

## Alkynyl-phosphine substituted Fe<sub>2</sub>S<sub>2</sub> clusters: synthesis, structure and spectroelectrochemical characterization of a cluster with a Class III mixed-valence [FeFe]<sup>3+</sup> core

Gregory L. Newman, Mohammad A.R. Jamil, Josef B.G. Gluyas, Dmitry S. Yufit, Jusith A.K. Howard, Paul J. Low

### Abstract

Phosphinoalkynes P(C≡CC<sub>6</sub>H<sub>4</sub>Me-4)Ph<sub>2</sub> (**1**) and P(C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>Me-4)Ph<sub>2</sub> (**2**) have been prepared from CuI catalysed reactions of the corresponding 1-alkyne and PClPh<sub>2</sub>. The trimethylamine-*N*-oxide promoted reaction of PPh<sub>3</sub>, **1** or **2** with [Fe<sub>2</sub>(μ-pdt)(CO)<sub>6</sub>] (pdt = propanedithiolate) affords derivatives [Fe<sub>2</sub>(μ-pdt)(CO)<sub>5</sub>{PRPh<sub>2</sub>}] [R = Ph (**3**), C≡CC<sub>6</sub>H<sub>4</sub>Me (**5**), C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>Me (**6**)] or, at elevated temperatures, [Fe<sub>2</sub>(μ-pdt)(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**4**). The cyclic voltammograms of compounds **3** and **4** feature almost fully reversible one-electron oxidation processes and an irreversible reduction, whilst the electrochemical response of the alkynyl phosphine substituted complexes **5** and **6** is irreversible for both oxidation and reduction. IR spectroelectrochemical studies of **4** are consistent with an oxidation processes leading to a delocalized or (Class III) mixed valence [FeFe]<sup>3+</sup> core in which the iron centers have an average oxidation state of 1.5. The molecular structures of the alkynyl phosphine substituted clusters **5** and **6** are also reported.

**Keywords** iron-only hydrogenase, spectroelectrochemistry, phosphino alkyne, trimethylamine-*N*-oxide, mixed-valence

## Introduction

The ready reaction of  $[\text{Fe}_3(\text{CO})_{12}]$  with dithiols, HSRSH, leading to dithiolate complexes  $[\text{Fe}_2(\mu\text{-SRS})(\text{CO})_6]$  has been widely exploited in the development of models for the active site in iron-only hydrogenases. Whilst the great majority of bioinorganic models are based on  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$  or, more rarely,  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}]$  cores,[1, 2] in the active enzyme the  $[\text{FeFe}]$  subunit is likely in a mixed-valent  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}]$  state [3]. However, only a relatively small number of mixed-valent  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}]$  model complexes have been isolated, and despite the use of spectroelectrochemical methods to study enzyme based systems,[4-8] there are surprisingly few spectroelectrochemical investigations of the model  $[\text{Fe}_2(\mu\text{-SRS})(\text{CO})_{6-x}\text{L}_x]^n$  systems.[9-15]

As well as being fascinating models for the biological system,[16] clusters  $[\text{Fe}_2(\mu\text{-SRS})(\text{CO})_{6-x}(\text{L})_x]^n$  are now attracting great attention as alternative, non-precious metal-based catalytic platforms for the reduction of water to dihydrogen for use as a future clean fuel [17-22]. Although examples of compounds with promising electrocatalytic performance have been explored in laboratory settings, a particular challenge that has been noted is the incorporation of additional photosensitizing motifs within the catalytic process [22-26]. These photosensitizing motifs have been either introduced as a separate molecular component of the catalyst solution, or covalently attached to the cluster with a view to promoting improved electronic coupling between the components. Many of these photosensitizing groups have been introduced into the backbone of the dithiolate bridging ligand, although a more close association with the metallic core might prove more effective.

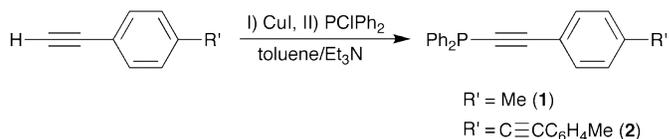
Against this background we considered the concept of introducing phosphino alkynes as wire-like conduits to channel electrons between a remote photosensitizer and a  $[\text{Fe}_2\text{S}_2]$  cluster [27-29]. Phosphinoalkynes are an appealing, if under-explored, class of molecular wire that could be well-suited to the task of tethering a catalyst center to a remote

photosensitizer, with alkyne-based  $\pi$ -conjugated compounds featuring prominently in the construction of wire-like molecules,[30] and phosphino moieties well established as ligands in transition metal coordination and cluster chemistry [31]. In this report we detail our first steps in this area, including the IR spectroelectrochemical investigation of a prototype phosphine-substituted model cluster.

