(η-Benzene)bis(trimethylphosphine)iron: A Useful Precursor to Polyene Iron Derivatives. Crystal Structure of 2—4-η:2′—4′-η-1,1′-bi(cyclohex-3-en-2-yl)-bis(trimethylphosphine)iron(II)†

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

(η-Benzene)bis(trimethylphosphine)iron reacts with 6,6-dimethylfulvene, 6-phenylfulvene, 6,6-diphenylfulvene, cyclobutene, indene, 1,2-bis(dimethylphosphino)ethane, and 1,2-bis(diphenylphosphino)ethane giving $[Fe(\eta^5,\eta^{5'}\text{-}C_5H_4CMe_2CMe_2C_5H_4)]$, $[Fe\{\eta^5,\eta^{5'}\text{-}C_5H_4CH(Ph)CH(Ph)C_5H_4\}]$, $[Fe(\sigma,\eta^5\text{-}C_5H_4CPh_2)(PMe_3)_2]$, $[Fe(\eta\text{-}C_4H_6)(PMe_3)_3]$, $[Fe(\eta^5\text{-}C_9H_7)(PMe_3)_2H]$, and $[Fe(\eta\text{-}C_6H_6)(R_2PCH_2CH_2PR_2)]$ (R = Me or Ph) respectively. Treatment of $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ with buta-1,3-diene gives a mixture of $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_4H_6)]$ and $[Fe(\eta\text{-}C_4H_6)_2(PMe_3)]$; with cycloheptatriene a mixture of $[Fe(\eta^4\text{-}C_7H_8)(PMe_3)_3]$, $[Fe(\eta\text{-}C_6H_6)(\eta^4\text{-}C_7H_8)]$, and $[Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ is obtained. $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ reacts with cyclohexa-1,3-diene causing an unusual coupling giving the compound $[Fe(\eta^3,\eta^{3'}\text{-}C_{12}H_{16})(PMe_3)_2]$ which has been characterized by ^1H–^1H COSY, heteronuclear ^1H–^{13}C shift correlation two-dimensional n.m.r. experiments and crystal structure determination. Protonation of $[Fe(\eta^3,\eta^{3'}\text{-}C_{12}H_{16})(PMe_3)_2]$ gives the cation $[Fe(\eta^3\text{-}C_6H_8\text{–}H)(PMe_3)_3]^+$ which contains an agostic hydrogen.

We have described the use of η-benzenebis(trimethylphosphine)iron (**1**) for the synthesis of η-cyclopentadienyl trimethylphosphine derivatives.[1,2] Here we report further studies of (**1**) as a synthetic intermediate for the synthesis of known and new organometallic compounds of iron.

Results and Discussion

Treatment of (**1**) with 6,6-dimethylfulvene and 6-phenylfulvene gives the orange-red crystalline bridged ferrocene derivatives $[Fe(\eta^5,\eta^{5'}\text{-}C_5H_4CMe_2CMe_2C_5H_4)]^3$ (**2**) and $[Fe\{\eta^5,\eta^{5'}\text{-}C_5H_4\text{-}CH(Ph)CH(Ph)C_5H_4\}]$ (**3**), respectively, in moderate yields. The data which characterize (**2**), (**3**), and all other new compounds are presented in Table 1, and will not be discussed further except where interpretation is not straightforward. Compound (**3**) could exist as distinct *cis–trans* isomers: however, the two hydrogens on the exocyclic carbons are chemically equivalent due to the presence of a mirror plane in the *cis* isomer, and a C_2 axis in the *trans* isomer. The available data do not allow the two isomers to be distinguished. Treatment of (**1**) with 6,6-diphenylfulvene gives $[Fe(\sigma,\eta^5\text{-}C_5H_4CPh_2)(PMe_3)_2]$ (**4**), which does not react with a two-fold excess of 6,6-diphenylfulvene in refluxing toluene to form a bridged ferrocene compound analogous to (**2**) and (**3**). We attribute this behaviour to the greater steric bulk of the two phenyl groups on the exocyclic carbon.

Treatment of (**1**) with cyclobutene gives low yields of the previously described $[Fe(\eta\text{-}C_4H_6)(PMe_3)_3]^4$ (**5**) in which the cyclobutene has undergone a ring-opening reaction. However, treatment of (**1**) with buta-1,3-diene forms a 4:1 mixture of $[Fe(\eta\text{-}C_4H_6)_2(PMe_3)]$ (**6**) and the known compound $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_4H_6)]^5$ (**7**). This observation excludes the possibility of the formation of (**5**) *via* a pre-equilibrium between cyclobutene and butadiene. Heating (**6**) at *ca.* 70 °C in the presence of an excess of PMe_3 in $[^2H_6]$benzene gives (**5**) in > 80% yield.

The reaction between (**1**) and cyclohexa-1,3-diene gives a 1:1 mixture of the previously described $[Fe(\eta\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]^5$ (**8**) and the new compound $[Fe(\eta^3,\eta^{3'}\text{-}C_{12}H_{16})\text{-}(PMe_3)_2]$ (**9**) in which a rare example of the dimerization of cyclohexa-1,3-diene has occurred.‡ The compounds (**8**) and (**9**) are not separable by sublimation or recrystallization. However, in pentane (**8**) crystallizes as long yellow needles and (**9**) as large brown prisms. This allowed their separation by hand and further purification by recrystallization. The molecular structure of (**9**) has been determined by *X*-ray diffraction studies and the structure, complete with numbering scheme, is shown in Figure 1. The crystal structure determination reveals two independent molecules in the asymmetric unit; however, no significant differences were found between their structural parameters during refinement and only one molecule is shown in Figure 1 for clarity. Crystal data, relevant bond lengths and angles, and atomic co-ordinates are presented in Tables 2—5.

The molecule possesses a non-crystallographic C_2 axis which

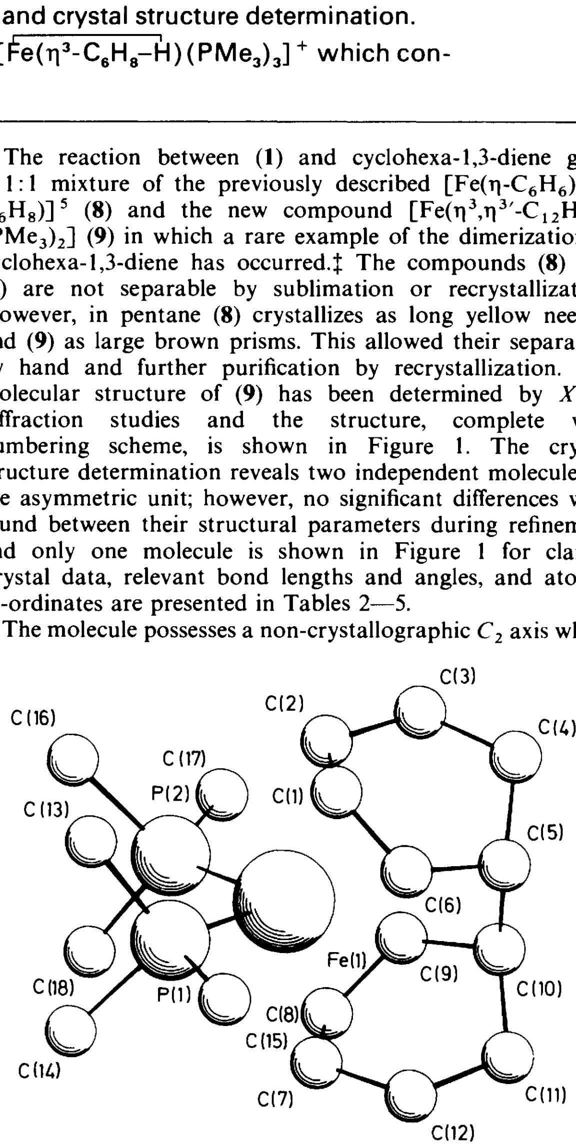

Figure 1. Molecular structure of (**9**) showing the coupled cyclohexadiene rings. Carbon atoms C(1),C(2),C(6) and C(7),C(8),C(9) are directly bonded to Fe(1). Only one molecule in the asymmetric unit is shown, and the hydrogen atoms are omitted, for clarity

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ *Note added in proof:* The coupling of cyclohexa-1,3-diene on ruthenium to give a $Ru(\eta^3,\eta^{3'}\text{-}C_{12}H_{16})$ system analogous to that in (**9**) has been reported by D. N. Cox and R. Roulet, *Organometallics*, 1986, **5**, 1886.

