η-Benzenebis(trimethylphosphine)iron as a Precursor to $[Fe(\eta\text{-}C_5R_5)(PMe_3)_2]$ (R = H or Me) Derivatives: the Equilibrium $[Fe](PMe_3)Et \rightleftharpoons [Fe](\eta\text{-}C_2H_4)H + PMe_3$, where $[Fe] = Fe(\eta\text{-}C_5Me_5)(PMe_3)$

Malcolm L. H. Green and Luet-Lok Wong
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

New or improved syntheses of the compounds $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$, $[Fe(\eta\text{-}C_5R_5)(PMe_3)_2X]$ (R = H or Me; X = H, Me, Et, or Cl), $[Fe(\eta\text{-}C_5H_4CH_2CH_2)(PMe_3)_2]$, $[Fe(\eta\text{-}C_5H_4CH_2CH_2I)(PMe_3)_2I]$, $[Hg\{Fe(\eta\text{-}C_5R_5)(PMe_3)_2\}_2]$ (R = H or Me), and $[Fe(\eta\text{-}C_5R_5)(PMe_3)_3]BF_4$ (R = H or Me) are described. The thermal equilibrium $[Fe(\eta\text{-}C_5Me_5)(PMe_3)(\eta\text{-}C_2H_4)H] + PMe_3 \rightleftharpoons [Fe(\eta\text{-}C_5Me_5)(PMe_3)_2Et]$ has been demonstrated and studied by variable-temperature n.m.r. spectroscopy.

We have found that co-condensation of metal atoms with mixtures of trimethylphosphine and potential hydrocarbon ligands such as arenes, cyclic olefins and, in some cases, cyclic alkanes, can give electron-rich, half-sandwich derivatives. Examples of new compounds prepared by this method include $[Re(\eta\text{-}C_6H_6)(PMe_3)_2H]$,[1] $[Cr(\eta\text{-}C_6H_6)(PMe_3)_3]$,[2] $[W(\eta\text{-}C_6H_6)(PMe_3)_2H_2]$,[2] $[W(\eta\text{-}C_6H_6)(PMe_3)_3]$,[2] $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$,[3] and $[Ru(\eta\text{-}C_6H_6)(PMe_3)(Ph)H]$.[4] We also found that co-condensation of iron atoms with benzene–trimethylphosphine gave high yields of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$.[5] Closely analogous compounds, of the class $[Fe(\eta\text{-arene})(PR_3)_2]$, where R = Me or OMe, had been synthesised independently by Ittel and Tolman[6] using iron atoms.

During a study of the chemistry of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (**1**) we found convenient syntheses of derivatives of the system $[Fe(\eta\text{-}C_5R_5)(PMe_3)_2]$ and, in particular, the ethylene–hydride compounds $[Fe(\eta\text{-}C_5R_5)(PMe_3)(\eta\text{-}C_2H_4)H]$.[5] We note that examples of the class $[Fe(\eta\text{-}C_5H_5)L_2X]$, where L = tertiary phosphine, have been described previously.[7]

It has been shown that the d^6 cobalt compounds $[Co(C_2H_4\text{–}H)(\eta\text{-}C_5Me_5)L]BF_4$ [L = $\eta\text{-}C_2H_4$, $P(C_6H_4Me\text{-}p)_3$,[9] PMe_3,[9] or $P(OMe)_3$[10]] have, as the stable ground-state structures, the agostic $Co(C_2H_4\text{–}H)$ group rather than having an ethylene–hydride grouping, $Co(\eta\text{-}C_2H_4)H$. These compounds were the first examples of agostic ethyl groups for a d^n metal centre, $n > 0$.

Therefore, we were interested to study the compounds $[Fe(\eta\text{-}C_5R_5)(PMe_3)(\eta\text{-}C_2H_4)H]$, which have the ethylene–hydride structure, and to examine whether there was an equilibrium between the ethylene–hydride structure and one with an agostic ethyl, *i.e.* as in $[Fe(C_2H_4\text{–}H)(\eta\text{-}C_5R_5)L]$. A preliminary communication of part of this work has been published.[5]

Results and Discussion

Compound (**1**) was readily prepared by co-condensation of iron atoms and a mixture (5:1, v/v) of benzene and trimethylphosphine. Typically 10 g of iron atoms were co-condensed with 200 cm^3 of the mixture for 4 h giving 15—25 g of black crystals of (**1**). Compound (**1**) is highly air sensitive and decomposes in solution at room temperature ($T_{\frac{1}{2}}$ = *ca.* 3 h) but it may be stored as the solid for several months at -80 °C. Compound (**1**) has been characterised by detailed n.m.r. studies (Table) and microanalysis. Thermal decomposition of (**1**) in light petroleum yields a residue of metallic appearance and a small yield of yellow crystalline $[Fe(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3H]$ (**2**) which has been described previously.[11]

Treatment of (**1**) with cyclopentadiene gives good yields of air-sensitive yellow crystals of the previously described $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2H]$[12] (**3**). The data which characterise (**3**) and all the other compounds are presented in the Table and will only be discussed where interpretation is not straightforward.

Treatment of (**1**) with pentamethylcyclopentadiene gives air-sensitive, brown crystals of $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2H]$ (**4**) in good yield. Compound (**4**) is thermally stable at room temperature (r.t.). However, on heating in $[^2H_6]$benzene at *ca.* 100 °C a metallic residue is slowly deposited. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the residual brown solution showed a 1:1:1 triplet at δ 30.3 p.p.m. (J = 11.3 Hz) indicating the presence of the compound $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2D]$ (**4′**). Comparison of the i.r. spectra of benzene solutions of (**4**) and (**4′**) identified ν(Fe–H) and ν(Fe–D) at 1 820 and *ca.* 1 300 cm^{-1}, respectively.

