

# Reduction of substituted cyclopropenes by $[\text{Fe}(\text{H})\text{H}_2-(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2][\text{BPh}_4]$ , and the validity of these reactions as models for nitrogenase function

David L. Hughes,<sup>b</sup> G. Jeffery Leigh<sup>\*a</sup> and C. Niamh Mc Mahon<sup>b</sup>

<sup>a</sup> School of Chemistry, Physics, and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ. E-mail: G.J.Leigh@Sussex.ac.uk

<sup>b</sup> Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Colney, Norwich, UK NR4 7UH

Received 20th November 1998, Accepted 21st January 1999

The complex  $[\text{FeH}(\text{H}_2)(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2][\text{BPh}_4]$  reacts with various substituted cyclopropenes to give mixtures of propenes and cyclopropanes. No further acid is required and the solvent, acetone, appears to be a ready source of protons. The only iron-containing product isolated is  $[\{\text{FeH}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\}_2(\mu\text{-Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)][\text{BPh}_4]_2$ , the structure of which was determined by X-ray crystal structure analysis. Evidence that a direct iron–cyclopropene interaction is necessary for hydrocarbon reduction to occur is outlined and the validity of this iron system as a model for nitrogenase function is assessed.

## Introduction

We have previously used platinum(0) complexes as models for the nitrogenase active site because platinum(0) is one of the few moieties that produce stable complexes containing cyclopropenes coordinated in an  $\eta^2$ -mode.<sup>1</sup> We treated platinum(0) cyclopropene adducts with protic acids to model events that may occur when cyclopropene is reduced by nitrogenases. However, it has been suggested that the active sites of nitrogenases contain metal hydrides,<sup>2</sup> and it is therefore of interest to investigate the reactions of cyclopropenes with iron and molybdenum hydrides. We have already reported briefly on the reaction of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  ( $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ) with cyclopropene,<sup>3</sup> and in more detail on its reaction with alkynes.<sup>4</sup> We showed that cyclopropene generates cyclopropane and dihydrogen, but no propene.<sup>3</sup> Reactions of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with alkynes produced iron–vinylidene complexes and alkene side-products.<sup>4</sup> In this paper we report on reactions of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with 3,3-dimethylcyclopropene and with 3,3- and 1,2-diphenylcyclopropene. Reactions of  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  with 3,3-dimethyl- and 3,3-diphenyl-cyclopropene are also outlined. Several other reactions were carried out to increase the understanding of the hydrocarbon reduction mechanism in these iron systems.

## Results and discussion

Reactions of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  and  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  were carried out in acetone under argon in order to avoid their facile reaction with dinitrogen, which yields  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$ .<sup>5</sup> Two equivalents of the cyclopropene were used but only one equivalent of cyclopropene was reduced, the second equivalent being recovered unchanged. All reactions were monitored by <sup>31</sup>P NMR spectroscopy and the iron–phosphine products were characterised using this technique. During the reaction the solution changed from clear yellow to a cloudy orange-brown. The hydrocarbon products from reaction of diphenylcyclopropenes were solvent-extracted from the reaction residue, purified by chromatography, and characterised by NMR spectroscopy. The volatiles from dimethylcyclopropene reactions were characterised using gas chromatography, by comparison of their retention times with those of likely reduction products. The absolute yields of hydrocarbon products were not determined.

## Iron-containing product

No iron–cyclopropene or iron–cyclopropane complexes were isolated from these reactions. Only one phosphorus- and iron-containing product was ever detected in the reaction mixtures and this was isolated and completely characterised as  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$ . This complex has already been characterised spectroscopically (see below). It has two signals in the <sup>31</sup>P NMR spectrum which indicates that the chelating phosphines are equivalent and implies a *trans* geometry for the hydride and the unidentate, bridging phosphine ligand. This was the major product as determined by <sup>31</sup>P NMR spectroscopy, and the yield varied from reaction to reaction, but never exceeded 50%, but as  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$  contains more than two moles of dmpe per iron atom there clearly must be at least one other iron-containing product. No other such compound was identified, but it is probably insoluble and causes the cloudiness observed in the reaction solution. A bridging diphosphine such as we observe here was first structurally characterised in the complex,  $[\{\text{Fe}(\text{NO})_2\text{-Cl}\}_2(\mu\text{-dppe})]$ .<sup>6</sup>

Baker *et al.*<sup>7</sup> reported that  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BF}_4]_2$  was formed after addition of dmpe to a methanolic solution of *cis*- $[\text{FeH}_2(\text{dmpe})_2]$ , which is known to contain an equilibrium amount of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2]^+$ , followed by precipitation with NaBF<sub>4</sub>. They showed that dmpe initially reacts to form  $[\text{FeH}(\text{dmpe-}P,P')_2(\text{dmpe-}P)]^+$ , which they also characterised spectroscopically, and that this complex then generates the dinuclear species isolated,  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BF}_4]_2$ . Our study of the reaction of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with dmpe did not yield  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$ . Instead,  $[\text{FeH}(\text{dmpe-}P,P')_2(\text{dmpe-}P)][\text{BPh}_4]$  was isolated. This difference in final product is probably due to the presence of the counter anion  $[\text{BPh}_4]^-$  in our solutions from the outset of our experiment, causing  $[\text{FeH}(\text{dmpe-}P,P')_2(\text{dmpe-}P)][\text{BPh}_4]$  to precipitate before it can rearrange in solution to the dinuclear species,  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$ . Several iron complexes with unidentate diphosphine have previously been structurally characterised.<sup>8,9</sup>

The complex  $[\{\text{FeD}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$  was formed analogously by reaction of  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  with substituted cyclopropenes. Its <sup>2</sup>H NMR spectrum is similar to the <sup>1</sup>H NMR spectrum of  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$  except that the Fe–D resonance was observed at  $\delta -16.6$ , with <sup>2</sup>J<sub>PD</sub>

values of *ca.* 7 and 2 Hz, about one sixth of the corresponding coupling constants found in the Fe–H compound, as expected.