Table 1. Spectroscopic and analytical data

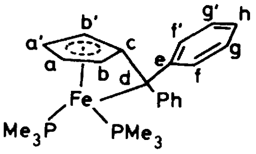
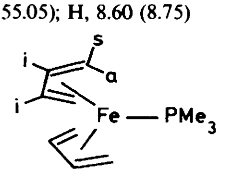
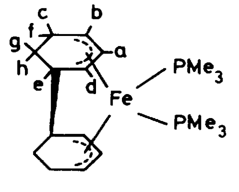
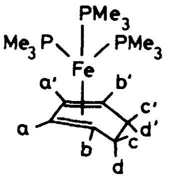
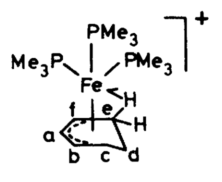
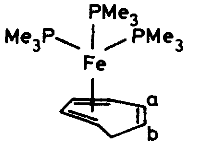
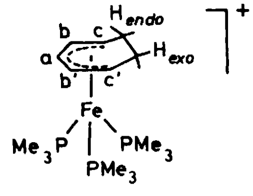
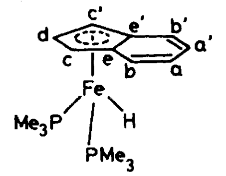
Compound [colour] and analysis[a] (%)	N.m.r. data[b]	
	^1H	^{31}P and ^{13}C
$[Fe(\eta^5,\eta^{5'}-C_5H_4CMe_2CMe_2C_5H_4)]$ (**2**) [orange-red] C, 72.1 (71.65); H, 7.55 (7.50); Fe, 19.95 (20.8)	4.51 [t, 4 H, *J*(H-H) 2, CH], 4.00 [t, 4 H, *J*(H-H) 2, CH], 1.12 (s, 12 H, 4 Me)	
$[Fe\{\eta^5,\eta^{5'}-C_5H_4CH(Ph)CH(Ph)C_5H_4\}]$ (**3**) [red] C, 79.0 (79.2); H, 5.40 (5.50)	7.25—7.10 [m, 10 H, 2 Ph], 5.15 (m, 2 H, C_5H_4), 4.80 (m, 2 H, C_5H_4), 4.63 [br s, 2 H, 2C*H*(Ph)], 4.25 (m, 2 H, C_5H_4), 3.90 (m, 2 H, C_5H_4)	
$[Fe(\sigma,\eta^5-C_5H_4CPh_2)(PMe_3)_2]$ (**4**) [red][c] C, 65.5 (65.8); H, 7.5 (7.3)  	7.65—6.95 (m, 10 H, 2 Ph), 4.20 (m, 2 H, C_5H_4), 3.51 (m, 2 H, C_5H_4), 0.95 (virtual t, 18 H, *J*′ 7.3, 2 PMe_3)	$^{31}P-\{^1H\}$: 27.3 (s) ^{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]
$[Fe(\eta-C_4H_6)_2(PMe_3)]$ (**6**) [red] C, 54.8 (55.05); H, 8.60 (8.75)  	4.33 (m, 4 H, 4 H_i), 0.92 (m, 4 H, 4 H_s), −1.25 (m, 4 H, 4 H_a), 1.35 [d, 9 H, *J*(P–H) 8, PMe_3]	$^{31}P-\{^1H\}$: 27.7 (s) ^{13}C: 82.5 [d, *J*(C–H) 165, 4 CH], 38.8 [dd, *J*(C–H) 145, ^2J(P–C) 10, 4 CH_2], 20.0 [q of m, *J*(C–H) 125, *J*(P–C) 17, PMe_3]
$[Fe(\eta^3,\eta^{3'}-C_{12}H_{16})(PMe_3)_2]$ (**9**) [orange-yellow] C, 58.45 (58.7); H, 9.10 (9.25)  	5.50 (m, 1 H, H_a), 2.90 (m, 1 H, H_b), 2.73 (m, 1 H, H_c), 2.60 (m, 1 H, H_d), 2.48 (m, 1 H, H_e), 2.30 (m, 1 H, H_f), 1.67 (m, 1 H, H_g), 1.35 (m, 1 H, H_h), 0.78 (virtual t, 18 H, *J*′ 7.7, 2 PMe_3)	$^{31}P-\{^1H\}$: 28.0 (s) ^{13}C: 95.3 [d, *J*(C–H) 159, CH_a], 74.0 [d, *J*(C–H) 153, CH_d], 54.1 [d, *J*(C–H) 123, CH_e], 46.5 [d, *J*(C–H) 149, CH_b], 32.1 [t, *J*(C–H) 123, CH_cH_f], 30.1 [t, *J*(C–H) 127, CH_gH_h], 17.6 [q of m, *J*(C–H) 121, *J*′ 21, 2 PMe_3]
$[Fe(\eta^4-C_6H_8)(PMe_3)_3]$ (**10**) [yellow-brown] C, 49.3 (49.45); H, 9.50 (9.60)  	4.15 (m, 2 H, $H_{a,a'}$ or $H_{b,b'}$), 1.80 (m, 2 H, $H_{b,b'}$ or $H_{a,a'}$), 1.70 (m, 2 H, $H_{d,d'}$), 1.05 (m, 27 H, 3 PMe_3), 0.93 (obscured, 2 H, $H_{c,c'}$)	$^{31}P-\{^1H\}$: 21.4 (s) $^{13}C-\{^1H\}$: 79.5 (s, $C_{a,a'}$ or $C_{b,b'}$), 46.5 (s, $C_{b,b'}$ or $C_{a,a'}$), 26.7 [q, ^3J(P–C) 3, 2 CH_2], 23.8 (virtual q, *J*′ 16, 3 PMe_3)
$[\overline{Fe(\eta^3-C_6H_8-H})(PMe_3)_3][BF_4]$ (**11**) [red][e] C, 35.3 (35.3); H, 7.05 (6.95)  	[d] 5.2 (m, 1 H, 1 CH), 2.5 (br, 2 H, 2 CH), 2.0 [d, *J*(P–H) 8, 9 H, PMe_3], 1.8 (br, 9 H, PMe_3), 1.5 (obscured, 1 H, CH), 1.3 (obscured, 1 H, CH), 1.2 (br, 9 H, PMe_3), 0.7 (m, 1 H, CH), −18.6 (br, 1 H, Fe ← H–C)	$^{31}P-\{^1H\}$:[e] 41.1 [t, *J*(P–P) 60, PMe_3], 15.5 [d, *J*(P–P) 60, 2 PMe_3] ^{13}C:[f] 90.8 [d, *J*(C–H) 161, C_a], 70.8 [d, *J*(C–H) 178, C_b or C_f], 52.7 [d, *J*(C–H) 151, C_f or C_b], 25.2 [t, *J*C–H) 127, C_c], 23.8 [q, 3 C,*J*(C–H) 125, PMe_3], 21.1 [q, 3 C, *J*(C–H) 126, PMe_3], 19.8 (obscured, C_d), 18.7 [q, 3 C, *J*(C–H) 125, PMe_3], 11.0 [dd, *J*(C–H) 150, 80, C_e]
$[Fe(\eta^4-C_7H_8)(PMe_3)_3]$ (**12**) [red] C, 50.85 (51.1); H, 9.10 (9.30)  	6.23 (m, 1 H, H_a or H_b), 5.22 (m, 1 H, H_b or H_a), 4.40 (m, 1 H, C_7H_8), 4.15 (m, 1 H, C_7H_8), 2.20 (m, 2 H, C_7H_8), 1.80 (m, 2 H, CH_2), 1.45 [d, *J*(P–H) 9, 9 H, PMe_3], 0.95 [d, *J*(P–H) 8, 9 H, PMe_3], 0.89 [d, *J*(P–H) 9, 9 H, PMe_3]	$^{31}P-\{^1H\}$: 12 (m, ABC system) ^{13}C: 134.5 [d, *J*(C–H) 147, CH_a or CH_b], 120.9 [d, *J*(C–H) 153, CH_b or CH_a], 90.8 [d, 1 C, *J*(C–H) 163, C_7H_8], 80.7 [d, 1 C, *J*(C–H) 148, C_7H_8], 43.3 [d, 1 C, *J*(C–H) 150, C_7H_8], 41.0 [d, 1 C, *J*(C–H) 150, C_7H_8], 32.5 [t, *J*(C–H) 128, CH_2], 24.8 [q of m, 3 C, *J*(C–H) 127, *J*(P–C) 18, PMe_3], 21.9 [q of m, 6 C, *J*(C–H) 126, *J*′ 26, PMe_3]

