Formation of a Bridged Vinylidenedi-iron Complex by Nucleophilic Attack on a Carbonyl Ligand of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, and the Synthesis and *X*-Ray Crystal Structure of $[(OC)_3\overline{Fe(\mu\text{-}Ph_2P\overline{C}HPPh_2)}FeH(CO)_3]$ *

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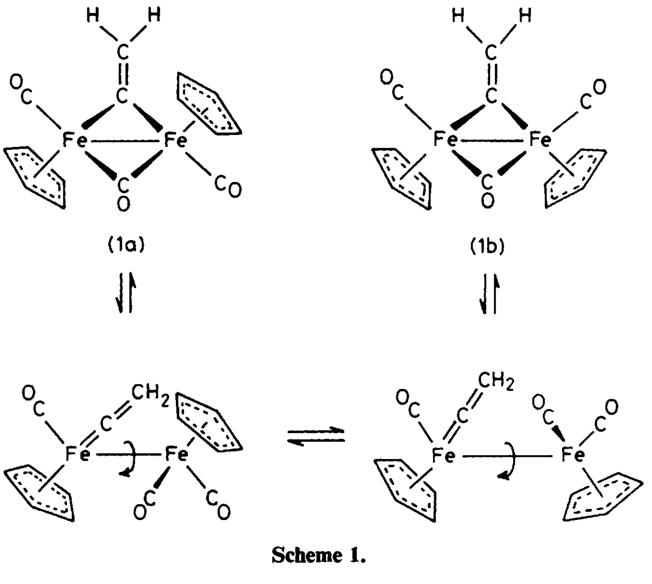
Reaction of $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ with an excess of methyl-lithium in tetrahydrofuran followed by treatment with CF_3CO_2H at low temperatures affords a mixture of *cis*- and *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$. The isomers can be separated by column chromatography, and are thermally interconvertible. Reaction of the *trans*-vinylidenedi-iron complex with $HBF_4{\cdot}Et_2O$ affords the salt $[Fe_2(\mu\text{-}CCH_3)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2][BF_4]$, which deprotonates on treatment with NEt_3 to form a mixture of *cis*- and *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$. In contrast, $[Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6]$ (dppm = $Ph_2PCH_2PPh_2$) is deprotonated by methyl-lithium to form an anionic species, which on protonation (CF_3CO_2H) affords the dinuclear iron complex $[(OC)_3\overline{Fe(\mu\text{-}Ph_2P\overline{C}HPPh_2)}FeH(CO)_3]$, characterised by n.m.r. spectroscopy and *X*-ray crystallography. Crystals are triclinic, space group $P\bar{1}$, $Z = 4$, in a unit cell with $a = 10.504(3)$, $b = 15.189(5)$, $c = 19.552(5)$ Å, $\alpha = 104.43(2)$, $\beta = 103.04(2)$, and $\gamma = 98.57(2)°$. There are two independent molecules in the asymmetric unit, and the structure has been refined to *R* 0.073 (*R*′ 0.072) for 2 669 reflections with $2\theta \leqslant 40°$ (Mo-K_α *X*-radiation) collected at 298 K. The two molecules have very similar geometries and contain a novel 1,2-diferra-3,5-diphosphabicyclo[2.1.0]pentane ring [mean separations within the ring system Fe–Fe 2.687(4), Fe–P 2.197(5) and 2.271(6), Fe–μ-C 2.15(2), and μ-C–P 1.79(2) and 1.76(2) Å]. Both iron atoms are bonded to three carbonyl groups, but one of these ligands semi-bridges the metal–metal bond [Fe–C–O 152.6(14)°]. The hydrido-ligand was not located by the *X*-ray diffraction study but from potential-energy minimisation methods was calculated to be bridging the metal–metal bond, in accord with the ^1H n.m.r. data for the compound.

As a result of renewed interest in Fischer–Tropsch chemistry (for a review see ref. 1) increasing attention is being paid to the chemistry of molecules containing carbon atoms bridging two or more metal centres. One such group of compounds contain the $\mu\text{-}C{=}CH_2$ group as found, for example, in $[Mn_2(\mu\text{-}C{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$,[2] $[Ru_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$,[3] and $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$[4] ($C_9H_7$ = indenyl). In the synthesis of these complexes the two carbon atoms in the $\mu\text{-}C{=}CH_2$ system have their origin in a molecule of acetylene. We became interested in the possibility of devising synthetic pathways to species containing the $\mu\text{-}C{=}CH_2$ ligand, where the ligated carbon was derived from a terminal or bridging carbonyl ligand. An indication that such an approach might be possible was provided by a brief comment by Rosenblum and co-workers[5] that salts of the type $[Fe_2(\mu\text{-}CR)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2][BF_4]$ are formed in moderate yield by treating $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ with alkyl-lithium reagents followed by acidification with HBF_4. This paper describes a detailed study of the reaction of the nucleophilic reagent methyl-lithium with $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ and $[Fe_2(\mu\text{-}CO)(dppm)(CO)_6]$ (dppm = $Ph_2PCH_2PPh_2$). A preliminary communication has described some aspects of this work.[6]

Results and Discussion

Addition of an excess of methyl-lithium to a tetrahydrofuran solution (0 °C) of $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ resulted in a change in colour from red-brown to dark brown, and examination of the i.r. spectrum of the reaction mixture showed the presence of a new band at 1 657s cm^{-1} assignable[7] to an acyliron group. Attempts to characterise the presumed anionic acyliron complex as a crystalline salt were unsuccessful. However, low-temperature protonation of the acylate with trifluoroacetic acid afforded a neutral deep purple material. Column chromatography on alumina and elution with toluene gave purple crystals of complex (1a) characterised by elemental analysis and by i.r. and n.m.r. spectroscopy as the *trans* isomer of $[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$. The i.r. spectrum



Scheme 1.