Treatment of (**3**) and (**4**), separately, with dichloromethane caused an immediate reaction giving purple-black crystals of $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Cl]$ (**5**) and $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2Cl]$ (**6**), respectively, in 70—80% yields. Prolonged reaction of (**3**) with CH_2Cl_2 resulted in a decreased yield (20%) of (**5**) and other products isolated from the reaction mixture included ferrocene and $[Fe(\eta\text{-}C_5H_5)(PMe_3)_3]Cl$.

Treatment of (**5**) with the Grignard reagents MgRBr (R = Me or Et) gives orange-red crystals of $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Me]$ (**7**) which has been previously described,[7] and $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Et]$ (**8**), respectively. Similarly, reaction of (**6**) with MgMeBr gave $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2Me]$ (**9**) as red crystals.

However, treatment of (**6**) with MgEtCl gave two products. The major product was red crystalline $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2Et]$ (**10**) and the minor product, which could be separated by fractional crystallisation from light petroleum at low temperature, was shown to be the ethylene–hydride $[Fe(\eta\text{-}C_5Me_5)(PMe_3)(\eta\text{-}C_2H_4)H]$ (**11**). The ^1H n.m.r. spectrum of apparently pure (**10**) showed bands assignable to (**11**) and PMe_3. Under vacuum (**10**) slowly loses PMe_3, giving pure (**11**). On addition of PMe_3 (*ca.* 5 mol equiv.) to a yellow solution of (**11**) it became orange and the ^1H n.m.r. spectrum showed the product to be mainly (**10**) with traces of (**11**) and PMe_3. Analytically pure (**10**) can be obtained by recrystallization of (**11**) using PMe_3 as solvent. We conclude that (**10**) and (**11**) are in equilibrium in solution.

The dynamic behaviour of (**11**) has been investigated by variable-temperature ^1H (Figure) and ^{13}C n.m.r. spectroscopy. At 236 K the ^1H n.m.r. spectrum shows the expected ABCX spin system for the η-ethylene hydrogens and a sharp doublet

[^2J(P–H) 96 Hz] for the Fe–H hydrogen. The ^{13}C n.m.r. spectrum at this temperature strongly supports a static ethylene–hydride structure, with a triplet at δ 27.2 p.p.m. [J(C–H) 151 Hz] and a triplet of doublets at δ 30.4 p.p.m. [J(C–H) 150, ^2J(P–C) 10 Hz] being observed for the carbons of the η-ethylene ligand. In the ^{1}H n.m.r. spectrum at 263 K resonances due to the ethylene hydrogens start to broaden. At room temperature the resonances due to two ethylene hydrogens (one at δ 0.5 p.p.m. and the other within the complex multiplet centred at δ 1.33 p.p.m. in the low-temperature spectrum) have disappeared into the baseline but the chemical shift of the resonances due to the remaining two hydrogens have not changed significantly. In the ^{13}C n.m.r. spectrum at 298 K the triplet resonance at δ 27.2 p.p.m. at 236 K has moved to δ 27.5 p.p.m. and become a multiplet with sharp outer lines and broad internal bands. At 353 K there is no evidence for an Fe–H hydrogen in the ^{1}H n.m.r. spectrum whereas in the ^{13}C n.m.r. spectrum a sharp quartet at δ 27.9 p.p.m. [apparent J(C–H) 101 Hz] and a triplet of doublets at δ 30.15 p.p.m. [J(C–H) 150, ^2J(P–C) 10 Hz] are observed for the carbons of the η-ethylene ligand.

We conclude that there is exchange between the Fe–H hydrogen and two hydrogens attached to one carbon atom, C_a (Scheme), of η-C_2H_4 at $T > ca.$ 253 K. Supporting evidence comes from the fact that the other carbon atom of η-C_2H_4 retains coupling to the phosphorus atom of PMe_3 at 353 K, hence ruling out any rapid rotation of the co-ordinated ethylene. Rapid scrambling of the Fe–H and C_aH_2 hydrogens would lead to a quartet with $J(\mathrm{C{-}H})_{\mathrm{average}} = [(2 \times 151) + 0]/3 = 100.7$ Hz for C_a in the fully proton-coupled ^{13}C n.m.r. spectrum, in close agreement with data at 353 K. It can be envisaged that this rapid exchange proceeds *via* an equilibrium between (**11**) and an intermediate (not observed) with an agostic Fe$\leftarrow$H–C_a structure for the Fe–Et group: the structure for this intermediate is shown in the Scheme. It is interesting that (**11**) does not have an agostic ground-state structure and is not a catalyst for ethylene polymerisation whilst the cobalt compounds $[\overline{\mathrm{Co}(\mathrm{C_2H_4{-}H}})(\eta\text{-}\mathrm{C_5Me_5})L]^+$ [$L = \eta$-C_2H_4,[8] $P(C_6H_4\text{-}Me\text{-}p)_3$,[9] or $P(OMe)_3$[10]] have the agostic ground-state structure, with the ethylene–hydride isomer occurring as a higher energy state, and they polymerize ethylene.