Table 1 (*continued*)

	N.m.r. data[b]	
Compound [colour] and analysis[a] (%)	^1H	^{31}P and ^{13}C
$[Fe(\eta^5\text{-}C_7H_9)(PMe_3)_3][BF_4]$ (**15**) [yellow] C, 41.7 (41.4); H, 7.70 (7.75) 	5.85 (m, 1 H, H_a), 4.80 (m, 2 H, $H_{b,b'}$ or $H_{c,c'}$), 3.25 (m, 2 H, $H_{c,c'}$ or $H_{b,b'}$), 2.16 (m, 2 H, 2 H_{exo}), 1.54 (br, 27 H, 3 PMe_3), 1.20 (m, 2 H, 2 H_{endo})	$^{31}P\text{-}\{^1H\}$: 11.2 (br) $^{13}C\text{-}\{^1H\}$: 97.1 (s, $C_{b,b'}$ or $C_{c,c'}$), 88.9 (s, C_a), 70.8 (s, $C_{c,c'}$ or $C_{b,b'}$), 22.9 [q, $^3J(P\text{–}C)$ 9, 2 CH_2], 23.5 (br, 3 C, PMe_3), 20.2 (br, 6 C, 2 PMe_3)
$[Fe(\eta^5\text{-}C_9H_7)(PMe_3)_2H]$ (**16**) [purple][g] C, 55.35 (55.6); H, 7.90 (8.05) 	7.42 (m, 2 H, $H_{a,a'}$ or $H_{b,b'}$), 6.85 (m, 2 H, $H_{b,b'}$ or $H_{a,a'}$), 5.22 [q, 1 H, $J(H_d\text{–}H_c)$ = $^2J(P\text{–}H_d)$ 2.5, H_d], 4.21 [dt, 2 H, $J(H_c\text{–}H_d)$ 2.5, $^2J(P\text{–}H_c)$ 1.8, 2 H_c], 1.05 (virtual t, 18 H, J' 9.1, 2 PMe_3), −21.71 [t, $J(P\text{–}H)$ 79, Fe–H]	$^{31}P\text{-}\{^1H\}$: 29.1 (s) ^{13}C: 125.6 [d, $J(C\text{–}H)$ 170, $C_{a,a'}$ or $C_{b,b'}$], 121.6 [d, $J(C\text{–}H)$ 157, $C_{b,b'}$ or $C_{a,a'}$], 98.6 (s, 2 $C_{e,e'}$), 82.8 [d, $J(C\text{–}H)$ 173, C_d], 63.3 [d, $J(C\text{–}H)$ 174, 2 C_c], 24.7 [q of m, 6 C, $J(C\text{–}H)$ 125, J' 22, 2 PMe_3]
$[Fe(\eta\text{-}C_6H_6)(dmpe)]$ (**17**)[f] [red-orange] C, 50.4 (50.5); H, 7.95 (8.4)	4.75 [t, 6 H, $J(P\text{–}H)$ 2.5, C_6H_6], 1.20 (m, 4 H, 2 CH_2), 1.11 [virtual t, 12 H, J' 4.6, 2 PMe_2]	$^{31}P\text{-}\{^1H\}$: 56.5 (s) ^{13}C: 75.8 [d, $J(C\text{–}H)$ 167, C_6H_6], 31.4 [t of virtual t, $J(C\text{–}H)$ 130, J' 13.8, 2 CH_2], 23.6 [q of m, 4 C, $J(C\text{–}H)$ 126, J' 13, 2 PMe_2]
$[Fe(\eta\text{-}C_6H_6)(dppe)]$ (**18**) [dark red] C, 71.7 (72.2); H, 5.20 (5.65)	7.7—7.0 (m, 20 H, 4 Ph), 4.63 [t, 6 H, $J(P\text{–}H)$ 2.2, C_6H_6], 1.79 (m, 4 H, 2 CH_2)	$^{31}P\text{-}\{^1H\}$: 89.3 (s) $^{13}C\text{-}\{^1H\}$: 142.9 (virtual t, J' 12.5, *ipso*-C), 132.7 (virtual t, 5.4, *ortho*-C), 128.7 (s, *meta*-C), 127.4 (s, *para*-C), 78.8 (s, C_6H_6), 30.7 (virtual t, J' 25, 2 CH_2)

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (δ), multiplicity, relative intensity, J/Hz, assignment; J' = separation of the outer lines of virtual triplets. ^1H N.m.r. spectra were determined at 300 MHz, unless otherwise stated, ^{13}C N.m.r. spectra at 62.9 MHz, and ^{31}P n.m.r. spectra at 101.3 MHz. All spectra were determined at room temperature (r.t.) and the solvent was $[^2H_6]$benzene, unless otherwise stated. [c] P, 14.4 (14.6). [d] In $[^2H_6]$acetone at −70 °C; resonances due to other ring hydrogens are obscured by broad PMe_3 peaks. [e] In $[^2H_6]$acetone at r.t. [f] In $[^2H_6]$acetone at −104 °C. [g] ν(Fe–H) = 2 050 cm^{-1} (Nujol mull).

Table 2. Crystal data

Formula	$C_{18}H_{34}FeP_2$
M	368.26
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.970(4)
b/Å	19.125(4)
c/Å	14.457(9)
β/°	113.9(4)
U/Å^3	3 784.3
Z	8
D_c/g cm^{-3}	1.292
μ/cm^{-1}	9.56
F(000)	1 584
$\theta_{min.}$—$\theta_{max.}$/°	1—22.5
Scan mode	ω—2θ
Total data collected	7 358
No. of observations	3 548
No. of parameters	384
No. of restraints	0
Observations/parameters	9.24
Weighting scheme[a]	4-term Chebyshev
Weighting coefficients	220.62, 311.33, 105.56, 10.00
Crystal size (mm)	1.6 × 0.12 × 0.24
Sum of (shift/e.s.d.)^2 at convergence	0.52
Maximum peak in final difference map (e Å^{-3})	0.51
Final residuals[b] R, R'	0.0348, 0.0450
Extinction parameter[16]	67 (16)

[a] $w = \sum_{i}^{4} a_i T_i^* F_o$ where a_i are the coefficients; for details of the function T_i^* see ref. 17. [b] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$, $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w\text{-}|F_o|^2]^{\frac{1}{2}}$.