We obtained crystals of the dinuclear deuterio-isotopomer suitable for X-ray structure analysis from an extended NMR experiment. The material is as expected, with a dmpe bridge and with deuteride ligands *trans* to the phosphorus atoms of the bridging dmpe. The structure of the cation is represented in Fig. 1, and selected bond lengths and angles are in Table 1.

There is a distorted octahedral geometry about each Fe atom; the D–Fe–P angles are 171(2) and 177(2)°, and the iron atoms are displaced from the mean planes of the four equatorially coordinated P atoms, towards the phosphorus atoms of the bridging dmpe ligand, by 0.349(1) and 0.329(1) Å. Each chelating dmpe is slightly different, with P–C–C–P torsion angles in the range –15.9(7) to –44.3(8)°. The bridging dmpe is twisted, with P–C–C–P = 145.3(4)°, and the Fe centres are *trans* with respect to the P...P link; this reduces the interaction between the chelating dmpe ligands, which have a staggered conformation, at opposite ends of the cation.

Dimensions in the chelating dmpe ligands are different from those in the bridge. For example, the *trans*-effect of the deuteride ligand lengthens the Fe–P bonds in the bridge to 2.260(2) and 2.254(2) Å compared to an average of 2.207(3) Å in the chelating ligands. In addition, the Fe–P–C(–C) and P–C–C

angles are both affected by steric constraints either to form the five-membered chelate ring or to extend the bridging system. As a consequence of these effects, the angles in the bridging ligand are consistently larger than those in the chelate rings.

## Reduction of cyclopropenes

Hydrocarbon materials produced by reduction of cyclopropenes with [FeH(H<sub>2</sub>)(dmpe)<sub>2</sub>][BPh<sub>4</sub>] and [FeD(D<sub>2</sub>)(dmpe)<sub>2</sub>][BPh<sub>4</sub>] are listed in Table 2. The reaction stoichiometries appeared to be close to 1:1. When 2 equivalents of the cyclopropene were used in these reactions, one equivalent of unreacted cyclopropene was always detected in the reaction mixture. The product yields given in Table 2 are expressed as percentages of the total material converted.

The predominant product from 3,3-dimethylcyclopropene was ring-opened 3-methylbut-1-ene and some 1,1-dimethylcyclopropane was also observed. This is in contrast to the reaction with cyclopropene which produces only cyclopropane. This difference between the kinds of products from reaction of cyclopropene and disubstituted cyclopropenes was also seen in platinum chemistry.<sup>1</sup> There is NMR evidence that the unidentified hydrocarbon from the reaction of [FeH(H<sub>2</sub>)(dmpe)<sub>2</sub>][BPh<sub>4</sub>] and 3,3-diphenylcyclopropene, which accounts for less than 5% of the total yield, is a dimeric species. Previous work has shown that iron–hydride systems can produce dimeric species from unsaturated substrates.<sup>7</sup> The reduced products from 1,2-diphenylcyclopropene were *E*-1,2-diphenylpropene, *Z*-1,2-diphenylpropene and 2,3-diphenylpropene. The ring-intact product, 1,2-diphenylcyclopropane, was not observed.

The only product unequivocally identified from the reaction of [FeD(D<sub>2</sub>)(dmpe)<sub>2</sub>][BPh<sub>4</sub>] with 3,3-dimethylcyclopropene was 3-methylbut-1-ene, and no 1,1-dimethylcyclopropane was detected. It was, of course, impossible to determine by gas chromatography the extent of deuteration, and we were not able to interpret the NMR spectra. However, products formed from reaction of [FeD(D<sub>2</sub>)(dmpe)<sub>2</sub>][BPh<sub>4</sub>] with 3,3-diphenylcyclopropene were analysed using <sup>1</sup>H and <sup>2</sup>H NMR spectroscopies. The presence of non-deuteriated material was confirmed by analysis of the multiplicities of signals and the coupling constants in the <sup>1</sup>H NMR spectrum. Signals were present in the <sup>2</sup>H NMR spectrum but the multiplets for protons

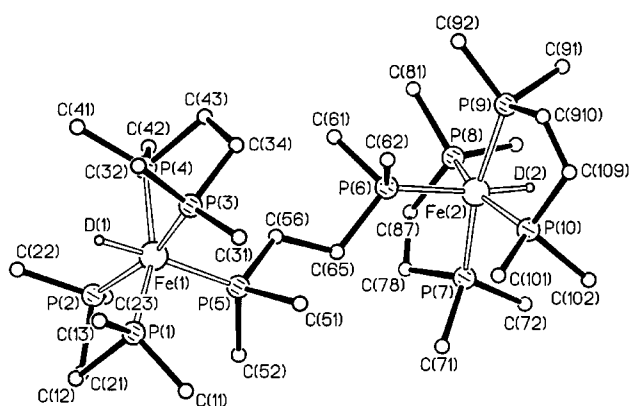


Fig. 1 ORTEP<sup>30</sup> representation of the structure of the cation in [FeD(dmpe)<sub>2</sub>]<sub>2</sub>(μ-dmpe)[BPh<sub>4</sub>]<sub>2</sub>.

