** to **5a**. But the replacement occurs on the phenyl ring and is far away from the diiron centre, and thus the resultant electronic effect is rather limited.^[24] As in complex **4a**, its demethylated product **5a** possesses two isomers at a rather similar ratio to that in complex **4a**.

Crystallographic Analysis

Diffusion of hexanes into a dichloromethane solutions of complexes **4b** and **4c** and storing of the mixtures at -20 °C for several days afforded dark red crystals of complexes **4b** and **4c** suitable for X-ray single crystal diffraction analysis. Their selected bond lengths and angles are tabulated in Table 2. Figure 3 shows the structural views of the two complexes. Geometries of these complexes show no drastic differences from currently existing diiron hexacarbonyl analogues. Crystals for complex **5a** were also crystallised in a

Table 2. Selected bond lengths [Å] and angles [°] of complexes 4b and 4c.

| and He. | | |
|------------|------------|------------|
| Complex | 4b | 4c |
| Fe1–Fe2 | 2.5174(5) | 2.5224(14) |
| Fe1–S1 | 2.2726(5) | 2.2624(17) |
| Fe1–S2 | 2.2570(5) | 2.2550(18) |
| Fe2–S1 | 2.2706(5) | 2.262(2) |
| Fe2–S2 | 2.2683(5) | 2.2491(17) |
| Fe1–C1 | 1.7990(18) | 1.815(6) |
| Fe1-C2 | 1.7893(18) | 1.773(5) |
| Fe1–C3 | 1.7954(17) | 1.792(5) |
| Fe2–C4 | 1.815(2) | 1.781(6) |
| Fe2–C5 | 1.7883(18) | 1.793(5) |
| Fe2–C6 | 1.788(2) | 1.819(6) |
| C2-Fe1-C3 | 99.22(8) | 90.8(2) |
| C2-Fe1-C1 | 91.10(8) | 97.6(2) |
| C3-Fe1-C1 | 99.11(8) | 100.1(2) |
| C2–Fe1–S2 | 91.25(6) | 94.42(16) |
| C3–Fe1–S2 | 102.75(6) | 156.79(17) |
| C1-Fe1-S2 | 157.34(6) | 101.57(16) |
| C2-Fe1-S1 | 157.97(6) | 156.07(18) |
| C3–Fe1–S1 | 102.61(6) | 85.62(16) |
| C1–Fe1–S1 | 88.34(6) | 106.29(18) |
| S2–Fe1–S1 | 81.167(19) | 80.50(6) |
| S2–Fe1–Fe2 | 56.414(16) | 55.83(5) |
| S1–Fe1–Fe2 | 56.313(13) | 56.12(5) |
| C5–Fe2–C6 | 90.68(9) | 103.3(2) |
| C5–Fe2–C4 | 97.26(9) | 92.1(2) |
| C6–Fe2–C4 | 99.77(10) | 98.6(3) |
| C5–Fe2–S2 | 93.80(6) | 156.61(17) |
| C6–Fe2–S2 | 158.20(7) | 98.63(17) |
| C4–Fe2–S2 | 100.80(6) | 92.64(16) |
| C5–Fe2–S1 | 157.81(6) | 87.26(16) |
| C6–Fe2–S1 | 86.86(7) | 100.77(18) |
| C4–Fe2–S1 | 104.90(6) | 160.2(2) |
| S2–Fe2–S1 | 80.97(2) | 80.62(6) |
| S2-Fe2-Fe1 | 55.987(11) | 56.05(5) |
| S1–Fe2–Fe1 | 56.388(15) | 56.12(5) |



similar procedure to give **5a** \cdot 0.25CH₂Cl₂. But its poor quality gave no satisfactory results in the structure refinements (Table S1 and Figure S1). Nevertheless, an approximate structure was generated, and the structural information revealed that it is essentially analogous to the other two complexes.



Figure 3. Crystal structures of model complexes **4b** (top) and **4c** (bottom) with ellipsoids drawn at a thermal probability of 50% (hydrogen atoms were omitted for clarity reasons).

