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Coordination and organometallic complexes of iron containing *o*-phenylenebis(dimethylphosphine) (pdmp). Crystal and molecular structure of $[Fe(\eta^2-C_2H_4)(pdmp)_2]$

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Routes to hydrido- and organo-iron complexes of the bidentate ligand *o*-phenylenebis(dimethylphosphine), *o*-$C_6H_4(PMe_2)_2$ (pdmp), have been developed, starting from *trans*-$[FeCl_2(pdmp)_2]$. Reduction of *trans*-$[FeCl_2(pdmp)_2]$ with $LiAlH_4$ gives the dihydride, *cis*-$[FeH_2(pdmp)_2]$, there being no evidence for an intermediate monohydride $[FeHCl(pdmp)_2]$. Treatment of *trans*-$[FeCl_2(pdmp)_2]$ with an excess of methyllithium gives $[FeMe_2(pdmp)_2]$, isolated as a *cis*/*trans*-mixture, the methyl groups of which are cleaved by an excess of HX to give $[FeX_2(pdmp)_2]$ (X = Cl, Br), predominantly in the form of the *cis*-isomers. Other new complexes include $[FeCl(Me)(pdmp)_2]$ (*cis*/*trans*-mixture) and $[Fe(L)(pdmp)_2]$ [L = CO, η^2-C_2H_4, η^2-C_8H_8, η^2-1,4-$C_8H_6(SiMe_3)_2$, η^2-C_4H_6, η^2-PhC_2Ph and η^2-MeC_2Me]. Treatment of *trans*-$[FeCl_2(pdmp)_2]$ with sodium–naphthalene generates the hydrido(naphthyl)iron(II) complex $[FeH(\eta^1-C_{10}H_7)(pdmp)_2]$ as a *cis*/*trans*-mixture in tautomeric equilibrium with a zerovalent iron naphthalene complex $[Fe(\eta^2-C_{10}H_8)(pdmp)_2]$. Single crystal X-ray analysis shows that $[Fe(\eta^2-C_2H_4)(pdmp)_2]$ has a distorted octahedral structure in which the ethylene is twisted by *ca.* 15° relative to the FeP_4 skeleton, probably because of steric effects. In solution the coordinated ethylene rotates about the coordination axis with a free energy of activation $\Delta G^{\ddagger}$ at 324 K of 67 kJ mol^{-1}, as estimated from variable temperature ^1H and ^{31}P NMR spectra. In the cyclooctatetraene complexes $[Fe(\eta^2-C_8H_8)(pdmp)_2]$ and $[Fe\{(\eta^2-1,4-C_8H_6)(SiMe_3)_2\}(pdmp)_2]$ there is also a lower energy process in which the $Fe(pdmp)_2$ unit migrates between the double bonds of the eight-membered ring. The strong electron-donating ability of the $Fe(pdmp)_2$ fragment is indicated by the low value of $\nu(CO)$ in $[Fe(CO)(pdmp)_2]$, the highly shielded ^1H and ^{13}C nuclei of coordinated ethylene in $[Fe(\eta^2-C_2H_4)(pdmp)_2]$, the Fe–C and C=C bond lengths in the Fe–C_2H_4 unit [2.052(8) and 1.418(10) Å, respectively], and the facile reversible protonation of the coordinated ethylene by methanol or ethanol. Treatment of $[Fe(\eta^2-C_2H_4)(pdmp)_2]$ with $HBF_4 \cdot OEt_2$ gives initially a complex *cis*-$[Fe(BF_4)(Et)(pdmp)_2]$, in which the ethyl group may be agostic, and finally *cis*-$[Fe(BF_4)_2(pdmp)_2]$. The coordinated BF_4 groups of the latter compound are displaced by acetonitrile to give *cis*-$[Fe(NCMe)_2(pdmp)_2](BF_4)_2$. The BPh_4 salts of the cations $[FeBr(NCMe)(pdmp)_2]^+$ and $[Fe(NCMe)_2(pdmp)_2]^{2+}$ have also been isolated as mixtures of *cis*/*trans*-isomers from *cis*-$[FeX_2(pdmp)_2]$ (X = Cl, Br) and acetonitrile.

Building on the pioneering studies of Nyholm and coworkers on the coordination chemistry of *o*-phenylenebis(dimethylarsine), *o*-$C_6H_4(AsMe_2)_2$ (pdma),[1] Warren and Bennett,[2] and, more recently, Levason and coworkers[3–6] have shown that the corresponding ditertiary phosphine, *o*-$C_6H_4(PMe_2)_2$ (pdmp), forms complexes with the d-block elements in which the metal atom attains unexpectedly high formal oxidation states, *e.g.* +3 and +4 in *trans*-$[MX_2(pdmp)_2]^{n+}$ (X = Cl, Br, M = Mn,[2] Fe,[2,3] Ni,[2,4] Os,[2,5] $n = 1, 2$), +3 in $[CuCl(pdmp)_2]^{2+}$ and $[Cu(pdmp)_2]^{3+}$,[2] and +6 in *trans*-$[OsO_2Cl_2(pdmp)]$ and *trans*-$[OsO_2(pdmp)_2]^{2+}$.[6] The stability of such compounds can be attributed to a combination of the geometrical rigidity and strong electron-donating ability of pdmp. However, the application of pdmp in organometallic chemistry has not been as widespread as that of its more flexible aliphatic counterparts of similar steric bulk, *viz.*, 1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$ (dmpe) or 1,2-bis(diethylphosphino)ethane, $Et_2PCH_2CH_2PEt_2$ (depe) (see refs. 7 and 8 for recent examples). This remains true even though the earlier low-yielding syntheses of pdmp[2,7,9,10] have been replaced by a reliable, high-yield alternative.[11] In view of the extensive low oxidation state, organometallic and C–H activation chemistry based on $3d^8$ fragments such as $Fe(dmpe)_2$ and $Fe(depe)_2$,[12–21] we thought it worthwhile to make a preliminary survey of the organometallic chemistry of the $Fe(pdmp)_2$ moiety. The results are reported in this paper.

Results and discussion

Since most of the $Fe(pdmp)_2$ complexes reported here are pseudooctahedral, their ^{31}P-$\{^1H\}$ NMR data, collected in Table 1, provide useful stereochemical information.

The starting material for most of the syntheses is *trans*-$[FeCl_2(pdmp)_2]$, *trans*-**1**, which precipitates as a pale green, diamagnetic solid when pdmp is added to a solution of ferrous chloride in ethanol.[2] If the preparation is carried out in thf instead of ethanol, a mixture of the red-brown *cis*- and green *trans*-isomers can be isolated. Supersaturated solutions containing mixtures of *cis*- and *trans*-**1** are formed when the organo- or hydrido-complexes of pdmp (see below) react with chlorinated solvents, thus enabling the ^{31}P parameters of these poorly soluble complexes to be determined. As expected, *trans*-**1** shows a singlet whereas *cis*-**1** shows a pair of well separated triplets arising from an A_2X_2 spin system. The *cis*-dihalides $[FeX_2(pdmp)_2]$ (X = Cl **1**, Br **2**) are also obtained by addition of an excess of HX to the dimethyl compound $[FeMe_2(pdmp)_2]$ (see below).

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Table 1 $^{31}P-\{^1H\}$ NMR data for Fe–pdmp complexes[a]

