Ethylene elimination upon addition of acids to the μ-ethenyl complex [Fe$_2$(CO)$_4$(μ-η^2-HC=CH$_2$)(μ-PCy$_2$)(μ-dppm)]: synthesis of halide- and carboxylate-bridged diiron carbonyl complexes

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Abstract

Addition of acids to the μ-ethenyl complex [Fe$_2$(CO)$_4$(μ-η^2-HC=CH$_2$)(μ-PCy$_2$)(μ-dppm)] 1 results in selective proton transfer to the α-carbon and loss of ethylene. When the anion is coordinating, subsequent attack at the diiron centre provides a convenient synthesis of halide- and carboxylate-bridged diiron complexes [Fe$_2$(CO)$_4$(μ-X)(μ-PCy$_2$)(μ-dppm)] 2a–c (X = F, Cl, Br) and [Fe$_2$(CO)$_4$(μ-η^2-O$_2$CY)(μ-PCy$_2$)(μ-dppm)] 3a–e (Y = H, CF$_3$, CCl$_3$, CBr$_3$, CO$_2$H) respectively. When it is poorly coordinating, scavenging of two carbonyls affords the hexacarbonyl complexes [Fe$_2$(CO)$_6$(μ-PCy$_2$)(μ-dppm)][Z] 4 (Z = F, BF$_4$, PF$_6$, 0.5SO$_4$), the yield of which is increased under a carbon-monoxide atmosphere. In order to elucidate mechanistic details the reactions have been monitored by IR, ^{1}H and ^{31}P NMR spectroscopies. These reveal the formation of an intermediate, spectroscopically characterised as the vinyl-hydride [HFe$_2$(CO)$_4$(μ-η^2-HC=CH$_2$)(μ-PCy$_2$)(μ-dppm)][BF$_4$] 5, which is stable in the presence of ethylene and propene. Crystallographic studies have been carried out on [Fe$_2$(CO)$_4$(μ-Cl)(μ-PCy$_2$)(μ-dppm)] 2b, [Fe$_2$(CO)$_4$(μ-Br)(μ-PCy$_2$)(μ-dppm)] 2c and [Fe$_2$(CO)$_4$(μ-η^2-O$_2$CH)(μ-PCy$_2$)(μ-dppm)] 3a. All contain a short iron–iron vector bridged symmetrically by diphosphine and phosphido moieties with a relative *trans* orientation, and the halide or carboxylate anion which lies *cis* to both the latter.

Keywords: Diiron; Ethenyl; Diphosphine; Protonation; Halide; Carboxylate

1. Introduction

The reactivity of small organic fragments when bound to two or more metal atoms is an area of continuing interest, primarily since such complexes act as models for surface species in heterogeneous catalysis. In this context, complexes containing a vinyl moiety, and specifically the parent ethenyl ligand, are particularly interesting due to their implication in the Fischer–Tropsch process [1]. Vinyl complexes have been shown to undergo a range of facile carbon–carbon bond forming processes when bound to a binuclear metal centre. For example, Knox and coworkers [2] have shown that reactions with alkynes occur to give μ-butadienyl complexes which subsequently undergo deprotonation to yield metallacyclopentadienyl complexes [2], while

Maitlis et al. [3] have reported the facile coupling with methylene ligands in the presence of one-electron oxidizers. Perhaps the simplest transformation of a metal bound organic moiety (after isomerisation) is its protonation, which may afford new metal-bound organics. Specifically, protonation of a cluster-bound μ-ethenyl complex can follow a number of possible pathways: initial attack of the electrophile may occur at one or more metal centres, followed by transfer to the vinyl ligand; or direct attack at the latter. In either case, transfer of the proton to the organic can occur at the α-carbon, affording an ethylene complex, or at the β-carbon to yield a methylidene ligand. A number of such protonation studies have been carried out on both ethenyl and other vinyl complexes with proton addition to the α-carbon being predominant. Thus, Werner et al. [4] have shown the facile elimination of primary alkenes upon addition of hydrogen chloride to arene–phosphine complexes, [Os(η^6-arene)(PR$_3$)Cl(η^1-HC=CHR')], while most relevantly to this work Stone and coworkers

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[5] have reported that thiolate-bridged diiron complexes [Fe$_2$(CO)$_6$(μ-η^2-HC=CH$_2$)(μ-SR)] eliminate ethylene upon thermolysis with carboxylic acids. Herein we describe protonation studies of the phosphine-stabilized diiron μ-ethenyl complex [Fe$_2$(CO)$_4$(μ-η^2-HC=CH$_2$)-(μ-PCy$_2$)(μ-dppm)] 1 employing a variety of acids. In all cases, selective protonation at the α-carbon leads to the formation of ethylene, which is readily lost from the complex. The nature of the products formed upon ethylene loss, however, depends critically on the nature of the counterion. Thus, when acids of strongly coordinating anions are used, it provides a convenient and high yield synthesis of halide and carboxylate-bridged diiron complexes; while with poorly coordinating anions, cationic diiron complexes result. A number of spectroscopic studies have also been carried out which lend an insight into the nature of these transformations.

2. Experimental details

2.1. General comments

All reactions were carried out under N$_2$ in predried solvents. NMR spectra were recorded on a Varian VXR 400 spectrometer and IR spectra on a Nicolet 205 Fourier-Transform spectrometer. Chromatography was carried out on columns of deactivated alumina (6% w/w water). Elemental analyses were performed in the Chemistry Department of University College. Acids were purchased from Aldrich and used without further purification and [Fe$_2$(CO)$_4$(μ_2-η^2-HC=CH$_2$)(μ-PCy$_2$)(μ-dppm)] 1 was prepared as previously described [6].

2.2. Synthesis of [Fe$_2$(CO)$_4$(μ-X)(μ-PCy$_2$)(μ-dppm)] 2

2b – Addition of 40% HCl (0.1 cm^3) to a dichloromethane solution (10 cm^3) of 1 (0.20 g, 0.24 mmol) resulted in a rapid colour change from yellow to red. The solvent was removed under reduced pressure and the resulting red solid was absorbed onto alumina. Chromatography eluting with light petroleum–diethylether (4: 1) gave an orange band which yielded 2b (0.15 g, 74%) as a pale orange solid. 2c (75%) was prepared in an analogous fashion upon addition of aqueous HBr and elution with light petroleum–ethylacetate (4: 1). Addition of 40% HF resulted in the isolation after chromatography of 2a in 40% yield upon elution with light petroleum–diethyl ether (4: 1). Further elution with light petroleum–dichloromethane (1: 4) gave a yellow band which afforded 4 (Z = F) (28%) as an orange solid. Crystallisation of 2b–c was effected upon slow diffusion of methanol into dichloromethane solutions, affording large orange crystals, while the more soluble 2a was crystallised upon cooling of a concentrated hexane solution to − 40°C.

2a. Anal. Found: C, 59.56; H, 5.40. Fe$_2$C$_{41}$H$_{44}$O$_4$P$_3$F$_1$ Calc.: C, 59.71; H, 5.34%.

2b. Anal. Found: C, 54.08; H, 5.34. Fe$_2$C$_{41}$H$_{44}$O$_4$-P$_3$Cl$_1$ · CH$_2$Cl$_2$ Calc.: C, 54.45; H, 4.97%.

2c. Anal. Found: C, 52.40; H, 4.89. Fe$_2$C$_{41}$H$_{44}$O$_4$-P$_3$Br$_1$ · CH$_2$Cl$_2$ Calc.: C, 51.96; H, 4.74%.

