Substitution Reactions of the Zerovalent Iron Complexes $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ and $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ (dmpe = $Me_2PCH_2CH_2PMe_2$)†

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Substitution reactions of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ with two-electron donor ligands occur with loss of the PMe_3 ligands, whereas those of the $Me_2PCH_2CH_2PMe_2$ (dmpe) analogue $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ result in displacement of the η-benzene ligand. Treatment of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ with 6,6-diphenylfulvene gives the compound $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ which reacts reversibly with methanol to form the cationic species $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]^+$.

It has been shown that the zerovalent iron compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (**1**), available in 20—30 g quantities by the cocondensation of iron atoms with benzene and trimethylphosphine, is a versatile synthetic intermediate towards a wide range of organoiron compounds.[1,2] In particular, treatment of (**1**) with the chelating phosphine dmpe [1,2-bis(dimethylphosphino)ethane] gives the red crystalline compound $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ (**2**), in high yield.[2] Although (**1**) decomposes steadily at room temperature, the chelating dmpe ligand in (**2**) imparts greater thermal stability and light petroleum solutions of (**2**) at 80 °C show no evidence of decomposition. We were interested to explore and compare the substitution reactions of compounds (**1**) and (**2**), and investigate the possibility of using (**2**) as a synthetic intermediate towards organoiron complexes containing the Fe(dmpe) moiety, as described below.

Results and Discussion

Compounds (**1**) and (**2**) were prepared as previously described.[1,2] Both are highly basic and their treatment with suspensions of the weak acid ammonium hexafluorophosphate in tetrahydrofuran (thf) gave the expected protonation products $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2H]PF_6$ (**3**) and $[Fe(\eta\text{-}C_6H_6)(dmpe)H]PF_6$ (**4**), respectively, in high yield. The data characterising (**3**), (**4**), and all other new compounds are summarised in the Table and will not be discussed further except where the interpretation is not straightforward. Attempts further to protonate (**3**) and (**4**) using the strong acid $HBF_4\cdot OEt_2$ resulted in decomposition and, in the case of (**3**), the salt $[PMe_3H]BF_4$ was recovered in high yield. Treatment of (**4**) with $LiBu^n$ readily gave (**2**). Compound (**2**) was also the product of the reaction of (**4**) with $LiAlH_4$. When the reaction was carried out with $LiAlD_4$ there was no incorporation of deuterium into the η-benzene ligand (^2H n.m.r. spectroscopy). This suggests that formation of (**2**) from (**4**) does not proceed *via* an η-cyclohexadienyl complex such as $[Fe(\eta\text{-}C_6H_7)(dmpe)H]$ which then eliminates dihydrogen.

The reaction of (**1**) with an excess of carbon monoxide at room temperature gave mainly $[Fe(PMe_3)_2(CO)_3]$ (**5**),[3-5] together with a small amount of the monocarbonyl complex $[Fe(\eta\text{-}C_6H_6)(PMe_3)(CO)]$ (**6**), which is the first example of the class of compounds $[Fe(\eta\text{-}arene)L(L')]$. There was no evidence for the dicarbonyl compound $[Fe(\eta\text{-}C_6H_6)(CO)_2]$. The only other example of an areneiron carbonyl compound is $[Fe(\eta\text{-}C_6Me_6)(CO)_2]$ prepared by Weber and Brintzinger[6] *via* the reaction of $[Fe(\eta\text{-}C_6Me_6)_2]$ with carbon monoxide. The observation of a single ν(C–O) stretching frequency (1 880 cm^{-1}) in the i.r. spectrum of (**5**) suggests that the *trans* isomer of D_{3h} symmetry is present. This agrees with the general observation, made from detailed analysis of the i.r. data for $[Fe(CO)_3L_2]$ complexes,[5,7] that strong σ donors prefer the axial sites, and thus the *trans* isomer is favoured. Treatment of (**2**) with carbon monoxide gave a red microcrystalline solid which appears to contain an inseparable mixture of two uncharacterised iron phosphine carbonyl compounds.

Treatment of compound (**1**) with an excess of trimethylphosphite at room temperature gave $[Fe(\eta\text{-}C_6H_6)(PMe_3)\{P(OMe)_3\}]$ (**7**). Heating (**7**) with an excess of $P(OMe)_3$ at 70 °C gave the previously described compound $[Fe(\eta\text{-}C_6H_6)\{P(OMe)_3\}_2]$.[8] The reaction of (**2**) with $P(OMe)_3$ at room temperature gave the arene-displacement product $[Fe(dmpe)\{P(OMe)_3\}_3]$ (**8**).

The reaction of (**1**) with tris(dimethylphosphinomethyl)methylsilane (tdms) results in phosphine substitution and arene ring slippage to form $[Fe(\eta^4\text{-}C_6H_6)(tdms)]$.[9,10] In contrast, treatment of (**2**) with tdms at 60 °C gave the arene-displacement product [Fe(dmpe)(tdms)] (**9**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this presumably trigonal bipyramidal complex shows a triplet for the ^{31}P nuclei of the tdms [δ 13.0 p.p.m., *J*(P–P) 30 Hz] and a quartet for those of the dmpe [δ 55.6 p.p.m., *J*(P–P) 30 Hz] ligands at temperatures down to 193 K. This suggests that (**9**) is highly fluxional on the n.m.r. time-scale. Treatment of (**9**) with NH_4PF_6 gave the pseudo-octahedral protonation product $[Fe(dmpe)(tdms)H]PF_6$ (**10**), as an orange crystalline solid. Compound (**10**) is stereochemically rigid on the n.m.r. time-scale, as shown by the ^1H spectrum (Figure) in which the hydride resonance is a clearly resolved doublet of triplets of triplets. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows three multiplets of integrated intensity ratio 2:2:1. The chemical shift (δ 57.7 p.p.m.) of the resonance assigned to the phosphorus nuclei of the dmpe ligand is not significantly different from that (δ 55.6 p.p.m.) of (**9**). This is consistent with the isomer of (**10**) in which the hydride ligand is *trans* to a phosphorus atom of tdms. This regioselectivity presumably arises from electrophilic attack by the ammonium ion in the equatorial plane of (**9**) so as to give the preferred *fac* arrangement of the phosphorus atoms of the tdms ligand.