Table 1 Selected bond lengths (Å), bond angles (°) and torsion angles (°) in the cation

### (a) About the metal atoms

Fe(1)–D(1)	1.44(5)	Fe(2)–D(2)	1.33(5)
Fe(1)–P(1)	2.206(3)	Fe(2)–P(6)	2.260(2)
Fe(1)–P(2)	2.211(2)	Fe(2)–P(7)	2.210(2)
Fe(1)–P(3)	2.208(2)	Fe(2)–P(8)	2.214(2)
Fe(1)–P(4)	2.204(2)	Fe(2)–P(9)	2.217(2)
Fe(1)–P(5)	2.254(2)	Fe(2)–P(10)	2.188(2)
D(1)–Fe(1)–P(1)	77.6(24)	D(2)–Fe(2)–P(6)	171.3(24)
D(1)–Fe(1)–P(2)	82.2(19)	D(2)–Fe(2)–P(7)	90.0(24)
D(1)–Fe(1)–P(3)	82.0(19)	D(2)–Fe(2)–P(8)	81.7(19)
D(1)–Fe(1)–P(4)	81.7(24)	D(2)–Fe(2)–P(9)	76.8(24)
D(1)–Fe(1)–P(5)	176.7(24)	D(2)–Fe(2)–P(10)	77.7(19)
P(1)–Fe(1)–P(2)	86.8(1)	P(6)–Fe(2)–P(7)	98.7(1)
P(1)–Fe(1)–P(3)	92.5(1)	P(6)–Fe(2)–P(8)	100.4(1)
P(1)–Fe(1)–P(4)	159.2(1)	P(6)–Fe(2)–P(9)	94.6(1)
P(1)–Fe(1)–P(5)	99.1(1)	P(6)–Fe(2)–P(10)	100.6(1)
P(2)–Fe(1)–P(3)	63.9(1)	P(7)–Fe(2)–P(8)	82.4(1)
P(2)–Fe(1)–P(4)	92.6(1)	P(7)–Fe(2)–P(9)	166.6(1)
P(2)–Fe(1)–P(5)	97.3(1)	P(7)–Fe(2)–P(10)	93.1(1)
P(3)–Fe(1)–P(4)	82.4(1)	P(8)–Fe(2)–P(9)	93.3(1)
P(3)–Fe(1)–P(5)	98.7(1)	P(8)–Fe(2)–P(10)	159.0(1)
P(4)–Fe(1)–P(5)	101.6(1)	P(9)–Fe(2)–P(10)	86.5(1)

### (b) Torsion angles in the dmpe ligands

P(1)–C(12)–C(21)–P(2)	–44.3(8)	P(3)–C(34)–C(43)–P(4)	–15.9(7)
P(5)–C(56)–C(65)–P(6)	–145.3(4)	P(7)–C(78)–C(87)–P(8)	–20.9(9)
P(9)–C(910)–C(109)–P(10)	–36.4(13)		

**Table 2** Hydrocarbon products from reduction reactions with  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  and  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$ 

Cyclopropene added	Products from $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$	Products from $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$
Cyclopropene <sup>a</sup>	Cyclopropane (100%)	
3,3-Dimethylcyclopropene	1,1-Dimethylcyclopropane (8%) 3-Methylbut-1-ene (92%)	Methylbutenes, with some deuteration
3,3-Diphenylcyclopropene	1,1-Diphenylpropene (86%) Uncharacterised dimer (5%) 1,1-Diphenylcyclopropene (9%)	3,3- <i>d</i> <sub>2</sub> -1,1-Diphenylpropene 1,1-Diphenylpropene 1,1-Diphenylcyclopropane Other unidentified products
1,2-Diphenylcyclopropene	<i>E</i> -1,2-Diphenylpropene (50%) <i>Z</i> -1,2-Diphenylpropene (17%) 2,3-Diphenylpropene (33%)	Unidentified products

<sup>a</sup> See ref. 3.

split by deuterium in the  $^1\text{H}$  NMR spectrum were weak and in most cases were obscured by resonances for hydrogenated rather than deuteriated material. The origin of the hydrogenated products is not obvious, but the source of the protons is probably acetone. The deuteriated product was 3,3-*d*<sub>2</sub>-1,1-diphenylpropene. Monodeuteriated products are also likely to have been present, but the complexity of the  $^1\text{H}$  and  $^2\text{H}$  NMR spectra made it difficult to confirm their presence.

The low degree of deuteration of cyclopropenes by stoichiometric amounts of  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  was unexpected. Acetone must be the source of protons for the reaction and iron may activate these external protons for cyclopropene reduction. Acetone exists with small equilibrium concentrations of the enolate,  $\text{CH}_3\text{C}(\text{OH})=\text{CH}_2$ , which has an available acidic proton. Evidence that iron hydride species can interact with solvents exists.<sup>7</sup>  $[\text{FeH}_2(\text{dmpe})_2]$  in acetone forms  $\{[\text{FeH}(\text{dmpe})_2]_2(\mu\text{-dmpe})\}^+$  over a few days. It is suspected that a small amount of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2]^+$  is formed in acetone and that this is subsequently attacked by acetone to release  $\text{H}_2$  and dmpe. Dmpe can react with  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2]^+$  to generate  $\{[\text{FeH}(\text{dmpe})_2]_2(\mu\text{-dmpe})\}^+$ , as discussed earlier.<sup>7</sup> We dissolved  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  in  $(\text{CD}_3)_2\text{CO}$  and  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  in  $(\text{CH}_3)_2\text{CO}$  routinely with no evidence of exchange with the solvent ever observed by NMR spectroscopy. Presumably the acetone must provide protons only after loss of  $\text{D}_2$  from the initial iron complex or there is some other interaction with the incoming cyclopropene, which allows the iron centre to utilise protons from the solvent.