Coordination of the Phenol Groups in Complex 5a to the Diiron Centre Upon Deprotonation

In our previous report, deprotonation of complex 1H led to the formation of a monoanionic diiron pentacarbonyl complex with a bond between Fe^I and the phenolate.^[24] Complex 5a was treated in the same manner in acetonitrile and a group of neat absorption bands were observed, Figure 4, which accompanied a distinct colour change upon deprotonation from yellow-brown to dark red. Upon addition of an acid (HBF₄·Et₂O) under Ar, about 30% of the parent complex was recovered as estimated from the intensities of the infrared absorption bands, Figure 4. Close inspection of the spectral profile of the product reveals a similarity to those of diiron tetracarbonyl complexes.[23,30-32] Relative to the absorption bands of the parent complex 5a, the absorption bands of the formed product are shifted to lower frequencies by about 85 cm⁻¹ on average. This is comparable to those analogous shifts found for the conversion from hexacarbonyl to tetracarbonyl. By considering the partial recovery of the parent complex and the spectral features of the product upon deprotonation, it is assumed that the two pendant phenolates bind to the diiron centre, probably in a manner shown in Scheme 4. The structure proposed is based on the facts that the anti form is dominant in complexes of this type and that it is not unprecedented that one of the phenolate groups coordinates the iron atom in a basal position rather than in an axial position.^[26,33] Plotting the absorption bands of a known diiron tetracarbonyl complex against the bands of the product produces a linear correlation (Figure S2), which serves as further support for the proposed tetracarbonyl product. Despite our attempts at using bulky organic cations, for example, Ph₄PBr or But₄NBF₄, isolating this product was not successful because of its instability as we observed previously for the monophenolate analogue.^[24]



Figure 4. Infrared spectral variations for the interconversion from complex **5a** (solid line) to the product (presumably **6a**) (dashed line) and its partial recovery after acidification (dotted line).



Scheme 4. Deprotonation of the pendant phenol groups and their possible binding modes to the two iron atoms.

Influence of Substituents of the Phenyl Rings in the Complexes (4a–c, 5a, 1Me, and 1H) on Their Electrochemical Behaviour

It is well understood that the reduction of complexes possessing the core {Fe₂(CO)_n} (n = 4-6) is an ECE process but often appears with one reduction peak or with the second reduction potential slightly more negative than the first.^[23,28,34-35] Indeed, the reduction of the complexes in-

vestigated here followed the proposed ECE mechanism when ferrocene was used as an external standard (data not shown). On the other hand, the redox behaviour of the complexes depends very much on the nature of the bridging linkage of the diiron centre. The complexes examined in this work fall into two categories, that is, complexes 1Me and 1H is in one group, while complexes 4a-c and 5a are in the other. Furthermore, complexes 1H and 5a possess pendant phenol groups, whereas in complexes 1Me and 4a-c, these phenols are methylated. The variation of these bridging linkages in both bulkiness and whether the two bridging thiolates are from an integrated multidentate ligand or two monothiolates makes these diiron complexes suitable for investigating the correlation between their electrochemical properties and the bridging moieties. Particularly, the pendant phenol group shows structural flexibility in its ability to coordinate to the diiron centre upon deprotonation as discussed above. Therefore, the pairs of complexes 1Me/1H and 4a/5a can be appropriate systems to examine how the pendant phenol group affects their electrochemical reduction and hence their catalysing proton reduction, i.e., whether this internal weak acid (pendant phenol) plays any role in the catalysis of proton reduction. Such a correlation would have particular interest with regard to guiding the designing and assembling of novel artificial analogues for the subunit of the [FeFe]-hydrogenase.