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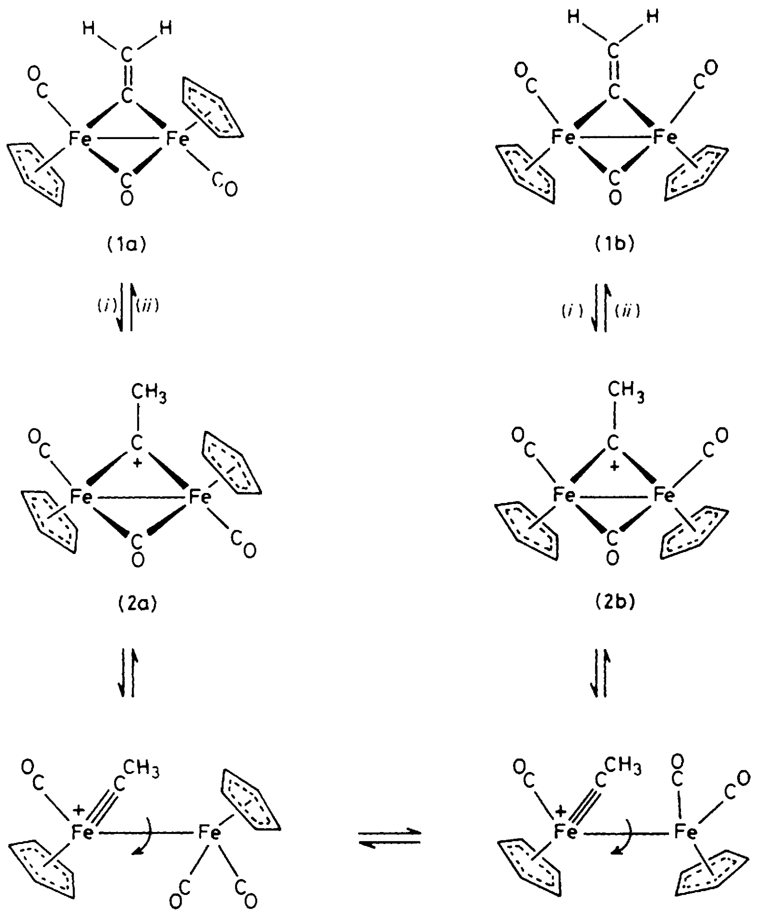
* μ-[Bis(diphenylphosphino)methyl-*PC*(Fe¹):*P*′(Fe²)]-μ-carbonyl-1,1,2,2,2-pentacarbonyl-μ-hydrido-di-iron (*Fe–Fe*).

Supplementary data available (No. SUP 23476, 32 pp.): thermal parameters, H-atom co-ordinates, complete bond parameters for both molecules, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



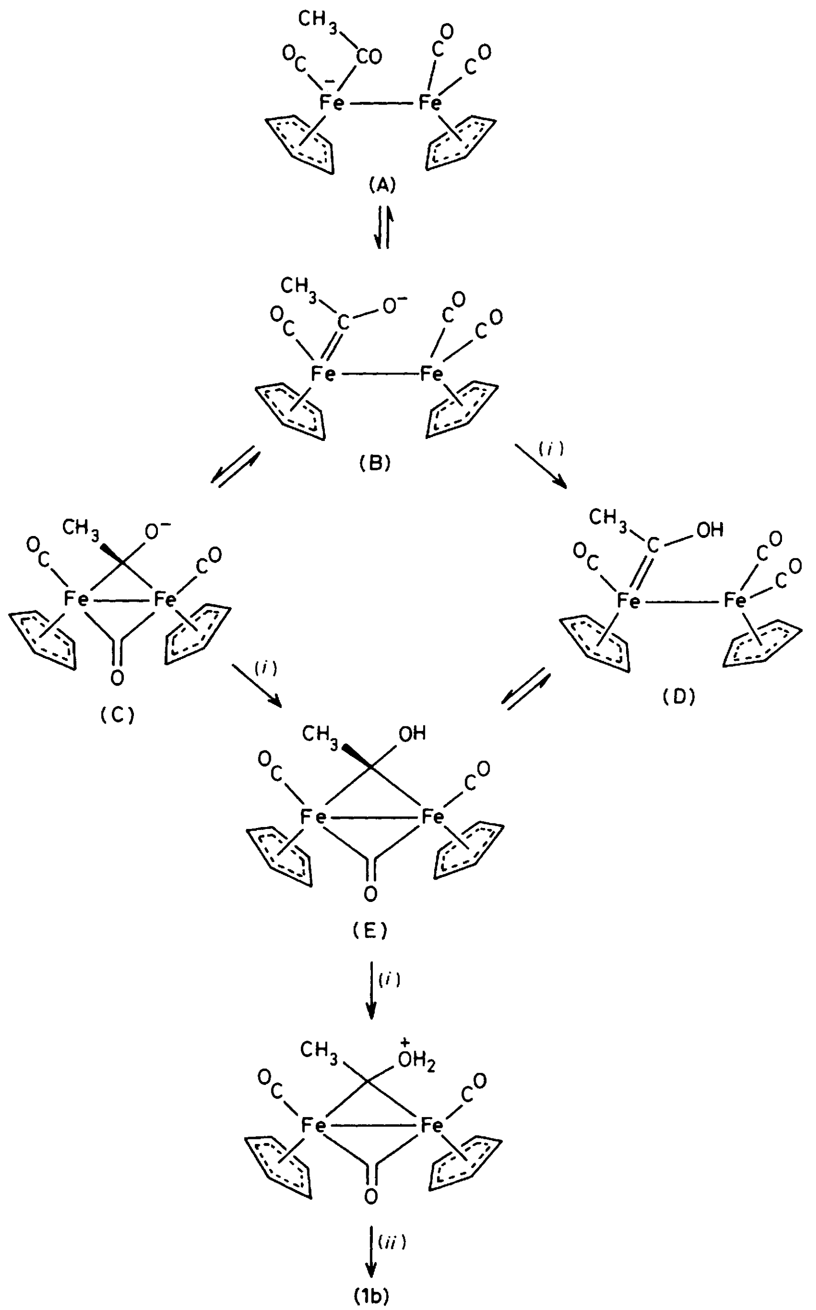
Scheme 2. (*i*) HBF_4; (*ii*) NEt_3

showed one terminal carbonyl band at 1 957s cm^{-1} and one bridging carbonyl absorption at 1 804m cm^{-1}. Further elution of the chromatography column gave an orange band containing a mixture of starting material $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$, and the *cis* isomer (1b) of $[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$, which showed carbonyl bands in the i.r. at 1 998s, 1 963w, and 1 804m cm^{-1}. A pure sample of (1b) was obtained by refluxing the *trans* isomer in toluene for 0.5 h, followed by chromatography and recrystallisation. The orange-red complex (1b) was characterised by elemental analysis and mass, i.r., and n.m.r. spectroscopy. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of complexes (1a) and (1b) showed low-field resonances at δ 279 and 277 p.p.m., respectively, which can be assigned to the contact carbon atom of the $\mu\text{-}C{=}CH_2$ ligand, on the basis of the observation that these resonances are more intense than the CO peaks at 270 and 269 p.p.m., due to a nuclear Overhauser effect from the nearby CH_2 group. Partial decoupling of the signals at δ 125.4 and 125.8 p.p.m., assignable to the $\mu\text{-}C{=}CH_2$ carbons present in (1a) and (1b), respectively, resulted in their appearance as triplets, thus confirming the presence in these isomeric molecules of the $Fe_2(\mu\text{-}C{=}CH_2)$ system, rather than the alternative $Fe_2[\mu\text{-}(\sigma{:}\sigma'\text{-}HC_2H)]$ arrangement.