#### Evidence for iron–cyclopropene interactions

Experiments were carried out to determine the order of events in these hydrocarbon reduction reactions. A standard reaction of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with an excess of 3,3-diphenylcyclopropene was carried out under an  $\text{H}_2$  atmosphere instead of argon. It was hoped that  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  could catalytically reduce cyclopropenes, because catalytic hydrogenation of alkynes has been shown to occur for similar systems.<sup>10,11</sup> However, the presence of  $\text{H}_2$  in the reaction mixture inhibited all reduction and only starting materials were recovered. This implies that the initial reaction step is likely to be the equilibrium loss of  $\text{H}_2$  from  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ , a process which would clearly be inhibited under an atmosphere of  $\text{H}_2$ .<sup>12</sup>

The kinetics of the substitution of  $\text{H}_2$  in  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  by acetonitrile, in solution in thf, have been studied previously by IR spectroscopy.<sup>13</sup> This reaction is first-order with respect to  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  concentration and zero-order with respect to acetonitrile concentration, with a rate constant of *ca.*  $1.6 \times 10^{-3} \text{ s}^{-1}$ . Similarly, the reaction of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with acetonitrile is first-order with respect to the concentration of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (dmpe =  $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PET}_2$ ) and zero-order with respect to acetonitrile concen-

tration.<sup>12,14</sup> The kinetics of the replacement of dihydrogen in phosphine complexes of iron, ruthenium, and osmium trihydrides by donors such as nitriles have also been studied by NMR spectroscopy. The rate-determining step in every case is the loss of  $\text{H}_2$ .<sup>9</sup>  $[\text{FeH}(\text{dmpe})_2]^+$  may be a short-lived reactive species in solution, but a recent kinetic study of the substitution of  $\text{H}_2$  in *trans*- $[\text{FeH}(\text{H}_2)(\text{dppe})_2][\text{BF}_4]$  (dppe =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) by acetonitrile, benzonitrile or dmsO (L) has been interpreted in terms of a different mechanism.<sup>15</sup> The rate-determining step is deduced to be the attack of L on an intermediate formed by detachment of one arm of a chelating phosphine ligand from the iron. However, we have not studied any dppe complexes.

Further evidence that a cyclopropene–iron interaction is involved in the reduction of cyclopropenes is detailed below. Reaction of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with dmsO resulted in the spectroscopically characterised complex  $[\text{FeH}(\text{dmsO})(\text{dmpe})_2][\text{BPh}_4]$ . It has a methyl resonance at  $\delta$  2.93 and an IR band at  $911 \text{ cm}^{-1}$  implying coordination *via* the oxygen atom rather than sulfur atom.<sup>16</sup> Several iron–dmsO complexes have been reported and they show coordination through the oxygen atom.<sup>17,18</sup> As there is only one  $^{31}\text{P}$  NMR resonance arising from this compound it implies a *trans* geometry for dmsO and the hydride ligand on iron. The substitution reaction of  $[\text{FeH}(\text{H}_2)(\text{dppe})_2][\text{BF}_4]$  by dmsO also gave a similar *trans* species, as judged by  $^{31}\text{P}$  NMR spectroscopy.<sup>15</sup> When a mixture of cyclopropene and dmsO is added to  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  the product is spectroscopically identical to that formed with dmsO alone. The cyclopropenes remain unreduced. This implies that an adduct of dmsO forms preferentially, and that this blocks the iron site where cyclopropenes coordinate and undergo reduction.

Loss of  $\text{H}_2$  from  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  could be followed by coordination of the cyclopropene. It has already been shown that  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  and ethene form  $[\text{FeH}(\text{C}_2\text{H}_4)(\text{dmpe})_2][\text{BPh}_4]$  by displacement of  $\text{H}_2$  by  $\text{C}_2\text{H}_4$ , which shows that iron in this kind of environment can form complexes with compounds containing double bonds.<sup>5</sup> The next step could be the insertion of the cyclopropene double bond into the remaining Fe–H bond. There is precedent for this in the reaction of allene with  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ .<sup>3</sup> Subsequently either  $\text{H}_2$  re-enters the reaction sphere or acetone provides protons, and reduced cyclopropanes or propenes are released. Chelating dmpe on iron is capable of unfastening and refastening one coordinated phosphorus,<sup>15,19</sup> thus creating further vacant coordination sites on iron. It is conceivable that both  $\text{H}_2$  and the cyclopropene could be coordinated at the same time.

In contrast to the reactions reported here, in the reactions of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with alkynes a characterisable iron derivative such as a bis(alkynyl) complex or a butenyne complex can be isolated, provided at least three equivalents of alkyne are added.<sup>4</sup> The corresponding alkene is also formed. We did not isolate a complex of a cyclopropene, possibly because

the iron centre more rapidly forms  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})]\text{-}[\text{BPh}_4]_2$ , a compound that was never observed in reactions of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  with the more reactive alkynes.

