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The reactivity of bridging hydride ligands at the di-iron centre. Synthesis and reactivity towards alkynes of $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$. X-ray crystal structure of $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}dppm)][BF_4]$ *

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Abstract

Addition of $HBF_4 \cdot Et_2O$ to $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) results in rapid and quantitative proton addition across the di-iron vector to yield $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$ (**2**). Unlike **1**, in which all carbonyls are fluxional even at low temperatures, those in **2** are all static at room temperature, a feature that is attributed to the blocking of the previously vacant bridging site by the hydride ligand. The hydride in **2** is acidic. Thus upon addition of water, amines, or phosphines rapid and quantitative regeneration of **1** occurs. In contrast, alkyne insertion into the di-iron hydride function is rapid, and yields $\sigma-\pi$ vinyl complexes. With ethyne the previously characterised μ-ethenyl complex $[Fe_2(CO)_6(\mu\text{-}HC{=}CH_2)(\mu\text{-}dppm)][BF_4]$ (**3**) is formed in high yield. Addition of phenylacetylene occurs with high regioselectivity to give predominantly the 1-phenylvinyl isomer $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}dppm)][BF_4]$ (**4a**), which has been characterised crystallographically, and shown to contain a *trans* arrangement of vinyl and diphosphine ligands. Insertion of diphenyacetylene gives two products, which are tentatively characterised as isomers of $[Fe_2(CO)_6\{\mu\text{-}PhC{=}CH(Ph)\}(\mu\text{-}dppm)][BF_4]$ (**5**) with different relative orientations of vinyl and diphosphine ligands.

Introduction

The diphosphine bis(diphenylphosphino)methane (dppm) has found widespread use as a bridging ligand capable of binding two metal centres in close proximity, thus allowing studies of the chemistry of the binuclear metal centre [1,2]. We have utilised this approach to bind together iron carbonyl sites, as in the di-iron nonacarbonyl derivative $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**), which provides a convenient entry into the chemistry of this dinuclear centre [3,4], notorious for its fragmentation into mononuclear species. More recently, we have also adopted this

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* Dedicated to Professor Alwyn G. Davies in honour of his outstanding contribution to organometallic chemistry.

approach in the synthesis of complexes containing a di-iron centre bridged by a hydride ligand, which shows a high reactivity towards a variety of organic [5] and inorganic [6] reagents.

Di-iron nonacarbonyl is not readily protonated; indeed the usual method of synthesis involves the irradiation of iron pentacarbonyl in acetic acid [7]. It does react with hydrogen halides under UV irradiation, but gives dinuclear complexes $[Fe_2(CO)_6(\mu\text{-}X)_2]$ rather than protonated derivatives [8]. Replacement of two carbonyls by stronger donor phosphine ligands might be expected to increase the basicity of the di-iron centre, thus facilitating protonation. Herein we describe the synthesis of $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-dppm})][BF_4]$ (**2**), a diphosphine stabilised derivative of protonated di-iron nonacarbonyl, and its reactions with bases and alkynes, the latter resulting in rapid carbonyl loss and insertion into the hydride function to yield σ–π vinyl complexes.

Experimental

General comments

All reactions were carried out under N_2 using predried solvents unless otherwise stated. NMR spectra were recorded on a Varian VXR 400 spectrometer. IR spectra were recorded in solution on a Perkin-Elmer 983 spectrometer. Column chromatography was carried out on columns of deactivated alumina (6% w/w water). The elemental analyses were carried out in our department. $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) was prepared by the literature method [4], and fluoroboric acid, phenylethyne, and diphenylacetylene were purchased from Aldrich and used without further purification. Ethyne was passed through two propanol slush traps before use.