In refluxing toluene, the pure *trans* (1a) and *cis* (1b) vinylidene di-iron complexes isomerise to form an equilibrium mixture of the two isomers (1 : 2.1, *trans* : *cis*), which could be separated by chromatography. It is likely that this isomerisation reaction involves the intermediacy of species containing terminally bonded vinylidene ligands formed in a pairwise exchange process as illustrated in Scheme 1, and analogous to that postulated [8,9] to explain the *cis–trans* isomerisation of $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(\mu\text{-}CMe_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$. Terminally bonded vinylidene complexes of Mo,[10] Mn,[11] Fe,[12] and Ru[13] have now been isolated and characterised, thus providing support for this suggestion.

Formation of the isomeric vinylidene complexes (1a) and (1b) by protonation of an anionic acyl complex is particularly interesting in view of the earlier isolation [5] of a cationic bridged carbyne complex from a very similar reaction. This apparent anomaly was resolved by examining the effect of the stronger acid HBF_4 on the isomers (1). A rapid reaction occurred at low temperatures to give a light red cation identified as the carbyne complex (2) [5] by i.r. and by ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectroscopy. The ^{13}C spectrum of (2) showed a low-field resonance at 499 p.p.m. characteristic [14] of the ligated carbon atom of a bridging carbyne group, and is the most deshielded signal of this type so far reported.

The cation (2) readily deprotonates on treatment with triethylamine to reform the vinylidene di-iron complex. Particularly interesting was the observation that protonation of the pure *trans*-vinylidene complex (1a), followed by deprotonation, afforded a mixture of the *trans* and *cis* vinylidene complexes [1 : 2.1, (1a) : (1b)]. In order to effect this isomerisation thermally in toluene a few days at room temperature are required, whereas the protonation–deprotonation sequence can effect the same transformation in minutes. This can be explained if the important assumption is made that complexes containing $\mu\text{-}CCH_3$ ligands can readily reversibly convert into terminally bonded cationic carbyne complexes, with simultaneous bridge to terminal CO exchange, thus allowing

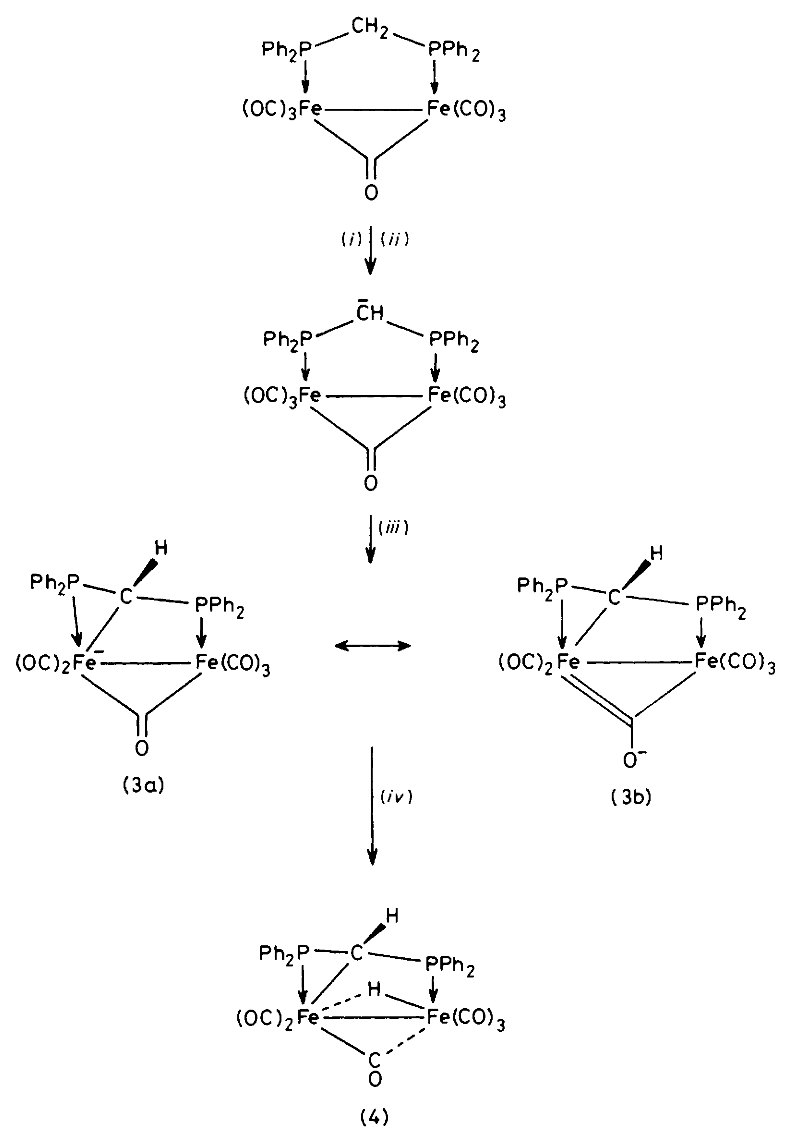


Scheme 3. (*i*) $+CF_3CO_2H$; (*ii*) $-H_3O^+$

rotation about the Fe–Fe bond as is shown in Scheme 2. It is interesting that protonation of the vinylidene di-iron complexes occurs *via* attack on the methylene carbon, as has been observed [15] in the formation of $[Mn_2(\mu\text{-}CCH_3)(CO)_4(\eta\text{-}C_5H_5)_2][O_2CCF_3]$ from $[Mn_2(\mu\text{-}C{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$. This contrasts with the dirhodium system $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$, where reaction with the diethyl etherate of HBF_4 gives $[Rh_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}CO)(CO)(\eta^5\text{-}C_9H_7)_2][BF_4]$, there being no evidence for the formation of a bridged carbyne complex.[4]