Table 3. Selected bond distances (Å) for (**9**), with estimated standard deviations (e.s.d.s) in parentheses. Data for both molecules in the asymmetric unit are given

Fe(1)–P(1)	2.194(1)	Fe(2)–P(3)	2.200(1)
Fe(1)–P(2)	2.202(1)	Fe(2)–P(4)	2.202(1)
Fe(1)–C(1)	2.037(4)	Fe(2)–C(25)	2.146(4)
Fe(1)–C(2)	2.155(4)	Fe(2)–C(26)	2.034(4)
Fe(1)–C(6)	2.134(4)	Fe(2)–C(27)	2.140(4)
Fe(1)–C(7)	2.159(4)	Fe(2)–C(31)	2.132(4)
Fe(1)–C(8)	2.035(4)	Fe(2)–C(32)	2.037(4)
Fe(1)–C(9)	2.131(4)	Fe(2)–C(33)	2.161(4)
P(1)–C(13)	1.834(5)	P(3)–C(19)	1.841(5)
P(1)–C(14)	1.824(5)	P(3)–C(20)	1.840(5)
P(1)–C(15)	1.862(6)	P(3)–C(21)	1.837(5)
P(2)–C(16)	1.842(5)	P(4)–C(22)	1.837(5)
P(2)–C(17)	1.847(6)	P(4)–C(23)	1.829(5)
P(2)–C(18)	1.842(5)	P(4)–C(24)	1.833(5)
C(1)–C(2)	1.393(6)	C(25)–C(26)	1.400(6)
C(1)–C(6)	1.392(6)	C(25)–C(30)	1.522(6)
C(2)–C(3)	1.513(6)	C(26)–C(27)	1.394(6)
C(3)–C(4)	1.525(7)	C(27)–C(28)	1.528(6)
C(4)–C(5)	1.519(7)	C(28)–C(29)	1.522(7)
C(5)–C(6)	1.536(6)	C(28)–C(36)	1.532(6)
C(5)–C(10)	1.536(6)	C(29)–C(30)	1.525(7)
C(7)–C(8)	1.400(6)	C(31)–C(32)	1.391(6)
C(7)–C(12)	1.512(7)	C(31)–C(36)	1.522(6)
C(8)–C(9)	1.398(6)	C(32)–C(33)	1.407(6)
C(9)–C(10)	1.513(6)	C(33)–C(34)	1.515(6)
C(10)–C(11)	1.517(7)	C(34)–C(35)	1.523(7)
C(11)–C(12)	1.521(6)	C(35)–C(36)	1.526(7)

Table 4. Selected bond angles (°) for (**9**), with e.s.d.s in parentheses. Data for both molecules in the asymmetric unit are given

P(2)–Fe(1)–P(1)	94.06(5)	P(4)–Fe(2)–P(3)	94.46(5)
C(8)–Fe(1)–C(1)	143.7(2)	C(32)–Fe(2)–C(26)	143.9(2)
C(6)–C(1)–C(2)	116.4(4)	C(30)–C(25)–C(26)	118.4(4)
C(3)–C(2)–C(1)	119.4(4)	C(27)–C(26)–C(25)	116.5(4)
C(4)–C(3)–C(2)	111.1(4)	C(28)–C(27)–C(26)	120.3(4)
C(5)–C(4)–C(3)	115.7(4)	C(29)–C(28)–C(27)	109.5(4)
C(6)–C(5)–C(4)	109.4(4)	C(36)–C(28)–C(27)	108.7(4)
C(10)–C(5)–C(4)	113.3(4)	C(36)–C(28)–C(29)	113.6(4)
C(10)–C(5)–C(6)	108.0(3)	C(30)–C(29)–C(28)	114.9(4)
C(5)–C(6)–C(1)	120.1(4)	C(29)–C(30)–C(25)	111.8(4)
C(12)–C(7)–C(8)	118.4(4)	C(36)–C(31)–C(32)	120.4(4)
C(9)–C(8)–C(7)	116.5(4)	C(33)–C(32)–C(31)	116.8(4)
C(10)–C(9)–C(8)	120.3(4)	C(34)–C(33)–C(32)	118.6(4)
C(9)–C(10)–C(5)	109.2(4)	C(35)–C(34)–C(33)	111.6(4)
C(11)–C(10)–C(5)	113.5(4)	C(36)–C(35)–C(34)	115.8(4)
C(11)–C(10)–C(9)	110.2(4)	C(31)–C(36)–C(28)	109.2(4)
C(13)–P(1)–Fe(1)	121.7(2)	C(35)–C(36)–C(28)	112.8(4)
C(14)–P(1)–Fe(1)	120.7(2)	C(35)–C(36)–C(31)	109.7(4)
C(14)–P(1)–C(13)	97.5(3)	C(19)–P(3)–Fe(2)	120.8(2)
C(15)–P(1)–Fe(1)	113.6(2)	C(20)–P(3)–Fe(2)	121.3(2)
C(15)–P(1)–C(13)	99.3(3)	C(21)–P(3)–Fe(2)	114.9(2)
C(15)–P(1)–C(14)	99.7(3)	C(20)–P(3)–C(19)	97.7(3)
C(16)–P(2)–Fe(1)	120.7(2)	C(21)–P(3)–C(19)	99.4(3)
C(17)–P(2)–Fe(1)	115.5(2)	C(21)–P(3)–C(20)	98.2(3)
C(17)–P(2)–C(16)	98.5(3)	C(22)–P(4)–Fe(2)	121.8(2)
C(18)–P(2)–Fe(1)	121.0(2)	C(23)–P(4)–Fe(2)	120.5(2)
C(18)–P(2)–C(16)	98.2(3)	C(23)–P(4)–C(22)	98.5(3)
C(18)–P(2)–C(17)	98.2(3)	C(24)–P(4)–Fe(2)	114.8(2)
		C(24)–P(4)–C(22)	97.8(3)
		C(24)–P(4)–C(23)	98.8(3)

is defined by the vector connecting the iron atom to the mid-point of P(1)–P(2). The six Fe–C(allyl) distances in each molecule range from 2.034(4) to 2.161(4) Å. The angle between the normals to the planes of the two allyl groups in the molecule shown in Figure 1 is 93.05°. The corresponding value for the other molecule in the asymmetric unit is 86.48°. The bond lengths of the central carbon of the allyl groups [C(1), C(8), C(26), C(32)] to the iron atoms are significantly shorter than the remaining eight bond distances by 0.10—0.12 Å, a phenomenon which has been observed in the related complex [Ru($\eta^3,\eta^{3'}$-$C_{12}H_{20}$)$(CO)_2$].[6]

The ^1H and ^{13}C n.m.r. spectra of (**9**) are complicated because, although the C_2 axis in the molecule allows equivalence of the two rings, within each ring all the hydrogen and carbon atoms are chemically and magnetically inequivalent. However, a combination of ^1H–^1H COSY (shown in Figure 2) and ^1H–^{13}C heteronuclear shift correlation experiments allow the complete assignment of the spectra.

The coupling of 1,3-dienes catalysed by transition and metal atoms[7] and zero-valent nickel complexes[8] is well established. However, there are very few analogous reactions for iron compounds; one example is the reaction between [$Fe_3(CO)_{12}$] and 1,2-dimethylenecyclobutane to give [Fe($\eta^3,\eta^{3'}$-$C_{12}H_{16}$)$(CO)_2$].[9] In the formation of (**9**) no intermediates were observed. It appears that the other product of the reaction, (**8**), is not a precursor to (**9**); for example, it does not react with a 1:2 mixture of cyclohexa-1,3-diene and PMe_3. Further, treatment of [$Fe(CH_2PMe_2)(PMe_3)_3H$][10] with an excess of cyclohexa-1,3-diene forms only [Fe(η^4-C_6H_8)$(PMe_3)_3$] (**10**), hence ruling out (**10**) as an intermediate towards (**9**). Treatment of (**9**) with cyclohexa-1,3-diene did not give rise to catalytic dimerization.