Compound (**1**) has been shown to react readily with cyclic and acyclic polyenes to give predominantly products arising from arene displacement.[1,2] Treatment of (**1**) with 6,6-diphenylfulvene gave the dark red, highly air-sensitive compound $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ (**11**). In an earlier publication,[2] the molecular formula of (**11**) was incorrectly assigned as $[Fe(\eta^5\text{-}C_5H_4CPh_2)(PMe_3)_2]$ due to erroneous analytical data. The correct formulation of (**11**) was eventually arrived at by careful integration of the ^1H n.m.r. spectrum, by the quartet fine

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† *Non-S.I. units employed:* atm = 101 325 Pa, bar = 10^5 Pa.

Table. Analytical and spectroscopic data

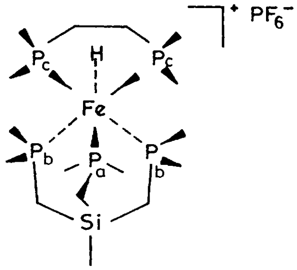
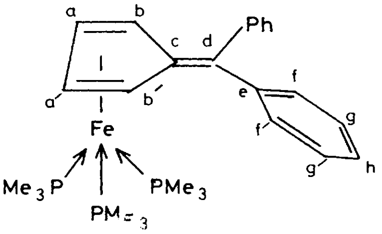
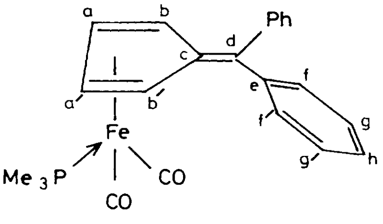
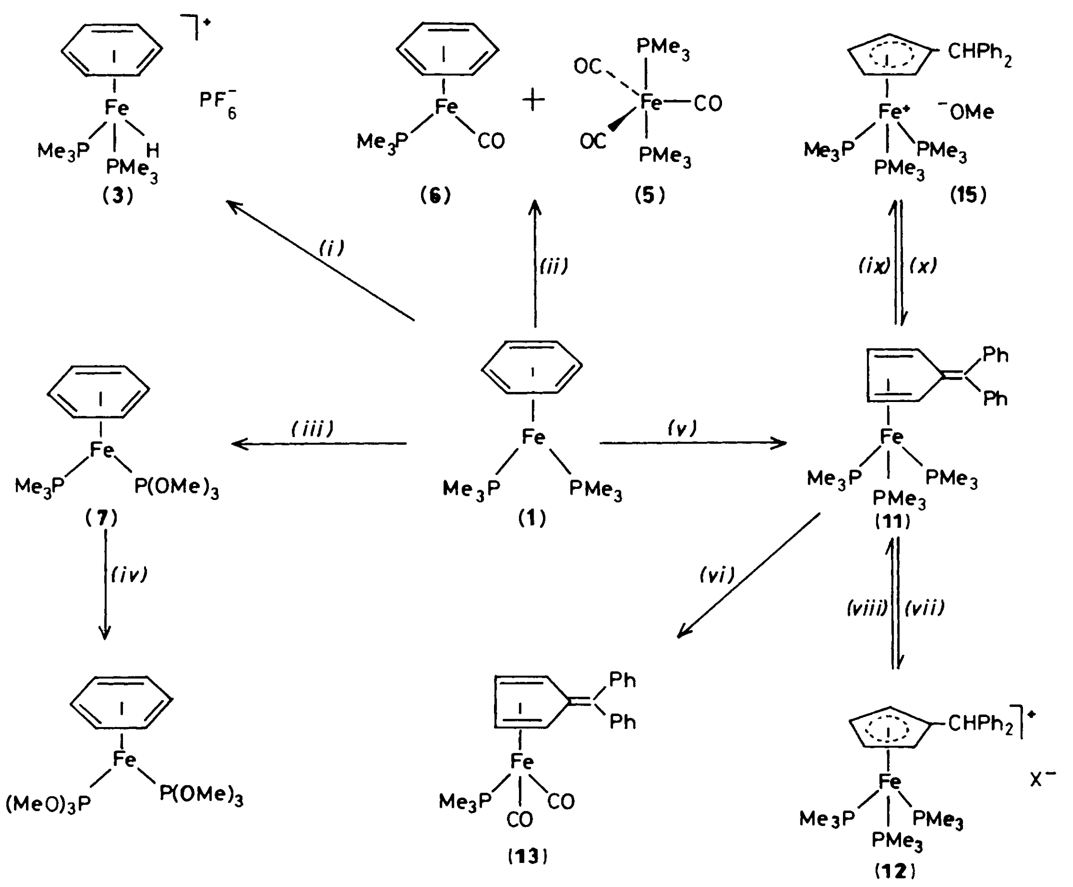
Compound, colour, and analysis[a]	N.m.r. data[b]	
	^{1}H	^{31}P and ^{13}C
(**3**) $[Fe(\eta-C_6H_6)(PMe_3)_2H]PF_6$[c] Yellow C, 33.15 (33.35); H, 5.60 (5.80)	5.75 [t, 6 H, *J*(P–H) 2, $\eta-C_6H_6$],[d] 1.45 (virtual t, 18 H, *J′* 10, 2 PMe_3), −13.28 [t, 1 H, *J*(P–H) 93, Fe–H]	$^{31}P-\{^1H\}$: 21.0 (s, 2 PMe_3)[d] $^{13}C-\{^1H\}$:[d] 90.2 (s, $\eta-C_6H_6$), 22.7 (virtual t, *J′* 20.5, 2 PMe_3)
(**4**) $[Fe(\eta-C_6H_6)(dmpe)H]PF_6$[e] Yellow C, 33.70 (33.50); H, 5.35 (5.35)	5.60 [t, 6 H, *J*(P–H) 2.2, $\eta-C_6H_6$],[f] 1.70 (m, 2 H, 2 CH of dmpe backbone), 1.65 (virtual t, 6 H, *J′* 10.2, 2 PMe), 1.55 (m, 2 H, 2 CH of dmpe backbone), 1.50 (virtual t, 6 H, *J′* 12.4, 2 PMe), −15.00 [t, 1 H, *J*(P–H) 85, Fe–H]	$^{31}P-\{^1H\}$: 72.2 (s, dmpe)[f]
(**6**) $[Fe(\eta-C_6H_6)(PMe_3)(CO)]$[g] Orange-red $m/z = 237, M^+$	4.82 [d, 6 H, *J*(P–H) 2.8, $\eta-C_6H_6$], 1.00 [d, 9 H, *J*(P–H) 8.8, PMe_3]	$^{31}P-\{^1H\}$: 15.5 (s, PMe_3) $^{13}C-\{^1H\}$: 81.7 (s, $\eta-C_6H_6$), 22.2 [d, *J*(P–C) 26.5, PMe_3]
(**7**) $[Fe(\eta-C_6H_6)(PMe_3)\{P(OMe)_3\}]$ Red C, 42.90 (43.15); H, 7.10 (7.20)	4.84 {t, $J_d(PMe_3\text{-}H) = J_d[P(OMe)_3\text{-}H]$ 2.5, $\eta-C_6H_6$}, 3.41 [d, *J*(P–H) 12, $P(OMe)_3$], 1.64 [d, *J*(P–H) 7.5, PMe_3]	$^{31}P-\{^1H\}$: 181.5 [d, *J*(P–P) 156, $P(OMe)_3$], 12.4 [d, *J*(P–P) 156, PMe_3] $^{13}C-\{^1H\}$: 77.6 (s, $\eta-C_6H_6$), 49.3 [s, $P(OMe)_3$], 24.0 [d, *J*(P–C) 21.5, PMe_3]
(**8**) $[Fe(dmpe)\{P(OMe)_3\}_3]$ Yellow $m/z = 577, M^+$	3.60 [m, 3 $P(OMe)_3$], 1.61 (m, 4 H, 2 CH_2), 1.50 (m, 12 H, 2 PMe_2)	$^{31}P-\{^1H\}$: 177.6 [t, *J*(P–P) 58, 3 $P(OMe)_3$], 62.5 [q, *J*(P–P) 58, dmpe]
