Models of the iron-only hydrogenase: Reactions of [Fe$_2$(CO)$_6$(μ-pdt)] with small bite-angle diphosphines yielding bridge and chelate diphosphine complexes [Fe$_2$(CO)$_4$(diphosphine)(μ-pdt)]

Fatima I. Adam, Graeme Hogarth *, Idris Richards

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Abstract

Reactions of [Fe$_2$(CO)$_6$(μ-pdt)] (**1**) (pdt = SCH$_2$CH$_2$CH$_2$S) and small bite-angle diphosphines have been studied. A range of products can be formed being dependent upon the nature of the diphosphine and reaction conditions. With bis(diphenylphosphino)methane (dppm), thermolysis in toluene leads to the formation of a mixture of bridge and chelate isomers [Fe$_2$(CO)$_4$(μ-dppm)(μ-pdt)] (**2**) and [Fe$_2$(CO)$_4$(κ^2-dppm)(μ-pdt)] (**3**), respectively. Both have been crystallographically characterised, **3** being a rare example of a chelating dppm ligand in a first row binuclear system. At room temperature in MeCN with added Me$_3$NO · 2H$_2$O, the monodentate complex [Fe$_2$(CO)$_5$(κ^1-dppm)(μ-pdt)] (**4**) is initially formed. Warming **4** to 100 °C leads the slow conversion to **2**, while oxidation (on alumina) gives [Fe$_2$(CO)$_5$(κ^1-dppmO)(μ-pdt)] (**5**). With bis(dicyclohexylphosphino)methane (dcpm), heating in toluene cleanly affords [Fe$_2$(CO)$_4$(μ-dcpm)(μ-pdt)] (**6**). With Me$_3$NO · 2H$_2$O in MeCN the reaction is not clean as the phosphine is oxidised but monodentate [Fe$_2$(CO)$_5$(κ^1-dcpm)(μ-pdt)] (**7**) can be seen spectroscopically. With 1,2-bis(diphenylphosphino)benzene (dppb) and *cis*-1,2-bis(diphenylphosphino)ethene (dppv) the chelate complexes [Fe$_2$(CO)$_4$(κ^2-dppb)(μ-pdt)] (**8**) and [Fe$_2$(CO)$_4$(κ^2-dppv)(μ-pdt)] (**9**), respectively are the final products under all conditions, although a small amount of [Fe$_2$(CO)$_5$(κ^2-dppvO)(μ-pdt)] (**10**) was also isolated. Protonation of **2** with HBF$_4$ affords a cation with poor stability while with the more basic diiron centre in **6** readily forms the stable bridging-hydride complex [(μ-H)Fe$_2$(CO)$_4$(μ-dcpm)(μ-pdt)][BF$_4$] (**11**) which has been crystallographically characterised.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Iron-only hydrogenase; Diphosphine; Dithiolate; Diiron; Chelating; dppm

1. Introduction

While being known for over forty years [1], there has recently been a tremendous resurgence in interest in the chemistry of dithiolate-bridged diiron complexes of the type [Fe$_2$(CO)$_6$(μ-SR)$_2$]. This has resulted primarily from the realisation that they closely resemble the two-iron unit of the H-cluster active site of iron-only hydrogenases [2].

One particularly widely studied complex is [Fe$_2$(CO)$_6$(μ-pdt)] (**1**) (pdt = SCH$_2$CH$_2$CH$_2$S) [3–8], since in the iron-only hydrogenase a three atom unit bridges the two sulfur atoms. Initially this was thought to be a propane chain [9], although recent studies suggest that it more likely contains a central NH unit [10]. A key role of the two-iron unit of the H-active cluster is to promote the reduction of protons to dihydrogen, which most probably involves proton binding to the diiron unit, possibly to one of the iron atoms. Clearly, any complex which aims to model this active site should be basic enough to bind a proton; unfortunately this does not apply to **1**.

* Corresponding author.
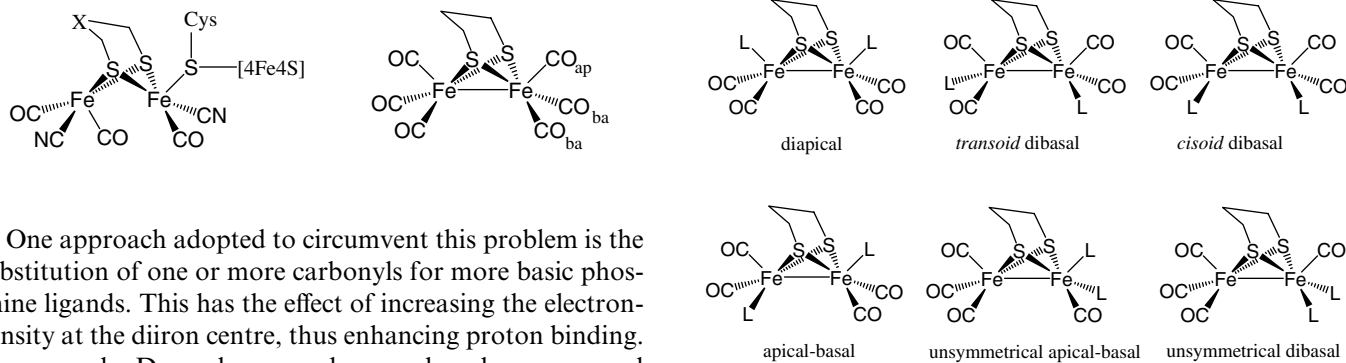 *E-mail address:* g.hogarth@ucl.ac.uk (G. Hogarth).

Chart 1.

One approach adopted to circumvent this problem is the substitution of one or more carbonyls for more basic phosphine ligands. This has the effect of increasing the electron-density at the diiron centre, thus enhancing proton binding. For example, Darensbourg and co-workers have prepared [Fe₂(CO)₄(PMe₃)₂(μ-pdt)] and shown that it can be readily protonated [4b]. The addition of phosphines to the diiron centre, however, introduces a further level of complexity into the system as isomers can result. Phosphines can substitute at either apical or basal sites with the former being generally preferred. For disubstitution, six possible conformations are possible (Chart 1). Two monodentate phosphines always substitute at different metal centres and the diapical and *transoid* dibasal conformations are most common. Thus, in the solid-state both [Fe₂(CO)₄(PTA)₂-(μ-pdt)] (PTA = 1,3,5-triaza-7-phosphaadamantane) [4f] and [Fe₂(CO)₄(PMe₃)₂(μ-pdt)] [4b] adopt the *transoid* dibasal configuration, while in contrast in [Fe₂(CO)₄-(PMe₂Ph)₂(μ-pdt)] and [Fe₂(CO)₄(PPh₃)₂(μ-pdt)] both phosphines occupy apical positions [8a].

In solution the situation is potentially more complex since the different isomers may be in equilibrium as the well-known trigonal-twist of Fe(CO)₂L fragments can occur with only low activation barriers, and potentially leads to an increase in complexity of the system. One potential way of simplifying the situation is to use diphosphine ligands capable of offering a more rigid coordination environment. Thus, the *cisoid* dibasal conformation is not seen with monodentate phosphines presumably because it is sterically unfavourable with respect to the *transoid* dibasal geometry. However, a diphosphine capable of bridging between two metal centres should favour this geometry while making the alternative diapical and *transoid* dibasal arrangements inaccessible. In this regard, bis(diphenylphosphino)methane (dppm) is an ideal choice as it exhibits a high propensity to bridge metal–metal vectors leading to the formation of a stable five-membered rings [11]. Likewise, diphosphines with rigid two-carbon backbones such as *cis*-bis(diphenylphosphino)ethene (dppv) and 1,2-bis(diphenylphosphino)benzene (dppb) should favour unsymmetrical chelating coordination thus affording elec-

tronic and steric asymmetry to the diiron centre. Herein we report details of the reaction of **1** with a number of small bite-angle diphosphines showing that the three disubstituted conformations inaccessible with monodentate phosphines are all available with diphosphines provided the correct choice of ligand is made. While this publication was in preparation two contributions in this area were reported. Thus, Liu, Åkermark, Sun and co-workers have detailed aspects of the reaction of **1** with dppm [12], and De Gioia, Rauchfuss and co-workers reported the formation of [Fe₂(CO)₄(κ²-dppv)(μ-pdt)] [13]. Further, in closely related work we have recently shown that reaction of **1** with bis(2-diphenylphosphino-ethyl)phenylphosphine (triphos) affords the novel tricarbonyl complex, [Fe₂(CO)₃(μ,κ¹,κ²-triphos)(μ-pdt)], in which the triphosphine chelates to one metal centre in a apical–basal manner, while also bridging the diiron centre *via* a dibasal coordination [14].

2. Results and discussion

2.1. With bis(diphenylphosphino)methane (dppm)

Heating a toluene solution of **1** with a slight excess of dppm results in a slow reaction in which the hexacarbonyl was consumed over 16 h. After washing with hexanes in order to remove any unreacted starting materials, the IR spectrum showed the relatively clean formation of [Fe₂(CO)₄(μ-dppm)(μ-pdt)] (**2**) characterised by a singlet at δ 53.2 in the ³¹P NMR spectrum. A second minor resonance was also observed at δ 12.5 being attributed to the isomeric chelate complex, [Fe₂(CO)₄(κ²-dppm)(μ-pdt)] (**3**) (see below).
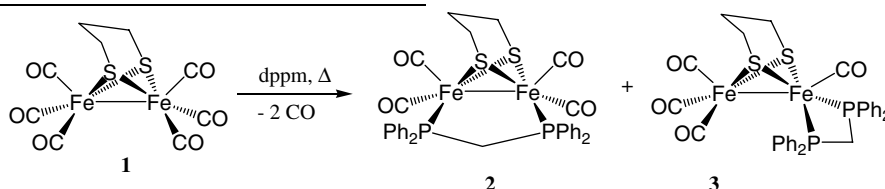
Crystallisation of **2** upon slow diffusion of methanol into a dichloromethane solution gave small orange blocks shown to be [Fe$_2$(CO)$_4$(μ-dppm)(μ-pdt)] (**2**) (Fig. 1). These contain one whole and two half molecules of **2** in the asymmetric unit, together with half a molecule of hexane and half a molecule of methanol. Differences in the independent molecules of **2** are small, and for comparison data are shown only for the unique whole molecule. Frustratingly, despite many efforts we failed to isolate significant amounts of the pure chelate isomer [Fe$_2$(CO)$_4$(κ^2-dppm)(μ-pdt)] (**3**). However, after heating **1** and a slight excess of dppm in toluene for 4 h, chromatography gave a red band which comprised mainly **4** (see below) but also contained significant amounts of **3**. The latter is easily detected by IR spectroscopy, showing a distinctive strong band at 2023 cm^{-1}. Fortunately, crystallisation of this mixture upon slow diffusion of hexane into a concentrated diethyl ether solution afforded a small number of red blocks of [Fe$_2$(CO)$_4$-(κ^2-dppm)(μ-pdt)] (**3**) suitable for X-ray diffraction (Fig. 2).