#### $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ as a model system for nitrogenases

We have employed three different systems thus far to try to mimic the cyclopropene chemistry of nitrogenase, and none has yet reproduced it exactly. First, we studied simple adducts of cyclopropenes with platinum,<sup>1,20</sup> and inferred that the active site within the enzyme must be in a fairly acid environment, otherwise cyclopropane would be expected to be the predominant product. The formation of propene by the nitrogenases implies the ready availability of acid protons. Secondly, the reactions of cyclopropenes with  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  are reported here and elsewhere,<sup>3</sup> and we observed the formation of reduced hydrocarbon products without addition of any further acid. Unexpectedly, current studies suggest that the solvent appears to provide protons in addition to any present initially on the iron. Thirdly, the reactions of  $[\text{MoH}_4(\text{dppe})_2]$  with cyclopropene yielded cyclopropane and propene,<sup>3</sup> but with proportionately more propene than is normally produced by the enzyme. However, acid was necessary to provoke reaction, and the ratio of cyclopropane to propene was a function of the acid employed. This all tends to show that the nature of the products is influenced in part by the acidity of the system, and implies that there is ready access of protons to the reactive site of nitrogenase. More model studies on this aspect of the enzymes' reactivity are needed to confirm this inference.

Like all the model systems so far investigated in any detail, the iron system with cyclopropene itself generates primarily cyclopropane. This could mean that the product of insertion of cyclopropene into a metal-hydrogen bond, probably a cyclopropyl complex, is relatively quickly protonated on the hydrocarbon before it undergoes any rearrangement leading to ring-opening. In the iron case, the hydrogen atoms for the second protonation, if not from the first, may arise from the solvent. In the platinum case they are also provided externally by the acid. The production of both ring-opened and ring-retained materials in the platinum system was ascribed<sup>1</sup> to a competition between proton flow from solution and electron flow from the metal in a cyclopropyl intermediate. Our only firm evidence is that high acid strength promotes ring opening,<sup>1</sup> but the mechanism of that promotion is far from clear.

A trihydride has been postulated as the dinitrogen-binding intermediate in nitrogenases.<sup>2</sup> The complex  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2]\text{-}[\text{BPh}_4]$  also reacts with substrates of nitrogenase such as allene and ethyne and even with dinitrogen.<sup>4</sup> Free cyclopropene is also a substrate and the hydridic iron has the means to reduce the cyclopropene without the addition of acid. It may be this model resembles the nitrogenase active site more closely than any other. Nitrogenase has coordinatively unsaturated iron atoms within FeMoco (iron-molybdenum cofactor) and these may indeed constitute the active site, although hitherto molybdenum has generally been regarded as the more likely candidate.<sup>21</sup> Molybdenum model systems do not show as wide a range of nitrogenase substrate chemistry as the iron compound discussed here, although they do mediate the reduction of dinitrogen itself.<sup>22</sup> The oxidation state of molybdenum that binds dinitrogen in most model systems is zero, which is unlikely to be accessible in a biological environment. On the other hand, we have shown elsewhere<sup>23</sup> that these iron-diphosphine systems are capable of mediating the reduction of dinitrogen to ammonia in cyclical fashion if the pH is cycled between acidic and alkaline values. When this occurs the formal oxidation state of iron apparently changes between the oxidation states II and 0, neither of which is inconceivable within an enzyme. The current studies therefore favour iron rather than molybdenum as the active site of the classical nitrogenase.

## Experimental

NMR spectra were recorded on a JEOL GSX-270 spectrometer using the solvent as reference for  $^1\text{H}$  NMR and the values quoted are upfield from  $\text{Me}_4\text{Si}$ .  $\text{H}_3\text{PO}_4$  was used as the external reference for  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectra. Chemical shifts are in ppm, and coupling constants in Hz. Elemental analyses were carried out by Butterworth Laboratories. Dmpe was supplied by Dr J. R. Sanders of the Nitrogen Fixation Laboratory. The complex  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ ,<sup>24</sup> and 3,3-dimethyl-, 3,3-diphenyl- and 1,2-diphenyl-cyclopropene were synthesised as described elsewhere.<sup>1</sup> The GC standards, 2-methylbut-2-ene, 3-methylbut-1-ene, 2-methylbut-1-ene were supplied by Aldrich and 1,1-dimethylcyclopropane was synthesised according to ref. 25. EI MS was carried out on a Fisons VG Autospec with a source of 70 eV at the University of Sussex. IR spectra were recorded on a Shimadzu DR-8001 FTIR machine and the samples were prepared as Nujol mulls. Solvents were routinely dried and distilled under dinitrogen. Standard Schlenk and syringe techniques were used. A Philips PU4400 gas chromatograph was used with a Porapak-Q column. NMR data used for product determination are presented in ref. 1 unless otherwise stated.

#### $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$

To a purple solution of  $[\text{FeCl}_2(\text{dmpe})_2]$  (1.18 g, 2.8 mmol) in argon-saturated MeOD (10 cm<sup>3</sup>) was added  $\text{Na}[\text{BD}_4]$  (0.13 g, 3.1 mmol) in degassed MeOD (*ca.* 10 cm<sup>3</sup>). The solution turned orange immediately. This solution was stirred for 5 min and then  $\text{Na}[\text{BPh}_4]$  (1.05 g, 3.1 mmol) dissolved in MeOD (5 cm<sup>3</sup>) was added. Precipitation of an off-white powder was immediate. This was stirred for 1 h, after which the precipitate was filtered off. The off-white precipitate was filtered and dried *in vacuo*. Yield: 1.57 g (83%). IR: 1341 cm<sup>-1</sup>  $\nu_{\text{FeD}}$ .  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ :  $\delta$  1.47, 1.5, 1.96 (3 br s, 32H, dmpe), 6.8, 6.9, 7.3 (3m, 20H, Ph).  $^2\text{H}$  NMR  $[(\text{CH}_3)_2\text{CO}, -60^\circ\text{C}]$ :  $\delta$  -11.1 (br s, 2D,  $\text{FeD}_2$ ), -16.3 (quin,  $^2J_{\text{PD}} = 8$ , 1D,  $\text{FeD}$ ).  $^{31}\text{P}$  NMR  $[(\text{CH}_3)_2\text{CO}, 25^\circ\text{C}]$ :  $\delta$  69.6 (s, dmpe).