We associate the stabilisation of the agostic structure in the cobalt compounds with their cationic nature. The empty orbital in the 16-electron ethyl compound $[\mathrm{Co}(\eta\text{-}\mathrm{C_5Me_5})L(\mathrm{Et})]^+$

Table. Spectroscopic and analytical data

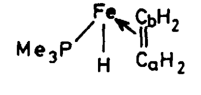
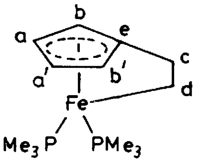
	N.m.r. data[b]	
Compound, colour, and analysis (%)[a]	^{1}H	^{31}P and ^{13}C
(**1**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_6H_6})(\mathrm{PMe_3})_2]$ Black-red C, 50.1 (50.4); H, 8.20 (8.40)	At −65 °C in [$^2H_8$]toluene: 4.71 [s, 6 H, η-C_6H_6], 1.05 [br s, 18 H, 2 PMe_3]	At −65 °C in [$^2H_8$]toluene: ^{31}P-{^{1}H}: −16 [s] ^{13}C-{^{1}H}: 74.5 [s, η-C_6H_6], 25.4 [br s, 2 PMe_3]
(**3**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{PMe_3})_2\mathrm{H}]$ Yellow C, 47.9 (48.2); H, 8.65 (8.80)[c]	4.06 [t, 5 H, ^3J(P–H) 2, η-C_5H_5], 1.12 [vt, 18 H, J' 7.7, 2 PMe_3], −16.2 [t, 1 H, ^2J(P–H) 76.6, Fe–H]	^{31}P-{^{1}H}: 33.5 [s] ^{13}C-{^{1}H}: 73.57 [s, η-C_5H_5], 26.1 [vt, J' 22.4, 2 PMe_3]
(**4**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{PMe_3})_2\mathrm{H}]$ Yellow C, 55.6 (55.8); H, 9.8 (10.0)[d]	1.87 [s, 15 H, η-C_5Me_5], 1.19 [vt, 18 H, J' 7.1, 2 PMe_3], −17.5 [t, 1 H, ^2J(P–H) 75.1, Fe–H]	^{31}P-{^{1}H}: 30.3 [s] ^{13}C-{^{1}H}: 84.47 [s, η-C_5Me_5], 26.20 [vt, J' 20.2, 2 PMe_3], 13.05 [s, Me_5]
(**5**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{PMe_3})_2\mathrm{Cl}]$ Purple-red C, 42.7 (42.8); H, 7.3 (7.5)[e]	3.81 [br s, 5 H, η-C_5H_5], 1.19 [vt, 18 H, J' 7.1, 2 PMe_3]	
(**6**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{PMe_3})_2\mathrm{Cl}]$ Purple-red C, 50.3 (50.8); H, 8.5 (8.8)[f]	1.45 [s, 15 H, η-C_5Me_5], 1.27 [vt, 18 H, J' 8, 2 PMe_3]	
(**7**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{PMe_3})_2\mathrm{Me}]$ Orange-red C, 49.9 (50.0); H, 8.9 (9.1)	3.83 [t, 5 H, ^3J(P–H) 1.6, η-C_5H_5], 1.00 [vt, 18 H, J' 7.7, 2 PMe_3], −0.31 [t, 3 H, ^3J(P–H) 8.0, Fe–Me]	^{31}P-{^{1}H}: 34.07 [s] ^{13}C-{^{1}H}: 77.54 [s, η-C_5H_5], 21.44 [vt, J' 20, 2 PMe_3], −24.00, [t, ^2J(P–C) 24.3, Fe–Me]
(**8**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{PMe_3})_2\mathrm{Et}]$ Orange-red C, 51.1 (51.7); H, 9.0 (9.3)	3.84 [t, 5 H, ^3J(P–H) 1.7, η-C_5H_5], 1.56 [tt, 3 H, J(H–H) 7.6, ^4J(P–H) 1.5, CH_2CH_3], 1.00 [vt, 18 H, J' 7.6, 2 PMe_3], 0.60 [sxt, 2 H, J(H–H) = ^3J(P–H) 7.6, CH_2CH_3]	^{31}P-{^{1}H}: 33.7 [s] ^{13}C-{^{1}H}: 78.10 [s, η-C_5H_5], 23.47 [t, ^3J(P–C) 6.0, CH_2CH_3], 21.89 [vt, J' 21.6, 2 PMe_3], −6.0 [t, ^2J(P–C) 23, CH_2CH_3]
(**9**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{PMe_3})_2\mathrm{Me}]$ Red C, 56.0 (57.0); H, 9.9 (10.1)	1.57 [s, 15 H, η-C_5Me_5], 1.05 [vt, 18 H, J' 7, 2 PMe_3], −0.71 [t, 3 H, ^3J(P–H) 7.6, Fe–Me]	^{31}P-{^{1}H}: 32.45 [s] ^{13}C: 84.32 [s, η-C_5Me_5], 21.53 [q of vt, J(C–H) 124, J' 18, 2 PMe_3], 11.28 [q, J(C–H) 132, Me_5], −15.41 [qt, J(C–H) 122, ^3J(P–C) 23, Fe–Me]
(**10**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{PMe_3})_2\mathrm{Et}]$ Red C, 57.7 (58.1); H, 9.95 (10.2)	1.67 [s, 15 H, η-C_5Me_5], 1.07 [vt, 18 H, J' 8, 2 PMe_3], 1.45 [m, 3 H, CH_2CH_3], 0.32 [m, 2 H, CH_2CH_3]	^{31}P-{^{1}H}: 30.81 [s] ^{13}C: 84.83 [s, η-C_5Me_5], 21.57 [qt, J(C–H) 125, ^3J(P–C) 6.5, CH_2CH_3], 21.37 [q of m, J(C–H) 125, 2 PMe_3], 13.5 [q, J(C–H) 125, Me_5], −1.16 [tt, J(C–H) 121, ^2J(P–C) 23, CH_2CH_3]
(**11**) $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{PMe_3})(\eta\text{-}\mathrm{C_2H_4})\mathrm{H}]$ Yellow C, 60.8 (60.9); H, 9.75 (9.8) 	At −37 °C in [$^2H_8$]toluene: 1.65 [s, 15 H, η-C_5Me_5], 1.33 [m, 3 H, ABC system, 3 H of η-C_2H_4], 0.69 [d, 9 H, ^2J(P–H) 7.7, PMe_3], 0.52 [m, 1 H of η-C_2H_4], −11.7 [d, 1 H, ^2J(P–H) 96, Fe–H]	^{13}C (−37 °C in [$^2H_8$] toluene): 87.3 [s, η-C_5Me_5], 30.4 [td, J(C–H) 150, ^2J(P–C) 10, C_bH_2], 27.2 [t, J(C–H) 151, C_aH_2], 18.40 [qd, J(C–H) 128, J(P–C) 26, PMe_3], 10.55 [q, J(C–H) 126, Me_5] ^{13}C (r.t.): 87.4 [s, η-C_5Me_5], 30.00 [td, J(C–H) 150, ^2J(P–C) 10, C_bH_2], 27.5 [m, separation of outer lines 302, C_aH_2], 18.50 [qd, J(C–H) 125, J(P–C) 26, PMe_3], 10.55 [q, J(C–H) 126, Me_5] ^{31}P-{^{1}H}: 40.1 [s] ^{13}C (+80 °C): 87.40 [s, C_5Me_5], 30.15 [td, J(C–H) 150, ^2J(P–C) 10, C_b of η-C_2H_4], 27.9 [q, J(C–H) 101, C_a cf η-C_2H_4], 18.50 [qd, J(C–H) 128, J(P–C) 26, PMe_3], 10.55 [q, J(C–H) 126, Me_5]

