Dinuclear Hydride and η^3-Bonded Dithioformate Complexes of Iron(II) *

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Iron(II) chloride reacts consecutively with bis(diphenylphosphino)methane (dppm), activated magnesium and cyclopentadiene to give the mono- and di-iron hydrides [FeH(η-C_5H_5)(dppm)] **1** and [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)] **2**. Compound **2** contains three bridging units (average separation of the hydride from the metal atoms, 1.73 Å) in the solid state and crystallizes in the space group $P2_1/c$ with $a = 10.004(2)$, $b = 20.134(7)$, $c = 19.353(10)$ Å, $\beta = 95.00(3)°$ and $Z = 4$. Compound **1** reacts with CS_2 to form the dithioformate complex [Fe(η-C_5H_5)(dppm-*P*)(S_2CH)] **4**. The sulfur-donor ligand is η^3 co-ordinated in solution.

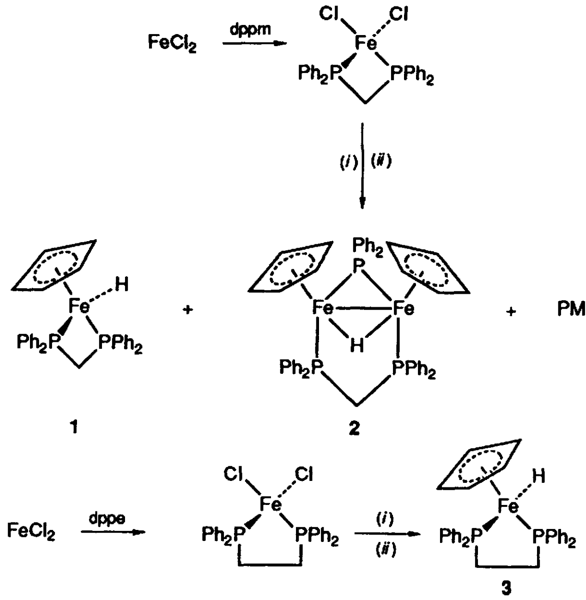
A number of synthetic routes for the preparation of complexes of the type [FeH(η-C_5H_5)(L^1L^2)] [L^1,L^2 = PPh_3, dppe-*P* (dppe = $Ph_2PCH_2CH_2PPh_2$), CO, PMe_3 or $P(OMe)_3$; L^1L^2 = dppe-*P,P′*][1–6] are known. While our work was in progress, Ruiz and co-workers[7] described the reduction of [Fe(η-C_5H_5)(NCMe)(dppm)]$^+$ (dppm = $Ph_2PCH_2PPh_2$) with the electron-reservoir complex [Fe(η-C_5H_5)(η-C_6Me_6)] to afford, with the solvent tetrahydrofuran (thf) acting as the source of protons, a new member [FeH(η-C_5H_5)(dppm)] **1** of the above class of compounds containing a four-membered chelate ring. Reaction of [Fe(η-C_5H_5)(η-C_6H_5Me)] with dppm or dppe also yields [FeH(η-C_5H_5)(dppm)] and [FeH(η-C_5H_5)(dppe)] and once again the solvent acts as a source of protons.[7]

While studying the synthesis and reactions of various cyclopentadienylmetal compounds stabilized by phosphine ligands,[8,9] we became interested in preparing the mononuclear hydride compound **1** along a short and simple route. A new preparation for **1**, based on a method developed by Frings,[10] as well as the unexpected formation of the dinuclear complex [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)] **2**, are described. Carbonyl analogues of **2**, [{Fe(η-C_5H_5)}$_2$H(μ-PR_2)(CO)$_2$] (R = Me or Ph), were prepared previously by Hayter,[11] but the location of the hydrogen atom in these complexes is uncertain. It may either undergo rapid exchange between the two iron atoms or form a hydrogen bridge. We now report the crystal and molecular structure of complex **2**, which is the first hydrogen-bridged iron complex fully characterized by X-ray crystallography.

Treichel and Molzahn[12] have described the insertion of CS_2 into the Fe–H bond of [FeH(η-C_5H_5)(dppe)] **3** to form a S-bonded dithioformate complex. The reaction between the mononuclear hydride complex **1** and CS_2 produced a further example of the rare dihetera π-allylic ligands observed previously in related iron complexes.[9]

Results and Discussion

Preparation and Structural Characterization of the Compounds [FeH(η-C_5H_5)(dppm)] **1**, [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)] **2**, [FeH(η-C_5H_5)(dppe)] **3** *and* [Fe(η-C_5H_5)(dppm-*P*)(S_2CH)] **4**.—Successive treatment of $FeCl_2$ in thf at room temperature with dppm, magnesium, 1,2-dibromoethane (to activate the Mg) and cyclopentadiene afforded a mixture of products (Scheme 1) which, according to the ^1H NMR spectrum, contained compound **1**, ferrocene, $PMePh_2$ and an unexpected and unknown product **2**, in a ratio of *ca.* 23:1:2:2. Treatment with CuCl followed by filtration removed the excess of phosphine and chromatography on a short Florisil column the ferrocene. Crystallization of the products afforded yellow-orange crystals of **1** and brown crystals of **2** which were separated mechanically, and characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy and an X-ray crystal structure determination of **2**. Crystals of **2** decompose within 3 months under argon at −20 °C. Substituting dppm for dppe in the syntheses afforded only **3**[1,7] and 1% ferrocene.