Treatment of (**9**) with tetrafluoroboric acid etherate or ammonium ions (in ammonium hexafluorophosphate) gives [Fe(η^3-C_6H_8–H)$(PMe_3)_3$][BF_4] (**11**) and [Fe(η^3-C_6H_8–H)$(PMe_3)_3$][PF_6] (**11′**), respectively. This reaction involves uncoupling of the dienes and disproportionation. The cation (**11**) is also the product of the protonation of (**10**) with tetrafluoroboric acid etherate. Hydrogen-1 n.m.r. studies on (**11**) show it to contain an agostic M←H–C bond, analogous to the cyclohexenyl compound [Fe(η^3-C_6H_8–H){$P(OMe)_3$}$_3$][BPh_4],[11,12] and is fluxional at room temperature. The data show that there is exchange between the *endo*-hydrogens on C_c and C_e (Table 1). In the fully proton-coupled ^{13}C n.m.r. spectrum of (**11**) at −104 °C ([$^2H_6$]acetone), when the slow exchange limit is reached, the resonance due to C_e is a doublet of doublets with J(C–H) of 150 and 80 Hz.

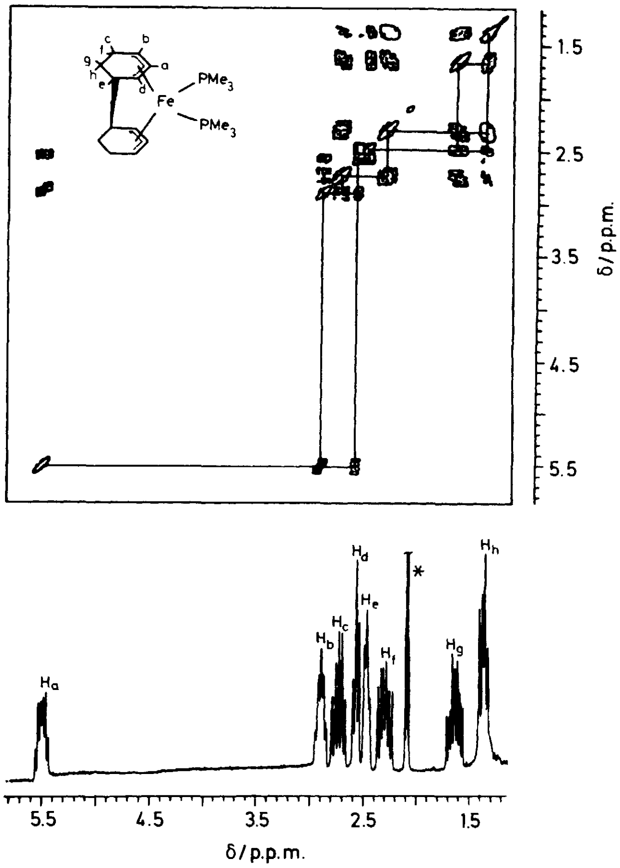
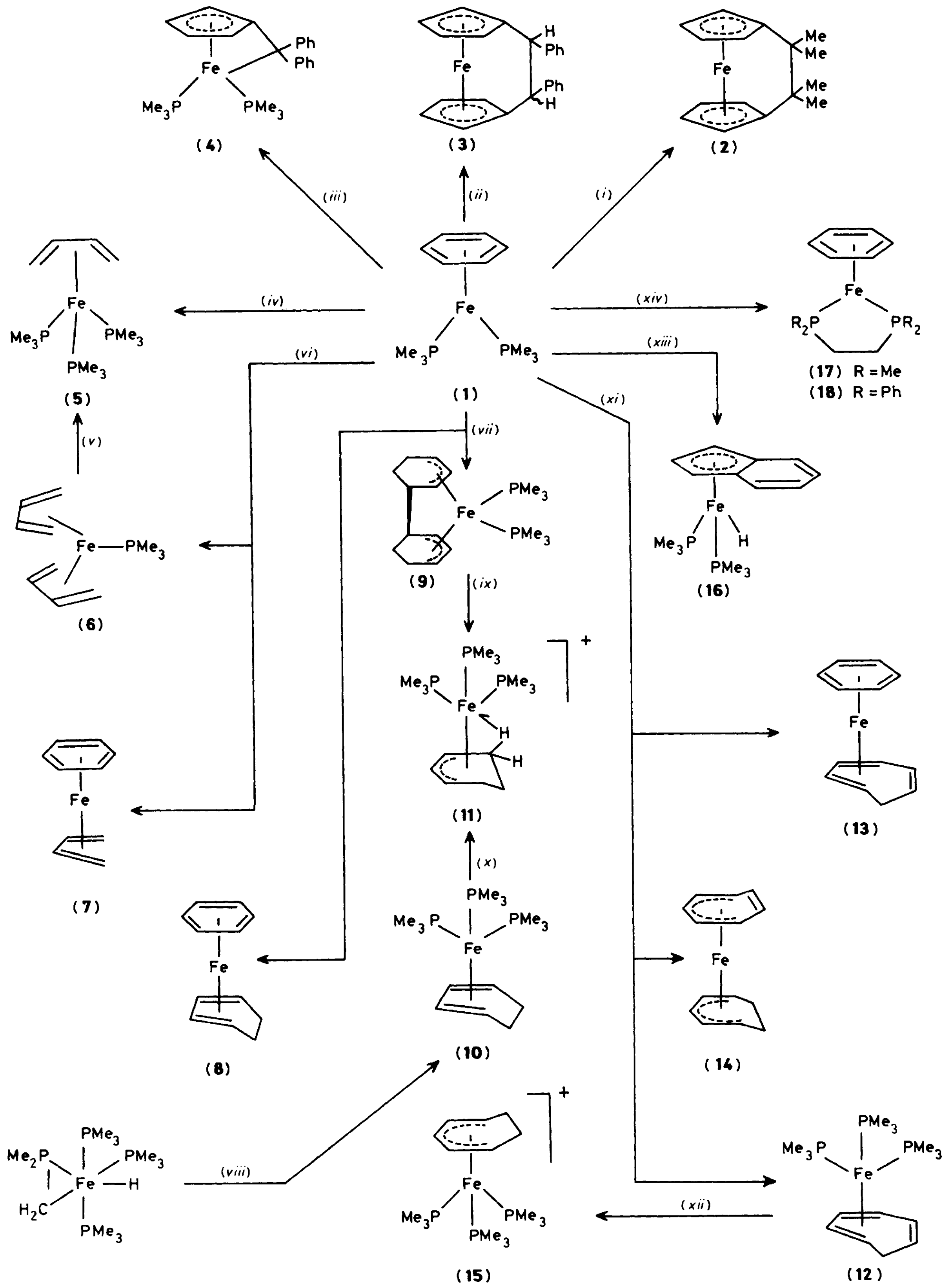


Figure 2. 250 MHz ^1H–^1H COSY-45 n.m.r. spectrum of (**9**); (*) denotes solvent [$^2H_8$]toluene

Treatment of (**1**) with cycloheptatriene gives [Fe(η^4-C_7H_8)$(PMe_3)_3$] (**12**), and the known compounds [Fe(η-C_6H_6)(η^4-C_7H_8)] (**13**)[5] and [Fe(η^5-C_7H_7)(η^5-C_7H_9)] (**14**),[13] in the ratio 4:1:1 (^1H n.m.r.). Compounds (**13**) and (**14**) may be separated from (**12**) by sublimation, leaving (**12**) which can be isolated as red crystals. Treatment of (**12**) with $HBF_4{\cdot}Et_2O$ gives yellow [Fe(η^5-C_7H_9)$(PMe_3)_3$][BF_4] (**15**) in high yield. Treatment of (**1**) with indene gives [Fe(η^5-C_9H_7)$(PMe_3)_2H$] (**16**), as purple crystals, in high yield.

