Synthesis and Reactivity towards Unsaturated Organics of the Diiron Hydride Complex $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCH_2PPh_2)]$†

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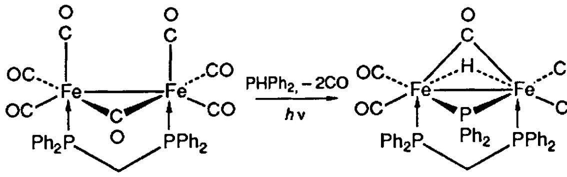
Ultraviolet irradiation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ **1** (dppm = $Ph_2PCH_2PPh_2$) with diphenylphosphine results in phosphorus–hydrogen bond cleavage to give $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **2**. The hydride functionality in **2** readily inserts unsaturated organics. Thus reaction with ethyne yields the μ-ethenyl complex $[Fe_2(CO)_4(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **3**. Both allene and propyne insert into **2** to give $[Fe_2(CO)_4(\mu\text{-}MeC{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ which exists in two isomeric forms **4a**, **4b**. Both contain the 1-methylvinyl ligand but differ in the relative orientations of diphosphine and vinyl moieties. A third isomer $[Fe_2(CO)_4(\mu\text{-}HC{=}CHMe)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **4c** containing a 2-methylvinyl ligand has been isolated from the reaction of **1** with allyldiphenylphosphine *via* phosphorus–carbon bond cleavage at the diiron centre. Reaction of **2** with phenylethyne gives two isomeric forms of $[Fe_2(CO)_4(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **5a**, **5b**. The nature of these isomers is deduced from ^{31}P NMR data and an X-ray crystallographic study of one isomer of the propyne insertion product. Compound **4a** crystallises in the monoclinic space group $P2_1/c$ with $a = 10.749(8)$, $b = 18.122(15)$, $c = 19.854(9)$ Å, $\beta = 94.32(5)°$ and $Z = 4$. On the basis of 3492 unique reflections and 478 parameters the structure has been refined to $R = 0.055$ and $R' = 0.054$. The structure confirms the formation of a 1-methylvinyl ligand which lies *trans* to the diphosphine moiety but *cis* to the diphenylphosphido bridge. A variable-temperature ^{31}P NMR study allows monitoring of the σ–η vinyl fluxionality in each isomer. Reaction of **2** with ethyl diazoacetate results in insertion of the nitrogen–nitrogen bond into the hydride to give the unusual zwitterionic product $[Fe_2(CO)_4\{\mu\text{-}HN\text{-}N{=}CH(CO_2Et)\}(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **6** which is stable to prolonged thermolysis in toluene.

Transition-metal complexes containing hydride ligands continue to attract considerable attention due to the critical importance of such species in many stoichiometric and catalytic reactions.[1] While the chemistry of mononuclear hydride complexes is well understood, in contrast, the synthesis and reactivity of hydrogen bridging two or more metal centres remains relatively unexplored.[1,2]

The photochemically induced reactivity of transition-metal carbonyl complexes is a well documented process which has been extensively utilised towards the substitution of carbon monoxide for other donor ligands.[3] Indeed, in a number of recent papers we have described how the binuclear complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)]$ **1** (dppm = $Ph_2PCH_2PPh_2$), whilst unreactive in the absence of UV irradiation, reacts readily with alkynes[4] and phosphines[5,6] upon photolysis to yield a variety of CO-loss products. Herein we describe the photochemically induced reaction of diphenylphosphine with **1** which results in both carbonyl loss and ready oxidative addition of the phosphorus–hydrogen bond to the diiron centre yielding $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **2**. The bridging hydride moiety at the diiron centre exhibits high reactivity towards alkynes and other unsaturated organics, the former resulting in the isolation of σ:η vinyl complexes.

Results and Discussion

Synthesis of $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **2**.—Ultraviolet irradiation of a toluene solution of **1** and a slight excess of diphenylphosphine results in the generation of the new complex $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **2** in 77% yield [equation (1)]. The formation of **2** is conveniently monitored by IR spectroscopy. Significantly the bridging carbonyl of **1** at 1755 cm^{-1} gradually diminishes to be replaced by a new absorption at 1711 cm^{-1}. In the ^1H NMR spectrum the hydride moiety appears as a doublet of triplets at δ −9.50 (*J* 51.0, 26.5 Hz) while in the ^{31}P NMR spectrum a triplet at δ 150.3 (*J* 45 Hz) is assigned to the phosphido bridge.[7] The magnitude of this phosphorus–phosphorus coupling constant indicates that the diphosphine and phosphido bridge lie *cis*, while the phosphorus–hydrogen coupling constants of 51.0 and 26.5 Hz between the hydride and the phosphido and diphosphine moieties respectively indicate that it lies *trans* to the former and *cis* to the latter. In the ^{13}C NMR spectrum the bridging carbonyl appears as a broad signal at δ 268.1 and the terminal carbonyls appear as doublets at δ 218.1 (*J* 10) and 216.1 (*J* 7 Hz). On the basis of these data the structure is assigned.