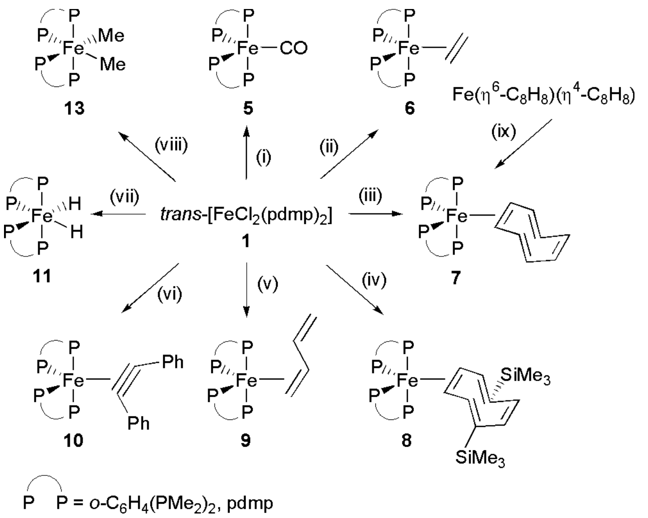
Complex	Isomer	Solvent	δ_P
$[FeCl_2(pdmp)_2]$ **1**	*trans*	$CDCl_3$	59.7 (s)[b]
	cis	$CDCl_3$	58.4 (t), 72.2 (t, $^2J_{PP}$ 49)[b]
$[FeX(NCMe)(pdmp)_2]^+$ **3a**	*trans*	CD_3CN	62.7 (s)[c]
	cis	CD_3CN	60.6 (q, sep 48.2, 52.3, 52.8), 66.7 (q, sep 53.2, 51.3, 54.3), 70.8 (q, sep 43.9, 52.0, 42.5)[c]
$[FeX(NCMe)(pdmp)_2]^+$ **3b**	*trans*	CD_3CN	61.1 (s)[c]
		CD_2Cl_2	58.8 (s)[d]
	cis	CD_3CN	58.4 (t, sep 57.0), 64.4 (q, sep 52.4), 75.7 (q, sep 53.6)[c]
		CD_2Cl_2	57.2 (8-line m), 62.6 (q, sep 53.0), 74.0 (6-line m)[d]
$[Fe(NCMe)_2(pdmp)_2]^{2+}$ **4**	*trans*	CD_3CN	60.7 (s)[e]
	cis	CD_3CN	59.6 (t), 63.3 (t, $^2J_{PP}$ 42.4)[e]
		acetone-d_6	58.3 (t), 62.1 (t, $^2J_{PP}$ 43.5)[f]
$[Fe(CO)(pdmp)_2]$ **5**		C_6D_6	57.6 (s)
$[Fe(\eta^2-C_2H_4)(pdmp)_2]$ **6**		C_6D_6	50.8 (t), 69.8 (t, $^2J_{PP}$ 46.9)
$[Fe(\eta^2-C_8H_8)(pdmp)_2]$ **7**		C_6D_6	46.0–48.4 (11-line m), 50.0–52.5 (6-line m), 63.6–66.2 (8-line m)
$[Fe\{\eta^2-1,4-C_8H_6(SiMe_3)_2\}(pdmp)_2]$ **8**		C_6D_6	46.7 (m), 47.7 (m), 51.9 (m), 65.8 (m)
$[Fe(\eta^2-C_4H_6)(pdmp)_2]$ **9**		C_6D_6	45.4 (6-line m, sep 13.8, 43.6, 43.6), 51.8 (6-line m, sep 13.8, 47.8, 47.8), 59.0 (6-line m, sep 118.7, 48.7, 43.6)
$[Fe(\eta^2-PhC_2Ph)(pdmp)_2]$ **10**		C_6D_6	52.6 (t), 63.8 (t, $^2J_{PP}$ 43.0)
cis-$[FeH_2(pdmp)_2]$ **11**		C_6D_6	61.8 (t), 70.7 (t, $^2J_{PP}$ 29.8)
cis-$[Fe(AlH_4)Cl(pdmp)_2]$ **12**		C_6D_6	68.0 (m)
$[FeMe_2(pdmp)_2]$ **13**	*trans*	C_6D_6	74.2 (s)
	cis	C_6D_6	59.8 (t), 69.6 (t, $^2J_{PP}$ 34.6)
$[FeCl(Me)(pdmp)_2]$ **14**	*trans*	C_6D_6	68.7 (s)
	cis	C_6D_6	53.1 (1:2:1 td), 64.4–65.4 (7-line m), 78.3 (8-line m)
$[FeH(\eta^1-C_{10}H_7)(pdmp)_2]$ **15**	*trans*	thf-d_8	73.2 (s), 73.5 (s)
	cis	thf-d_8	44.7 (br m), 61.4 (br m), 67.5 (br m)
trans-$[FeHCl(pdmp)_2]$ **17**		Et_2O	69.3 (s)
$[Fe(BF_4)(C_2H_5)(pdmp)_2]$ **18**	*trans*	C_6D_6	66.3 (s)
	cis	C_6D_6	47.1 (8-line m), 58.2–68.5 (15-line m), 66.4–68.0 (8-line m)
cis-$[Fe(BF_4)_2(pdmp)_2]$ **19**		CD_2Cl_2	53.0 (t), 70.6 (t, $^2J_{PP}$ 42.0)

[a] Separations and couplings in Hz. [b] Data from solutions of **6** or **11** in $CDCl_3$ that had been set aside for *ca*. 0.5 h. [c] Data from *cis*/*trans*-**1** in CD_3CN. [d] Data from BPh_4 salt of **3b** in CD_2Cl_2. [e] Data from BPh_4 salt of **4** in CD_3CN. [f] Data from BF_4 salt of **4** in acetone-d_6.

Addition of *cis*-**1** or *cis*-**2** to neat acetonitrile gives immediately at room temperature a mixture of *cis*- and *trans*-$[FeX(NCMe)(pdmp)_2]X$ [X = Cl **3a**, Br **3b**], as shown by the $^{31}P-\{^1H\}$ NMR spectra. The cation of **3b** (**3**, X = Br; *cis*/*trans*-mixture) was isolated as its BPh_4 salt. On heating to 80 °C for 24 h in the presence of $NaBPh_4$, the bis(acetonitrile) complex $[Fe(NCMe)_2(pdmp)_2](BPh_4)_2$ **4a** is formed, also consisting of an approximately 1 : 1 mixture of *cis*- and *trans*-isomers. There is no reaction between *trans*-**1** and acetonitrile at room temperature, but at 80 °C in the presence of $NaBPh_4$ the 1 : 1 mixture of *cis*- and *trans*-**4a** is formed again. The crystalline solid that separates on cooling appears to be pure *trans*-**4a** according to an X-ray crystallographic study.[22] The isolation of pure *cis*-**4** as its BF_4 salt **4b** is discussed below. In its $^{31}P-\{^1H\}$ NMR spectrum *trans*-**3b** shows a singlet whereas in *cis*-**3b** all the phosphorus atoms are inequivalent and give rise to three complex multiplets in a 2 : 1 : 1 ratio arising from an ABCD spin system. Correspondingly, the ^1H NMR spectrum of *trans*-**3b** contains a pair of quintets due to the inequivalent P–Me groups, whereas in *cis*-**3b** all the P–Me groups are inequivalent and appear as eight doublets. The ^{31}P NMR spectra of *cis*- and *trans*-$[Fe(NCMe)_2(pdmp)_2]^{2+}$ **4** resemble those of the corresponding isomers of **1** and **2**. Acetonitrile complexes *trans*-$[FeCl(NCMe)(L–L)_2]BPh_4$ (L–L = pdma,[23] depe[24]) and *trans*-$[Fe(NCMe)_2(depe)_2](BPh_4)_2$[24] are known, but the *cis*-isomers of these cations or of $[FeCl_2(L–L)_2]$ have not been reported and are presumably more labile than their pdmp analogues.

An unsuccessful attempt was made to generate the cation $[FeCl(N_2)(pdmp)_2]^+$, an analogue of $[FeCl(N_2)(dmpe)_2]^+$,[25] by treatment of a suspension of *trans*-**1** in ethanol with $NaBPh_4$ under dinitrogen.

Despite its low solubility, *trans*-**1** reacts rapidly with reducing agents and alkylating agents, as outlined in Scheme 1. In the dmpe series, the *cis*/*trans*-mixture of hydrido(2-naphthyl) complexes $[FeH(C_{10}H_7)(dmpe)_2]$ obtained from *trans*-$[FeCl_2(dmpe)_2]$ and $NaC_{10}H_8$ (2 equiv.) is a convenient room temperature source of the 16-electron $Fe(dmpe)_2$ fragment,[12] but the analogous pdmp system seems generally to work only at *ca*. 65 °C (see below). Reaction of *trans*-**1** with sodium-amalgam in thf gives a deep red, thermally unstable solution which we have been unable to characterise but which functions as a source of $Fe(pdmp)_2$ in some of its reactions. Thus, in the presence of CO, the red 18e complex $[Fe(CO)(pdmp)_2]$ **5** is formed in high yield. Its IR spectrum in thf shows one ν(CO) band at 1825 cm⁻¹, *cf.* 1812 cm⁻¹ (C_6D_6),[12] 1830 cm⁻¹ (thf)[26] for $[Fe(CO)(dmpe)_2]$.[12] The ^{31}P NMR spectrum contains only a



Scheme 1 (i) Na/Hg, CO; (ii) Na/Hg, C_2H_4; (iii) $K_2C_8H_8$; (iv) $Li_2\{1,4-C_8H_6(SiMe_3)_2\}$; (v) $C_4H_6Mg·2thf$; (vi) $NaC_{10}H_8$, PhC_2Ph; (vii) Na/Hg, H_2 or $LiAlH_4$; (viii) MeLi (excess); (ix) pdmp.

singlet, indicating that complex **5**, which is probably trigonal bipyramidal with equatorial CO, is highly fluxional at room temperature.

Sodium-amalgam reduction of *trans*-**1** under ethylene gives the iron(0)–ethylene complex $[Fe(\eta^2\text{-}C_2H_4)(pdmp)_2]$ **6**. After separation from a pyrophoric by-product, this can be isolated in good yield as a red, crystalline, air-sensitive solid. The ^1H NMR spectrum at 20 °C shows a broad resonance at δ 1.24 corresponding to two of the ethylene protons; the resonance due to the other two is masked by broad singlets due to the P–Me groups. On cooling the latter sharpen and resolve into four singlets.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum at 20 °C in C_6D_6 consists of a pair of triplets, corresponding to the presence of a pair of mutually *cis*-pdmp ligands. In the ^1H NMR spectrum of $[Fe(\eta^2\text{-}C_2H_4)(o\text{-}C_6H_4\{P(CD_3)_2\}_2)]$ **6**-d_{12} at 0 °C, the ethylene protons appear as a pair of broad resonances at δ 1.22 and 0.90, which sharpen on cooling to a pair of multiplets; in the ^{13}C NMR spectrum of **6** at room temperature the ethylene carbon atoms resonate at δ 17.04. These data are consistent with a representation of **6** either as a trigonal bipyramidal iron(0) complex with ethylene occupying an equatorial site or as a pseudooctahedral iron(II) complex (ferracyclopropane); confirmation is provided by the X-ray crystal structure discussed below. The marked upfield shifts of the ethylene ^1H and ^{13}C nuclei presumably reflect strong back-bonding into the ethylene π^*-orbital, although comparison with the value for the average chemical shift of the ethylene protons in $[Fe(\eta^2\text{-}C_2H_4)(dmpe)_2]$ (δ 0.59) suggests that back-bonding from the $Fe(dmpe)_2$ fragment may be even stronger.