(**9**) [Fe(dmpe)(tdms)] Red C, 40.0 (40.5); H, 9.4 (9.1) $m/z = 474, M^+$	1.45 (m, 4 H, 2 PCH_2 of dmpe), 1.35 (m, 18 H, 3 PMe_2 of tdms), 1.30 (m, 12 H, 2PMe_2 of dmpe), 0.77 (m, 6 H, 3PCH_2 of tdms), 0.10 (br s, 3 H, Me of tdms)	$^{31}P-\{^1H\}$: 55.6 [q, *J*(P–P) 30, dmpe], 13.0 [t, *J*(P–P) 30, tdms]
(**10**) $[Fe(dmpe)(tdms)H]PF_6$[h] Orange C, 31.1 (31.0); H, 7.6 (7.2)  	1.67 (m, 2 H, P_cCH_2),[d] 1.61 (m, 2 H, P_cCH_2), 1.59 (m, 6 H, 2P_bMe), 1.55 (m, 6 H, 2P_bMe), 1.50 [virtual t, 6 H, *J′* 7.8, 2 P_cMe], 1.43 [virtual t, 6 H, *J′* 8.1, 2 P_cMe], 1.36 [d, 6 H, *J*(P–H) 6.0, P_aMe_2], 0.90 (m, 4 H, 2 P_bCH_2), 0.81 (m, 2 H, P_aCH_2), 0.25 (m, 3 H, SiMe), −15.6 [dtt, 1 H, J_d(P–H) 59.2, J_t(P–H) 50.3, 18.5, Fe-H]	$^{31}P-\{^1H\}$:[i] 57.7 (m, 2 P, 2 P_c), 22.8 (m, 2 P, 2 P_b), 11.2 (m, 1 P, P_a)
(**11**) $[Fe(\eta^4-C_5H_4CPh_2)(PMe_3)_3]$ Red C, 62.95 (63.05); H, 7.85 (8.00); P, 18.00 (18.10)  	7.65—6.95 (m, 10 H, 2 C_6H_5), 4.20 (m, 2 H, 2 H of $\eta-C_5H_4$), 3.51 (m, 2 H, 2 H of $\eta-C_5H_4$), 0.95 (m, 27 H, *J′* 7.3, 3 PMe_3)	$^{31}P-\{^1H\}$: 27.3 (s, 3 PMe_3) ^{13}C: 147.0 (s, C_e), 143.1 (s, C_d), 130.1 [d, *J*(C–H) 156, $C_{f,f'}$ or $C_{g,g'}$], 128.1 [d, *J*(C–H) 158, C_h], 122.0 [d, *J*(C–H) 160, $C_{g,g'}$ or $C_{f,f'}$], 92.4 (s, C_c), 76.2 [d, *J*(C–H) 178, $C_{a,a'}$ or $C_{b,b'}$], 51.4 [d, *J*(C–H) 178, $C_{b,b'}$ or $C_{a,a'}$], 23.7 [q of m, *J*(C–H) 124, *J′* 22, 2 PMe_3]
(**12**) $[Fe(\eta^5-C_5H_4CHPh_2)(PMe_3)_3]$-$BF_4$ Yellow C, 53.70 (53.85); H, 6.70 (7.00)	7.50 [dd, 4 H, *J*(H–H) 7.2, 1.2, 4 H_{ortho}],[j] 7.32 [t, 4 H, *J*(H–H) 7.2, 4 H_{meta}], 7.20 [tt, 2 H, *J*(H–H) 7.2, 1.2, 2H_{para}], 4.52 [sxt, 2 H, *J*(H–H) = *J*(P–H) 2, 2 η-CH], 4.40 [sxt, 2 H, *J*(H–H) = *J*(P–H) 2, 2 η-CH], 1.51 (m, 27 H, *J′* 9.5, 3 PMe_3)	$^{31}P-\{^1H\}$: 20.4 (s, 3 PMe_3)[j] $^{13}C-\{^1H\}$:[k] 140.5 (s, 2 C_{ipso}), 129.5 (d, 4 C_{ortho} or 4 C_{meta}), 129.3 (d, 4 C_{meta} or 4 C_{ortho}), 126.5 (d, 2 C_{para}), 86.4 (d, 2 η-CH), 74.3 (d, 2 η-CH), 52.7 (d, $CHPh_2$), 24.7 (qm, 3 PMe_3)
(**13**) $[Fe(\eta^4-C_5H_4CPh_2)(PMe_3)$-$(CO)_2]$[l] Dark red C, 65.95 (66.05); H, 5.55 (5.50)  	7.46 (m, 4 H, 4 H_{ortho}), 7.22 (m, 4 H, 4 H_{meta}), 7.02 (m, 2 H, 2 H_{para}), 4.75 [q, 2 H, *J*(H–H) = *J*(P–H) 2.5, 2 η-CH], 4.41 [q, 2 H, *J*(H–H) = *J*(P–H) 2.5, 2 η-CH], 0.62 [d, 9 H, *J*(P–H) 9, PMe_3]	$^{31}P-\{^1H\}$: 22.9 (s, PMe_3) $^{13}C-\{^1H\}$: 215.1 [d, *J*(P–C) 15, 2 CO], 144.7 (s, C_e), 144.0 (s, C_d), 142.7 (s, C_c), 130.6 (s, $C_{f,f'}$ or $C_{g,g'}$), 128.6 (s, $C_{g,g'}$ or $C_{f,f'}$), 124.7 (s, C_h), 82.6 (s, $C_{a,a'}$ or $C_{b,b'}$), 61.7 (s, $C_{b,b'}$ or $C_{a,a'}$), 19.8 [d, *J*(P–C) 28, PMe_3]