## Results and Discussion

### Synthesis

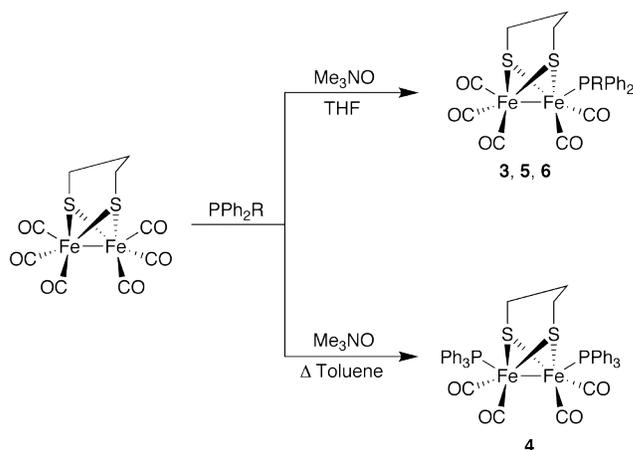
Phosphino alkynes have typically been prepared from reactions of lithiated acetylenes with mono-, di- or tri-chlorophosphanes [31]. Recently, Beletskaya and colleagues have shown that Ni(acac)<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> [32], CuI [33] and related complexes smoothly catalyse the cross-coupling of terminal alkynes with chlorophosphanes in the presence of NEt<sub>3</sub> to give alkynylphosphanes in excellent yields. The Beletskaya route [33] was duly employed in the synthesis of the phosphinoalkynes P(C≡CC<sub>6</sub>H<sub>4</sub>Me)Ph<sub>2</sub> (**1**) and P(C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>Me)Ph<sub>2</sub> (**2**) (Scheme 1).



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

The phosphine substituted iron clusters **3–6** were synthesized according to Scheme 2 by treatment of [Fe<sub>2</sub>( $\mu$ -pdt)(CO)<sub>6</sub>] [34] [35] (pdt = propanedithiolate) with the appropriate phosphine (PPh<sub>3</sub>, **1**, **2**). Mono substitution of a carbonyl ligand (**3**, **5**, **6**) could be achieved at room temperature by addition of anhydrous trimethylamine-*N*-oxide (TMNO) [27]. Synthesis of the bis(PPh<sub>3</sub>) complex **4** required prolonged reaction in refluxing toluene

even in the presence of TMNO to achieve even modest conversion, as noted earlier by Wang, Sun and colleagues in thermally driven phosphine substitution reactions [36].



Scheme 2. Synthesis of phosphine substituted iron clusters **3** (R = Ph), **4**, **5** (R = C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>Me-4), **6** (R = C≡CC<sub>6</sub>H<sub>4</sub>Me-4).

Compounds **3** and **4** have been described previously, having been prepared from thermal substitution reactions of [Fe<sub>2</sub>(μ-pdt)(CO)<sub>6</sub>] with excess PPh<sub>3</sub> in refluxing toluene (6h: **3**, 64%; **4** 20%) [36]. The milder TMNO activation permits preparation of **3** (62%) in comparable yield after only 3 h, although the preparation of **4** still proceeded sluggishly and not even prolonged reaction times (3 d) could drive yields of the compound higher, 16% isolated yield being achieved. Spectroscopic data for **3** and **4** were similar to those reported earlier [36], and include characteristic <sup>31</sup>P NMR signals at δ 64.0 (**3**) and 61.0 (**4**) ppm and IR ν(CO) spectra indicative of all terminal CO ligands (CH<sub>2</sub>Cl<sub>2</sub> /cm<sup>-1</sup>: **1** 2044, 1984, 1933; **2** 1998, 1952, 1934). The ν(CO) band patterns associated with the phosphinoalkyne substituted complexes **5** and **6** are characteristic of their general [Fe<sub>2</sub>(μ-pdt)(CO)<sub>5</sub>L] composition (CH<sub>2</sub>Cl<sub>2</sub> /cm<sup>-1</sup>: **5** 2047, 1988, 1937; **6** 2046, 1986, 1936), and the frequencies suggest that there is little electronic difference between the donor ability of PPh<sub>3</sub> and the phosphinoalkynes **1** and **2**. The <sup>31</sup>P NMR spectra of **5** and **6**

contained singlets at 38.9 and 38.1 ppm, respectively.

The cleavage of the P-C bond in phosphinoalkynes within metal coordination spheres has been exploited in the preparation of a wide range of phosphido-supported alkynyl clusters under mild conditions [31]. The thermal stability of **5** was therefore investigated by way of example. A toluene solution of **5** was heated at reflux for 6h and monitored by IR spectroscopy ( $\nu(\text{CO})$ ). No change could be detected, and **5** was recovered essentially quantitatively by preparative TLC. This stability of the P-C bond in **5** is in contrast to the facile thermal reactions of  $[\text{Fe}_3(\text{CO})_{11}(\text{Ph}_2\text{PC}\equiv\text{CR})]$  systems leading readily to the formation of  $[\text{Fe}_2(\mu\text{-C}_2\text{R})(\mu\text{-PPh}_2)(\text{CO})_6]$  [37-39].

