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Improved Access to 'Butterfly' Di-Iron Dithiolates $Fe_2(\mu\text{-}SR)_2(CO)_6$ and their Mono- and Bis(phosphine) Adducts

Atheer M. Madlool,[a] Grace E. Wingrove,[a] Ben J. Paran Rutterford,[a] Ahmad Malik,[a] Heather K. Butcher,[a] and Joseph A. Wright*[a]

A series of $Fe_2(\mu\text{-}SR)_2(CO)_6$ complexes {R=Me ($\mathbf{1}^{Me}$), Et ($\mathbf{1}^{Et}$), Pr ($\mathbf{1}^{Pr}$), *i*Pr ($\mathbf{1}^{iPr}$), *t*Bu ($\mathbf{1}^{tBu}$), $PhCH_2$ ($\mathbf{1}^{Bn}$) and Ph ($\mathbf{1}^{Ph}$)} have been synthesised. Complexes $\mathbf{1}^{Me}$, $\mathbf{1}^{tBu}$, $\mathbf{1}^{Bn}$ and $\mathbf{1}^{Ph}$ were produced by addition of S_2R_2 to $Fe_3(CO)_{12}$, with all but $\mathbf{1}^{tBu}$ giving excellent yields. Two isomers of $\mathbf{1}^{Me}$ and $\mathbf{1}^{Ph}$ were isolated: the *anti*- and 'open' *syn*-products. Complexes $\mathbf{1}^{Et}$, $\mathbf{1}^{Pr}$ and $\mathbf{1}^{iPr}$ were synthesised by treatment of RSH with $Fe_3(CO)_{12}$; two isomers of each complex were isolated. Addition of one equivalent of PR'$_3$ (R' = Me, Cy, Ph) yields the corresponding mono(phosphine) adducts, whilst use of two equivalents of the phosphine (under mild condition, reflux, or irradiation using a deep blue LED depending on SR group) affords the corresponding bis(phosphine) adducts in good to excellent yield. Treatment of $\mathbf{1}^{Ph}$ or $\mathbf{1}^{Me}$ with two equivalents of PMe_3 gives the corresponding bis-substituted phosphines when carried out in the absence of light but leads to oxidative cleavage to $Fe(\mu\text{-}SPh)_2(PMe_3)_2(CO)_2$ and $Fe(\mu\text{-}SMe)_2(PMe_3)_2(CO)_2$, respectively, under blue light irradiation. Treatment of $\mathbf{1}^{Pr}$ with two equivalents of PCy_3 under blue light irradiation leads to reductive breakdown of the Fe–Fe bond to yield $Fe(CO)_3(PCy_3)_2$, but in the dark at room temperature the desired product $Fe_2(\mu\text{-}SPr)_2(PCy_3)_2(CO)_4$ may be isolated. Single crystal X-ray structures were obtained for most family members of 'butterfly' $\{Fe_2S_2\}$ cores. Cyclic voltammetry shows PMe_3-containing complexes undergo irreversible oxidation, whereas both PCy_3 and PPh_3 complexes show one (quasi)reversible oxidation, IR of *in situ* protonation showed CO_v blue shifting around 80–100 cm^{-1}, while $^{31}P\{^1H\}$ NMR spectroscopy showed shifting to low field.

Introduction

Alternatives to classical fossil fuels continue to attract significant interest in the scientific community, with dihydrogen as one of the leading examples. For H_2 to deliver on its potential to be one of the 'clean' fuels projected for future use, efficient, scalable, and sustainable methods for generating the gas are required. Whilst platinum-based methods are potentially very efficient, they are neither scalable nor sustainable. Similarly, steam reforming fossil fuels to generate hydrogen simply moves the unsustainable chemistry from the point of use to point of generation. In contrast, the [FeFe]-hydrogenases can produce dihydrogen by proton reduction using only earth-abundant metals and (in principle) without needing any fossil fuel input.[1,2] The challenge is therefore to take this biological chemistry and mimic it in small, scalable, synthetic systems.[3]

Whilst accessing fully elaborated models for the core of the [FeFe]-hydrogenase requires a significant amount of imaginative chemistry, routes to $Fe_2(\mu\text{-}SR)_2(CO)_6$, particularly where there is a bridge between the sulfur atoms, are more tractable. These hexacarbonyl complexes are not sufficiently electron-rich to undergo protonation with typical mineral or organic acids, although they can be protonated using super-acids. Introduction of electron-donating ligands, particularly phosphines, increases the reactivity of the metal centres.

To date, most research efforts have been directed toward sulfur-bridged synthetic models, primarily as they are closer to the structure of the enzyme. This area has been extensively reviewed, and the interested reader is directly to the many excellent articles covering the 'butterfly' systems.[4,5] However, there is now increasing interest in the 'open' (unbridged) analogues, which may offer unique reactivity, and which are also potential starting materials for novel chemistry in their own right.[6–10]

Complexes of general formula $Fe_2(\mu\text{-}SR)_2(CO)_6$ have been synthesised by many methods: (*i*) treatment of $Fe_3(CO)_{12}$ with RSH derivatives in several hydrocarbon solvents with reflux[11] or photochemically,[12] (the mechanism is believed to involve formation of $Fe_3(CO)_9(H)(RS)$[13]) (*ii*) the Hieber-Gruber reaction,[14] (*iii*) treatment of $(C_5H_4SPh)_2Fe$ with $Fe_2(CO)_9$ under photolytic conditions,[15] (*iv*) reduction of $Fe_2(\mu\text{-}S)_2(CO)_6$by Na or KH followed by treatment with alkyl halide to give the corresponding derivatives,[16] (*v*) treatment of $Fe(CO)_5$ with RSH or RSSR under CO atmosphere,[17] and (*vi*) King's method by the reaction of RSSR with $Fe_3(CO)_{12}$ under reflux.[18]

Here, we have explored optimisations of King's method and subsequent introduction of phosphine in 'open' systems featuring aromatic and the aliphatic groups at the sulfur centres, and the effect of phosphine substituted on structural parameters, carbonyl stretching, and voltammetry. In our hands,