Scheme 1 (*i*) activated Mg; (*ii*) C_5H_6

Since Felkin *et al.*[5] have shown that species such as [(dppe)(η-C_5H_5)FeMgBr] which contain an iron–magnesium bond can deprotonate ethanol and even acetone, it is feasible that, after the reduction of [$FeCl_2$(dppm)] with magnesium, C_5H_6 (pK_a = 17)[13] partakes in protonolysis and Cl^- substitution of

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

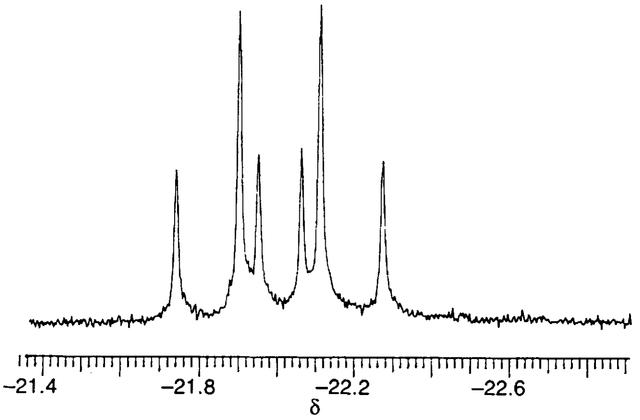


Fig. 1 Expansion of a part of the ^{1}H NMR spectrum of complex **2** at room temperature showing the bridging hydrogen {J[HP(dppm)] = 32.0 and J[HP(PPh$_2$)] = 42.2 Hz}

Table 1 Selected bond distances (Å) and angles (°) for complex **2** with estimated standard deviations (e.s.d.s) in parentheses

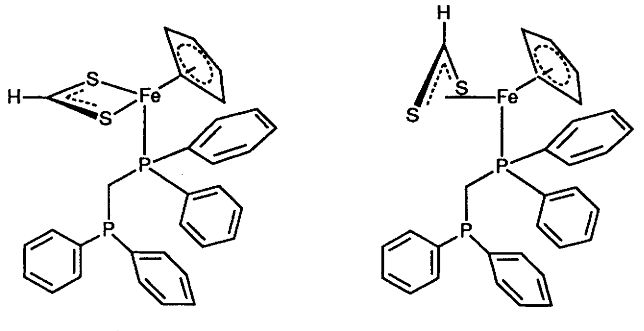
Fe(1)–C(1)	2.086(4)	Fe(2)–C(18)	2.087(4)
Fe(1)–C(2)	2.098(3)	Fe(2)–C(19)	2.088(3)
Fe(1)–C(3)	2.110(3)	Fe(2)–C(20)	2.091(4)
Fe(1)–C(4)	2.103(4)	Fe(2)–C(21)	2.082(4)
Fe(1)–C(5)	2.075(4)	Fe(2)–C(22)	2.079(4)
	Fe(1)–Fe(2)	2.787(1)	
Fe(1)–HFe	1.78(2)	Fe(2)–HFe	1.68(2)
Fe(1)–P(1)	2.189(1)	Fe(2)–P(1)	2.194(1)
Fe(1)–P(3)	2.177(1)	Fe(2)–P(2)	2.173(1)
P(3)–C(35)	1.838(3)	P(2)–C(35)	1.825(3)
	Fe(1)–P(1)–Fe(2)	79.0(1)	
P(1)–Fe(1)–Fe(2)	50.6(1)	Fe(1)–Fe(2)–P(1)	50.5(1)
	Fe(1)–HFe–Fe(2)	107.6(12)	
HFe–Fe(1)–Fe(2)	35.0(7)	Fe(1)–Fe(2)–HFe	37.5(8)
	P(2)–C(35)–P(3)	111.7(2)	
Fe(1)–P(3)–C(35)	116.0(1)	Fe(2)–P(2)–C(35)	114.0(1)
Fe(2)–Fe(1)–P(3)	92.0(1)	Fe(1)–Fe(2)–P(2)	94.5(1)
P(2)–Fe(2)–HFe	78.7(8)	P(3)–Fe(1)–HFe	77.7(8)
P(1)–Fe(2)–P(2)	97.5(1)	P(1)–Fe(1)–P(3)	95.6(1)
P(1)–Fe(2)–HFe	86.4(8)	P(1)–Fe(1)–HFe	84.2(7)

the iron Grignard complex to form **1**. Formally, in a parallel pathway, a P–C and two Fe–P bonds in the adduct complex **1** are broken, the phosphide formed, one hydride and the free phosphorus atom of the then dangling dppm co-ordinate again in bridging fashion and thus hold the two iron atoms in close proximity for stable metal–metal bond formation. The remaining hydrogen is transferred to the Ph$_2$PCH$_2$ residue to form methyldiphenylphosphine.