Both isomers show the expected dithiolate-bridged diiron core. In **2** the diphosphine bridges the iron–iron vector in a *cisoid* dibasal fashion which renders the two thiolate bridges inequivalent. This arrangement is adopted in other diiron dithiolate complexes [15]. As alluded to in the introduction, while this manuscript was in preparation, the independent synthesis and structural characterisation of **2** was reported [12]. Our preparation excludes the use of Me$_3$NO which results in higher yields (76% vs. 27%). In **3** the diphosphine binds to a single iron atom occupying the two basal positions and rendering the two dithiolate-bridges equivalent and while in **2** the two sulphurs bind approximately symmetrically to the two iron atoms, in **3**
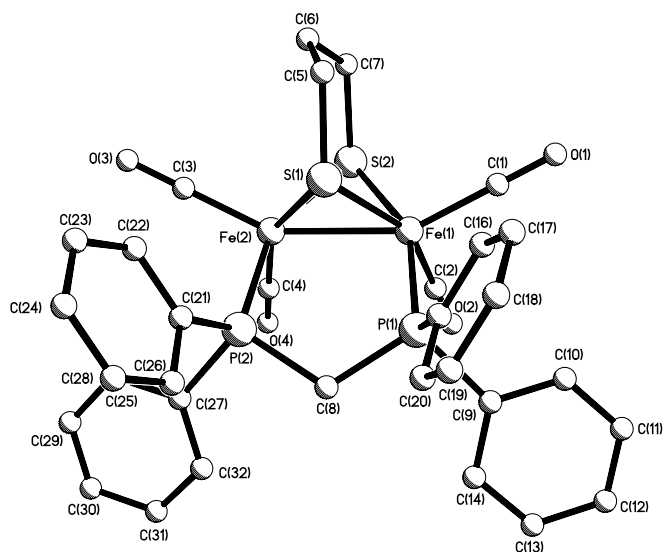

Fig. 2. Molecular structure of [Fe$_2$(CO)$_4$(κ^2-dppm)(μ-pdt)] (**3**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(2) 2.5879(7), Fe(1)–P(1) 2.2123(11), Fe(1)–P(2) 2.2217(11), Fe(1)–S(1) 2.2222(10), Fe(1)–S(2) 2.2250(10), Fe(2)–S(1) 2.2614(11), Fe(2)–S(2) 2.2650(11), P(1)–Fe(1)–S(1) 156.89(4), P(2)–Fe(1)–S(2) 163.34(4), P(1)–Fe(1)–P(2) 74.55(4), P(1)–C(8)–P(2) 93.53(17), Fe(1)–S(1)–Fe(2) 70.50(3), Fe(1)–S(2)–Fe(2) 70.39(3).

they are quite asymmetric, lying closer to the phosphine bound metal centre [Fe(1)–S(av) 2.224(2), Fe(2)–S(av) 2.263(2) Å]. While there are a number of examples of dppm acting in a chelating manner in polynuclear complexes containing the larger second and third row transition metals [16], the only crystallographically characterised example of this behaviour at a first row metal centre is in [CpMo-(CO)$_2$(μ-H)(μ-PPh$_2$)Mn(κ^2-dppm)(CO)$_2$] [17].

In **3** both phosphorus atoms occupy basal sites and this seems unusual since apical substitution is generally preferred. For example, both [Fe$_2$(CO)$_5$(PPh$_3$)(μ-pdt)] and [Fe$_2$(CO)$_5$(PPhMe$_2$)(μ-pdt)] [8a] are substituted in the apical positions. The adoption of the dibasal geometry may be favoured in order to minimise adverse steric interactions between the phenyl rings and dithiolate-bridge. The bite-angle of 74.55(4)° for the diphosphine in **3** is very small, but in line with values found in dppm-chelate complexes [16,17]. Its adoption requires a significant decrease in the preferred dibasal angle as can be seen when compared with that at the unsubstituted iron centre [C(3)–Fe(2)–C(4) 90.85(19)°] [4a]. There is also a significant reduction in the P–C–P angle to 93.53(17)° upon chelation which can be compared with that of 114.3(2)° in **2**. In **3** this leads to the close contact of the two phosphorus nuclei [P(1)–P(2) 2.6854(12) Å] when compared to that in the **2** [P(1)–P(2) 3.094(3) Å].

NMR spectra of **2** show significant temperature dependence. At room temperature the ^{1}H NMR spectrum shows two broad methylene resonances associated with the μ-pdt ligand suggesting that the ligand "flips" rapidly at this temperature and this is in accord with the observation of a singlet in the ^{31}P NMR spectrum. Upon cooling the latter

Fig. 1. Molecular structure of [Fe$_2$(CO)$_4$(μ-dppm)(μ-pdt)] (**2**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(2) 2.5076(9), Fe(1)–P(1) 2.2134(13), Fe(2)–P(2) 2.2104(13), Fe(1)–S(1) 2.2531(12), Fe(2)–S(1) 2.2489(12), Fe(1)–S(2) 2.2597(13), Fe(2)–S(2) 2.2592(13), P(1)–Fe(1)–S(1) 85.12(4), P(2)–Fe(2)–S(1) 85.56(5), P(1)–Fe(1)–S(2) 152.90(5), P(2)–Fe(2)–S(2) 153.26(5), Fe(1)–S(1)–Fe(2) 67.70(4), Fe(1)–S(2)–Fe(2) 67.41(4), C(1)–Fe(1)–Fe(2) 152.62(15), P(2)–C(8)–P(1) 114.3(2).

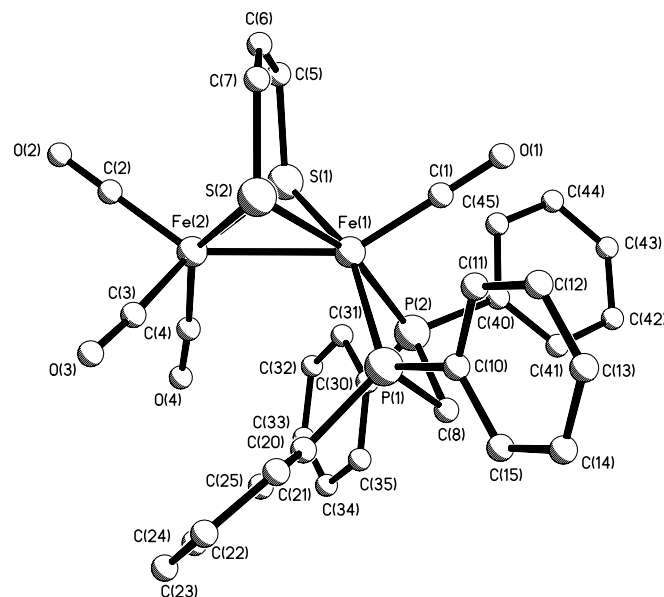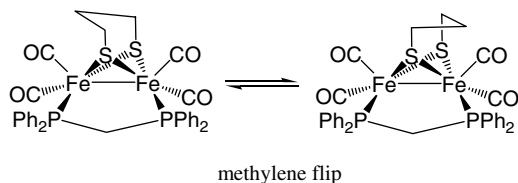broadens and collapses and at 213 K is replaced by two well-resolved AB doublets (J_{PP} 54 Hz) suggesting that now the flipping of the central methylene is slow on the NMR timescale. From the coalescence temperature (243 K) a free energy of activation is estimated at 45 ± 1 kJ mol^{-1}.


methylene flip

Significant changes also occur to the ^{1}H NMR spectrum upon cooling being associated with the inequivalence of all six μ-pdt protons, but signal overlap and resolution prevented full assignment. At room temperature the two methylene protons of the diphosphine ligand are also inequivalent being consistent with the solid-state structure. Upon warming, however, these broaden and collapse into a single broad resonance at 333 K. From the coalescence temperature (315 K) a free energy of activation is estimated at 61 ± 1 kJ mol^{-1}. While this high energy process could involve either dissociation of one end of the bridging dppm ligand or the reversible cleavage of Fe–Fe or Fe–S bonds, we favour a double trigonal-twist of the diphosphine in the basal site. The trigonal-twist process is known to occur in μ-pdt and related diiron dithiolate complexes although here a major difference is the requirement for both phosphorus atoms to undergo the process *simultaneously*. This is not unexpected since the movement of one of the phosphorus atoms (as shown) would be expected to lead to a significant strain at the backbone carbon in the intermediate state.