2.3. Synthesis of [Fe$_2$(CO)$_4$(μ-η^2-O$_2$CY)(μ-PCy$_2$)(μ-dppm)] 3

3a – Addition of an excess of formic acid (0.1 cm^3) to a dichloromethane solution (40 cm^3) of 1 (0.30 g, 0.36 mmol) resulted in a gradual colour change from yellow to red over a period of 1 h. Removal of the solvent under reduced pressure afforded an oily red solid which was absorbed onto alumina. Chromatography eluting with light petroleum gave an orange band which afforded 3a (0.22 g, 72%) as an orange solid. Addition of trifluoroacetic acid to 1 resulted in an immediate colour change to red which, after chromatography, afforded orange 3b (84%) upon elution with light petroleum–dichloromethane (9: 1). 3c (77%) and 3d (87%) were prepared in a similar fashion upon addition of excess trichloro- and tribromoacetic acid respectively, however, purification was via extraction of the reaction mixture with diethylether (3 × 20 cm^3) as chromatography led to some decomposition. Addition of oxalic acid (0.05 g, 0.56 mmol) to a toluene solution (50 cm^3) of 1 (0.20 g, 0.24 mmol) resulted in the formation of a red solution after stirring for 12 h. Removal of the solvent under reduced pressure afforded an oily orange solid which was absorbed onto alumina. Chromatography eluting with light petroleum–dichloromethane (4: 1) afforded 3e (0.13 g, 61%) as an orange solid. Some of the compound stuck to the column and could not be eluted. Yields were higher (75%) upon extraction of the reaction mixture into diethylether (2 × 10 cm^3) and washing with water (3 × 5 cm^3). Compounds 3a,b,e were recrystallised upon slow diffusion of methanol into dichloromethane solutions.

3a. Anal. Found: C, 58.93; H, 5.34. Fe$_2$C$_{42}$H$_{45}$O$_6$P$_3$ Calc.: C, 59.29; H, 5.29%.

3b. Anal. Found: C, 56.48; H, 5.01. Fe$_2$C$_{43}$H$_{44}$O$_6$-P$_3$F$_3$ Calc.: C, 56.20; H, 4.79%.

3e. Anal. Found: C, 54.44; H, 5.38. Fe$_2$C$_{43}$H$_{45}$O$_8$P$_3$ Calc.: C, 53.96; H, 4.84%.

Satisfactory elemental analyses were not obtained for 3c,d due to persistent contamination with small amounts of the corresponding halide complexes 2b,c respectively.

2.4. Synthesis of [Fe$_2$(CO)$_6$(μ-PCy$_2$)(μ-dppm)][Z] 4

Addition of a slight excess of HBF$_4$ · Et$_2$O in diethylether to a dichloromethane solution (20 cm^3) of 1 (0.20 g, 0.24 mmol) resulted in a rapid colour change

from yellow to dark orange, while after stirring for a further 10 min the solution became lighter. An IR spectrum after the initial addition showed only the presence of 5, but absorptions due to 4 grew steadily with time. Removal of solvent under vacuum afforded an oily pale orange solid which was washed with diethylether (2×5 cm^3) to remove excess acid. Extraction with dichloromethane (10 cm^3) followed by addition of light petroleum lead to precipitation of 4 (Z = BF$_4$) (0.16 g, 78%) as a pale orange solid. Other salts of 4 were made in an analogous manner upon addition of HPF$_6$ or H$_2$SO$_4$ and yields were similar. Addition of nitric acid did not afford 4 and the nature of this product remains uncertain. Purification could also be carried out by column chromatography. Residual solvent proved difficult to remove from samples of 4, and repeated attempts to recrystallise it from a range of solvents proved unsuccessful.

4 (Z = BF$_4$). Anal. Found: C, 54.76; H, 4.62. Fe$_2$C$_{43}$H$_{44}$O$_6$P$_3$B$_1$F$_4$ Calc.: C, 54.43; H, 4.64%.

Mass spectrum (FAB): m/e 862 (M + 1).

2.5. Mechanistic studies

(i) Room temperature addition of small amounts of CF$_3$CO$_2$H to a CDCl$_3$ solution of 1 whilst monitoring by ^{1}H NMR spectroscopy showed the quantitative formation of equal amounts of ethylene (δ 5.42) and 3b,

while the latter was also confirmed using ^{31}P NMR spectroscopy. (ii) Addition of a slight excess of HBF$_4$ · Et$_2$O to a dichloromethane solution of 1 saturated with ethylene, and with a slow purge of the gas still passing through the solution, resulted in the formation of an orange solution shown by IR to consist solely of 5. When the ethylene purge was stopped the solution became lighter and the IR spectrum revealed the formation of 4 over approximately 20 min. Removing the ethylene purge and replacing it with CO resulted in the instantaneous formation of 4. Addition of a variety of bases to the dichloromethane solution immediately after cessation of the ethylene purge resulted in the quantitative reformation of 1. NMR spectra of 5 were obtained upon addition of HBF$_4$ · Et$_2$O to CDCl$_3$ solutions of 1 saturated with ethylene. (iii) Addition of a small amount of 40% hydrofluoric acid to a dichloromethane solution (20 cm^3) of 1 (0.20 g, 0.24 mmol) whilst purging with CO afforded 4 (Z = F) (0.18 g, 86%) as the sole reaction product, while purging a similar reaction with ethylene for 20 min afforded a mixture of 2a and 4 (Z = F) in an approximate 4:1 ratio. (iv) Addition of HBF$_4$ · Et$_2$O to a propene saturated dichloromethane solution of 1, whilst still purging with propene, resulted in the rapid formation of 5 as shown by IR spectroscopy. Under this propene atmosphere, 5 was quite stable and after 20 min only small absorptions associated with 4 (Z = BF$_4$) were noted. Quenching the reac-

Table 1
Crystallographic data

	2b · CH$_2$Cl$_2$	2c · CH$_2$Cl$_2$	3a · CH$_2$Cl$_2$
Formula	Fe$_2$C$_{42}$H$_{46}$O$_4$P$_3$Cl$_3$	Fe$_2$C$_{42}$H$_{46}$O$_4$P$_3$Br$_1$Cl$_2$	Fe$_2$C$_{43}$H$_{47}$P$_3$O$_6$Cl$_2$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.859(2)	11.817(2)	11.873(2)
b (Å)	12.890(2)	12.896(2)	13.068(3)
c (Å)	16.668(2)	16.662(2)	17.116(5)
α (deg)	73.73(1)	73.30(1)	93.21(2)
β (deg)	76.50(1)	76.51(1)	104.70(2)
γ (deg)	64.22(1)	64.12(1)	116.68(1)
V (Å^3)	2183.92	2171.07	2250.48
Z	2	2	2
$F(0000)$	956	992	904
d_{calc} (g cm^{-3})	1.41	1.48	1.29
Crystal size (mm^3)	$0.52 \times 0.44 \times 0.26$	$0.60 \times 0.40 \times 0.06$	$0.40 \times 0.30 \times 0.20$
μ(Mo Kα) (cm^{-1})	9.95	1.85	9.00
Orientations, reflections no.; range	30; $17 \le 2\theta \le 30$	30; $19 \le 2\theta \le 29$	37; $16 \le 2\theta \le 30$
Data measured	8406	8356	8398
Unique data	8142	8095	8226
No. of unique data with $I \ge 3.0\sigma(I)$	6383	5581	5680
No. of parameters	460	472	481
R [a]	0.062	0.063	0.067
R_w [b]	0.072	0.069	0.073
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.001159F^2$	$w^{-1} = \sigma^2(F) + 0.001080F^2$	$w^{-1} = \sigma^2(F) + 0.000748F^2$
Largest shift/esd, final cycle	0.03	0.02	0.001
Largest peak (e Å^{-3})	1.81	1.63	1.78