Finally, treatment of (**1**) with the chelating phosphines 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diphenylphosphino)ethane (dppe) results in replacement of the PMe_3 ligands giving thermally stable [Fe(η-C_6H_6)($R_2PCH_2CH_2PR_2$)] [R = Me (**17**) or Ph (**18**)].

The reactions and the structures proposed for the new compounds are shown in the Scheme. In conclusion, compound (**1**), which may be prepared readily in quantities of *ca.* 20 g, shows unexpected reactivity and is a useful synthetic intermediate.



Scheme. (*i*) 6,6-Dimethylfulvene in light petroleum at r.t. for 30 min, yield 43%; (*ii*) 6-phenylfulvene in light petroleum at r.t. for 2 h, 52%; (*iii*) 6,6-diphenylfulvene in light petroleum at r.t. for 2 h, 85%; (*iv*) cyclobutene in light petroleum at r.t. for 2 h, *ca.* 27%; (*v*) 10 mol equiv. of PMe_3 in $[^2H_6]$benzene at 70 °C for 2 d, >80% (n.m.r.); (*vi*) buta-1,3-diene in light petroleum at r.t. for 3 h, total yield 80%; (*vii*) cyclohexa-1,3-diene in light petroleum at r.t. for 6 h, yield 30% for (**9**); (*viii*) cyclohexa-1,3-diene in light petroleum at r.t. for 2 h, 79%; (*ix*) tetrafluoroboric acid in diethyl ether or ammonium hexafluorophosphate in thf at r.t., 40—45%; (*x*) tetrafluoroboric acid in diethyl ether at r.t., 89%; (*xi*) cycloheptatriene in light petroleum at r.t. for 3 h, yield 34% for (**12**); (*xii*) tetrafluoroboric acid in diethyl ether at r.t., 86%; (*xiii*) indene in light petroleum at r.t. for 4 h, 75%; (*xiv*) R = Me, 1,2-bis(dimethylphosphino)ethane in light petroleum at r.t. for 3 h, 85%; R = Ph, 1,2-bis(diphenylphosphino)ethane in light petroleum–diethyl ether (1:1) at r.t. for 2 h, 54%

Table 5. Atomic co-ordinates (× 10^4) for (**9**), with e.s.d.s in parentheses. Data for both molecules in the asymmetric unit are given

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) Molecule 1				(*b*) Molecule 2			
Fe(1)	9 907.4(4)	726.5(3)	2 286.1(4)	Fe(2)	4 846.8(4)	2 064.7(3)	2 472.6(4)
P(1)	11 022.0(9)	1 074.1(7)	3 742.8(8)	P(3)	5 705.3(8)	1 287.9(6)	3 607.2(8)
P(2)	10 428.5(9)	−362.7(6)	2 482.7(8)	P(4)	4 019.4(8)	1 278.8(6)	1 335.2(8)
C(1)	8 883(9)	1 000(3)	2 813(3)	C(19)	6 452(5)	632(3)	3 311(4)
C(2)	8 618(3)	329(3)	2 422(3)	C(20)	5 122(4)	694(3)	4 198(4)
C(3)	7 732(3)	232(3)	1 438(4)	C(21)	6 641(4)	1 657(3)	4 768(3)
C(4)	7 321(3)	935(3)	954(4)	C(22)	4 614(4)	705(3)	736(4)
C(5)	8 072(3)	1 492(3)	1 034(3)	C(23)	3 284(4)	621(3)	1 625(4)
C(6)	8 851(3)	1 519(2)	2 125(3)	C(24)	3 074(4)	1 638(3)	177(4)
C(7)	10 656(3)	1 375(3)	1 604(3)	C(25)	3 503(3)	2 312(2)	2 600(3)
C(8)	10 242(3)	768(3)	1 056(3)	C(26)	4 332(3)	2 388(2)	3 506(3)
C(9)	9 225(3)	714(2)	675(3)	C(27)	5 004(3)	2 896(2)	3 518(3)
C(10)	8 594(3)	1 361(3)	329(3)	C(28)	4 656(4)	3 568(2)	2 905(3)
C(11)	9 205(4)	1 977(3)	261(4)	C(29)	3 552(4)	3 629(3)	2 538(4)
C(12)	10 176(4)	2 069(3)	1 194(4)	C(30)	2 984(4)	2 969(3)	2 050(4)
C(13)	11 028(4)	772(4)	4 949(4)	C(31)	4 673(3)	2 899(2)	1 436(3)
C(14)	12 317(4)	941(4)	4 048(4)	C(32)	5 349(3)	2 401(2)	1 434(3)
C(15)	11 021(5)	2 035(3)	3 944(5)	C(33)	6 193(3)	2 325(2)	2 335(3)
C(16)	10 580(5)	−859(3)	3 629(4)	C(34)	6 700(4)	2 977(3)	2 898(4)
C(17)	9 641(5)	−988(3)	1 526(4)	C(35)	6 117(4)	3 634(2)	2 431(4)
C(18)	11 600(4)	−594(3)	2 427(5)	C(36)	5 010(4)	3 568(2)	2 048(3)

Experimental

All preparations, manipulations, and reactions were carried out under an inert 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 column containing BTS 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 and distilled immediately before use. Deuteriated solvents for n.m.r. samples were stored in Rotaflo ampoules over 4 Å activated molecular sieves or over a potassium film, and were transferred by vacuum distillation.

Infrared spectra were recorded on a Perkin-Elmer 1510 FT interferometer. ^{1}H N.m.r. spectra were determined at 300 MHz using a Bruker WH-300 spectrometer. Carbon-13 and ^{31}P n.m.r. spectra were determined at 62.9 and 101.26 MHz, respectively, using a Bruker AM 250 spectrometer. Spectra were referenced internally using the residual solvent resonance (^{1}H, ^{13}C) relative to $SiMe_4$ (δ 0), or externally using trimethyl phosphate in D_2O(^{31}P). All chemical shifts are quoted in δ and coupling constants in Hz. The two-dimensional n.m.r. experiment was acquired using the AM250 spectrometer with standard Bruker software, and processed using the ASPECT 3000 computer.

Cycloheptatriene (Aldrich) was distilled and stored under nitrogen over activated molecular sieves before use. Alumina for chromatography (Fluka) was deactivated by addition of water (6% w/w). Celite 545 filtration acid (Koch-Light) was pre-dried at 80 °C before use. Indene (Aldrich) was stood over activated alumina for 24 h, distilled, and then dried over activated molecular sieves (type 4 Å). Buta-1,3-diene was purified by passage through columns [5 cm (diameter) × 60 cm] of potassium hydroxide-activated alumina and then activated molecular sieves (type 4 Å). The compound $[Fe(\eta\text{-}C_6H_6)(PMe_3)_2]$ (**1**) was prepared as described.[2] All other reagents were used as supplied.

1,1′-(*Tetramethylethylene*)*ferrocene*, (**2**).—A solution of (**1**) (200 mg, 0.7 mmol) in light petroleum (20 cm^3) was cooled to −20 °C and treated with a solution of 6,6-dimethylfulvene (200 mg, excess) in light petroleum (10 cm^3). A brown solid was precipitated upon mixing and the solution turned from dark red to orange. After warming to room temperature (r.t.) and stirring for 30 min, volatiles were removed *in vacuo* leaving a red oil. This oily residue was extracted with light petroleum (2 × 30 cm^3) and filtered. The combined filtrates were concentrated to *ca.* 2 cm^3 and adsorbed onto an alumina column (6% w/w water). Elution with pentane gave an orange band which was collected, concentrated to *ca.* 3 cm^3, and cooled to −80 °C overnight to give an orange-red solid. Recrystallization from pentane gave red prisms of $[Fe(\eta^5,\eta^{5'}\text{-}C_5H_4CMe_2CMe_2\text{-}C_5H_4)]$. Yield: 80 mg, 43%.