As the temperature of the solution of **6**-d_{12} is raised, the ethylene resonances reversibly broaden and coalesce to a singlet at δ 1.0; the free energy of activation $\Delta G^\ddagger$ for the fluxional process at the coalescence temperature (324 K) calculated from the equation $k = \pi\Delta\nu/\sqrt{2}$[27] is 67.3 kJ mol^{-1}. An independent estimate of $\Delta G^\ddagger$ can be made from the broadening of the ^{31}P resonances of **6**, which becomes evident at 50–60 °C. The linewidths at half-height of the deconvoluted ^{31}P NMR peaks at 324 K and 273 K were 40.0 Hz and 3.54 Hz, respectively, and application of the equation $k = \pi(W_{\frac{1}{2}}{}^* - W_{\frac{1}{2}}{}^\circ)$, which is valid in the slow exchange regime,[27] gave a value of $\Delta G^\ddagger$ of 66.8 kJ mol^{-1} ($W_{\frac{1}{2}}{}^*$ and $W_{\frac{1}{2}}{}^\circ$ are the linewidth at half height at temperature T and the natural linewidth, respectively). As in the case of $[Fe(\eta^2\text{-}C_2H_4)(dmpe)_2]$,[12] the process responsible for these changes must be a 90° rotation of the coordinated ethylene, but the dmpe complex is stereochemically more mobile than the pdmp complex, **6**. Its olefinic protons appear as a single broad resonance at 25 °C and split into two resonances only at −25 °C; similarly, its $^{31}P\{^1H\}$ resonances are broad at 25 °C. In agreement with previous experimental and theoretical work,[27–31] these differences imply a strong connection between the processes of olefin rotation and pseudorotation of the FeP_4 unit, the latter process having a higher barrier for the more rigid pdmp system.

The coordinated ethylene of complex **6** is firmly bound but is displaced by CO at room temperature and atmospheric pressure over a period of several days to give the carbonyl complex **5**. The protonation of complex **6** is discussed below.

In the course of investigating alternative routes to complex **6**, we found that bis(cyclooctatetraene)iron(0), $[Fe(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$,[32,33] reacts with pdmp to give $[Fe(\eta^2\text{-}C_8H_8)(pdmp)_2]$ **7** as a red, thermally robust and fairly air-stable complex. Complex **7** can also be made directly from the reaction of *trans*-**1** with $K_2C_8H_8$, but in much lower yield and purity. The $^{31}P\text{-}\{^1H\}$ NMR spectrum consists of complex overlapping multiplets showing the four phosphorus atoms to be inequivalent, suggesting that the eight-membered ring is non-planar, probably with a tub conformation similar to that found in $[Mn(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_8H_8)]$.[34] At room temperature, the ^1H NMR spectrum contains a pair of broad resonances, at δ 3.30 ($W_{\frac{1}{2}} = 180$ Hz) and 6.40 ($W_{\frac{1}{2}} = 35$ Hz), attributable to the coordinated and uncoordinated protons, respectively, of the eight-membered ring. These coalesce at higher temperature and separate at −60 °C into six multiplets of equal intensity at δ 2.51, 3.28, 5.22, 5.42, 6.38 and 6.51; the protons of the coordinated C=C bond are probably masked by the P–Me resonances. In addition to rotation of the C_8H_8 ring about the iron–alkene bond, therefore, there is a lower energy process in which the $Fe(pdmp)_2$ unit migrates between the double bonds. In contrast, the eight-membered ring in $[Mn(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_8H_8)]$ shows no fluxional behaviour below its decomposition temperature (*ca.* 75 °C).[34] The lower energy process is hindered in the corresponding η^2-1,4-bis(trimethylsilyl)cyclooctatetraene complex, $[Fe\{\eta^2\text{-}1,4\text{-}C_8H_6(SiMe_3)_2\}(pdmp)_2]$ **8**, which is formed in high yield from the reaction of *trans*-**1** with $Li_2\{1,4\text{-}C_8H_6(SiMe_3)_2\}$. At room temperature, the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows four separate multiplets and the ^1H NMR spectrum shows broad multiplets at δ 2.79(1H), 3.52(1H) and 6.30(2H); the absence of proton resonances in the region δ 5–6 implies that the iron atom is probably bound to carbon atoms 6 and 7, thus placing the bulky $SiMe_3$ groups as far as possible from the $Fe(pdmp)_2$ unit.

Attempts to prepare a butadiene complex by reaction of *trans*-**1** with Na/Hg in the presence of butadiene were unsuccessful, but treatment with but-2-ene-1,3-diylmagnesium, $C_4H_6Mg\cdot 2thf$,[35,36] gives the deep red, very air-sensitive complex $[Fe(\eta^2\text{-}C_4H_6)(pdmp)_2]$ **9** whose complex $^{31}P\text{-}\{^1H\}$ NMR spectrum indicates that the phosphorus atoms are inequivalent, as expected. The ^1H NMR spectrum in C_6D_6 shows three broad resonances of equal intensity at δ 6.35, 5.25 (doublet) and 4.95 assignable to the uncoordinated diene protons and a peak at δ 2.95 that may be due to one of the coordinated diene protons.

Reduction of *trans*-**1** with Na/Hg in the presence of alkynes such as diphenylacetylene or but-2-yne did not yield alkyne complexes cleanly, but use of $NaC_{10}H_8$ in the presence of an excess of diphenylacetylene gives $[Fe(\eta^2\text{-}PhC_2Ph)(pdmp)_2]$ **10** as a red, air-stable solid. Complex **10** shows bands in its solid state IR spectrum at 1710 and 1685 cm^{-1}, *cf.* 1720 cm^{-1} in $[Fe(\eta^2\text{-}PhC_2Ph)(dmpe)_2]$,[12] and the acetylenic carbon atoms give a signal at δ 143.4 in the ^{13}C NMR spectrum. The $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra are consistent with the presence of a pair of mutually *cis*-pdmp ligands. These data indicate that the alkyne is acting as a 2e donor in a trigonal bipyramidal structure similar to that of the η^2-ethylene complex **6**. The corresponding but-2-yne complex, $[Fe(\eta^2\text{-}MeC_2Me)(pdmp)_2]$, was formed similarly to complex **10** and identified on the basis of its A_2X_2 $^{31}P\text{-}\{^1H\}$ NMR spectrum. The compound could not be isolated because it decomposed in solution to a second, unidentified species containing four inequivalent phosphorus atoms.

Sodium-amalgam reduction of *trans*-**1** under hydrogen gas gave a low yield of the dihydride *cis*-$[FeH_2(pdmp)_2]$ **11**, which could be separated only with difficulty from a pyrophoric by-product. Complex **11** is obtained in higher yield and purity as a yellow solid by reduction of *trans*-**1** with an excess of $LiAlH_4$ and subsequent hydrolysis. If the hydrolysis step is omitted, an intermediate orange solid can be isolated, whose composition, based on microanalysis and mass spectrometry, corresponds to the formula $[Fe(AlH_4)Cl(pdmp)_2]$ **12**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum consists of a complex, symmetrical multiplet centred at δ 68.0; the ^1H NMR spectrum contains four one-proton triplet resonances in the range δ 0.2–2.2, which may be due to Al–H protons, in addition to a pair of 12H-resonances suggestive of the presence of *cis*-pdmp ligands. The nature of this intermediate requires further investigation. In contrast to the $LiAlH_4$ reduction of $[FeCl_2(dmpe)_2]$ or $[FeCl_2(depe)_2]$,[18,37,38] the monohydride *trans*-$[FeHCl(pdmp)_2]$ could not be detected as an intermediate.

Reaction of *trans*-**1** with two equivalents of methyllithium gives the dimethyl complex $[FeMe_2(pdmp)_2]$ **13**, which we isolated in 64% yield as a mixture of the *cis*- and *trans*-isomers. Monitoring by ^{31}P NMR spectroscopy showed that *cis*-**13** was formed initially but this underwent partial isomerisation as the solution was concentrated, and at equilibrium the ratio of *trans*- to *cis*-**13** in d_8-thf was *ca.* 1 : 4. Consistent with the electron-rich nature of the fragment Fe(pdmp)$_2$, the iron–methyl resonances of both isomers in C_6D_6 are highly shielded, *viz.* a quintet at δ −1.80 (J_{PH} 5.9 Hz) for *trans*-**13** and a multiplet at δ −0.27 for *cis*-**13**. As in the case of the ethylene complexes, however, the shieldings are not as high as those of the corresponding dimethyliron(II) complexes containing dmpe, *viz.*, *trans*-[FeMe$_2$(dmpe)$_2$]: δ −2.02(toluene-d_8);[39] *cis*-[FeMe$_2$(dmpe)$_2$]: δ −0.99(toluene-d_8),[39] −0.64(C_6D_6).[40]

Addition of one equivalent of HCl in ether to a mixture of *cis*- and *trans*-**13** in toluene gives a red-brown solid containing the corresponding chloro(methyl)iron(II) complexes, *cis*- and *trans*-[FeCl(Me)(pdmp)$_2$] **14**. The *trans*-isomer was obtained in reasonable purity, as shown by ^{31}P NMR spectroscopy, by washing the mixture with pentane, in which it is poorly soluble. The chloro(methyl) complexes could not be obtained by treatment of *trans*-**1** with one equivalent of methyllithium, nor could they be detected as intermediates in the formation of the dimethyl complex **13**. Treatment of complex **13** with more than two equivalents of HCl or HBr in ether precipitated brown-red and brown-green solids, respectively, identified as containing mainly *cis*-**1** and *cis*-**2**, on the basis of their elemental analysis and ^{31}P-{^{1}H} NMR spectra in CD_3CN (see above).