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 2 equivalents of 3,3-dimethylcyclopropene

To  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.40 g, 0.59 mmol) dissolved in degassed acetone (20 cm<sup>3</sup>) in a closed system was added 3,3-dimethylcyclopropene (*ca.* 0.08 g, 1.21 mmol) *via* syringe. GC samples were taken with a gas-tight syringe after 5, 30 and 60 min. Hydrocarbon products are tabulated in Table 2. The GC standard compounds were sampled from the head space of an acetone solution, in order to mimic the reaction conditions. After 60 min a gold precipitate started to form. This was filtered off, dried *in vacuo* and characterised as  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$ , yield before recrystallisation 0.10 g (29%). IR: 1865 (shoulder at 1877 cm<sup>-1</sup>)  $\nu_{\text{FeH}}$ , 1580 cm<sup>-1</sup>. EI MS: *m/z* 356 [52,  $\text{Fe}(\text{dmpe})_2$ ], 135 (80%,  $\text{dmpe-CH}_3$ ).  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ :  $\delta$  -17.53 (dquin, 2H,  $^2J_{\text{PH}} = 55.1$ ,  $^2J_{\text{PaH}} = 18.8$ ,  $\text{FeH}$ ), 1.27, 1.50, 1.67, 1.97 (4 br s, 80H, dmpe), 6.8, 6.9, 7.3 (3 m, 40H, Ph).  $^{31}\text{P}$  NMR  $[(\text{CH}_3)_2\text{CO}]$ :  $\delta$  68.5 (br m, dmpe), 15.2 (br quin,  $^2J_{\text{PP}} = 30$ ,  $\mu\text{-dmpe}$ ).

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 2 equivalents of 3,3-diphenylcyclopropene

The compound  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.36 g, 0.53 mmol) was dissolved in argon-saturated acetone (10 cm<sup>3</sup>) and 3,3-diphenylcyclopropene (0.20 g, 1.04 mmol) was added *via* syringe. The solution was stirred for 1 h, and changed from clear yellow to a cloudy orange-brown. Precipitation of a gold solid,  $[\{\text{FeH}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$  occurred. The reaction mixture was taken to dryness and extracted with hexane. The hexane extract was purified on an alumina column by elution with hexane, and the products analysed by  $^1\text{H}$  NMR spec-

troscopy. The hydrocarbon products are listed in Table 2. Only 10% 3,3-diphenylcyclopropene remained when the reaction was repeated with one equivalent of 3,3-diphenylcyclopropene, but a similar mixture of reduced products was produced.

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 2 equivalents of 1,2-diphenylcyclopropene

The reaction of  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.44 g, 0.65 mmol) with 1,2-diphenylcyclopropene (0.25 g, 0.13 mmol) was undertaken in the same manner as the reaction with 3,3-diphenylcyclopropene. The  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$  data for *E*- and *Z*-1,2-diphenylpropene are as follows: *Z*-1,2-diphenylpropene  $\delta$  2.27 (d, 3H,  $^4J_{\text{HH}} = 1.7$ ,  $\text{CH}_3$ ), 6.56m (br m, 1H, *I-H*), 7.38–7.58 (m, 10H, Ph). *E*-1,2-diphenylpropene:  $\delta$  2.27 (d, 3H,  $^4J_{\text{HH}} = 1.5$ ,  $\text{CH}_3$ ), 6.85 (q, 1H, *I-H*), 7.2–7.6 (m, 10H, Ph).

#### Reaction of $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 2 equivalents of 3,3-dimethylcyclopropene

The reaction of  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.38 g, 0.56 mmol) was carried out with 2 equivalents of 3,3-dimethylcyclopropene in acetone in a closed system as above. Gas chromatographic analysis of the hydrocarbon products was carried out. Yellow crystals of  $[\{\text{FeD}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$  were formed at *ca.* 20 °C overnight from an acetone solution, isolated crude yield 0.50 g (15%). IR: 1578  $\text{cm}^{-1}$   $\nu_{\text{FeD}}$ .  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ :  $\delta$  1.29, 1.50, 1.70, 1.97 (4 br s, 80H, dmpe), 6.80, 6.94, 7.32 (3 m, 40H, Ph).  $^2\text{H}$  NMR  $[(\text{CH}_3)_2\text{CO}]$ :  $\delta$  –16.63 (br q,  $^2J_{\text{PD}} = 7.3$ ,  $^2J_{\text{PaD}} = 2.5$ ,  $\text{FeD}$ ).  $^{31}\text{P}$  NMR  $[(\text{CH}_3)_2\text{CO}]$ :  $\delta$  68.5 (br m, dmpe), 15.2 (br q,  $^2J_{\text{PP}} = 30$ ,  $\mu\text{-dmpe}$ ).