1 2 (1)

The oxidative addition of the phosphorus–hydrogen bond of diphenylphosphine to yield μ-hydride and μ-phosphido moieties is well documented.[8] While the process probably occurs *via* initial photochemical substitution of a carbonyl for diphenylphosphine, no evidence for this species was observed. This may imply that the later oxidative-addition reaction proceeds very rapidly. In support of this we have previously found that in the photochemical reaction of **1** with diphosphines[5] and vinylphosphines[6] no hexacarbonyl products

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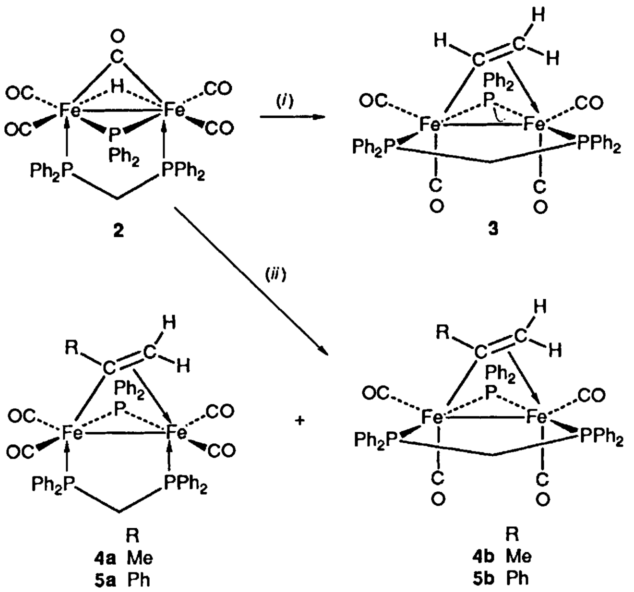
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 (*i*) HC_2H, $-CO$, toluene; (*ii*) R = Me, MeC_2H or $H_2C{=}C{=}CH_2$, $-CO$, toluene; R = Ph, PhC_2H, $-CO$, toluene

Table 1 Crystallographic data for $[Fe_2(CO)_4(\mu\text{-}MeC{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCH_2PPh_2)]$ **4a**

Formula	$C_{44}H_{37}Fe_2O_4P_3$
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a/Å	10.7491(82)
b/Å	18.1217(148)
c/Å	19.8545(88)
β/°	94.320(50)
U/Å^3	3856.51
Z	4
$F(000)$	1720
D_c/g cm^{-3}	1.44
Crystal size/mm	0.40 × 0.40 × 0.40
μ(Mo-Kα)/cm^{-1}	9.16
Orientation reflections: no.; range	21; $8 \leqslant 2\theta \leqslant 20$
T/°C	19
Data measured	7679
Unique data	7181
No. of unique with $I \geqslant 3.0\sigma(I)$	3492
No. of parameters	478
R[a]	0.055
R'[b]	0.054
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000\,629F^2$
Largest shift/e.s.d., final cycle	0.035
Largest peak/e Å^{-3}	0.50

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}|F_o|$.

could be observed, rather in both cases substitution of two carbonyls resulted in the isolation of pentacarbonyl products. Complex **2** is formally the dppm-substituted derivative of the heptacarbonyl complex $[Fe_2H(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ which has been reported by a number of groups but has not been fully characterised due to difficulties in obtaining crystalline samples.[9] Data for this and **2** correlate well however and it is tempting to speculate that the unsubstituted complex also contains a bridging hydride ligand.

Reaction of Complex **2** *with Primary Alkynes.*—Complex **2** reacts readily with primary alkynes in the absence of UV irradiation resulting in insertion into the metal–hydrogen bonds (Scheme 1). Thus, room-temperature addition of ethyne results in the isolation of $[Fe_2(CO)_4(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **3** in 59% yield. We have previously synthesised **3** from the carbon–phosphorus bond cleavage of ethenyldiphenylphosphine.[6] It is produced as a single isomeric form *via* both synthetic routes and, on the basis of the large phosphorus–phosphorus coupling constants (*J* 91, 81 Hz), a structure is assigned containing a *trans* orientation of diphosphine and phosphido moieties. This contrasts with their *cis* orientation in **2**, showing that during the reaction one, or both, of the phosphorus-containing ligands is mobilised.

Addition of either propyne or allene to **2** affords $[Fe_2(CO)_4(\mu\text{-}MeC{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **4** in 64–70% yield, as a mixture of two isomers in the approximate ratio of 2:1, as shown by ^1H NMR spectroscopy at −50 °C. Thus at room temperature, the ^1H NMR spectrum is broad, but sharpens appreciably at −50 °C. The absence of resonances between δ 4.3 and 6.0, the expected position of a proton bound to the α carbon of a σ:η vinyl, leads us to conclude that both components of **4** are substituted at this position. The methyl resonances of each isomer are clearly distinguished at δ 3.06 (**4a**) and 1.66 (**4b**), as are the vinylic resonances of **4a** at δ 2.08 (*J* 9) and 2.63 (*J* 13 Hz), and **4b** at δ 2.57 (*J* 14) and 2.90 (*J* 2 Hz). Addition of phenylethyne to **2** affords $[Fe_2(CO)_4(\mu\text{-}PhC{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **5** in 72% yield, again as an inseparable mixture of two isomers **5a**, **5b** in the approximate ratio of 10:1. In the ^1H NMR spectrum at −70 °C resonances due to **5a** are clearly resolved, one vinyl proton appearing as a doublet of triplets at δ 2.38 (*J* 13.5, 4.3 Hz) and the second as a multiplet at δ 2.12. Resonances due to the minor isomer are not clearly resolved, and may be partly obscured.