Table (*continued*)

Compound, colour, and analysis (%)[a]	N.m.r. data[b] ^1H	 ^{31}P and ^{13}C
(**12**) $[Fe(\eta\text{-}C_5H_4CH_2CH_2)(PMe_3)_2]$ Brown C, 52.0 (52.0); H, 8.5 (8.7) 	4.05 [m, 5 lines, 2 H, $H_{a,a'}$ or $H_{b,b'}$], 4.02 [m, 5 lines, 2 H, $H_{b,b'}$ or $H_{a,a'}$], 3.07 [dd, 2 H, $J(H_{c,c'}\text{–}H_{d,d'})$ 8.5, 7.4, $H_{c,c'}$], 1.08 [vt, 18 H, J' 7.2, 2 PMe_3], −0.9 [dddd, 2 H, $J(H_{d,d'}\text{–}H_{c,c'})$ 8.5, 7.4, $^3J(P\text{–}H_{d,d'})$ 7.0, 5.5, $H_{d,d'}$]	$^{31}P\text{-}\{^1H\}$: 32.1 [s] ^{13}C: 81.5 [s, C_e], 80.8 [d, J(C–H) 160, $C_{a,a'}$ or $C_{b,b'}$], 72.8 [d, J(C–H) 168, $C_{b,b'}$ or $C_{a,a'}$], 24.9 [t, J(C–H) 131, C_c], 22.9 [q of vt, J(C–H) 124, J' 21, 2 PMe_3], −45.3 [tt, J(C–H) 137, ^2J(P–C) 20.5, C_d]
(**13**) $[Fe(\eta\text{-}C_5H_4CH_2CH_2I)(PMe_3)_2I]$ Dark green C, 28.35 (28.2); H, 4.65 (4.7)[g]	3.9 [m, 5 lines, 2 H of $\eta\text{-}C_5H_4$], 3.05 [m, 8 lines, AA′BB′, 4 H, $(CH_2)_2$], 2.65 [m, 5 lines, 2 2 H of $\eta\text{-}C_5H_4$], 1.2 [vt, J' 8.3, 18 H, 2 PMe_3]	
(**14**) $[Hg\{Fe(\eta\text{-}C_5H_5)(PMe_3)_2\}_2]$ Red C, 34.5 (35.4); H, 6.2 (6.1)	3.84 [br s, 5 H, $\eta\text{-}C_5H_5$], 1.23 [br s, 18 H, 2 PMe_3]	$^{31}P\text{-}\{^1H\}$: 7.67 [s, $J(P\text{–}^{199}Hg)$ 490] $^{13}C\text{-}\{^1H\}$: 72.53 [s, $\eta\text{-}C_5H_5$], 26.48 [vt, J' 21.1, 2 PMe_3],
(**15**) $[Hg\{Fe(\eta\text{-}C_5Me_5)(PMe_3)_2\}_2]$ Red C, 43.1 (43.3); H, 7.35 (7.45)	1.81 [s, 15 H, $\eta\text{-}C_5Me_5$], 1.4 [br s, 18 H, 2 PMe_3]	$^{31}P\text{-}\{^1H\}$: 6.0 [s, $J(P\text{–}^{199}Hg)$ 374] $^{13}C\text{-}\{^1H\}$: 82.1 [s, $\eta\text{-}C_5Me_5$], 26.0 [vt, J' 20. 2 PMe_3], 12.7 [s, Me_5]
(**16**) $[Fe(\eta\text{-}C_5H_5)(PMe_3)_3]BF_4\cdot 2H_2O$ Yellow C, 36.9 (36.9); H, 7.7 (7.9)[i]	4.5 [q, J(P–H) 1.6, 5 H, $\eta\text{-}C_5H_5$], 1.6 [m, 27 H, 3 PMe_3][h]	
(**17**) $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_3]BF_4$ Yellow C, 41.2 (42.1); H, 7.7 (7.75)[j]	1.72 [s, 15 H, $\eta\text{-}C_5Me_5$], 1.56 [m, 27 H, 3 PMe_3][h]	