Oxidative-addition reactions of dppm[14,15] and of the sulfur compound MeSCH$_2$SMe,[16] affording dinuclear compounds containing bridging Ph$_2$P or MeS groups, are known and have been discussed in detail recently.[14] In complex **2**, however, the Ph$_2$PCH$_2$ fragment is not retained as a ligand but is converted into the neutral phosphine, PMePh$_2$. Neutral phosphine is also produced during the cleavage of co-ordinated dppm in an aqueous basic medium[17] or in liquid ammonia.[18]

Treatment of the mononuclear hydride complex **1** with an excess of carbon disulfide led to the insertion of CS$_2$ into the Fe–H bond and the formation of a dithioformate ligand in **4**.

The hydride ligand in compound **2** resonates as a doublet of triplets (δ −22.00, Fig. 1) upfield from the triplet of doublets shown by the mononuclear compound **1** at δ −12.01.[7] These chemical shifts are in accordance with literature values for dinuclear iron hydrides,[1,11,19–22] *e.g.* δ −36.9 for [{Fe(η-C$_5$H$_5$)(CO)}$_2$H(μ-dppe)]$^+$, to which a bridged structure was assigned.[1] In both **1** and **2** the two CH$_2$ protons of the dppm ligand are chemically inequivalent and appear in **1** as two multiplets at δ 3.21 and 4.15, whereas each appears as a doublet of triplets of doublets in **2** (δ 0.90 and 1.60), indicating significant coupling with each other [J(HH) ≈ 12 Hz] and with dppm phosphorus atoms [J(HP) ≈ 12 Hz] but weak coupling with the bridging phosphorus atom [J(HP) = 2.5 Hz]. In **4** they give rise to a doublet of doublets due to different coupling with the free and co-ordinated phosphorus atoms. The cyclopentadienyl signals of **1**–**3** are singlets, whereas for **4** a doublet appears [J(PH) = 1.6 Hz]. The proton of the dithioformate ligand in **4** also couples with the phosphorus atom and J(PH) = 0.6 Hz. The ^{31}P NMR spectra of **1** and **3** gave signals at δ 48.3 and 112.2 respectively. In **2** the phosphorus atoms of dppm appear as a doublet [J(PP) = 36 Hz] at δ 76.7 due to coupling with the bridging phosphide which resonates as a triplet at δ 172.3 [J(PP) = 36 Hz]. The ^{1}H and ^{31}P NMR spectra of **2** remained unchanged over the temperature range 193–298 K. The dppm ligand in **4** gave signals at δ 49.7 and −26.0 for the co-ordinated and free phosphorus atoms respectively. This indicates that the dppm is a monodentate ligand and that the dithioformate is not monodentate.



4

The 81 MHz ^{31}P NMR spectra of compound **4** at 183 K did not show an exchange between *S,S′* and η^3(*S,C,S′*) co-ordinated linkage isomers as was observed previously for the dithioacetate ligand in [Fe(η-C$_5$H$_5$)(dppm)(S$_2$CMe)].[9] This indicated that only one isomer exists in solution. The results of the nuclear Overhauser effect (NOE) difference experiments shown in Fig. 2 indicated that the dithioformate ligand in **4** is η^3 co-ordinated. A comparison of traces (*b*) and (*c*) clearly indicates an NOE between the cyclopentadienyl protons and the proton of the dithioformate ligand. The larger separation between the cyclopentadienyl protons and the thioformate proton in the *S,S′* bonded isomer would have precluded the observation of an NOE.

This result for compound **4**, [Fe(η-C$_5$H$_5$)(dppm)(S$_2$CH-*S,C,S′*)] in solution, and the results observed for the dithioacetate {the ratio [Fe(η-C$_5$H$_5$)(dppm)(S$_2$CMe-*S,S′*)]: [Fe(η-C$_5$H$_5$)(dppm)(S$_2$CMe-*S,C,S′*)] is 5:95 in solution} and the dithiobenzoate {ratio of [Fe(η-C$_5$H$_5$)(dppm) (S$_2$CPh-*S,S′*)]: [Fe(η-C$_5$H$_5$)(dppm)(S$_2$CPh-*S,C,S′*)] is 70:30 in solution} complexes suggests that the R group in [Fe(η-C$_5$H$_5$)(dppm)(S$_2$CR)] compounds is an important factor in determining the isomer ratios in solution. The smaller H and Me groups favour η^3 co-ordination. The η^3 co-ordination as such seems to accommodate the goal of maximum configurational entropy of the phosphine ligand. If R = Ph, however, the phenyl–cyclopentadienyl interaction determines the *S,S′* co-ordination of the dithiobenzoate ligand at the expense of a loss in configurational entropy for the phosphine ligand.