Because some of the complexes are not sufficiently soluble in acetonitrile, all the complexes, 4a-c, 5a, 1Me and 1H were electrochemically examined in dichloromethane, and their redox potentials are tabulated in Table 3. Their redox processes are shown in Figures 5 and S3. In general, the redox potentials are related to the capability of electron donation of the bridging linkages. It is interesting to note the difference between the reduction peak potential and the oxidation peak potential of the investigated complexes, $^{\rm red}E_{\rm c}$ – $^{\rm ox}E_{\rm a}$, as shown in Table 3. The potential differences are significantly affected by the replacement of a methoxy group by a hydroxy group and much less by the variation in the bridging linkages, although fluctuations in both reduction and oxidation potentials with the linkages are obvious. For complexes 4a-c and 1Me, the potential difference is about 2.3 V, whereas for complexes 5a and 1H, which were derived from demethylation of their parent complexes, the potential difference is about 2.1 V. Since reduction and oxidation potentials are directly correlated to the energy

Table 3. Redox potentials [V] of complexes 4a-c, 5a, 1Me and 1H in dichloromethane.

| Complex | Reduction, $E_{\rm c}/E_{\rm a}$ | Oxidation, $E_{a}^{[a]}$ | $^{\rm red}E_{\rm c}-{}^{\rm ox}E_{\rm a}$ |
|---------|----------------------------------|-----------------------------|--|
| 4a | -1.656 ^[b] | 0.629 | -2.29 |
| 4b | -1.618 ^[b] | 0.731 | -2.35 |
| 4c | -1.740 ^[b] | 0.596 | -2.34 |
| 5a | -1.501 ^[b] | 0.635, 0.879 ^[c] | -2.14 |
| 1Me | -1.550/-1.477 | 0.857 | -2.33 |
| 1H | -1.508/-1.386 | 0.767 | -2.15 |

[a] Irreversible oxidation. [b] Irreversible reduction. [c] From a daughter product and is not used in the calculation of the potential difference.

levels of HOMO and LUMO of a molecule, respectively, these observations imply that the hydroxy groups decrease the energy gap between the frontier orbitals more than that observed for the non-hydroxy groups. It is certain that the hydroxy groups electronically influence the redox potentials, but exactly how the hydroxy groups exert the influence on the frontier orbitals is hard to explain without further theoretical exploration.



Figure 5. Reduction behaviour of complex 4a–c, 5a (top) and 1Me and 1H (bottom) in dichloromethane (scan rate = 0.1 V s^{-1} , 298 K).

The bridging linkages of the complexes not only exert an electronic influence on the redox potentials, but also affect the reversibility of the reduction processes. As shown in Figure 5, under the same conditions, complexes 1Me and 1H exhibit decent reversibility, whereas for the others, no reversibility was observed. As mentioned earlier, the reduction of the diiron complexes follows a unique ECE mechanism. The results observed in this work further shed some light on the nature of the coupled chemical reaction. It seems that one of the two bridging thiolate groups might entirely de-coordinate in this chemical reaction. If this is the case, the fact that the reversibility varies with the bridging linkage can be explained. In complexes 1Me and 1H, the dithiolate that bridges the two iron atoms is an integrated bidentate ligand, which allows the de-coordinated

thiolate to dangle around and re-coordinate to the metal centre when necessary. However, in the other complexes, such a de-coordination would lead to a permanent departure of the de-coordinated thiolate group.

By considering the different reduction behaviours between the two categories of diiron complexes (Figure 5), it is not surprising that they respond rather differently upon the addition of an acid (acetic acid). Figure 6 shows the catalytic reduction of a proton by complex 4a. As suggested by their cyclic voltammograms (Figures S4 and S5), the catalysis of the other two analogues (4b and 4c) is essentially similar to that of complex 4a. For complex 1Me, catalysis occurs at a potential more negative by ca. 300 mV relative to the reduction potential of the first process, which is hardly affected by the addition of the acid (Figure 7). This is rather different from the catalysis by complexes 4a-c (Figures 6, S4 and S5). The experimental observations support the suggestion that the monoanion generated from the first one-electron reduction is not responsible for the catalysis.^[23] The striking difference in catalytic potentials for the two categories of complexes is thought to be associated with the difference in the chemical reaction coupled with the electron-transfer process as discussed above.



Figure 6. Cyclic voltammograms of complex 4a ($C = 3.30 \text{ mmol } \text{L}^{-1}$) without and with the addition of acetic acid in dicholormethane (scan rate = 0.1 Vs⁻¹, 298 K).