#### Crystal structure analysis of $[\{\text{FeD}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$

**Crystal data.**  $\text{C}_{78}\text{H}_{110}\text{B}_2\text{D}_2\text{Fe}_2\text{P}_{10}$ ,  $M = 1504.9$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 16.033(2)$ ,  $b = 16.535(1)$ ,  $c = 18.624(2)$  Å,  $\alpha = 109.758(6)$ ,  $\beta = 106.764(7)$ ,  $\gamma = 106.708(7)^\circ$ ,  $V = 4022.7(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.242$  g  $\text{cm}^{-3}$ ,  $F(000) = 1604$ ,  $\mu(\text{Mo-K}\alpha) = 6.0$   $\text{cm}^{-1}$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $T = 293(1)$  K. Suitable crystals of the material prepared from the reaction of  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$  with 2 equivalents of 3,3-dimethylcyclopropene (see above) were formed from an acetone solution in a 10 mm NMR tube. They were beautiful, small, pale yellow prisms, air-stable for short periods. Several crystals were selected and mounted on fine glass fibres but many were twinned. Photographic examination showed that one, *ca.*  $0.11 \times 0.12 \times 0.24$  mm was single and this was transferred to an Enraf-Nonius CAD-4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the settings of 25 reflections,  $\theta = 10\text{--}10.5^\circ$ , each centred in four orientations) and for measurement of diffraction intensities (7466 unique reflections, to  $\theta_{\text{max}} = 20^\circ$ ; 4994 were observed with  $I > 2\sigma_I$ ).

During processing, corrections were applied for Lorentz-polarisation effects, slight crystal deterioration (*ca.* 3.5% overall), absorption (by semi-empirical  $\psi$ -scan methods) and to remove negative net intensities (by Bayesian statistical methods). The structure was determined by the automated Patterson routines in the SHELXS program<sup>26</sup> and refined by the large-block-matrix least-squares methods, on  $F$ , in SHELXN.<sup>27</sup> All the non-hydrogen atoms were refined anisotropically. The hydrogens on the phenyl rings and in the methylene groups were placed in idealised positions and set to ride on the parent carbon atoms. Hydrogen atoms in the methyl groups were refined with geometrical constraints. The isotropic thermal parameters of all the hydrogen atoms were refined freely. At the conclusion of the refinement,  $R = 0.074$  and  $R_w = 0.060$ <sup>27</sup> for all 7466 reflections weighted  $w = (\sigma_F^2 + 0.00029F^2)^{-1}$ . In the final difference map, the highest peaks (to *ca.*  $0.5$  e Å<sup>−3</sup>) were close to the dmpe ligands.

The scattering factors for neutral atoms were taken from ref. 28. Computer programs used in this analysis have been

noted above or in Table 4 of ref. 29, and were run on a Micro-VAX 3600 machine in the Nitrogen Fixation Laboratory at the University of Sussex.

CCDC reference number 186/1323.

#### Reaction of $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 2 equivalents of 3,3-diphenylcyclopropene

This reaction was carried out in an analogous manner to the reaction with  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  using 0.47 g (0.69 mmol) of  $[\text{FeD}(\text{D}_2)(\text{dmpe})_2][\text{BPh}_4]$ . The products of this reaction are 1,1-diphenylpropene, 1,1-diphenylcyclopropane and 3,3-*d*<sub>2</sub>-1,1-diphenylpropene. The  $^1\text{H}$  and  $^2\text{H}$  NMR data for 3,3-*d*<sub>2</sub>-1,1-diphenylpropene can be found in ref. 1.  $[\{\text{FeD}(\text{dmpe})_2\}_2(\mu\text{-dmpe})][\text{BPh}_4]_2$  was also isolated.

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with an excess of dmpe

$[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.15 g, 0.22 mmol) was dissolved in degassed acetone (30  $\text{cm}^3$ ) and dmpe (1.5  $\text{cm}^3$ , 9.0 mmol) was added *via* a syringe. The reaction was allowed to stir for 3 h. Degassed ethanol was added and the volume reduced under a stream of argon with gentle heating. The solution was held at  $-20^\circ\text{C}$  overnight and the resulting yellow precipitate was filtered and dried *in vacuo*. The product was characterised as  $[\text{FeH}(\text{dmpe-}P, P')_2(\text{dmpe-}P)][\text{BPh}_4]$ . Yield: 0.11 g (61%). IR ( $\text{cm}^{-1}$ ): 1846  $\nu_{\text{FeH}}$ , 1578.  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ :  $\delta$  –17.63 (dq, 1H,  $^2J_{\text{PH}} = 55.5$ ,  $^2J_{\text{PaH}} = 17.5$ ,  $\text{FeH}$ ), 0.97, 1.22, 1.24, 1.50, 1.67, 1.95 (br s, 48H,  $\text{CH}_2$  and  $\text{CH}_3$  of dmpe), 6.76, 6.91, 7.32 (m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{31}\text{P}$  NMR  $[(\text{CH}_3)_2\text{CO}]$ :  $\delta$  69.0 (d,  $^2J_{\text{PP}} = 33$ ), 15.3 (dq,  $^3J_{\text{PP}} = 19$ ), –46.5 (d, dmpe-*P*) (Found: C, 60.0; H, 8.5.  $\text{C}_{42}\text{H}_{69}\text{BFeP}_6$  requires: C, 61.0; H, 8.3%).

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 5 equivalents of 3,3-diphenylcyclopropene under $\text{H}_2$

To  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.36 g, 0.53 mmol) in  $\text{H}_2$ -saturated acetone (50  $\text{cm}^3$ ) was added 3,3-diphenylcyclopropene (0.51 g, 2.7 mmol) *via* syringe and the mixture stirred for 1 h with  $\text{H}_2$  bubbling through the solution. The  $^{31}\text{P}$  NMR spectrum of a sample showed only  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  and this was ultimately the only iron complex isolated. The remaining acetone was evaporated under a stream of  $\text{H}_2$  and the hydrocarbon material was extracted with hexane and purified using an alumina column, eluting with hexane. A  $^1\text{H}$  NMR spectrum showed more than 95% of starting material, 3,3-diphenylcyclopropene.