### *Molecular structures*

The structures of  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  [40], **3** [36] and **4** [41] have been reported previously, and those of **5** (Figure 1) and **6** (Figure 2) are now described (Table 1, Table 2). In each case, the Fe centers are found in distorted octahedral environments if the Fe-Fe bond is included in the description of the coordination sphere, although descriptions in terms of edge-sharing square-pyramidal fragments are more commonly employed [40]. The phosphine ligands occupy apical positions approximately trans to the Fe-Fe bond. The propane back bone of the dithiolate ligand in the five-membered  $\text{S}_2(\text{CH}_2)_3$  ring is folded towards the  $\text{Fe}(\text{CO})_3$  fragment in **6**, but is disordered over both proximal and distal sites in **5** (and likely also in **3** given the large thermal ellipsoid depicted for this compound [36]). The Fe-Fe bond length is relatively insensitive to the nature of the supporting ligands, spanning a range 2.5048(10) - 2.5239(4) Å (Table 2). As might be expected, the Fe-CO bond lengths were more responsive to the change in ligand environment, averaging ca. 1.80 Å in the  $\text{Fe}(\text{CO})_3$  fragments, contacting to ca. 1.77 Å in the  $\text{Fe}(\text{CO})_2(\text{PR}_3)$  sites. The phosphinoalkyne ligands displayed typical C≡C bond lengths (**6** 1.209(3) Å; **5** 1.202(3), 1.197(3) Å), whilst the  $\text{Fe}_2\text{S}_2$  butterfly core was also similar to the many other examples of clusters of this type [36] [34, 40, 42-44].

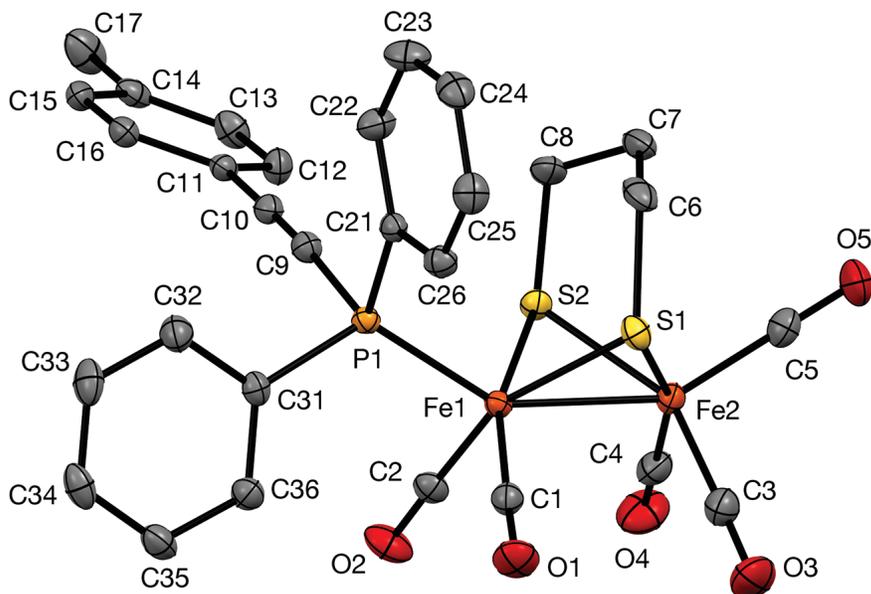
**Table 1.** Crystallographic and refinement details for **5** and **6**.

Compound	<b>5</b>	<b>6</b>
Empirical formula	C <sub>37</sub> H <sub>27</sub> Fe <sub>2</sub> O <sub>3</sub> PS <sub>2</sub>	C <sub>29</sub> H <sub>23</sub> Fe <sub>2</sub> O <sub>3</sub> PS <sub>2</sub>
Formula weight	758.38	658.26
Temperature/K	120	120
Crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
a/Å	21.6939(12)	13.1798(4)
b/Å	9.8301(6)	15.6043(5)
c/Å	16.2886(9)	14.4029(4)
β/°	101.6710(10)	105.205(3)
Volume/Å <sup>3</sup>	3401.8(3)	2858.43(15)
Z	4	4
ρ <sub>calc</sub> /mg/mm <sup>3</sup>	1.481	1.530
m/mm <sup>-1</sup>	1.065	1.254
F(000)	1552.0	1344.0
Reflections collected	43520	40261
Independent reflections	9910[R(int) = 0.0480]	8326[R(int) = 0.0616]
Data/restraints/parameters	9910/0/507	8326/0/432
Goodness-of-fit on F <sup>2</sup>	1.028	1.047
Final R <sub>1</sub> indexes [I ≥ 2σ (I)]	0.0386	0.0375
Final wR <sub>2</sub> indexes [all data]	0.1048	0.0825
Largest diff. peak/hole / e Å <sup>-3</sup>	0.56/-0.43	0.46/-0.35