Preparation of $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-dppm})][BF_4]$ (2)

Dropwise addition of $HBF_4 \cdot Et_2O$ to a dichloromethane solution (50 cm^3) of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) (500 mg, 0.72 mmol) resulted in an immediate colour change from red to orange. The progress of the reaction was conveniently monitored by IR spectroscopy by observing the decrease in intensity of the band from the bridging carbonyl of **1** at 1755 cm^{-1} and the growth of that in **2** at 1785 cm^{-1}. After removal of solvent *in vacuo* the orange oil was washed with 3×10 cm^3 portions of diethyl ether and dried, to afford an orange microcrystalline solid. This was redissolved in 20 cm^3 of dichloromethane, and the solution was filtered via a cannula and layered with 40 cm^3 of light petroleum (40–60°C). Slow diffusion afforded large orange crystals, which were dried under vacuum. Yield 540 mg, 96%. ^1H NMR ($CDCl_3$): δ 8.1–7.1 (m, 20H, Ph), 4.08 (br, 2H, CH_2), -11.33 (t, J 8.8, 1H, μ-H). ^{13}C NMR (CD_2Cl_2): δ 257.9 (t, J 11, μ-CO), 206.6 (t, J 18, 2CO), 202.9 (s, 2CO), 201.4 (t, J 18, 2CO), 138–126 (m, Ph), 33.5 (t, J 22, CH_2). ^{31}P NMR (CD_2Cl_2): δ 49.3 (s). IR [ν(CO)] (CH_2Cl_2): 2098s, 2072m, 2047m, 2016m, 1785m cm^{-1}. Anal. Found: C, 45.70; H, 3.25; P, 6.33. $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-dppm})][BF_4] \cdot CH_2Cl_2$ calc.: C, 45.78; H, 2.89; P, 7.16%.

Reaction of 2 with ethyne

A few drops of $HBF_4 \cdot Et_2O$ were added to a dichloromethane solution (50 cm^3) of **2** (500 mg, 0.64 mmol). Ethyne was slowly bubbled through the solution which darkened significantly during 90 min. Removal of solvent *in vacuo* gave a red oil, which was washed with 3 × 10 cm^3 portions of diethyl ether and dried. The dry orange solid was redissolved in 20 cm^3 of dichloromethane and filtered through a cannula. Addition of light petroleum (b.p. 40–60°C) produced a cloudy solution which was cooled to −20°C. Orange microcrystals of $[Fe_2(CO)_6(\mu\text{-HC=CH}_2)(\mu\text{-dppm})][BF_4]$ (**3**) were collected, and dried under vacuum. Yield: 414 mg, 83%. ^1H NMR (CD_2Cl_2): δ 8.15 (dd, *J* 11, 7, 1H, H_α), 7.8–6.9 (m, 20H, Ph), 4.90 (q, *J* 10, 1H, PC*H*HP), 4.12 (dd, *J* 11, 3, 1H, H_{trans}), 4.05 (dd, *J* 7, 3, 1H, H_{cis}), 3.73 (dt, *J* 10, 5, 1H, PCH*H*P). ^{13}C NMR (CD_2Cl_2): δ 207.0 (br, CO), 171.9 (d, *J* 22, Cα), 137–127 (m, Ph), 70.8 (s, Cβ), 37.8 (dd, *J* 24, 18, PCH_2P). ^{31}P NMR ($CDCl_3$): δ 96.3 (d, *J* 51), 60.4 (d, *J* 51). IR [ν(CO)] (CH_2Cl_2): 2083s, 2048s, 2027m, 2002sh, 1987sh cm^{-1}. Anal. Found: C, 50.61; H, 3.40. $[Fe_2(CO)_6(\mu\text{-HC=CH}_2)(\mu\text{-CO})(\mu\text{-dppm})][BF_4]$ calc.: C, 50.90; H, 3.21%.