[a] Dr. A. M. Madlool, G. E. Wingrove, B. J. Paran Rutterford, A. Malik, H. K. Butcher, Dr. J. A. Wright
Energy Materials Laboratory, School of Chemistry, University of East Anglia, Norwich Research Park, NR4 7TJ Norwich, United Kingdom
E-mail: joseph.wright@uea.ac.uk

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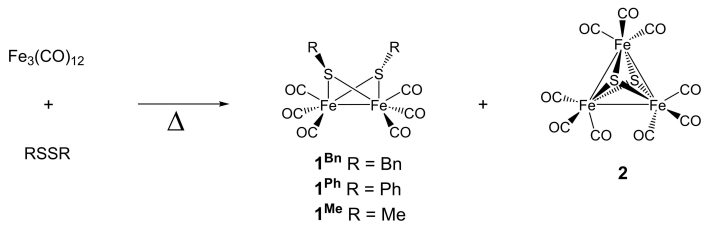
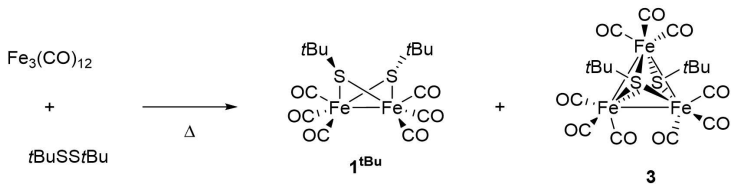


Scheme 1. Synthesis of complexes $\mathbf{1}^{Me}$, $\mathbf{1}^{Ph}$ and $\mathbf{1}^{Bn}$; reactions took place in THF at reflux and were monitored by IR spectroscopy.



Scheme 2. Synthesis of $\mathbf{1}^{tBu}$; reaction took place in THF at reflux and was monitored by IR spectroscopy.

the use of King's approach gave the highest yields of reliably pure material.

Results and Discussion

Synthesis of $Fe_2(\mu\text{-}SR)_2(CO)_6$

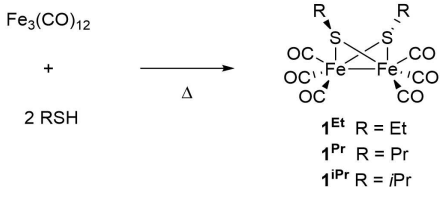
To study the effect of open aliphatic and aromatic substituted thiolate bridging of {2Fe2S} 'butterfly' systems, King's method was utilised to prepare $Fe_2(\mu\text{-}SR)_2(CO)_6$ (**1**) (R=Me, Et, Pr, *i*Pr, *t*Bu, Ph, CH_2Ph). Compounds $Fe_2(\mu\text{-}SMe)_2(CO)_6$ ($\mathbf{1}^{Me}$) $Fe_2(\mu\text{-}StBu)_2(CO)_6$ ($\mathbf{1}^{tBu}$), $Fe_2(\mu\text{-}SBn)_2(CO)_6$ ($\mathbf{1}^{Bn}$) and $Fe_2(\mu\text{-}SPh)_2(CO)_6$ ($\mathbf{1}^{Ph}$) were synthesised by reaction of $Fe_3(CO)_{12}$ with the appropriate dialkyl disulfide under reflux (Scheme 1). In the case of $\mathbf{1}^{Me}$ and $\mathbf{1}^{Ph}$, two isomers could be identified by thin layer chromatography (TLC). Separation of the two required that the reaction was carried out with a starting material ratio of 1:1, to avoid contamination by unreacted disulfide. This yielded *anti*-**1** (one R 'up', one 'down') as the major isomer in a ratio of around 9:1 to the *syn* isomer (both R groups 'down') in $\mathbf{1}^{Ph}$, and 3:1 in $\mathbf{1}^{Me}$. IR spectroscopy could distinguish the two isomers of $\mathbf{1}^{Ph}$, with a diagnostic peak at 1943 cm^{-1} for the *syn* isomer contrasting with one at 1979 cm^{-1} in the *anti* product. However, IR shows identical CO stretches for the two isomers of $\mathbf{1}^{Me}$, likely due to the small size of the methyl substituent. Proton NMR spectroscopy of *anti*-$\mathbf{1}^{Me}$ in $CDCl_3$ shows a singlet at δ 1.54 ppm arising from the axial Me group, with the equatorial methyl groups exhibiting a signal at δ 2.07 ppm. The *syn* isomer in contrast shows a singlet at δ 2.03 ppm. The identities of both isomers were unambiguously confirmed by X-ray crystallography, in accord with previous reports of synthesis $\mathbf{1}^{Me}$ and $\mathbf{1}^{Ph}$.[19,20] In contrast to earlier reports,[21] in our hands the isolated by-product of the hexacarbonyl synthesis of $\mathbf{1}^{Me}$, $\mathbf{1}^{Ph}$ and $\mathbf{1}^{Bn}$ was the tri-iron complex **2**.

The synthesis of $\mathbf{1}^{tBu}$ was best achieved by reaction of $Fe_3(CO)_{12}$ with two equivalents of $(tBuS)_2$ under reflux for 30 minutes. This led to isolation of three separate red products in addition to recovery of starting material: purification by column chromatography gave $\mathbf{1}^{tBu}$ in 30% yield and $Fe_3(\mu\text{-}tBuS)_2(CO)_9$ (**3**) in 17% yield, along with 10% of recovered $Fe_3(CO)_{12}$ and an unidentified brown solid material which did not elute under the conditions used (Scheme 2). Refluxing pure **3** in THF for 30 min produced $\mathbf{1}^{tBu}$ in around 65% yield, and a brown precipitate similar to that seen in the direct reaction, suggesting that **3** is an intermediate on the reaction pathway.