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$; [b] $R_w = \Sigma w^{1/2} \cdot [|F_o| - |F_c|]/\Sigma w^{1/2} \cdot |F_o|$.

tion after 30 min, upon addition of a slight excess of NEt$_3$, resulted in the formation of **1** and **4** (Z = BF$_4$) in an approximate 9:1 ratio as shown by ^{31}P NMR spec-

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A} \times 10^3$) for **2b**

Atom	x	y	z	U_{eq} *
Fe(1)	514(1)	2797(1)	7782(1)	29(1)
Fe(2)	2733(1)	2696(1)	7187(1)	30(1)
P(1)	−395(1)	4718(1)	7829(1)	29(1)
P(2)	2293(1)	4611(1)	7041(1)	29(1)
P(3)	2199(1)	1153(1)	7620(1)	33(1)
O(1)	−1632(4)	2203(4)	7910(3)	63(2)
O(2)	589(5)	2225(4)	9562(3)	67(2)
O(3)	5065(6)	1965(7)	6057(5)	112(4)
O(4)	3851(5)	2043(4)	8701(3)	62(2)
Cl(1)	1171(1)	3305(1)	6363(1)	36(1)
C(1)	−795(5)	2453(5)	7836(4)	40(2)
C(2)	567(5)	2448(5)	8859(4)	41(2)
C(3)	4143(6)	2264(6)	6480(4)	51(8)
C(4)	3402(5)	2312(5)	8102(4)	38(2)
C(5)	801(5)	5330(5)	7684(3)	35(2)
C(11)	−1338(5)	5079(4)	8824(3)	32(2)
C(12)	−2266(6)	4644(5)	9149(4)	45(3)
C(13)	−3062(6)	4932(6)	9870(4)	54(3)
C(14)	−2942(6)	5644(6)	10293(4)	52(3)
C(15)	−2017(6)	6070(6)	9990(4)	55(3)
C(16)	−1210(6)	5781(6)	9260(4)	46(3)
C(21)	−1524(5)	5754(5)	7098(3)	35(2)
C(22)	−2117(6)	6917(6)	7150(4)	52(3)
C(23)	−2963(7)	7720(6)	6567(5)	66(3)
C(24)	−3232(7)	7336(7)	5993(5)	68(4)
C(25)	−2650(7)	6175(7)	5948(4)	66(4)
C(26)	−1802(6)	5356(6)	6511(4)	48(3)
C(31)	2137(5)	5557(5)	5994(3)	36(2)
C(32)	1013(7)	6190(6)	5677(4)	61(3)
C(33)	937(8)	6894(7)	4893(5)	70(4)
C(34)	1974(8)	7002(7)	4393(4)	64(4)
C(35)	3103(9)	6371(9)	4688(5)	93(5)
C(36)	3210(7)	5630(8)	5476(4)	78(4)
C(41)	3382(5)	5012(5)	7379(3)	34(2)
C(42)	2996(6)	6132(5)	7525(4)	49(8)
C(43)	3846(7)	6464(6)	7732(5)	60(3)
C(44)	5062(7)	5695(7)	7794(5)	61(4)
C(45)	5448(6)	4588(6)	7655(5)	54(3)
C(46)	4611(5)	4247(5)	7453(4)	42(2)
C(51)	2335(5)	219(5)	6903(4)	41(2)
C(52)	3225(7)	320(7)	6084(5)	63(4)
C(53)	3364(8)	−494(8)	5551(5)	75(4)
C(54)	2094(9)	−264(8)	5329(5)	83(5)
C(55)	1228(8)	−408(7)	6124(5)	73(4)
C(56)	1061(6)	409(6)	6709(4)	54(8)
C(61)	2783(6)	67(5)	8583(4)	41(2)
C(62)	1965(7)	−630(6)	9014(4)	54(3)
C(63)	2422(9)	−1406(7)	9833(5)	75(4)
C(64)	3828(10)	−2212(7)	9724(6)	89(6)
C(65)	4602(8)	−1519(7)	9285(6)	77(4)
C(66)	4165(6)	−758(5)	8446(4)	52(3)
Cl(2)	2792	9704	2624	292
Cl(3)	734	11359	1783	312
C(70)	2386	10580	1389	235

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent displacement parameters ($\mathring{A} \times 10^3$) for **2c**

Atom	x	y	z	U_{eq} *
Fe(1)	2230(1)	2317(1)	2822(1)	33(1)
Fe(2)	4464(1)	2213(1)	2236(1)	32(1)
Br(1)	3824(1)	1661(1)	3740(1)	42(1)
P(1)	2670(2)	411(2)	2960(1)	31(1)
P(2)	5352(2)	309(2)	2175(1)	31(1)
P(3)	2780(2)	3846(2)	2397(1)	35(1)
O(1)	−157(7)	3095(8)	3897(6)	104(5)
O(2)	1205(6)	2943(6)	1259(4)	67(3)
O(3)	6600(6)	2824(5)	2100(4)	65(3)
O(4)	4380(6)	2803(6)	442(4)	68(3)
C(1)	790(8)	2780(8)	3478(6)	57(4)
C(2)	1623(8)	2688(6)	1893(5)	43(4)
C(3)	5760(7)	2554(6)	2194(5)	42(3)
C(4)	4402(7)	2569(7)	1163(5)	46(4)
C(5)	4149(6)	−280(6)	2297(5)	36(3)
C(11)	1584(7)	−1(6)	2628(4)	35(3)
C(12)	349(7)	796(7)	2503(5)	45(4)
C(13)	−460(7)	469(8)	2287(6)	56(4)
C(14)	−83(8)	−662(9)	2186(6)	58(5)
C(15)	1130(9)	−1459(8)	2291(7)	65(5)
C(16)	1941(8)	−1112(7)	2510(6)	58(4)
C(21)	2040(7)	−541(6)	4011(4)	33(3)
C(22)	3949(9)	−1378(9)	4267(7)	83(6)
C(23)	3995(11)	−2053(11)	5053(7)	95(6)
C(24)	2977(13)	−2009(10)	5586(6)	80(7)
C(25)	1895(13)	−1187(14)	5358(7)	122(5)
C(26)	1798(10)	−452(12)	4585(6)	104(6)
C(31)	6471(7)	−776(6)	2902(4)	36(3)
C(32)	7035(8)	−1944(7)	2836(6)	58(4)
C(33)	7884(8)	−2770(8)	3379(7)	70(5)
C(34)	3201(10)	−2433(11)	3961(7)	80(6)
C(35)	7704(9)	−1290(10)	4004(8)	70(5)
C(36)	6846(8)	−461(8)	3481(5)	52(4)
C(41)	6285(6)	−45(6)	1183(4)	33(0)
C(42)	6177(7)	−751(7)	740(5)	44(4)
C(43)	6969(8)	−1045(8)	41(5)	53(4)
C(44)	7907(8)	−610(7)	−268(5)	51(4)
C(45)	8013(8)	100(8)	134(5)	57(4)
C(46)	7204(7)	399(7)	848(5)	46(4)
C(51)	2643(7)	4782(6)	3109(5)	42(3)
C(52)	3903(8)	4583(7)	3327(6)	54(4)
C(53)	3755(9)	5422(9)	3882(6)	66(5)
C(54)	2820(12)	5309(10)	4661(6)	82(6)
C(55)	1580(10)	5545(9)	4444(7)	73(5)
C(56)	1700(9)	4729(8)	3896(6)	58(6)
C(61)	2193(7)	4923(6)	1442(5)	40(3)
C(62)	809(8)	5750(7)	1571(6)	55(4)
C(63)	384(11)	6511(9)	738(8)	88(6)
C(64)	1143(12)	7230(9)	304(8)	91(1)
C(65)	2558(12)	6441(9)	178(6)	79(6)
C(66)	3012(9)	5635(7)	1009(5)	58(4)
C(70)	7110(20)	5737(19)	1374(14)	188(8)
Cl(1)	7749(15)	4804(13)	2359(9)	404(7)
Cl(2)	5519(9)	6510(8)	1763(6)	261(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

troscopy. which revealed no signals due to μ-propenyl complexes. (v) Addition of HBF$_4$ · Et$_2$O to a dichloromethane solution of [Fe$_2$(CO)$_4$-