There remains the important question as to how the isomeric vinylidene di-iron complexes (1a) and (1b) are formed when trifluoroacetic acid is used. Nucleophilic attack by methyllithium at either a terminal or a bridged CO ligand of the starting material $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ could provide access to the interconvertible anionic species (A)—(C) illustrated in Scheme 3, where for the sake of simplicity only the *cis* isomers are shown, it being assumed that intermediates without bridging ligands could undergo *cis–trans* isomerisation *via* rotation about a single Fe–Fe bond. As previously mentioned, the i.r. spectrum of the anionic species in tetrahydrofuran shows a band at 1 657 cm^{-1}, which is consistent with the presence of the isomeric species (A). Protonation of the anion could then lead to the formation of the bridged hydroxy-substituted carbene complex (E), which on further protonation could either undergo an elimination reaction to form (1b) directly (S_E2 reaction) or the bridged carbyne complex (2b) could be formed (S_E1 reaction), which then deprotonates.

The successful synthesis of these $\mu\text{-}C{=}CH_2$ and $\mu\text{-}CCH_3$ di-iron complexes encouraged us to examine the possibility of



Scheme 4. (*i*) LiMe; (*ii*) $-CH_4$; (*iii*) $-CO$; (*iv*) H^+

carrying out a similar sequence of reactions with the known [16] complex $[Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6]$, it being assumed that the presence of the bridging dppm ligand could help to stabilise the resultant di-iron complex. In the event a reaction of a different type intervened.

Treatment of $[Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6]$ with an excess of methyl-lithium in refluxing tetrahydrofuran afforded a salt (3), which with CF_3CO_2H (−60 °C) gave red crystalline complex (4) in good yield. Since the spectroscopic properties of this complex did not define the molecular structure, a single-crystal *X*-ray diffraction study was carried out.

There are two independent molecules of (4) in the asymmetric unit having very similar geometries. One of these is shown in the Figure with the atom-numbering scheme and is discussed herein. Table 1 contains selected bond lengths and interbond angles for both molecules. The complex contains a novel 1,2-diferra-3,5-diphosphabicyclo[2.1.0]pentane ring system, the dppm ligand of the starting complex having been deprotonated at the CH_2 group so as to form an iron–carbon σ bond. The Fe(11)–C(17) distance of 2.18(2) Å is close to the average of those found for such separations in a variety of organoiron compounds containing Fe–C (sp^3) bonds.[17] The iron–iron distance [2.684(4) Å] is shorter than that [2.709(2) Å] in $[Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6]$.[16] Moreover, whereas in the latter the Fe–P bond lengths [mean 2.253(3) Å] are essentially the same, in structure (4) this is not so, with Fe(11)–P(11) 2.200(5) Å and Fe(12)–P(12) 2.260(6) Å. This probably reflects torsional strain in the bicyclic ring system; the three-membered ring has angles of 65.5(5), 66.4(6), and 48.2(5)° at P(11), C(17), and Fe(11), respectively.

The ^1H n.m.r. spectrum of complex (4) (see below) shows a hydrido-ligand. This was not located by the *X*-ray diffraction study, but probable locations for this ligand were calculated from the *X*-ray co-ordinates using the steric potential-energy minimisation method of Orpen.[18] The results of this calculation strongly suggest that the hydride ligand edge-bridges the Fe–Fe bond as illustrated in Scheme 4. This is consistent with the n.m.r. data. Moreover, the semi-bridging carbonyl C(11)–O(11) [Fe(11)–C(11)–O(11) 152.6(14)°], which evidently serves to delocalise electron density from Fe(11) to Fe(12), is also present in solution [$\nu_{max.}$(CO) at 1 811 cm^{-1}].

It was not possible to obtain suitable crystals of complex (3), the anionic precursor of (4), for an *X*-ray diffraction study.

Table 1. Selected bond lengths (Å) and interbond angles (°) for complex (4), with estimated standard deviations in parentheses

Molecule 1		Molecule 2		Molecule 1		Molecule 2	
Fe(11)-Fe(12)	2.684(4)	Fe(21)-Fe(22)	2.691(4)	P(11)-Fe(11)-Fe(12)	98.2(2)	P(21)-Fe(21)-Fe(22)	99.0(2)
Fe(11)-P(11)	2.200(5)	Fe(21)-P(21)	2.195(6)	P(11)-Fe(11)-C(17)	48.2(5)	P(21)-Fe(21)-C(27)	48.7(4)
Fe(11)-C(17)	2.18(2)	Fe(21)-C(27)	2.12(2)	Fe(12)-Fe(11)-C(17)	82.0(5)	Fe(22)-Fe(21)-C(27)	81.7(5)
Fe(11)-C(11)	1.82(2)	Fe(21)-C(21)	1.85(3)	P(12)-Fe(12)-Fe(11)	71.9(2)	P(22)-Fe(22)-Fe(21)	74.4(2)
Fe(11)-C(12)	1.72(2)	Fe(21)-C(22)	1.69(2)	Fe(11)-P(11)-C(17)	65.5(6)	Fe(21)-P(21)-C(27)	63.4(6)
Fe(11)-C(13)	1.77(2)	Fe(21)-C(23)	1.76(3)	Fe(12)-P(12)-C(17)	105.7(7)	Fe(22)-P(22)-C(27)	101.9(7)
Fe(12)-P(12)	2.260(6)	Fe(22)-P(22)	2.282(7)	Fe(11)-C(17)-P(11)	66.4(6)	Fe(21)-C(27)-P(21)	67.9(6)
Fe(12)-C(14)	1.76(3)	Fe(22)-C(24)	1.81(3)	Fe(11)-C(17)-P(12)	95.1(8)	Fe(21)-C(27)-P(22)	100.9(9)
Fe(12)-C(15)	1.77(2)	Fe(22)-C(25)	1.70(3)	P(11)-C(17)-P(12)	124.5(10)	P(21)-C(27)-P(22)	120.0(9)
Fe(12)-C(16)	1.69(3)	Fe(22)-C(26)	1.74(3)	Fe(11)-C(11)-O(11)	152.6(14)	Fe(21)-C(21)-O(21)	149(2)
P(11)-C(17)	1.79(2)	P(21)-C(27)	1.78(2)	Fe(12)-C(11)-O(11)	125.0(14)	Fe(22)-C(21)-O(21)	128(2)
P(12)-C(17)	1.76(2)	P(22)-C(27)	1.79(2)	Fe(11)-C(11)-Fe(12)	82.3(6)	Fe(21)-C(21)-Fe(22)	83.3(7)
Fe(12) ··· C(11)	2.23(2)	Fe(22) ··· C(21)	2.19(2)				