1,1′-(1″,2″-*Diphenylethylene*)*ferrocene*, (**3**).—A solution of (**1**) (700 mg, 2.5 mmol) in light petroleum (30 cm^3) was cooled to −20 °C and treated with a solution of 6-phenylfulvene (1.0 g, excess) in light petroleum (20 cm^3). The mixture turned red and large amounts of a brown solid were precipitated. After stirring for 2 h, volatiles were removed *in vacuo* at 40 °C and the red solid residue extracted with light petroleum (40 cm^3). The filtrate was concentrated to *ca.* 2 cm^3 and then adsorbed onto an alumina column (6% w/w water). Elution with light petroleum gave two bands; the slower moving one was collected and the eluant removed to give a red oil. Crystallization from light petroleum gave red crystals of $[Fe\{\eta^5,\eta^{5'}\text{-}C_5H_4CH(Ph)\text{-}CH(Ph)C_5H_4\}]$. Yield: 200 mg, 52%.

(σ,η^5-*Diphenylmethylenecyclopentadienediyl*)*bis*(*trimethylphosphine*)*iron*, (**4**).—Compound (**1**) (1.5 g, 5.3 mmol) in thf (40 cm^3) was treated with 6,6-diphenylfulvene (1.2 g, 5.2 mmol) as a solution in thf (20 cm^3). The mixture turned from dark red to orange after 5 min. After stirring for 2 h, volatiles were removed *in vacuo* at 50 °C giving a red solid residue. The residue was washed with light petroleum (2 × 20 cm^3) to remove any unreacted 6,6-diphenylfulvene, then extracted with diethyl ether (3 × 100 cm^3) and filtered. The combined filtrates were concentrated to *ca.* 70 cm^3 and cooled to −80 °C overnight to give a red solid which was recrystallized from diethyl ether to give red prisms of $[\text{Fe}(\sigma,\eta^5\text{-C}_5\text{H}_4\text{CPh}_2)(\text{PMe}_3)_2]$. Yield: 2.0 g, 85%.

(η-Buta-1,3-diene)tris(trimethylphosphine)iron, (**5**).—A solution of (**1**) (300 mg, 1.1 mmol) in light petroleum (20 cm^3) was frozen at 77 K and cyclobutene (0.5 cm^3, excess) was distilled under reduced pressure onto the frozen solid. Upon warming to r.t. and stirring for 2 h, the solution was yellow with large amounts of a brown precipitate. The solution was filtered, and volatiles removed *in vacuo* at 25 °C leaving a yellow solid. Sublimation at 25 °C and 10^{-2} mbar (1 Pa) gave a yellow solid. The ^{1}H n.m.r. spectrum ($[^2\text{H}_6]$benzene) of the sublimate showed it to be $[\text{Fe}(\eta\text{-C}_4\text{H}_6)(\text{PMe}_3)_3]$ by comparison with that of an authentic sample. Yield: *ca.* 100 mg, 27%.

Synthesis of Bis(η-buta-1,3-diene)(trimethylphosphine)iron, (**6**), *and (η-Benzene)(η-buta-1,3-diene)iron*, (**7**).—A solution of (**1**) (1.0 g, 3.5 mmol) in light petroleum (50 cm^3) was frozen at 77 K and buta-1,3-diene (3 cm^3, excess) was distilled under reduced pressure onto the frozen solid. Upon warming to r.t. and stirring for 3 h, the solution turned orange. Volatiles were removed *in vacuo* at 40 °C giving a red solid which was extracted with light petroleum (2 × 30 cm^3) and the extracts were filtered. The combined filtrates were concentrated (to *ca.* 5 cm^3) and cooled to −80 °C overnight to give an orange solid together with a small amount of a red solid. Recrystallization from pentane gave $[\text{Fe}(\eta\text{-C}_4\text{H}_6)_2(\text{PMe}_3)]$ as orange prisms. A ^{1}H n.m.r. spectrum ($[^2\text{H}_6]$benzene) of the crude reaction mixture showed that the red solid was $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_4\text{H}_6)]$ by comparison with literature data.[5] The integration showed that the ratio of $[\text{Fe}(\eta\text{-C}_4\text{H}_6)_2(\text{PMe}_3)]:[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_4\text{H}_6)]$ was 4:1. Total yield: 650 mg, 80%.

Reaction of $[\text{Fe}(\eta\text{-C}_4\text{H}_6)_2(\text{PMe}_3)]$ *with Trimethylphosphine.*—Compound (**6**) (20 mg, 0.06 mmol) in $[^2\text{H}_6]$benzene (0.5 cm^3) in an n.m.r. tube was treated with a ten-fold excess (by integration) of trimethylphosphine at 70 °C for 2 d. The ^{1}H n.m.r. spectrum of the resulting solution indicated that the only organometallic compound present was $[\text{Fe}(\eta\text{-C}_4\text{H}_6)(\text{PMe}_3)_3]$.

Synthesis of (η-Benzene)(η-cyclohexa-1,3-diene)iron, (**8**), *and [η^3,η$^{3'}$-Bi(cyclohex-3-en-2-yl)]bis(trimethylphosphine)iron*(II), (**9**).—A solution of (**1**) (1.5 g, 5.3 mmol) in light petroleum (50 cm^3) was frozen at 77 K and cyclohexa-1,3-diene (1 cm^3, excess) was distilled under reduced pressure onto the frozen solid. The mixture was allowed to warm to r.t. and stirred for 6 h, during which the solution turned yellow. Volatiles were removed *in vacuo* giving a brown solid, which was extracted with light petroleum (2 × 40 cm^3) and the extracts were filtered through a Celite bed. The combined filtrates were concentrated to *ca.* 15 cm^3 and cooled to −80 °C to afford a mixture of long yellow needles and a brown solid. This mixture was taken into a glove-box, separated by hand, and then recrystallized from pentane. The yellow needles were shown to be $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\eta^4\text{-C}_6\text{H}_8)]$ by comparison of its ^{1}H n.m.r. spectrum ($[^2\text{H}_6]$benzene) with literature data.[5] The brown solid gave large brown prisms of $[\text{Fe}(\eta^3,\eta^{3'}\text{-C}_{12}\text{H}_{16})(\text{PMe}_3)_2]$ upon recrystallization in pentane. Yield: 300 mg, 30%. A ^{1}H n.m.r. spectrum of the crude mixture ($[^2\text{H}_6]$benzene) showed that the two products were present in 1:1 ratio.

(η-Cyclohexa-1,3-diene)tris(trimethylphosphine)iron, (**10**).—A solution of $[\overline{\text{Fe}(\text{CH}_2\text{P}}\text{Me}_2)(\text{PMe}_3)_3\text{H}]$ (1.5 g, 4.2 mmol) in light petroleum (40 cm^3) was frozen at 77 K and cyclohexa-1,3-diene (1 cm^3, excess) was distilled under reduced pressure onto the frozen solid. After warming to r.t. and stirring for 2 h, volatiles were removed *in vacuo* at 35 °C giving a dark brown solid. This solid was extracted with light petroleum (2 × 30 cm^3) and the extracts were filtered through a Celite bed. The combined extracts were concentrated to *ca.* 20 cm^3 and then cooled to −80 °C to afford a brown solid. Extraction with the minimum volume of pentane at −20 °C, filtration into a Schlenk vessel which was cooled to −20 °C, followed by cooling to −80 °C overnight gave large yellow prisms of $[\text{Fe}(\eta^4\text{-C}_6\text{H}_8)(\text{PMe}_3)_3]$. Yield: 1.2 g, 79%.