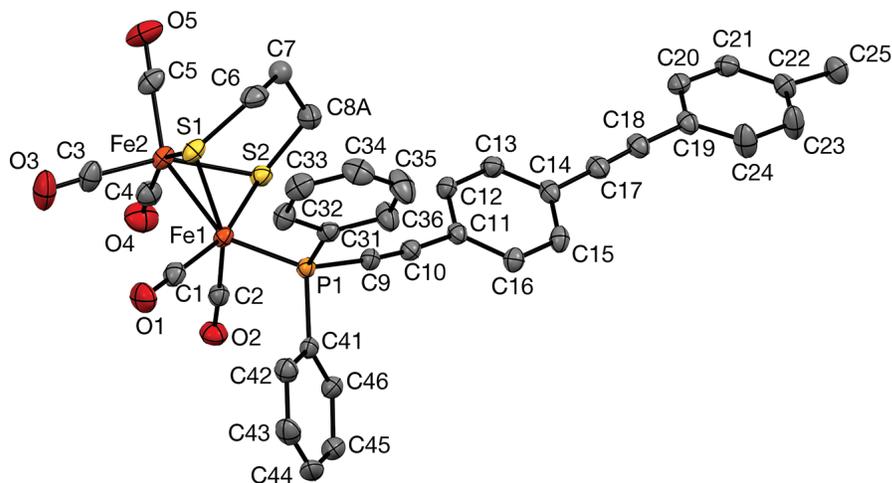
**Table 2.** Selected bond lengths (Å) from the crystallographically determined structures of  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  and **3–6**.

	$\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6$	<b>3</b> [36]	<b>4</b> [41]	<b>5</b>	<b>6</b>
	[40]				
Fe(1)-Fe(2)	2.5103(11)	2.5048(10)	2.5167(16)	2.5064(4)	2.5239(4)
Fe(1)-S(1, 2)	2.2542(10), 2.2491(10)	2.2617(13), 2.2653(14)	2.285(2), 2.254(2)	2.2653(6), 2.2638(6)	2.2598(5), 2.2571(6)
Fe(2)-S(1, 2)		2.2653(14), 2.2707(13)	2.276(2), 2.287(2)	2.2695(7), 2.2651(6)	2.2606(6), 2.2687(6)
Fe(1)-P(1)		2.2222(15)	2.237(2) <sup>a</sup>	2.1958(6)	2.2083(6)
Fe(1)-C(1)		1.791(5)	1.773(8)	1.778(2)	1.776(2)
Fe(1)-C(2)		1.772(5)	1.719(8)	1.770(2)	1.776(2)
Fe(2)-C(3)	1.801(3)	1.776(6)	1.720(8)	1.792(3)	1.789(2)
Fe(2)-C(4)	1.797(3)	1.797(6)	1.720(8)	1.790(3)	1.790(2)
Fe(2)-C(5)	1.802(3)	1.788(6)	-	1.802(3)	1.806(2)

<sup>a</sup> Fe(2)-P(2) 2.230(2)



**Figure 1.** A plot of a molecule of **5** showing the atom labeling scheme (thermal ellipsoids are plotted at 50% and hydrogen-atoms omitted for clarity).

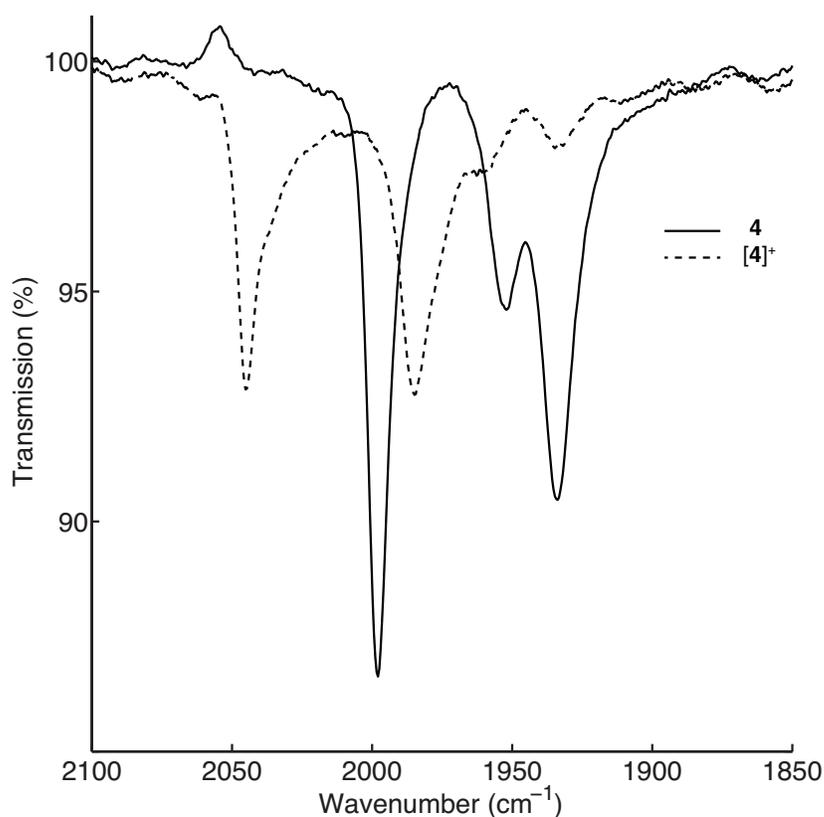


**Figure 2.** A plot of a molecule of **6** showing the atom labeling scheme (thermal ellipsoids are plotted at 50% and hydrogen-atoms omitted for clarity).