Complexes **1**–**4** gave molecular ions in their mass spectra and fragmented by various pathways, two of which involve the initial loss of either a hydrogen atom and a cyclopentadienyl group or the phosphine ligand(s).

Structure of [{Fe(η-C$_5$H$_5$)}$_2$(μ-H)(μ-PPh$_2$)(μ-dppm)] **2**.—A

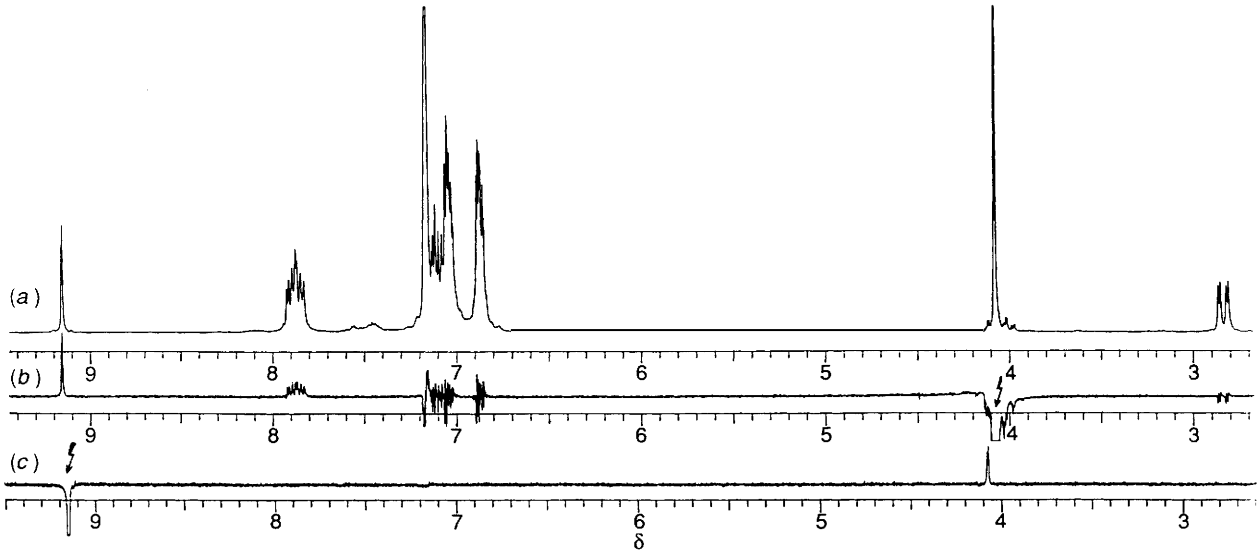


Fig. 2 Proton NMR spectra (200.06 MHz) of [Fe(η-C_5H_5)(dppm)(S_2CH)] **4** in C_6D_6 at 293 K: (*a*) normal spectrum; (*b*) and (*c*) NOE difference spectra, where the irradiated signal is marked by an arrow and absorption lines stem from spatially neighbouring protons

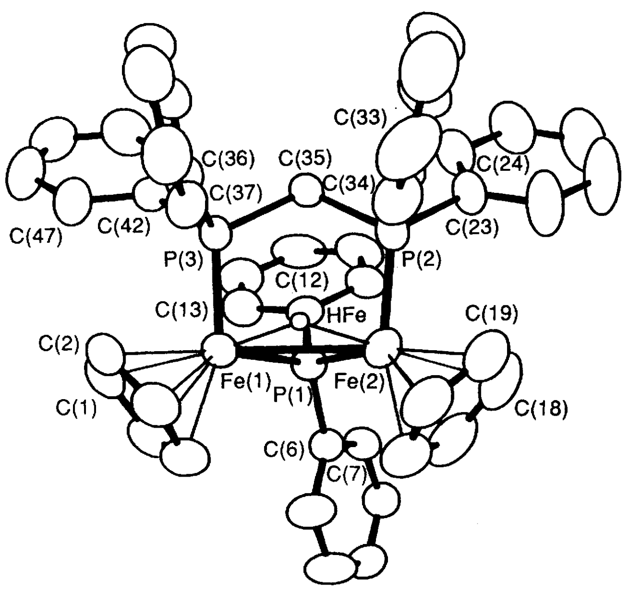


Fig. 3 An ORTEP[23] drawing of the structure of [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)] **2**

view of the molecule is shown in Fig. 3. Selected bond lengths and angles are given in Table 1 and final atomic coordinates in Table 2. The crystal structure of **2** is the first example of a diiron complex containing a bridging hydrogen. The Fe–Fe bond length is 2.787(1) Å and the two cyclopentadienyl groups are situated in *cis* positions. The three Fe–P distances in **2** do not differ much and are also similar to such separations {*e.g.* 2.199(1) and 2.174(3) Å in [Fe(η-C_5H_5)Ph(dppm)][9]} in other iron compounds.[24,25] The Fe–C(cyclopentadienyl) separations are similar to those in [Fe(η-C_5H_5)Ph(dppm)].[9]