Table (*continued*)

Compound, colour, and analysis[a]	N.m.r. data[b] ^{1}H	N.m.r. data[b] ^{31}P and ^{13}C
(**17**) $[\{Fe(\eta^5-C_5H_4CHPh_2)(dmpe)\}_2-(\mu-dmpe)][PF_6]_2$ Yellow C, 49.30 (49.30); H, 6.30 (6.10)	7.35—7.2 (m, 20 H, 4 C_6H_5),[m] 5.05 (s, 2 H, 2 C*H*Ph_2), 4.40 (m, 4 H, η-CH), 4.30 (m, 4 H, η-CH), 1.50 (virtual t, 12 H, *J*′ 9.7, 2 PMe_2 of chelating dmpe), 1.35 (virtual t, 12 H, *J*′ 9.0, 2 PMe_2 of chelating dmpe), 1.10 [d, 12 H, *J*(P–H) 7.2, 2 PMe_2 of bridging dmpe]	$^{31}P-\{^1H\}$:[n] 67.5 [d, *J*(P–P) 69, chelating dmpe], 31.7 [t, *J*(P–P) 69, bridging dmpe]

[a] Calculated values (%) in parentheses. [b] Given as: chemical shift (δ/p.p.m.), multiplicity, relative intensity, *J*/Hz, assignment; all spectra were obtained in C_6D_6 at room temperature and ^1H at 300 MHz, ^{31}P at 101.26 MHz, and ^{13}C at 62.89 MHz, unless otherwise stated. The *J*′ values given are the separations of the outer lines in virtually coupled multiplets. [c] ν(Fe–H) 1 883 cm^{-1}. [d] In CD_3OD. [e] ν(Fe–H) 1 878 cm^{-1}. [f] In CD_2Cl_2. [g] ν(C–O) 1 870 cm^{-1}. [h] ν(Fe–H) 1 824 cm^{-1}. [i] Determined at 124.5 MHz in CD_2Cl_2. [j] In $(CD_3)_2CO$. [k] Distortionless enhancement by polarisation transfer; in CD_2Cl_2. [l] ν(C–O) 1 961 and 1 910 cm^{-1}. [m] Determined at 500 MHz in CD_3CN; the methylene hydrogens of the dmpe backbones were obscured by the solvent and PMe_2 resonances. [n] Determined at 121.5 MHz in CD_3CN.



Scheme 1. (*i*) NH_4PF_6 in thf, yield 84%; (*ii*) CO at −10 °C for 3 h; (*iii*) $P(OMe)_3$ at room temperature (r.t.) for 2 h, 83%; (*iv*) $P(OMe)_3$ at 70 °C for 2 h, 70%; (*v*) 6,6-diphenylfulvene at r.t. for 2 h, 88%; (*vi*) CO (2 atm) at 65 °C for 4 h, 92%; (*vii*) acids such as $HBF_4{\cdot}OEt_2$ in Et_2O, X = BF_4, 72%; (*viii*) $LiBu^n$ in thf at −78 °C for 1 h, >95%; (*ix*) MeOH in toluene–thf; (*x*) *in vacuo*

structure [*J*(P–H) 2.5 Hz] of the $H_{a,a'}$ resonance of the η^4-C_5 ring upon irradiation of the $H_{b,b'}$ resonance, microanalysis, and from chemical evidence. Thus treatment of (**11**) with $HBF_4{\cdot}OEt_2$ gave the yellow crystalline complex $[Fe(\eta^5-C_5H_4CHPh_2)(PMe_3)_3]BF_4$ (**12**), in high yield. Compound (**11**) was reformed in >95% yield by the reaction of (**12**) with n-butyllithium.

The compound (**11**) reacts with carbon monoxide (2 atm) at 60 °C to give the air-stable, red compound $[Fe(\eta^4-C_5H_4CPh_2)(PMe_3)(CO)_2]$ (**13**), in high yield. The ν(C–O) stretching modes of (**13**) were observed at 1 961 and 1 910 cm^{-1} in the i.r. spectrum. When the reaction was carried out at room temperature there was spectroscopic evidence for the presence of the monocarbonyl compound $[Fe(\eta^4-C_5H_4CPh_2)(PMe_3)_2(CO)]$ (**14**). The ^1H n.m.r. spectrum of the product mixture showed the presence of (**11**), (**13**), and (**14**) in approximately 2:1:1 ratio. Attempts to isolate (**14**) were, however, unsuccessful. The PMe_3 hydrogens of (**14**) were observed as a virtual triplet at δ 0.90 in the ^1H n.m.r. spectrum. The ν(C–O) stretch was observed at 1 895 cm^{-1} in the i.r. spectrum. It is likely that the reaction of (**11**) with carbon monoxide proceeds by stepwise substitution, and (**14**) is the precursor to (**13**).