Reaction of 2 with phenylacetylene

A few drops of $HBF_4 \cdot Et_2O$ were added to a dichloromethane solution (50 cm^3) of **2** (500 mg, 0.64 mmol). Phenylacetylene (100 mg, 0.98 mmol) was added to the solution which darkened during 40 min. Removal of solvent *in vacuo* gave a red oil, which was washed with 3 × 10 cm^3 portions of diethyl ether to give a red solid which was redissolved in 20 cm^3 of dichloromethane. The solution was filtered through a cannula. Careful layering with 40 cm^3 of light petroleum (b.p. 40–60°C) and slow diffusion of the solvents produced large orange crystals of $[Fe_2(CO)_6(\mu\text{-PhC=CH}_2)(\mu\text{-dppm})][BF_4]$ (**4a**), which were collected and dried under vacuum. Yield: 470 mg, 86%. **4a**: ^1H NMR ($CDCl_3$): δ 8.1–7.1 (m, 25H, Ph), 5.32 (br, 1H, H_{trans}), 4.72 (br, 2H, CH_2), 4.01 (br, 1H, H_{cis}). ^{31}P NMR ($CDCl_3$): δ 45.5 (d, *J* 51), 37.4 (d, *J* 51). IR [ν(CO)] (CH_2Cl_2): 2079m, 2046m, 2010s cm^{-1}. Anal. Found: C, 50.69; H, 3.18; P. 5.66. $[Fe_2(CO)_6(\mu\text{-PhC=CH}_2)(\mu\text{-CO})(\mu\text{-dppm})][BF_4] \cdot CH_2Cl_2$ calc: C, 51.12; H, 3.30; P, 6.60%. Monitoring of the reaction by ^{31}P NMR spectroscopy revealed the concomitant formation of **4a** and a second product **4b** in a ratio of 10/1, constant with time. **4b**: ^{31}P NMR ($CDCl_3$): δ 52.4 (d, *J* 57), 49.8 (d, *J* 57).

Reaction of 2 with diphenylacetylene

A few drops of $HBF_4 \cdot Et_2O$ were added to a dichloromethane solution (50 cm^3) of **2** (500 mg, 0.64 mmol). Diphenylacetylene (200 mg, 1.12 mmol) was added to the solution resulting in a colour change from orange to red during 2 h. Removal of the solvent *in vacuo* gave a red oil which was washed with 3 × 10 cm^3 of diethyl ether to give a dry red solid. This was redissolved in 30 cm^3 of dichloromethane and the solution filtered through a cannula. Removal of solvent gave a red microcrystalline solid, which was used for recording of spectra. Attempted recrystallisation of this solid always resulted in extensive decomposition. ^{31}P NMR (CD_2Cl_2): δ 69.8 (d, *J* 61) (**5b**), 47.3 (d, *J* 61) (**5b**), 43.5 (d, *J* 49) (**5a**), 39.2 (d, *J* 49) (**5a**). IR [ν(CO)] (CH_2Cl_2): 2098s, 2054m, 2040m, 2022s, 2010m cm^{-1}.

Deprotonation experiments

Addition of triphenylphosphine (20 mg, 0.07 mmol) to a dichloromethane solution (5 cm^3) of **2** (40 mg, 0.05 mmol) resulted in the quantitative formation of **1**

Table 1

Crystallographic data for $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}Ph_2PCH_2PPh_2)][BF_4]\cdot CH_2Cl_2$

Formula	$Fe_2C_{40}O_6P_2B_1F_4Cl_2H_{31}$	Data collection instrument	Nicolet R3mV
Space group	$P\bar{1}$	Radiation	Mo-K_α ($\lambda = 0.71073$)
a (Å)	11.1829(23)	Orientation reflections: no.; range	29; $15 \leqslant 2\theta \leqslant 31$
b (Å)	11.5761(14)	Temp. (°C)	19
c (Å)	17.3049(32)	Data measured	7618
α (deg)	73.551(13)	Unique data	7435
β (deg)	88.259(16)	No. of unique with $I \geqslant 3.0\sigma(I)$	5577
γ (deg)	69.853(13)	No. of parameters	514
V (Å^3)	2011.43	R [a]	0.055
Z	2	R_w [b]	0.061
$F(000)$	952.0	Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000797F^2$
d_{calc} (g cm^{-3})	1.55	Largest shift/e.s.d. final cycle	0.15
Crystal size (mm)	$0.72 \times 0.60 \times 0.30$	Largest peak (e Å^{-3})	1.25
μ(Mo-K_α) (cm^{-1})	9.96		

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

during 10 min as indicated by IR spectroscopic monitoring. Reactions of **2** with water and triethylamine also gave **1**.

X-ray crystallographic study of $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}dppm)][BF_4]\cdot CH_2Cl_2$ *(4a)*

An orange single crystal of approximate size 0.72 × 0.60 × 0.30 mm was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-K_α radiation ($\lambda = 0.71073$ Å). Important crystallographic details are summarised in Table 1.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 29 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 7618 reflections (7435 unique) in the range $5 \leqslant 2\theta \leqslant 50$. 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 5577 unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the triclinic space group $P\bar{1}$.