The Fe–HFe bond lengths of compound **2** [1.78(2) and 1.68(2) Å] are significantly longer than the reported distances between iron and terminal hydrogen atoms, *e.g.* 1.37(3) and 1.47(1) Å in [FeH(η^5-C_6H_7)(dippp)] [dippp = 1,3-bis(diisopropylphosphino)propane] and [FeH(η^5-C_6H_6Et-*endo*)(dippp)].[10] The Fe(1)–HFe–Fe(2) angle is 107.6(12)°. Although the bond angles P(2)–Fe(2)–HFe [78.7(8)°], P(3)–Fe(1)–HFe [77.7(8)°], P(1)–Fe(2)–P(2) [97.5(1)°] and P(1)–Fe(1)–P(3) [95.6(1)°] suggest that the two iron atoms and the bridging hydrogen and PPh_2 groups lie essentially in one plane and perpendicular to the five-membered chelate ring, deviations from planarity of up to 0.5 Å occur in the planes Fe(1)–Fe(2)–P(1)–HFe–Fe and Fe(1)–Fe(2)–P(2)–C(35)–P(3), and the dihedral angle between the two planes is 69(3)°.

Experimental

Materials.—The ligands dppm and dppe were purchased from Strem Chemicals, magnesium turnings from Fluka and 1,2-dibromoethane from Hopkin & Williams. Anhydrous $FeCl_2$ was prepared from $FeCl_3$,[26] CuCl from $CuCl_2$[27] and cyclopentadiene was obtained by cracking dicyclopentadiene. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium diphenylketyl, CH_2Cl_2 and CS_2 from P_2O_5, and hexane and pentane from CaH_2.

Physical Methods.—All reactions and manipulations were performed under an argon atmosphere with standard vacuum-line and Schlenk techniques. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument, the infrared spectra on a Perkin-Elmer 841 spectrometer and NMR spectra on a VXR 200 FT spectrometer. Elemental analyses were carried out by the Mikroanalitisches Labor Pascher, Bonn.

Preparations.—[FeH(η-C_5H_5)(dppm)] **1** *and* [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)] **2**. A suspension of $FeCl_2$ (0.50 g, 4.0 mmol), dppm (1.53 g, 4.0 mmol) and magnesium (0.97 g, 4.0 mmol) in thf (30 cm^3) was treated with 1,2-dibromoethane (0.03 cm^3, 0.4 mmol) and cyclopentadiene (0.33 cm^3, 4.0 mmol) at −30 °C. The mixture was stirred for 24 h. The dark brown reaction mixture that had reached 10 °C was then allowed to warm to room temperature. After removal of the solvent *in vacuo*, extraction with diethyl ether (2 × 60 cm^3), filtration through Florisil (9 g) and concentration to 80 cm^3, the filtrate was left at −20 °C for 4 d. Brown crystals of compound **2** formed. The mother-liquor was removed and the crystals (0.03 g, 1%) were washed with pentane, stripped of solvent and characterized. Free phosphines in the mother-liquor were precipitated with copper(I) chloride (0.79 g, 8.0 mmol) and removed by filtration. The filtrate was concentrated and absorbed on Florisil at −20 °C. Chromatography on Florisil (56 g, at −10 °C) with hexane yielded ferrocene and with ether–hexane (1:10 to 2:1) yielded **1**, 1.7 g (85%). Complex **2** decomposed on the column. Larger amounts of **2** were obtained by removing the ferrocene by chromatography on Florisil (18 g) with hexane after filtration of the extract. The free phosphines