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for 3a

Atom	x	y	z	U_{eq} *
Fe(1)	4518(1)	2456(1)	2135(1)	33(1)
Fe(2)	6707(1)	2230(1)	2725(1)	33(1)
P(1)	3100(2)	545(1)	2019(1)	32(1)
P(2)	5616(2)	313(1)	2818(1)	31(1)
P(3)	6619(2)	3872(1)	2520(1)	35(1)
O(1)	4364(6)	2979(5)	3756(3)	60(3)
O(2)	2911(8)	3551(7)	1445(5)	94(5)
O(3)	7094(6)	2826(5)	4468(3)	64(3)
O(4)	9542(6)	2961(6)	3123(4)	76(4)
O(5)	4628(5)	2017(4)	1020(3)	46(2)
O(6)	6398(5)	1748(4)	1518(3)	46(3)
C(1)	4444(7)	2770(6)	3117(4)	39(3)
C(2)	3516(8)	3100(7)	1682(5)	53(4)
C(3)	6911(8)	2582(6)	3759(4)	44(3)
C(4)	8428(8)	2624(6)	2946(5)	44(4)
C(5)	3867(7)	−161(5)	2721(4)	34(3)
C(6)	5495(8)	1742(6)	950(5)	48(4)
C(10)	2375(7)	−380(6)	992(4)	39(3)
C(11)	2410(9)	−1419(7)	826(5)	63(5)
C(12)	1764(11)	−2091(10)	15(6)	87(6)
C(13)	1103(11)	−1751(11)	−583(6)	91(6)
C(14)	1062(10)	−733(9)	−421(5)	79(5)
C(15)	1698(8)	−54(8)	363(5)	59(4)
C(20)	1573(6)	124(6)	2311(4)	34(3)
C(21)	1232(8)	946(7)	2554(4)	46(4)
C(22)	97(8)	602(8)	2794(5)	57(4)
C(23)	−682(8)	−532(8)	2793(5)	61(5)
C(24)	−381(9)	−1369(8)	2550(6)	67(5)
C(25)	731(8)	−1051(7)	2294(6)	60(4)
C(30)	5566(6)	−870(6)	2134(4)	34(3)
C(31)	6273(7)	−623(7)	1586(4)	45(4)
C(32)	6230(9)	−1542(8)	1089(5)	57(5)
C(33)	5517(9)	−2667(7)	1161(5)	59(4)
C(34)	4817(10)	−2926(7)	1708(5)	64(5)
C(35)	4840(8)	−2025(6)	2204(4)	49(4)
C(40)	6215(6)	−36(5)	3822(4)	33(3)
C(41)	5398(7)	−719(6)	4234(4)	45(3)
C(42)	5901(9)	−1025(7)	4963(4)	54(4)
C(43)	7231(9)	−625(7)	5274(5)	55(4)
C(44)	8075(8)	78(7)	4879(5)	57(4)
C(45)	7578(8)	374(6)	4148(5)	47(4)
C(50)	7168(7)	4997(6)	3463(4)	43(3)
C(51)	8682(8)	5646(7)	3861(5)	53(4)
C(52)	9064(10)	6495(8)	4664(5)	74(5)
C(53)	8485(10)	7307(8)	4525(6)	78(5)
C(54)	6989(11)	6647(8)	4119(6)	77(6)
C(55)	6599(8)	5833(6)	3299(5)	54(4)
C(60)	7432(7)	4782(6)	1810(4)	45(4)
C(61)	6463(8)	4828(7)	1051(5)	59(4)
C(62)	7183(9)	5650(8)	531(5)	66(5)
C(63)	8184(11)	5384(9)	329(6)	78(6)
C(64)	9146(9)	5375(8)	1077(6)	67(5)
C(65)	8475(8)	4539(7)	1612(5)	58(4)
Cl(1)	1898	6720	3264	186(2)
Cl(2)	2873	5134	3224	420(7)
C(100)	2451	5793	3714	216(9)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

(μ-HC=CHMe)(μ-PCy$_2$)(μ-dppm)] [6] resulted in the rapid formation of 4 via an intermediate with IR absorptions at 2023(m), 1994(s) and 1976(m) cm^{-1}; when this reaction was carried out under an ethylene atmosphere and quenched after 7 min via addition of NEt$_3$, formation of approximately 15% of 1 was shown by ^{31}P NMR spectroscopy. (vi) Reactions between 1 and Cl$_{3-x}$H$_x$CCO$_2$H ($x = 0$–3) in CDCl$_3$ were monitored by ^{31}P NMR spectroscopy. Approximately 95% conversion of 1 to the respective carboxylate-bridged complex occurred over a period of less than 1 min ($x = 0$), 5 min ($x = 1$) and 120 min ($x = 2$), while with acetic acid ($x = 0$) no significant reaction was observed even after extended periods.

2.6. X-ray data collection and solution

For all structures, a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Important crystallographic parameters are summarised in Table 1. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure reflections in the range $5° \leq 2\theta \leq 50°$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects, and empirically for absorption. The unique data with $I \geq 3.0\sigma(I)$ were used to solve and refine the structures.

Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. Non-hydrogen atoms of the diiron complex were refined anisotropically, while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2). The non-hydrogen atoms of the dichloromethane were refined only isotropically in 2c; in 3a and 2b they were refined anisotropically with their positions fixed, while in 2b their thermal parameters were also fixed for the last cycle of refinement. Final difference-Fourier maps contained a number of peaks greater than 1.00 e Å^{-3} close to the dichloromethane solvate. Structure solution used the SHELXTL PLUS program package on a microVax II computer [7].

Tables 2–4 give atomic coordinates and equivalent isotropic displacement parameters for 2b, 2c and 3a respectively. A complete list of bond lengths and angles and tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
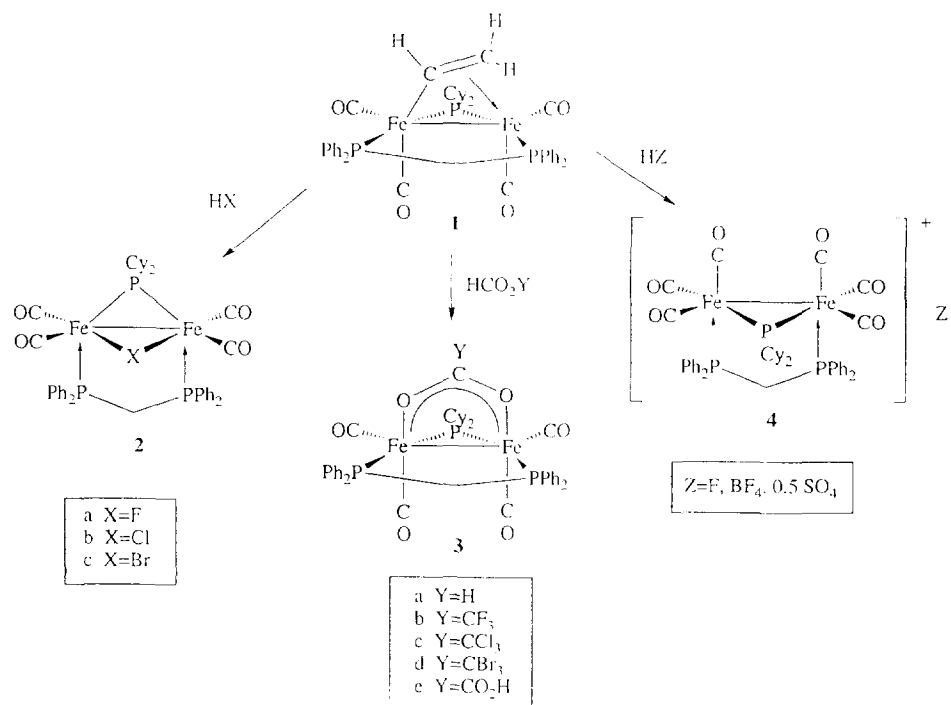
3. Results and discussion