However, having established the molecular structure of (4) it became possible to interpret the spectroscopic data for both species and thus propose a likely structure for (3) (Scheme 4). The i.r. spectrum of the latter complex showed a band at relatively low frequency (1 647 cm^{-1}) suggesting the presence of a bridging CO ligand with negative charge on the oxygen, (3b), which would be partially associated with the lithium cation.[7] Addition of [N(PPh$_3$)$_2$]Cl to the lithium salt caused the band at 1 647 cm^{-1} to shift to 1 731 cm^{-1} in accord with a preference for the canonical form (3a). In agreement with the proposed structure, the ^{31}P-{^{1}H} n.m.r. spectrum (in tetrahydrofuran) showed two resonances at δ 5.85 and 33.4 p.p.m., appearing as doublets [*J*(PP) 28 Hz]. The ^{13}C-{^{1}H} spectrum of complex (3), measured in tetrahydrofuran-[^{2}H$_6$]benzene (4 : 1), showed only one CO resonance (δ 220.5 p.p.m.) at room temperature, and this was also the case for the spectrum measured at −50 °C. Evidently there is a low-energy dynamic process which interchanges the bridging and terminal CO ligands. The ^{13}C-{^{1}H} spectrum of (3) also showed a resonance at −15.9 p.p.m., appearing as a multiplet due to ^{31}P coupling [*J*(P$_A$C) 29 Hz, *J*(P$_B$C) not resolved], which is ascribed to the bridgehead CH of the bicyclo[2.1.0]pentane ring system. This was confirmed by off-resonance experiments which showed one proton attached to the bridgehead carbon.

The ^{13}C-{^{1}H} spectrum of complex (4) also showed an unusual high-field resonance at −11.7 p.p.m., which appeared as a doublet [*J*(CH) 160 Hz] in a fully coupled spectrum, and is assigned to the μ-CH fragment of the deprotonated dppm ligand. However, in contrast with the anionic system (3), the ^{13}C-{^{1}H} spectrum of (4) showed four resonances due to the CO ligands (Experimental section), indicating the absence of a dynamic process exchanging bridging and terminal CO ligands.

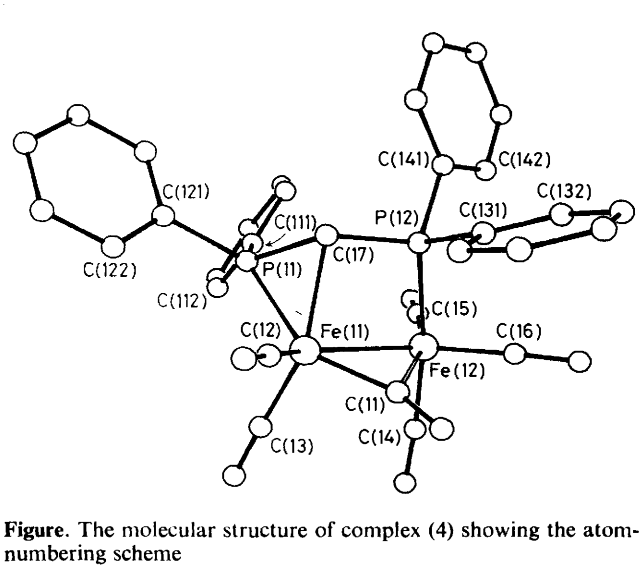


Figure. The molecular structure of complex (4) showing the atom-numbering scheme

The ^{1}H n.m.r. spectrum of complex (4) exhibited a high-field signal at δ −9.2 p.p.m., with coupling to two ^{31}P nuclei, consistent with the presence of a hydrido-ligand bonded to two non-equivalent iron atoms. Confirmation that the hydrido-ligand had its origin in the protonation step was provided by the observation that quenching of complex (3) with CF$_3$CO$_2$D gave the deuterio-analogue of (4) showing a resonance at δ −9.4 p.p.m. in the ^{2}H n.m.r. spectrum.

The formation of complexes (3) and (4) can be understood in terms of the deprotonation of the PCH$_2$P group of the μ-dppm ligand, followed by an *intramolecular* nucleophilic attack on one of the two iron atoms (Scheme 4). Such a process could afford the anionic acyl species (3). It is interesting that deprotonation of [Fe$_2$(μ-CO)(μ-dppm)(CO)$_6$] with methyllithium occurs rather than the alternative attack on a carbonyl ligand, the pathway observed with [Fe$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. Moreover, the related compound [Fe$_2$(μ-PPh$_2$)$_2$(CO)$_6$] reacts with lithium alkyls to form acylate complexes.[19]

Although the formation of (3) is the first example of such a deprotonation reaction, it is interesting to note that complexes of the type [M(CO)$_4$(dppm)] (M = Cr, Mo, or W) have recently been reported [20] to be deprotonated readily by strong bases, forming carbanions, which react with electrophiles at the carbon atom of the Ph$_2$P$\bar{\text{C}}$HPPh$_2$ system. Also, the cationic vinylidene iron complex [Fe(=C=CMe$_2$)(dppe)(η-C$_5$H$_5$)][PF$_6$] [dppe = Ph$_2$P(CH$_2$)$_2$PPh$_2$] reacts with bases to form a ferradiphosphabicyclo[2.1.1]hexane system.[12] Mononuclear complexes containing the related three-membered ring arrangement $\overline{\text{MCH}_2\text{P}}$ have also been reported.[21-23]

Experimental

The n.m.r. measurements were made with JEOL PS-100, JNM-90Q, and FX 200 instruments. Chemical shifts, δ (p.p.m.), are relative to SiMe$_4$ for the ^{1}H and ^{13}C-{^{1}H} spectra and to 85% H$_3$PO$_4$ (external) for the ^{31}P-{^{1}H} spectra. A Nicolet MX-1 FT i.r. spectrophotometer was used to record i.r. spectra, and mass spectra for measurement of molecular ions were recorded on an A.E.I. MS 902 instrument. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. Chromatography was carried out on columns of alumina (Brockman Activity II)