Table 2 Fractional coordinates ($\times 10^4$) for complex **2**

Atom	*X/a*	*Y/b*	*Z/c*
C(1)	1046(4)	2575(2)	1360(2)
C(2)	839(3)	2064(2)	851(2)
C(3)	1881(4)	1603(2)	973(2)
C(4)	2727(3)	1821(2)	1558(2)
C(5)	2189(4)	2413(2)	1777(2)
Fe(1)	775(1)	1668(1)	1851(1)
P(1)	939(1)	1600(1)	2984(1)
C(6)	2403(3)	1884(1)	3559(1)
C(7)	2308(3)	2017(2)	4263(2)
C(8)	3413(3)	2158(2)	4714(1)
C(9)	4654(3)	2183(2)	4487(2)
C(10)	4784(3)	2063(2)	3789(2)
C(11)	3685(3)	1918(2)	3347(2)
C(12)	−315(3)	2021(1)	3462(1)
C(13)	−611(3)	2680(2)	3328(2)
C(14)	−1445(4)	3033(2)	3722(2)
C(15)	−2002(3)	2729(2)	4255(2)
C(16)	−1760(3)	2075(2)	4386(2)
C(17)	−909(3)	1713(2)	4001(1)
Fe(2)	1000(1)	547(1)	2696(1)
C(18)	1756(4)	−143(2)	3436(2)
C(19)	1463(4)	−463(2)	2775(2)
C(20)	2247(4)	−173(2)	2311(2)
C(21)	3028(4)	324(2)	2670(3)
C(22)	2710(4)	331(2)	3347(2)
P(2)	−1146(1)	362(1)	2636(1)
C(23)	−1939(3)	74(2)	3412(1)
C(24)	−2953(4)	406(2)	3702(2)
C(25)	−3501(4)	167(2)	4293(2)
C(26)	−3050(5)	−410(2)	4576(2)
C(27)	−2093(5)	−750(2)	4290(2)
C(28)	−1539(4)	−511(2)	3708(2)
C(29)	−1869(3)	−271(1)	2020(1)
C(30)	−3187(4)	−480(2)	2032(2)
C(31)	−3706(5)	−952(3)	1557(3)
C(32)	−2915(7)	−1215(2)	1078(3)
C(33)	−1661(6)	−1004(2)	1061(2)
C(34)	−1111(4)	−534(2)	1523(2)
C(35)	−2172(3)	1083(1)	2373(1)
P(3)	−1402(1)	1585(1)	1721(1)
C(36)	−2150(3)	1175(1)	923(1)
C(37)	−1347(3)	811(2)	512(2)
C(38)	−1920(5)	479(2)	−70(2)
C(39)	−3262(5)	495(2)	−243(2)
C(40)	−4082(4)	853(2)	159(2)
C(41)	−3513(3)	1188(2)	738(2)
C(42)	−2477(3)	2328(1)	1704(1)
C(43)	−3383(4)	2466(2)	2170(2)
C(44)	−4165(4)	3028(2)	2120(2)
C(45)	−4083(4)	3473(2)	1601(2)
C(46)	−3207(5)	3346(2)	1130(2)
C(47)	−2406(4)	2784(2)	1170(2)
H(1)	434(25)	2963(12)	1432(12)
H(2)	81(24)	2061(11)	464(12)
H(3)	1966(24)	1188(12)	718(12)
H(4)	3547(24)	1600(12)	1788(12)
H(5)	2499(25)	2643(12)	2111(12)
H(7)	1530(25)	1992(12)	4416(12)
H(8)	3340(25)	2267(12)	5200(12)
H(9)	5383(25)	2283(12)	4793(12)
H(10)	5644(25)	2087(11)	3674(12)
H(11)	3793(25)	1860(11)	2885(12)
H(13)	−211(24)	2902(12)	2994(12)
H(14)	−1611(24)	3432(12)	3618(12)
H(15)	−2589(25)	2949(12)	4500(12)
H(16)	−2016(25)	1861(12)	4669(12)
H(17)	−693(24)	1268(12)	4134(12)
H(18)	1290(24)	−230(12)	3886(12)
H(19)	730(24)	−824(11)	2694(12)
H(20)	2207(24)	−222(12)	1834(12)
H(21)	3679(24)	596(11)	2480(12)
H(22)	3125(24)	583(12)	3693(12)
H(24)	−3344(24)	804(11)	3558(12)
H(25)	−4214(24)	457(12)	4471(12)
H(26)	−3461(24)	−574(12)	4969(12)
H(27)	−1579(24)	−1067(12)	4437(12)
H(28)	−724(24)	−689(12)	3613(12)
H(30)	−3713(24)	−285(12)	2350(12)
H(31)	−4515(30)	−1071(16)	1555(16)
H(32)	−3381(29)	−1491(14)	754(14)
H(33)	−1110(30)	−1195(15)	789(15)
H(34)	−227(28)	−358(14)	1508(14)
H(35A)	−3162(28)	979(13)	2204(13)
H(35B)	−2180(27)	1361(13)	2770(13)
H(37)	−428(27)	778(14)	645(14)
H(38)	−1346(29)	259(14)	−313(14)
H(39)	−3710(28)	303(13)	−660(14)
H(40)	−5025(29)	904(14)	16(14)
H(41)	−4044(28)	1442(14)	982(14)
H(43)	−3445(30)	2183(14)	2512(14)
H(44)	−4695(32)	3056(16)	2372(16)
H(45)	−4708(28)	3833(14)	1561(14)
H(46)	−3152(31)	3610(14)	801(14)
H(47)	−1780(28)	2700(14)	846(14)
HFe	528(24)	795(12)	1885(12)

were then precipitated with CuCl and removed by filtration. The filtrate was concentrated and left at −20 °C for 24 h. Yellow-orange crystals of **1** [0.85 g, 45%, based on $FeCl_2$ (0.48 g, 3.8 mmol)] and brown crystals of **2** [0.15 g, 5% based on $FeCl_2$ (0.48 g, 3.8 mmol)] formed and were separated and dried under vacuum.