3.1. Synthesis and characterisation

Addition of a slight excess of aqueous acids (HX; X = F, Cl, Br) to dichloromethane solutions of $[Fe_2(CO)_4(\mu_2\text{-}\eta^2\text{-}HC=CH_2)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$ 1 resulted in the rapid formation of the new halide-bridged complexes $[Fe_2(CO)_4(\mu\text{-}X)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$ 2a–c, isolated after chromatography in yields of 40–75%. While with HCl and HBr this was the only reaction product, with HF a second product was also produced (see later). Addition of carboxylic acids HCO_2Y (Y = H, CF_3, CCl_3, CBr_3, CO_2H) to 1 similarly results in the isolation of the carboxylate-bridged complexes $[Fe_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CY)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$ 3a–e in yields of 72–87% as the only reaction products (Scheme 1). The timescale of the latter reaction was, however, strongly dependent upon the nature of the carboxylic acid, being a function of acidity. For example, with CF_3CO_2H reaction was complete within seconds, while with CBr_3CO_2H a slow conversion was noted over 2 h. Addition of oxalic acid afforded only a single product identified as the monosubstituted complex $[Fe_2(CO)_4(\mu\text{-}\eta^2\text{-}O_2CCO_2H)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$ 3e, and even upon addition of excess 1 the disubstituted complex was not observed. The latter may indicate that metal coordination to one end of the oxalic acid strongly affects the acidity of the second carboxylic functionality, however, steric effects cannot be discounted. Indeed, inspection of the structure of 3a (see later) reveals that un-

favourable steric interactions might be expected between substituents on phosphorus upon disubstitution. Complexes 3a,b were easily purified by column chromatography, however, chromatography of 3c,d led to the slow formation of the corresponding halide complexes, while some decomposition of 3e was also noted under these conditions.

Characterisation proved straightforward on the basis of both spectroscopic and analytical data (Table 5). All show similar absorptions in the carbonyl region of the IR spectrum, the pattern being characteristic of two iron dicarbonyl units. The absorptions for the carboxylate complexes appear at slightly higher frequencies than those of the halides, indicating that all are poorer donor ligands than the latter. Two absorptions were observed due to the symmetric and asymmetric CO_2 stretches of the carboxylate ligand, the difference of approximately 140 cm^{-1} being indicative of a symmetrically bridging ligand [8]. In the ^{31}P NMR spectrum, all show a low field triplet and a high field doublet in a 1:2 ratio assigned to dicyclohexylphosphido and equivalent diphosphine atoms respectively. The chemical shifts of the dicyclohexylphosphido moiety are in the range 217–220 ppm for 2, while for 3 they are shifted to lower field, lying between 238 and 242 ppm. This observation is consistent with an earlier report by Mott and Carty [9] of the ^{31}P NMR chemical shifts of the related diphenylphosphido-bridged complexes $[Fe_2(CO)_6(\mu\text{-}X)(\mu\text{-}PPh_2)]$ (146–154 ppm) and $[Fe_2(CO)_6(\mu\text{-}\eta^2\text{-}O_2CY)]$ (183–185 ppm), and is attributed to the longer diiron vectors and consequently larger Fe–P–Fe bond

Scheme 1.

Table 5
Spectroscopic data for new complexes

	IR (ν_{CO}) (cm^{-1}) [a]	31p (δ), J (Hz) [b]	^{1}H (δ), J (Hz) [b]
2a	1978(m), 1948(m), 1916(m), 1897(sh)	217.0(t, J = 99), 62.5(d)	7.6–7.2 (20H, mPh), 3.48 (1H, q, J = 11.0, CH$_2$), 2.97 (1H, q, J = 11.4, CH$_2$), 2.2–1.2 (22H, m, Cy)
2b	1981(m), 1951(s), 1916(m), 1896(sh)	217.0(t, J = 98), 60.7(d)	7.8–7.3 (20H, m, Ph), 3.51 (1H, q, J = 11.4, CH$_2$), 3.00 (1H, q, J = 10.4, CH$_2$), 2.3–1.1 (22H, m, Cy)
2c	1980(m), 1950(s), 1916(m), 1897(sh)	220.1(t, J = 95), 62.7(d)	7.9–7.2 (20 H, m, Ph), 3.55 (1H, q, J = 10.7, CH$_2$), 3.33 (1H, q, J = 14.0, CH$_2$), 2.4–1.1 (22H, m, Cy)
3a	1987(m), 1947(s), 1912(s), 1893(sh), 1572(m), 1435(m)	238.1(t, J = 90), 59.2(d)	7.8–7.1 (21H, m, Ph + CH), 4.10 (1H, q, J = 11.3, CH$_2$), 2.2–1.2 (22H, m, Cy)
3b	1993(m), 1960(s), 1931(m), 1910(sh), 1574(m), 1435(m)	234.1(t, J = 87), 59.5(d)	7.8–7.2 (20H, m, Ph), 4.02 (2H, t, J = 10.2, CH$_2$), 2.4–1.3 (22H, m, Cy)
3c	1983(m), 1954(s), 1920(m), 1901(sh), 1575(m), 1434(m)	237.4(t, J = 87), 58.6(d)	7.8–7.2 (20, m, Ph), 4.07 (2H, m, CH$_2$), 2.4–1.1 (22H, m, Cy)
3d	1982(m), 1952(s), 1917(m), 1898(sh), 1574(m), 1435(m)	238.3(t, J = 88), 58.7(d)	8.1–7.2 (20H, m, Ph), 3.55 (2H, m, CH$_2$), 2.4–1.3 (22H, m, Cy)
3e	1985(m), 1956(s), 1923(s), 1635(m), 1436(m)	234.3(t, J = 87), 62.2(d)	7.9–7.1 (20H, m, Ph), 4.31 (1H, br, CH$_2$), 4.08 (1H, q, J = 9.0, CH$_2$), 3.75 (1H, br, CO$_2$H), 2.4–.0 (22H, m, Cy)
4	2032(m), 2003(s), 1991(sh)	257.5(t, J = 35), 52.7(d)	8.1–7.1 (20H, m, Ph), 4.61 (2H, m, CH$_2$), 2.4–1.1 (22H, m, Cy)
5	2025(m), 1998(s), 1980(s)	186.6(d, J = 45), 55.1(dd, J = 45, 17), 4.7(d, J = 17)	8.0–7.1 (20H, m, Ph), 7.00 (1H, br, H$_\alpha$), 2.02 (1H, br, H$_\beta$), 1.80 (1H, br, H$_\beta$), 2.0–1.1 (22H, m, Cy), −8.69 (1H, t, J = 40, Fe–H)

[a] In CH$_2$Cl$_2$; [b] in CDCl$_3$.

angles. The size of the phosphorus–phosphorus coupling constants in all complexes (90–100 Hz) is clearly indicative of a relative *trans* configuration of phosphorus-containing ligands, which is maintained throughout the reaction. Proton NMR data were generally uninformative, showing only complex signals for the phenylic and cyclohexyl protons and signal(s) assigned to the methylene protons. For **3a** the unique proton was not located by ^{1}H NMR spectroscopy, probably due to masking by the phenylic resonances, while for **3e** it appeared as a broad singlet at δ 3.75.