Treatment of $Fe_3(CO)_{12}$ with two equivalents of RSH was the most effective route to the complexes $\mathbf{1}^{Et}$, $\mathbf{1}^{Pr}$, and $\mathbf{1}^{iPr}$, all of which were obtained in excellent yield (Scheme 3). Two isomers were observed for each of these materials, in *syn*:*anti* ratios of 3:1, 4:1 and 4:1, respectively. Proton NMR spectroscopy showed that the axial and equatorial alkyl group signals can be distinguished, which can clearly be attributed to the increasing of shielding due to the steric effect (see Supporting Information).

Synthesis of mono-substituted phosphine derivatives

Replacement of the CO groups in $Fe_2(\mu\text{-}SR)_2(CO)_6$ is of broad interest as it allows control of the electronic properties of the iron centres, in particular in mimicking the active side of [FeFe]-hydrogenase enzymes.[1,2,20,21] Mono-substituted phosphine {2Fe2S} complexes are normally synthesised by using



Scheme 3. Synthesis of $\mathbf{1}^{Et}$, $\mathbf{1}^{Pr}$, and $\mathbf{1}^{iPr}$; reactions took place in THF at reflux and were monitored by IR spectroscopy.

$Me_3NO \cdot 2H_2O$ as decarbonylation reagent;[22–24] these reactions are typically carried out at room temperature. However, reaction of **1** proceeded without the need for active decarbonylation, irrespective of the alkyl substituent involved. Addition of one equivalent of phosphine to solutions of the hexacarbonyls proceeded smoothly either at room temperature (PMe_3) or under reflux/blue (455 nm) light irradiation (PPh_3, PCy_3) (Scheme 4). Yields in these reactions were moderate to high and did not appear to be compromised by the omission of $Me_3NO \cdot 2H_2O$. By surveying the conditions for these reactions, we have established reliable and (moderately) high-yielding access to the full family of these complexes.

Treatment of $\mathbf{1}^{Bn}$, $\mathbf{1}^{Ph}$ and $\mathbf{1}^{tBu}$ with one equivalent of PMe_3 at room temperature cleanly produce the corresponding substitution phosphine, confirmed by the presence of low-field singlets in the $^{31}P\{^1H\}$ NMR spectra (δ 13.2 ppm, 25.6 ppm and 34.3 ppm, respectively, for $\mathbf{4a}^{Bn}$, $\mathbf{4a}^{Ph}$ and $\mathbf{4a}^{tBu}$).^{1}H NMR spectroscopy shows that $\mathbf{4a}^{Bn}$ exhibits two isomers in solution, in a 6:1 ratio in $CDCl_3$ and approximately 1:1 in CD_2Cl_2, driven by ready interchange of isomers and indicating a 'flat' energy surface in which small solvent interactions can tip the energy balance.

Moving to the synthesis of mono-PCy_3 substituted derivatives, treatment of $\mathbf{1}^{Me}$, $\mathbf{1}^{Et}$, $\mathbf{1}^{iPr}$, $\mathbf{1}^{tBu}$, $\mathbf{1}^{Ph}$ and $\mathbf{1}^{Bn}$ with one equivalent of PCy_3 under reflux give the corresponding mono-substituted complexes $Fe_2(\mu\text{-}SR)_2(PCy_3)(CO)_5$ (**4b**), $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ showed singlet signals for the bound phosphine in the range 55–66 ppm. The equivalent mono-PPh_3 complexes **4c** could also be accessed by refluxing the starting materials in a 1:1 ratio. NMR spectroscopy showed that $\mathbf{4c}^{Me}$, $\mathbf{4c}^{Et}$, $\mathbf{4c}^{Pr}$ and $\mathbf{4c}^{iPr}$ exists in two isomers in $CDCl_3$ solution.

Infrared spectroscopy for all the phosphine complexes confirmed a blue shift of the CO bands (Table S1). As anticipated, the largest shifts compared with the parent hexacarbonyl complexes were seen in the PCy_3 derivatives (65–45 cm^{-1}), with the smallest shifts for the PPh_3 systems (40–15 cm^{-1}), reflecting the electron-donating abilities of the phosphine ligands. The magnitudes of these changes are in line with those reported for other mono-phosphine substituted {2Fe2S} systems.

Synthesis of bis-substituted phosphine derivatives

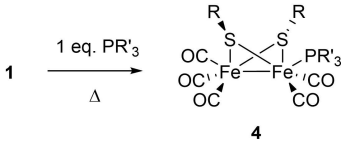
Bis-substitution by monodentate phosphines is usually achieved through addition of excess phosphine to the hexacarbonyl.[21–25] However, this can proceed poorly, particularly when using PPh_3, which is both bulky and a poor electron donor. Irradiating a reaction mixture containing a 1:2 ratio of hexacarbonyl and phosphine with a 455 nm LED gave smooth reaction to produce $Fe_2(\mu\text{-}SR)_2(PR'_3)_2(CO)_4$ (**5**) in moderate to high yields for PMe_3, PCy_3 and PPh_3 (Scheme 5). $^{13}C\{^1H\}$ NMR spectra showed shifting of CO signals toward high frequency by around 7.0–8.0 ppm comparing with the corresponding hexacarbonyl complexes, and showed that $\mathbf{5a}^{Me}$, $\mathbf{5a}^{Et}$ and $\mathbf{5a}^{Pr}$ existed single isomers in solution which showed triplet signals (1:2:1) due to the effect of two phosphine groups and the coupling average of J_{PC} = 3.8 Hz. In the case of $\mathbf{5a}^{Ph}$, two polymorphs could be isolated depending on reaction temperature, a phenomenon that has been observed in related {2Fe2Se} systems isomers.[3]

Infrared spectroscopy showed a blue shift in the carbonyl stretching with increasing electron density on the metal centres (Table S2). The symmetry of the bis-phosphine complexes means that in most cases only three bands were resolved in the carbonyl region: in contrast, many of the lower-symmetry mono-phosphines exhibited four or five distinct bands.

