The Reaction of Phosphines with $[Fe_2(CO)_4L_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$ [L = CO or $P(OPh)_3$]; Cyclopropane Ring-opening of the Bicyclo[5.1.0]octadienyl Groups, and the *X*-Ray Crystal Structure of $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2\cdot0.5C_6H_5Me$ *

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Tributylphosphine and $[Fe_2(CO)_4L_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})][PF_6]_2$ (1; L = CO) form the symmetrical bis(phosphonium)salt $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PBu^n{}_3)_2\}][PF_6]_2$ (2) in which one phosphine ligand has added to the terminal carbon atom of each of the two dienyl units of the bis(bicyclo[5.1.0]octadienyl) carbon skeleton of (1; L = CO). By contrast, PPh_3 and (1; L = CO) yield $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ (3), *X*-ray studies of which show that the dication comprises two open C_7 rings joined by a *trans* ethylenic bridge of four coplanar carbon atoms, and that the two phosphine ligands are bonded to the two carbon atoms adjacent to the bridgehead of *one* C_7 ring. The remaining carbon atoms of this ring are η^4-bonded to an $Fe(CO)_3$ group. In the other C_7 ring, however, four atoms adjacent to the bridgehead are η^4-bonded to another $Fe(CO)_3$ group while the other two atoms form an ethylenic moiety not bonded to the metal. The complex crystallises in the monoclinic space group $P2_1/c$, and the asymmetric unit comprises two molecules of the dication, four $[PF_6]^-$ counter ions, and two half-molecules of solvent (toluene), one of which is disordered. The structure has been refined to $R = 0.142$ for 6 436 reflections [$I \geqslant 2.0\sigma(I)$]. The high R value is a consequence of poor crystal quality: of 22 019 unique reflections measured, 15 583 were rejected. Cyclopropane ring opening also occurs on reacting [1; L = $P(OPh)_3$] with $PBu^n{}_3$ or PPh_3; the hydrocarbon ligand of the resulting complex $[Fe_2(CO)_4\{P(OPh)_3\}_2(\eta^4:\eta'^5\text{-}C_{16}H_{16}L')][PF_6]_2$ (4; L′ = $PBu^n{}_3$ or PPh_3) is related to that of (3). $NaBH_4$ and (2) react to give $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$ but (3) is reduced to $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{16})]$ (5), a complex of *trans*-1,2-di(cycloheptatrienyl)ethylene.

The stereospecific oxidative dimerisation of $[Fe(CO)_2L(\eta^4\text{-}cot)]$ [L = CO or $P(OPh)_3$, cot = cyclo-octatetraene] yields [1] $[Fe_2(CO)_4L_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$ [1; L = CO or $P(OPh)_3$] on which unusual reactivity is conferred by the juxtaposition of two cyclopropane rings. Although hydride ions can be simply added to the terminal carbon atoms of the two pentadienyl units, giving $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$, the reaction with halide ions leads [1] to reductive ring closure (Scheme 1). We now give details of a study of the reactions of (1) with P-donor ligands, preliminary results on which have previously appeared.[2] Whereas $PBu^n{}_3$ and (1; L = CO) give the simple adduct $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PBu^n{}_3)_2\}][PF_6]_2$ (2), structurally similar to $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$, the reaction with PPh_3 leads to cyclopropane ring-opening. An *X*-ray structural study of the product, $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ (3), has revealed that the two phosphine ligands are co-ordinated to one cycloheptadiene ring. The mechanism by which both (2) and (3) may be formed has been probed *via* a study of the reactions of [1; L = $P(OPh)_3$] with $PBu^n{}_3$ and PPh_3. Reduction of (3) with $NaBH_4$ to give $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{16})]$, a derivative of *trans*-1,2-di(cycloheptatrienyl)-ethylene, is also reported.

Results and Discussion

The addition of $PBu^n{}_3$ to (1; L = CO) (2 : 1 ratio) in cold acetone (−78 °C) yields, on slow warming to room temperature, a pale yellow solution from which moderate yields of yellow, crystalline $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PBu^n{}_3)_2\}][PF_6]_2$ (2) are readily isolable. The identity of (2) as a symmetrical bis(phosphonium)salt (Scheme 2) was established by elemental analysis, the i.r. carbonyl spectrum (Table 1), and by n.m.r. spectroscopy (Table 2). The ^{31}P n.m.r. spectrum shows only one resonance (apart from that of the $[PF_6]^-$ anion), due to the two equivalent phosphonium phosphorus atoms, and the proton spectrum is very similar to that of $[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{18})]$ (Scheme 1). Addition of the phosphines to the terminal carbon atoms of the dienyl units of (1) is in accord with the Davies–Green–Mingos rules for the addition of nucleophiles to co-ordinated hydrocarbons.[3]