As previously mentioned, with HF a second reaction product was isolated, and with other acids of poorly coordinating anions such as HBF$_4$ and H$_2$SO$_4$ this same product was formed exclusively. On the basis of spec-

troscopic data it was characterised as the ionic diiron complex [Fe$_2$(CO)$_6$(μ-PCy$_2$)(μ-dppm)][Z] **4** (Z = F, BF$_4$, 0.5SO$_4$). In the carbonyl region of the IR spectrum, absorptions at 2032, 2003 and 1991 cm^{-1} are clearly indicative of a cationic diiron centre. Further evidence for this formulation comes from the FAB mass spectrum, the highest peak being at 862 m/e (M + 1). In the ^{31}P NMR spectrum, a low-field triplet at 256.5 is assigned to the dicyclohexylphosphido moiety, and a high-field doublet at 52.3 ppm to equivalent ends of the diphosphine. Most notable is the relatively small phosphorus–phosphorus coupling constant of 36 Hz, suggestive of a relative *cis* configuration of phosphorus-containing ligands. This is apparently contradicted by the ^{1}H NMR spectrum which shows a single broad signal at

Table 6
Selected bond lengths (Å) and angles (°) for **2b**, **2c**, **3a** and [Fe$_2$(CO)$_4$(μ-I)(μ-PCy$_2$)(μ-dppm)] **2d** [6]

	2b	2c	3a	2d
Fe–Fe	2.546(1)	2.550(2)	2.692(2)	2.580(2)
Fe–PPh$_2$	2.242(2)	2.232(2)	2.260(2)	2.235(3)
	2.242(2)	2.233(2)	2.284(2)	2.245(3)
Fe–PCy$_2$	2.222(1)	2.216(3)	2.228(2)	2.219(3)
	2.226(2)	2.210(2)	2.237(2)	2.224(2)
Fe–CO(*trans*)	1.767(7)	1.751(8)	1.797(11)	1.783(10)
	1.770(6)	1.751(10)	1.796(9)	1.760(12)
Fe–CO(*cis*)	1.733(6)	1.713(9)	1.742(8)	1.714(11)
	1.733(7)	1.723(9)	1.731(8)	1.740(10)
Fe–X	2.311(1)	2.412(1)	2.015(5)	2.604(2)
	2.291(2)	2.434(1)	2.015(5)	2.606(1)
Fe–X–Fe	67.2(1)	63.5(1)	—	59.4(1)
Fe–PCy$_2$–Fe	69.8(1)	70.4(1)	74.2(1)	71.0(1)

δ 4.61 assigned to both methylene protons, indicative of a relative *trans* orientation. We suggest that the molecule contains a *cis* configuration as shown in Scheme 1, the proton NMR data being interpreted in terms of an accidental near equivalence of the chemical shifts of the methylene protons. Formation of 4 clearly involves scavenging of two carbonyls and, consistent with this, isolated yields were enhanced under a CO atmosphere.

3.2. Structural studies

Three of the complexes synthesized during this study, namely [Fe₂(CO)₄(μ-Cl)(μ-PCy₂)(μ-dppm)] 2b, [Fe₂(CO)₄(μ-Br)(μ-PCy₂)(μ-dppm)] 2c, and [Fe₂(CO)₄(μ-η²-O₂CH)(μ-PCy₂)(μ-dppm)] 3a were characterised by X-ray crystallography, the results of which are shown in Table 5 and Fig. 1, the former also containing a comparison with the analogous iodo-bridged complex [Fe₂(CO)₄(μ-I)(μ-PCy₂)(μ-dppm)] [6]. All show the same gross structural features, namely two iron dicarbonyl units bridged symmetrically by diphosphine and phosphido moieties, which adopt a

relative *trans* disposition, and the halide or carboxylate group which lies *cis* to both the latter. The halide complexes 2b,c are characterised by a relatively short iron–iron vector [2b, 2.546(1); 2c, 2.550(2) Å], while in the formate complex this is somewhat elongated [3a, 2.692(2) Å]. A direct consequence of this is the opening up of the Fe(1)–P(3)–Fe(2) bond angle as compared with the halide-bridged complexes [2b, 69.8(1); 2c, 70.4(1); 3a, 74.2(1)°], an effect which is manifested in the down-field shift of approximately 20 ppm of this phosphorus atom in carboxylate complexes 3 as compared with 2 [9]. It is interesting to compare these bond lengths and angles with those reported for the related chloro-bridged complex [Fe₂(CO)₆(μ-Cl)(μ-PPh₂)] [9] [Fe(1)–Fe(2) 2.560(1) Å, Fe(1)–P–Fe(2) 69.7(1)°], which varies little from those found in 2b, indicating that the diphosphine ligand is not sterically demanding. The elongation of the iron–iron bond in 3a is, then, a direct result of the steric and electronic requirements of the carboxylate ligand. The halides bridge the diiron vector approximately symmetrically [2b, Fe(1)–Cl(1) 2.311(1), Fe(2)–Cl(1) 2.291(2); 2c, Fe(1)–Br(1)

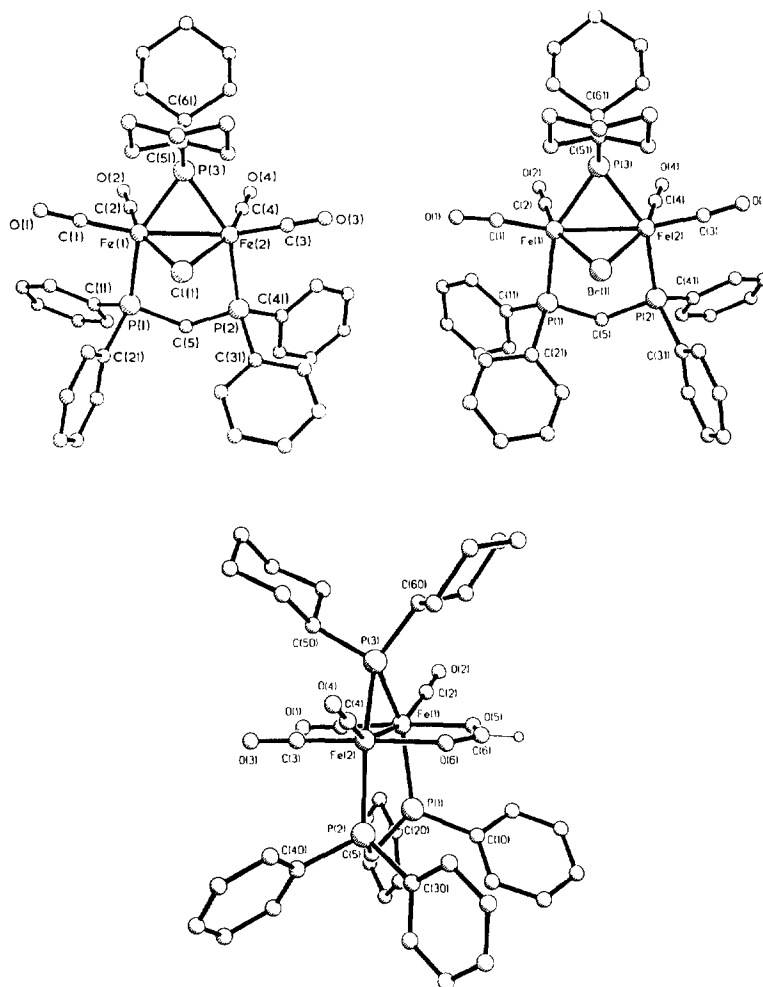Fig. 1. Molecular structures of 2b, 2c and 3a respectively.