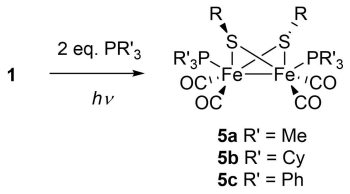
Most hexacarbonyl complexes containing *bridging* dithiolene ligation are resistant to breakdown even if reacted with excess phosphine at elevated temperatures. In contrast, the 'open' hexacarbonyls are more reactive, and therefore control of conditions is important to avoid cleavage of the Fe–Fe bond. Treatment of $\mathbf{1}^{Me}$ with two equivalents of PMe_3 with reflux or blue light irradiation led to breakdown to the {2Fe2S} core to the Fe(II) species $Fe(SMe)_2(CO)_2(PMe_3)_2$ ($\mathbf{6}^{Me}$). In the case of $\mathbf{1}^{Ph}$, application of the LED route gave complex $Fe(SPh)_2(CO)_2(PMe_3)_2$ ($\mathbf{6}^{Ph}$) as a second product, but in contrast to $\mathbf{1}^{Me}$, this was not an issue under reflux conditions. Similar decomposition has been reported recently in the reactions of $\{(\mu\text{-}S)_2(C_4N_2H_2)\}Fe_2(CO)_6$ with excess of PMe_3,[26] and treatment of $\mathbf{1}^{Ph}$ with dppe (dppe = 1,2-diphenylphosphinethane).[27]

The treatment of $\mathbf{1}^{Pr}$ with two equivalents of PCy_3 leads to Fe–Fe bond cleavage *via* reductive elimination to give Fe(0) complex of $Fe(PCy_3)_2(CO)_3$ **7** as a bipyramidal complex. Typically, this complex is accessed by reaction of PCy_3 with $Fe(CO)_5$.

Notably, we have largely been able to avoid the use of excess phosphine by appropriate selection of reaction conditions. This saving of expensive starting materials, and reduction in the formation of by-products, means that our reported protocols are preferable to those reported previously: minor adjustments to conditions here make a significant difference in synthetic utility.



Scheme 4. Synthesis of mono-phosphine complexes **4** {R' = Me (**a**), Cy (**b**), Ph (**c**)}; reactions took place in hexane at reflux and were monitored by $^{31}P\{^1H\}$ NMR spectroscopy.



Scheme 5. Photochemical synthesis of complex **5**; reactions took place in hexane illuminated using a 455 nm LED and were monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

Table 1. Summary of X-ray structural data collections.

R group (SR)	1	4			5		
		PMe_3 (**a**)	PPh_3 (**b**)	PCy_3 (**c**)	PMe_3 (**a**)	PPh_3 (**b**)	PCy_3 (**c**)
Me	Refs. [20, 28]	–	This work	This work	Ref. [32][a]	This work	This work
Et	*Anti*: Ref. [11][a]	–	Ref. [30][a]	This work	Ref. [33][a]	Ref. [34][a]	This work
	Syn: this work						
Pr	–	–	This work	–	This work	This work	This work
*i*Pr	*Anti*: this work[b]	This work	Ref. [31][a]	This work[c]	–	This work	–
	Syn: this work						
*t*Bu	Ref. [29][a]	This work	This work	This work	This work	This work	–
Bn	Ref. [6]	This work	This work	This work	Ref. [7][a]	This work	This work
Ph	Ref. [28]	This work	This work	This work	This work	This work	This work

[a] Data set from this work included in Supplementary Information; [b] Alternative polymorph reported in ref. [30]; [c] Alternative polymorph reported in ref. [31].

X-ray crystallography

Single crystal X-ray diffraction studies were carried out for most complexes reported here and were used to confirm the anticipated structures (see Supporting Information). A summary of the data sets collected, included details of those previously reported, is given in Table 1.

The structures for the hexacarbonyls are unremarkable, and as detailed in Table 1, the majority have been reported previously. The structures confirm the isolation of both *syn*- and *anti*-isomers for $\mathbf{1}^{Ph}$, $\mathbf{1}^{Me}$, $\mathbf{1}^{Et}$ and $\mathbf{1}^{iPr}$; complexes $\mathbf{1}^{Bn}$ and $\mathbf{1}^{tBu}$ were isolated only as the *anti* isomers. Structural data for *syn*-$\mathbf{1}^{Et}$ and *syn*-$\mathbf{1}^{iPr}$ has not previously been reported, whilst for *anti*-$\mathbf{1}^{iPr}$, a novel polymorph was obtained. The metrical data for these previously unreported structures are comparable with the known materials,[6,20,28,29] suggesting that a relatively flat energy surface for interchange of the sulfur-substituents exists, and the preferred polymorph form is driven by temperature and concentration factors.

In contrast to the hexacarbonyls, most of the phosphine-containing structures have not previously been reported: only the Me and Et-substituted thiolates have been extensively studied in the past. Example ORTEP representations are shown in Figure 1 (monophosphine complexes featuring the tBu thiolate) and Figure 2 (bulky bis-phosphines).

The metrical parameters for the set of structures are in accord with previous reports[7,30–34] and are available as Supporting Information. The steric effect of phosphine substitution largely forces the complexes to the *syn*-geometry, the only exceptions being $\mathbf{4c}^{Me}$ and $\mathbf{4c}^{Et}$. In these systems, the small size of the alkyl group combines with the π-acceptor nature of PPh_3 to enable access to the *anti*-isomers.

Electrochemistry and protonation activity

To investigate the effect of phosphine ligands on the electrochemical properties of the diiron centres, cyclic voltammograms (CVs) of the phosphine complexes were recorded in CH_2Cl_2 under an argon atmosphere. We have previously established that oxidation potential for 'butterfly' {2Fe2S} complexes correlates with protonation rates for these systems.[35] We therefore examined the oxidation potentials of the novel 'open' systems described here. Cyclic voltammetry showed the inverse relationship between E_{ox} and the electron density surrounding the metal centre. The PMe_3-substituted complexes ($\mathbf{4a}^{Bn}$, $\mathbf{4a}^{Ph}$, $\mathbf{5a}^{Bn}$, $\mathbf{5a}^{Ph}$) show only irreversible oxidation, while, with the exception of $\mathbf{4c}^{Ph}$ and $\mathbf{4a}^{iPr}$, the PPh_3 and Pcy_3 systems show one (quasi)reversible oxidation (Table 2, Supplementary Information). Compared with our earlier data for 'butterfly' systems containing Pme_3 ligands, these values are shifted to lower potential by up to 200 mV. We therefore anticipate that the open systems will protonate very rapidly: this will be the subject of further study. Notably, the published literature lacks comparison oxidation potentials for other 'open' {2Fe2S} centres, as the focus of electrochemistry has been almost exclusively on studies of reduction.