As indicated by the redox potentials in Table 3, demethylation causes noticeable variation in the energies of the frontier orbitals for the pairs of complexes 4a and 5a, 1Me and 1H. However, with regard to their catalysis, no essential difference is observed for these complexes (Figures 6, 7, S6 and S7). The only noticeable difference observed is the neat cyclic voltammograms observed for the complexes without pendant phenol groups (4a–c and 1Me). This can probably be attributed to the adsorbing preference on the surface of a vitreous carbon electrode possessed by species with phenol groups as the surface of a vitreous carbon electrode is rich in functional groups, for instance, hydroxy and carboxylic groups. However, the presence of a pendant phenol group does not lead to a significant change in the catalytic efficiency of proton reduction (Figures S8 and S9).



Figure 7. Cyclic voltammograms of complex 1Me ($C = 3.24 \text{ mmol } \text{L}^{-1}$) without and with the addition of the acid in dichloromethane (scan rate = 0.1 V s^{-1} , 298 K).

Conclusions

In this work, four diiron hexacarbonyl complexes, 4a-c and 5a, in addition to two complexes 1Me and 1H reported previously,^[24] were investigated electrochemically without and with the presence of acetic acid in dichloromethane. These complexes are believed to adopt the unique ECE mechanism for electron transfer, in which the potential for the second reduction could be either more positive or marginally more negative than the first one. Our results also show that the bridging linkages of the diiron complexes significantly affect the chemical reaction coupled to the first electron-transfer process. When the two thiolate groups are from two monothiolates, the coupled chemical reaction may be associated with the partial deconstruction of the diiron moiety, for example, the permanent cleavage of one of the two thiolates. Such a destruction is much less significant for complexes 1Me and 1H, as suggested by their quasireversible reductions; the bidentate ligand certainly made the difference. Demethylation of complexes 4a and 1Me led to complexes (5a and 1H) with pendant phenol group(s). However, this pendant weak acid does not seem to exert much influence on the catalysis of proton reduction.

Experimental Section

General Procedures: All reactions were carried out under an argon atmosphere by using standard Schlenk technique. Solvents for reactions and electrochemistry were freshly distilled by using appropriate drying agents prior to use. Infrared spectroscopic data were collected on a Scimitar 2000 (Varian) instrument in an appropriate solvent by using a solution cell (spacer = 1 mm). NMR spectra were recorded on an Avance DRX-400 or–600 (Bruker) instrument. Electrochemistry was performed as described elsewhere.^[23,28,33,36] All potentials were quoted against the ferrocenium/ferrocene couple, F_C^+/F_C . The microanalysis service was provided by the Centre of Analysis and Testing at Nanchang University and Nanjing University.

Synthesis

Preparation of $[Fe_2(\mu-S)_2(CO)_6]$: After being flushed with Ar, a three-necked round-bottomed flask (1 L) was charged with Fe-(CO)₅ (25 mL, 186 mmol), followed by dry MeOH (125 mL) and finally freshly prepared aqueous KOH (75 mL, 75%). After stirring for 30 min, the homogeneous solution was cooled to ice temperature in an ice bath, and then S_8 (33 g, 1.03 mol) was slowly added. After the addition and further stirring for 1 h, the reaction mixture was treated with H₂O (250 mL), hexanes (150 mL), and finally NH_4Cl (85 g, 1.6 mol). The ice bath was then removed, and the reaction solution was stirred at room temperature for an additional 16 h. The reaction mixture was then extracted with petroleum ether $(4 \times 200 \text{ mL})$. The extracts were combined, and the solvents were removed to give a crude product, which was purified by using flash chromatography (eluent: petroleum ether) to produce a red solid (9.7 g, 30%). Mp: 46–47 °C. IR [acetonitrile]: $v_{CO} = 2084.0, 2041.8,$ 2002.7 cm^{-1} .