Table 2. Atomic positional parameters (fractional co-ordinates) for the non-hydrogen atoms in complex (4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(11)	0.388 3(3)	0.902 8(2)	0.359 12(13)	C(241)	0.947 3(14)	0.160 4(9)	0.291 5(6)
Fe(12)	0.347 2(3)	0.728 6(2)	0.351 35(13)	C(246)	0.869 7(14)	0.124 2(9)	0.330 9(6)
Fe(21)	0.719 1(3)	0.333 1(2)	0.174 92(14)	C(245)	0.931 6(14)	0.106 7(9)	0.395 4(6)
Fe(22)	0.945 9(3)	0.285 3(2)	0.153 87(14)	C(244)	1.070 9(14)	0.125 3(9)	0.420 5(6)
P(11)	0.282 5(5)	0.888 7(4)	0.244 8(3)	C(243)	1.148 5(14)	0.161 4(9)	0.381 1(6)
P(12)	0.459 3(5)	0.749 6(3)	0.268 8(3)	C(242)	1.086 6(14)	0.178 9(9)	0.316 6(6)
P(22)	0.858 4(6)	0.188 5(4)	0.209 1(3)	C(141)	0.425 0(13)	0.663 8(8)	0.179 5(6)
P(21)	0.757 2(6)	0.346 2(4)	0.292 6(3)	C(142)	0.369 6(13)	0.574 3(8)	0.169 3(6)
C(13)	0.283(2)	0.940 1(11)	0.413 8(9)	C(143)	0.346 9(13)	0.511 3(8)	0.101 3(6)
O(13)	0.208 9(13)	0.960 1(9)	0.449 2(7)	C(144)	0.379 7(13)	0.537 8(8)	0.043 4(6)
C(12)	0.505(2)	1.002 1(12)	0.385 6(10)	C(145)	0.435 1(13)	0.627 4(8)	0.053 5(6)
O(12)	0.587 4(13)	1.068 4(9)	0.403 9(7)	C(146)	0.457 7(13)	0.690 3(8)	0.121 6(6)
C(14)	0.270(2)	0.736 5(12)	0.423 2(10)	C(22)	0.551(2)	0.316 4(13)	0.145 7(11)
O(14)	0.218 7(13)	0.748 1(9)	0.470 9(7)	O(22)	0.435(2)	0.306 9(10)	0.125 9(8)
C(11)	0.489(2)	0.855 5(12)	0.422 5(10)	C(23)	0.739(2)	0.439 2(13)	0.161 0(11)
O(11)	0.575 9(12)	0.861 8(8)	0.475 3(7)	O(23)	0.743 4(15)	0.510 7(10)	0.152 9(8)
C(17)	0.438(2)	0.853 2(11)	0.255 8(9)	C(26)	0.975(3)	0.203 5(15)	0.085 0(12)
C(111)	0.133 0(11)	0.804 7(8)	0.191 3(7)	O(26)	0.991 9(15)	0.147 7(10)	0.037 1(9)
C(112)	0.018 3(11)	0.818 6(8)	0.213 1(7)	C(24)	0.976(3)	0.372(2)	0.109 9(12)
C(113)	−0.104 8(11)	0.760 2(8)	0.175 0(7)	O(24)	0.993(2)	0.428 7(12)	0.083 4(10)
C(114)	−0.113 1(11)	0.688 0(8)	0.114 9(7)	C(25)	1.098(3)	0.330(2)	0.215 0(14)
C(115)	0.001 5(11)	0.674 2(8)	0.093 0(7)	O(25)	1.213(2)	0.357 6(12)	0.251 8(10)
C(116)	0.124 6(11)	0.732 5(8)	0.131 2(7)	C(21)	0.739(2)	0.262 6(14)	0.088 8(11)
C(121)	0.288 6(12)	0.975 7(7)	0.200 4(7)	O(21)	0.688 9(14)	0.219 0(9)	0.025 2(8)
C(122)	0.333 3(12)	1.065 3(7)	0.242 0(7)	C(27)	0.724(2)	0.235 7(11)	0.232 3(9)
C(123)	0.334 4(12)	1.132 3(7)	0.207 3(7)	C(211)	0.917 6(10)	0.390 3(8)	0.362 6(6)
C(124)	0.290 6(12)	1.109 8(7)	0.130 9(7)	C(212)	1.006 2(10)	0.461 3(8)	0.356 5(6)
C(125)	0.245 9(12)	1.020 2(7)	0.089 2(7)	C(213)	1.129 2(10)	0.497 5(8)	0.409 3(6)
C(126)	0.244 9(12)	0.953 2(7)	0.124 0(7)	C(214)	1.163 6(10)	0.462 6(8)	0.468 2(6)
C(131)	0.640 0(9)	0.764 3(8)	0.302 7(6)	C(215)	1.075 0(10)	0.391 7(8)	0.474 2(6)
C(132)	0.693 3(9)	0.688 0(8)	0.297 4(6)	C(216)	0.952 0(10)	0.355 5(8)	0.421 4(6)
C(133)	0.829 5(9)	0.696 1(8)	0.328 5(6)	C(231)	0.777 1(13)	0.074 7(7)	0.148 2(6)
C(134)	0.912 3(9)	0.780 5(8)	0.364 9(6)	C(236)	0.638 9(13)	0.044 9(6)	0.118 2(6)
C(135)	0.859 0(9)	0.856 8(8)	0.370 1(6)	C(235)	0.585 4(13)	−0.043 7(6)	0.075 7(6)
C(136)	0.722 9(9)	0.848 7(8)	0.339 0(6)	C(234)	0.669 9(13)	−0.102 5(6)	0.063 0(6)
C(221)	0.628 6(10)	0.347 8(8)	0.341 4(6)	C(233)	0.808 1(13)	−0.072 7(6)	0.093 0(6)
C(222)	0.561 5(10)	0.417 9(8)	0.348 0(6)	C(232)	0.861 7(13)	0.015 9(6)	0.135 5(6)
C(223)	0.466 5(10)	0.421 5(8)	0.387 8(6)	C(15)	0.209(3)	0.647 5(14)	0.287 3(11)
C(224)	0.438 7(10)	0.354 9(8)	0.420 8(6)	O(15)	0.110(2)	0.597 1(10)	0.250 0(8)
C(225)	0.505 8(10)	0.284 8(8)	0.414 2(6)	O(16)	0.541 0(15)	0.634 9(9)	0.410 1(8)
C(226)	0.600 7(10)	0.281 2(8)	0.374 4(6)	C(16)	0.456(3)	0.669 1(13)	0.383 2(11)

unless otherwise stated. Light petroleum refers to the fraction boiling in the range 40—60 °C.

