Preparation and Reactions of [Fe(Ph$_2$PCH$_2$PPh$_2$-*P*)(CO)(COMe)(η^5-C$_5$H$_5$)] and its Derivatives

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Treatment of [Fe(CO)$_2$Me(η^5-C$_5$H$_5$)] with Ph$_2$PCH$_2$PPh$_2$ (dppm) gave the yellow complex [Fe(dppm-*P*)(CO)(COMe)(η^5-C$_5$H$_5$)] (**1**) which reacted with HBF$_4$·Et$_2$O, *via* the intermediate [Fe{CMe(OH)PPh$_2$CH$_2$PPh$_2$}(CO)(η^5-C$_5$H$_5$)][BF$_4$] (**2**), to give [Fe{C(=CH$_2$)PPh$_2$CH$_2$PPh$_2$}(CO)(η^5-C$_5$H$_5$)][BF$_4$] (**3**). This stable orange salt was reduced with sodium tetrahydroborate to give [Fe{CH(Me)PPh$_2$CH$_2$PPh$_2$}(CO)(η^5-C$_5$H$_5$)][BF$_4$] (**4**) and deprotonated with LiMe to give the neutral complex [Fe{C(=CH$_2$)PPh$_2$CHPPh$_2$}(CO)(η^5-C$_5$H$_5$)] (**5**). Hydrogen-1 and ^{31}P-{^{1}H} n.m.r., and i.r. data are presented and discussed.

Recently, compounds of the type [Fe(PPh$_3$)(CO)R(η^5-C$_5$H$_5$)] (R = alkyl, aryl, or acyl) have had a significant impact upon the field of asymmetric organic synthesis.[1–3] The reactivity and specific steric limitations of such complexes have enabled highly stereoselective reactions of R groups to be performed. The chemistry of similar complexes with chelating diphosphine ligands has been less extensively investigated[4–6] and appears to have less potential in organic synthesis. As part of continuing investigations on the reaction of dppm (Ph$_2$PCH$_2$PPh$_2$) with transition metals, we have synthesised a complex in this area containing monodentate dppm. We describe here the preparation of this complex, and some chemistry associated with it.

Results and Discussion

Treatment of [Fe(CO)$_2$Me(η^5-C$_5$H$_5$)] with Ph$_2$PCH$_2$PPh$_2$ (dppm) at 115 °C gave the new complex [Fe(dppm-*P*)(CO)(COMe)(η^5-C$_5$H$_5$)] (**1**) in high yield. This complex was characterised by elemental analysis; the i.r. spectrum, which had bands at 1 918 and 1 593 cm^{-1} assigned to a terminal ν(C≡O) and an acyl ν(C=O), respectively; and the ^{31}P-{^{1}H} n.m.r. spectrum, which consisted of an AX pattern. The monodentate nature of the phosphine co-ordination was evident from the substantial downfield shift of one resonance (P$_A$), the other (P$_B$) being similar to that of free dppm (δ −21.6 p.p.m.)[7] (see Table 1). The ^{1}H n.m.r. spectrum showed the MeCO resonance at δ 2.27 p.p.m. with J(P$_A$H) = 0.7 Hz, and also showed that the two hydrogens of the CH$_2$ group were not chemically equivalent (Table 2). This reaction of [Fe(CO)$_2$Me(η^5-C$_5$H$_5$)] with dppm is similar to that with PPh$_3$, which gives [Fe(PPh$_3$)(CO)(COMe)(η^5-C$_5$H$_5$)].[8]

