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

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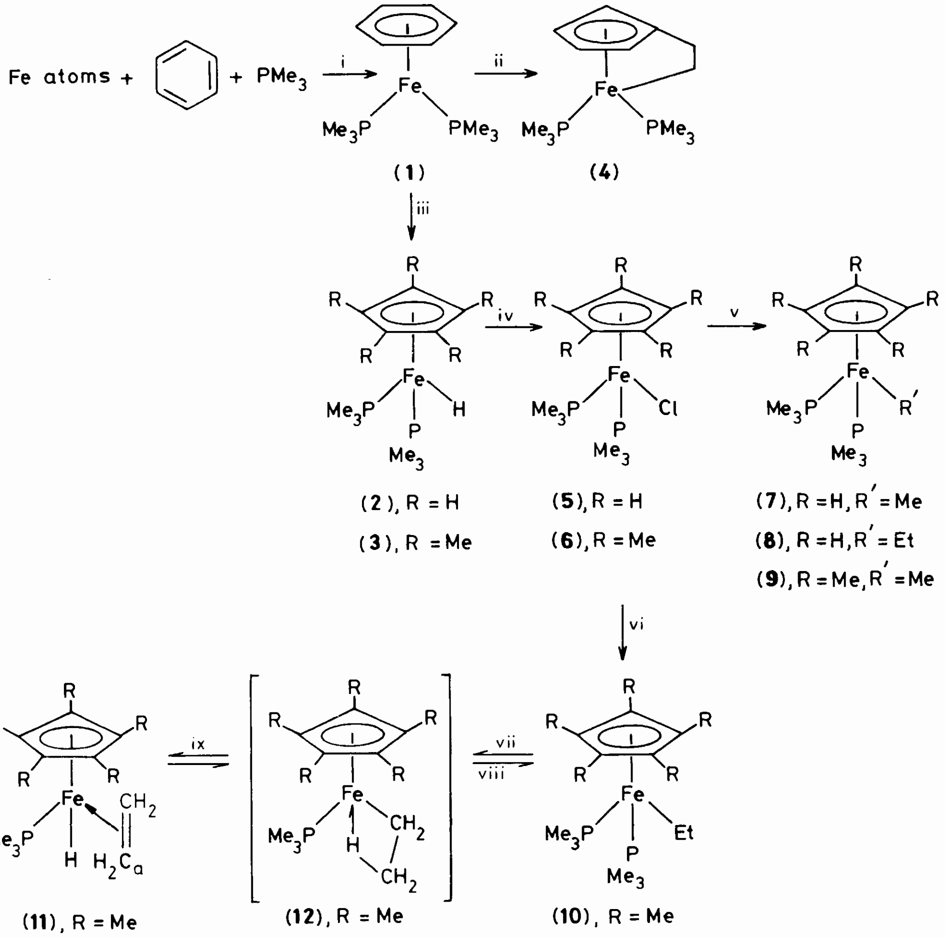
The compounds Fe(η-C_5R_5)(PMe_3)$_2$X, where R = H, Me, X = H, Cl, Me, Et, and Fe(CH_2CH_2-η^5-C_5H_4)(PMe_3)$_2$ are readily prepared from Fe(η-benzene)(PMe_3)$_2$; the equilibrium [Fe](PMe_3)Et ⇌ [Fe](η-C_2H_4)H + PMe_3, where [Fe] = Fe(η-C_5Me_5)(PMe_3), is described.

There is an extensive and useful chemistry of the Fe(η-C_5H_5)(CO)$_2$ system.[1] Derivatives of the mono-triphenylphosphine analogue Fe(η-C_5H_5)(CO)(PPh_3) have applications in stereospecific carbon–carbon bond formation.[2] It is to be expected that the Fe(η-C_5H_5)(PR_3)$_2$ system will provide a related extensive chemistry. However, relatively few studies have been described.