Compound [FeH(η-C_5H_5)(dppm)] **1**: m.p. 124 °C (decomp.) (Found: M^+, 506.101 33. $C_{30}H_{29}FeP_2$ requires *M*, 506.101 38); ν_{max}(Fe–H) 1842w cm^{-1} (Nujol); δ_H(200.06 MHz, solvent C_6D_6, standard $SiMe_4$) −12.01 [1 H, dt, *J*(HH) 5, *J*(PH) 66.4 Hz, FeH], 3.21 and 4.15 (1 H each, m, PCH_2P), 4.42 (5 H, s, C_5H_5) and 7.09, 7.56 and 7.75 (20 H, m, PC_6H_5); δ_C(50.31 MHz, solvent C_6D_6, standard $SiMe_4$) 50.3 [1 C, t, *J*(PC) 19.9 Hz, PCH_2P], 72.8 (5 C, s, C_5H_5) and 126.2–143.4 (24 C, m, PC_6H_5); δ_P(80.98 MHz, solvent C_6D_6, external standard H_3PO_4) 48.3 (2 P, s, PC_6H_5); *m/z* 506 (M^+, 46) and 440 [*M* − (η-C_5H_5) − H, 70%].

Compound [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)}] **2**: m.p. 125 °C (decomp.) (Found: C, 69.9; H, 5.6; P, 11.8%; M^+, 812.127 34. $C_{47}H_{43}Fe_2P_3$ requires C, 69.5; H, 5.3; P, 11.4%; *M*, 812.127 34); ν_{max} 1127w, 1027vw, 892vw and 769w cm^{-1} (Nujol); δ_H(200.06 MHz, solvent C_6D_6, standard $SiMe_4$) −22.00 {1 H, dt, *J*[HP(dppm)] 32.0, *J*[HP(PPh_2)] 42.2, FeHFe}, 0.90 and 1.60 {1 H each, dtd, *J*(HH) ≈12, *J*[HP(dppm)] ≈12, *J*[HP(PPh_2)] 2.5 Hz, PCH_2P}, 4.33 (10 H, s, C_5H_5), 6.84, 7.00, 7.16, 7.39 and 7.58 (30 H, m, PC_6H_5); δ_C(50.31 Hz, solvent C_6D_6, standard $SiMe_4$) 29.5 [1 C, t, *J*(PC) 16.9 Hz, PCH_2P], 76.2 (10 C, s, C_5H_5) and 128.0–142.4 (36 C, m, PC_6H_5); δ_P(80.98 MHz, solvent C_6D_6, external standard H_3PO_4) 76.7 [2 P, d, *J*(PP) 36] and 172.3 [1 P, t, *J*(PP) 36 Hz]; *m/z* 812 (M^+, 26%) and 746 [*M* −(η-C_5H_5) − H, 8%].

[FeH(η-C_5H_5)(dppe)] **3**. A suspension of $FeCl_2$ (0.94 g, 7.4 mmol), dppe (2.96 g, 7.4 mmol) and magnesium (0.18 g, 7.4 mmol) in thf (30 cm^3) was treated with 1,2-dibromoethane (0.05 cm^3, 0.7 mmol) and cyclopentadiene (0.61 cm^3, 7.4 mmol) at −40 °C. The mixture was stirred for 12 h while the temperature rose to 10 °C, and was then allowed to reach room temperature. After removal of the solvent *in vacuo*, extraction with diethyl ether (2 × 60 cm^3), filtration through Florisil (9 g) and concentration to 30 cm^3, the filtrate was left at −20 °C. Yellow-orange crystals of [FeH(η-C_5H_5)(dppe)] **3** (2.7 g, 69%) formed, m.p. 143 °C (decomp.) (Found: M^+, 520.

$C_{31}H_{30}FeP_2$ requires *M*, 520.38); ν_{max}(Fe–H) 1876w and 1827w cm^{-1} (Nujol); δ_H(200.06 MHz, solvent C_6D_6, standard $SiMe_4$) −16.06 [1 H, t, *J*(PH) 71.5 Hz, FeH], 1.70–2.30 (4 H, m, PCH_2CH_2P), 4.19 (5 H, s, C_5H_5) and 6.40–8.80 (20 H, m, PC_5H_5); δ_C(50.31 MHz, solvent C_6D_6, standard $SiMe_4$) 31.1 [2 C, t, *J*(PC) 22.9 Hz, PCH_2CH_2P], 75.7 (5 C, s, C_5H_5) and 126.0–133.5 (24 C, m, PC_6H_5); δ_P(80.98 MHz, solvent C_6D_6, external standard H_3PO_4) 112.2 (2 P, s, PC_6H_5); *m*/*z* 520 (M^+, 37) and 454 [*M* − (η-C_5H_5) − H, 11%].