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (δ/p.p.m.) [multiplicity (*J* in Hz), relative intensity, assignment]; J' = separation of the outer lines of virtual triplets (vt); s = singlet, d = doublet, t = triplet, q = quartet, sxt = sextet, m = multiplet. ^1H N.m.r. spectra were determined at 300 MHz, ^{13}C n.m.r. spectra at 62.8 MHz. All spectra were determined at room temperature in $[^2H_6]$benzene as solvent, unless otherwise stated. [c] Fe, 20.35 (20.45%). ν(Fe–H), 1 845 cm^{-1} (Nujol mull, CsI plates). [d] ν(Fe–H), 1 820 cm^{-1} (Nujol mull, CsI plates). [e] Fe, 18.1 (18.3); Cl, 11.5 (11.7%). [f] Fe, 14.8 (14.6); Cl, 9.4 (9.7%). [g] I, 45.8 (46.05%). [h] In $[^2H_6]$acetone. [i] Fe, 11.7 (12.3%). [j] Fe, 9.7 (10.3%).

would be expected to be lower in energy than the corresponding orbital in the 16-electron, neutral $[Fe(\eta\text{-}C_5Me_5)L(Et)]$ and, hence, better able to accept electrons from a donor C_β–H group.

In a further study of the chemistry of (**1**), we found that addition of spiro[2.4]hepta-4,6-diene gave compound $[Fe(\eta\text{-}C_5H_4CH_2CH_2)(PMe_3)_2]$ (**12**) as air-sensitive brown crystals in good yield. Homonuclear decoupling experiments show that the C_5-ring hydrogens are not coupled to the CH_2 hydrogens and that the hydrogens of the Fe–CH_2 group are coupled both to the two ^{31}P nuclei and to the other CH_2 hydrogens. Treatment of (**12**) with iodine gives dark green crystals of $[Fe(\eta\text{-}C_5H_4CH_2CH_2I)(PMe_3)_2I]$ (**13**).

Reduction of (**5**) and (**6**) with sodium amalgam gave red crystals of $[Hg\{Fe(\eta\text{-}C_5H_5)(PMe_3)_2\}_2]$ (**14**) and $[Hg\{Fe(\eta\text{-}C_5Me_5)(PMe_3)_2\}_2]$ (**15**),[13] respectively. Reduction of (**5**) and (**6**) in thf using a potassium film gave (**3**) and (**4**), respectively, in quantitative yield.

Treatment of (**3**) and (**4**) with tetrafluoroboric acid in diethyl ether gave the previously described[11] yellow compounds $[Fe(\eta\text{-}C_5H_5)(PMe_3)_3]BF_4$ (**16**) and $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_3]BF_4$ (**17**) respectively. The compound (**17**) was also formed in the reaction between the chloro derivative (**6**) and thallium tetrafluoroborate in *ca.* 35% yield.

The structures proposed for the compounds (**1**)—(**17**) are shown in the Scheme. It is clear that the readily available compound (**1**) is a useful and reactive precursor for η-cyclopentadienyl–iron derivatives.

Experimental

All preparations and reactions described were carried out under an atmosphere of nitrogen (< 10 p.p.m. oxygen or water) using standard Schlenk-tube and vacuum-line techniques or in a dry-box. Nitrogen was purified by passage through a gas-drying column containing BASF catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of nitrogen. Solvents were pre-dried over molecular sieves and then distilled from potassium (tetrahydrofuran, thf), sodium–potassium alloy [pentane, light petroleum (b.p. 40—60 °C throughout), diethyl ether], or phosphorus pentoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for n.m.r. were stored in Rotaflo ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation.

Elemental analyses were performed by the Analysis Department in this laboratory, or in the case of very air-sensitive materials, by Analytische Laboratorien, 5270 Gummersbach, 1 Elbach, W. Germany.

Infrared spectra were recorded on a Pye Unicam SP2000 double-beam, grating spectrophotometer, or on a Perkin-Elmer 1510 Fourier-transform interferometer. Hydrogen-1 n.m.r. spectra were determined using a 300-MHz Bruker WH-300 spectrometer. Carbon-13 and ^{31}P n.m.r. spectra were determined at 62.8 and 101.3 MHz, respectively, using a Bruker AM-250 spectrometer. Spectra were referenced internally using the residual protio solvent resonance (^1H, ^{13}C) relative to $SiMe_4$ (δ = 0 p.p.m.), or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts are quoted in δ (p.p.m.), and coupling constants in Hz.

Metal-vapour synthesis experiments were carried out using the 10-kW bell-jar reactor[4,14] operated in the positive hearth mode using a pre-melted ingot of iron. A pre-melted ingot is required to minimise outgassing during the reaction which would lead to deterioration of the vacuum.