### *Electrochemistry and IR Spectroelectrochemistry*

The redox properties of complexes  $[\text{Fe}_2(\mu\text{-dithiolate})(\text{CO})_{6-n}\text{L}_n]$  have attracted considerable interest as part of the strategy to study their capacity to serve as functional models of the iron-only hydrogenases. Although initial CV investigations of **5** and **6** revealed only irreversible electrochemical processes in  $\text{CH}_2\text{Cl}_2 / 0.1 \text{ M NBu}_4\text{PF}_6$  the  $\text{PPh}_3$  substituted compounds **3** and **4** were much better behaved. Both compounds underwent an irreversible reduction, the peak potential of which was quite sensitive to the degree of substitution ( $E_{\text{pc}} = -2.08$  (**3**),  $-1.75$  (**4**) V) corresponding to the reduction of the  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$  cluster core to (formally)  $[\text{Fe}^{\text{I}}\text{Fe}^0]$ . In contrast to the behavior of **3** in  $\text{NCMe} / 0.1 \text{ M NBu}_4\text{PF}_6$  [36], oxidation of this compound in  $\text{CH}_2\text{Cl}_2 / 0.1 \text{ M NBu}_4\text{PF}_6$  was almost fully reversible ( $E_{1/2}(\mathbf{3}) +0.37 \text{ V vs FeCp}_2 / [\text{FeCp}_2]^+ = 0.0 \text{ V}$ ). The greater solubility of **4** in  $\text{CH}_2\text{Cl}_2$  than in  $\text{NCMe}$  also allowed good oxidative electrochemistry to be observed in this solvent with an almost fully reversible wave observed ( $E_{1/2}(\mathbf{4}) +0.58 \text{ V}$ ).

Although the  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}]$  redox state has been implicated in the hydrogenase enzyme active sites [45, 46], and during electrocatalysis by synthetic models [47-50], direct spectroscopic observation of complexes featuring this redox state are limited [49, 51-53]. We therefore took advantage of the comparatively well-behaved electrochemical response of **4** in  $\text{CH}_2\text{Cl}_2 / 0.1 \text{ M NBu}_4\text{PF}_6$  to  $[\mathbf{4}]^+$  by IR spectroelectrochemical methods, and assess the effect of the phosphine ligands on the nature of the formally  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}]$  mixed valence cluster core.



**Figure 3.** IR data obtained spectroelectrochemically for **4** and  $[4]^+$  in  $\text{CH}_2\text{Cl}_2$  / 0.1 M  $\text{NBu}_4\text{PF}_6$  using an OTTLE cell [54].

The IR spectrum of **4** is characteristic of the distribution of carbonyl ligands in  $\text{L}(\text{CO})_2\text{Fe}-\text{Fe}(\text{CO})_2\text{L}$  formulations with  $\nu(\text{CO})$  bands, shifting from 2075 – 1975  $\text{cm}^{-1}$  in  $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6$  to 2050 – 1920  $\text{cm}^{-1}$  in the case of **3** and further to 2000 – 1920  $\text{cm}^{-1}$  for the most electron-rich complex **4**. Upon oxidation of **4** to  $[4]^+$  in a spectroelectrochemical cell, the parent  $\nu(\text{CO})$  band pattern (**4** 1998, 1952, 1934  $\text{cm}^{-1}$ ) is shifted by ca. +50  $\text{cm}^{-1}$  ( $[4]^+$  2045, 1985, 1958  $\text{cm}^{-1}$ ) (Figure 3). On re-reduction the spectrum of **4** was largely recovered, confirming the assignment of the spectroelectrochemically generated spectrum to that of  $[4]^+$ . The  $\nu(\text{CO})$  spectrum of  $[4]^+$  is remarkably similar in band-pattern to that of the related hydride complex  $[\text{Fe}_2(\mu\text{-H})(\mu\text{-pdt})(\text{CO})_4(\text{PMe}_3)_2]$  (**7**) ( $\nu(\text{CO})$  1948, 1900,