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with dmsO

The complex  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.11 g, 0.16 mmol) was treated with an excess of dmsO (0.3  $\text{cm}^3$ , 7 mmol) in degassed acetone (15  $\text{cm}^3$ ) and stirred for 1 h. A  $^{31}\text{P}$  NMR analysis of the clear, yellow reaction solution showed no signal corresponding to the iron-containing starting material. The solvent was removed *in vacuo* and the isolated yellow material was characterised spectroscopically as  $[\text{FeH}(\text{dmsO})(\text{dmpe})_2][\text{BPh}_4]$ . IR ( $\text{cm}^{-1}$ ): 1885, 1858  $\nu_{\text{FeH}}$ , 1051  $\nu_{\text{S=O}}$  (free dmsO), 911  $\nu_{(\text{O-coordinated dmsO})}$ .  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ :  $\delta$  –19.38 (q, 1H,  $^2J_{\text{PH}} = 55.1$ ,  $\text{FeH}$ ), 1.49, 1.76, 1.94 (3 br s, 32 H, dmpe), 2.51 (s, 6H, free dmsO), 2.93 (s, 6H,  $\text{CH}_3$  of coordinated dmsO), 6.7–7.3 (m, 20H, Ph).  $^{31}\text{P}$  NMR  $[(\text{CH}_3)_2\text{CO}]$ :  $\delta$  65.0 (br m, dmpe).

#### Reaction of $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ with 2 equivalents of 3,3-diphenylcyclopropene in the presence of dmsO

The complex  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.16 g, 0.24 mmol) was added to an acetone solution of 3,3-diphenylcyclopropene (0.10 g, 0.52 mmol) and dmsO (0.5  $\text{cm}^3$ , 7.05 mmol). The mixture was stirred for 1 h, after which a  $^{31}\text{P}$  NMR spectrum of the reaction solution showed no  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ . The reaction was brought to dryness and the hydrocarbon products purified as usual. The  $^1\text{H}$  NMR spectrum showed more than 95% 3,3-

diphenylcyclopropene.  $[\text{FeH}(\text{dmso})(\text{dmpe})_2][\text{BPh}_4]$  was also spectroscopically identified as the sole iron-containing product.

## Acknowledgements

We are grateful to Dr J. R. Sanders for assistance and to the BBSRC for providing facilities.

## References

- 1 G. J. Leigh, C. E. McKenna and C. N. McMahon, *Inorg. Chim. Acta*, 1998, **280**, 193.
- 2 D. J. Lowe and R. N. F. Thorneley, *Biochem. J.*, 1984, 887.
- 3 A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh, C. A. McGearry, A. T. Rowley, M. Bravo, C. E. McKenna and M.-C. McKenna, *J. Chem. Soc., Chem. Commun.*, 1991, 522.
- 4 D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 3151.
- 5 A. Hills, D. L. Hughes, M. Jimenez-Tenorio and G. J. Leigh, *J. Organomet. Chem.*, 1990, **391**, C41.
- 6 H. Li Kam Wah, M. Postel and M. Pierrot, *Inorg. Chim. Acta*, 1989, **165**, 215.
- 7 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1988, 546.
- 8 F. R. Askham, S. E. Saum and G. G. Stanley, *Organometallics*, 1987, **6**, 1370.
- 9 R. L. Keiter, A. L. Rheingold, J. J. Hamerski and C. K. Castle, *Organometallics*, 1983, **2**, 1635.
- 10 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, F. Zanobini and P. Frediani, *Organometallics*, 1989, **8**, 2080.
- 11 C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics*, 1992, **11**, 138.
- 12 C. A. Hellere, D.Phil. Thesis, University of Sussex, 1998.
- 13 M. Jimenez-Tenorio, D.Phil. Thesis, University of Sussex, 1990.
- 14 D. A. Hall, D.Phil. Thesis, University of Sussex, 1994.
- 15 M. G. Basallote, J. Duran, M. J. Fernandez-Trujillo, G. Gonzalez, M. A. Manez and M. Martinez, *Inorg. Chem.*, 1998, **37**, 1623.
- 16 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.
- 17 V. I. Ponomarev, O. S. Filipenko and L. O. Atovmyan, *Koord. Khim.*, 1982, **8**, 98.
- 18 M. Mylrajan, L. A. Andersson, J. Sun, T. M. Loehr, C. S. Thomas, E. P. Sullivan, M. A. Thomson, K. M. Long, O. P. Anderson and S. H. Strauss, *Inorg. Chem.*, 1995, **34**, 3953.
- 19 L. D. Field, A. V. George, E. Y. Malouf, H. M. Slip and T. W. Hambley, *Organometallics*, 1991, **10**, 3842.
- 20 D. L. Hughes, G. J. Leigh and C. N. McMahon, *J. Chem. Soc., Dalton Trans.*, 1997, 1301.
- 21 B. K. Burgess, in *Metal Ions in Biology*, ed. T. G. Spiro, John Wiley & Sons, New York, 1985, p. 161.
- 22 G. J. Leigh, *Eur. J. Biochem.*, 1995, **229**, 14.
- 23 D. A. Hall and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1996, 3539.
- 24 A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 3041.
- 25 C. N. McMahon, D.Phil. Thesis, University of Sussex, 1995.
- 26 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 27 G. M. Sheldrick, SHELX-Program for crystal structure determination, University of Cambridge, 1976; also an extended version, SHELXN, 1977.
- 28 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
- 29 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.
- 30 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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