double trigonal-twist
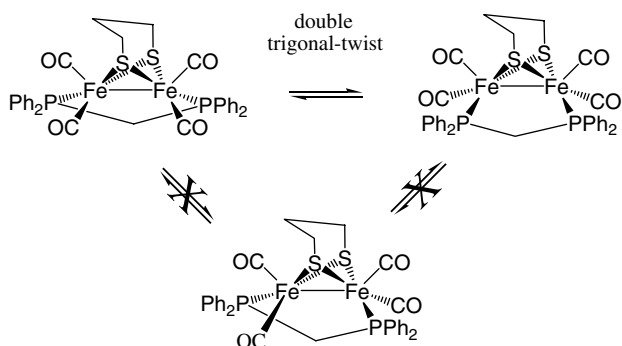
While this manuscript was in preparation, Liu, Åkermark, Sun and co-workers reported the synthesis of the monodentate diphosphine complex, [Fe$_2$(CO)$_5$(κ^1-dppm)-(μ-pdt)] (**4**) (77%) from the reaction of **1** with dppm and Me$_3$NO · 2H$_2$O in MeCN [12],[1] confirming that basal sub-

station has occurred *via* a crystallographic study. We independently carried out this reaction under essentially identical conditions (although we added the diphosphine before Me$_3$NO · 2H$_2$O and stirred for 14 h rather than 4 h). In our hands, the reaction leads to the formation of **4** (J_{PP} 84 Hz) as the major product, but two further products were also seen in the crude reaction mixture. Small amounts (*ca.* 5%) of the tetracarbonyl chelate **3** were seen but the bridge isomer **2** was notably absent. A second minor product (*ca.* 15%) appeared as doublets at δ 55.7 and 23.1 (J_{PP} 19 Hz). In an attempt to separate these products the mixture was chromatographed on alumina which resulted in the isolation of a pure sample of **4** along with substantial amounts of [Fe$_2$(CO)$_5$(κ^1-dppmO)(μ-pdt)] (**5**), characterised by a phosphorus–phosphorus coupling constant of 19 Hz. Initial formation of **5** presumably results from oxidation of **4** by Me$_3$NO · 2H$_2$O since dppm itself is oxidised very slowly by this reagent. Isolation of significant amounts of **5** after chromatography suggests that some degree of oxidation of **4** has been facilitated on the column. Complex **5** is presumed to be the basal isomer and in this instance a second isomer was not observed.
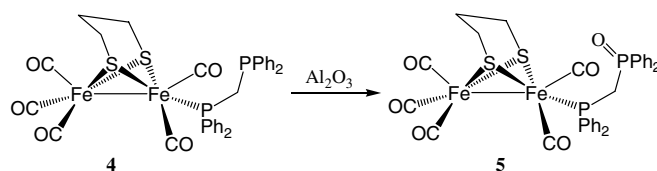
Heating **4** for a prolonged period results in a second carbonyl loss and formation of **2**. In a similar manner to that observed for **2**, cooling a CD$_2$Cl$_2$ solution of **4** results in a gradual broadening of the phosphorus resonances such that at 213 K each doublet splits into two separate signals (J_{PP} unresolved) in an approximate 2:1 ratio. We attribute these changes to the flipping of the pdt ligand. Intuitively, one would expect the minor low temperature species to be that with the central methylene moiety orientated away from the substituted iron centre, however it is noteworthy that in the solid-state it is this conformation which is found [12].

Since apical substitution is generally favoured in these diiron μ-pdt complexes, we were somewhat surprised the apically substituted isomer of **4** was not observed at room temperature or below. In order to probe whether this transformation was accessible at higher temperatures, a d^8-toluene of **4** was warmed to 373 K while monitoring by ^{31}P NMR spectroscopy. No significant changes were seen over this temperature range, although the high temperature (373 K) phosphorus–phosphorus coupling constant of 78 Hz was slightly smaller than that of 90 Hz seen at room temperature. In these complexes the methylene protons of the μ-pdt are typically poorly resolved at room temperature, appearing as what seems to be a series of overlapping broad singlets. At 373 K, however, **4** shows

three well defined quintets (two overlapping). This is consistent with the fast flipping of the pdt ligand but also requires that the phosphine is averaged over either both basal positions or all three possible sites, since if the phosphine remains in a single basal site all six methylene protons of the pdt ligand remain inequivalent. To further probe the phosphine position in solution we recorded a ^{13}C NMR spectrum. The key feature of this is the observation of only two carbonyl resonances (ratio 3:2) showing that at room temperature the carbonyls at both iron sites are mobile. Hence, while the solid-state structure shows phosphine coordination at a basal site, in solution the situation is clearly more complex.

2.2. With bis(dicyclohexylphosphino)methane (dcpm)

Heating a toluene solution of **1** and dcpm for 16 h results in the clean formation of $[Fe_2(CO)_4(\mu\text{-dcpm})(\mu\text{-pdt})]$ (**6**) in high yield. Formation of the bridge isomer was immediately clear from the IR spectrum which showed four carbonyl absorptions at 1975s, 1942vs, 1906s, 1889w cm^{-1}. These compare well with those for **2** at 1988s, 1957vs, 1921s, 1908sh cm^{-1}, being shifted to lower wavenumbers by *ca.* 15–16 cm^{-1}, suggesting that the diiron centre is considerably more basic. Significantly, under these conditions no evidence was seen for the formation of a chelate isomer. In order to confirm the nature of **6** a crystallographic study was carried out (Fig. 3). The structure contains four independent diiron molecules (and two molecules of dichloromethane) in the asymmetric unit but the former vary only slightly in their coordination geometry and only one is shown. General features are the same as seen for **2**, the diphosphine binding in a *cisoid* dibasal fashion.
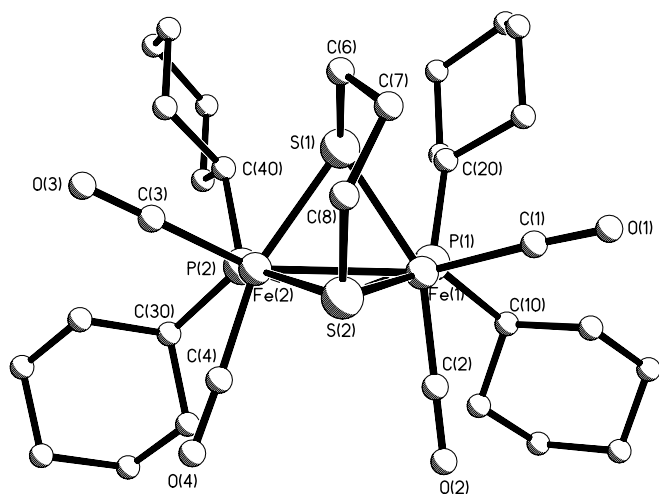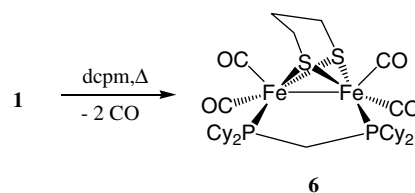

As with dppm, the reaction of **1** with dcpm was also carried out in MeCN in the presence of $Me_3NO \cdot 2H_2O$. In this case, however, the reaction was not clean, the major reaction product being doubly oxidised dcpm. The major diiron containing component was tentatively identified on the basis of ^{31}P NMR data as $[Fe_2(CO)_5\text{-}(\kappa^1\text{-dcpm})(\mu\text{-pdt})]$ (**7**) being characterised by doublets at δ 62.9 and −9.2 ($J_{PP} = 23.8$ Hz). Generation of **7** is in line with the IR crude spectra and it is probably the basal isomer since the dcpm ligand is more sterically demanding than dppm. It is not clear why the oxidised variant of **7** is not seen, and this suggests that phosphine oxidation must be slower once coordinated to iron. A number of other minor products were seen in the crude reaction mixture but the bridging dcpm complex **6** was noticeably absent.
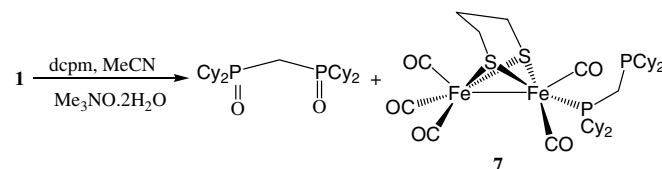
2.3. With dppb and dppv

Heating **1** with either of the more rigid diphosphines, 1,2-bis(diphenylphosphino)benzene (dppb) or *cis*-1,2-bis(diphenylphosphino)ethene (dppv), in toluene for two days led to the slow formation of the chelate complexes $[Fe_2(CO)_4(\kappa^2\text{-dppb})(\mu\text{-pdt})]$ (**8**) and $[Fe_2(CO)_4(\kappa^2\text{-dppv})(\mu\text{-pdt})]$ (**9**), respectively as the major reaction products. Both were readily characterised as chelate complexes on the basis of their IR spectra which are characteristic. Thus, **8** shows three bands in dichloromethane at 2019vs, 1950s and 1905w cm^{-1}, and **9** is similar; 2020vs, 1950s and 1912w cm^{-1}. In the ^{31}P NMR spectra both showed two singlets in an approximate 10:1 ratio, the low-field resonance being most intense. While this manuscript was in preparation, De Gioia, Rauchfuss and co-workers reported the independent synthesis of **9** [13]. Their data generally agree with our own, although we do not see a resonance in the ^1H NMR spectrum at δ 4.3 which they have assigned with the vinylic protons. We observe no peaks in this region and assume that the vinylic protons are hidden by the aromatic resonances as indeed they are in the free ligand.