The Nature of σ:η *Vinyl Isomers.*—This is deduced from low-temperature ^{31}P NMR data and an X-ray crystallographic study of the major isomer of **4**, namely **4a**. Thus at −40 °C, the ^{31}P NMR spectrum of **4** shows two clearly defined doublets of doublets at low field assigned to the phosphido-bridge moieties of each isomer: **4a**, δ 166.1 (*J* 47, 26); **4b** δ 203.4 (*J* 87, 77 Hz). Similarly at −80 °C, phosphido-bridge resonances of **5** appear as a doublet of doublets and pseudotriplet respectively: **5a**, δ 160.1 (*J* 46, 25); **5b**, δ 199.0 (*J* 83 Hz). The size of the coupling constants allows assignment of **4a** and **5a** as isomers containing a *cis* configuration of diphosphine and phosphido moieties, and **4b** and **5b** to those containing the *trans* arrangement. Since the two three-electron-donor ligands must adopt a *cis* arrangement, then the structures shown are deduced.

Slow diffusion of methanol into a dichloromethane solution of **4** led to the formation of orange crystals of **4a** suitable for X-ray crystallography. The results are summarised in Table 1, and Fig. 1 shows the molecular geometry with the crystallographic numbering scheme. The molecule consists of two iron atoms separated by 2.658(3) Å, bridged symmetrically by phosphido and diphosphine moieties which adopt a *cis* geometry. The vinyl ligand bridges the diiron centre in the familiar σ,η mode, with C(5) σ-bound to Fe(1) and the C(5)–C(7) bond π-bound to Fe(2). The C(5)–C(7) bond length of 1.403(12) Å corresponds to a bond order of between one and two. The methyl group C(6) is bound to the α carbon C(5) and oriented away from the sterically demanding diphenylphosphido moiety. As expected, the two three-electron-donor ligands adopt a *cis* configuration, the vinyl ligand being orientated *trans* to the diphosphine moiety. On the basis of the *cis* configuration of diphosphine and phosphido moieties the crystallographically characterised molecule corresponds to the major isomer of **4**, namely **4a**.

While no 2-methylvinyl isomers of **4** were isolated from the insertion of either propyne or allene into the bridging hydride, one of these was synthesised using a different synthetic method. Thus, irradiation of a toluene solution of **1** and allyldiphenylphosphine gave a yellow air-sensitive solution which upon thermolysis led to the isolation of $[Fe_2(CO)_4(\mu\text{-}HC{=}CHMe)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$ **4c** in 28% yield [equation (2)]. Characterisation as a 2-methylvinyl isomer is easily made on the basis of the ^1H NMR spectrum. Thus the α-bound proton is observed as a

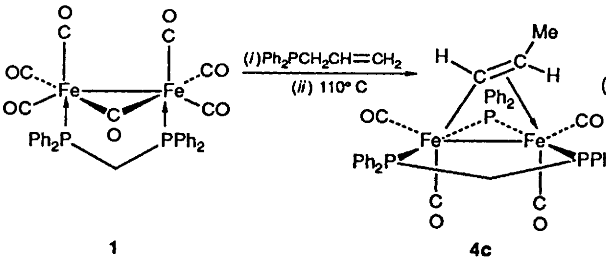
Table 2 Atomic coordinates (× 10^4) for complex **4a**

Atom	*x*	*y*	*z*
Fe(1)	2 531(1)	7 740(1)	1 793(1)
Fe(2)	4 539(1)	6 883(1)	1 947(1)
P(1)	2 691(2)	8 218(1)	753(1)
P(2)	5 258(2)	7 513(1)	1 086(1)
P(3)	2 665(2)	6 577(1)	1 406(1)
O(1)	−118(6)	7 827(4)	2 031(4)
O(2)	2 803(6)	9 245(4)	2 337(3)
O(3)	6 731(6)	7 326(4)	2 825(3)
O(4)	5 434(7)	5 377(4)	1 787(3)
C(1)	928(9)	7 783(5)	1 926(4)
C(2)	2 769(8)	8 657(5)	2 128(4)
C(3)	5 873(8)	7 178(5)	2 474(4)
C(4)	5 100(8)	5 972(5)	1 836(4)
C(5)	3 372(7)	7 347(5)	2 653(3)
C(6)	3 854(8)	7 872(5)	3 221(4)
C(7)	3 567(7)	6 598(5)	2 804(3)
C(8)	4 130(6)	7 866(4)	405(3)
C(11)	2 784(8)	9 239(4)	719(4)
C(12)	1 700(9)	9 626(5)	825(5)
C(13)	1 691(11)	10 379(5)	898(5)
C(14)	2 813(12)	10 762(5)	886(5)
C(15)	3 881(11)	10 393(5)	784(5)
C(16)	3 893(8)	9 630(5)	688(4)
C(21)	1 502(7)	8 069(4)	41(3)
C(22)	1 810(7)	8 121(5)	−619(4)
C(23)	931(9)	7 982(5)	−1 150(4)
C(24)	−271(8)	7 798(5)	−1 023(4)
C(25)	−604(8)	7 775(5)	−373(4)
C(26)	276(7)	7 900(4)	163(4)
C(31)	6 153(7)	8 364(4)	1 282(4)
C(32)	5 884(7)	8 801(5)	1 832(4)
C(33)	6 434(9)	9 490(5)	1 920(4)
C(34)	7 271(9)	9 736(5)	1 485(5)
C(35)	7 575(8)	9 299(5)	959(5)
C(36)	7 017(7)	8 628(5)	854(4)
C(41)	6 368(6)	6 979(4)	612(3)
C(42)	7 373(7)	6 645(4)	963(4)
C(43)	8 163(8)	6 189(5)	649(4)
C(44)	7 968(8)	6 040(5)	−31(5)
C(45)	6 992(8)	6 382(5)	−400(4)
C(46)	6 191(7)	6 849(4)	−85(4)
C(51)	1 694(8)	5 819(4)	1 724(3)
C(52)	675(8)	5 955(5)	2 088(4)
C(53)	−51(10)	5 386(6)	2 306(5)
C(54)	248(10)	4 664(7)	2 169(5)
C(55)	1 250(9)	4 520(5)	1 805(5)
C(56)	1 975(9)	5 093(5)	1 578(4)
C(61)	2 589(7)	6 248(4)	527(3)
C(62)	3 659(7)	5 953(4)	253(4)
C(63)	3 567(8)	5 672(5)	−405(4)
C(64)	2 460(9)	5 686(5)	−788(4)
C(65)	1 409(8)	5 965(4)	−521(4)
C(66)	1 480(8)	6 240(5)	134(4)