Here we report a general route to derivatives of the system Fe(η-C_5R_5)(PMe_3)$_2$, R = H, Me using Fe(η-C_6H_6)(PMe_3)$_2$ as a highly reactive intermediate. The compounds Fe(η-C_5H_5)(PMe_3)$_2$X, X = Me, SiR'$_3$, SnR'$_3$ and Fe(η-C_5H_5)($R_2PCH_2CH_2PR_2$)X, R = Me, Ph, X = Cl, Br, I, have been previously prepared *via* photoinduced substitutions from Fe(η-C_5H_5)(CO)$_2$X precursors.[3,4]

Tolman and Ittel have shown that co-condensation of arenes and iron atoms in the presence of PR_3, R=OMe or Me, gives high yields of the compounds Fe(η-arene)(PR_3)$_2$, *e.g.* Fe(η-C_6H_5Me)(PMe_3)$_2$.[5] Co-condensation of iron atoms with



Scheme 1. *Reagents and conditions:* i, typically 3—6 g of iron atoms with benzene–PMe_3 (5 : 1) (150—250 cm^3) gives 10—20 g (85%); ii, spiro-[2.4]hepta-4,6-diene in light petroleum (b.p. 40—60 °C) at room temp. for 2 h, 65%; iii, R=H, cyclopentadiene in light petroleum (b.p. 40—60 °C) at room temp. for 5 h, 65%; R=Me, pentamethylcyclopentadiene in light petroleum (b.p. 40—60 °C) at room temp for 12 h, 67%; iv, in CH_2Cl_2 at room temp.; R=H, 2 h, 70%, R=Me, 30 min, 79%; v, R'MgBr, R'=Et or Me, in tetrahydrofuran (thf) at room temp. for 1 h, 85%; vi, EtMgCl in thf, *ca.* 20% (**10**), 80% (**11**); combined yield 80%; vii, $-PMe_3$; viii, + PMe_3; ix, slow exchange at < -37 °C, fast exchange at $> +60$ °C.

a mixture of benzene–trimethylphosphine (5:1) gives the expected, new compound $Fe(\eta-C_6H_6)(PMe_3)_2$, (**1**) [typically, 3—6 g of iron atoms gave 10—20 g of (**1**)]. Compound (**1**) may be stored for months at −80 °C but steadily decomposes at room temperature.

Treatment of (**1**) with cyclopentadiene, pentamethylcyclopentadiene, or spiro[2.4]hepta-4,6-diene gives the compounds $Fe(\eta-C_5H_5)(PMe_3)_2H$, (**2**), $Fe(\eta-C_5Me_5)(PMe_3)_2H$, (**3**), or $Fe(CH_2CH_2-\eta^5-C_5H_4)(PMe_3)_2$, (**4**), respectively, in good yields (see Scheme 1). The photoelectron spectra of (**2**) and (**3**) show that the first ionisation potentials are 5.9 and 5.6 eV, respectively, classifying them as high energy compounds.[6]

The compounds (**2**) and (**3**) react with dichloromethane giving the corresponding chloro derivatives $Fe(\eta-C_5H_5)(PMe_3)_2Cl$, (**5**) and $Fe(\eta-C_5Me_5)(PMe_3)_2Cl$, (**6**), respectively. Treatment of (**4**) with iodine gives $Fe(\eta-C_5H_4CH_2CH_2I)(PMe_3)_2I$. Reduction of (**5**) with sodium amalgam forms $\{[Fe(\eta-C_5H_5)(PMe_3)_2]_2Hg\}$. This observation contrasts strongly with the reaction of $Fe(\eta-C_5H_5)(CO)_2Cl$ or the dimer $[Fe(\eta-C_5H_5)(CO)_2]_2$ with sodium amalgam in which the long-known sodium salt $Na[Fe(\eta-C_5H_5)(CO)_2]$ is formed.[7]

The alkyl derivatives $Fe(\eta-C_5H_5)(PMe_3)_2Me$, (**7**), and $Fe(\eta-C_5H_5)(PMe_3)_2Et$, (**8**), and $Fe(\eta-C_5Me_5)(PMe_3)_2Me$, (**9**) are prepared in high yield by treatment of (**5**) and (**6**), respectively, with the corresponding Grignard reagents RMgBr, R=Me or Et.