Synthesis of 2-Methylanisol, 2a: A stirred suspension of NaH (6.0 g, 150 mmol, 60% dispersion in mineral oil) in dry THF (120 mL) was cooled to ice temperature in an ice bath. To the suspension was slowly added a solution of *o*-cresol (1a, 10.8 g, 100 mmol) in dry THF (20 mL). When there was no more hydrogen gas evolving, CH₃I (7.2 mL, 115 mmol) was added dropwise. The reaction mixture was warmed to 85 °C and stirred overnight. Completion of the reaction was confirmed by using TLC (petroleum ether/ethyl acetate = 10:1). After removal of the solvent, water (50 mL) was added. After extraction with ethylacetate (3 × 50 mL) and purification by column chromatography (petroleum ether/ethyl acetate, 10:1), the desired compound was obtained as a colourless liquid (11.8 g, 97%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.16 (m, 2 H, Ar*H*), 6.84 (m, 2 H, Ar*H*), 3.82 (s, 3 H, OC*H*₃), 2.22 (s, 3 H, C*H*₃) ppm.

Synthesis of 1,4-Dimethoxy-2-methylbenzene, 2b: Compound 2b was synthesised in the same procedure as described above for compound 2a by using 2-methylhydroquinone (6.3 g, 50 mmol), NaH (6 g, 150 mmol), 60% dispersion in mineral oil) and CH₃I (10 mL, 150 mmol). It was isolated as a colourless liquid (6.8 g, 88%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 6.59-6.69$ (m, 3 H, ArH), 3.69 (s, 3 H, OCH₃), 3.66 (s, 3 H, OCH₃), 2.18 (s, 3 H, CH₃) ppm.

Synthesis of Methyl(3-methoxy-2-methyl)benzoate (2c): 3-Hydroxy-2-methylbenzoic acid (1c, 3.2 g, 20 mmol) was dissolved in dry MeOH (20 mL, 500 mmol) and mixed with concentrated H₂SO₄ (2 mL, 35.5 mmol, 95%). The solution was heated at reflux overnight. Removal of the solvents gave a residue to which water (30 mL) was then added. Extraction with ethyl acetate (3 × 30 mL) and routine work-up gave compound 2c as a colourless liquid (3.3 g, 95%) without further purification for the next reaction. ¹H NMR (CDCl₃, 400 MHz): δ = 7.30 (d, *J* = 7.76 Hz, 1 H, Ar*H*), 7.07 (t, *J* = 7.98 Hz, 1 H, Ar*H*), 6.86 (d, *J* = 8.12 Hz, 1 H, Ar*H*), 4.53 (s, 2 H, *CH*₂), 3.77 (s, 3 H, COOC*H*₃), 3.71 (s, 3 H, OC*H*₃), 2.33 (s, 3 H, *CH*₃) ppm.

Synthesis of 2-Bromomethylanisol (3a): A solution of compound 2a (7.3 g, 60 mmol), NBS (10.7 g, 60 mmol) and AIBN (160 mg, 1 mmol) in CCl₄ (250 mL) was heated at reflux for about 1 h until a white solid was floating on the surface. The mixture was filtered, and the filtrate was then concentrated under reduced pressure to produce a residue. Recrystallisation of the residue in hexanes afforded a white solid (11.5 g, 93%). Mp: 47–50 °C. ¹H NMR (CDCl₃, 600 MHz): δ = 7.30 (m, 2 H, Ar*H*), 6.93 (m, 1 H, Ar*H*), 6.88 (m, 1 H, Ar*H*), 4.57 (s, 2 H, 2 × CH*H*), 3.88 (s, 3 H, OC*H*₃) ppm. ¹³C NMR (CDCl₃, 600 MHz): δ = 157.45, 130.89, 130.21, 126.07, 120.67, 110.95, 55.57, 29.06 ppm.