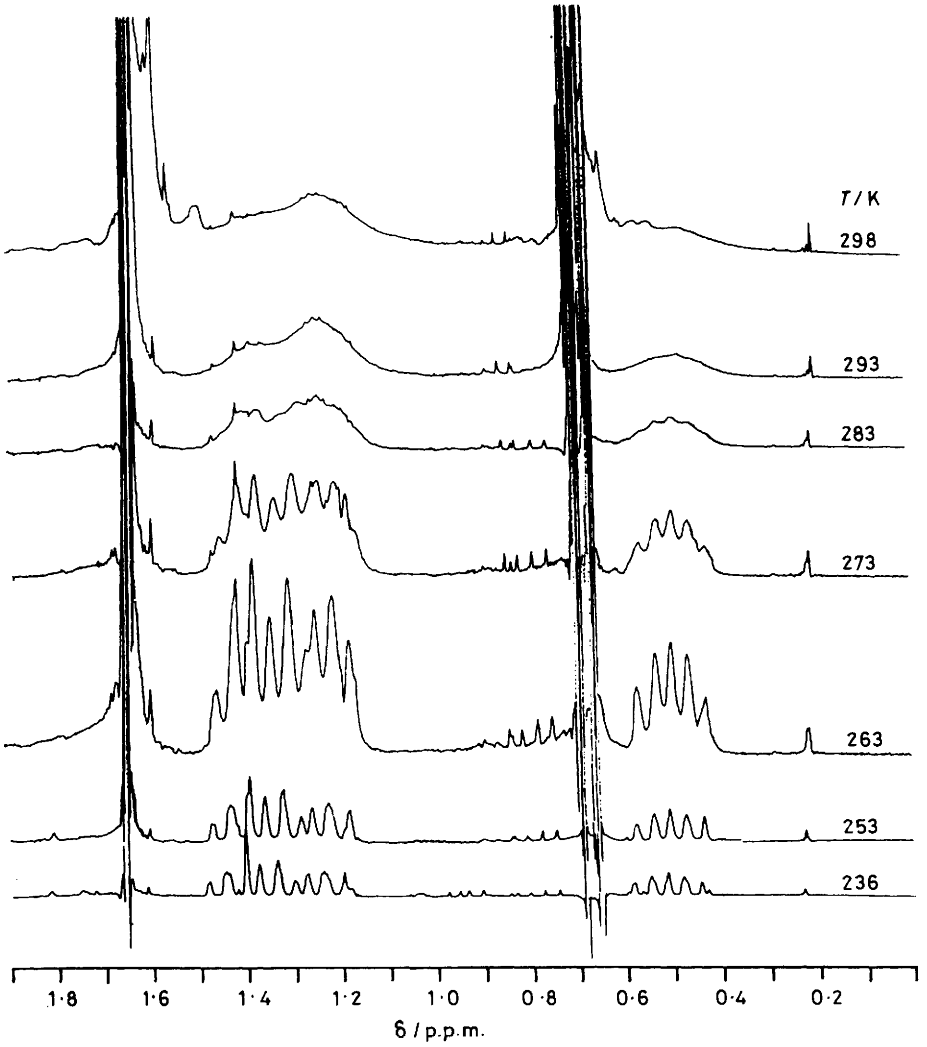


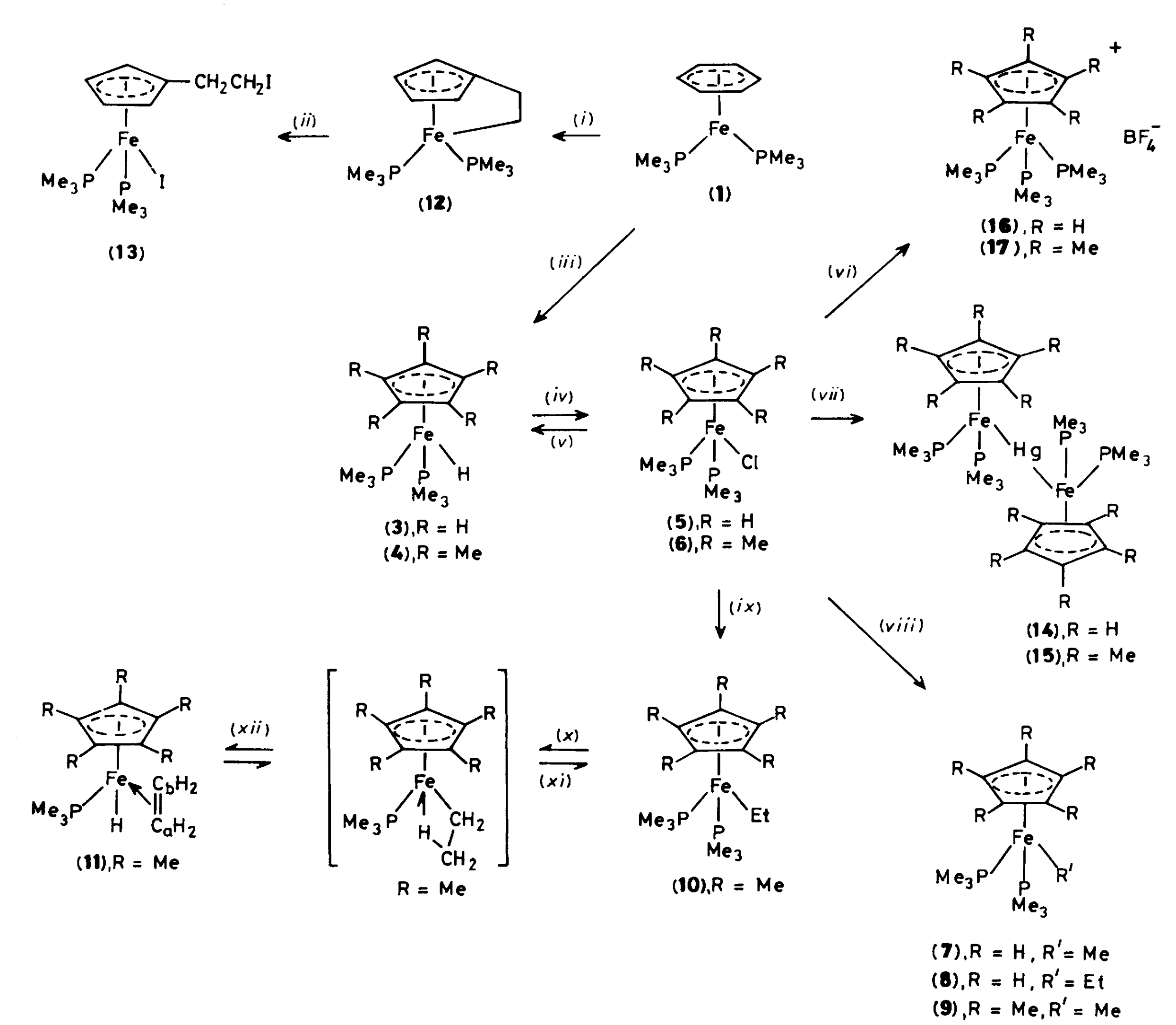
Figure. Variable-temperature 300-MHz ^{1}H n.m.r. spectrum of (**11**) in [$^2H_8$]toluene