[Fe(η-C_5H_5)(dppm)(S_2CH)] **4**. The crude reaction product containing compounds **1** and **2** was extracted with diethyl ether (60 cm^3) and the extract filtered and stripped of solvent. The residue was dissolved in thf (20 cm^3) and an excess of CS_2 (5.0 cm^3, 83.9 mmol) in thf (20 cm^3) slowly added at 0 °C. After stirring the reaction mixture for 18 h at room temperature it was stripped of solvent and extracted with diethyl ether (60 cm^3). The extract was filtered through Florisil (9 g) and dried *in vacuo*. The residue was dissolved in the minimum of CH_2Cl_2, an equal volume of diethyl ether was added, the mixture was layered with pentane (10 cm^3) and left at −20 °C for crystallization. The dark brown crystals (0.49 g, 22% based on 4.0 mmol $FeCl_2$) were washed with pentane, m.p. 143 °C (decomp.) (Found: C, 64.0; H, 4.8; P, 11.0%; M^+, 582. $C_{31}H_{28}FeP_2S_2$ requires C, 63.9; H, 4.85; P, 11.0%; *M*, 582.49); ν_{max} (C–S range) 824m, 875m, 1013w, 1117w and 1173vw (Nujol); 821m, 874m, 1012vw, 1110vw and 1266w cm^{-1} ($CHCl_3$); δ_H(200.06 MHz, solvent C_6D_6, standard $SiMe_4$) 2.18 [2 H, dd, *J*(HPFe) 8.2, *J*(HP) 2.2, PCH_2P], 4.16 [5 H, d, *J*(HP) 1.6, C_5H_5], 6.77, 6.97, 7.23 and 7.69 (20 H, m, PC_6H_5) and 8.73 [1 H, d, *J*(HP) 0.6 Hz, S_2CH]; δ_C(50.31 MHz, solvent C_6D_6, standard $SiMe_4$), 27.0 [1 C, t, *J*(PC) 21.9, PCH_2P], 80.6 [5 C, d, *J*(PC) 1.6 Hz, C_5H_5], 127.0–140.5 (24 C, m, PC_6H_5) and 252.3 (1 C, s, S_2CH); δ_P(80.98 MHz, solvent C_6D_6, external standard H_3PO_4) −26.0 [1 P, d, *J*(PP) 32.2, P–Fe], 49.7 [1 P, d, *J*(PP) 32.2 Hz, P]; *m*/*z* 582 (M^+, 1) and 517 [*M* − (η-C_5H_5), 2%].

Crystallography.—Crystal data for [{Fe(η-C_5H_5)}$_2$(μ-H)(μ-PPh_2)(μ-dppm)] **2**. $C_{47}H_{43}Fe_2P_3$, *M* = 812.1, monoclinic, space group $P2_1/c$ (no. 14), *a* = 10.004(2), *b* = 20.134(7), *c* = 19.353(10) Å, β = 95.00(3)°, *U* = 1688(1) Å^3 [based on the least-squares refinement of the diffractometer angles for 25 centred reflections with $18 \leqslant \theta \leqslant 20°$, using Mo-Kα (λ = 0.7107 Å) radiation], *Z* = 4, D_c = 1.39 g cm^{-3}. Dark brown spear-shaped crystals, crystal dimensions 0.44 × 0.62 × 0.75 mm, μ(Mo-Kα) 8.0 cm^{-1}, *F*(000) = 1688.

Data collection and processing. CAD4 diffractometer, graphite-monochromated Mo-Kα radiation, ω–2θ scan mode with ω = 0.54 + 0.34 tanθ, variable ω scan rate 5.49° min^{-1}, maximum scan time 60 s per reflection, 12 166 unique reflections (*h* 0–14, *k* 0–28, *l* −27 to 27) with $3 \leqslant \theta \leqslant 30°$ measured. Data correction for Lorentz and polarization factors, yielding 7861 reflections with $I > 3\sigma(I)$ used for the analysis and refinement. Decay 3.2% (uncorrected).

Structure analysis and refinement. Direct methods (SHELX 86),[28] followed by conventional Fourier-difference techniques using SHELX 76.[29] Full-matrix least-squares refinement (in two blocks for final cycles) with all non-hydrogen atoms anisotropic, all hydrogen atoms refined in experimental positions with a common isotropic thermal parameter that converged to U_{iso} = 0.067(1) Å^2 using $\sigma(F)^{-2}$ weights and refining 601 parameters. Final *R*, *R′* are 0.052, 0.032. The maximum shift/e.s.d. during the final refinement was <0.19:1. Atomic scattering factors were taken from ref. 30.

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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