Treatment of (**6**) with EtMgCl gave two products: the expected $Fe(\eta-C_5Me_5)(PMe_3)_2Et$, (**10**) as red crystals and yellow crystalline $Fe(\eta-C_5Me_5)(PMe_3)(\eta-C_2H_4)H$, (**11**). The ^1H n.m.r. spectrum of apparently pure (**10**) showed bands assignable to (**11**) and PMe_3. *In vacuo*, (**10**) slowly loses PMe_3 giving (**11**). On addition of PMe_3 (*ca.* 5 equiv.) to a yellow benzene 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. We conclude that (**10**) and (**11**) are in equilibrium in solution. The low temperature n.m.r. data (−37 °C) of (**11**) strongly support the ethylene–hydride structure shown in Scheme 1. The ^1H n.m.r. spectrum at room temperature shows marked broadening of the resonances at δ 1.37 and −11.7 assigned to a C_2H_4 and an Fe–H group, respectively. Similarly, in the ^{13}C n.m.r. spectrum, the resonance assigned to carbon C_a moves from δ 27.2 (−37 °C) to 27.0 (room temp.) and changes from a binomial triplet to a multiplet with sharp outer lines and broad internal bands. The data are consistent with an exchange between the C_aH_2 hydrogens and the Fe-hydrogen.

At +80 °C the ^1H. n.m.r. spectrum of (**11**) shows no evidence for an Fe-hydrogen. A spin-echo Fourier transform experiment[8] at +80 °C showed that the methyl groups of the PMe_3 and $\eta-C_5$-ring had negative intensities as had the resonance assignable to the C_a carbon, for which hydrogen exchange was observed at room temperature. Further, the fully proton-coupled ^{13}C n.m.r. spectrum showed a *quartet* for C_a, for which the value of $J(C-H)_{av.}$ was 101 Hz.

We conclude that at +80 °C there is fast intramolecular exchange between the Fe–H and C_aH_2 of (**11**). The magnitude of 101 Hz for $J(C-H)_{av.}$ corresponds to $[2 \times J(C-H) = 302 + 0]/3 = 100.7$ Hz. It can be envisaged that this rapid exchange proceeds *via* an equilibrium between (**11**) and an intermediate with an agostic $Fe-H-CH_2$ structure for the Fe-ethyl group:[9] the structure for this intermediate, (**12**), is shown in Scheme 1. The presence of an agostic $Co-H-CH_2$ group has been demonstrated in the closely related ethyl–cobalt cation $[Co(\eta-C_5Me_5)(PPh_3)(\eta^2-Et)]^+$.[10] The new compounds (**1**)—(**11**) have been fully characterised by n.m.r. spectroscopy and microanalysis.[†] The reactions are shown in Scheme 1 and they all proceed in high yields. Further, the precursor $Fe(\eta-C_6H_6)(PMe_3)_2$, (**1**), is readily available since iron can be vaporised from simple resistance heating furnaces.