The reaction of compound (**11**) with methanol is unusual. Addition of a dark red toluene solution of (**11**) to a mixture of methanol and thf resulted in an instantaneous reaction giving a yellow solution. When volatiles were removed at room temperature a yellow oil (**15**) slowly separated from the solution. Upon drying *in vacuo* (**15**) gradually turned red and the red crystalline solid thus obtained was shown to be (**11**) (^{1}H n.m.r. spectroscopy). In the ^{1}H n.m.r. spectrum of compound (**15**) (C_6D_6–CH_3OH mixture) the resonances due to the phenyl hydrogens are at δ 7.26, 7.14, and 7.00, those due to the η-CH hydrogens are at δ 4.03 and δ 3.94, and the PMe_3 hydrogens are observed as a broad singlet at δ 1.08. In addition to the resonances due to methanol, there is a one hydrogen resonance at δ 4.79. The data are consistent with the formulation $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]OMe$. However, the resonance due to the methoxy hydrogens is not observed, presumably due to rapid scrambling with excess of methanol. There is no evidence for the presence of (**11**) in the ^{1}H n.m.r. spectrum at 70 °C, indicating that (**15**) is thermally stable in the presence of excess of methanol. When $NaPF_6$ is added to (**15**) the expected metathesis product $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]PF_6$ can be isolated.

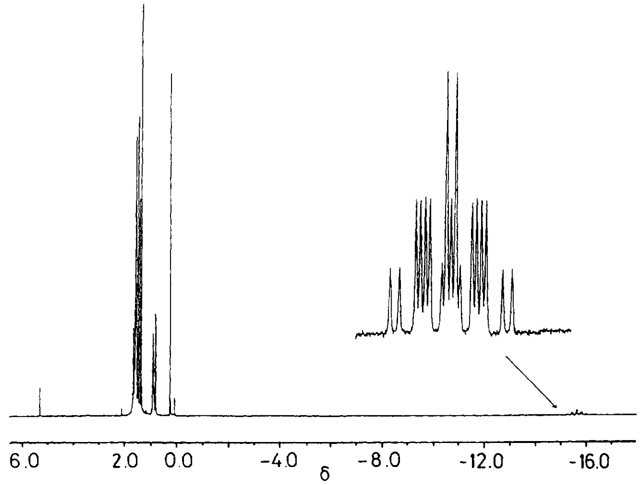
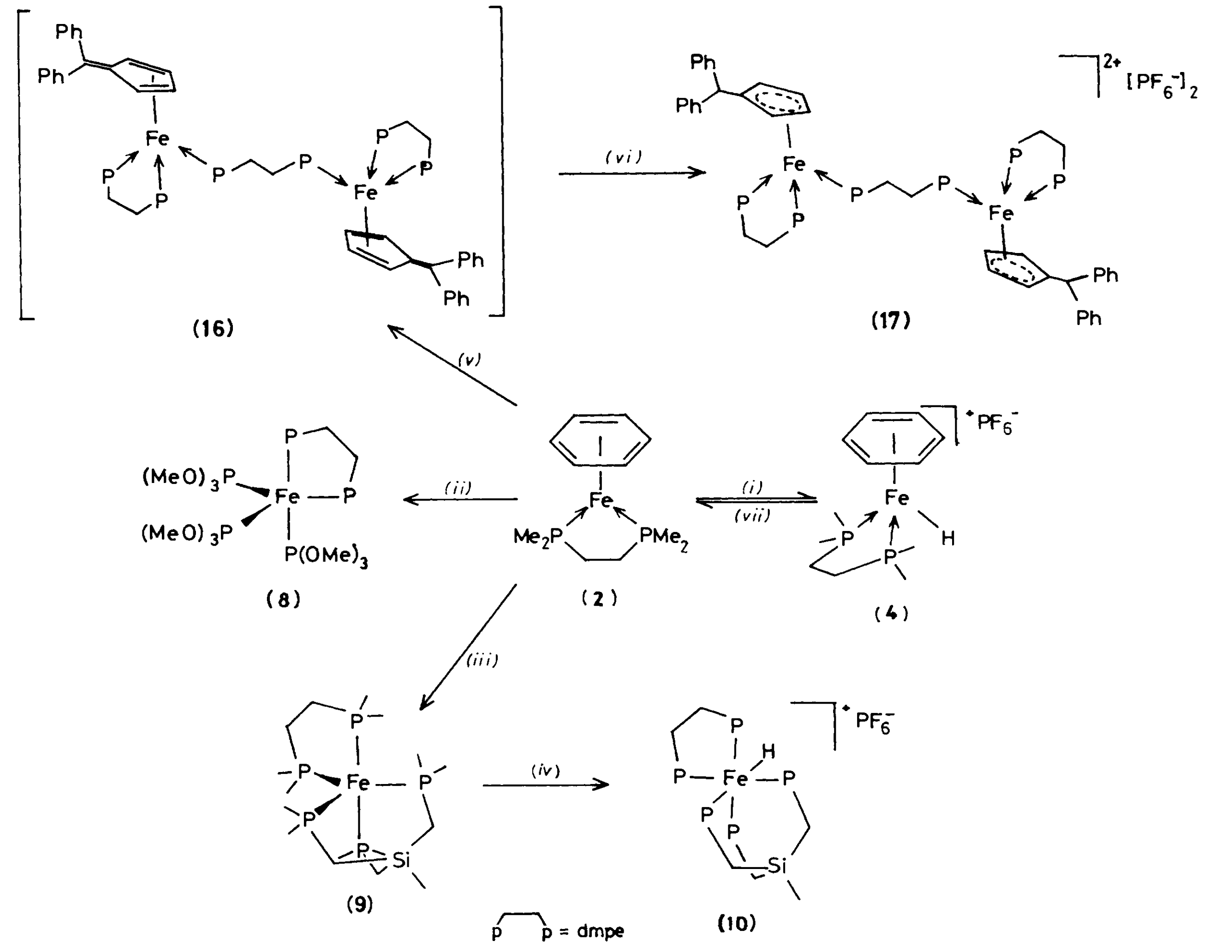


Figure. 300-MHz ^{1}H N.m.r. spectrum of $[Fe(dmpe)(tdms)H]PF_6$ (**10**), in $[^2H_2]$dichloromethane

The reversible reactions of *cis*-$[Fe(R_2PCH_2CH_2PR_2)_2H_2]$ (R = Me, Et, or Pr^i) with alcohols have been reported.[11] Unlike the reversible reaction of (**11**) with methanol, the protonation equilibrium was found to be temperature dependent and complete protonation was observed at −50 °C. It is likely that the pK_a values of compound (**11**) and methanol are very similar, and the protonation products such as (**15**) are stabilised in solution by strong solvation of the alkoxide counter ion by the excess of alcohol.