Reaction of *trans*-1 with sodium–naphthalene (two equivalents)

The IR spectrum of the very air-sensitive solid (**15**) isolated from this reaction carried out under argon in thf shows *ν*(FeH) bands at 1721 and 1765 cm^{-1}, and the ^{1}H NMR spectrum contains multiplet hydride resonances at δ −13.6 and −18.2. The chemical shifts are close to those reported[12] for *cis*- and *trans*-[FeH(η^1-2-$C_{10}H_7$)(dmpe)$_2$], respectively. Unexpectedly, however, the ^{31}P-{^{1}H} NMR spectrum shows *two* sharp singlets at δ 73.2 and 73.5, whereas *trans*-[FeH(η^1-2-$C_{10}H_7$)(dmpe)$_2$] has the expected singlet, at δ 74.2.[12] In addition, there are three very broad resonances at δ 44.7, 61.4 and 67.5 in a ratio of 1 : 1 : 2 in the ^{31}P-{^{1}H} NMR spectrum of the pdmp complex, whereas the corresponding complex multiplets in *cis*-[FeH(η^1-2-$C_{10}H_7$)(dmpe)$_2$] in the range δ 50–75 are well-resolved. We suggest tentatively that [FeH(η^1-$C_{10}H_7$)(pdmp)$_2$] **15** contains both 1- and 2-naphthyl derivatives, each as a *cis*/*trans*-mixture, and that the *cis*-isomers are in rapid equilibrium with an undetected, zerovalent iron naphthalene complex, [Fe(η^2-$C_{10}H_8$)(pdmp)$_2$] **16**. Treatment of compound **15** with an excess of DCl gives naphthalene containing no deuterium, *i.e.* deuterolysis must proceed entirely *via* the reactive tautomer **16**. In contrast, reaction of *cis*-[FeH(η^1-2-$C_{10}H_7$)(dmpe)$_2$] with DCl gives naphthalene containing *ca.* 20% of 2-$C_{10}H_7D$, as shown by ^{2}H NMR spectroscopy and GC-MS; a similar result has been reported for the reaction of DCl with *cis*-[RuH(η^1-2-$C_{10}H_7$)(dmpe)$_2$].[41]

Attempts to obtain a dinitrogen complex analogous to [Fe(η^1-N_2)(depe)$_2$][42] by treatment of *trans*-**1** in thf with sodium–naphthalene under nitrogen gave a mixture of **15** and the dihydride **11**. The same mixture is formed if a solution of **15** in thf is exposed to nitrogen; in *n*-hexane or cyclohexane, however, **11** is not observed. This behaviour has not been investigated further.

Addition of an equimolar quantity of HCl to complex **15** gives mainly **1** as a *cis*/*trans*-mixture and unchanged starting material. Only a small amount of a compound assumed to be *trans*-[FeHCl(pdmp)$_2$] **17**, identified by its quintet hydride resonance and singlet ^{31}P-{^{1}H} NMR signal (Table 1), could be detected. Complex **15** is unaffected by ethylene at room temperature and reacts to give [Fe(η^2-C_2H_4)(pdmp)$_2$] **6** only at 65 °C; in contrast, *cis*-[FeH(η^1-2-$C_{10}H_7$)(dmpe)$_2$] reacts with ethylene at room temperature.[12] Preliminary experiments show that complex **15** also reacts with hex-3-yne only at 65 °C, whereas reactions with benzene and terminal alkynes occur at room temperature.

Table 2 Selected bond distances (Å) and interbond angles (°) in [Fe(η^2-C_2H_4)(pdmp)$_2$] **6**

Molecule 1		Molecule 2	
Fe(1)–C(21)	2.052(8)	Fe(2)–C(51)	2.052(8)
Fe(1)–C(22)	2.045(9)	Fe(2)–C(52)	2.047(8)
C(21)–C(22)	1.409(14)	C(51)–C(52)	1.427(14)
Fe(1)–P(11)	2.173(2)	Fe(2)–P(21)	2.174(2)
Fe(1)–P(12)	2.154(2)	Fe(2)–P(22)	2.147(2)
Fe(1)–P(13)	2.176(2)	Fe(2)–P(23)	2.168(2)
Fe(1)–P(14)	2.142(2)	Fe(2)–P(24)	2.139(2)
C(21)–Fe(1)–C(22)	40.2(4)	C(51)–Fe(2)–C(52)	40.7(4)
C(21)–Fe(1)–P(12)	110.0(3)	C(52)–Fe(2)–P(23)	109.5(4)
C(22)–Fe(1)–P(14)	106.9(3)	C(52)–Fe(2)–P(22)	106.6(4)
P(11)–Fe(1)–P(13)	179.6(1)	P(21)–Fe(2)–P(23)	179.2(1)
P(11)–Fe(1)–P(12)	84.6(1)	P(21)–Fe(2)–P(22)	85.3(1)
P(13)–Fe(1)–P(14)	85.3(1)	P(23)–Fe(2)–P(24)	85.1(1)
P(12)–Fe(1)–P(14)	104.0(1)	P(22)–Fe(2)–P(24)	104.3(1)

Protonation reactions

As expected for an alkene coordinated to an electron-rich, low-valent metal centre,[43] the ethylene in [Fe(η^2-C_2H_4)(pdmp)$_2$] **6** is readily protonated. Addition of one equivalent of HBF_4·OEt_2 to a solution of **6** in ether gave a pale yellow, air- and moisture-sensitive solid, the ^{1}H NMR spectrum of which in CD_2Cl_2 shows broad multiplets due to an ethyl group at δ 0.60(2H) and δ 1.44(3H). The ^{31}P-{^{1}H} NMR spectrum contains a complex pattern of overlapping multiplets due to inequivalent phosphorus atoms. The microanalysis corresponds approximately to the formula [Fe(BF_4)(C_2H_5)(pdmp)$_2$] **18**, but further work is required to establish whether the compound would be better represented as an agostic ethyl complex, [Fe(CH_2CH_2-μ-H)(pdmp)$_2$]BF_4.[44] The ^{31}P-{^{1}H} NMR spectrum of the yellow solution of complex **6** in ethanol is very similar to that of **18**, suggesting that even ethanol is sufficiently acidic to protonate the coordinated ethylene; removal of ethanol regenerates complex **6** almost quantitatively. This behaviour is reminiscent of the protonation of [FeH_2(dmpe)$_2$] by ethanol to give [FeH(η^2-H_2)(dmpe)$_2$]$^+$, the labile η^2-dihydrogen of which is readily replaced by Cl$^-$ to give *trans*-[FeHCl(dmpe)$_2$].[18] The dihydride **11** also reacts with methanol and ethanol but we have not been able to identify conclusively the analogous cation [FeH(η^2-H_2)(pdmp)$_2$]$^+$.

Addition of an excess of HBF_4·OEt_2 to complexes **6**, **7** or **11** cleaves the Fe–H (**11**) or Fe–C (**6**, **7**) bonds to give the mauve-grey solid *cis*-[Fe(BF_4)$_2$(pdmp)$_2$] **19**. The corresponding bis(triflato) complex *cis*-[Fe(CF_3SO_3)$_2$(pdmp)$_2$] can be made similarly by use of triflic acid. We assume that in these compounds the anions are bound weakly to iron in a monodentate fashion,[45] perhaps similarly to the perchlorate groups in the monoclinic modification of *trans*-[Co(ClO_4)$_2$(pdma)$_2$].[46] Complex **19** immediately forms an orange solution in acetonitrile from which the salt *cis*-[Fe(NCMe)$_2$(pdmp)$_2$](BF_4)$_2$, *cis*-**4b**, can be isolated as a yellow powder. The ^{31}P-{^{1}H} NMR spectrum shows that the pdmp groups retain their *cis*-arrangement and there is no trace of the corresponding *trans*-isomer (see above).

Molecular structure of [Fe(η^2-C_2H_4)(pdmp)$_2$] 6

Crystals of **6** contain two crystallographically independent but metrically similar molecules in each asymmetric scattering unit. The molecules are separated by normal van der Waals contacts and exhibit virtual C_2 symmetry. Diagrams of each, one viewed parallel and one viewed perpendicular to the virtual twofold axis, are shown in Fig. 1, together with the atom numbering schemes; hydrogen atoms of the pdmp ligands are omitted for

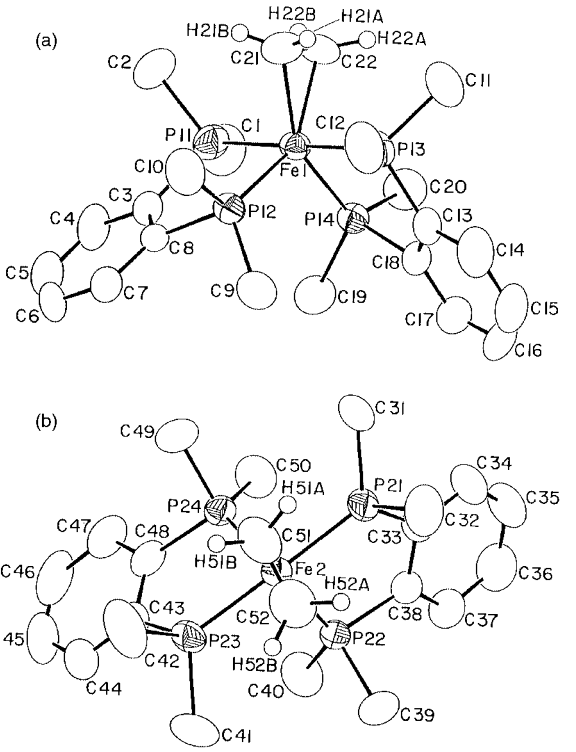


Fig. 1 Molecular structure of $[Fe(\eta^2-C_2H_4)(pdmp)_2]$ **6**, viewed (a) parallel and (b) perpendicular to the virtual twofold axis, with atom labelling and 30% probability ellipsoids.

clarity. Selected bond lengths and interbond angles are listed in Table 2. The coordination geometry about the metal atom can be described as approximately trigonal bipyramidal, with two axial and two equatorial phosphorus atoms of pdmp and the third equatorial site occupied by the mid-point of dihapto-ethylene, or as a slightly distorted octahedron with the ethylene occupying one edge. In both molecules the ethylene ligands are twisted by about 15° relative to the FeP_4 skeleton, probably owing to intramolecular steric interaction between the ethylene hydrogen atoms and neighbouring phosphorus and methyl groups of the pdmp ligands. In addition, the ethylene ligands also exhibit an in-plane tilting displacement, which is manifested in the inequivalence of the P(equatorial)–Fe–C angles and of the P · · · C non-bonding contact distances. This deformation is, again, metrically similar in both molecules [Δ{P(equatorial)–Fe–C} = 3.1, 2.9°] but, unlike the twist deformation, it does not conform to the virtual C_2 symmetry of the $Fe(pdmp)_2$ fragment.