Treatment of complex (**1**) with an excess of HBF$_4$ rapidly gave an orange complex. We formulate this complex as [Fe{C(=CH$_2$)PPh$_2$CH$_2$PPh$_2$}(CO)(η^5-C$_5$H$_5$)][BF$_4$] (**3**) on the basis of (*i*) elemental analysis (Table 1); (*ii*) the i.r. spectrum, which had bands at 1 949 and 1 050 cm^{-1}, assigned to ν(C≡O) and ν(B–F), respectively; (*iii*) the ^{31}P-{^{1}H} n.m.r. spectrum, which consisted of an AX pattern with δ (P$_B$) being significantly downfield from δ (P$_B$) in complex (**1**) (Table 1); (*iv*) the ^{1}H n.m.r. spectrum which contained two vinylidene resonances at δ 6.93, ^3J(P$_B$H) = 65.4, and δ 6.37 p.p.m., ^3J(P$_B$H) = 34.6, ^4J(P$_A$H) = 4.0 Hz; and (*v*) electrical conductivity in acetonitrile solution, typical of a 1:1 electrolyte (see Experimental section). When the above addition, *viz.* (**1**) + HBF$_4$·Et$_2$O, was carried out at −50 °C and the mixture slowly warmed to room temperature, an intermediate was observed by ^{31}P-{^{1}H} n.m.r. spectroscopy. This intermediate complex was formulated as [Fe{CMe(OH)PPh$_2$CH$_2$PPh$_2$}(CO)(η^5-C$_5$H$_5$)][BF$_4$] (**2**) on the basis of the ^{31}P-{^{1}H} n.m.r. spectrum, which consisted of the expected AX splitting pattern (Table 1), and the ^{1}H n.m.r. spectrum, which contained an Me resonance at δ 2.48 p.p.m. ^3J(P$_B$H) = 21.6 Hz (Table 2). The reaction sequence shown in the Scheme has no direct analogy in the literature although it has been reported[9] that treatment of [Fe(PPh$_3$)(CO)(COMe)(η^5-C$_5$H$_5$)] with (CF$_3$SO$_2$)$_2$O gives an intermediate complex which loses CF$_3$SO$_3$H to give a vinylidene–iron complex [Fe(PPh$_3$)(=C=CH$_2$)(CO)(η^5-C$_5$H$_5$)][SO$_3$CF$_3$]. This intermediate showed an Me resonance at δ 2.38 p.p.m., somewhat similar to that shown by our Me-containing intermediate (**2**) (2.48 p.p.m.). The reaction of the neutral complex (**1**) with HBF$_4$ to give the intermediate (**2**) involves the protonation of the acyl oxygen to generate a cationic carbene, which is in turn attacked by the lone pair of the uncomplexed phosphorus (P$_B$). The newly formed P$_B$ to quaternary C linkage is evidenced by the coupling (21.6 Hz) (Table 2), between ^{31}P$_B$ and the Me group. Loss of water from the intermediate (**2**) gives the vinylidene complex (**3**).

The vinylidene ligand in the cationic complex [Fe(PPh$_3$)(=C=CH$_2$)(CO)(η^5-C$_5$H$_5$)][SO$_3$CF$_3$][9] is susceptible to attack by nucleophiles such as alcohols and amines.[10] In this cationic complex ν(CO) has the high value of 2 035 cm^{-1}. In contrast, our vinylidene complex (**3**) has a ν(C≡O) value of 1 949 cm^{-1} and the vinylidene group resists attack by amines such as pyrrolidine.

We attempted to reverse the reactions (**1**)→(**2**)→(**3**) by treating (**1**) with HBF$_4$·Et$_2$O until all of (**1**) had reacted and then adding 1,8-bis(dimethylamino)naphthalene (proton sponge). This reformed some of complex (**1**) as evidenced from the ^{31}P-{^{1}H} n.m.r. spectrum but simple reversibility did not occur because, regardless of the amount of proton sponge added, the amount of complex (**1**) regenerated decreased as the time between adding HBF$_4$·Et$_2$O and proton sponge increased. This result strongly suggests that, on addition of base, (**2**) is converted back to (**1**), but (**3**) is not.

A tetrahydrofuran solution of the vinylidene complex (**3**) reacted slowly with NaBH$_4$ to give an orange crystalline complex. We formulate this orange complex as [Fe{CH(Me)PPh$_2$CH$_2$PPh$_2$}(CO)(η^5-C$_5$H$_5$)][BF$_4$] (**4**) on the basis of elemental analysis (Table 1); the ^{31}P-{^{1}H} n.m.r. spectrum which showed the expected AX pattern (Table 1); and particularly from the ^{1}H n.m.r. spectrum (Table 2) which showed one CH and one Me resonance coupled both to each