Although compound (**1**) has been shown to react readily with polyenes under mild conditions,[1,2] (**2**) showed no reaction with cyclopentadiene, indene, or even the highly reactive



Scheme 2. (*i*) NH_4PF_6 in thf, yield 73%; (*ii*) $P(OMe)_3$ at r.t. for 30 min; (*iii*) tdms in toluene at 60 °C for 8 h, 72%; (*iv*) NH_4PF_6 in thf, 64%; (*v*) 6,6-diphenylfulvene in toluene at 65 °C for 48 h; (*vi*) NH_4PF_6 in thf for 2 h, overall yield of (*v*) and (*vi*) from 450 mg of (**2**) was 600 mg; (*vii*) $LiBu^n$ in thf at r.t. for 30 min, >85%; $LiAlH_4$ or $LiAlD_4$ in thf at −40 °C for 30 min, 68%

6,6-dimethylfulvene at 80 °C. However, heating (**2**) with 6,6-diphenylfulvene in toluene gave a purple crystalline precipitate (**16**) which was insoluble in thf and dichloromethane. Compound (**16**) was soluble in methanol giving a yellow solution which gave a purple solid when the methanol was removed *in vacuo*. Treatment of (**16**) with NH_4PF_6 gave the yellow compound $[\{Fe(\eta^5\text{-}C_5H_4CHPh_2)(dmpe)\}_2(\mu\text{-dmpe})][PF_6]_2$ (**17**). By analogy with (**11**), we propose that (**16**) is the dmpe-bridged di-iron complex $[\{Fe(\eta^4\text{-}C_5H_4CPh_2)(dmpe)\}_2(\mu\text{-dmpe})]$, and its reaction with methanol is also reversible.

Conclusions

The reactions of compounds (**1**) and (**2**) described are summarised in Schemes 1 and 2. It is clear that (**2**), with the chelating phosphine dmpe, is much more thermally and kinetically stable compared to (**1**). All the substitution reactions of (**1**) proceed rapidly at room temperature whereas those of (**2**) require heating, usually at 60 °C. Photolysis had no effects on the rate of such reactions with compound (**2**). In the reactions of (**1**) and (**2**) with two-electron donor ligands the PMe_3 ligands of (**1**) are displaced whereas the $\eta\text{-}C_6H_6$ ligand is displaced in (**2**). This has allowed the synthesis of the first examples of compounds of the class $[Fe(\eta\text{-arene})L(L')]$. The reversible reaction of (**11**) and (**16**) with methanol is interesting and further work on whether this reaction is more general, *e.g.* with other alcohols and other $[Fe(\eta\text{-diene})L_3]$ complexes, is in progress.

Experimental

All preparations, manipulations, and reactions were carried out under an atmosphere of dinitrogen (<10 p.p.m. oxygen, <20 p.p.m. water) using standard Schlenk-tube and vacuum-line techniques, or in a dry-box. Dinitrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Solvents were pre-dried over activated molecular sieves and then distilled from potassium (tetrahydrofuran, thf), sodium [petroleum ether (b.p. 100—120 °C unless otherwise stated), toluene], sodium–potassium alloy [light petroleum (b.p. 40—60 °C unless otherwise stated), diethyl ether], or phosphorus pentoxide (dichloromethane) under an atmosphere of dinitrogen before use. Methanol was dried over activated molecular sieves and deoxygenated before use. Deuteriated solvents for n.m.r. samples were stored in Rotaflo ampoules over activated molecular sieves and transferred by vacuum distillation. Celite 545 filtration aid (Koch–Light) was pre-dried in an oven at 80 °C before use.

Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 1510 FT interferometer. Hydrogen-1 n.m.r. spectra were obtained at 300 MHz using a Bruker WH-300 or AM-300 spectrometer, ^{13}C and ^{31}P n.m.r. spectra at 62.89 and 101.26 MHz, respectively, using a Bruker AM-250 spectrometer. Spectra were referenced internally using a residual solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ 0 p.p.m.), or externally using trimethyl phosphate $[PO(OMe)_3]$ in D_2O (^{31}P). All chemical shifts are quoted in δ (p.p.m.) and coupling constants in Hz.

Low-resolution mass spectra were obtained on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services Ltd. Elemental analysis was performed by the Analysis Department in this laboratory or, in the cases of very air-sensitive compounds, by Analytische Laboratorien, Elbach, West Germany.

Reactions with NH_4PF_6.—(*a*) $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$. The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (250 mg, 0.88 mmol) in thf (50 cm^3) was added to a suspension of NH_4PF_6 (500 mg, excess) in thf (30 cm^3) at −50 °C. The dark red solution of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ became yellow instantaneously upon mixing. The mixture was warmed to ambient temperature with stirring and, after 10 min, volatiles were removed *in vacuo* at *ca.* 50 °C leaving a yellow solid. Water (100 cm^3) was added, the suspension transferred onto a frit and washed through with water (30 cm^3). Extraction of the yellow residue with warm (*ca.* 50 °C) methanol and filtration through the frit gave a yellow solution which was concentrated to *ca.* 20 cm^3 and cooled at −80 °C to afford yellow, analytically pure $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2H]PF_6$. Yield 255 mg, 84%.

(*b*) *With* $[Fe(\eta\text{-}C_6H_6)(dmpe)]$. As above, yellow $[Fe(\eta\text{-}C_6H_6)(dmpe)H]PF_6$ was obtained in 73% yield.