1863  $\text{cm}^{-1}$ ) generated by reduction from the  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}]$  precursor  $[\text{Fe}_2(\mu\text{-H})(\mu\text{-pdt})(\text{CO})_4(\text{PMe}_3)_2]^+$  ( $[\mathbf{7}]^+$ ;  $\nu(\text{CO})$  1986, 2031  $\text{cm}^{-1}$ ) (the lower electron density in  $[\mathbf{4}]^+$  vs  $\mathbf{7}$  accounting for the ca. 100  $\text{cm}^{-1}$  difference in  $\nu(\text{CO})$  frequencies) [52]. Calculations on a model of neutral  $\mathbf{7}$  indicates that the iron atoms carry ca. 70% of the unpaired spin density leading to a description in terms of an average oxidation state at each iron of 1.5. In the case here, the formal oxidation state of the bimetallic core is realised by oxidation of the bis-triphenylphosphine supported  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$  cluster  $\mathbf{4}$  to give a cationic analogue with a similarly delocalized electronic structure. DFT studies of  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$  complexes of the general type  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4\text{L}_2]$  typically feature substantial Fe-Fe bond character in the HOMO [55] [56], and the results here are consistent with depopulation of such a metal-metal bonding orbital on oxidation. However, it must be noted that fuller models suggest a more localized electronic structure within the mixed-valence enzyme active site [57]. Nevertheless, the work here demonstrates that relatively stable model complexes of the ‘mixed valence’  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}]$  type can be accessed from the oxidation of simple  $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$  precursors and studied spectroelectrochemically.

## Conclusion

Phosphinoalkyne substituted complexes  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{Ph}_2\text{PC}\equiv\text{CR})]$  can be readily obtained from TMNO-promoted carbonyl ligand substitution reactions. The presence of the  $\mu\text{-pdt}$  ligand appears to engineer substantial thermal resilience to the cluster core and surprisingly P-C bond activation is suppressed in these complexes. The simpler,  $\text{PPh}_3$  derivatives  $\mathbf{3}$  and  $\mathbf{4}$  give rise to relatively stable oxidation products in an electrochemical cell with  $[\mathbf{4}]^+$  being formulated as a Class III (or fully delocalized) mixed-valence complex. Further steps towards the use of phosphine alkynes as robust tethers to secure photosensitizers to the model hydrogenase site are under way in our laboratory.

## General Experimental Procedures

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran and toluene were purified and dried using an Innovative Technology SPS-400 and degassed before use, triethylamine was dried and distilled according to standard procedures and degassed before use, and all other solvents were reagent grade and used as received. No special precautions were taken to exclude air or moisture during workup except where otherwise indicated. Trimethylamine *N*-oxide was freshly sublimed before use,  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  [35] and compound **2** [33] were synthesised by minor variation to the procedures described in the literature, as detailed below. The precursor alkyne 1-ethynyl-4-(*p*-tolylethynyl)benzene was prepared as described elsewhere [58]. All other reagents were commercially available and used as received.

Column chromatography was performed using silica gel. NMR spectra were recorded at 23 °C on a Varian NMR Systems 700 ( $^1\text{H}$ , 699.7 MHz;  $^{31}\text{P}$ , 283.3 MHz) or a Bruker Avance 400 ( $^1\text{H}$ , 400.1 MHz;  $^{31}\text{P}$ , 162.0 MHz) spectrometer using  $\text{CDCl}_3$  as the solvent. Chemical shifts were determined relative to internal  $\text{CHCl}_3$  ( $^1\text{H}$ ,  $\delta = 7.26$  ppm;  $\text{CDCl}_3$ ) [59] or external  $\text{H}_3\text{PO}_4$  (85%,  $^{31}\text{P}$ ,  $\delta = 0.00$  ppm). MALDI-MS spectra were measured on a Bruker Daltonik Autoflex II ToF/ToF MS and ASAP-MS (APCI) spectra were recorded on an LCT Premier XE mass spectrometer. MS data was processed using MassLynx 4.1. IR spectra were recorded on a Nicolet Avatar 6700 FT-IR from samples in solution cells fitted with  $\text{CaF}_2$  windows.

Cyclic voltammetry was carried out using an EcoChemie Autolab PG-STAT 30 potentiostat, with a platinum disc working electrode, a platinum wire counter electrode, and a platinum wire pseudo-reference electrode, from solutions in dichloromethane containing 0.1 M  $\text{NBu}_4\text{PF}_6$  as the electrolyte. Either the ferrocene/ferrocinium ( $\text{FeCp}_2/[\text{FeCp}_2]^+$ ; 0.00 V) couple or decamethylferrocene/decamethylferrocinium ( $\text{FeCp}^*_2/[\text{FeCp}^*_2]^+$ ; -0.55 V vs.  $\text{FeCp}_2/[\text{FeCp}_2]^+$  at 0.00 V) couple was used as an internal reference for potential measurements. Spectroelectrochemical measurements were made in an OTTLE cell of Hartl design [54] from dichloromethane containing

0.1 M NBu<sub>4</sub>PF<sub>6</sub> as the electrolyte. The cell was fitted into the sample compartment of a Nicolet Avatar 6700 FT-IR and electrolysis in the cell was performed with an EcoChemie Autolab PG-STAT 30 potentiostat.