Table 1. Analytical, i.r., and $^{31}P-\{^1H\}$ n.m.r. data

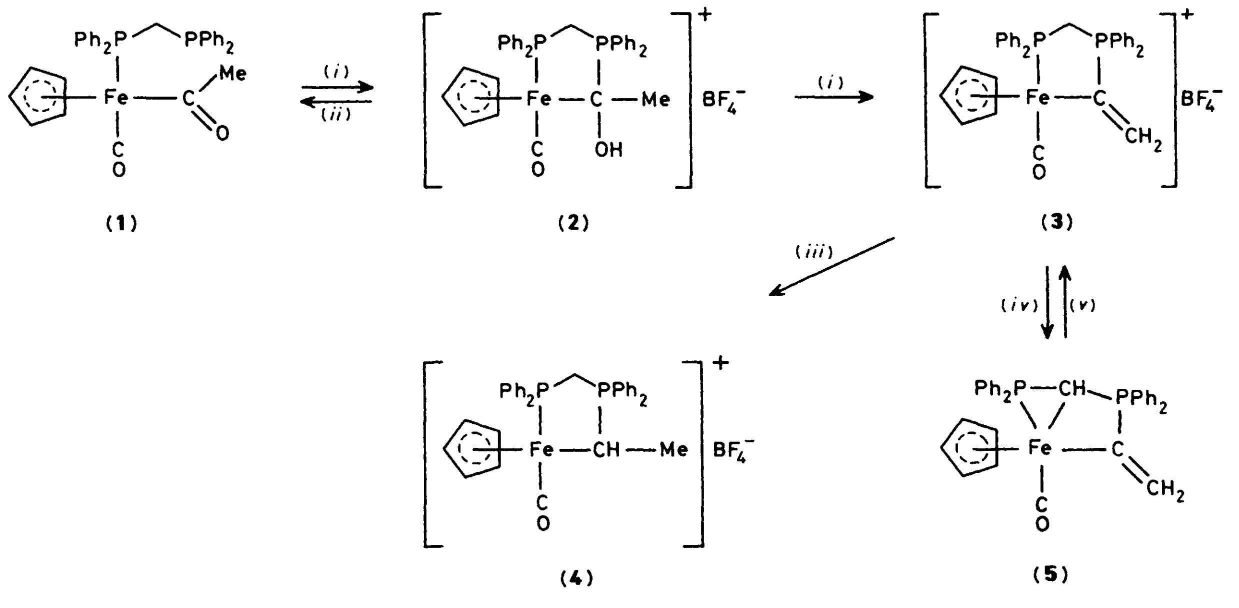
			Analysis (%)[a]		I.r. (cm^{-1})		$^{31}P-\{^1H\}$ n.m.r.[d]		
Complex	M.p./°C	Yield/%	C	H	ν(C≡O)[b]	ν(B–F)[c]	δ(P_A)	δ(P_B)	$^2J(P_AP_B)$
(1)	135—136	91	68.55 (68.75)	5.25 (5.25)	1 918vs	1 593s[e]	73.3	−23.9	79
(2)							88.9[f]	40.7[f]	71[f]
(3)	106—108	100[g]	62.0 (61.85)	5.20 (5.2)	1 949vs	1 050vs,br	88.0	41.0	65
(4)	170—175[h]	52	61.0 (61.15)	5.15 (4.8)	1 940vs	1 052vs,br	83.2	50.3	54
(5)					1 928vs		75.4[i]	47.4[i]	133[i]

[a] Required values are given in parentheses. [b] In dichloromethane (solution). [c] As Nujol mull (solid). [d] Spectra (40.25 MHz) measured at *ca.* +21 °C unless otherwise indicated. Chemical shifts (δ) in p.p.m. (± 0.01) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±3). P_A is bonded to iron. Solvent $CDCl_3$. [e] ν(C=O) in dichloromethane solution. [f] Spectrum (40.25 MHz) measured at −20 °C. [g] The crude product contained small amounts of solvent of crystallisation. A sample was recrystallised from tetrahydrofuran for analytical purposes. [h] With decomposition. [i] In benzene solution.

Table 2. Hydrogen-1 n.m.r. data[a]

	Alkene				Cyclopentadienyl		Methyne			Methylene					Methyl	
Complex	δ(H)	^3J(PH)	δ(H)	J(PH)	δ(H)	J(PH)	δ(H)	J(PH)	^3J(HH)	δ(H)	J(PH)	δ(H)	J(PH)	^2J(HH)	δ(H)	J(PH)
(1)[b]					4.56	1.0				3.61	10.8, 2.9	3.29	11.5, 2.9	14.3	2.27	0.7
(2)[c]					4.43					3.86				10.0	2.48	21.6
(3)	6.93	65.4	6.37	34.6, 4.0	4.58	1.3				4.31	10.4	3.61	12.9, 10.0	15.9		
(4)					4.50	1.2	4.18	11.7	7.0	3.81	10.2	3.59	15.5, 9.7	16.1	1.58	20.4
(5)	6.34	56.8	6.09	29.9, 3.5	4.14		1.90	14.8, 8.7								

[a] Spectra measured at 400 MHz and 21 °C unless otherwise indicated. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$, and coupling constants (J) in Hz (±0.1). Solvent $CDCl_3$. [b] Spectrum measured at 100 MHz and 21 °C. [c] Spectrum measured at 400 MHz and −20 °C.