Synthesis of the Complex [Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)$_2$].—A solution of methyl-lithium (35 cm^3, 1.5 mol dm^{-3} in diethyl ether, 52 mmol) was added dropwise (40 min) to a solution of [Fe$_2$(μ-CO)$_2$(CO)$_2$(η-C$_5$H$_5$)$_2$] (12 g, 34 mmol) in tetrahydrofuran (240 cm^3) and the resultant mixture stirred for 30 min (0 °C). The reaction mixture was cooled to −60 °C (solid CO$_2$-ethanol), and CF$_3$CO$_2$H (4 cm^3) in tetrahydrofuran (40 cm^3) added dropwise over 10 min, with vigorous stirring. The reaction mixture changed from dark brown to purple in colour. Stirring was continued for 15 min at −60 °C, and during warming to room temperature (45 min). The volume of solvent was then reduced to 40 cm^3, and the concentrate filtered through Celite (4 × 4 cm). The Celite plug was washed with tetrahydrofuran, and the resultant solution concentrated to 40 cm^3 and chromatographed (19 × 5.5 cm column). Elution with diethyl ether gave a deep red band which was collected. Removal of the solvent gave a mixture of *cis*- and *trans*-[Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)$_2$] (1), which was separated as follows. The crude isomeric mixture (9.7 g) was dissolved in toluene (40 cm^3) and then chromatographed. Elution with toluene gave first a purple band which was collected and the residual solid recrystallised from a mixture of tetrahydrofuran–light petroleum (1 : 3) affording purple *crystals* of *trans*-[Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)$_2$] (1a) (6.5 g, 54%) (Found: C, 51.0; H, 3.4. C$_{15}$H$_{12}$Fe$_2$O$_3$ requires C, 51.1; H, 3.4%), m.p. 152 °C; $\nu_{\text{max.}}$ (CO) at 1 957s and 1 804m cm^{-1} (light petroleum). N.m.r. ([^{2}H$_6$]benzene): ^{1}H, δ 4.37 (s, 10 H, C$_5$H$_5$), 7.03 (s, 2 H, μ-C=CH$_2$); ^{13}C-{^{1}H}, δ 279.2 (μ-*C*=CH$_2$), 269.7 (μ-CO), 212.3 (CO), 125.4 (μ-C=*C*H$_2$), and 90.0 p.p.m. (C$_5$H$_5$).

Further elution with toluene afforded an orange band containing a mixture (2.9 g) of *cis*-[Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)$_2$] (1b) and [Fe$_2$(μ-CO)$_2$(CO)$_2$(η-C$_5$H$_5$)$_2$]. Pure (1b) was obtained by refluxing complex (1a) in toluene for 30 min. Chromatography, and elution with toluene followed by recrystallisation from tetrahydrofuran–light petroleum afforded orange-red *crystals* of *cis*-[Fe$_2$(μ-C=CH$_2$)(μ-CO)(CO)$_2$(η-C$_5$H$_5$)$_2$] (1b), m.p. 160 °C (Found: C, 50.8; H, 3.6%; *M* 352. C$_{15}$H$_{12}$Fe$_2$O$_3$ requires C, 51.1; H, 3.4%; *M* 352); $\nu_{\text{max.}}$ (CO) at 1 998s, 1 963w, and 1 804m cm^{-1} (light petroleum). N.m.r. ([^{2}H$_6$]benzene): ^{1}H, δ 4.23 (s, 10 H, C$_5$H$_5$), 6.97 (s, 2 H, μ-C=CH$_2$); ^{13}C-{^{1}H}, δ 276.7 (μ-*C*=CH$_2$), 269.2 (μ-CO), 211.7 (CO), 125.8 (μ-C=*C*H$_2$), and 87.6 p.p.m. (C$_5$H$_5$).

Protonation of Complex (1a).—A solution of $HBF_4·Et_2O$ (0.2 cm^3) was added dropwise with stirring to a solution of the *trans*-vinylidene complex (1a) (0.1 g, 0.28 mmol) in toluene (10 cm^3). The resultant red precipitate was allowed to settle and washed with toluene (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3) to give light red *crystals* of complex (2), $\nu_{max.}$ (CO) at 2 047s, 2 021m, and 1 849m cm^{-1} (CH_2Cl_2). N.m.r. ([$^2H_3$]-nitromethane): ^{1}H, δ 5.2 (s, 3 H, CH_3), 5.48 (s, 10 H, C_5H_5); ^{13}C-{^{1}H}, δ 498.7 (μ-CCH_3), 207.5 (CO), 93.7 (C_5H_5), and 65.6 p.p.m. (Me, partially obscured by solvent). This compound decomposes in solution within a few hours.

Deprotonation of Complex (2b).—Triethylamine (0.1 cm^3) was added to the light red material described above, dissolved in methylene chloride (5 cm^3). The cation dissolved to give a purple solution. Removal of the solvent, followed by chromatography, using diethyl ether as eluant afforded (100% yield) a mixture of complexes (1a) and (1b) (1 : 2.1) characterised by i.r. and ^{1}H n.m.r. spectroscopy.