η-Benzenebis(trimethylphosphine)iron, (**1**).—Iron atoms (6 g, 0.11 mol) were vaporised from a pre-melted ingot (*ca.* 50 g) and were co-condensed with a mixture of benzene and trimethylphosphine (5:1, v/v; total volume 200 cm^3) onto a liquid-nitrogen cooled surface over a period of 4 h. The resultant mixture was allowed to warm slowly to r.t. under an atmosphere of nitrogen. The product was washed out with diethyl ether (1 500 cm^3) and filtered through a Celite bed. Volatile components were removed under reduced pressure to give a dark solid which was extracted with light petroleum (200 cm^3) and filtered through a Celite bed. The extract was concentrated to *ca.* 40 cm^3 and cooled to −80 °C to obtain a dark crystalline solid. Yield: 18 g, 58.7% relative to metal evaporated.

η-Cyclopentadienyl(hydrido)bis(trimethylphosphine)iron, (**3**).—To a solution of the compound [Fe(η-C_6H_6)(PMe_3)$_2$] (9 g, 31 mmol) in light petroleum (100 cm^3) at −20 °C was added a light petroleum (10 cm^3) solution of cyclopentadiene (3 cm^3, 36 mmol) at −20 °C with stirring. The reaction mixture was warmed slowly to r.t. and stirred for 6 h. After the removal of volatile components under reduced pressure, the residue was extracted with light petroleum (3 × 30 cm^3) and the extracts filtered through a Celite bed. The combined extracts were evaporated to dryness and re-extracted with light petroleum (3 × 20 cm^3) and filtered through a Celite bed. The combined extracts were concentrated to 10 cm^3; cooling to −80 °C afforded a brown solid which melted on warming to room temperature. Recrystallization (three times) from pentane afforded yellow prisms. Overall yield: 6.0 g, 70%.

Hydrido(η-pentamethylcyclopentadienyl)bis(trimethylphosphine)iron, (**4**).—The procedure was similar to that for (**3**) but the reaction time was 12 h. [Fe(η-C_6H_6)(PMe_3)$_2$] (**1**) (4.0 g) gave brown prisms of [Fe(η-C_5Me_5)(PMe_3)$_2$H] (**4**). Yield: 3.2 g, 67%.

Chloro(η-cyclopentadienyl)bis(trimethylphosphine)iron, (**5**).—The compound [Fe(η-C_5H_5)(PMe_3)$_2$H] (3.0 g, 11 mmol) in light petroleum (20 cm^3) was added dropwise to dichloromethane (15 cm^3, excess) with stirring. The solution turned from brown to purple within 30 s of the addition of a small volume of the light petroleum solution. The mixture was stirred for 2 h and volatile components were then removed under reduced pressure. The purple residue was extracted with light petroleum (3 × 50 cm^3). The combined extracts were concentrated to 30 cm^3; cooling to −80 °C afforded black needles. Yield: 2.4 g, 70%.



Scheme. (*i*) Spiro[2.4]hepta-4,6-diene in light petroleum at room temperature for 2 h, yield 65%; (*ii*) iodine in toluene at −20 °C, 2 h, 85%; (*iii*) R = H, cyclopentadiene in light petroleum at r.t., 6 h, 70%; R = Me, pentamethylcyclopentadiene in light petroleum at r.t., 12 h, 67%; (*iv*) in CH_2Cl_2 at room temperature: R = H, 2 h, 70%; R = Me, 30 min, 79%; (*v*) potassium film, in thf, 16 h, >95%; (*vi*) R = Me, thallium tetrafluoroborate in acetone, *ca.* 35%; (*vii*) sodium amalgam in thf, 16 h: R = H, 60%; R = Me, 58%; (*viii*) MgR′Br, R′ = Et or Me, in thf at r.t., 1 h, 85%; (*ix*) MgEtCl in thf, *ca.* 20% (**11**), 80% (**10**) (combined yield 80%); (*x*) $-PMe_3$; (*xi*) $+PMe_3$; (*xii*) slow exchange at < −30 °C, fast exchange at > +60 °C

Chloro(η-pentamethylcyclopentadienyl)bis(trimethylphosphine)iron, (**6**).—The same method as for the preparation of $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Cl]$ was used, except for the duration of the reaction which was 30 min. $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2H]$ (1.5 g) gave (**6**). Yield: 1.3 g, 79%.

η-Cyclopentadienyl(methyl)bis(trimethylphosphine)iron, (**7**).—To a solution of $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Cl]$ (200 mg, 0.65 mmol) in tetrahydrofuran (15 cm^3) was added MgMeBr (1.0 cm^3 of 2 mol dm^{-3} solution in diethyl ether, 2 mmol) with stirring. The solution turned from purple to orange within 1 min. The mixture was stirred for 30 min, volatile components were then removed under reduced pressure. The orange residue was extracted with light petroleum (50 cm^3) and filtered through a Celite bed. Removal of solvent under reduced pressure was followed by extraction with light petroleum (30 cm^3). The extract was concentrated to *ca.* 3 cm^3; cooling to −80 °C afforded red prisms. Further concentration and cooling of the mother-liquor gave more product. Total yield: 150 mg, 80%.