Table 3 Selected bond lengths (Å) and angles (°) for complex **4a**

Fe(1)–Fe(2)	2.658(3)	Fe(2)–C(4)	1.778(10)
Fe(1)–P(1)	2.258(3)	Fe(1)–C(5)	2.002(7)
Fe(2)–P(2)	2.241(3)	Fe(2)–C(5)	2.124(8)
Fe(1)–P(3)	2.252(3)	Fe(2)–C(7)	2.126(8)
Fe(2)–P(3)	2.279(3)	P(1)–C(8)	1.854(7)
Fe(1)–C(1)	1.764(10)	P(2)–C(8)	1.860(7)
Fe(1)–C(2)	1.802(9)	C(5)–C(6)	1.535(11)
Fe(2)–C(3)	1.793(9)	C(5)–C(7)	1.403(12)

Fe(1)–Fe(2)–P(2)	86.5(1)	Fe(1)–Fe(2)–C(7)	77.9(2)
Fe(1)–Fe(2)–P(3)	53.6(1)	P(1)–Fe(1)–C(5)	148.9(2)
Fe(2)–Fe(1)–P(1)	102.3(1)	P(2)–Fe(2)–C(5)	89.0(3)
Fe(2)–Fe(1)–P(3)	54.6(1)	P(3)–Fe(1)–C(5)	85.5(2)
P(1)–Fe(1)–P(3)	92.0(1)	P(3)–Fe(2)–C(5)	82.1(2)
P(2)–Fe(2)–P(3)	96.2(1)	P(3)–Fe(1)–C(2)	168.1(3)
Fe(2)–Fe(1)–C(1)	143.3(3)	P(3)–Fe(2)–C(3)	171.1(3)
Fe(2)–Fe(1)–C(2)	113.9(3)	Fe(1)–P(3)–Fe(2)	71.8(1)
Fe(1)–Fe(2)–C(3)	120.0(3)	Fe(2)–C(5)–C(7)	70.8(4)
Fe(1)–Fe(2)–C(4)	144.0(3)	Fe(1)–C(5)–C(7)	125.2(5)
Fe(1)–Fe(2)–C(5)	47.9(2)	Fe(1)–C(5)–C(6)	120.8(6)
Fe(2)–Fe(1)–C(5)	51.9(2)	Fe(2)–C(5)–C(6)	123.1(5)
Fe(1)–C(5)–Fe(2)	80.2(3)	C(6)–C(5)–C(7)	114.0(6)



1 4c (2)

clearly resolved multiplet at δ 6.23, and the vinyl proton as a multiplet at δ 3.55. The methyl group appears as a doublet at δ 0.25 (*J* 6 Hz). In the ^{31}P NMR spectrum the phosphido bridge is observed as a triplet at δ 199.6 (*J* 84 Hz) and the diphosphine as a doublet of doublets at δ 73. The magnitude of the phosphorus–phosphorus coupling constants indicates that the diphosphine and phosphido moieties adopt a *trans* configuration. The synthesis of **4c** is similar to that which we have previously reported for **3** from **1** and ethenyldiphenylphosphine.[6] Thus, UV irradiation of **1** in the presence of the substituted phosphine results in carbonyl loss and pre-co-ordination. In this instance no attempt was made to characterise this intermediate. Thermolysis, however, results in carbon–phosphorus bond cleavage generating bridging phosphido and organic ligands. Clearly at some stage during the reaction a 1,3-hydrogen shift has occurred.