Scheme. (*i*) HBF_4; (*ii*) 1,8-bis(dimethylamino)naphthalene; (*iii*) $NaBH_4$; (*iv*) LiMe; (*v*) HBF_4

other and to P_B, but no vinylidene resonances: this showed that $C=CH_2$ had been reduced to CHMe. The values of $^2J(P_BCH)$ (11.7 Hz) and $^3J(P_BMe)$ (20.4 Hz) are typical of two-bond or three-bond P–H couplings in systems of the type P–CH–CH–, when the phosphorus is co-ordinated, quaternised, or is phosphorus(V). See, for example, the values of ^2J(PH) and ^3J(PH) in $[Pd(Ph_2PCHMePPh_2)Cl_2]$, which are 12.0 and 17.5 Hz, respectively.[11] In the reaction between the vinylidene complex $[Fe(PPh_3)(=C=CH_2)(CO)(\eta^5-C_5H_5)][BF_4]$ and $[BH_4]^-$ a vinyl complex $[Fe(PPh_3)(CH=CH_2)(CO)(\eta^5-C_5H_5)]$ forms,[12] *i.e.* there is simple hydride addition. It has been shown that $[Fe(dppm-PP')(CO)(\eta^5-C_5H_5)]^+$ reacts with $LiAlH_4$ with reduction of CO to Me, *i.e.* $[Fe(dppm-PP')Me(\eta^5-C_5H_5)]$ is formed.[6]

We also tried to attack the vinylidene double bond of (**3**) with methanide ion by treatment with LiMe. A complex was formed which we formulate as $[\mathrm{Fe\{C({=}CH_2)PPh_2CHPPh_2\}(CO)(\eta^5\text{-}C_5H_5)}]$ (**5**), *i.e.* LiMe had acted as a base and removed a $\mathrm{CH_2}$ proton. The complex was not isolated pure but appeared to be neutral since it was very soluble in non-polar solvents such as light petroleum. The complex was formulated as (**5**) on the basis of the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ and hydrogen-1 n.m.r. spectra (Tables 1 and 2); in particular the large value of $^2J(\mathrm{PP})$ (133 Hz) suggested a fundamental change in the ring system containing the two P nuclei, *i.e.* the formation of a substituted bicyclo[2.1.0]pentane ring system. It has been shown previously[13] that $[\mathrm{Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(CO)_6}]$, when treated with LiMe, is similarly deprotonated to give a complex containing a bicyclo[2.1.0]pentane. A three-membered Fe–C–P ring system has also been reported in $[\mathrm{Fe(CH_2PMe_2)H(PMe_3)_3}]$.[14] In a similar reaction to those described above $[\mathrm{Fe(Ph_2PCH_2CH_2PPh_2)(C{=}CR_2)(\eta^5\text{-}C_5H_5)}]^+$ (R = Me) reacted with base to give a complex containing a bicyclo[2.1.1]hexane ring system,[4] whereas for R = H, treatment with base gave $[\mathrm{Fe(Ph_2PCH_2CH_2PPh_2)(C{\equiv}CH)(\eta^5\text{-}C_5H_5)}]$. We found that the complex (**5**), when treated with $\mathrm{HBF_4}$, was immediately converted to the vinylidene salt (**3**).

Experimental

General methods were as described previously.[15] The complex $[\mathrm{Fe(CO)_2Me(\eta^5\text{-}C_5H_5)}]$ was made by a literature method.[16]

Preparation of $[\mathrm{Fe(dppm\text{-}\mathit{P})(CO)(COMe)(\eta^5\text{-}C_5H_5)}]$ (**1**).—A mixture of $[\mathrm{Fe(CO)_2Me(\eta^5\text{-}C_5H_5)}]$ (1.00 g, 5.20 mmol) and dppm (2.00 g, 5.20 mmol) was heated at 115 °C under nitrogen for 0.8 h. The melt was allowed to cool to *ca.* 80 °C and then light petroleum (b.p. 30—40 °C, 5 $\mathrm{cm^3}$) was cautiously added. The resultant yellow solid was washed four times with degassed light petroleum (b.p. 100—120 °C, 10 $\mathrm{cm^3}$) and the supernatant solution filtered off under nitrogen to give the required product as the residue. Yield 2.66 g. The product was stored at −20 °C.