Table 2. Oxidation potentials for (quasi)reversible electrochemical processes[a]

R′	R	$E_{1/2}$/V[b]	
		Mono	Bis
Cy	Bn	0.0500	−0.3589
	Ph	0.2486	−0.3287
	Me	0.1862	−0.2901
	Et		−0.2940
	Pr	0.1870	−0.0880
Ph	Bn	0.3517	−0.2086
	Ph	–	−0.1366
	Me	0.2361	−0.0380
	Pr	0.2971	0.4140

[a] Recorded in 0.1 M CH_2Cl_2-Bu_4NPF_6 with complex concentrations of 1 mM at a scan rate of 100 mV s^{-1}; [b] *Versus* Fc^+/Fc.

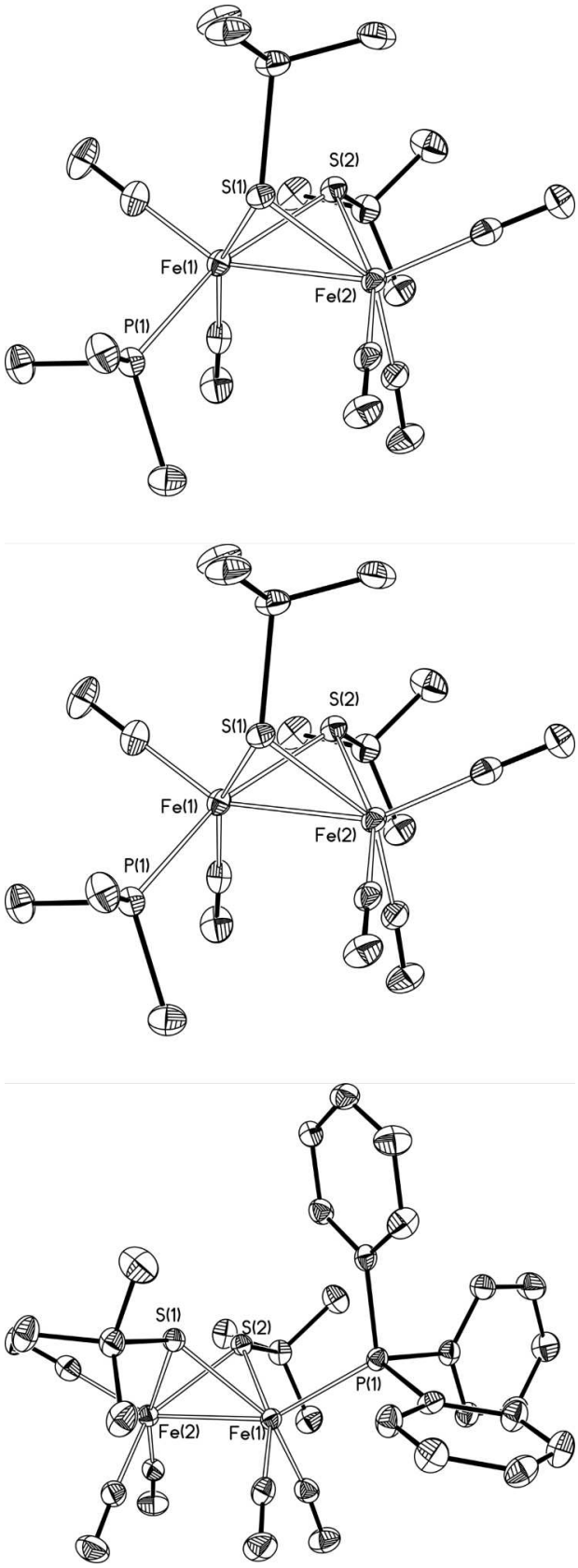


Figure 1. Example ORTEP representations for structures **4a**^{tBu}, **4b**^{tBu} and **4c**^{tBu} showing 50% probability ellipsoids; hydrogen atoms have been omitted for clarity.

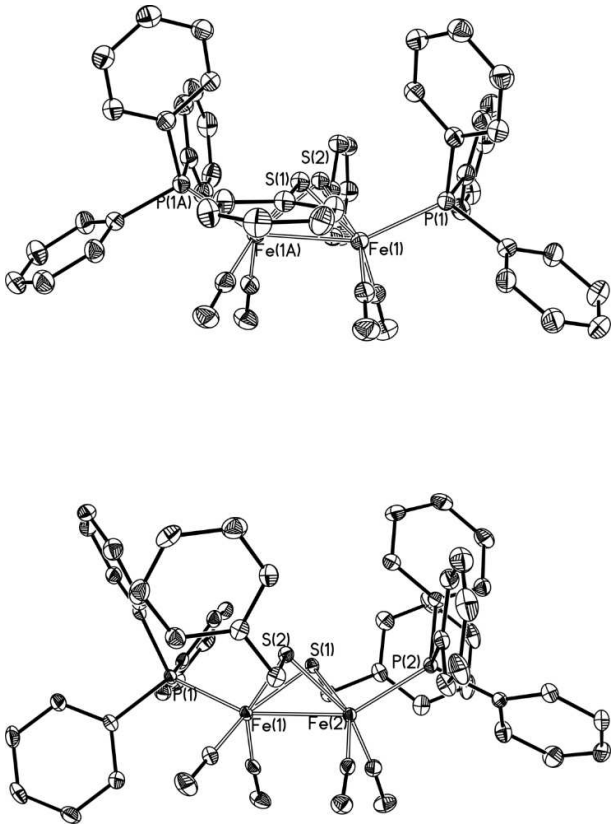


Figure 2. Example ORTEP representations for structures **5c**^{Ph} and **5c**^{Bn} showing 50% probability ellipsoids; hydrogen atoms have been omitted for clarity.