Reactions between alkynes and mononuclear metal hydrides are well known to afford σ-vinyl complexes, proceeding by *cis* addition of the M–H unit to the carbon–carbon triple bond.[10] More recently, examples of this type of reactivity have been reported at the binuclear metal centre resulting in the formation of bridging σ:η vinyl complexes.[11] The high regioselectivity for Markovnikov addition observed in the formation of **4** and **5** has previously been noted.[12] This appears not to be a result of thermodynamic preference for the 1-substituted isomer, since it is a 2-methylvinyl complex which is formed preferentially *via* a selective 1,3-proton shift, in the reaction of **1** with diphenylallylphosphine. The formation of σ:η vinyl complexes *via* the insertion of allene into a bridging hydride has recently been reported at a dimolybdenum centre.[13] In other examples however, formation of allyl complexes (*via* transfer of the hydride to the central carbon) competes with σ:η vinyl formation,[13] indeed in some instances this route is dominant.[14]

The formation of isomers containing different relative positions of phosphido and diphosphine ligands can easily be envisaged upon consideration of the X-ray crystal structure of the *cis* isomer **4a**. Thus exchange of the carbonyls CO(2) and CO(3) for dppm gives rise to the *trans* isomer **4b**. The ethenyl complex **3** is found solely in the *trans* form suggesting that, on electronic grounds, this isomer is preferred. Substitution at the 1 position of the vinyl gives rise to unfavourable steric interactions with the phenyl groups of the dppm ligand in the *trans* form. Thus, as the steric bulk increases at this position, formation of the *cis* isomer is expected to be preferred. This accounts for the observed changes in the *trans*:*cis* ratios on

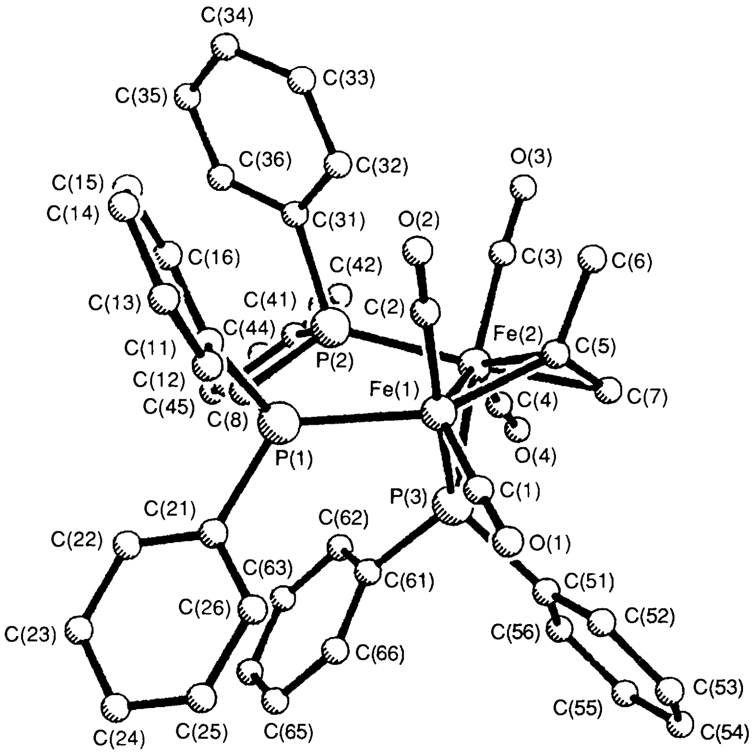


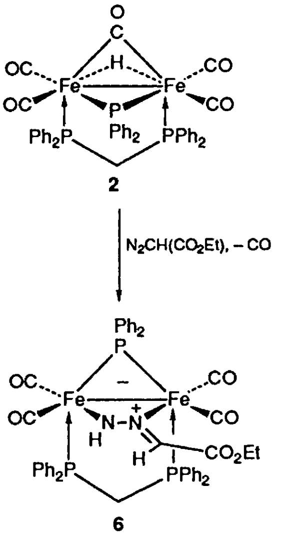
Fig. 1 Molecular structure of compound **4a** with the labelling scheme

going from H (>100:1), to Me (1:2), and Ph (1:10). The 2-methylvinyl complex **4c** is found solely as the *trans* form, again indicating that it is this form which is preferred electronically, since now steric interaction of substituents at the 2 position with the diphosphine ligand are anticipated to be small.

σ–η *Vinyl Fluxionality*.—At low temperatures all 1-substituted vinyl complexes display well resolved signals in the ^{31}P NMR spectra, and in each case the observation of two signals for the diphosphine ligand indicates asymmetrical structures consistent with a static σ:η vinyl moiety. Upon warming however, spectra broaden with the onset of 'windshield wiper' fluxionality.[15] Thus, resonances due to both isomers of **4** are significantly broadened at room temperature indicating slow σ–η vinyl fluxionality and collapse further upon warming to 80 °C. At higher temperatures however, and before resonances re-sharpen, secondary processes occur leading to the conversion of both isomers into new and as yet unidentified products.

The 1-phenylvinyl complexes **5** are somewhat better behaved. At room temperature the major isomer **5a** appears as three well resolved doublets of doublets at δ 160.1 (*J* 46, 25), 51.6 (*J* 94, 24) and 34.7 (*J* 94, 46 Hz), indicative of a static vinyl moiety. In contrast the minor isomer **5b** appears as a triplet at δ 199.0 (*J* 83 Hz) and doublet at δ 71.4 at this temperature indicating rapid σ–η vinyl fluxionality. The resonances due to **5a** only collapse upon raising the temperature to 70 °C. From these data approximate free energies of activation for the process are calculated as 63 ± 1 (**5a**) and 45 ± 1 (**5b**) kJ mol^{-1}. It is surprising that the orientation of the diphosphine can have such a pronounced effect upon the rate of σ–η vinyl fluxionality. The different behaviour is almost certainly a consequence of steric factors, since while in **5a** the 1-phenyl substituent is directed well away from all the bulky phenyl substituents on phosphorus, in the minor *trans* isomer **5b** this interaction is expected to be quite considerable.