Preparation of $[\mathrm{Fe\{C(C{=}CH_2)PPh_2CH_2PPh_2\}(CO)(\eta^5\text{-}C_5H_5)][BF_4]}$ (**3**).—$\mathrm{HBF_4{\cdot}Et_2O}$ (0.075 $\mathrm{cm^3}$, 0.090 g, 0.5 mmol) was added to a solution of $[\mathrm{Fe(dppm\text{-}\mathit{P})(CO)(COMe)(\eta^5\text{-}C_5H_5)}]$ (**1**) (0.283 g, 0.491 mmol) in dichloromethane (3 $\mathrm{cm^3}$) to give an orange solution. The mixture was put aside for 15 min and then light petroleum (b.p. 40—60 °C, 10 $\mathrm{cm^3}$) was added with vigorous shaking. The resultant viscous orange oil was washed twice with light petroleum (b.p. 40—60 °C, 10 $\mathrm{cm^3}$) and dried *in vacuo*. Yield 0.32 g; $\Lambda = 133\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$ for a 10^{-3} mol $\mathrm{dm^{-3}}$ solution in acetonitrile at 20 °C.

The above-mentioned reaction was also carried out in n.m.r. tubes with the addition of $\mathrm{HBF_4{\cdot}Et_2O}$ made when the temperature was −50 °C. An unstable intermediate, characterised as $[\mathrm{Fe\{CMe(OH)PPh_2CH_2PPh_2\}(CO)(\eta^5\text{-}C_5H_5)][BF_4]}$ (**2**) (see Tables 1 and 2 for $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ and $^1\mathrm{H}$ n.m.r. data) was formed. As the temperature was allowed to increase, the vinylidene complex (**3**) was formed at the expense of the intermediate complex (**2**). At room temperature complex (**3**) was the only detectable species present.

Preparation of $[\mathrm{Fe\{CH(Me)PPh_2CH_2PPh_2\}(CO)(\eta^5\text{-}C_5H_5)][BF_4]}$ (**4**).—$\mathrm{NaBH_4}$ (0.0048 g, 0.13 mmol) was added to a solution of (**3**) (0.030 g, 0.046 mmol) in tetrahydrofuran (1.5 $\mathrm{cm^3}$), to give an orange solution from which a gas was steadily evolved. The mixture was set aside for 2 d, during which time orange crystals and a fine white precipitate formed. The solids were filtered off, air dried, and extracted with dichloromethane (1 $\mathrm{cm^3}$). This extract was triturated with the original orange tetrahydrofuran-containing filtrate to give the required product. Yield 0.16 g.

Preparation of $[\mathrm{Fe\{C({=}CH_2)PPh_2CHPPh_2\}(CO)(\eta^5\text{-}C_5H_5)}]$ (**5**).—A solution of LiMe (0.39 mmol) in diethyl ether (0.30 $\mathrm{cm^3}$) was added to a solution of (**3**) (0.041 g, 0.063 mmol) in tetrahydrofuran (2 $\mathrm{cm^3}$) at 0 °C under nitrogen. The solution became dark orange upon mixing. The resultant mixture was put aside for 1 h at 0 °C, and degassed methanol (0.3 $\mathrm{cm^3}$) was then added. After a further 0.5 h at 0 °C, the solvent was evaporated under reduced pressure. The residue was extracted twice with benzene (4 $\mathrm{cm^3}$), the extract filtered, and the solvent evaporated similarly to give a viscous orange oil, which was stored at −20 °C. Attempts to induce the product to crystallise by treatment with either polar or non-polar solvents failed. Upon addition of $\mathrm{HBF_4{\cdot}Et_2O}$ the product completely reverted to $[\mathrm{Fe\{C({=}CH_2)PPh_2CH_2PPh_2\}(CO)(\eta^5\text{-}C_5H_5)][BF_4]}$.

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