η-Cyclopentadienyl(ethyl)bis(trimethylphosphine)iron, (**8**).—The procedure was similar to that for $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Me]$ but the Grignard reagent, MgEtBr, was a 3 mol dm^{-3} solution in diethyl ether. Orange-red prisms of the product were isolated in 75% yield.

Methyl(η-pentamethylcyclopentadienyl)bis(trimethylphosphine)iron, (**9**).—The procedure was similar to that for $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Me]$. Red prisms of the product were obtained in 85% yield.

Ethyl(η-pentamethylcyclopentadienyl)bis(trimethylphosphine)iron, (**10**), *and η-Ethylene(hydrido)(η-pentamethylcyclopentadienyl)(trimethylphosphine)iron*, (**11**).—The compound $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2Cl]$ (500 mg, 1.3 mmol) in thf (20 cm^3) was treated with MgEtCl (1 cm^3 of a 2 mol dm^{-3} solution in diethyl ether, 2 mmol) by slow addition, with stirring. The solution turned from purple to orange in 1 min. After stirring for 30 min, volatile components were removed under reduced pressure. The residue was extracted with light petroleum

(3×30 cm^3) and filtered through a Celite bed. The combined extracts were evaporated to dryness and the orange residue extracted with light petroleum (2×20 cm^3). After filtration through a Celite bed the combined extracts were concentrated to *ca.* 3 cm^3; cooling (-80 °C) afforded two compounds, one red and one yellow. Their separation was effected by low-temperature fractional crystallization.

$[\overline{\mathrm{Fe}(\eta\text{-}C_5H_4CH_2C}H_2)(PMe_3)_2]$, (**12**).—The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (1.0 g, 3.3 mmol) in light petroleum (30 cm^3) was added to a solution of spiro[2.4]hepta-4,6-diene (1 cm^3, 9 mmol) in light petroleum (10 cm^3) at -20 °C with stirring. The mixture was allowed to warm slowly to r.t. and stirred for 2 h. Volatile components were removed under reduced pressure and the residue extracted with light petroleum (50 cm^3). The extract was concentrated to *ca.* 10 cm^3 and cooling to -80 °C gave a brown solid. Recrystallization from pentane gave brown plates. Yield: 680 mg, 65%.

Iodo[η-(2-*iodoethyl*)*cyclopentadienyl*]*bis*(*trimethylphosphine*)*iron*, (**13**).—A solution of iodine (220 mg, 0.87 mmol) in toluene (20 cm^3) was added, in a dropwise manner and with stirring, to a toluene solution (20 cm^3) of $[\overline{\mathrm{Fe}(\eta\text{-}C_5H_4CH_2C}H_2)(PMe_3)_2]$ (250 mg, 0.83 mmol) at -20 °C. A brown solid was precipitated but which redissolved on warming to r.t. After stirring for 2 h at r.t., volatile components were removed under reduced pressure. The residue was extracted with diethyl ether (3×20 cm^3) and the combined extracts were concentrated to *ca.* 10 cm^3; cooling to -80 °C afforded a dark solid. Recrystallization from diethyl ether gave dark green plates. Yield: 450 mg, 85%.

Bis[η-*cyclopentadienylbis*(*trimethylphosphine*)*ferrio*]*mercury*, (**14**).—The compound $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2Cl]$ (250 mg, 0.8 mmol) in thf (30 cm^3) was added to an approximately 2% sodium amalgam (1.2—1.5 g of metallic sodium in 70 g of mercury). The solution was stirred for 16 h (the solution turned from purple to yellow and then red) and then filtered. The solvent was removed under reduced pressure and the red residue extracted with light petroleum (3×40 cm^3). The combined extracts were concentrated to *ca.* 15 cm^3; cooling to -80 °C gave red needles. Recrystallization from pentane gave red prisms. Yield: 180 mg, 60%.

Bis[η-*pentamethylcyclopentadienylbis*(*trimethylphosphine*)*ferrio*]*mercury*, (**15**).—The procedure was similar to that for $[Hg\{Fe(\eta\text{-}C_5H_5)(PMe_3)_2\}_2]$. Dark red prisms of the product were isolated in 58% yield (250 mg).

η-*Cyclopentadienyltris*(*trimethylphosphine*)*iron*(II) *Tetrafluoroborate*, (**16**).—The compound $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2H]$ (500 mg, 1.8 mmol) in diethyl ether (20 cm^3) was treated with tetrafluoroboric acid etherate (1 cm^3, excess) under an atmosphere of nitrogen by dropwise addition with stirring. An orange precipitate was formed immediately upon addition of the acid. After stirring for 2 h the solution was filtered and the residue washed with thf (3×30 cm^3). Extraction with acetone followed by addition of water precipitated a yellow solid which was collected and dried *in vacuo*. Yield: *ca.* 30%.

η-*Pentamethylcyclopentadienyltris*(*trimethylphosphine*)*iron*(II) *Tetrafluoroborate*, (**17**).—*Method A*. The reaction was carried out in diethyl ether using procedures similar to those for the protonation of $[Fe(\eta\text{-}C_5H_5)(PMe_3)_2H]$. A yellow solid was obtained in *ca.* 30% yield.

Method B. The compound $[Fe(\eta\text{-}C_5Me_5)(PMe_3)_2Cl]$ (200 mg, 0.5 mmol) in degassed acetone (15 cm^3) was added to a suspension of excess $TlBF_4$ in acetone with stirring. The solution turned from deep purple to red. After stirring under nitrogen for 2 h the red solution was filtered and solvent removed under reduced pressure. The orange residue was washed with diethyl ether (2×20 cm^3) and then extracted with acetone. An orange solid was precipitated from the extract by addition of diethyl ether (20 cm^3). The solid was collected and dried *in vacuo*. Yield: *ca.* 35%.

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