Synthesis of 1,4-Dimethoxy-2-bromomethylbenzene (3b): Compound 3b was prepared by following the same experimental procedure described for compound 3a by using compound 2b (6.1 g, 40 mmol), NBS (7 g, 40 mmol) and AIBN (160 mg, 1 mmol). The compound was obtained as a needle-shaped crystalline solid (8.5 g, 92%). Mp: 71–73 °C. ¹H NMR (CDCl₃, 600 MHz): $\delta = 6.89$ (d, J = 2.4 Hz, 1 H, ArH), 6.79–6.83 (m, 2 H, ArH), 4.53 (s, 2 H, CH₂), 3.84 (s, 3 H, OCH₃), 3.76 (s, 3 H, OCH₃) ppm.

Synthesis of Methyl(3-methoxy-2-bromomethyl)benzoate (3c): The same procedure was adopted to produce compound 3c as a white solid (4.5 g, 96%) by using compound 2c (3.3 g, 18 mmol), NBS (3.3 g, 18 mmol) and AIBN (60 mg, 0.4 mmol) in CCl₄ (160 mL). Mp: 112–114 °C. ¹H NMR (CDCl₃, 600 MHz): δ = 7.05 (m, 1 H, Ar*H*), 7.32 (t, *J* = 8.1 Hz, 1 H, Ar*H*), 7.06 (d, *J* = 8.4 Hz, 1 H, Ar*H*), 5.0 5 (s, 2 H, C*H*₂), 3.92 (s, 3 H, COOC*H*₃), 3.91 (s, 3 H, OC*H*₃) ppm.

Synthesis of [Fe₂(μ -SCH₂-o-C₆H₄OMe)₂(CO)₆] (4a): A solution of [Fe₂(μ -S)₂(CO)₆] (1.2 g, 3.5 mmol) in dry THF (60 mL), precooled to $-78 \,^{\circ}$ C with a dry-ice/acetone bath, was treated with LiBHEt₃ (7 mL, 1 mol L⁻¹ in dry THF). After stirring the mixture for 30 min, compound **3a** (1.4 g, 7.0 mmol) was added. The mixture was stirred at $-78 \,^{\circ}$ C for 30 min and was then warmed to room temperature for an additional 2 h. Removal of the solvent produced a crude product, which was purified by using flash chromatography (petroleum ether/ethyl acetate, 20:1) to give a red solid (1.6 g, 78%). Mp: 141–142 °C. IR [dichloromethane]: $v_{CO} = 2069.2$, 2033.5, 1991.8 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta = 6.77-7.33$ (m, 9 H, Ar*H*, *antilsyn* ratio 8:1), 3.94 (s, 3 H, *anti*-OCH₃), 3.84 (s, 0.75 H, *syn*-OCH₃), 3.71 (s, 3 H, *anti*-OCH₃), 3.67 (s, 2 H, *anti*-CH₂), 3.61 (s, 0.5 H, *syn*-CH₂), 3.25 (s, 2 H, *anti*-CH₂) ppm. C₂₂H₁₈Fe₂O₈S₂ (586.19): calcd. C 45.08, H 3.10; found C 44.94, H 3.29.

Synthesis of $[Fe_2\{\mu$ -SCH₂C₆H₃(OMe)₂ $\}_2(CO)_6]$ (4b): Complex 4b was prepared from $[Fe_2(\mu-S)_2(CO)_6]$ (1.05 g, 3 mmol), LiBHEt₃ (6 mL, 1 M in dry THF) and compound **2b** (1.5 g, 6 mmol) following the same procedure used to prepare complex 4a. Complex 4b was obtained as a red solid (1.2 g, 63%). Mp: 136-137 °C. IR [dichloromethane]: $v_{CO} = 2069.8$, 2033.9, 1993.3 cm⁻¹. ¹H NMR (CDCl₃, 600 MHz): δ = 6.56–6.92 (m, 6 H, ArH, antilsyn 6:1), 3.89 (s, 3 H, anti-OCH₃), 3.81 (s, 3 H, anti-OCH₃), 3.81 (s, 1 H, syn-OCH₃), 3.75 (s, 1 H, syn-OCH₃), 3.70 (s, 3 H, anti-OCH₃), 3.65 (s, 3 H, anti-OCH₃), 3.63 (s, 2 H, anti-CH₂), 3.58 (s, 0.63 H, syn-CH₂), 3.23 (s, 2 H, anti-CH₂) ppm. ¹³C NMR (CDCl₃, 600 MHz): δ = 209.98, 208.86, 153.56, 153.46, 153.28, 151.61, 151.45, 151.28, 128.61, 127.98, 127.68, 116.45, 116.10, 115.77, 114.17, 113.96, 113.75, 111.78, 111.60, 111.54, 55.80.55.78, 55.70, 55.63, 55.56, 55.43, 38.28, 36.83, 31.60, 23.85 ppm. C₂₄H₂₂Fe₂O₁₀S₂ (646.26): calcd. C 44.60, H 3.43; found C 44.46, H 3.30.