The reaction of (1) with PPh_3, in a 1 : 2 ratio, also gave a bis(phosphonium) salt, namely $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ (3). However, the i.r. carbonyl spectrum (Table 1) is very different from that of (2), with five absorptions implying the presence of two, inequivalent, $Fe(CO)_3$ groups. The ^{31}P n.m.r. spectrum (Table 2) also suggested an asymmetric structure for (3), with two doublet resonances [$J(PP') = 4$ Hz] due to two inequivalent, but coupled, phosphonium phosphorus atoms. The ^1H and ^{13}C n.m.r. spectra of (3) (Table 2) are also very different from those of (2), but full assignments were only made after the molecular structure of (3) had been determined by *X*-ray crystallography.

The results of the diffraction study are illustrated in Figure 1, which also shows the crystallographic numbering of the molecule. Selected bond lengths and angles are in Table 3. The hydrocarbon moiety in (3) comprises two seven-membered rings linked by a *trans* ethylenic bridge. The portions of the rings adjoining the four atoms of the bridge [C(7)—C(10)] are themselves approximately perpendicular to the plane defined by [C(7)—C(10)]. The two triphenylphosphine ligands are each bonded to a carbon atom adjacent to the bridgehead and are both attached to the same ring. The plane of the bridge is also an approximate plane of symmetry for this C_7 ring and for the two attached phosphines and the η^4-co-ordinated

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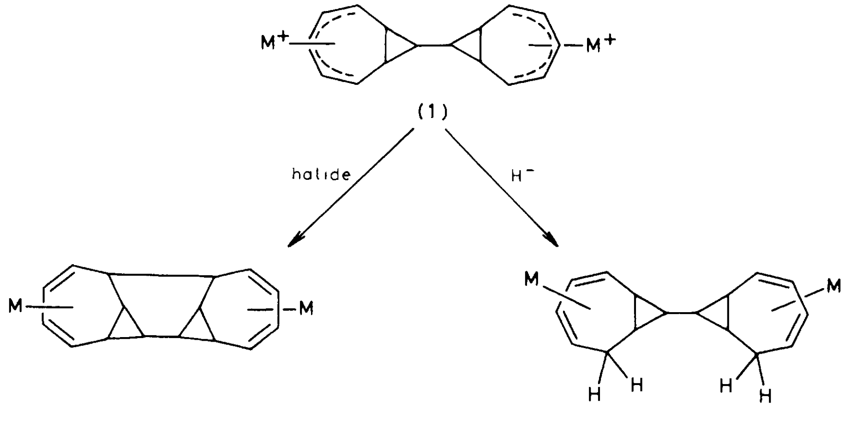
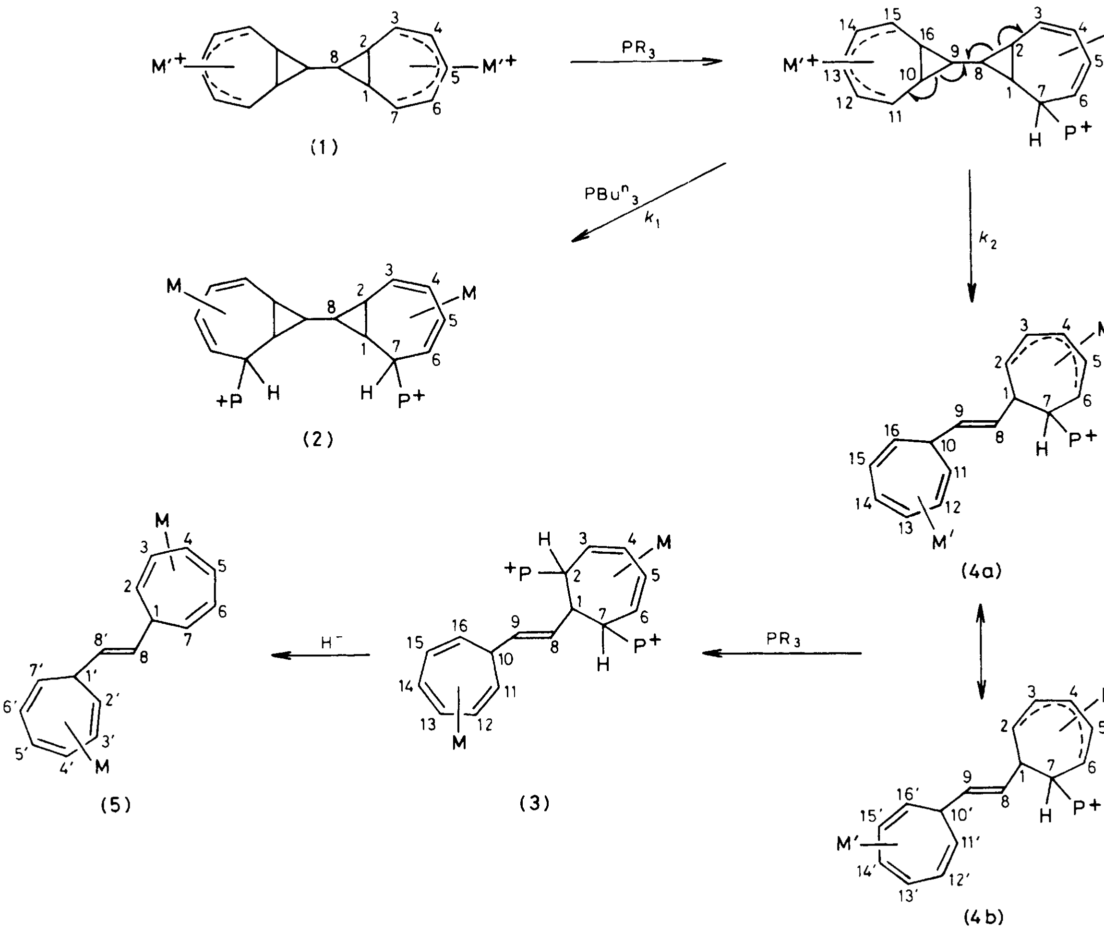
* μ-{*trans*-(1—4-η-Cyclohepta-1,3,5-trien-7-yl)[1′—4′-η-5′,7′-bis(triphenylphosphonium)cyclohepta-1′,3′-dien-6′-yl]ethylene}-bis(tricarbonyliron) bis(hexafluorophosphate)-toluene (2/1).