2.412(1), Fe(2)–Br(1) 2.434(1) Å] and, as expected, the angle subtended decreases with increasing atomic weight [Fe–X–Fe; X = Cl, 67.2(1); X = Br, 63.5(1); X = I, 59.4(1)°]. In **3a** the formate ligand also bridges the diiron vector symmetrically [Fe(1)–O(5) 2.015(5), Fe(2)–O(6) 2.015(5) Å], although there are slight, but not significant, differences in the carbon–oxygen bond lengths [C(6)–O(5) 1.262(13), C(6)–O(6) 1.248(10) Å], and the angle at the backbone carbon [O(5)–C(6)–O(6) 127.3(8)°] is within the expected range [10]. In all three structures, two of the carbonyls lie *trans* to the metal–metal vector, while the others lie *cis* to it and *trans* to the anionic bridging ligand. It is noteworthy that the Fe–C bonds of the former are elongated with respect to the latter by an average amount δ which is significantly greater for the formate complex in comparison with the halide-bridged compounds [δ, **2b**, 0.036; **2c**, 0.033; **3a**, 0.060 Å]. This effect is a σ-inductive effect of the metal–metal bond [11] and is therefore sensitive to the nature of the metal–metal interaction, most notably the metal–metal bond length. Hence the elongation of the latter in **3a** results in a significant lengthening of the metal–carbon bonds *trans* to it.

3.3. Mechanistic studies and discussion

In order to gain further insight into the nature of the transformation of [Fe$_2$(CO)$_4$(μ-η^2-CH=CH$_2$)(μ-PCy$_2$)(μ-dppm)] **1** upon addition of acids, a number of the reactions were followed by IR and NMR spectroscopy. Addition of trifluoroacetic acid to a CDCl$_3$ solution of **1** immediately and quantitatively afforded **3b** as shown by ^{31}P NMR spectroscopy, while monitoring by ^{1}H NMR spectroscopy revealed the release of one equivalent of ethylene, as shown by the appearance of a singlet at δ 5.42 in chloroform.

During protonation studies with acids of non-coordinating anions an intermediate species was observed spectroscopically. Thus, upon addition of either HBF$_4$ · Et$_2$O or H$_2$SO$_4$ to a dichloromethane solution of **1**, an initial colour change from yellow to orange was noted. This new species, **5**, is characterised by absorptions at 2025(m), 1998(s) and 1980(s) cm^{-1} in the IR spectrum, the positions of which indicate that it contains a cationic diiron centre. Under a nitrogen atmosphere, **5** is transformed into **4** over a period of a few minutes, as shown by the appearance of absorptions at 2032(m), 2002(s) and 1981(m) cm^{-1} and a colour change from orange to yellow. Under an ethylene atmosphere, however, the intermediate orange complex **5** is indefinitely stable, suggesting that the secondary transformation involves ethylene loss. Indeed, purging the orange solution with carbon-monoxide resulted in the immediate and complete conversion to **4**.

In order to further probe the nature of **5**, HBF$_4$ · Et$_2$O was added to a CDCl$_3$ solution of **1** saturated with

ethylene, while monitoring by both ^{1}H and ^{31}P NMR spectroscopy. In the former, a broad hydride signal was observed at δ −8.69 (t, J = 40 Hz), while in the latter, signals at 186.7 (d, J = 45), 55.1 (dd, J = 45, 17) and 4.7 (d, J = 17 Hz) were assigned to the phosphido-bridge and inequivalent ends of the diphosphine respectively. The nature of the ^{31}P NMR spectrum varies considerably from that observed for the neutral vinyl complex **1**, for example, the small coupling constants between the phosphido-bridge and the diphosphine (45 and 0 vs. 88 and 77 Hz in **1**) suggest a *cis* configuration of these two ligands. From an inspection of the molecular structure of **1** [6], it is not apparent where the most sterically favourable site for protonation is. In order, however, for proton transfer to the α-vinyl carbon to occur, the two moieties must adopt a relative *cis* orientation. Thus, we believe that a substantial rearrangement of the core geometry of **1** occurs upon protonation. We considered that this may take the form of a *trans–cis* rearrangement of the two phosphorus-containing ligands. If indeed this were the case then one might anticipate that deprotonation of the orange intermediate **5** would yield the unknown *cis* isomer of **1**. In order to test this hypothesis, deprotonation of **5** was effected by addition of a slight excess of NEt$_3$ to a dichloromethane solution, which resulted in an instantaneous colour change from orange to yellow and quantitative regeneration of **1**. Two possible explanations are consistent with these experimental observations: addition of acid does not lead to *trans–cis* isomerisation of the phosphorus containing ligands, or conversion of the *cis* isomer of **1** to the more stable *trans* isomer is a very facile process. We tend to favour the former since we have previously synthesized mixtures of *trans* and *cis* isomers of closely related vinyl complexes [Fe$_2$(CO)$_4$(μ-η^2-RC=CH$_2$) (μ-PPh$_2$)(μ-dppm)] (R = Me, Ph) [12] and found no evidence for their interconversion. Thus, while the precise nature of **5** has not been determined, we favour the formulation [HFe$_2$(CO)$_4$(μ-η^2-HC=CH$_2$)(μ-PCy$_2$)(μ-dppm)][BF$_4$], in which the hydride is bound to a single metal centre, probably that to which the vinyl ligand is σ-bound. Coordination at this centre is expected to be favoured since it is the least sterically congested, and it is anticipated that a twisting of the diphosphine phosphorus at this centre might occur as a result of the increase in coordination number. A number of the spectroscopic observations support this formulation. For example, the hydride appears as a triplet in the ^{1}H NMR spectrum, suggesting coupling to only two of the phosphorus atoms, while its chemical shift is some 3 ppm to higher field than seen for the related cationic diiron hydride [Fe$_2$(CO)$_6$(μ-H)(μ-CO)(μ-dppm)][BF$_4$] (δ −11.33) [13]. A twisting of the diphosphine is suggested from the relatively small coupling constant of 16 Hz between the two ends of the diphosphine, which is considerably lower than in the neutral vinyl complex

1 [6] and related diiron diphosphine complexes [6,12]. This may also account for the unusually small coupling constants between the diphosphine ligand and the phosphido-bridge moiety. On the basis of the above data, and the tentative assignment of the intermediate orange complex 5, the reaction is believed to proceed as shown in Scheme 2.

Initial protonation is proposed to occur at the σ-bound metal centre and this cationic hydride 5 is in equilibrium with the neutral complex 1, the equilibrium position being determined by the pK_a of the acid. Slow but selective transfer of the hydride to the α-carbon of the vinyl unit can then occur, affording an ethylene complex. Such a complex is a 32-electron species, and as such is coordinatively unsaturated. While this unsaturation could be overcome in a number of ways, we favour the formation of a metal–metal double bond as shown. In support of this formulation, it is noteworthy that a number of isoelectronic 32-electron bis(phosphido) complexes have recently been prepared, and are shown to have similar structures [14]. We cannot, however, rule out the possibility that the ethylene bridges the diiron centre, and although such bridging ethylene complexes are comparatively rare, a number of related diosmium complexes have been prepared [15].