The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference Fourier synthesis. The non-hydrogen atoms 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 final cycle of least-squares refinement included 514 parameters for 5577 observations and did not shift any parameter by more than 0.15 times its standard deviation. The final R values were 0.055 and 0.061. The final difference Fourier was featureless except for two peaks slightly greater than 1.00 e Å^{-3} close to a chloride Cl(1) of the solvent. Structure solution involved use of the SHELXTL PLUS program package on a microVax II computer. Atomic coordinates are listed in Table 2. Tables of hydrogen atom coordinates, anisotropic thermal parameters, and structure factors are available from the authors.

Table 2

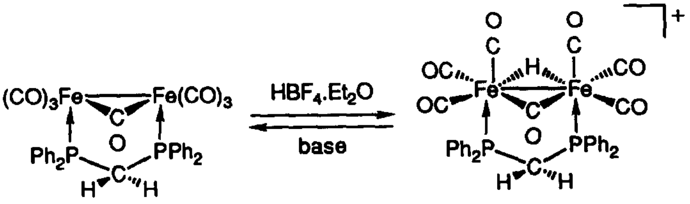
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
Fe(1)	3793(1)	2082(1)	6916(1)	29(1)
Fe(2)	2851(1)	428(1)	7889(1)	33(1)
P(1)	4752(1)	−1207(1)	8024(1)	31(1)
P(2)	5893(1)	953(1)	7290(1)	30(1)
O(1)	3914(4)	4319(4)	5667(2)	59(2)
O(2)	3619(4)	3667(4)	8004(2)	63(2)
O(3)	3886(3)	654(3)	5741(2)	45(1)
O(4)	1870(4)	−472(4)	6704(2)	52(2)
O(5)	4041(4)	875(4)	9225(2)	63(2)
O(6)	1210(4)	−665(5)	8984(3)	71(2)
F(1)	1619(6)	3151(5)	−609(3)	122(3)
F(2)	−223(5)	3278(7)	−83(4)	163(4)
F(3)	1059(5)	1428(4)	−238(3)	104(3)
F(4)	1519(6)	2227(5)	710(3)	116(3)
B(1)	997(8)	2498(7)	−43(4)	62(3)
Cl(1)	728(4)	4164(5)	2369(2)	193(3)
Cl(2)	−1196(4)	3162(5)	2224(3)	226(3)
C(1)	3379(5)	3446(5)	6143(3)	38(2)
C(2)	3698(4)	3000(5)	7627(3)	40(2)
C(3)	3844(4)	1180(4)	6211(3)	34(2)
C(4)	2260(4)	−85(4)	7131(3)	36(2)
C(5)	3576(5)	756(5)	8694(3)	42(2)
C(6)	1870(5)	−261(5)	8578(3)	44(2)
C(7)	1940(4)	2359(4)	7001(3)	38(2)
C(8)	1431(5)	2347(5)	7744(3)	42(2)
C(9)	1026(4)	2610(4)	6295(3)	38(2)
C(10)	1250(5)	3184(5)	5509(3)	46(2)
C(11)	398(6)	3478(6)	4857(3)	58(2)
C(12)	−712(6)	3209(6)	4992(4)	64(3)
C(13)	−969(5)	2646(6)	5759(4)	64(3)
C(14)	−108(5)	2358(6)	6403(4)	55(2)
C(15)	6096(4)	−630(4)	8006(3)	34(2)
C(16)	−420(9)	4131(8)	1562(8)	137(6)
C(21)	5197(5)	−2512(3)	8970(3)	35(2)
C(22)	4535(5)	−2423(5)	9653(3)	44(2)
C(23)	4969(6)	−3403(5)	10367(3)	52(2)
C(24)	6044(6)	−4450(5)	10405(3)	55(2)
C(25)	6719(6)	−4536(5)	9732(3)	53(2)
C(26)	6284(5)	−3568(5)	9014(3)	48(2)
C(31)	5007(5)	−2109(4)	7289(3)	36(2)
C(32)	5915(5)	−2075(5)	6712(3)	45(2)
C(33)	6050(6)	−2824(5)	6185(3)	57(2)
C(34)	5303(6)	−3568(5)	6223(3)	58(2)
C(35)	4442(6)	−3601(5)	6780(3)	55(2)
C(36)	4287(5)	−2879(5)	7314(3)	46(2)
C(41)	6753(4)	1658(4)	7796(3)	34(2)
C(42)	6653(5)	2923(5)	7427(3)	46(2)
C(43)	7310(5)	3496(5)	7773(4)	55(2)
C(44)	8077(5)	2827(5)	8468(3)	47(2)
C(45)	8196(5)	1583(6)	8826(3)	51(2)
C(46)	7522(5)	994(5)	8502(3)	45(2)
C(51)	6949(4)	580(4)	6498(3)	32(2)
C(52)	6540(4)	1191(5)	5688(3)	37(2)
C(53)	7335(5)	855(5)	5088(3)	43(2)
C(54)	8506(5)	−93(5)	5296(3)	48(2)
C(55)	8940(5)	−670(5)	6099(3)	52(2)
C(56)	8168(5)	−323(5)	6701(3)	43(2)