Fig. 3. Molecular structure of one of the four independent molecules of $[Fe_2(CO)_4(\mu\text{-dcpm})(\mu\text{-pdt})]$ (**6**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(2) 2.5259(10), Fe(1)–P(1) 2.2486(14), Fe(2)–P(2) 2.2477(15), Fe(1)–S(1) 2.2701(14), Fe(2)–S(1) 2.2539(14), Fe(1)–S(2) 2.2654(14), Fe(2)–S(2) 2.2640(15), P(1)–Fe(1)–S(1) 86.74(5), P(2)–Fe(2)–S(1) 87.98(5), P(1)–Fe(1)–S(2) 153.52(6), P(2)–Fe(2)–S(2) 150.58(6), Fe(1)–S(1)–Fe(2) 67.88(4), Fe(1)–S(2)–Fe(2) 67.79(4), C(1)–Fe(1)–Fe(2) 155.13(17), P(2)–C(5)–P(1) 114.6(3).
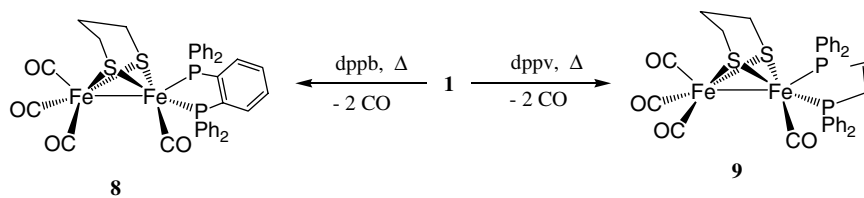
Single crystals of **8** suitable for X-ray crystallography were grown upon slow diffusion of hexane into a dichloromethane solution. The molecular structure (Fig. 4) reveals the apical–basal coordination of the 1,2-bis(diphenylphosphino)benzene ligand. The bite-angle of the diphosphine [P(1)–Fe(2)–P(2)] at 86.80(3)° is significantly larger than that of 74.55(4)° found in the dibasal **3**. In **8**, the angle between the dibasal positions [P(1)–Fe(2)–C(4)] is 89.14(10)° showing that the dppb ligand could sterically occupy both sites and suggesting that the dibasal geometry found in **3** is a result of the extremely small bite-angle of the dppm ligand. Unlike **3**, the sulphur atoms in **8** bridge the diiron vector approximately symmetrically and it is also noteworthy that the central methylene unit of the pdt ligand is proximal to the substituted iron atom.

De Gioia and Rauchfuss investigated **9** by variable temperature ^{31}P NMR spectroscopy. While at room temperature two singlets are observed, cooling to −90 °C results in the appearance of six signals associated with four isomers. These are proposed to result from the different orientations of the central methylene group of the pdt ligand (either proximal or distal to the phosphine-substituted

metal centre) and the orientation of the diphosphine (dibasal or basal–apical). We have previously observed very similar behaviour for the triphos complex, [Fe$_2$(CO)$_3$-(μ,κ^1,κ^2-triphos)(μ-pdt)] [14]. For **9**, the apical–basal conformation is preferred (ca. 82%) at low temperature.

The room temperature ^{31}P NMR spectrum of **8** in CD$_2$Cl$_2$ shows two singlets at δ 90.3 and 82.3 (ca. 10:1) which we attribute to apical–basal (**8a**) and dibasal (**8b**) isomers, respectively. Cooling results in a gradual broadening of the major singlet resonance δ 90.3 in the ^{31}P NMR spectrum. This collapses into the baseline around 213 K to be replaced by two sets of singlets in a ca. 13:1 ratio at 178 K; the major pair being observed at δ 94.5 and 88.1 and the minor set at δ 93.9 and 90.7. The line-width of the major signals at half-height is 17 Hz at this temperature and thus the phosphorus–phosphorus coupling (which could not be resolved) must be small. This splitting of the single high temperature resonance is associated with the freezing out of the trigonal-twist between basal and apical sites and for the major component a free energy of activation is estimated at 38 ± 1 kJ mol^{-1}. The observation of two low temperature conformations relates to the different possible orientations of the central methylene unit of the pdt ligand and similar to **4**, in the solid-state this is found to be proximal to the substituted iron centre in **8** and we suppose that this is the major solution component. Unfortunately, we could not ascertain the precise fate of the minor room temperature component of **8**, although at 178 K a small singlet was still apparent at δ 83.5 which may be due to a dibasal isomer.
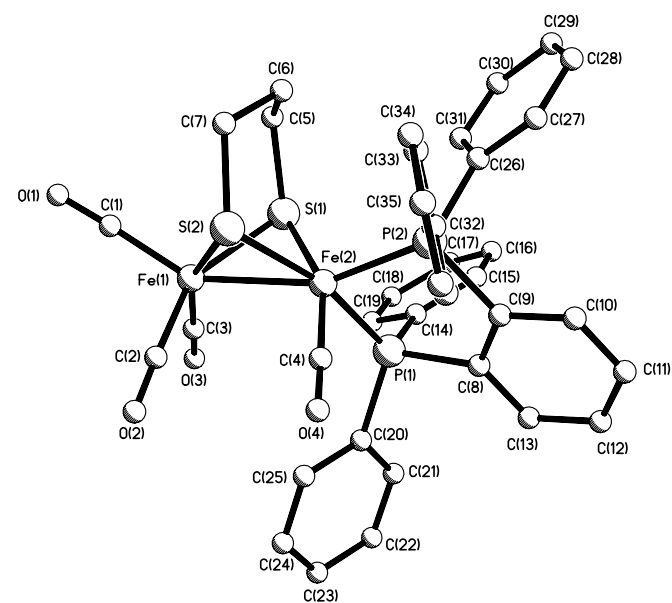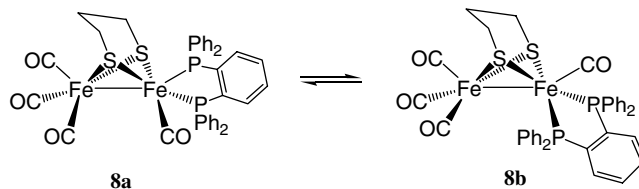

Fig. 4. Molecular structure of [Fe$_2$(CO)$_4$(κ^2-dppb)(μ-pdt)] (**8**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(2) 2.5382(6), Fe(2)–P(1) 2.2008(9), Fe(2)–P(2) 2.1843(9), Fe(2)–S(1) 2.2616(9), Fe(2)–S(2) 2.2587(9), Fe(1)–S(1) 2.2698(9), Fe(1)–S(2) 2.2752(9), P(1)–Fe(2)–S(1) 93.59(3), P(1)–Fe(2)–S(2) 166.17(3), P(2)–Fe(2)–S(2) 106.47(3), P(2)–Fe(2)–S(1) 112.18(3), P(2)–Fe(2)–Fe(1) 157.34(3), P(1)–Fe(2)–P(2) 86.80(3), Fe(1)–S(1)–Fe(2) 68.13(3), Fe(1)–S(2)–Fe(2) 68.09(3).

Reactions of dppb and dppv with **1** were also carried out in MeCN with added Me$_3$NO · 2H$_2$O. In both cases, formation of the desired tetracarbonyls was shown to be ca. 80% complete within 2 h at room temperature. In order to complete the conversions, the mixtures were heated overnight at 60 °C. This synthetic method is preferable to toluene reflux as work-up is simple and yields are higher. When **9** prepared by this method was purified by column chromatography, significant amounts of [Fe$_2$(CO)$_5$-(κ^1-dppvO)(μ-pdt)] (**10**) were also isolated. This was shown

to be a mixture of isomers in an approximate 3:1 ratio characterised by phosphorus–phosphorus coupling constants of 11–12 Hz. We suggest that the major isomer **10a** contains the phosphine in a basal site.
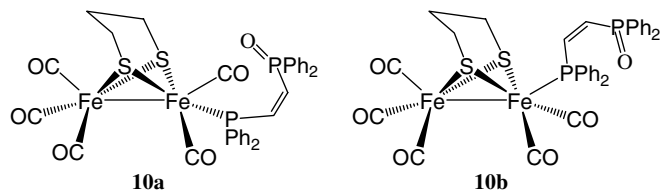
2.4. Protonation of [Fe₂(CO)₄(μ-R₂PCH₂PR₂)(μ-pdt)] (R = Ph, Cy) (2 and 6)

A key function of the diiron unit in the iron-only enzyme is its ability to bind protons. Addition of concentrated HCl to a methanol suspension of **2** did not result in the formation of a protonated product, consistent with the hypothesis that the dppm ligand is not a strong enough electron–donor to render the diiron centre basic enough. Addition of an excess of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of **2** in air did lead to significant changes in the carbonyl region of the IR spectrum, albeit over a prolonged timescale. Thus, absorptions at 1988s, 1957vs, 1921s, 1908sh in **2** were replaced over 3d with new peaks at 2053w, 2034vs, 2000s, 1965w. All attempts to isolate this new species were unsuccessful.

In contrast, addition of a drop of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of **6** resulted in an immediate colour change from orange to yellow with the clean and quantitative formation of [(μ-H)Fe₂(CO)₄(μ-dcpm)(μ-pdt)][BF₄] (**11**). The carbonyl region of the IR spectrum displays three absorptions at 2047m, 2029vs, 1993s cm⁻¹ the shift to higher wavenumbers of *ca.* 80 cm⁻¹ confirming the formation of a three-centre two-electron Fe₂H unit. The appearance of a singlet in the ³¹P NMR spectrum suggests that the symmetrical nature of the diiron centre is retained upon protonation and formation of the hydride was confirmed with the observation of a low-field triplet at $-\delta$ 14.54 (*J* 26.8 Hz) in the ¹H NMR spectrum.
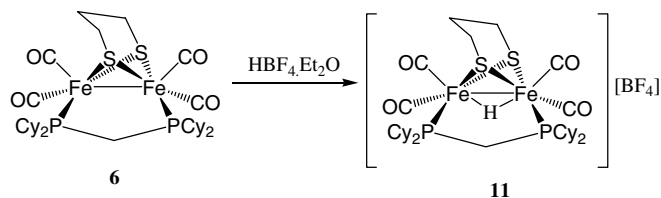
In order to confirm the formation of a bridging hydride and to probe any structural changes occurring upon protonation, single crystals of **11** grown from diethyl ether and hexane were analysed by X-ray crystallography (Fig. 5). Unfortunately, the overall quality of the X-ray data was
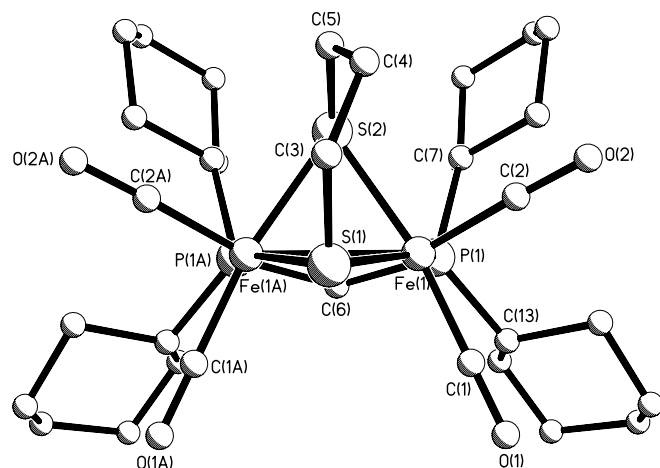