Synthesis of [Fe₂{μ-SCH₂C₆H₃(COOMe)OMe}₂(CO)₆] (4c): Complex 4c was synthesised as described for 4a from $[Fe_2(\mu-S)_2(CO)_6]$ (1.2 g, 3.6 mmol), LiBHEt₃ (7 mL, 1 M in dry THF) and compound 3c (1.8 g, 7 mmol) as a red solid (1.6 g, 65%). Mp: 174–176 °C. IR [dichloromethane]: $v_{CO} = 2068.6$, 2032.9, 1990.8 cm⁻¹. ¹H NMR (CDCl₃, 600 MHz): $\delta = 7.56$ (d, J = 7.2 Hz, 1 H, *anti*-ArH), 7.46 (d, J = 7.2 Hz, 1 H, *syn*-ArH), 7.37 (d, J = 7.2 Hz, 1 H, *anti*-ArH), 7.33 (t, J = 7.8 Hz, 1 H, *anti*-ArH), 7.25 (t, J = 9.6 Hz, 1 H, *syn*-ArH), 7.21 (t, J = 7.8 Hz, 1 H, *anti*-ArH), 7.10 (d, J = 8.4 Hz, 1 H, *anti*-ArH), 7.00 (d, J = 7.8 Hz, 1 H, *syn*-ArH), 7.90 (d, J = 8.4 Hz, 1 H, *anti*-ArH), 7.00 (d, J = 8.4 Hz, 1 H, *anti*-ArH), 7.00 (d, J = 8.4 Hz, 1 H, *anti*-ArH), 7.90 (d, J = 8.4 Hz, 1 H, *anti*-ArH), 167.52, 167.43, 167.21, 157.79, 157.55, 157.45, 131.33, 130.57, 130.24, 129.74, 129.17, 128.52, 128.42, 128.35, 128.11, 122.89, 122.85, 122.59, 114.01, 113.83, 55.60, 55.51, 55.16,



52.29, 52.18, 52.12, 34.47, 32.35, 21.42 ppm. $C_{26}H_{22}Fe_2O_{12}S_2$ (702.28): calcd. C 44.47, H 3.16; found C 44.62, H 3.53.

Synthesis of [Fe₂(µ-SCH₂-o-C₆H₄OH)₂(CO)₆] (5a): To a precooled solution of $[Fe_2(\mu$ -SCH₂C₆H₄OCH₃)₂(CO)₆] (680 mg, 1.16 mmol) in dry dichloromethane (50 mL) in a dry-ice/acetone bath was added a solution of BBr₃ (1 mol L⁻¹, 5 mL) in dry dichloromethane under argon. After the addition, the reaction mixture was stirred at -78 °C for 2 h and then warmed to room temperature for an additional 6 h. The reaction mixture was cooled in an ice bath, and methanol (2 mL) was slowly added to quench the reaction. Removal of the solvents left a residue, which was purified by using flash chromatography in a gradient eluting manner (petroleum ether/ethyl acetate, 10:1, 8:1 and 5:1) to give a dark red solid (377 mg, 58.2%). Mp: 138 °C. IR [dichloromethane]: $v_{CO} = 2070.9$, 2035.9, 1994.6 cm⁻¹. ¹H NMR (CDCl₃, 600 MHz): $\delta = 6.75-7.27$ (m, 9 H, ArH, anti/syn 8:1), 5.34 (s, 1 H, anti-PhOH), 5.25 (s, 1 H, anti-PhOH), 5.08 (s, 0.25 H, syn-PhOH), 3.70 (s, 2 H, anti-CH₂), 3.63 (s, 0.5 H, syn-CH₂), 3.26 (s, 2 H, anti-CH₂) ppm. C₂₀H₁₄Fe₂O₈S₂ (558.14): calcd. C 43.04, H 2.53; found C 42.65, H 2.71.