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

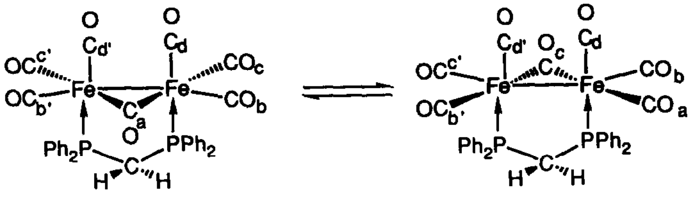
Results and discussion

Addition of a slight excess of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ (**1**) results in a rapid lightening of the solution and quantitative formation of the protonated species $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$ (**2**) which was readily identified from spectroscopic and analytical data. Thus in the IR spectrum absorptions are shifted to higher wavenumbers with respect to **1** indicating protonation at the dinuclear centre, the bridging carbonyl appearing at 1785 cm^{-1}. In the ^{31}P NMR spectrum a singlet at δ 49.3 ppm suggests retention of the mirror symmetry of the starting material **1** indicating that the hydride spans the metal–metal vector. This is confirmed by the ^1H NMR spectrum in which the hydride is observed as a triplet at $-\delta$ 11.33 ($J(P\text{-}H) = 8.8$ Hz), the magnitude of the coupling constant indicating that the hydride lies *cis* to the diphosphine ligand. In the ^{13}C NMR spectrum, four distinct carbonyl resonances are observed at δ 257.9 (t, J 11), 206.6 (t, J 18), 202.9 (s), and 201.4 (t, J 18 Hz) ppm in the ratio 1/2/2/2 indicating that even at room temperature they do not interconvert. This is in stark contrast to the rapid scrambling in **1** of all carbonyls at room temperature [9] which has been attributed to two processes: (i) trigonal rotation at each iron centre, and (ii) equilibration of the five carbonyls in the plane perpendicular to the diphosphine ligand. In **1**, neither of these processes are frozen out at temperatures "well below $-100°C$" [9]. The radical difference in fluxional behaviour between **1** and **2** is a result of the hydride ligand blocking the vacant coordination site *trans* to the bridging carbonyl, which stops the in-plane scrambling, and the change in coordination number of each iron centre from five to six, trigonal rotation being a significantly higher energy process at the latter. The hydride in $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$ (**2**) is acidic. Thus addition of triethylamine, water or even triphenylphosphine results in the rapid and quantitative regeneration of **1**.