The Fe–C(ethylene) distance in complex **6** [2.052(8) Å] is significantly less than those reported for the trigonal bipyramidal iron(0) complexes $[Fe(CO)_4(\eta^2-C_2H_4)]$ **20** [2.117(3) Å],[47] $[Fe(CO)_3(PPh_3)(\eta^2-C_2H_4)]$ **21** [2.095(7), 2.102(7) Å],[48] $[Fe(CO)_2\{P(OMe)_3\}_2(\eta^2-C_2H_4)]$ **22** [2.111(4) Å],[49] and $[Fe(CO)_2\{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2\}(\eta^2-C_2H_4)]$ **23** [2.125(4), 2.113(4) Å],[50] all of which contain auxiliary ligands that are probably stronger π-acceptors than pdmp. Correspondingly, the C–C (ethylene) distance in **6** [av. 1.418(10) Å] exceeds those in **22** and **23** [1.369(6) and 1.362(7) Å, respectively], although it is not significantly different from that in **21** [1.398(8) Å]. These data indicate strong $Fe–C_2H_4$ back-donation in **6** induced by the strong σ-donor and poor π-acceptor abilities of the $Fe(pdmp)_2$ fragment. The $Fe–C_2H_4$ unit in **6** has ferracyclopropane character, as is evident from the average dihedral angle between the H–C–H planes of 64°, *cf.* 0° for free ethylene and 109° 47′ for the eclipsed form of ethane.

As was also observed in complex **23**, the Fe–P(axial) bond distances in **6** [av. 2.172(2) Å] are significantly greater than the Fe–P(equatorial) distances [av. 2.145(2) Å]; a presumably associated contraction of the P(axial)–C(phenyl) relative to the P(equatorial)–C(phenyl) distance [1.830(4) Å, 1.849(3) Å, respectively; $\Delta/\sigma \approx 4$] is also evident.

Conclusion

The electron-rich fragment $Fe(pdmp)_2$, like its more extensively studied $Fe(dmpe)_2$ counterpart, forms complexes with CO and with unsaturated hydrocarbons in which there is strong back-bonding to the added ligands. The π-donor ability of $Fe(pdmp)_2$ may be slightly less than that of $Fe(dmpe)_2$ as a consequence of the presence of the aromatic linking group but this feature may serve to stiffen the chelate ring so that one-ended dissociation is less likely. The greater rigidity may also be responsible for the apparently higher barrier to rotation of coordinated ethylene in the $Fe(pdmp)_2$ complex. The iron chemistry of pdmp differs from that of dmpe and depe in other subtle ways, *e.g.* the zerovalent iron tautomer $[Fe(\eta^2-C_{10}H_8)(L–L)_2]$ plays a more significant role in the chemistry of $[FeH(\eta^1-C_{10}H_7)(L–L)_2]$ for L–L = pdmp than for L–L = dmpe, and the behaviour of *cis*-$[FeH_2(pdmp)_2]$ towards protons is more complex than that established for the dmpe and depe analogues. These differences may also arise from the tighter and more compact binding of the aromatic-based ligand but at present we cannot offer a detailed explanation. So far, we have been unable to isolate intermediates that could be used to generate the $Fe(pdmp)_2$ fragment at room temperature and thus allow access under mild conditions to a wider range of zerovalent iron complexes of pdmp. This problem may limit the utility of $Fe(pdmp)_2$ as an electron-rich fragment in organometallic chemistry.

Experimental

All reactions and subsequent manipulations were carried out under dry nitrogen or argon with use of standard Schlenk techniques. Solvents were dried and distilled before use by standard methods. NMR spectra were recorded at 20 °C on Varian XL200E (^2H at 30.7 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz), Gemini 300BB and Varian VXR300 (^{13}C at 75.4 MHz, ^{31}P at 121.4 MHz) and Inova 500 spectrometers and were referenced to the residual protons of deuterated solvents (^1H), the signals of the solvent (^{13}C), and to external 85% H_3PO_4 (^{31}P). $^{31}P-\{^1H\}$ NMR data are listed in Table 1. Variable temperature NMR spectra were measured on the VXR300 instrument. IR spectra were measured on Perkin-Elmer 683 grating or 1800 Fourier-transform spectrometers. Mass spectra were measured by the electron impact (EI) method at 70 eV on a VG Micromass 7070F spectrometer or by the fast-atom bombardment (FAB) technique on a VG ZAB2-SEQ spectrometer. Elemental analyses were performed in-house.

The compounds pdmp,[11] dmpe,[51] *trans*-$[FeCl_2(dmpe)_2]$,[40] $[Fe(\eta^6-C_8H_8)(\eta^4-C_8H_8)]$,[33] $K_2[C_8H_8]$,[52] $Li_2[1,4-C_8H_6(SiMe_3)_2]$[53] and $C_6H_4Mg\cdot 2thf$[35,36] were prepared by published procedures. The ligand *o*-$C_6H_4\{P(CD_3)_2\}_2$, pdmp-d_{12}, was made similarly to pdmp with use of CD_3I in place of CH_3I. Anhydrous ferrous chloride was made by reduction of anhydrous $FeCl_3$ with iron powder in thf;[54] the resulting solid was heated *in vacuo* at 85 °C to give a material whose composition corresponded approximately to the formula $[FeCl_2(thf)]$.[55]

Preparations

***trans*-$[FeCl_2(pdmp)_2]$, *trans*-1.**[2] *Method* (*i*). A vigorously stirred solution of $[FeCl_2(thf)]$ (1.98 g, 9.9 mmol) in ethanol (70 cm^3) was treated dropwise with pdmp (3.6 cm^3, 19.2 mmol). After an initial red coloration, a green precipitate formed. The suspension was stirred for 1 h at room temperature and the light green precipitate was separated from the pale pink solution by filtration. After the solid had been washed with ethanol (3 × 20 cm^3) and dried *in vacuo*, the yield was 4.50 g (87%).

Method (*ii*). A vigorously stirred solution of [$FeCl_2$(thf)] (1.90 g, 9.5 mmol) in thf (50 cm^3) was treated dropwise with pdmp (3.45 cm^3, 19.2 mmol). The mixture was stirred for 1 h at room temperature and the mixture of brown-red and green solids (*cis*- and *trans*-**1**) was separated from the colourless solution by filtration. After the solid had been washed with hexane (3 × 20 cm^3) and dried *in vacuo*, the yield was 4.3 g (87%). The mixture was converted into *trans*-**1** after stirring in ethanol for 1 h (Found: C, 46.6; H, 6.5; Cl, 13.1; P, 22.2%; $C_{20}H_{32}Cl_2FeP_4$ requires: C, 45.9; H, 6.2; Cl, 13.55; P, 23.7%); FAB-MS (ethanol) *m*/*z* 522(M^+), 487(M^+ − Cl).

***cis*-[FeCl$_2$(pdmp)$_2$], *cis*-1.** A suspension of freshly prepared *cis*-[$FeMe_2$(pdmp)$_2$] **12** (see below) (0.32 g, 0.66 mmol) in toluene (30 cm^3) was cooled to −25 °C and treated dropwise from a syringe with a solution of HCl in ether (2.0 cm^3, 1.43 M, 2.9 mmol) to give a red-brown precipitate. The colourless supernatant liquid was removed by cannulation and the residue was washed with pentane (3 × 15 cm^3) and dried *in vacuo*. The yield was 0.22 g (64%) (Found: C, 45.7; H, 6.3%. $C_{20}H_{32}Cl_2FeP_4$ requires: C, 45.9; H, 6.2%).

***cis*-[FeBr$_2$(pdmp)$_2$], *cis*-2.** A suspension of [$FeMe_2$(pdmp)$_2$] **12** (see below) (0.18 g, 0.37 mmol) in toluene (30 cm^3) was cooled to −25 °C and treated dropwise with a solution of HBr in ether (4.0 cm^3, 0.2 M, 0.8 mmol) to give a red-brown precipitate. The colourless supernatant liquid was removed by cannulation and the brown solid was washed with pentane (2 × 10 cm^3) to give *cis*-**2** (0.10 g, 44%) (Found: C, 40.3; H, 5.6; Br, 26.0%. $C_{20}H_{32}Br_2FeP_4$ requires: C, 39.2; H, 5.3; Br, 26.1%).