Fig. 5. Molecular structure of the cation in [(μ-H)Fe₂(CO)₄(μ-dcpm)(μ-pdt)][BF₄] (**11**) with selected bond lengths (Å) and angles (°); Fe(1)–Fe(1A) 2.531(2), Fe(1)–P(1) 2.291(3), Fe(1)–S(1) 2.265(4), Fe(1)–S(2) 2.259(3), P(1)–Fe(1)–S(1) 153.63(11), P(1)–Fe(1)–S(2) 85.67(14), Fe(1)–S(1)–Fe(1A) 67.93(13), Fe(1)–S(2)–Fe(1A) 68.12(12), C(1)–Fe(1)–Fe(2) 114.9(3), C(2)–Fe(1)–Fe(1A) 144.0(4), P(1)–C(6)–P(1A) 122.5(10).

poor as the crystal was only weakly diffracting, and the included half molecule of diethylether and a disordered BF₄ anion both of which could only be poorly modeled. Nevertheless, the main structural features of the cation could be discerned. The diiron unit lies on a plane of symmetry with the central carbon of pdt ligand being disordered over two sites (50:50). The metal–metal bond at 2.531(2) Å is slightly elongated as compared to **6** [Fe–Fe(av) 2.520 Å] and the diiron centre is more *open* as shown by the increasing bond angle between the basal carbonyl and *trans* thiolate sulfur; C(1)–Fe(1)–S(2) 170.6(3)° in **11** as compared to C(2)–Fe(1)–S(1) 152.3° and C(4)–Fe(2)–S(1) 162.9° in **6**. Three pairs of protonated–unprotonated pdt complexes have previously been crystallographically characterised, being derived from [Fe₂(CO)₄(PMe₃)₂(μ-pdt)], [Fe₂(CO)₄(PMe₂Ph)₂(μ-pdt)] and [Fe₂(CO)₄(κ²-Ph₂PCH₂CH₂PPh₂)-(μ-pdt)] [4c,4d,7e,8a]. In all cases a lengthening of the iron–iron vector is noted, but here protonation is also associated with significant ligand rearrangements; for example, diapically substituted [Fe₂(CO)₄(PMe₂Ph)₂(μ-pdt)] rearranges to dibasal [(μ-H)Fe₂(CO)₄(PMe₂Ph)₂(μ-pdt)][PF₆] [4d,8a]. Transformation of **6**–**11** occurs without significant rearrangement of the diphosphine ligand and thus the coordination geometry about the metal centre.

3. Conclusions

It is clear from the work described herein and from that of others [7e,12,13] that reactions of [Fe₂(CO)₆(μ-pdt)] (**1**) with diphosphines can lead to a range of products the nature of which is dependent upon both the backbone flexibility of the diphosphine and the reaction conditions employed. For diphosphines with a single methylene backbone (dppm and dcpm), symmetrically disubstituted *cisoid* complexes are thermodynamically favoured. In separate

work we have shown that this complexity increases upon lengthening the methylene backbone, such that for 1,3-bis(diphenylphosphino)propane (dppp) a range of co-existing products including chelate, bridged and linked binuclear complexes are available [18]. In contrast, for the more rigid diphosphines (*cis*-dppv and dppb), the asymmetrically disubstituted complexes are exclusively formed, although reaction times can be long. An aim of our research is to prepare such asymmetrically substituted complexes [19] and investigate their reactivity towards cyanide and proton sources. Complexes **8** and **9** fulfil this requirement as do complexes derived from the reaction of **1** amino-diphosphines, $Ph_2PN(R)PPh_2$ and these studies will be reported in the near future.

4. Experimental

All reactions were carried out under a nitrogen atmosphere in dried degassed solvents unless otherwise stated. Phosphines were purchased from Aldrich and used as supplied and $[Fe_2(CO)_6(\mu\text{-pdt})]$ was prepared as described in the literature [3]. NMR spectra were run on a Bruker AMX400 spectrometer and referenced internally to the residual solvent peak (^{1}H) or externally to $P(OMe)_3$ (^{31}P). Infrared spectra were run on Nicolet 205 or Shimadzu 8700 FT-IR spectrometers in a solution cell fitted with calcium fluoride plates, subtraction of the solvent absorptions being achieved by computation. Fast atom bombardment mass spectra were recorded on a VG ZAB-SE high resolution mass spectrometer and elemental analyses were performed in house. Chromatography was carried out on deactivated alumina support. The crude mixtures were dissolved in a small amount (*ca.* 5 ml) of dichloromethane, absorbed onto alumina (*ca.* 10 g) and dried. This was then added to the top of the wet chromatography column.

4.1. Thermolysis of 1 and dppm in toluene: synthesis of [Fe₂(CO)₄(dppm)(μ-pdt)] (2–3)

A toluene solution (80 cm^3) of **1** (0.20 g, 0.52 mmol) and dppm (0.26 g, 0.68 mmol) was refluxed for 16 h leading to a colour change from orange to dark red. After cooling to room temperature volatiles were removed by rotary evaporation to give an oily red solid which was washed with hexane (3 × 10 cm^3) to remove a small amount of unreacted **1** and excess dppm. After drying an orange-red solid was obtained shown to be a mixture of isomers of $[Fe_2(CO)_4(\mu\text{-dppm})(\mu\text{-pdt})]$ (0.28 g, 76%). Alternatively, the crude reaction mixture was dissolved in a minimum of dichloromethane (*ca.* 5 cm^3) and absorbed onto deactivated alumina. Chromatography on alumina in hexane gave an orange band eluting with hexane which gave a small amount (0.03 g) of unreacted **1**. Eluting with Et$_2$O:hexane 1:1 gave an orange band which afforded $[Fe_2(CO)_4(\mu\text{-dppm})(\mu\text{-pdt})]$ (**2**) as a bright orange solid (0.21 g, 57%). Crystallisation from the slow diffusion of methanol into a dichloromethane solution gave **2** as small

orange blocks. For **2**: IR v(CO) (CH$_2$Cl$_2$): 1988s, 1957vs, 1921s, 1908sh cm^{-1}; ^{1}H NMR (CDCl$_3$, 298 K): δ 7.80–7.10 (m, br, 20H, Ph), 3.70 (br, 1H, PCH$_2$), 3.21 (br, 1H, PCH$_2$), 2.17 (br, 4H, SCH$_2$), 1.97 (br, 2H, CH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 53.2 (s); (CD$_2$Cl$_2$, 213 K): 54.6 (d, J 54.6), 51.4 (d, J 54.6). Anal. Calc. for Fe$_2$P$_2$S$_2$O$_4$-C$_{32}$H$_{28}$ · 0.5CH$_2$Cl$_2$: C, 51.55; H, 3.83. Found: C, 51.66; H, 3.93%.

A toluene solution (80 cm^3) of **1** (0.20 g, 0.52 mmol) and dppm (0.26 g, 0.68 mmol) was refluxed for 5 h. Volatiles were removed under reduced pressure, the crude reaction mixture was dissolved in a minimum of dichloromethane (*ca.* 5 cm^3) and absorbed onto deactivated alumina. Chromatography on alumina in hexane gave unreacted **1** and dppm. Eluting with Et$_2$O:hexane 1:4 gave a red band which afforded 0.08 g of a red solid. This was shown to be a mixture of **3** and **4** (approximate ratio 1:4 by ^{31}P NMR spectroscopy). Crystallisation of this mixture upon slow diffusion of hexane into a diethyl ether solution afforded a small number of red blocks of $[Fe_2(CO)_4(\kappa^2\text{-dppm})\text{-}(\mu\text{-pdt})]$ (**3**). Unfortunately, there were insufficient for elemental analysis. Eluting with Et$_2$O:hexane 1:1 gave an orange band which afforded **2** (0.10 g, 27%). For **3**: IR v(CO)(C$_6$H$_{14}$): 2023vs, 1952 s, 1917m cm^{-1}; ^{1}H NMR (CDCl$_3$, 298 K): δ 7.80–7.24 (m, br, 20H, Ph), 4.78 (br, 1H, PCH$_2$), 4.22 (br, 1H, PCH$_2$), 2.28 (br, 2H, SCH$_2$), 2.16 (br, 2H, SCH$_2$), 2.01 (br, 2H, CH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 12.5 (s).