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[†] Selected n.m.r. data, in C_6D_6 unless otherwise stated. (δ, p.p.m., J in Hz, J' = separation of the outer lines of virtual triplets). (**1**), ^1H δ 4.71 (s, 6H, C_6H_6), 1.05 (br.s, 18H, $2PMe_3$); $^{31}P\{^1H\}$ δ −16 (s); $^{13}C\{^1H\}$ δ 74.5 (s, C_6H_6), 25.4 (br.s, $2PMe_3$). (**2**), ^1H δ 4.06 [t, 5H, $^3J(P-H)$ 2, C_5H_5], 1.12 (virtual t, 18H, J' 7.7, $2PMe_3$), −16.2 [t, 1H, $^2J(P-H)$ 76.6, FeH]; $^{31}P\{^1H\}$ δ 33.5 (s); $^{13}C\{^1H\}$ δ 73.57 (s, C_5), 26.1 (virtual t, J' 22.4, $2PMe_3$); ν(Fe–H) 1845 cm^{-1} (mull). (**4**) ^1H δ 4.05 (m, 5 lines, 2H, $H_{a,a'}$ or $H_{b,b'}$), 4.02 (m, 5 lines, 2H, $H_{b,b'}$ or $H_{a,a'}$), 3.07 [dd, 2H, $J(H_{c,c'}-H_{d,d'})$ 8.5, 7.4, $H_{c,c'}$], 1.08 (virtual t, 18H, J' 7.2, $2PMe_3$), −0.9 [dddd, 2H, $J(H_{d,d'}-H_{c,c'})$ 8.5, 7.4, $^3J(P-H_{d,d'})$ 7.0, 5.5, $H_{d,d'}$]; $^{31}P\{^1H\}$ δ 32.1 (s); ^{13}C δ 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 $C_{a,a'}$], 22.9 [q of virtual t, $J(C-H)$ 124, J' 21, $2PMe_3$], 24.9 [t, $J(C-H)$ 131, C_c], −45.3 [tt, $^2J(C-H)$ 137, $^2J(P-C)$ 20.5, C_d]. (**5**), ^1H δ 3.81 (br.s, 5H, C_5H_5), 1.19 (virtual t, 18H, J' 7.1, $2PMe_3$). (**7**), ^1H δ 3.83 [t, 5H, $^3J(P-H)$ 1.6, C_5H_5], 1.00 (virtual t, 18H, J' 7.7, $2PMe_3$), −0.31 [t, 3H, $^3J(P-H)$ 8.0, Fe–Me]; $^{31}P\{^1H\}$ δ 34.07 (s); $^{13}C\{^1H\}$ 77.54 (s, C_5H_5), 21.44 (virtual t, J' 20, $2PMe_3$), −24.00 [t, $^2J(P-C)$ 24.3, Fe–Me]. (**10**), ^1H δ 1.67 (s, 15H, C_5Me_5), 1.07 (virtual t, 18H, J' 8, $2PMe_3$), 1.45 (m, 3H, Me of Et), 0.32 (m, 2H, CH_2, of Et); $^{31}P\{^1H\}$ δ 30.81 (s); ^{13}C δ 84.83 (s, C_5), 21.57 [qt, $J(C-H)$ 125, $^3J(P-C)$ 6.5, Me of Et], 21.37 [q of multiplets, $J(C-H)$ 125, $2PMe_3$], 13.5 [q, $J(C-H)$ 125, Me_5], −1.16 [tt, $J(C-H)$ 121, $^2J(P-C)$ 23, CH_2 of Et]. (**11**), at −37 °C in $[^2H_8]$toluene, ^1H δ 1.65 (s, 15H, C_5Me_5), 0.69 [d, 9H, $^2J(P-H)$ 7.7, PMe_3], 1.37 (m, 4H, C_2H_4), −11.7 [d, 1H, $^2J(P-H)$ 96, Fe–H]; ^{13}C δ 87.3 (s, C_5), 30.4 [td, $J(C-H)$ 150, $^2J(P-C)$ 10, CH_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]; at +80 °C, ^{13}C δ 87.40 (s, C_5), 30.15 [td, $J(C-H)$ 150, $^2J(P-C)$ 10, CH_2 of Et], 27.9 [q, $J(C-H)$ 101, Me of Et], 18.50 [qd, $J(C-H)$ 128, $J(P-C)$ 26, PMe_3], 10.55 [q, $J(C-H)$ 126, Me_5]; at room temp., ^{13}C δ 87.4 (s, C_5), 30.00 [td, $J(C-H)$ 150, $^2J(P-C)$ 10, CH_2], 27.05 (m, separation of outer lines 302, CH_2), 18.50 [qd, $J(C-H)$ 125, $J(P-C)$ 26, PMe_3], 10.55 [q, $J(C-H)$ 126, Me_5]; $^{31}P\{^1H\}$ δ 40.1 (s).