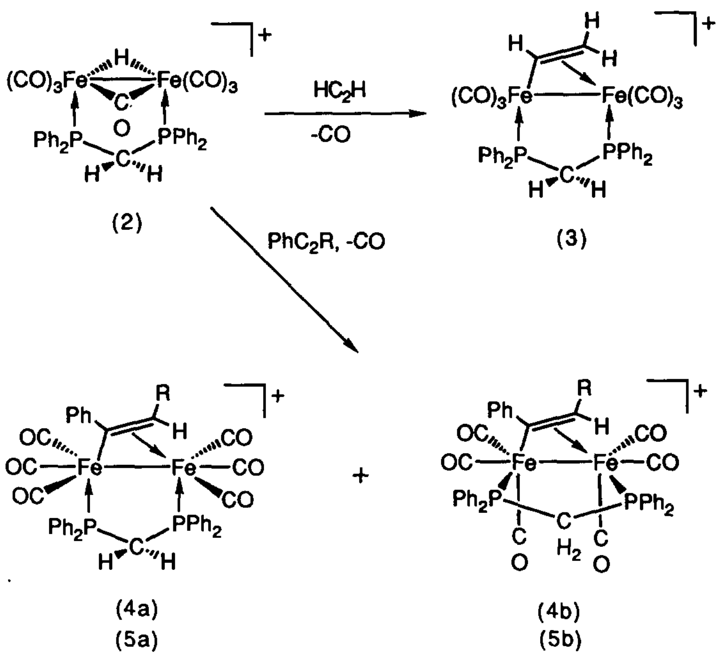


(1) (2)

In related studies Haines and co-workers [10] have reported that protonation of the bisdiphosphine complexes $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)_2]$ (R = Me, Ph)



Scheme 1. Shows the in-plane scrambling of five carbonyls in **1** via concerted opening and closing of carbonyl bridges, which is blocked in **2**.



Scheme 2.

with $HBF_4 \cdot Et_2O$ similarly gives μ-hydrido cations. While these more basic di-iron centres could be deprotonated, it required use of strong bases such as $NaBH_4$. A number of papers on related di-ruthenium complexes [10,11] also report similar behaviour, although, as expected, the diruthenium centre is significantly more basic.

Complex **2** reacts readily with alkynes in the presence of a slight excess of acid. Thus, purging a dichloromethane solution with ethyne results in the formation of $[Fe_2(CO)_6(\mu\text{-}CH{=}CH_2)(\mu\text{-dppm})][BF_4]$ (**3**) in 83% yield. This results from carbon monoxide loss and insertion of ethyne into the di-iron hydride moiety, behaviour we have recently noted at other diphosphine stabilised di-iron centres [5]. We have also recently synthesised **3** by a different method involving initial UV mediated ethyne addition to **1** to give the acyl bridging complex $[Fe_2(CO)_5\{\mu\text{-}HC{=}CHC(O)\}(\mu\text{-dppm})]$ followed by protonation [4]. The synthesis reported here has several advantages: (i) UV irradiation is not required for carbonyl loss, the facile loss of carbon monoxide from **2** being a result of the decreased electron density at the di-iron centre, which leads to a weaker metal–carbonyl interaction; (ii) the UV mediated reaction of **1** with ethyne is not selective, and leads to three products, which must be separated by chromatography; and (iii) it provides a one-pot high yield synthesis.

Addition of phenylacetylene to an acidified solution of **2** results in a rapid darkening, and isolation of $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-dppm})][BF_4]$ (**4a**) in 86% yield. In the ^{31}P NMR spectrum AB doublets at δ 45.5 and 37.4 (J 51 Hz) ppm indicate inequivalent iron centres. In the ^{1}H NMR spectrum at room temperature resonances are broadened somewhat, indicating slow σ–π vinyl fluxionality, but the formation of the 1-phenylvinyl complex is clearly illustrated by resonances at δ