Deprotonation of Complex 5a: To NaH (60% in oil, 13.2 mg, 0.33 mmol) in a Schlenk tube precooled with an ice bath was added a solution of complex **5a** (40 mg, 0.079 mmol) in dry acetonitrile (5 mL) under rapid stirring. The colour of the solution changed quickly from yellow–brown to dark red. The reaction was complete within 2 h, as confirmed by infrared spectroscopic monitoring. IR [acetonitrile]: $v_{CO} = 2020.8$, 1993.4, 1944.0, 1909.7 cm⁻¹.

X-ray Single-Crystal Diffraction: Standard procedures were used for mounting the crystals on a Bruker 98 APEX2 area-detector diffractometer at 296(2) K. The crystals were routinely wrapped with paraffin oil before being mounted. Intensity data were collected by using Mo-Ka radiation ($\lambda = 0.71073$ Å) under 296(2) K with a ϕ - and ω -scan mode. The SAINT and SADABS programs in the APPEX(II) software package were used for integration and absorption correction. The structures were solved by using direct methods with the SHELXS-97 program and refined on F^2 with XSHELL6.3.1; all non-hydrogen atoms were anisotropically modelled. All hydrogen atoms were geometrically positioned. Crystallo-

Table 4. Crystallographic data and processing parameters for complexes **4b,c**.

| Complex | 4b | 4c | |
|--|--|--|--|
| Empirical formula | C ₂₄ H ₂₂ Fe ₂ O ₁₀ S ₂ | C ₂₆ H ₂₂ Fe ₂ O ₁₂ S ₂ | |
| Fw | 646.26 | 702.28 | |
| <i>T</i> / K | 296(2) | 296(2) | |
| Crystal system | triclinic | triclinic | |
| Space group | $P\overline{1}$ | $P\overline{1}$ | |
| a [Å] | 8.9004(17) | 11.018(8) | |
| b [Å] | 9.5959(18) | 11.061(8) | |
| c [Å] | 17.285(4) | 13.150(9) | |
| | 101.806(3) | 88.948(8) | |
| b [°] | 95.464(3) | 79.530(9) | |
| | 107.528(2) | 70.571(8) | |
| $V/Å^3$ | 1358.3(5) | 1484.6(18) | |
| Ζ | 2 | 2 | |
| $q_{\rm calcd} / \rm g cm^{-3}$ | 1.580 | 1.571 | |
| F(000) | 660 | 716 | |
| Reflections collected (unique) | 12866(6842) | 12625(7290) | |
| Reflections [<i>R</i> _{int}] | 6842(0.0170) | 7290(0.0282) | |
| Goodness-of-fit on F^2 | 1.017 | 1.073 | |
| Final $R_1^{[a]}$ [I > 2 $\sigma(I)$] | 0.0264 | 0.0583 | |
| Final $wR_2^{[a]}$ | 0.0684 | 0.1350 | |
| $\boxed{\begin{bmatrix} 1 & D & -\sum \ E\ & \ E\ / \sum \ E\ and \end{bmatrix}}$ | $m D = \Gamma \Sigma (1E^2)$ | $= 21)2/\Sigma(\dots E 2)211/2$ | |

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ and $wR_2 = [\sum (|F_0^2 - F_c^2|)^2 / \sum (wF_0^2)^2]^{1/2}$.

graphic details of these complexes are summarised in Table 4. CCDC-795447 (**4b**), -795448 (**4c**) and -795449 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic data, the structural view of complex **5a**, further spectroscopic data and cyclic voltammograms are included.

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