Reactions of $[Fe(\eta\text{-}C_6H_6)(dmpe)H]PF_6$.—(*a*) With $LiBu^n$. n-Butyl-lithium (0.5 cm^3 of a 2 mol dm^{-3} solution) was added to a yellow solution of $[Fe(\eta\text{-}C_6H_6)(dmpe)H]PF_6$ (100 mg, 0.23 mmol) in thf (10 cm^3) and stirred for 30 min. During this time the solution gradually turned a deep orange. Volatiles were removed *in vacuo* and the resulting red solid was extracted with light petroleum (10 cm^3), filtered, and concentrated. After cooling overnight at −80 °C red prisms of $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ were obtained in >85% yield.

(*b*) *With* $LiAlH_4$. The compound $[Fe(\eta\text{-}C_6H_6)(dmpe)H]PF_6$ (200 mg, 0.47 mmol) was placed in a Schlenk tube containing $LiAlH_4$ (45 mg, excess), then cooled to −40 °C and thf (30 cm^3) added. The mixture was stirred and the colour changed from yellow to orange. After 30 min the orange solution was filtered and volatiles removed *in vacuo* leaving a red solid. This solid was extracted with light petroleum (20 cm^3), filtered, and concentrated. Upon cooling at −80 °C red crystals of $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ were obtained. Yield 90 mg, 68%.

Reaction of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ *with Carbon Monoxide.*—The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (720 mg, 2.52 mmol) in light petroleum (60 cm^3) was degassed by two freeze–pump–thaw cycles and then exposed to carbon monoxide (35 cm^3 at 2 atm, 2.9 mmol) at −10 °C for 3 h. Large amounts of a grey precipitate were formed and the solution was orange-red. Filtration and removal of volatiles *in vacuo* at 25 °C gave a red residue which was extracted into light petroleum and filtered. The orange filtrate was concentrated to *ca.* 10 cm^3 and cooled at −80 °C to give an orange solid. The ^1H n.m.r. spectrum ($[^2H_6]$benzene) showed it to be a 9:1 mixture of $[Fe(PMe_3)_2(CO)_3]$ and $[Fe(\eta\text{-}C_6H_6)(PMe_3)(CO)]$. Concentration and cooling of the supernatant gave another crop of solid consisting of the same mixture in 7:2 ratio. Sublimation at 35 °C and 10^{-2} mbar gave an orange solid which upon recrystallisation gave a *ca.* 85% pure sample of $[Fe(\eta\text{-}C_6H_6)(PMe_3)(CO)]$. Yield *ca.* 50 mg, 8.5%. Pure $[Fe(\eta\text{-}C_6H_6)(PMe_3)(CO)]$ may be obtained as red crystals by slow recrystallisation from light petroleum. Yield *ca.* 10 mg. Recrystallisation of the residue after sublimation from light petroleum gave white needles of $[Fe(PMe_3)_2(CO)_3]$, yield 200 mg (19.6%).

Reactions with Trimethyl Phosphite.—(*a*) *With* $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$. The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (250 mg, 0.87 mmol) in light petroleum (50 cm^3) was treated with a solution of trimethyl phosphite (220 mg, 1.75 mmol) in light petroleum (10 cm^3) at −20 °C with stirring. The solution rapidly turned from dark red to orange upon mixing, and the mixture was warmed to ambient temperature after addition was complete. Volatiles were removed *in vacuo* at *ca.* 40 °C, the red residue was extracted into light petroleum (2 × 40 cm^3) and filtered. Upon concentration to *ca.* 20 cm^3 and cooling at −80 °C red crystals were obtained. Recrystallisation from light petroleum gave analytically pure red prisms of $[Fe(\eta\text{-}C_6H_6)(PMe_3)\{P(OMe)_3\}]$. Yield 240 mg, 83%.

(*b*) *With* $[Fe(\eta\text{-}C_6H_6)(PMe_3)\{P(OMe)_3\}]$. The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)\{P(OMe)_3\}]$ (100 mg, 0.3 mmol) in toluene (20 cm^3) was heated with trimethyl phosphite (0.5 cm^3, excess) at 70 °C for 20 h. No colour change was apparent. Volatiles were removed *in vacuo* and extraction of the red residue with light petroleum (2 × 20 cm^3), filtration, concentration to *ca.* 5 cm^3, and cooling at −80 °C overnight gave red prisms of $[Fe(\eta\text{-}C_6H_6)\{P(OMe)_3\}_2]$. The product was identified by comparison of the ^1H n.m.r. spectrum with that of an authentic sample. Yield 80 mg, 70%.

(*c*) *With* $[Fe(\eta\text{-}C_6H_6)(dmpe)]$. The compound $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ (200 mg, 0.88 mmol) in toluene (30 cm^3) was stirred with trimethyl phosphite (0.5 cm^3, excess) at room temperature. The reaction mixture turned from red to green after 30 min. Volatiles were removed *in vacuo* leaving a green solid which was extracted with light petroleum and filtered. The solvent was removed *in vacuo* leaving a greenish yellow solid. Sublimation at 50 °C and 10^{-4} mbar gave a green solid (*ca.* 350 mg) which was shown to be a mixture of $[Fe(dmpe)\{P(OMe)_3\}_3]$ and *ca.* 5% of other $P(OMe)_3$-containing impurities (^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra). It was not possible to obtain pure $[Fe(dmpe)\{P(OMe)_3\}_3]$ by recrystallisation from light petroleum, or by sublimation.

Reaction of $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ *with* $MeSi(CH_2PMe_2)_3$ (tdms).—The compound $[Fe(\eta\text{-}C_6H_6)(dmpe)]$ (400 mg, 1.76 mmol) in toluene (30 cm^3) was heated with tdms (500 mg, excess) in a glass ampoule equipped with a Teflon stopcock at 60 °C for 8 h. The solution turned from dark red to orange-red. Volatiles were removed *in vacuo*, and the excess of tdms was removed by sublimation at 25 °C and 10^{-2} mbar. The resulting red crystalline solid was extracted with light petroleum (50 cm^3) and filtered. Upon concentrating to *ca.* 10 cm^3 and cooling at −80 °C overnight red crystals of [Fe(dmpe)(tdms)] were obtained. Yield 600 mg, 72%.