Crystal data and experimental details are listed in Tables 1 and 2. The single-crystal X-ray data for the compounds **5** and **6** were collected at the temperatures of 120.0(1)K on a Bruker SMART CCD 6000 and an Agilent Gemini S-Ultra diffractometers respectively (graphite monochromator,  $\lambda$ MoK $\alpha$ ,  $\lambda=0.71073\text{\AA}$ ). The structure was solved by direct method and refined by full-matrix least squares on  $F^2$  for all data using SHELXTL [60] and OLEX2 [61] software. All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters, non-disordered H-atoms were located on the difference map and refined isotropically. Disordered atoms were refined isotropically with fixed SOF=0.5 and the hydrogen atoms there were placed into the calculated positions and refined in riding mode. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 996300 and 996301 for compounds **5** and **6**. Copies of this information may be obtained free of charge from The Director, CCDC 12 Union Rd, Cambridge, CB2 1EZ, UK [or [http:// www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)].

### **Preparation of [Fe<sub>2</sub>( $\mu$ -pdt)(CO)<sub>6</sub>]**

1,3-Propanedithiol (pdt, 1.20 mL) was added to a solution of triiron dodecacarbonyl (3.00 g, 5.96 mmol) in toluene (40 mL) and the reaction mixture was heated to reflux. The reaction mixture was stirred at reflux for 15 min resulting in colour change from dark green to dark red. Heating was continued for 1.5 h whereupon IR spectroscopy and TLC analysis indicated complete consumption of the starting material. Following cooling to ambient temperature the solvent was removed under reduced pressure and the residue purified by column chromatography (eluent 80:20, hexanes/dichloromethane (v/v); isolation of an intense red band) followed by recrystallization from hexanes to afford [Fe<sub>2</sub>( $\mu$ -pdt)(CO)<sub>6</sub>] in 85% yield (1.96 g, 5.09 mmol) as a dark red crystalline powder. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.81 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.14 (4H, t, <sup>3</sup>J<sub>H-H</sub> = 7 Hz, CH<sub>2</sub>) ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 2073, 2033, 1999, 1990(sh) cm<sup>-1</sup>. ASAP-MS: 358.1 [M –

CO]<sup>+</sup>, 281.1 [M – pdt]<sup>+</sup>.

### Preparation of diphenyl(*p*-tolylethynyl)phosphine (1)

A Schlenk flask was charged with 1-ethynyl-4-methylbenzene (1.91 g, 16.4 mmol) in toluene (25 mL), before copper(I) iodide (3.10 mg, 164 μmol), chlorodiphenylphosphine (3.62 g, 16.4 mmol) and triethylamine (10 mL) were added sequentially in single portions at ambient temperature resulting in a thick mixture with a cream precipitate. The reaction mixture was stirred at ambient temperature for 18 h whereupon IR spectroscopy indicated complete consumption of the starting material. Subsequently the solvent was removed under reduced pressure and the residue crystallised from methanol to afford **1** in 57% yield (2.80 g, 9.31 mmol) as a white crystalline solid. <sup>1</sup>H NMR (699.7 MHz, CDCl<sub>3</sub>): δ = 2.37 (3H, s, Me), 7.16 (2H, d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, Ph), 7.33–7.38 (6H, m, PPh), 7.45 (2H, d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, Ph), 7.69 (4H, m, PPh) ppm. <sup>31</sup>P NMR (283.3 MHz, CDCl<sub>3</sub>): δ = –33.3 ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(C≡C) 2158 (m) cm<sup>-1</sup>.

### Preparation of diphenyl((4-(*p*-tolylethynyl)phenyl)ethynyl)phosphine (2)

In a manner similar to that described for **1**, 1-ethynyl-4-(*p*-tolylethynyl)benzene (600 mg, 2.77 mmol), copper(I) iodide (5.00 mg, 18.0 mmol) and chlorodiphenylphosphine (612 mg, 2.77 mmol) were added sequentially in single portions to a mixture of toluene (20 mL) and triethylamine (10 mL) at ambient temperature resulting in a thick mixture with a cream precipitate. The reaction mixture was stirred at ambient temperature for 18 h whereupon IR spectroscopy indicated complete consumption of the starting material. Subsequently the solvent was removed under reduced pressure and the residue crystallised from methanol to afford **2** in 81% yield (893 mg, 2.23 mmol) as a pale yellow crystalline solid. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.37 (3H, s, Me), 7.16 (2H, d, <sup>3</sup>J<sub>H-H</sub> = 8 Hz, Ph), 7.33–7.46 (12H, m, PPh), 7.68 (4H, m, Ph). <sup>31</sup>P NMR (162.0 MHz, CDCl<sub>3</sub>): δ = –34.1 ppm. ASAP-MS: 401.1 [M]<sup>+</sup>, 323.1 [M – Ph]<sup>+</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(C≡C) 2159 (w),

2218 (w)  $\text{cm}^{-1}$ .