Protonation of several complexes was undertaken using AcOH. IR of *in situ* protonation of **5a**^{Pr} and **5b**^{Ph} showed CO_v blue shifting from 1909 cm^{-1}, 1934 cm^{-1} and 1978 cm^{-1} to 1996 cm^{-1}, 2035 cm^{-1} and 2044 cm^{-1} for **5a**^{Pr}**H**$^{+}$, and from 1904 cm^{-1}, 1931 cm^{-1} and 1973 cm^{-1} to 2002 cm^{-1}, 2043 cm^{-1} and 2053 cm^{-1} for **5b**^{Ph}**H**$^{+}$, while $^{31}P\{^{1}H\}$ NMR spectroscopy of crude solution showed protonation of **5a**^{Pr} changing the symmetry in **5a**^{Pr}**H**$^{+}$ with shifting from δ 8.2 ppm to 17.7 ppm and 20.7 ppm, and in **5b**^{Ph} showed similarity of symmetry changing in **5b**^{Ph}**H**$^{+}$ to give two signals at δ 50.8 ppm and 62.3 ppm. These data are in accord with changes seen in 'butterfly' {2Fe2S} systems on protonation and suggest that further pursuit of these reactions may be fruitful.

Conclusions

In conclusion, we report here a facile route to pure 'open' $Fe_2(\mu\text{-}SR)_2(CO)_6$ systems and improving the access of mono- and bis-substitution of PR_3 ligands without using decarbonylation reagent. Comparison of synthesis routes, the effect of symmetry on carbonyl stretching (C≡O bonds), the solid-state structures, oxidative electrochemistry and the protonation behaviour with AcOH have been reported. Some of the by-products of synthesis of hexacarbonyl complexes have been isolated and

characterized, in addition to the isolation of Fe–Fe bond decomposition products.

Experimental Section

General

All reactions were carried out under argon atmosphere using standard Schlenk techniques. Reagent-grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Starting materials were purchased from Aldrich or Alfa Aesar and did not require further purification. NMR spectra were recorded on Bruker AvanceIII 400 or a Bruker AvanceIII 500. NMR spectra were referenced using the residual solvent peak (^{1}H: 7.26 δ; ^{13}C 77.16 δ). IR spectra were recorded using a Bruker Vertex 80 instrument using a 4 cm^{-1} resolution. Mass spectra were obtained using an Atmospheric Solids Analysis Probe (ASAP) with a Single Quadrupole Time-of-Flight instrument at Newcastle University. Elemental analysis was investigated at University of Manchester. Cyclic voltammetric measurements were carried out using an Autolab PGSTAT 30 potentiostat. All measurements were made in dry degassed CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. A conventional three-electrode arrangement was employed, consisting of a vitreous carbon working electrode, a platinum wire as the auxiliary electrode and a silver wire *pseudo*-reference electrode in conjunction with the ferrocenium/ferrocene couple.

Synthesis of $Fe_2(\mu\text{-SR})_2(CO)_6$ (1)

All hexacarbonyl complexes were synthesised using the same general procedure. To a solution of $Fe_3(CO)_{12}$ (10 mmol) in THF (200 mL) was added R_2S_2 (2 eq) or RSH (3 eq), followed by reaction at reflux until consumption of the starting material by IR spectroscopy. The solvent was removed *in vacuo*, then the dark red material was purified by column chromatography using hexane or a hexane–CH_2Cl_2 mixture as eluent.

Synthesis of $Fe_2(\mu\text{-SR})_2(CO)_5(PR'_3)$ (4)

These were synthesised using General Procedures **A** (**4a^{tBu}**, **4b^{iPr}**, **4b^{tBu}**, **4c^{tBu}**) or **B** (**4a^{Bn}**, **4b^{Me}**, **4b^{Et}**, **4b^{Ph}**, **4b^{Bn}**, **4c^{Me}**, **4c^{Et}**, **4c^{Pr}**, **4c^{iPr}**, **4c^{Ph}**, **4c^{Bn}**) other than **4a^{Ph}**.

General Procedure A

To a solution of **1** (0.5 mmol) in THF (30 mL) was added PR'_3 (0.5 mmol). The reaction was stirred under argon whilst illuminating with a 450 nm LED until $^{31}P\{^1H\}$ NMR spectroscopy showed consumption of free PR_3. The solvent then removed *in vacuo*, and the dark red material was purified by column chromatography.

General Procedure B

To a solution of **1** (2.0 mmol) in THF (50 mL) was added PR_3 (0.5 mmol). The reaction was stirred at reflux until $^{31}P\{^1H\}$ NMR spectroscopy showed consumption of free PR_3. The solvent then removed *in vacuo*, and the dark red material was purified by column chromatography.

$Fe_2(\mu\text{-SPh})_2(CO)_5(PMe_3)$ 4a^{Ph}

To a solution of **1^{Ph}** (0.46 g, 1.0 mmol) in THF (50 mL) was added PMe_3 (1.0 M in THF, 0.5 mL, 0.5 mmol). The reaction was stirred under argon at room temperature for 16 h. The solvent then removed *in vacuo*, and the dark red material was purified by column chromatography in hexane–CH_2Cl_2 (10:1), to give gave $Fe_2(\mu\text{-SPh})_2(CO)_5(PMe_3)$ (0.20 g, 36%).

Synthesis of $Fe_2(\mu\text{-SR})_2(CO)_4(PR'_3)_2$ (5)

These were synthesised using General Procedures **C** (**5a^{Me}**, **5a^{Et}**, **5a^{Pr}**, **5a^{Bn}**) or **D** (**5b^{Me}**, **5b^{Et}**, **5b^{Me}**, **5b^{iPr}**, **5b^{Ph}**, **5b^{Bn}**, **5c^{Me}**, **5c^{Et}**, **5c^{Pr}**, **5c^{iPr}**, **5c^{tBu}**, **5c^{Ph}**, **5c^{Bn}**) other than **5a^{tBu}** and **5a^{Ph}**.