Further insight comes from carrying out the protonation reaction under a propene atmosphere. Thus, addition of HBF_4 to a propene saturated dichloromethane solution of 1 resulted in the generation of 5, which was again quite stable under these conditions, 4 growing in

slowly over a period of 30 min. The stabilization of 5 under such conditions suggests that the propene is metal-bound. However, deprotonation after 30 min upon addition of excess triethylamine revealed the reformation of 1 along with small quantities (up to 10%) of 4 and no evidence could be found for the formation of a μ-propenyl complex. This seems surprising and we have previously prepared and characterised the isomeric pair $[Fe_2(CO)_4(\mu\text{-}\eta^2\text{-MeC=CH}_2)(\mu\text{-PCy}_2)(\mu\text{-dppm})]$ and $[Fe_2(CO)_4(\mu\text{-}\eta^2\text{-HC=CHMe})(\mu\text{-PCy}_2)(\mu\text{-dppm})]$ [6]. Such an observation is consistent with the formation of a bis(alkene) complex as shown in Scheme 2. Thus, further addition of an alkene to the unsaturated ethylene complex would afford a saturated 34-electron species bearing two alkenes. Since the stability of 5 is greater in the presence of ethylene versus propene, we deduce that the latter is held less strongly to the diiron centre, probably a manifestation of the extreme steric crowding caused by the bulky phosphorus-containing ligands. This also accounts for the selective loss of propene versus ethylene from this complex, as gleaned from the lack of any propene incorporation into the vinyl site upon deprotonation. We also carried out the protonation reaction in the presence of excess styrene, however, no stabilization of 5 was noted and we attribute this to the increased steric demands of this alkene.

Addition of $HBF_4 \cdot Et_2O$ to the μ-propenyl complex $[Fe_2(CO)_4(\mu\text{-HC=CHMe})(\mu\text{-PCy}_2)(\mu\text{-dppm})]$ [6] also results in formation of 4 with concomitant release of propene. As with 1, the solution initially darkens and
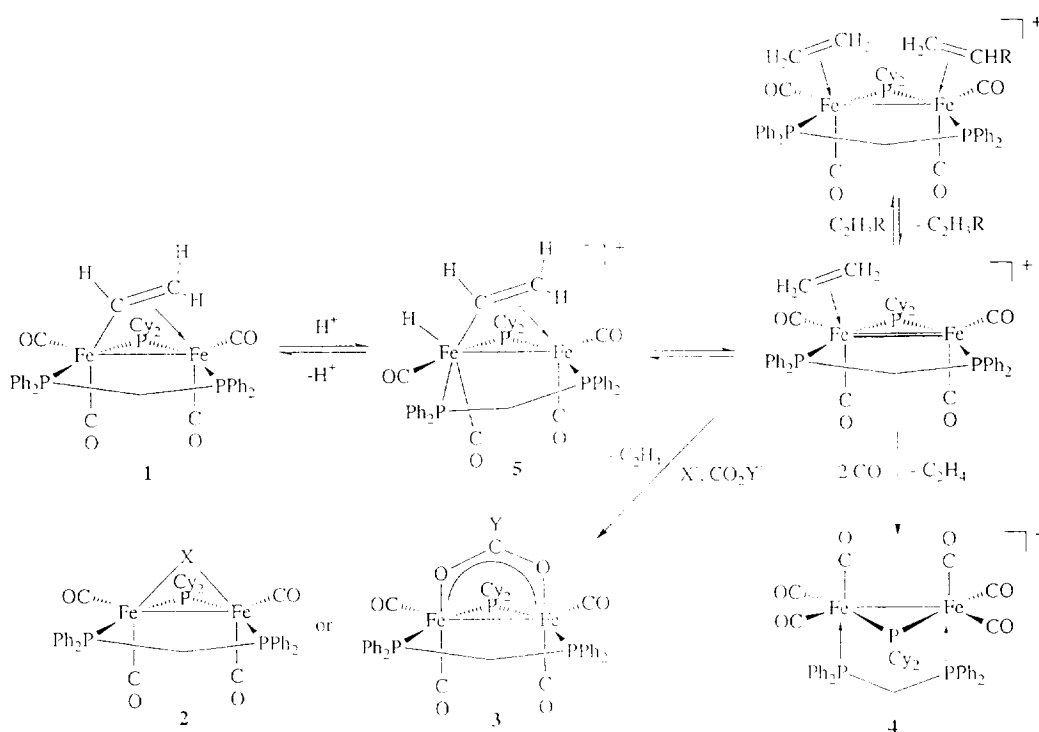
Scheme 2.

new absorptions are seen at 2023(m), 1994(s) and 1976(m) cm^{-1} in the IR spectrum together with those due to **4**, the latter being the only detectable species after approximately 10 min. When this reaction was carried out under an ethylene atmosphere, followed by deprotonation upon addition of triethylamine approximately 7 min after acid addition, the ^{31}P NMR spectrum revealed the formation of approximately 15% of the μ-ethenyl complex **1**, thus confirming the reaction mechanism outlined in Scheme 2. This observation also discounts the possibility that the role of the alkene is simply to inhibit the formation of adventitious CO via stabilization of **5**.

Further support for the formation of bis(alkene) complexes comes from a number of reports in which such dinuclear complexes have been prepared and studied [16,17]. For example, Koelle et al. [7] have detailed synthesis and X-ray crystal structure of the bis(ethylene) complex [(η^5-C$_5$Me$_4$Et)Ru(η^2-C$_2$H$_4$)(μ-Cl)]$_2$. Indeed, in support of our proposed reaction scheme, carbonylation of this diruthenium complex results in displacement of ethylene for CO.

Thus, a picture is beginning to emerge of the precise nature of the seemingly simple transformation of **1** to **2–4**. In the presence of coordinating anions, ethylene is readily displaced from the unsaturated complex to afford the observed halide- or carboxylate-bridged complexes **2** and **3** respectively. When the anion is poorly coordinating, a second reaction pathway is favoured, namely the displacement of ethylene by two moles of carbon-monoxide to afford the cationic hexacarbonyl **4**, and in support of this, the yield of **4** is increased in the presence of added carbon-monoxide. The reaction of **1** with HF is of special interest since it allows a comparison of the two possible pathways. Under a nitrogen atmosphere, addition of HF to **1** affords a mixture of **2a** and **4** (Z = F) (4:3), indicating that under these conditions the rate of attack of the poor nucleophile (fluoride) and carbonyl scavenging are similar. Addition of HF to a carbon-monoxide saturated solution of **1**, however, led to exclusive formation of **4** (Z = F) in 86% yield, while addition to an ethylene saturated solution gave **2a** as the major product. Both of these observations are consistent with the proposed reaction scheme.

In order to probe the basicity of **1**, reactions with a number of carboxylic acids, Cl$_{3-x}$H$_x$CCO$_2$H ($x = 0–3$), of differing pK_as. were followed by ^{31}P NMR spectroscopy. Addition of Cl$_3$C–CO$_2$H ($x = 0$, pK_a 0.65) resulted in the instantaneous and quantitative formation of **3c**, while as the pK_a increases the rate of formation of the carboxylate-bridged complexes decreases ($x = 1$, pK_a 1.29, 5 min: $x = 2$, pK_a 2.86, 2 h), and even after prolonged reaction times no reaction was detected between **1** and acetic acid ($x = 3$, pK_a 4.75). It is noteworthy that even with HCl$_2$C–CO$_2$H, the orange intermediate was not detected. indicating that while the

equilibrium between **1** and **5** lies well over to the former, subsequent proton transfer and nucleophile attack are rapid.

Acknowledgements

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