Reaction of Complex **2** *with Ethyl Diazoacetate*.—Addition of the activated diazoalkane, ethyl diazoacetate, to a toluene solution of **2** produces the zwitterionic complex $[Fe_2(CO)_4\{\mu\text{-HN-N=CH}(CO_2Et)\}(\mu\text{-PPh}_2)(\mu\text{-dppm})]$ **6** in 72% yield [equation (3)], resulting from the insertion of the dinitrogen functionality into the hydride moiety. In the ^{31}P NMR spectrum the *trans* orientation of diphosphine and phosphido ligands, and the inequivalence of the two ends of the former, are clearly shown by resonances at δ 205.2 (dd, *J* 124, 82), 50.9 (dd, *J* 82, 72) and 46.0 (dd, *J* 124, 72 Hz). In the ^1H NMR spectrum the nitrogen-bound hydrogen atom is observed as a broad singlet at δ 8.96 while in the ^{13}C NMR spectrum four inequivalent carbonyl resonances are observed at δ 218.5 (t, *J* 21), 218.1 (t, *J* 20), 214.4 (t, *J* 3) and 212.8 (t, *J* 3 Hz).



(3)

The insertion of the dinitrogen functionality of a diazoalkane into the dimetal hydride functionality is unusual and appears not to have been previously noted. In a somewhat related system, Curtis *et al.*[16] have found that addition of ethyl diazoacetate to the dimolybdenum triple bond of $[\{Mo(CO)_2(\eta\text{-}C_5Me_5)\}_2]$ gives crystallographically characterised

[Mo$_2$(CO)$_4$(η-C$_5$Me$_5$)$_2${μ-N–N=CH(CO$_2$Et)}]. This contains the unprotonated ligand acting as a four-electron donor to the dimolybdenum centre.[16] In contrast, in **6** the protonated ligand formally donates three electrons to the diiron centre. This form of ligation is extremely stable, no degradation or dinitrogen loss being observed upon prolonged thermolysis.

Experimental

General Comments.—All reactions were carried out under an N$_2$ atmosphere using pre-dried solvents unless otherwise stated. The NMR spectra were recorded on a Varian VXR 400 spectrometer, IR spectra as KBr disks on a Perkin Elmer 983 spectrometer. Column chromatography was carried out on columns of deactivated alumina (6% w/w water). Elemental analysis was performed within the chemistry department of University College. The compound [Fe$_2$(CO)$_6$(μ-CO)(μ-dppm)] **1** was prepared by the literature method.[4] Ultraviolet photolysis was carried out using a Hanovia medium pressure lamp. Diphenylphosphine and allyldiphenylphosphine were purchased from Aldrich and used as supplied.

Syntheses.—[Fe$_2$(CO)$_4$(μ-CO)(μ-H)(μ-PPh$_2$)(μ-dppm)] **2**. Ultraviolet irradiation of a toluene solution (150 cm^3) of [Fe$_2$(CO)$_6$(μ-CO)(μ-dppm)] **1** (1.00 g, 1.45 mmol) and diphenylphosphine (0.3 g, 1.61 mmol) for 4 h whilst purging with a steady stream of nitrogen resulted in a colour change from red to dark yellow. Concentration of the toluene solution to 50 cm^3 and cooling to −20 °C resulted in the formation of a yellow-orange precipitate which after washing with light petroleum (b.p. 40–60 °C) afforded [Fe$_2$(CO)$_4$(μ-CO)(μ-H)(μ-PPh$_2$)(μ-dppm)] **2** (720 mg). Further batches (*ca.* 200 mg) of **2** were isolated upon further concentration of the filtrate giving a total yield of 77% (Found: C, 60.75; H, 4.35; P, 11.55. C$_{42}$H$_{33}$Fe$_2$O$_5$P$_3$ requires C, 61.30; H, 4.00; P, 11.30%). NMR(CDCl$_3$): ^{1}H, δ 7.9–7.1 (30 H, m, Ph), 3.00 (1 H, ddt, *J* 2.0, 10.3, 9.8, PCH$_2$P), 2.68 (1 H, dt, *J* 14.04, 9.8, PCH$_2$P) and −9.50 (1 H, dt, *J* 26.5, 51.0 Hz, μ-H); ^{31}P, δ 150.3 (t, *J* 45, μ-PPh$_2$) and 65.6 (d, *J* 45 Hz, dppm); ^{13}C, δ 268.1 (m, μ-CO), 218.1 (d, *J* 10, 2CO), 216.1 (d, *J* 7 Hz, 2CO), 141–127 (m, Ph) and 35.2 (m, PCH$_2$P). IR(CH$_2$Cl$_2$): 1973s, 1938s, 1890m and 1711m cm^{-1}.