General Procedure C

To a solution of **1** (1.0 mmol) in hexane (40 mL) was added PR'_3 (2.0 mmol), and the reaction stirred under argon atmosphere for 72 h. The concentrated solution then recrystallised at −20 °C to give the product as red blocks.

General Procedure D

To a solution of **1** (1.0 mmol) in THF (50 mL) was added PR'_3(2.0 mmol). The solution was stirred and irradiated with a 450 nm LED until $^{31}P\{^1H\}$ NMR spectroscopy showed consumption of the free phosphine. The solvent then removed *in vacuo*, and the red oily material was purified by column chromatography using hexane–CH_2Cl_2.

Synthesis of $Fe_2(\mu\text{-StBu})_2(CO)_4(PMe_3)_2$ 5a^{tBu}

To a hot solution of **1^{tBu}** (0.23 g, 0.5 mmol) in hexane (30 mL) was added PMe_3 (1.0 M solution in THF, 1.0 mL, 1.0 mmol) with stirring under argon. The solution left to cool down for 16 h without stirring. The solution then concentrated *via* slow evaporation to 5.0 mL, then recrystallization at −20 °C gave $Fe_2(tBuS)_2(Me_3P)_2(CO)_4$ (0.20 g, 80%).

Synthesis of $Fe_2(\mu\text{-SPh})_2(CO)_4(PMe_3)_2$ 5a^{Ph}

Two methods were used to synthesise **5a^{Ph}**. Method **a**: To a solution of **1^{Ph}** (0.46 g, 1.0 mmol) in THF (50 mL) was added PMe_3 (1.0 M solution in THF, 3.0 mL, 3.0 mmol). The reaction was refluxed for 3 h to give dark red solution. The solvent was removed *in vacuo*, and the oily red material was extracted with hot hexane (50 mL) to give the product (0.33 g, 55%).

Method **b**: To a solution of 1.0 mmol. of **1^{Ph}** (0.46 g, 1.0 mmol) in toluene (50 mL) was added PMe_3 (1.0 M solution in THF, 2.0 mL, 2.0 mmol). The solution was stirred whilst irradiating with a 450 nm LED for 16 h to give dark red solution. The solvent was removed *in vacuo*, and the product was purified by column chromatography using hexane–CH_2Cl_2 (10:1) as eluent to give red solution. Recrystallisation by slow evaporation gave the product (0.30 g, 49%).

X-Ray Crystallography

For each sample, crystals were suspended in oil, and one was mounted on a glass fibre and fixed in the cold nitrogen stream of the diffractometer. Data were collected using Rigaku Synergy diffractometer equipped with confocal mirrors and were processed

using CrysAlisPro.[36] Structures were determined using a dual-space approach in SHELXT and refined by full-matrix least-squares methods on F^2 in SHELXL.[37] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions and their U_{iso} values were set to ride on the U_{eq} values of the parent atom.

Supporting Information Summary

Characterisation data for all compounds, NMR spectra, ORTEP figures for crystal structures including key metrical parameters and cyclic voltammograms.[38]