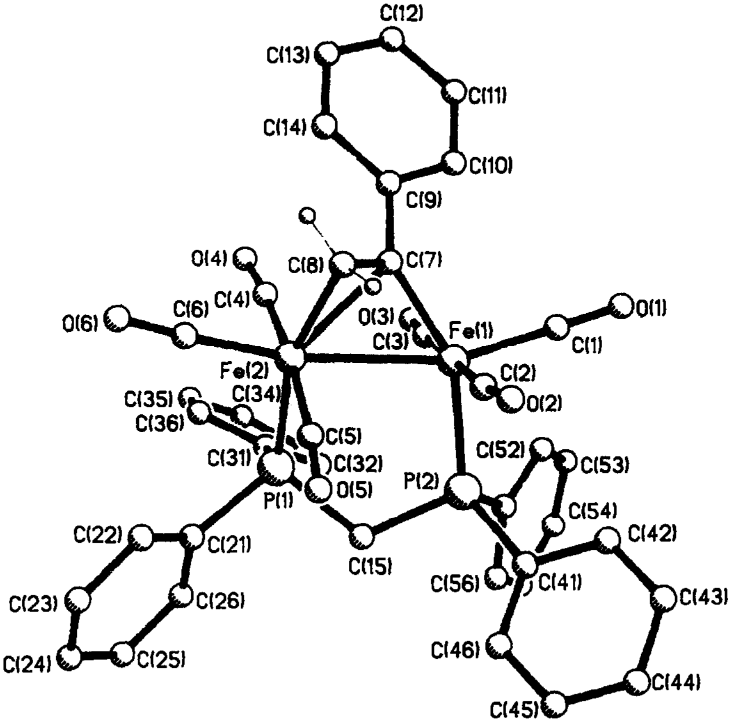


Fig. 1. X-ray crystal structure of the cation $[Fe_2(CO)_6(\mu\text{-PhC=CH}_2)(\mu\text{-dppm})]^+$ (**4a**).

5.32 and 4.01 assigned to protons on the β-carbon, *trans* and *cis* to the phenyl group, respectively.

In order to confirm the nature of **4a** an X-ray crystallographic study was carried out on the dichloromethane solvate, and the results are summarised in Fig. 1 and Table 3. Complex **4** contains two iron atoms separated by 2.658(1) Å and bridged symmetrically by a dppm ligand [Fe(1)–P(2) 2.268(1), Fe(2)–P(1) 2.273(1) Å]. Each iron atom also supports three terminally bound carbonyls, two being *trans* to one another [C(2)–Fe(1)–C(3) 178.6(2), C(4)–Fe(2)–C(5) 173.4(2)°] and the third *trans* to the di-iron vector [Fe(2)–Fe(1)–C(1) 160.9(2), Fe(1)–Fe(2)–C(6) 164.1(2)°]. Also bridging the dimetal centre is a 1-phenylvinyl ligand lying approximately *trans* to the diphosphine. We have previously noted the preferred *trans* orientation of diphosphine and σ–π vinyl ligands at the di-iron centre [5]. The α-carbon C(7) of the vinyl ligand carries the phenyl group and is bound asymmetrically to both iron atoms [Fe(1)–C(7) 1.992(5), Fe(2)–C(7) 2.231(4) Å], while the β-carbon C(8) is attached to only a single metal centre [Fe(2)–C(8) 2.190(4) Å]. The two vinyl carbons are separated by 1.388(7) Å, indicative of a bond order intermediate between one and two, as found in related σ–π vinyl species [5,12].

Examination of the crude reaction mixture from the addition of phenyacetylene to **2** by ^{31}P NMR spectroscopy indicates that *ca.* 10% of a second complex (**4b**) is present, characterised by resonances at δ 52.4 and 49.8 (J 57 Hz) ppm. We initially thought that this second species might be an intermediate in the formation of **4a**, but monitoring of the reaction by ^{31}P NMR spectroscopy revealed the gradual

Table 3

Selected bond lengths (Å) and angles (deg) in **4a**

Fe(1)–Fe(2)	2.658(1)	Fe(1)–Fe(2)–P(1)	91.3(1)
Fe(1)–P(2)	2.268(1)	Fe(2)–Fe(1)–P(2)	97.9(1)
Fe(2)–P(1)	2.273(1)	Fe(2)–Fe(1)–C(1)	160.9(2)
Fe(1)–C(1)	1.787(5)	Fe(2)–Fe(1)–C(2)	94.4(2)
Fe(1)–C(2)	1.818(6)	Fe(2)–Fe(1)–C(3)	84.9(2)
Fe(1)–C(3)	1.806(6)	Fe(1)–Fe(2)–C(4)	98.5(2)
Fe(2)–C(4)	1.810(6)	Fe(1)–Fe(2)–C(5)	84.3(2)
Fe(2)–C(5)	1.823(6)	Fe(1)–Fe(2)–C(6)	163.1(2)
Fe(2)–C(6)	1.802(6)	Fe(1)–Fe(2)–C(7)	47.1(1)
Fe(1)–C(7)	1.992(5)	Fe(2)–Fe(1)–C(7)	55.1(1)
Fe(2)–C(7)	2.231(4)	Fe(1)–Fe(2)–C(8)	73.6(1)
Fe(2)–C(8)	2.190(4)	P(1)–Fe(2)–C(7)	135.1(1)
P(1)–C(15)	1.839(6)	P(2)–Fe(1)–C(7)	153.0(1)
P(2)–C(15)	1.840(4)	P(1)–Fe(2)–C(8)	161.6(2)
C(7)–C(8)	1.388(7)	Fe(1)–C(7)–Fe(2)	77.8(1)
C(7)–C(9)	1.514(7)	C(1)–Fe(1)–C(2)	87.2(2)
		C(1)–Fe(1)–C(3)	93.0(2)
		C(2)–Fe(1)–C(3)	178.6(2)
		C(4)–Fe(2)–C(5)	173.4(2)
		C(4)–Fe(2)–C(6)	87.2(3)
		C(5)–Fe(2)–C(6)	91.8(3)
		Fe(1)–C(7)–C(9)	123.9(3)
		Fe(2)–C(7)–C(9)	123.6(4)
		Fe(2)–C(8)–C(7)	73.3(3)
		C(8)–C(7)–C(9)	117.0(4)