***cis*- and *trans*-[FeBr(NCMe)(pdmp)$_2$]BPh$_4$, 3b.** To a mixture of *cis*-**2** (55 mg, 0.09 mmol) and $NaBPh_4$ (33 mg, 0.1 mmol) was added a solution of acetonitrile (3 μl) in CH_2Cl_2 (5 cm^3). The orange-brown supernatant liquid was separated by decantation from a white precipitate (presumably NaBr) and evaporated to dryness under reduced pressure. The residue was redissolved in the minimum volume of CH_2Cl_2 and hexane was added slowly to the solution to give the mixture of *cis*- and *trans*-**3b** as an orange-brown solid (Found: C, 62.0; H, 6.4%. $C_{46}H_{55}BBrFeNP_4$ requires: C, 61.9; H, 6.2%). *cis*-**3b**: ^1H NMR (CD_2Cl_2) δ 0.62 (d, 3 H, PMe, J_{PH} 8.0 Hz), 0.69 (d, 3 H, PMe, J_{PH} 7.6 Hz), 1.18 (d, 3 H, PMe, J_{PH} 9.1 Hz), 1.51 (d, 3 H, PMe, J_{PH} 9.9 Hz), 1.80 (br s, 3 H, MeCN), 1.90 (d, 3 H, PMe, J_{PH} 7.1 Hz), 1.92 (d, 3 H, PMe, J_{PH} 5.4 Hz), 2.07 (d, PMe, 3 H, J_{PH} 7.1 Hz), 2.19 (d, 3 H, PMe, J_{PH} 7.1 Hz), 6.88 (t, 4 H, *J* 7.2 Hz), 7.03 (t, 8 H, *J* 7.2 Hz), 7.35 (m, 8 H) (BPh_4), 7.48 (ABq, 8 H, *J* 8.4 Hz, C_6H_4). *trans*-**3b**: ^1H NMR (CD_2Cl_2) δ 1.66 (qnt, 12 H, PMe), 2.12 (qnt, 12 H, PMe). FAB-MS (ethanol) *m*/*z* 573 (M^+ + H), 531 [FeBr(pdmp)$_2$].

***cis*- and *trans*-[Fe(NCCD$_3$)$_2$(pdmp)$_2$](BPh$_4$)$_2$, 4a-*d*$_6$.** A suspension of *cis*-**1** (30 mg, 0.06 mmol) in CD_3CN was treated with $NaBPh_4$ (24 mg, 0.07 mmol). After the mixture had been stirred for 5 min, an orange solution had formed together with a white solid, which was removed by centrifugation. The ^{31}P-{^1H} NMR spectrum of the orange solution showed the presence of *cis*- and *trans*-**3a**-*d*$_6$. Additional $NaBPh_4$ (24 mg, 0.07 mmol) was added and the mixture was heated at 60–80 °C for 96 h. At this stage the ^{31}P-{^1H}NMR spectrum showed the presence of *trans*-**4a**-*d*$_6$ (δ 61.0), *cis*-**4a**-*d*$_6$ [δ 59.9 (t), 63.6 (t, $^2J_{PP}$ 42.4 Hz)] and some unchanged *cis*- and *trans*-**3a**-*d*$_6$. Another 20 mg of $NaBPh_4$ was added and the mixture was heated again at 80 °C for 12 h. The ^{31}P-{^1H}NMR spectrum showed the main product to be *cis*-**4**-*d*$_6$, together with a small amount of *trans*-**4**-*d*$_6$. The product was isolated by evaporating to dryness and washing the yellow solid with ether (Found: C, 72.6; H, 6.65; N, 2.3%. $C_{70}H_{72}D_6B_2FeN_2P_4$ requires: C, 73.7; H, 6.7; N, 2.4%); IR (cm^{-1}, Nujol) 2100w [ν(CN)].

[Fe(CO)(pdmp)$_2$] 5. To a stirred suspension of 1% sodium-amalgam (5 mmol Na, excess) in thf (60 cm^3) under an atmosphere of CO was added solid *trans*-**1** (0.50 g, 0.96 mmol). The mixture was stirred for 2 h and the deep red solution was separated by decantation. Solvent was removed *in vacuo* and the solid residue was purified by crystallisation from hexane at −25 °C to give complex **5** as a red crystalline solid. The yield was 0.28 g (61%) (Found: C, 52.3; H, 7.0%. $C_{21}H_{32}FeOP_4$ requires: C, 52.5; H, 6.7%). ^1H NMR (C_6D_6) δ 1.55 (s, 24 H, PMe), 7.15 (br, 4 H), 7.37 (br, 4 H) (C_6H_4); IR (thf) 1825 cm^{-1} (ν_{CO}); EI-MS *m*/*z* 480 (M^+), 452 (M^+ − CO).

[Fe(η^2-C$_2$H$_4$)(pdmp)$_2$] 6. To a rapidly stirred suspension of 1% sodium-amalgam (10 mmol Na) in thf (100 cm^3) under ethylene was added solid *trans*-**1** (1.50 g, 2.87 mmol). After 1 h the deep red solution was separated by decantation and evaporated to dryness *in vacuo*. The residual solid was crystallised from hexane at −25 °C to give complex **6** as large red crystals, some of which were of X-ray quality. The yield was 0.95 g (69%) (Found: C, 54.7; H, 7.7; Fe, 11.5%. $C_{22}H_{36}FeP_4$ requires: C, 55.0; H, 7.6; Fe, 11.6%). ^1H NMR (C_6D_6) δ 0.94 (s, 14 H, PMe, CH_2CH_2), 1.24 (br s, 2 H, CH_2CH_2), 1.53 (s, 6 H, PMe), 1.63 (s, 6 H, PMe), 7.08 (br s, 4 H), 7.31 (br s, 4 H) (C_6H_4); ^{13}C-{^1H} NMR (C_6D_6) δ 14.36 (m, PMe, J_{CH} 124 Hz), 17.04 (m, C_2H_4, J_{CH} 144 Hz), 18.38 (m, PMe, $^1J_{CH}$ 128 Hz), 21.08 (m, PMe, $^1J_{CH}$ 126 Hz), 26.66 (m, PMe, $^1J_{CH}$ 126 Hz), 126.4 (m, C_6H_4, $^1J_{CH}$ 163 Hz), 150 (br s, C_6H_4), 153 (br s, C_6H_4); EI-MS *m*/*z* 452 (M^+ − C_2H_4).

[Fe(η^2-C$_8$H$_8$)(pdmp)$_2$] 7. *Method* (*a*). A solution of pdmp (1.26 g, 6.36 mmol) in thf (50 cm^3) was treated with solid [Fe(η^6-C_8H_8)(η^4-C_8H_8)] (0.84 g, 3.18 mmol) and the mixture was stirred for 18 h, after which time the reaction was complete as judged by ^{31}P NMR spectroscopy. The deep red solution was evaporated to dryness *in vacuo* to give a brick-red powder. Recrystallisation from ether gave violet crystals of **7** (1.41 g, 80%).

Method (*b*). A suspension of *trans*-**1** (0.20 g, 0.38 mmol) in thf (20 cm^3) was treated dropwise with a freshly prepared solution of $K_2[C_8H_8]$ (*ca*. 0.5 mmol) and the mixture was stirred at room temperature for 12 h. The solvent was removed *in vacuo* and the dark red residue was extracted with hexane at −25 °C. Crystallisation from hexane gave complex **7** in 5–10% yield (Found: C, 60.6; H, 7.6; Fe, 9.9%. $C_{28}H_{40}FeP_4$ requires: C, 60.45; H, 7.25; Fe, 10.0%). ^1H NMR (C_6D_6) δ 0.58 (d, 3H, PMe, J_{PH} 5.3 Hz), 0.66 (d, 3 H, PMe, J_{PH} 5.2 Hz), 1.07 (d, 3 H, PMe, J_{PH} 6.7 Hz), 1.52 (d, 3 H, PMe, J_{PH} 6.0 Hz), 1.60 (d, 3 H, PMe, J_{PH} 8.1 Hz), 1.66 (d, 3 H, PMe, J_{PH} 6.3 Hz), 1.81 (d, 3 H, PMe, J_{PH} 6.2 Hz), 1.88 (d, 3 H, PMe, J_{PH} 6.5 Hz), 3.30 (br, 2 H, C_8H_8), 6.40 (br, 6 H, C_8H_8), 7.1–7.5 (br m, C_6H_4); EI-MS *m*/*z* 556 (M^+), 452 [Fe(pdmp)$_2$$^+$].

[Fe{η^2-1,4-C$_8$H$_6$(SiMe$_3$)$_2$}(pdmp)$_2$] 8. Dropwise addition of *n*-butyllithium in hexane (3.25 cm^3, 1.6 M, 5.2 mmol) to a solution of 1,4-C_8H_8($SiMe_3$)$_2$ (0.65 g, 2.60 mmol) in thf (30 cm^3) at −30 °C caused the initially colourless solution to turn orange. *trans*-**1** (1.33 g, 2.54 mmol) was added to the solution at −30 °C. The mixture was allowed to warm to room temperature and was stirred for 12 h. The dark red solution was filtered and evaporated to dryness *in vacuo*. Recrystallisation of the residue from hexane gave complex **8** as a red solid (1.38 g, 78%). ^1H NMR (C_6D_6) δ 0.29 (s, 9 H, $SiMe_3$), 0.49 (s, 9 H, $SiMe_3$), 0.50 (d, 3 H, PMe, J_{PH} 6.9 Hz), 0.58 (d, 3 H, PMe, J_{PH} 5.2 Hz), 0.86 (d, 3 H, PMe, J_{PH} 6.6 Hz), 1.16 (d, 3 H, PMe, J_{PH} 8.5 Hz), 1.36 (d, 3 H, PMe, J_{PH} 6.1 Hz), 1.65 (d, 3 H, PMe, J_{PH} 6.2 Hz), 1.71 (d, 3 H, PMe, J_{PH} 6.5 Hz), 1.80 (d, 3 H, PMe, J_{PH} 6.1 Hz), 2.79 (br, 1 H), 3.52 (br, 1 H), 6.30 (m, 2 H) (C_8H_6; coordinated olefinic protons probably masked by P–Me resonances), 6.9–7.3 (br m, C_6H_4); EI-MS *m*/*z* 700 (M^+), 628 (M^+ − $SiMe_3$ + 1), 452 [Fe(pdmp)$_2$$^+$].