4.2. Reaction of 1 and dppm in MeCN: synthesis of [Fe₂(CO)₅(κ¹-dppm)(μ-pdt)] (4) and [Fe₂(CO)₅-(κ¹-dppmO)(μ-pdt)] (5)

To an MeCN solution (10 cm^3) of **1** (0.10 g, 0.24 mmol) and dppm (0.10 g, 0.26 mmol) at room temperature was slowly added an MeCN solution (5 cm^3) of Me$_3$NO · 2H$_2$O (0.058 g, 0.52 mmol). This resulted in a colour change from orange to red. IR v(CO)(CH$_2$Cl$_2$): 2044s, 1982br, 1928w cm^{-1}. The mixture was stirred for 14 h after which volatiles were removed under reduced pressure giving a dark red solid. IR v(CO)(CH$_2$Cl$_2$): 2044s, 2017w, 1982br, 1926w, cm^{-1}. ^{31}P NMR (CDCl$_3$, 298 K): δ −57.4 (d, J 84.5, **4**), 55.7 (d, J 18.9, **5**), 25.1 (s, dppmO$_2$), 23.1 (d, J 18.9, **5**), 12.5 (s, **3**), −25.7 (d, J 84.5, **4**). Ratio **3**:**4**:**5**:dppmO$_2$ *ca.* 1:10:3:1.5. In an attempt to convert **4** into **3** we carried out a similar reaction at 60 °C. To an MeCN solution (15 cm^3) of **1** (0.25 g, 0.65 mmol) and dppm (0.25 g, 0.65 mmol) was added an MeCN solution (5 cm^3) of Me$_3$NO · 2H$_2$O (0.058 g, 0.52 mmol). The mixture was stirred at room temperature for 1 h and then heated in a graphite bath maintained at 58 °C for 14 h. After cooling to room temperature, volatiles were removed under reduced pressure to give a dark red solid. IR v(CO)(CH$_2$Cl$_2$): 2043s, 1982br, 1959w, 1919w cm^{-1}; IR v(CO)(C$_6$H$_{14}$): 2048, 2042, 2023, 1986, 1966, 1952 cm^{-1}. The crude reaction mixture was dissolved in a minimum of dichloromethane (*ca.* 5 cm^3) and absorbed onto deacti-

vated alumina. Chromatography on alumina in hexane gave a yellow band eluting with hexane yielding a small quantity of **1**. Eluting with hexane:Et$_2$O (9:1) gave a red band which afforded [Fe$_2$(CO)$_5$(κ^1-dppm)(μ-pdt)] (**4**) as a red powder (0.29 g, 60%). Eluting with hexane:Et$_2$O (4:1) gave an orange band which afforded a small amount of a dark orange solid (*ca.* 30 mg) shown to be a mixture of **4**, **5** and **3** (ratio *ca.* 8:4:1) by ^{31}P NMR spectroscopy. Eluting with hexane:Et$_2$O (7:3) gave a second orange band which afforded **2** (0.08 g, 17%). Eluting CH$_2$Cl$_2$:Et$_2$O (3:7) gave an orange-brown band which afforded [Fe$_2$(CO)$_5$-(κ^1-dppmO)(μ-pdt)] (**5**) as a brown solid (0.12 g, 24%). Pure **4** was formed upon slow addition of hexanes to a concentrated dichloromethane solution. For **4**: IR v(CO) (CH$_2$Cl$_2$): 2043m, 1981vs, 1961sh, 1924w cm^{-1}; ^{1}H NMR (CDCl$_3$, 298 K): δ 7.62 (t, *J* 8.5, 4H, Ph), 7.29–7.20 (m, 16H, Ph), 3.30 (dd, *J* 8.9, 2.3, 2H, PCH$_2$), 1.85 (br, 2H, SCH$_2$), 1.62 (br, 4H, SCH$_2$); ^{1}H NMR (d^8-toluene, 373 K): δ 7.61 (brt, *J* 5.8, 4H, Ph), 7.18 (brt, *J* 6.0, 4H, Ph), 6.91 (brs, 12H, Ph), 3.29 (d, *J* 8.4, 2H PCH$_2$P), 1.57 (quin, *J* 7.0, 2H, SCH$_2$), 1.54 (quin, *J* 7.0, 2H, SCH$_2$), 1.32 (quin, *J* 5.8, CH$_2$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 215.21 (dd, *J* 14.0, 2.3, 2CO), 210.29 (s, 3CO), 138.70 (dd, *J* 15.5, 7.2), 136.40 (dd, *J* 35.6, 3.8), 133.20 (s), 133.13 (d, *J* 1.3), 133.03 (d, *J* 1.3), 132.99 (s), 130.52 (d, *J* 2.3), 129.00 (s), 128.75 (d, *J* 7.1), 128.56 (d, *J* 9.4), 33.61 (dd, *J* 31.3, 21.9, PCH$_2$P), 30.72 (s, CH$_2$), 22.86 (s, 2SCH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 57.7 (d, *J* 84.6, Fe–P), −26.1 (d, *J* 84.6, P); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 59.2 (d, *J* 86.3), −24.3 (d, *J* 86.3); ^{31}P{^{1}H} NMR (CDCl$_3$, 213 K): δ 61.5 (br), 57.7 (br), −25.9 (br), −28.2 (br); ^{31}P{^{1}H} NMR (d^8-toluene, 298 K): δ 63.3 (d, *J* 89.7), −20.4 (d, *J* 89.7); ^{31}P{^{1}H} NMR (d^8-toluene, 373 K): δ 63.1 (d, *J* 78.1), −18.9 (d, *J* 78.1). Anal. Calc. for Fe$_2$P$_2$S$_2$O$_5$C$_{33}$H$_{28}$ · 0.5CH$_2$Cl$_2$: C, 51.24; H, 3.70. Found: C, 51.84; H, 4.02%. For **5**: IR v(CO) (CH$_2$Cl$_2$): 2044m, 1982vs, 1961sh, 1928w cm^{-1}; ^{1}H NMR (CDCl$_3$, 298 K): δ 7.70 (t, *J* 8.7, 4H, Ph), 7.51 (t, *J* 8.7, 4H, Ph), 7.38 (d, *J* 6.4, 2H, Ph), 7.32–7.22 (m, 10H, Ph), 3.55 (dd, *J* 10.1, 8.0, 2H, PCH$_2$), 1.94,1.92,1.90 (brs, 2H, SCH$_2$), 1.73,1.72,1.69,1.66,1.64 (brs, 4H, SCH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, 298 K): δ 55.7 (d, *J* 18.8, Fe–P), 23.1 (d, *J* 18.8, P=O). Anal. Calc. for Fe$_2$P$_2$S$_2$O$_6$C$_{33}$H$_{28}$ · 0.5C$_6$H$_{14}$: C, 53.93; H, 4.37. Found: C, 53.47; H, 4.35%.

4.3. Thermolysis of **1** and dcpm in toluene: synthesis of [Fe$_2$(CO)$_4$(μ-dcpm)(μ-pdt)] (**6**)

A toluene solution (20 cm^3) of **1** (0.20 g, 0.52 mmol) and dcpm (0.20 g, 0.49 mmol) was refluxed for 16 h leading to a colour change from orange to dark red. After cooling to room temperature volatiles were removed by rotary evaporation to give an oily red solid which was washed with hexane (3 × 10 cm^3) and dried. The crude reaction mixture was dissolved in a minimum of dichloromethane (*ca.* 5 cm^3) and absorbed onto deactivated alumina. Chromatography on alumina in hexane gave an orange band which gave a

small amount (0.02 g) of unreacted **1**. Eluting with Et$_2$O:hexane 1:9 gave an orange band which afforded [Fe$_2$(CO)$_4$(μ-dcpm)(μ-pdt)] (**6**) as a bright orange solid (0.30 g, 84%). Crystallisation from dichloromethane–methanol afforded large orange plates suitable for X-ray diffraction. For **6**: IR v(CO) (CH$_2$Cl$_2$): 1975s, 1942vs, 1906s, 1889w cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.49 (dt, *J* 13.9, 10.2, 1H, CH$_2$), 2.53–1.23 (m, 45H, Cy + CH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 61.6 (s). Anal. Calc. for Fe$_2$P$_2$S$_2$O$_4$-C$_{32}$H$_{52}$ · 0.5CH$_2$Cl$_2$: C, 49.96; H, 6.80. Found: C, 49.72; H, 6.80%.

4.4. Reaction of **1** and dcpm in MeCN: identification of [Fe$_2$(CO)$_5$(κ^1-dcpm)(μ-pdt)] (**7**)

To an MeCN solution (10 cm^3) of **1** (0.10 g, 0.26 mmol) and dcpm (0.107 g, 0.26 mmol) was added Me$_3$NO · 2H$_2$O (0.076 g, 0.64 mmol) in MeCN (5 cm^3) Me$_3$NO · 2H$_2$O (0.076 g, 0.64 mmol) resulting in a colour change from orange to dark red. The reaction was stirred at room temperature for 14 h and volatiles removed under reduced pressure to give a dark red solid. IR v(CO) (CH$_2$Cl$_2$): 2038s, 1980vs, 1961m cm^{-1}; ^{31}P{^{1}H} NMR (CDCl$_3$): δ 62.7 (d, *J* 23.8, **7**), 49.5 (s, dcpmO$_2$), −9.3 (d, *J* 23.8, **7**). Ratio **7**: dcpmO$_2$ *ca.* 2:1.