growth of both species, in a ratio independent of time. We have been unable to characterise this complex further; it may contain either a 2-phenylvinyl ligand or differ from **4a** in the relative orientation of vinyl and diphosphine moieties. While one might initially favour the former, we have recently found that the related complexes [$Fe_2(CO)_4(\mu$-$RC{=}CH_2)(\mu$-$PPh_2)(\mu$-dppm)] exist in two isomeric forms that differ only in the relative disposition of the 1-substituted vinyl and diphosphine ligands, *i.e.* either *cis* or *trans* [5]. This and other evidence (*vida infra*) strongly suggests a similar isomerism in **4**. Irrespective of the nature of this minor product, insertion of phenylethyne into the hydride function of **2** occurs with high regioselectivity, in Markovnikov and *cis*-fashion. Indeed this appears to be. a general feature of such reactions, and has been noted previously [5,13].

Insertion of diphenylacetylene into **2** is not as clean as the reactions with primary alkynes, and results in a mixture of products the ratio of which varies with time. Thus addition of diphenylacetylene to an acidified solution of **2** results in a colour change from orange to red during 2 h. ^{31}P NMR analysis of the crude reaction mixture shows the presence of a number of species; the two major constituents, in the ratio 1/2, are characterised by AB doublets at δ 69.8, 47.3 (J 61 Hz) (**5b**) and 43.5, 39.2 (J 49 Hz) (**5a**) ppm, respectively. All attempts to purify **5** resulted in extensive decomposition, the major phosphorus-containing product being the mononuclear [$Fe(CO)_4(\eta^1$-dppm)], produced via fragmentation of the iron–iron bond [14]. The nature of these products is unclear, but it is tempting to suggest that they differ with respect to the relative disposition of vinyl and diphosphine ligands, since clearly in this instance vinyl isomerism is not possible.

Both ^{31}P NMR chemical shifts and coupling constants for **5** agree well with those observed for **4**, and on this basis we tentatively assign the structures shown to the isomers of **5**.

Conclusion

The di-iron centre in $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ is readily protonated by $HBF_4 \cdot Et_2O$ to give the μ-hydrido complex $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$ quantitatively. This complex can be considered as a model for the unknown species $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)_3]^+$. The hydride blocks the carbonyl scrambling observed in **1**, and is acidic, being rapidly deprotonated by PPh_3. Addition of alkynes results in facile loss of carbon monoxide and insertion of the alkyne into the hydrido moiety to yield σ–π vinyl complexes. In the case of phenylacetylene the process proceeds with high regioselectivity, the nature of which has been elucidated by an X-ray diffraction study of the major isomer $[Fe_2(CO)_6(\mu\text{-}PhC{=}CH_2)(\mu\text{-}dppm)][BF_4]$, which was found to involve a *trans* disposition of vinyl and diphosphine moieties. The nature of the isomerism in these complexes is uncertain, but is tentatively attributed to the relative dispositions of vinyl and diphosphine ligands. Further studies on the nature of this isomerism and the reactions of $[Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)][BF_4]$ are in progress.

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