[Fe(η^2-C_4H_6)(pdmp)$_2$] 9. A suspension of *trans*-**1** (0.52 g, 1.0 mmol) in thf (50 cm^3) was treated with [$C_4H_6Mg{\cdot}2thf$] (*ca.* 1.2 equiv.) and the mixture was stirred for 14 h at room temperature. Filtration through Celite and evaporation to dryness *in vacuo* gave **9** as a very air-sensitive red solid, which was recrystallised from thf/hexane (1:4). The yield was 68%. ^{1}H NMR(C_6D_6) δ 0.5–1.8 (br m, 26 H, PMe, 2 H of C_4H_6), 2.95 (br s), 4.95 (br s), 5.25 (d), 6.35 (br s) (each 1 H of C_4H_6), 6.95–7.35 (br m, 8 H, C_6H_4); EI-MS *m*/*z* 452 [Fe(pdmp)$_2$$^+$].

[Fe(η^2-PhC$_2$Ph)(pdmp)$_2$] 10. A mixture of *trans*-**1** (0.17 g, 0.32 mmol) and diphenylacetylene (0.12 g, 0.65 mmol) in thf (30 cm^3) was treated dropwise with a solution of $NaC_{10}H_8$ freshly prepared from naphthalene (2.5 mg, 0.33 mmol) and sodium (0.5 g, excess) in thf (50 cm^3). The colour changed from green to red. After the solution had been stirred for 2 h at room temperature, solvent was removed *in vacuo*. Naphthalene was removed from the residue by sublimation at 40 °C 10^{-4} mm and the residue was recrystallised from hexane to give complex **10** in *ca.* 30% yield (Found: C, 64.5; H, 6.9; Fe, 8.6%. $C_{34}H_{42}FeP_4$ requires: C, 64.8; H, 6.7; Fe, 8.9%). ^{1}H NMR(C_6D_6) δ 0.75 (d, 6 H, PMe, J_{PH} 4.5 Hz), 1.09 (t, 6 H, PMe, J_{PH} 3.4 Hz), 1.37 (t, 6 H, PMe, J_{PH} 2.3 Hz), 1.82 (d, 6 H, PMe, J_{PH} 5.1 Hz); EI-MS *m*/*z* 452 [Fe(pdmp)$_2$$^+$]; IR (cm^{-1}, KBr) 1710m, 1685m [ν(C=C)].

***cis*-[FeH$_2$(pdmp)$_2$] 11.** *Method* (*a*). Solid *trans*-**1** (0.155 g, 0.30 mmol) was added to a suspension of 1% sodium-amalgam (2 mmol Na) in thf (30 cm^3) and the mixture was stirred vigorously for 3 h at room temperature under hydrogen. The dark red supernatant liquid was removed by cannulation and evaporated to dryness *in vacuo* to give a red, pyrophoric solid. Extraction with hexane and several recrystallisations from this solvent gave a poor yield of a yellow solid identified by its ^{1}H and ^{31}P-{^{1}H} NMR spectra as complex **11**.

Method (*b*). An excess of $LiAlH_4$ (0.50 g, 13 mmol) was added to a vigorously stirred suspension of *trans*-**1** (0.50 g, 0.96 mmol) in thf (200 cm^3). After *ca.* 0.5–1 h the starting complex had been consumed and an olive-green solution had formed. This was filtered to remove the excess of $LiAlH_4$ and distilled water (0.10 cm^3) was added, causing vigorous gas evolution. The resulting yellow solution was evaporated to dryness *in vacuo* and the residue was recrystallised from hexane to give complex **11** as a yellow, microcrystalline solid. The yield was 0.37 g (85%) (Found: C, 51.1; H, 7.6%. $C_{20}H_{34}FeP_4$ requires: C, 52.9; H, 7.5%). ^{1}H NMR(C_6D_6) δ −13.08 (br m, 2 H, FeH), 1.18 (br s, 6 H, PMe), 1.56 (br s, 6 H, PMe), 1.70 (br s, 6 H, PMe), 1.85 (br s, 6 H, PMe), 7.30 (br m, 8 H, C_6H_4); EI-MS *m*/*z* 452 (M$^+$ + 2); IR (cm^{-1}, Nujol) 1762m br [ν(FeH)].

***cis*-[Fe(AlH$_4$)Cl(pdmp)$_2$] 12.** An excess of $LiAlH_4$ (0.05 g, 1.3 mmol) was added to a vigorously stirred suspension of *trans*-**1** (0.10 g, 0.19 mmol) in thf (40 cm^3). After *ca.* 1 h the resulting olive green solution was filtered and evaporated to dryness *in vacuo*. Crystallisation of the residue from toluene gave *cis*-[Fe(AlH$_4$)Cl(pdmp)$_2$] (0.08 g, 81%) as an orange microcrystalline solid (Found: C, 46.4; H, 6.45%. $C_{20}H_{36}AlClFeP_4$ requires: C, 46.3; H, 7.0%). ^{1}H NMR(C_6D_6) δ 0.24 (t, 1 H, AlH), 1.32 (t, 1 H, AlH), 1.47 (s, 12 H, PMe), 1.87 (s, 12 H, PMe), 1.90 (t, 1 H, AlH), 2.21 (t, 1 H, AlH), 7.40 (br, 8 H, C_6H_4); EI-MS *m*/*z* 487 (M$^+$ − AlH$_4$), 452 [Fe(pdmp)$_2$$^+$].

[FeMe$_2$(pdmp)$_2$] 13. A vigorously stirred suspension of *trans*-**1** (1.57 g, 3.00 mmol) in thf (100 cm^3) was treated dropwise at room temperature with an ether solution of methyllithium (4.20 cm^3, 1.44 M, 6.00 mmol) and stirring was continued for 2 d. The solution was evaporated to dryness *in vacuo* and the residual orange solid was extracted with toluene (50 cm^3). The orange solution was evaporated to dryness *in vacuo* and the solid was crystallised from hexane to give a mixture of *cis*- and *trans*-**13** (0.92 g, 64%). Recrystallisation from ether gave pure *cis*-**13** in the first fraction and a 1:1 mixture of *cis*- and *trans*-**13** in the second fraction (Found: C, 54.8; H, 8.4%. $C_{22}H_{38}FeP_4$ requires: C, 54.8; H, 7.9%). *cis*-**13**: ^{1}H NMR(C_6D_6) δ −0.27 (m, 6 H, FeMe), 0.68 (d, 6 H, PMe, J_{PH} 3.9 Hz), 1.20 (d, 6 H, PMe, J_{PH} 5.8 Hz), 7.30 (br m, 8 H, C_6H_4); *trans*-**13**: ^{1}H NMR(C_6D_6) δ −1.80 (qnt, 6 H, FeMe, J_{PH} 5.9 Hz), 1.46 (s, 24 H, PMe), 7.30 (br m, 8 H, C_6H_4).

[FeCl(Me)(pdmp)$_2$] 14. A solution of *cis*- and *trans*-**13** (0.35 g, 0.70 mmol) in toluene (100 cm^3) was cooled in dry ice and treated dropwise with an ether solution of HCl (7.50 cm^3, 0.095 M, 0.70 mmol). The initially red solution turned brown and a red-brown precipitate formed. The mixture was evaporated to dryness *in vacuo* and the residual solid was washed with pentane (3 × 20 cm^3). The solid (0.31 g) contained a mixture of *cis*- and *trans*-**14** together with small amounts of *cis*-**13**, *cis*-**1** and *trans*-**1** (Found: C, 49.1; H, 6.6%. $C_{21}H_{35}ClFeP_4$ requires: C, 50.2; H, 7.0%). *trans*-**14**: ^{1}H NMR(C_6D_6) δ −2.73 (qnt, 3 H, FeMe, J_{PH} 7.0 Hz), 1.28 (qnt, 12 H, PMe), 2.18 (qnt, 12 H, PMe). *cis*-**14**: ^{1}H NMR(C_6D_6) δ −0.72 (ddt, 3 H, FeMe, sep, 8.7, 5.6, 1.6 Hz), 0.26 (d, 3 H, PMe, J_{PH} 6.5 Hz), 0.66 (d, 3 H, PMe, J_{PH} 4.7 Hz), 0.89 (d, 3 H, PMe, J_{PH} 8.2 Hz), 1.49 (d, 3 H, PMe, J_{PH} 5.2 Hz), 1.61 (d, 3 H, PMe, J_{PH} 7.6 Hz), 1.79 (d, 3 H, PMe, J_{PH} 7.0 Hz), 1.84 (d, 3 H, PMe, J_{PH} 7.1 Hz), 1.88 (d, 3 H, PMe, J_{PH} 5.9 Hz), 6.84 (t, 1 H, *J* 6.5 Hz), 6.98 (t, 1 H, *J* 7.0 Hz), 7.08 (q, 4 H, *J* 7.4 Hz), 7.43 (q, 2 H, *J* 7.4 Hz) (C_6H_4). EI-MS *m*/*z* 503 (M$^+$), 489 (M$^+$ − Me), 452 [Fe(pdmp)$_2$$^+$].