Reaction of [Fe(dmpe)(tdms)] *with* NH_4PF_6.—The compound [Fe(dmpe)(tdms)] (300 mg, 0.63 mmol) in light petroleum (30 cm^3) was added slowly to a suspension of NH_4PF_6 (150 mg, excess) in thf (20 cm^3). An instantaneous reaction occurred: the red colour of the light petroleum solution was discharged and small amounts of a yellow solid were precipitated. Volatiles were removed *in vacuo* leaving an orange solid which was extracted with methanol (50 cm^3), filtered, and concentrated. Upon cooling at −25 °C overnight an orange crystalline solid was obtained. Pure $[Fe(dmpe)(tdms)H]PF_6$ was obtained by recrystallisation from methanol. Yield 250 mg, 64%.

Reaction of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ *with* 6,6-*Diphenylfulvene.*—The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (1.0 g, 3.5 mmol) in light petroleum (70 cm^3) was treated with 6,6-diphenylfulvene (0.7 g, 3.1 mmol) in toluene (20 cm^3) at −20 °C. The solution turned from dark red to red after stirring for 2 min and a red solid was precipitated. After warming to ambient temperatures and stirring for 2 h, volatiles were removed *in vacuo* leaving a red solid which was washed with light petroleum (100 cm^3) to remove any unreacted 6,6-diphenylfulvene. The crystalline residue was then extracted with warm toluene (2 × 70 cm^3 at 50 °C) and filtered. The filtrates were concentrated to *ca.* 20 cm^3 and light petroleum was added until a red solid started to appear. The mixture was cooled at −80 °C to give dark red crystalline $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$. Yield 1.05 g, 88% taking into account the partial decomposition.

Reaction of $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ *with* $HBF_4\cdot OEt_2$.—A suspension of $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ (500 mg, 1 mmol) in diethyl ether (100 cm^3) was treated with $HBF_4\cdot OEt_2$ by dropwise addition. The dark red colour was rapidly discharged as the acid was added, and a yellow crystalline solid was precipitated. Addition of the acid was stopped when the solution became colourless. The colourless liquid was filtered off, and the solid washed with diethyl ether (2 × 30 cm^3). The yellow residue was extracted with dichloromethane (2 × 50 cm^3) and filtered. The combined filtrates were concentrated to *ca.* 40 cm^3, and diethyl ether was added until solid began to appear. Cooling at −80 °C overnight gave the yellow complex $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]BF_4$ in 72% yield (420 mg).

Reaction of $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]PF_6$ *with n-Butyllithium.*—The compound $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]PF_6$ (300 mg, 0.45 mmol) in thf (40 cm^3) was treated with $LiBu^n$ (0.3 cm^3 of a 2.5 mol dm^{-3} solution in pentane, 0.75 mmol) at −78 °C. The mixture was stirred at −78 °C and the solution gradually turned from yellow to orange to red. After stirring for 1 h at −78 °C the solution was dark red. Volatiles were removed *in vacuo* at ambient temperature, the red residue was extracted with toluene (2 × 30 cm^3) and filtered. The combined filtrates were concentrated to *ca.* 10 cm^3 and light petroleum (*ca.* 10 cm^3) was added. The mixture was cooled at −80 °C to give red crystalline $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ in nearly quantitative yield.

Reaction of $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ *with Carbon Monoxide.*—The compound $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ (350 mg, 0.7 mmol) in toluene (70 cm^3) in a glass ampoule equipped with a Teflon stopcock was charged with carbon monoxide (2 atm) and heated at 55 °C. The solution changed from dark red to orange-red after 2 h. After 4 h, volatiles were removed *in vacuo* leaving a red solid which was extracted with toluene (2 × 30 cm^3) and filtered. The combined filtrates were concentrated to *ca.* 10 cm^3 and light petroleum was added until a red solid appeared. The solution was then cooled at −80 °C overnight to give red crystalline $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)(CO)_2]$. Yield 270 mg, 92%.

Reaction of $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ *with Methanol followed by Sodium Hexafluorophosphate.*—The compound $[Fe(\eta^4\text{-}C_5H_4CPh_2)(PMe_3)_3]$ (250 mg, 0.5 mmol) in thf (40 cm^3) was added to a mixture of thf (20 cm^3) and methanol (2 cm^3). A suspension of sodium hexafluorophosphate (excess) in thf (30 cm^3) was added to the yellow solution and the mixture was stirred. A small amount of a yellow crystalline solid was precipitated. Volatiles were removed *in vacuo* and the excess of sodium hexafluorophosphate was extracted into water and filtered through a frit. After washing with diethyl ether (40 cm^3) the yellow solid on the frit was extracted with thf (2 × 50 cm^3). The combined filtrates were concentrated to *ca.* 20 cm^3 and diethyl ether was added until yellow crystals appeared. The solution was then cooled at −80 °C to give yellow prisms of $[Fe(\eta^5\text{-}C_5H_4CHPh_2)(PMe_3)_3]PF_6$. Yield 250 mg, 76%.

Synthesis of $[\{Fe(\eta^5\text{-}C_5H_4CHPh_2)(dmpe)\}_2(\mu\text{-}dmpe)][PF_6]_2$.—$[Fe(\eta\text{-}C_6H_6)(dmpe)]$ (450 mg, 1.58 mmol) in toluene (30 cm^3) was added to a solution of 6,6-diphenylfulvene (365 mg, 1.58 mmol) in toluene (10 cm^3). The resulting red solution was heated at 65 °C for 48 h in a glass ampoule equipped with a Teflon stopcock. During this time a purple solid precipitated. The solution was cooled and volatiles removed *in vacuo*. A suspension of NH_4PF_6 (excess) in thf was added and after stirring for 2 h the purple solid was replaced by a yellow precipitate. The thf solution was filtered off and the yellow solid was slurried onto a frit with water (50 cm^3). The solid was washed with water and diethyl ether, then extracted with acetonitrile and filtered to give a yellow solution which was concentrated. The salt $[\{Fe(\eta^5\text{-}C_5H_4CHPh_2)(dmpe)\}_2(\mu\text{-}dmpe)][PF_6]_2$ was obtained as a yellow crystalline solid by vapour diffusion of diethyl ether into the solution. Yield 600 mg.

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