4.5. Synthesis of [Fe$_2$(CO)$_4$(κ^2-dppb)(μ-pdt)] (**8**)

A toluene solution (80 cm^3) of **1** (0.21 g, 0.54 mmol) and dppb (0.244 g, 0.55 mmol) was heated at reflux for 2 d to give a mud-green solution. After cooling to room temperature, the solvent was removed under vacuum and the resulting solid washed with hexanes (3 × 25 cm^3) giving a dark brown powder. This was dissolved in a minimum amount of dichloromethane and deactivated alumina (*ca.* 12 g) added. The solvent was removed under vacuum and the resulting solid purified by column chromatography. Eluting with hexane:Et$_2$O (9:1) afforded an orange band which gave [Fe$_2$(CO)$_4$(κ^2-dppb)(μ-pdt)] (**8**) (0.113 g, 26%) as a dry brown powder. A dark brown band then eluted with hexane:Et$_2$O (1:1) also yielded a further batch of **8** (0.115 g, 26%). Alternatively, to an MeCN solution (20 cm^3) of **1** (0.10 g, 0.26 mmol) and dppb (0.115 g, 0.26 mmol) at room temperature was added an MeCN solution (15 cm^3) of Me$_3$NO · 2H$_2$O (0.062 g, 0.56 mmol) resulting in a colour change from orange to dark red. The mixture was stirred at room temperature for 2 h and then placed in a graphite bath maintained at 60 °C for 14 h. After cooling to room temperature, volatiles were removed under vacuum giving the crude product as a dark red solid after washing with hexanes. This was then dissolved in dichloromethane, filtered under gravity and volatiles removed to give **8** as a red-brown solid (0.14 g, 69%). Recrystallisation upon slow diffusion of hexane into a concentrated dichloromethane solution gave crystals suitable for X-ray crystallography. For **8**: IR v(CO) (CH$_2$Cl$_2$): 2020s, 1949m, 1905w cm^{-1}; ^{31}P NMR (CDCl$_3$ 298 K): δ

88.1 (s), 80.5 (s) ratio *ca.* 10:1; ^{31}P NMR (CD$_2$Cl$_2$ 298 K): δ 90.3 (s), 82.3 (s); ^{31}P NMR (CD$_2$Cl$_2$ 178 K): δ 94.5 (s), 88.1 (s), 93.9 (s), 90.8 (s), ratio *ca.* 13:1; ^{1}H NMR (CDCl$_3$): δ 7.76–7.01 (m, 24H, Ar), 1.99–1.96 (m, 2H, SCH$_2$), 1.66, 1.63, 1.60 (brs, 4H, SCH$_2$); mass spectrum (FAB) *m/z* 776 (M$^+$, 1.05%), 748 (M$^+$−CO, 0.30%), 720 (M$^+$−2CO, 0.20%), 694 (M$^+$−3CO, 0.70%), 664 (M$^+$−4CO, 0.95%), 154 (100%). Anal. Calc. for Fe$_2$P$_2$S$_2$O$_4$C$_{37}$H$_{30}$ · 2CH$_2$Cl$_2$: C, 49.47; H, 3.60. Found: C, 50.30; H, 3.52%.

4.6. Synthesis of [Fe$_2$(CO)$_4$(κ^2-dppv)(μ-pdt)] (9) and [Fe$_2$(CO)$_5$(κ^1-dppvO)(μ-pdt)] (10)

A toluene solution (50 cm^3) of **1** (0.20 g, 0.53 mmol) and *cis*-dppv (0.208 g, 0.52 mmol) was refluxed for 2 d to give a dark red solution. After cooling to room temperature volatiles were removed under reduced pressure and the crude material washed with hexane (3 × 50 cm^3) to give a dark red powder consisting predominantly of [Fe$_2$(CO)$_4$-(κ^2-dppv)(μ-pdt)] (**9**) (0.26 g, 69%). Extraction into diethyl ether followed by filtration and removal of volatiles gave a purer product. Some of the desired product was extracted with hexane and upon cooling was precipitated as a red-brown solid. Crystallisation from slow diffusion of hexane into a concentrated dichloromethane solution gave a brown crystalline material suitable for analysis. Alternatively, an MeCN solution (10 cm^3) of Me$_3$NO · 2H$_2$O (0.06 g, 0.54 mmol) was added to a stirred MeCN solution (15 cm^3) of **1** (0.104 g, 0.27 mmol) and *cis*-dppv (0.105 g, 0.264 mmol) over 10 min, resulting in an instant colour change from orange to dark red. The reaction was stirred at room temperature for 2 h and then at 60 °C for 14 h. After cooling to room temperature, volatiles were removed under reduced pressure to give a dark red solid. This was adsorbed onto deactivated alumina (*ca.* 5 g) and column chromatography carried out. Eluting with hexane:Et$_2$O (3:2) gave a brown band which afforded **9** (0.057 g, 29%). Eluting with hexane:Et$_2$O (1:9) gave a pink band which afforded [Fe$_2$(CO)$_5$(κ^1-dppvO)(μ-pdt)] (**10**) (0.036 g, 18%) as a pale red solid. For **9**: IR ν(CO) (CH$_2$Cl$_2$): 2020vs, 1950s, 1912w cm^{-1}; ^{31}P NMR (CDCl$_3$ 298 K): δ 96.0 (s), 82.1 (s) ratio *ca.* 10:1; ^{1}H NMR (CDCl$_3$): δ 8.10–6.98 (m, 22H, Ar + CH=CH), 1.71 (brs, 2H, SCH$_2$), 1.41 (brs, 2H, SCH$_2$), 1.25 (brs, 2H, CH$_2$); mass spectrum (FAB) *m/z* 726 (M$^+$, 15%), 176 (100%). Anal. Calc. for Fe$_2$P$_2$-S$_2$O$_4$C$_{33}$H$_{28}$ · CH$_2$Cl$_2$: C, 50.31; H, 3.70. Found: C, 49.57; H, 4.13%. For **10**: IR ν(CO) (CH$_2$Cl$_2$): 2043s, 1987vs, 1962s, 1937w cm^{-1}; ^{31}P NMR (CDCl$_3$ 298 K): δ 55.3 (d, *J* 10.9, Fe–P, **10a**), 54.5 (d, *J* 11.0, Fe–P, **10b**), 17.5 (d, *J* 10.9, P=O, **10a**), 17.3 (d, *J* 11.0, P=O, **10b**) ratio **10a:10b** *ca.* 3:1; ^{1}H NMR (CDCl$_3$): δ 7.80–6.98 (m, 22H, Ar + CH=CH), 2.28 (brs, 1H, SCH$_2$, **10a**), 2.17 (brs, 1H, SCH$_2$, **10b**), 1.75 (brs, 2H, SCH$_2$, **10a**), 2.28 (brs, 1H, SCH$_2$, **10a**), 1.43 (brs, 4H, **10a** and **10b**); mass spectrum (FAB) *m/z* 726 (M$^+$, 15%), 176 (100%). Anal. Calc. for Fe$_2$P$_2$S$_2$O$_6$C$_{34}$H$_{28}$: C, 52.98; H, 3.66. Found: C, 52.81; H, 4.44%.

4.7. Synthesis of [(μ-H)Fe$_2$(CO)$_4$(dcpm)(μ-pdt)][BF$_4$] (11)

To a dichloromethane solution (10 cm^3) of **6** (50 mg, 0.068 mmol) was added one drop of HBF$_4$ · Et$_2$O. An immediate lightening of the orange solution was apparent and an IR spectrum showed the clean formation of [(μ-H)-Fe$_2$(CO)$_4$(μ-dcpm)(μ-pdt)][BF$_4$] (**11**). The solution was allowed to sit in air for 4 h and no further changes were observed. Removal of volatiles gave an oily orange solid which was dried and washed with diethyl ether (1 cm^3). This was quite strongly coloured and was thus layered with hexane. Slow mixing of the two solvents lead to the formation of crystals suitable for X-ray diffraction. The ether insoluble material was washed with hexane and dried to afford **11** as a pale orange solid (0.50 g, 89%). IR ν(CO) (CH$_2$Cl$_2$): 2047m, 2029vs, 1993s cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ 4.78 (q, *J* 11, 1H, CH$_2$), 3.68–1.15 (m, 45H, Cy + CH$_2$), 14.54 (t, *J* 26.8, 1H, μ-H); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 70.9 (s).

4.8. X-ray data collection and solution

Single crystals were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction was carried out with SAINT PLUS and absorption correction applied using the programme SADABS. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. For **3** all non-hydrogen atoms were refined anisotropically. The structure of **2** contains one whole and two half diiron molecules. The central methylene carbon, C(6), of the pdt group in the whole molecule was disordered (50:50) over two sites. The structure also contained half molecules of hexane and methanol. In all cases these atoms were refined only isotropically. Hydrogens were generally placed in calculated positions (riding model). The hydrogen atoms on the solvate molecules and the pdt methylene carbons were not included. Complex **6** contains four full diiron molecules and two molecules of dichloromethane in the asymmetric unit. All atoms were refined anisotropically. The crystal of **11** was only weakly diffracting. The central methylene carbon, C(4), of the pdt group was disordered (50:50) over two sites and the fluorines of the BF$_4$ were disordered over three sites (45:45:10). A solvate diethylether was best modeled at 25% site occupancy with atoms lying in a plane of symmetry. The *x* and *z* coordinates were fixed for refinement as two of the atoms, C(22) and C(23) kept drifting away from the central oxygen. The hydrogen atoms on the solvate molecule, the pdt methylene carbons and the bridging hydride were not included. Structure solution used SHELXTL PLUS V6.10 program package.

Crystallographic data for 2[Fe$_2$(CO)$_4$(μ-dppm)-(μ-pdt)] · 0.5C$_6$H$_{14}$ · 0.5MeOH (2). Orange block, dimensions $0.18 \times 0.13 \times 0.05$ mm, orthorhombic, space group

P_{nma}, $a = 16.1052(19)$ Å, $b = 40.759(5)$ Å, $c = 21.395(3)$ Å, $V = 14045(3)$ Å^3, $Z = 4$, $F(000)$ 6056, $d_{calc} = 1.399$ g cm^{-3}, $\mu = 1.072$ mm^{-1}. 120 128 reflections were collected, 17 467 unique [$R_{int} = 0.0992$] of which 11 245 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0687$, $wR_2 = 0.1616$ [$I > 2.0\sigma(I)$] and $R_1 = 0.1148$, $wR_2 = 0.1843$ (all data), for 822 parameters.

Crystallographic data for [Fe$_2$(CO)$_4$(κ^2-dppm)(μ-pdt)] (**3**). Red block, dimensions $0.14 \times 0.13 \times 0.11$ mm, triclinic, space group P_{1bar}, $a = 10.3556(13)$ Å, $b = 12.1406(15)$ Å, $c = 12.9298(16)$ Å, $\alpha = 91.174(2)°$, $\beta = 98.599(2)°$, $\gamma = 102.055(2)°$, $V = 1569.6(3)$ Å^3, $Z = 2$, $F(000)$ 732, $d_{calc} = 1.511$ g cm^{-3}, $\mu = 1.195$ mm^{-1}. 12 622 reflections were collected, 7042 unique [$R_{int} = 0.0378$] of which 5039 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0543$, $wR_2 = 0.1253$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0826$, $wR_2 = 0.1387$ (all data), for 379 parameters.