### Preparation of $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\text{PPh}_3)$ (**3**)

Trimethylamine *N*-oxide was added portionwise to a stirred solution of triphenylphosphine (680 mg, 2.59 mmol) and  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  (1.00 g, 2.59 mmol) in tetrahydrofuran (10 mL). Addition was continued over a period of 3 h until the complete consumption of both starting materials was determined by TLC analysis. Subsequently the volatile components of the reaction mixture were removed under reduced pressure and the crude product was purified by preparative TLC (eluent 80:20, hexanes/dichloromethane (v/v); isolation of an intense red band) followed by crystallisation (layer diffusion hexanes/dichloromethane) to afford **3** in 62% yield (1.00 g, 1.61 mmol) as dark red crystals.  $^1\text{H}$  NMR, (699.7 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.26–1.51 (4H, m,  $\text{SCH}_2$ ), 1.73 (2H, s,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 7.42 (9H, brs, Ph), 7.68 (6H, brs, Ph).  $^{31}\text{P}$  NMR (283.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 64.8 ppm. MALDI-MS ( $m/z$ ): 638.2  $[\text{M} + \text{CO}]^+$ . IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  (CO) 2044, 1984, 1933  $\text{cm}^{-1}$ .

### Preparation of $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4(\text{PPh}_3)_2$ (**4**)

A mixture of triphenylphosphine (272 mg, 1.04 mmol), TMNO,  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  (100 mg, 260  $\mu\text{mol}$ ) in toluene (10 mL) was heated at reflux for 3 d. Following cooling to ambient temperature the volatile components of the reaction mixture were removed under reduced pressure and the crude product was purified by preparative TLC (eluent 80:20, hexanes/dichloromethane (v/v); isolation of an intense red band) followed by crystallisation (layer diffusion hexanes/dichloromethane) to afford **4** in 16% yield (35.8 mg, 41.9  $\mu\text{mol}$ ) as a dark red powder.  $^1\text{H}$  NMR (699.7 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.74 (4H, m,  $\text{CH}_2$ ), 1.56 (2H, m,  $\text{CH}_3$ ), 7.25–7.84 (30H, m, Ph) ppm.  $^{31}\text{P}$  NMR (162.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  61.0 ppm. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$ (CO) 1998, 1952, 1934  $\text{cm}^{-1}$ .

### Preparation of $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\{\text{P}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})\text{Ph}_2\}$ (**5**)

Trimethylamine *N*-oxide was added portionwise to a stirred solution of **1** (212 mg, 697  $\mu\text{mol}$ ) and  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  (269 mg, 697  $\mu\text{mol}$ ) in tetrahydrofuran (10mL). Addition was continued over a period of 1 h until the complete consumption of both starting materials was determined by TLC analysis. Subsequently the volatile components of the reaction mixture were removed under reduced pressure and the crude product was purified by flash column chromatography (eluent 80:20, hexanes/dichloromethane (v/v); isolation of an intense red band), followed by crystallisation (layer diffusion dichloromethane/methanol) to afford **5** in 40% yield (180 mg, 279  $\mu\text{mol}$ ) as a dark red solid.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.60 (2H, m,  $\text{CH}_2$ ), 1.89 (4H, m,  $\text{CH}_2$ ), 2.40 (3H, s,  $\text{CH}_3$ ), 7.20 (2H, d,  $^3J_{\text{H-H}} = 8$  Hz, *PhMe*), 7.43–7.50 (8H, m, *Ph*), 7.96 (4H, m, *Ph*) ppm.  $^{31}\text{P}$  NMR (162.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  38.1 ppm. MALDI-MS (*m/z*): 714.2  $[\text{M} + 2\text{CO}]^+$ , 567.3  $[\text{M} - \text{PhMe}]^+$ . IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2046, 1986, 1936  $\text{cm}^{-1}$ .

### Preparation of $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\{\text{P}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})\text{Ph}_2\}]$ (**6**)

Trimethylamine *N*-oxide was added portionwise to a stirred solution of **2** (104 mg, 260  $\mu\text{mol}$ ) and  $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6]$  (100 mg, 260  $\mu\text{mol}$ ) in tetrahydrofuran (10mL). Addition was continued over a period of 1 h until the complete consumption of both starting materials was determined by TLC analysis. Subsequently the volatile components of the reaction mixture were removed under reduced pressure and the crude product was purified by flash column chromatography (eluent 70:30, hexanes/dichloromethane (v/v); isolation of an intense red band), followed by preparative TLC (eluent 70:30, hexanes/dichloromethane (v/v); isolation of an intense red band) and finally by crystallisation (layer diffusion dichloromethane/methanol) to afford **6** in 16% yield (31.2 mg, 40.9  $\mu\text{mol}$ ) as dark red crystals.  $^1\text{H}$  NMR (699.7 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.61 (2H, m,  $\text{CH}_2$ ), 1.89 (4H, m,

CH<sub>2</sub>), 2.39 (3H, s, CH<sub>3</sub>), 7.18 (2H, m, PhMe), 7.44–7.58 (12H, m, Ph), 7.95 (4H, m, Ph) ppm. <sup>31</sup>P NMR (162.0 MHz, CDCl<sub>3</sub>): δ 38.9 (s) ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2047, 1988, 1937 cm<sup>-1</sup>.

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