(η^3-Cyclohexenyl)tris(trimethylphosphine)iron(II) *Tetrafluoroborate*, (**11**).—Compound (**10**) (700 mg, 2 mmol) in diethyl ether (40 cm^3) was treated with 5 drops of $\text{HBF}_4\cdot\text{Et}_2\text{O}$. A red precipitate was formed immediately upon addition of the acid. The colourless liquid was filtered off and the residue was washed with diethyl ether (2 × 40 cm^3). Extraction with methanol (2 × 40 cm^3) and filtration gave an orange solution, which was concentrated to *ca.* 15 cm^3 and cooled to −80 °C overnight to yield analytically pure red prisms of $[\overline{\text{Fe}(\eta^3\text{-C}_6\text{H}_8\text{–H}})(\text{PMe}_3)_3][\text{BF}_4]$. Yield: 800 mg, 89%.

(η^3-Cyclohexenyl)tris(trimethylphosphine)iron(II) *Hexafluophosphate*, (**11′**).—Compound (**9**) (200 mg, 0.55 mmol) in thf (20 cm^3) was treated with an excess of a suspension of ammonium hexafluorophosphate in thf. The solution turned from orange-yellow to red immediately upon mixing. Volatiles were then removed *in vacuo* at 50 °C and the red residue was washed with light petroleum (2 × 30 cm^3). After washing with water, the red residue was extracted with methanol (2 × 40 cm^3) and filtered. The combined extracts were concentrated to *ca.* 5 cm^3 and cooled to −80 °C overnight to give $[\overline{\text{Fe}(\eta^3\text{-C}_6\text{H}_8\text{–H}})(\text{PMe}_3)_3][\text{PF}_6]$ as a red crystalline solid. Yield: 120 mg, 43%.

(η^4-Cycloheptatriene)tris(trimethylphosphine)iron, (**12**), *(η-Benzene)(η^4-cycloheptatriene)iron*, (**13**), *and [η^5-Cycloheptadienyl)(η^5-cycloheptatrienyl)iron*(II), (**14**).—A solution of (**1**) (1.0 g, 3.5 mmol) in light petroleum (50 cm^3) was cooled to −20 °C, and a cooled solution of cycloheptatriene (1 cm^3, excess) in light petroleum (10 cm^3) was added with stirring. After warming to r.t. and stirring for 3 h, during which time the solution turned orange-red, volatiles were removed *in vacuo* giving a red oil. Extraction with light petroleum (2 × 40 cm^3), followed by filtration of the extracts through a Celite bed, gave an orange solution which was reduced to an oil *in vacuo*. A ^{1}H n.m.r. spectrum ($[^2\text{H}_6]$benzene) of the crude mixture showed that the compounds $[\text{Fe}(\eta^4\text{-C}_7\text{H}_8)(\text{PMe}_3)_3]$ (**12**), $[\text{Fe}(\eta\text{-C}_6\text{H}_6)(\eta^4\text{-C}_7\text{H}_8)]$ (**13**), and $[\text{Fe}(\eta^5\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)]$ (**14**) were present in the ratio 4:1:1. The compounds (**13**) and (**14**), together with other more volatile impurities, were removed by sublimation at 20 °C and 10^{-2} mbar, leaving a red solid. Compound (**12**) was isolated as red prisms by recrystallization in pentane. Yield: 450 mg, 34%.

(η^5-Cycloheptadienyl)tris(trimethylphosphine)iron(II) *Tetrafluoroborate*, (**15**).—Compound (**12**) (300 mg, 0.8 mmol) in diethyl ether (30 cm^3) was treated with 5 drops of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ at r.t. A yellow precipitate was formed immediately upon addition of the acid and the colour of the solution was completely discharged. The solution was filtered and the solid was washed with diethyl ether (2 × 40 cm^3). Extraction with methanol (2 × 30 cm^3) followed by filtration gave a yellow solution which was concentrated to *ca.* 10 cm^3 and cooled to −80 °C to give yellow prisms of $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{PMe}_3)_3][\text{BF}_4]$. The supernatant liquid was concentrated to *ca.* 5 cm^3 and cooled to give a second crop of crystals. Total yield: 320 mg, 86%.

*Hydrido(η^5-indenyl)bis(trimethylphosphine)*iron(II), (**16**).—To a solution of (**1**) (1.0 g, 35 mmol) in light petroleum (50 cm^3) was added a solution of indene (1 cm^3, excess) in light petroleum

(10 cm^3) at -20 °C with stirring. After warming to r.t. and stirring for 4 h, volatiles were removed *in vacuo* at 35 °C. Excess indene was removed by sublimation at 20 °C and 10^{-2} mbar for 10 min. The dark red solid residue was extracted with light petroleum (2 × 40 cm^3) and filtered; the combined purple filtrates were concentrated to *ca.* 15 cm^3 and cooled to -80 °C to afford a purple solid. Recrystallization in pentane gave $[Fe(\eta^5-C_9H_7)(PMe_3)_2H]$ as purple prisms. Yield: 850 mg, 75%.

(η-*Benzene*)[1,2-*bis*(*dimethylphosphino*)*ethane*]*iron*, **(17)**.—A solution of **(1)** (2.0 g, 7 mmol) in light petroleum (50 cm^3) was cooled to -20 °C and dmpe (0.7 cm^3, excess) was added. After warming to r.t. and stirring for 3 h, the solution was bright orange. Volatiles were removed *in vacuo* at 50 °C leaving a red solid. Extraction followed by filtration with light petroleum (3 × 30 cm^3) gave a red solution which was concentrated to *ca.* 20 cm^3 and cooled to -80 °C overnight to give a red crystalline solid. Recrystallization in pentane gave large red prisms of $[Fe(\eta-C_6H_6)(dmpe)]$. Yield: 1.7 g, 85%.

(η-*Benzene*)[1,2-*bis*(*diphenylphosphino*)*ethane*]*iron*, **(18)**.— Compound **(1)** (100 mg, 0.35 mmol) in light petroleum (20 cm^3) was added slowly to a solution of dppe (100 mg, 0.25 mmol) in diethyl ether (20 cm^3) at -20 °C with stirring. The solution turned from dark red to orange upon mixing. After stirring for 2 h, volatiles were removed *in vacuo* at 35 °C leaving a red solid. Extraction with light petroleum (2 × 40 cm^3) and filtration gave a red solution which was concentrated to *ca.* 30 cm^3 and cooled to -80 °C to afford a red solid. Recrystallization from ether–pentane gave red prisms of $[Fe(\eta-C_6H_6)(dppe)]$. Yield: *ca.* 50 mg, 54%.

Crystal Structure Determination.—Crystals of compound **(9)** suitable for *X*-ray diffraction studies were obtained by slow recrystallization from pentane at -20 °C. A crystal of dimensions 1.6 × 0.24 × 0.12 mm was sealed under nitrogen in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4F diffractometer. Cell dimensions were obtained by least-squares methods from the positions of 25 carefully centred reflections. During data collection three intensity control reflections were measured every hour and four orientation controls checked after each 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout data collection.

Lorentz polarization corrections were applied together with an empirical absorption correction.[14] Equivalent reflections were merged and only those for which $I > 3\sigma(I)$ were included in the refinement [where $\sigma(I)$ is the standard deviation based on counting statistics].

The structure was solved by direct methods using the MULTAN program,[15] revealing the positions of the iron and phosphorus atoms; a subsequent electron-density difference synthesis revealed the location of all the carbon atoms. The iron atoms and the other non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares methods. All hydrogen atoms were located by electron-density difference synthesis after successive cycles of refinement and were refined with isotropic thermal parameters with their positional parameters linked to the carbon atoms to which they were attached. Corrections for anomalous dispersion and isotropic extinction[16] were made in the final cycles of refinement; a Chebyshev weighting scheme[17] was used with parameters as given in Table 2. Refinement converged at $R = 0.0348$ ($R' = 0.0450$) and the final electron-density synthesis revealed no peaks >0.51 e Å^{-3}, the largest peaks lying in close proximity to the iron atom positions.

All calculations were performed on the VAX11/750 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system[18] and plotted using the CHEMGRAF package.[19] Atomic scattering factors and anomalous dispersion coefficients were taken from International Tables.[20]

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