***cis*- and *trans*-[Fe(BF$_4$)(Et)(pdmp)$_2$] 18.** A red solution of complex **6** (0.17 g, 0.35 mmol) in ether (50 cm^3) was treated dropwise with a dilute solution of $HBF_4{\cdot}OEt_2$ in ether until the supernatant liquid became pale orange. The flocculent, pale yellow precipitate was collected by filtration and dried *in vacuo*. The yield of compound **19** was quantitative (Found: C, 45.0; H, 6.9%. $C_{22}H_{37}BF_4FeP_4$ requires: C, 44.2; H, 6.9%). ^{1}H NMR(CD_2Cl_2) δ 0.60 (br m, 2 H, CH$_2$), 0.80–1.1 (m, 12 H, PMe), 1.44 (br m, 3 H, CH$_2$C*H*$_3$), 1.6–2.0 (br m, 12 H, PMe), 7.5–8.1 (m, 8 H, C_6H_4).

The ^{31}P-{^{1}H} NMR spectrum of the yellow solution of complex **6** in ethanol was almost the same as that of complex **18**, suggesting that either [Fe(OEt)(η^1-C_2H_5)(pdmp)$_2$] or [Fe(η^2-C_2H_5)(pdmp)$_2$]$^+$ had been formed. There were also weak peaks at δ 62.8 (t), 69.8 (t, $^2J_{PP}$ 35.3 Hz), possibly due to *cis*-[Fe(OEt)$_2$(pdmp)$_2$].

***cis*-[Fe(BF$_4$)$_2$(pdmp)$_2$] 19.** Treatment of a solution of complex **6** (0.18 g, 0.38 mmol) in ether (40 cm^3) with an excess of $HBF_4{\cdot}OEt_2$ caused discharge of the red colour and precipitation of complex **19** as a mauve-grey solid, which was separated by filtration and dried *in vacuo*. The yield was quantitative (Found: C, 38.4; H, 5.7%. $C_{20}H_{32}B_2F_8FeP_4$ requires: C, 38.4; H, 5.15%). The compound is very hygroscopic and attempted recrystallisation from CH_2Cl_2/ether gave a monohydrate (Found: C, 37.1; H, 5.3%. $C_{20}H_{34}B_2F_8FeOP_4$ requires: C, 37.3; H, 5.3%). ^{1}H NMR(CD_2Cl_2) δ 0.55 (t, 6 H, PMe, sep, 8.8 Hz), 1.32 (d, 6 H, PMe, $^2J_{PH}$ 10.0 Hz), 1.94 (br m, 6 H, PMe), 2.26 (br m, 6 H, PMe), 7.47–8.15 (br m, 8 H, C_6H_4); IR (Nujol) 1158–1056 cm^{-1} (vs br, BF$_4$).

Complex **19** could be formed similarly from complexes **7** or **11**.

***cis*-[Fe(NCMe)$_2$(pdmp)$_2$](BF$_4$)$_2$·H$_2$O, *cis*-4b.** Addition of acetonitrile (10 cm^3) to complex **19** (50 mg, 0.08 mmol) gave immediately a pale orange solution. Evaporation to dryness *in vacuo* and crystallisation of the residue from CH_2Cl_2/ether gave *cis*-**4b** quantitatively as a yellow powder (Found: C, 39.3; H, 5.5; N, 3.6%. $C_{24}H_{40}B_2F_8FeN_2OP_4$ requires: C, 39.7; H, 5.55; N, 3.9%). ^{1}H NMR (acetone-d_6) δ 0.93 (t, 6 H, PMe, $^2J_{PH}$ + $^4J_{PH}$ 8.4 Hz), 1.57 (t, 6 H, PMe, $^2J_{PH}$ + $^4J_{PH}$ 10.1 Hz), 2.09 (t, 6 H, PMe, ${}^2J_{PH} + {}^4J_{PH}$ 8.7 Hz), 2.29 (t, 6 H, PMe, ${}^2J_{PH} + {}^4J_{PH}$ 8.4 Hz), 2.65 (t, 6 H, *J* 1.7 Hz, MeCN), 2.85 (br s, H_2O), 7.7–8.0 (m, 4 H), 8.4 (m, 4 H) (C_6H_4); IR (cm^{-1}, Nujol) 2100 w [*ν*(CN)].

Reaction of *trans*-1 with sodium–naphthalene. A suspension of *trans*-**1** (161 mg, 0.3 mmol) in thf (20 cm^3) was treated at room temperature with a solution of $NaC_{10}H_8$ that had been prepared from sodium (240 mg, *ca.* 10 mmol) and naphthalene (1.34 g) in thf (30 cm^3). The mixture gradually turned yellow and was stirred for a further 2 h. The solvent was removed *in vacuo* and the solid residue was extracted with pentane (3 × 15 cm^3). The solution was evaporated to dryness and the excess of naphthalene removed at room temperature/10^{-4} mm to give a very air-sensitive, orange-yellow solid believed to contain *cis*- and *trans*-[FeHR(pdmp)$_2$] (R = 1- or 2-$C_{10}H_7$) **15** (see text and Table 1). The yield was 124 mg (71%). ^{1}H NMR (thf-d_8) δ −18.2 (m, FeH of *trans*-**15**), −13.6 (m, FeH of *cis*-**15**), 0.55–1.85 (m, PMe), 6.40–8.15 (m, aromatic); IR (Nujol) 1721, 1765 cm^{-1} [*ν*(FeH)].

Reaction of 15 with DCl. A solution of **15** prepared *in situ* from *trans*-**1** (86 mg, 0.164 mmol) was treated with a solution of 37% DCl in D_2O (0.03 cm^3, 0.375 mmol). The mixture was stirred for 30 min and evaporated to dryness, and the residue was extracted with hexane. Naphthalene (40 mg, 87% of the initial amount) was recovered from the solution and identified by comparison of its EI-mass spectrum with that of a reference sample. The ^{2}H NMR spectrum showed that no deuterium had been incorporated.

In a similar experiment, a solution of [$FeCl_2$(dmpe)$_2$] (129 mg, 0.3 mmol) in thf (10 cm^3) was treated with $NaC_{10}H_8$ that had been prepared from naphthalene (77 mg) and sodium (300 mg) in thf (10 cm^3). The mixture was stirred for 3 h, treated with 37% DCl in D_2O, and stirred again for 10 min. Solvents were removed *in vacuo* and the residue was extracted with pentane. From the extract, a mixture of naphthalene and 2-deuterionaphthalene (75 mg, 97%) was recovered. ^{2}H NMR (hexane/acetone-d_6) δ 7.52 (s, 2-$DC_{10}H_7$); EI-MS *m*/*z* 128 (100%, M^+), 129 (58%, $M^+ + 1$); for pure $C_{10}H_8$, *m*/*z* 128 (100%, M^+), 129 (8%, $M^+ + 1$).

Reaction of 15 with ethylene. A solution of **15** in thf was made from *trans*-**1** (85 mg, 0.16 mmol) and ethylene was passed through it for 4 h. The ^{31}P-{^{1}H} NMR spectrum was unaffected. The solution was then heated to 65 °C with continued bubbling of ethylene. After 2 h, the ^{31}P-{^{1}H} NMR spectrum showed only peaks due to complex **6**.

X-Ray crystallography of 6

Crystal data and data collection parameters. $C_{22}H_{36}FeP_4$, *M* = 480.3, monoclinic, space group *P*2/*n* (non-standard setting of *P*2/*c*, No. 13), $a = 17.216(2)$, $b = 9.333(1)$, $c = 31.391(1)$ Å, $\beta = 97.93(1)°$, $V = 4995.6$ Å^3, $Z = 8$, $D_m = 1.27(1)$; $D_c = 1.28$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 8.84 cm^{-1}, T = 293(2) K, deep red prism with dimensions 0.45 × 0.23 × 0.19 mm. Philips PW 1100/20 diffractometer, θ–2θ scans, data collection range $4 < 2\theta < 50°$, 8848 unique reflections; reflection intensities corrected for crystal degradation (*ca.* 2%)[56] and for Lorentz, polarisation and specimen absorption effects (transmission range 0.81–0.87).[57] Sorting and averaging of equivalent forms yielded 4928 unique reflections with $I \geq 3\sigma(I)$, for which $R_s = 0.036$ and $R_{int} = 0.030$.

Structure solution and refinement. The structure was solved with MULTAN[58] and refined by full-matrix least-squares analysis, minimising $\Sigma w(|F_o| - |F_c|)^2$ with reflection weights $w = [(\sigma_s(F_o))^2 + 0.25(pF_o)^2]^{-1}$ and instrumental uncertainty parameter $p = 0.03$.[59] Hydrogen atoms were clearly apparent in difference maps and were included in the scattering model [ethylene hydrogens as refinable contributors (*x*,*y*,*z*,*B*; phosphine ligand hydrogens as fixed contributors at idealised sites (C–H = 0.95 Å, normal angles) with $B_H = 1.1\ B_C$]. Anisotropic thermal parameters were specified for all non-hydrogen atoms and a secondary extinction parameter β was also included in the refinement scheme.[60] Neutral atom scattering factors with dispersion corrections for Fe, P & C were taken from ref. 61. At convergence $R = 0.058$, $wR = 0.063$, goodness of fit = 2.10, maximum shift to error ratio = 0.04 and the maximum $\Delta\rho$ in a final difference map was 0.45 e Å^{-3}. Data reduction and refinement were performed with programs contained in the ANUCRYS package.[62] Fig. 1 was drawn with ORTEP.[63]

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