Deposition Numbers 2226975 (for $\mathbf{1}^{Et}$-ae), 2226976 (for $\mathbf{1}^{Et}$-ee), 2226973 (for $\mathbf{1}^{iPr}$-ae), 2226974 (for $\mathbf{1}^{iPr}$-ee), 2226977 (for $\mathbf{1}^{tBu}$), 2226986 (for $\mathbf{4a}^{iPr}$), 2226992 (for $\mathbf{4a}^{tBu}$), 2112318 (for $\mathbf{4a}^{Ph}$), 2112312 (for $\mathbf{4a}^{Bn}$), 2226989 (for $\mathbf{4b}^{Me}$), 2226984 (for $\mathbf{4b}^{Et}$), 2226987 (for $\mathbf{4b}^{iPr}$), 2226993 (for $\mathbf{4b}^{tBu}$), 2112323 (for $\mathbf{4b}^{Ph}$), 2112316 (for $\mathbf{4b}^{Bn}$), 2226990 (for $\mathbf{4c}^{Me}$), 2226985 (for $\mathbf{4c}^{Et}$), 2226991 (for $\mathbf{4c}^{Pr}$), 2226988 (for $\mathbf{4c}^{iPr}$), 2226994 (for $\mathbf{4c}^{tBu}$), 2112321 (for $\mathbf{4c}^{Ph}$), 2112314 (for $\mathbf{4c}^{Bn}$), 2227000 (For $\mathbf{5a}^{Me}$), 2226995 (for $\mathbf{5a}^{Et}$), 2227002 (for $\mathbf{5a}^{Pr}$), 2227005 (for $\mathbf{5a}^{tBu}$), 2112319 (for $\mathbf{5a}^{Ph}$ isomer a), 2112320 (for $\mathbf{5a}^{Ph}$ isomer b), 2112313 (for $\mathbf{5a}^{Bn}$ isomer a), 2287915 (for $\mathbf{5a}^{Bn}$ isomer b), 2226999 (for $\mathbf{5b}^{Me}$), 2226996 (for $\mathbf{5b}^{Et}$), 2227003 (for $\mathbf{5b}^{Pr}$), 2112324 (for $\mathbf{5b}^{Ph}$), 2112317 (for $\mathbf{5b}^{Bn}$), 2227001 (for $\mathbf{5c}^{Me}$), 2226997 (for $\mathbf{5c}^{Et}$), 2227004 (for $\mathbf{5c}^{Pr}$), 2226998 (for $\mathbf{5c}^{iPr}$), 2227006 (for $\mathbf{5c}^{tBu}$), 2112322 (For $\mathbf{5c}^{Ph}$), 2112315 (for $\mathbf{5c}^{Bn}$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[1] C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245–2274.
[2] Y. Li, T. B. Rauchfuss, *Chem. Rev.* **2016**, *116*, 7043–7077.
[3] M. Wang, L. Chen, L. Sun, *Energy Environ. Sci.* **2012**, *5*, 6763–6778.
[4] J. T. Kleinhaus, F. Wittkamp, S. Yadav, D. Siegmund, U.-P. Apfel, *Chem. Soc. Rev.* **2021**, *50*, 1668–1784.
[5] G. Hogarth, *Coord. Chem. Rev.* **2023**, *490(215)*, 174.
[6] L. Haley, L. N. Broadbent, L. S. McDaniel, S. T. Heckman, C. H. Hinkle, N. N. Gerasimchuk, J. C. Hershberger, C. A. Mebi, *Polyhedron* **2016**, *114*, 218–226.
[7] S. Lü, C.-R. Qin, H.-L. Ma, J.-M. Ouyang, Q.-L. Li, *Inorg. Chim. Acta* **2021**, *516(120)* 130.
[8] R. J. Day, A. J. Gross, E. S. Donovan, K. D. Fillo, G. S. Nichol, G. A. N. Felton, *Polyhedron* **2021**, *197(115)*, 043.
[9] J. A. Martinez, N. N. Gerasimchuk, C. A. Mebi, *Transition Met. Chem.* **2020**, *45*, 569–575.
[10] C. A. Mebi, J. H. Labrecque, A. A. Williams, *Transition Met. Chem.* **2020**, *45*, 577–581.
[11] S. Jeannin, Y. Jeannin, F. Robert, C. Rosenberger, *J. Organomet. Chem.* **1993**, *448*, 151–155.
[12] L. Maresca, F. Greggio, G. Sbrignadello, G. Bor, *Inorg. Chim. Acta* **1971**, *4*, 667–674.
[13] J. A. De Beer, R. J. Haines, *J. Organomet. Chem.* **1970**, *24*, 757–767.
[14] R. B. King, *Inorg. Chem.* **1963**, *2*, 326–327.
[15] J. A. Adeleke, Y. W. Chen, L. K. Liu, *Organometallics* **1992**, *11*, 2543–2550.
[16] D. Seyferth, R. S. Henderson, L. C. Song, *Organometallics* **1982**, *1*, 125–133.
[17] R. B. King, B. Bisnette, *Inorg. Chem.* **1965**, *4*, 1663–1664.
[18] R. B. King, *J. Am. Chem. Soc.* **1962**, *84*, 2460.
[19] W. Henslee, R. E. Davis, *Cryst. Struct. Commun.* **1972**, *1*, 403.
[20] Y.-C. Shi, Z.-D. Wu, X.-L. Hou, Z.-W. Li, Y. Wang, *J. Coord. Chem.* **2016**, *69*, 3603–3618.
[21] D. Schilter, J. M. Camara, M. T. Huynh, S. Hammes-Schiffer, T. B. Rauchfuss, *Chem. Rev.* **2016**, *116*, 8693–8749.
[22] X. Zhang, T. Zhang, B. Li, G. Zhang, L. Hai, X. Ma, W. Wu, *RSC Adv.* **2017**, *7*, 2934–2942.
[23] S. Ghosh, A. Rahaman, G. Orton, G. Gregori, M. Bernat, U. Kulsume, N. Hollingsworth, K. B. Holt, S. E. Kabir, G. Hogarth, *Eur. J. Inorg. Chem.* **2019**, *2019*, 4506–4515.
[24] H. N. Kagalwala, N. Lalaoui, Q. Li, L. Liu, T. Woods, T. B. Rauchfuss, *Inorg. Chem.* **2019**, *58*, 2761–2769.
[25] P. Li, M. Wang, C. He, G. Li, X. Liu, C. Chen, B. Åkermark, L. Sun, *Eur. J. Inorg. Chem.* **2005**, *2005*, 2506–2513.
[26] S. Gao, J. Fan, S. Sun, F. Song, X. Peng, Q. Duan, D. Jiang, Q. Liang, *Dalton Trans.* **2012**, *41*, 12064–12074.
[27] J. Takacs, L. Marko, *J. Organomet. Chem.* **1989**, *361*, 109–116.
[28] M. C. Ortega-Alfaro, N. Hernández, I. Cerna, J. G. López-Cortés, E. Gómez, R. A. Toscano, C. Alvarez-Toledano, *J. Organomet. Chem.* **2004**, *689*, 885–893.
[29] S. B. Katser, A. S. Antsyshkina, A. S. Katugin, A. S. Abdullaev, *Koord. Khim.* **1987**, *13*, 1132.
[30] E. Delgado, E. Hernández, O. Rossell, M. Seco, E. G. Puebla, C. Ruiz, *J. Organomet. Chem.* **1993**, *455*, 177–184.
[31] T. Agarwal, S. Kaur-Ghumaan, *Eur. J. Inorg. Chem.* **2023**, *26*, e202200623.
[32] G. L. Borgne, D. Grandjean, R. Mathieu, R. Poilblanc, *J. Organomet. Chem.* **1977**, *131*, 429–438.
[33] X. Zhao, I. P. Georgakaki, M. L. Miller, R. Mejia-Rodriguez, C.-Y. Chiang, M. Y. Darensbourg, *Inorg. Chem.* **2002**, *41*, 3917–3928.
[34] A. L. Rheingold, *CCDC 1437927: Experimental Crystal Structure Determination*, Cambridge Crystallographic Data Centre, 2015.
[35] A. Jablonskyte, L. R. Webster, T. R. Simmons, J. A. Wright, C. J. Pickett, *J. Am. Chem. Soc.* **2014**, *36*, 13038–13044.
[36] CrysAlisPro, Rigaku Oxford Diffraction, **2020**, Rigaku Corporation, Wroclaw, Poland.
[37] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
[38] X. Jiang, L. Long, H. Wang, L. Chen, X. Liu, *Dalton Trans.* **2014**, *43*, 9968–9975.

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