[Fe$_2$(CO)$_4$(μ-CH=CH$_2$)(μ-PPh$_2$)(μ-dppm)] **3**. Slow purging of ethyne through a toluene solution (20 cm^3) of **2** (400 mg, 0.48 mmol) for 5 h resulted in a colour change from yellow to red. Removal of the solvent and chromatography gave upon elution with light petroleum (b.p. 40–60 °C)–dichloromethane (4:1) an orange band which afforded **3** (240 mg, 59%) as an orange microcrystalline solid. Analytical and spectroscopic data agreed with those previously recorded (Found: C, 61.20; H, 4.45; P, 10.40. C$_{43}$H$_{35}$Fe$_2$O$_4$P$_3$·0.5CH$_2$Cl$_2$ requires C, 60.50; H, 4.15; P, 10.80%). NMR (CDCl$_3$): ^{1}H, δ 8.3–6.5 (30 H, m, Ph), 6.32 (1 H, m, H$_a$), 3.80 (1 H, ddt, *J* 2.6, 4.3, 9.0, PCH$_2$P), 2.69 (1 H, dt, *J* 18.0, 9.0, PCH$_2$P), 2.59 (1 H, qnt, *J* 5.9, H$_c$) and 2.38 (1 H, t, *J* 10.7 Hz, H$_b$); ^{31}P (20 °C), δ 202.1 (dd, *J* 91, 81, μ-PPh$_2$), 84.2 (dd, *J* 81, 65, PPh$_2$) and 72.1 (dd, *J* 91, 65, Hz, PPh$_2$); ^{13}C, δ 219.9 (dd, *J* 28, 22, CO), 219.3 (d, *J* 10, CO), 219.2 (dd, *J* 10, 5, CO), 213.9 (t, *J* 19, CO), 155.1 (t, *J* 23, C$_\alpha$), 142–127 (m, Ph), 74.7 (dd, *J* 17, 5, C$_\beta$) and 40.2 (dd, *J* 45, 28 Hz, PCH$_2$P). IR(CH$_2$Cl$_2$): 1979m, 1947s, 1915m and 1899m cm^{-1}.

[Fe$_2$(CO)$_4$(μ-MeC=CH$_2$)(μ-PPh$_2$)(μ-dppm)] **4a**, **4b**. A toluene solution (50 cm^3) of **2** (400 mg, 0.48 mmol) was purged periodically with propyne. After 4 h a colour change from yellow to red was noted and the solvent removed. Chromatography eluting with light petroleum (b.p. 40–60 °C)–dichloromethane (1:1) gave an orange band which afforded **4** (260 mg, 64%) as an orange microcrystalline solid. Slow diffusion of methanol into a dichloromethane solution of **4** gave orange crystals of **4a** suitable for X-ray crystallography. Complex **4** was also prepared upon periodically purging a toluene solution (40 cm^3) of **2** (280 mg, 0.34 mmol) with allene over 6 h. Chromatography afforded **4** (200 mg, 70%) (Found: C, 64.05; H, 4.60; P, 11.20. C$_{44}$H$_{37}$Fe$_2$O$_4$P$_3$ requires C, 63.30; H, 4.45; P, 11.15%). NMR (CD$_2$Cl$_2$): ^{1}H (−50 °C), δ 8.3–6.0 (m, Ph), 3.81 (1 H, m, PCH$_2$P, **4b**), 3.68 (2 H, m, PCH$_2$P, **4a** + **4b**), 3.27 (1 H, q, *J* 13.5, PCH$_2$P, **4a**), 3.06 (3 H, s, Me, **4a**), 2.90 (1 H, br, H$_{cis}$, **4b**), 2.63 (1 H, d, *J* 13.1, H$_{trans}$, **4a**), 2.57 (1 H, d, *J* 14.47, H$_{trans}$, **4b**), 2.08 (1 H, d, *J* 8.9 Hz, H$_{cis}$, **4a**) and 1.66 (3 H, s, Me, **4b**); ^{31}P (−40 °C), δ 203.4 (dd, *J* 87, 77, μ-PPh$_2$, **4b**), 166.1 (dd, *J* 47, 26, μ-PPh$_2$, **4a**), 72.2 (m, dppm, **4b**), 53.3 (dd, *J* 96, 26, $\frac{1}{2}$dppm, **4a**) and 32.3 (dd, *J* 96, 47 Hz, $\frac{1}{2}$dppm, **4a**). IR(CH$_2$Cl$_2$): 1976m, 1955s, 1945s, 1914s and 1900 (br) cm^{-1}.

[Fe$_2$(CO)$_4$(μ-HC=CHMe)(μ-PPh$_2$)(μ-dppm)] **4c**. Ultraviolet irradiation of a toluene solution (150 cm^3) of [Fe$_2$(CO)$_6$(μ-CO)(μ-dppm)] **1** (440 mg, 0.63 mmol) and allyldiphenylphosphine (0.15 g, 0.66 mmol) for 3 h whilst purging with nitrogen resulted in a colour change from red to yellow. The extremely air-sensitive yellow solution was characterised only by IR spectroscopy; ν(CO) (CH$_2$Cl$_2$) 2015s, 1943m, 1919s, 1882m and 1869m cm^{-1}. Thermolysis of the toluene solution for 6 h resulted in a slight darkening. After removal of solvent, chromatography gave a yellow band which afforded **4c** (150 mg, 28%) as a yellow microcrystalline solid (Found: C, 62.95; H, 4.55; P, 10.85. C$_{44}$H$_{37}$Fe$_2$O$_4$P$_3$ requires C, 63.30; H, 4.45; P, 11.15%). NMR(CDCl$_3$): ^{1}H, δ 7.9–7.2 (30 H, m, Ph), 6.23 (1 H, dddd, *J* 19.1, 12.8, 6.3, 6.1, H$_\alpha$), 3.93 (1 H, ddt, *J* 14.6, 4.3, 10.3, PCH$_2$P), 3.55 (1 H, qnt, *J* 6.1, H$_\beta$), 2.82 (1 H, dt, *J* 14.6, 9.7, PCH$_2$P) and 0.25 (3 H, d, *J* 6.1 Hz, Me); ^{31}P, δ 199.6 (t, *J* 84 Hz, μ-PPh$_2$) and 73.0 (br, dppm). IR(CH$_2$Cl$_2$): 1974m, 1940s, 1910m and 1882m cm^{-1}.