Synthesis of [$(OC)_3Fe(\mu\text{-}Ph_2PCHPPh_2)FeH(CO)_3$].—Methyl-lithium (2.9 cm^3, 1.5 mol dm^{-3} in diethyl ether, 4.3 mmol) was added dropwise with stirring to a solution of [$Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6$] (2.08 g, 2.89 mmol) in refluxing tetrahydrofuran (40 cm^3). The reaction was monitored by i.r. spectroscopy. After 1 h the spectrum showed ν(CO) bands at 2 033w(br), 1 983s(br), 1 929s, 1 909m, 1 893s, 1 875m, and 1 647m cm^{-1}, corresponding to the formation of an acyl species. Addition of an excess of [$N(PPh_3)_2$]Cl caused a shift in the frequency of the band at 1 647m to 1 731w(br) cm^{-1}. The reaction mixture was cooled (−60 °C) and one equivalent of trifluoroacetic acid (0.22 cm^3, 2.89 mmol) was added with stirring. The temperature of the mixture was allowed to rise to 25 °C, solvent was removed *in vacuo* from the deep red solution, and the residue extracted with diethyl ether (20 cm^3). Chromatography on Florisil (20 × 2.5 cm column) and elution with diethyl ether afforded a red band. After removal of solvent *in vacuo*, recrystallisation (−20 °C) of the residue from diethyl ether–light petroleum solvent gave red *crystals* of [$(OC)_3Fe(\mu\text{-}Ph_2PCHPPh_2)FeH(CO)_3$] (4) (1.2 g, 63%) (Found: C, 56.2; H, 3.4%; *M* 664. $C_{31}H_{22}Fe_2O_6P_2$ requires C, 56.0; H, 3.3%; *M* 664), m.p. 124—128 °C; $\nu_{max.}$ (CO) at 2 045s, 2 001s, 1 985m, 1 969m, 1 957m, and 1 811w(br) cm^{-1} (methylcyclohexane). N.m.r.: ^{1}H ([$^2H_6$]acetone), δ 7.2—8.0 (m, 20 H, C_6H_5), 1.3 [d of d of d, 1 H, CH, *J*(HH) 6, *J*(P_AH) 9, *J*(P_BH) 3], −9.2 [d of d of d, 1 H, FeH, *J*(HH) 6, *J*(P_AH) 35, *J*(P_BH) 43 Hz]; ^{13}C-{^{1}H} ([$^2H_2$]dichloromethane), δ 252.4 (μ-CO), 214.3 (CO), 213.6 (CO), 211.4 (CO), 140—122 (C_6H_5), −11.7 [d of d, CH, *J*(P_AC) 6, *J*(P_BC) 24, *J*(CH) 160 Hz (from coupled spectrum)]; ^{31}P-{^{1}H} ([$^2H_2$]dichloromethane), δ 37.9 [d, *J*(P_AP_B) 4] and 13.5 p.p.m. [d, *J*(P_AP_B) 4 Hz].

Crystal-structure Determination of Complex (4).—Crystals of (4) grow as ill formed red prisms of very poor diffracting power. Intensities were collected at 298 K from a crystal of dimensions *ca.* 0.2 × 0.2 × 0.1 mm in the range $2.9 \leqslant 2\theta \leqslant 40°$. Of the 5 279 independent intensities measured on a Syntex $P2_1$ diffractometer, only 2 669 had $(F) > 5.0\sigma(F)$ and these were used in the solution and refinement of the structure after corrections had been made for Lorentz and polarisation effects. In view of the comparatively small value of the mass-absorption coefficient (μ = 11.2 cm^{-1}), and the poor quality of the data, no absorption correction was applied.

Crystal data. $C_{31}H_{22}Fe_2O_6P_2$, M = 664.2, Triclinic, a = 10.504(3), b = 15.819(5), c = 19.552(5) Å, α = 104.43(2), β = 103.04(2), γ = 98.57(2)°, U = 2 992(1) Å^3, Z = 4, D_c = 1.47 g cm^{-3}, $F(000)$ = 1 352, space group $P\bar{1}$, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 11.2 cm^{-1}.

Solution and refinement of the structure. The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. Because of the limited number of observed intensities (see above), only the Fe and P atoms were refined with anisotropic thermal parameters. All remaining non-hydrogen atoms were refined with isotropic thermal parameters. For similar reasons the phenyl rings were treated as rigid groups (C–C 1.395 and C–H 0.960 Å) with the constituent carbon atoms being given individual refined isotropic thermal parameters. Refinement by blocked-cascade least squares led to *R* 0.073 (*R'* 0.072), and a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.001\,3|F_o|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > 1.5 e Å^{-3}. Scattering factors were from ref. 24. Atomic co-ordinates for the non-hydrogen atoms are given in Table 2. All computations were carried out on an Eclipse (Data General) mini-computer with the SHELXTL system of programs.[25]

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References

1 W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117.

2 K. Folting, J. C. Huffman, L. N. Lewis, and K. G. Caulton, *Inorg. Chem.*, 1979, **18**, 3483.

3 D. L. Davies, A. F. Dyke, A. Endersfelder, S. A. R. Knox, P. J. Naish, A. G. Orpen, D. Plaas, and G. E. Taylor, *J. Organomet. Chem.*, 1980, **198**, C43.

4 Y. N. Al-Obaidi, M. Green, N. D. White, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 319.

5 N. Nitay, W. Priester, and M. Rosenblum, *J. Am. Chem. Soc.*, 1978, **100**, 3620.

6 G. M. Dawkins, M. Green, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1980, 1120.

7 R. E. Ginsburg, J. M. Berg, R. K. Rothrock, J. P. Collman, K. O. Hodgson, and L. F. Dahl, *J. Am. Chem. Soc.*, 1979, **101**, 7218.

8 R. D. Adams and F. A. Cotton in ' Dynamic Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1975, ch. 12, p. 489.

9 A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 861.

10 G. K. Barker, P. K. Baker, M. Green, and A. J. Welch, *J. Am. Chem. Soc.*, 1980, **102**, 1812.

11 N. E. Kolobova, L. L. Ivanov, O. S. Zhanko, G. G. Aleksandrov, and Yu. T. Stuchkov, *J. Organomet. Chem.*, 1982, **228**, 265 and refs. therein.

12 R. D. Adams, A. Davison, and J. P. Selegue, *J. Am. Chem. Soc.*, 1979, **101**, 7232.

13 M. I. Bruce and R. C. Wallis, *J. Organomet. Chem.*, 1978, **161**, C1.

14 R. A. Anderson, A. L. Galyer, and G. Wilkinson, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 609.

15 L. N. Lewis, J. C. Huffmann, and K. G. Caulton, *J. Am. Chem. Soc.*, 1980, **102**, 403.

16 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 4422.

17 C. Krüger, B. L. Barnett, and D. Brauer, in ' The Organic Chemistry of Iron,' eds. E. A. Koerner Von Gustorf, F.-W. Grevels, and I. Fischler, Academic Press, New York, 1978, vol. 1, ch. 1.

18 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

19 J. P. Collman, R. K. Rothrock, R. G. Finke, E. J. Moore, and F. Rose-Munch, *Inorg. Chem.*, 1982, **21**, 146.

20 S. Al-Jibori and B. L. Shaw, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 286.

21 H. H. Karsch, H.-F. Klein, and H. Schmidbauer, *Angew. Chem.*, *Int. Ed. Engl.*, 1975, **14**, 637.

22 J. W. Rathke and E. L. Muetterties, *J. Am. Chem. Soc.*, 1975, **97**, 3272.

23 S. Al-Jibori, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 1572.

24 ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

25 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P*3*m* *X*-ray system, Cambridge, 1976.

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