Crystallographic data for 4[Fe$_2$(CO)$_4$(μ-dcpm)-(μ-pdt)] · 2CH$_2$Cl$_2$ (**6**). Orange plate, dimensions $0.48 \times 0.26 \times 0.03$ mm, orthorhombic, space group $Pca2_1$, $a = 15.7448(10)$ Å, $b = 20.2384(13)$ Å, $c = 45.917(3)$ Å, $V = 14631.6(16)$ Å^3, $Z = 8$, $F(000)$ 6576, $d_{calc} = 1.418$ g cm^{-3}, $\mu = 1.102$ mm^{-1}. 120 987 reflections were collected, 33 528 unique [$R_{int} = 0.0912$] of which 25 468 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0555$, $wR_2 = 0.1107$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0826$, $wR_2 = 0.1212$ (all data), for 1567 parameters.

Crystallographic data for [Fe$_2$(CO)$_4$(κ^2-dppb)(μ-pdt)] · CH$_2$Cl$_2$ (**8**). Brown block, dimensions $0.24 \times 0.08 \times 0.07$ mm, monoclinic, space group Pc, $a = 10.1181(13)$ Å, $b = 10.9537(14)$ Å, $c = 17.301(2)$ Å, $\beta = 106.262(2)°$, $V = 1840.7(4)$ Å^3, $Z = 2$, $F(000)$ 880, $d_{calc} = 1.554$ g cm^{-3}, $\mu = 1.174$ mm^{-1}. 15 525 reflections were collected, 8372 unique [$R_{int} = 0.0398$] of which 7769 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0381$, $wR_2 = 0.0856$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0422$, $wR_2 = 0.0874$ (all data), for 451 parameters.

Crystallographic data for [Fe$_2$(CO)$_4$(μ-dcpm)(μ-pdt)][BF$_4$] · 0.5Et$_2$O (**11**). Orange plate, dimensions $0.12 \times 0.04 \times 0.03$ mm, orthorhombic, space group $C2/m$, $a = 28.225(8)$ Å, $b = 14.318(4)$ Å, $c = 10.887(3)$ Å, $V = 4400(2)$ Å^3, $Z = 2$, $F(000)$ 6920, $d_{calc} = 1.238$ g cm^{-3}, $\mu = 0.868$ mm^{-1}. 12 742 reflections were collected, 4879 unique [$R_{int} = 0.1877$] of which 1485 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.1150$, $wR_2 = 0.2787$ [$I > 2.0\sigma(I)$] and $R_1 = 0.2523$, $wR_2 = 0.3186$ (all data), for 234 parameters.

Acknowledgements

Appendix A. Supplementary material

CCDC 614428, 614429, 641156, 639867 and 641658 contain the supplementary crystallographic data for **2**, **3**, **6**, **8** and **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.050.

References

[1] R.B. King, J. Am. Chem. Soc. 84 (1962) 2460.
[2] (a) Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian, J.C. Fontecilla-Camps, Structure 7 (1999) 13;
(b) I.P. Georgakaki, L.M. Thomson, E.J. Lyon, M.B. Hall, M.Y. Darensbourg, Coord. Chem. Rev. 238–239 (2003) 255;
(c) D.J. Evans, C.J. Pickett, Chem. Soc. Rev. 32 (2003) 268;
(d) T.B. Rauchfuss, Inorg. Chem. 43 (2004) 14;
(e) L. Sun, B. Åkermark, S. Ott, Coord. Chem. Rev. 249 (2005) 1653;
(f) X. Liu, S.K. Ibrahim, C. Tard, C.J. Pickett, Coord. Chem. Rev. 249 (2005) 1641.
[3] D. Seyferth, G.B. Womack, M.K. Gallagher, M. Cowie, B.W. Hames, J.P. Fackler, A.M. Mazany, Organometallics 6 (1987) 83.
[4] (a) E.J. Lyon, I.P. Georgakaki, J.H. Reibenspies, M.Y. Darensbourg, Angew. Chem., Int. Ed. Engl. 38 (1999) 3178;
(b) E.J. Lyon, I.P. Georgakaki, J.H. Reibenspies, M.Y. Darensbourg, J. Am. Chem. Soc. 123 (2001) 3268;
(c) X. Zhao, I.P. Georgakaki, M.L. Miller, J.C. Yarbrough, M.Y. Darensbourg, J. Am. Chem. Soc. 123 (2001) 9710;
(d) X. Zhao, I.P. Georgakaki, M.L. Miller, R. Mejia-Rodriguez, C.-Y. Chiang, M.Y. Darensbourg, Inorg. Chem. 41 (2002) 3917;
(e) D. Chong, I.P. Georgakaki, R. Mejia-Rodriguez, J. Sanabria-Chinchilla, M.P. Soriaga, M.Y. Darensbourg, Dalton Trans. (2003) 4158;
(f) R. Mejia-Rodriguez, D. Chong, J.H. Reibenspies, M.P. Soriaga, M.Y. Darensbourg, J. Am. Chem. Soc. 126 (2004) 12004.
[5] (a) F. Gloaguen, J.D. Lawrence, T.B. Rauchfuss, J. Am. Chem. Soc. 123 (2001) 9476;
(b) F. Gloaguen, J.D. Lawrence, T.B. Rauchfuss, M. Bénard, M.-M. Rohmer, Inorg. Chem. 41 (2002) 6573.
[6] J. Nehring, D.M. Heinekey, Inorg. Chem. 42 (2003) 4288.
[7] (a) J.-F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin, J. Electroanal. Chem. 566 (2004) 241;
(b) J.-F. Capon, S. El Hassnaoui, F. Gloaguen, P. Schollhammer, J. Talarmin, Organometallics 24 (2005) 2020;
(c) V. Vijaikanth, F. Gloaguen, P. Schollhammer, J. Talarmin, Electrochem. Commun. 7 (2005) 747;
(d) D. Morvan, J.-F. Capon, F. Gloaguen, A. Le Goff, M. Marchivie, F. Michaud, P. Schollhammer, J. Talarmin, J.-J. Yaouanc, R. Pichon, N. Kervarec, Organometallics 26 (2007) 2042;
(e) S. Ezzaher, J.-F. Capon, F. Gloaguen, F.Y. Petillon, P. Schollhammer, J. Talarmin, R. Pichon, N. Kervarec, Inorg. Chem. 46 (2007) 3426.
[8] (a) P. Li, M. Wang, C. He, G. Li, X. Liu, C. Chen, B. Åkermark, L. Sun, Eur. J. Inorg. Chem. 44 (2005) 2506;
(b) W. Gao, J. Liu, B. Åkermark, L. Sun, Inorg. Chem. 45 (2006) 9169;
(c) W. Gao, J. Liu, B. Åkermark, L. Sun, J. Organomet. Chem. 692 (2007) 1579;
(d) W. Dong, M. Wang, T. Liu, X. Liu, K. Jin, L. Sun, J. Inorg. Biochem. 101 (2007) 506;

(e) L. Duan, M. Wang, P. Li, N. Wang, L. Sun, Dalton Trans. (2007) 1277.
[9] (a) J.W. Peters, W.N. Lanzilotta, B. Lemon, L.C. Seefeldt, Science 282 (1998) 1853;
(b) B.J. Lemon, J.W. Peters, Biochemistry 38 (1999) 12969.
[10] (a) Y. Nicolet, A.L. De Lacy, X. Vernéde, V.M. Fernandez, E.C. Hatchikian, J.C. Fontecilla-Camps, J. Am. Chem. Soc. 123 (2001) 1596;
(b) H.-J. Fan, M.B. Hall, J. Am. Chem. Soc. 123 (2001) 3828.
[11] (a) R.J. Puddpehatt, Chem. Soc. Rev. (1983) 99;
(b) B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 134.
[12] W. Gao, J. Ekström, J. Liu, C. Chen, L. Eriksson, L. Weng, B. Åkermark, L. Sun, Inorg. Chem. 46 (2007) 1981.
[13] A.K. Justice, G. Zampella, L. De Gioia, T.B. Rauchfuss, J.I. van der Vlugt, S.R. Wilson, Inorg. Chem. 46 (2007) 1655.
[14] G. Hogarth, I. Richards, Inorg. Chem. Commun. 10 (2007) 66.
[15] G. Hogarth, M. O'Brien, D.A. Tocher, J. Organomet. Chem. 672 (2003) 29.
[16] (a) M.R. Awang, J.C. Jeffery, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1983) 2091;

(b) F.A. Cotton, W.J. Roth, Inorg. Chem. 22 (1983) 3654;
(c) P. Braunstein, C.deM. de Bellefon, M. Lanfranchi, A. Tiripicchio, Organometallics 3 (1984) 1772;
(d) K.-K. Lee, W.T. Pennington, A.W. Cordes, T.L. Brown, J. Am. Chem. Soc. 107 (1985) 631;
(e) B. Delavaux, B. Chaudret, F. Dahan, R. Poilblanc, Organometallics 4 (1985) 935;
(f) S. Guesmi, P.H. Dixneuf, N.J. Taylor, A.J. Carty, J. Organomet. Chem. 328 (1987) 193;
(g) C. Potvin, J.-M. Manoli, F. Secheresse, S. Marzak, Inorg. Chim. Acta 134 (1987) 9;
(h) J.T. Lin, S.Y. Wang, P.S. Huang, Y.M. Hsiao, Y.S. Wen, S.K. Yeh, J. Organomet. Chem. 388 (1990) 151.
[17] A.D. Horton, M.J. Mays, P.R. Raithby, J. Chem. Soc., Dalton Trans. (1987) 1557.
[18] G. Hogarth, I. Richards, unpublished.
[19] F.I. Adam, G. Hogarth, I. Richards, B.E. Sanchez, Dalton Trans. (2007) 2495.