[Fe$_2$(CO)$_4$(μ-PhC=CH$_2$)(μ-PPh$_2$)(μ-dppm)] **5a**, **5b**. Addition of phenylethyne (300 mg, 2.94 mmol) to a toluene solution (80 cm^3) of **2** (380 mg, 0.46 mmol), resulted over 2 d in a colour change from yellow to orange. Removal of solvent gave an oily orange solid. Careful chromatography eluting with light petroleum (b.p. 40–60 °C)–dichloromethane (1:1) gave an orange band which afforded **5a**, **5b** (300 mg, 72%) as a microcrystalline solid (Found: C, 59.60; H, 4.15; P, 9.30. C$_{49}$H$_{39}$Fe$_2$O$_4$P$_3$·1.5CH$_2$Cl$_2$ requires C, 59.20; H, 4.10; P, 9.10%). NMR: ^{1}H(CDCl$_3$) (−70 °C), δ 8.0–6.1 (35 H, m, Ph), 3.86 (1 H, q, *J* 11.2, PCH$_2$P), 3.24 (1 H, q, *J* 13.2, PCH$_2$P), 2.38 (1 H, dt, *J* 13.5, 4.3, H$_{trans}$) and 2.12 (1 H, dd, *J* 6.1 Hz, 4.5, H$_{cis}$); ^{31}P(CD$_2$Cl$_2$) (−80 °C), δ 199.0 (t, *J* 83, μ-PPh$_2$, **5b**), 160.1 (dd, *J* 46, 25, μ-PPh$_2$, **5a**), 73.9 (dd, *J* 80, 65, $\frac{1}{2}$dppm, **5b**), 68.5 (dd, *J* 85, 65, $\frac{1}{2}$dppm, **5b**), 51.6 (dd, *J* 94, 24, $\frac{1}{2}$dppm, **5a**) and 34.7 (dd, *J* 94, 46 Hz, $\frac{1}{2}$dppm, **5a**). IR(CH$_2$Cl$_2$): 1980m, 1959vs and 1911s cm^{-1}.

[Fe$_2$(CO)$_4${μ-HN–N=CH(CO$_2$Et)}(μ-PPh$_2$)(μ-dppm)] **6**. Addition of ethyl diazoacetate (400 mg, 3.50 mmol) to a toluene solution (60 cm^3) of **2** (400 mg, 0.48 mmol) resulted after 1 d in a colour change from yellow to red. After removal of solvent, washing with light petroleum (b.p. 40–60 °C) gave an oily orange solid. Chromatography eluting with light petroleum (b.p. 40–60 °C)–diethyl ether (7:3) gave an orange band which afforded **6** (320 mg, 72%) as an orange microcrystalline solid (Found: C, 59.85; H, 4.50; N, 2.85; P, 8.90. C$_{45}$H$_{39}$Fe$_2$N$_2$O$_6$P$_3$ requires C, 59.15; H, 4.50; N, 2.80; P, 9.35%). NMR(CDCl$_3$): ^{1}H, δ 8.96 (1 H, s, NH), 8.0–7.1 (30 H, m, Ph), 5.29 (1 H, t, *J* 2.6, CH), 3.70 (1 H, m, PCH$_2$P), 3.59 (1 H, m, PCH$_2$P), 3.47 (2 H, q, *J* 7.2, CH$_2$) and 0.93 (3 H, t, *J* 7.2 Hz, Me); ^{31}P, δ 205.2 (dd, *J* 124, 82, μ-PPh$_2$), 50.9 (dd, *J* 82, 72, $\frac{1}{2}$dppm) and 46.0 (dd, *J* 124, 72 Hz, $\frac{1}{2}$dppm); ^{13}C, δ 218.5 (t, *J* 21, CO), 218.1 (t, *J* 20, CO), 214.4 (t, *J* 3, CO), 212.8 (t, *J* 3, CO), 162.9 (s, C=O), 141–127 (m, Ph), 125.4 (s, CH), 57.9 (s, CH$_2$), 35.6 (t, *J* 20 Hz, PCH$_2$P) and 14.4 (s, CH$_3$). IR(CH$_2$Cl$_2$): 1983s, 1952s, 1920m, 1903m, 1637w and 1481m cm^{-1}.

Details of the Crystal Structure Determination of [Fe$_2$(CO)$_4$(μ-MeC=CH$_2$)(μ-PPh$_2$)(μ-dppm)] **4a**.—An orange single crystal 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-Kα radiation (λ = 0.710 73 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 21 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure the reflections. 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 were used to solve and refine the structure.

The structures was solved by direct methods and developed by using alternating cycles of least-squares refinement and Fourier difference 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 478 parameters for 3492 variables and did not shift any parameter by more than 0.035 times its standard deviation. The final R values were 0.055 and 0.054, and the final Fourier difference map was featureless with no peaks greater than 0.50 e Å^{-3}. Structure solution used the SHELXTL PLUS[17] program package on a microVax II computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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