Supplementary data available (No. SUP 23766, 50 pp.): structure factors, thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme 1. M = Fe(CO)$_3$



Scheme 2. M = Fe(CO)$_3$; M′ = Fe(CO)$_2$L, L = CO or P(OPh)$_3$

Fe(CO)$_3$ group. The ring shows two folds along the lines C(1)—C(6) and C(2)—C(5): interplanar angles 123 and 138°. These folds continue in the same sense as that introduced at atom C(7) between the bond C(8)–C(7) and the plane C(1), C(7), C(6), giving this ring structure a markedly concave configuration with the Fe(CO)$_3$ moiety co-ordinated on the convex face of the ring. The remaining portion of the dication comprises the other (unsubstituted) C$_7$ ring and its η^4-co-ordinated Fe(CO)$_3$ group. Here the carbon atoms co-ordinated to Fe(2) are co-planar and the ring is folded once only (interplanar angle 140°) along the line C(13)—C(16). The atoms C(10)—C(13) and C(16) are also coplanar and enclose an ethylenic bond C(11)–C(12). As with the first ring, however, the angle between C(9)–C(10) and the adjoining ring plane is continued in the same sense at the next fold to give a concave ring with an *exo* Fe(CO)$_3$ group. The molecule as a whole thus has two concave ring structures joined in converse orientation by the *trans* ethylenic bridge. Further-

Table 1. I.r. and analytical data

Complex	$\tilde{\nu}$(CO) [a]/cm^{-1}	Analysis [b] (%)	
		C	H
$[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PBu^n_3)_2\}][PF_6]_2$ (2)	2 049, 1 985	46.9 (46.7)	6.1 (5.9)
$[Fe_2(CO)_6\{\eta^4:\eta'^5\text{-}C_{16}H_{16}(PPh_3)\}][PF_6]_2$	2 121, 2 085, 2 079, 2 047, 1 981br	45.9 (46.2)	3.2 (3.0)
$[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ (3)	2 069, 2 051, 2 003 (sh), 1 991, 1 971 (sh)	52.9 (53.5)	3.5 (3.5)
$[Fe_2(CO)_4\{P(OPh)_3\}_2\{\eta^4:\eta'^5\text{-}C_{16}H_{16}(PBu^n_3)\}][PF_6]_2$ (4; L′ = PBu^n_3)	2 077, 2 041, 2 003, 1 949	53.0 (52.8)	4.8 (4.7)
$[Fe_2(CO)_4\{P(OPh)_3\}_2\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PBu^n_3)_2\}][PF_6]_2$	2 006br, 1 957br	54.4 (55.0)	6.3 (5.7)
$[Fe_2(CO)_4\{P(OPh)_3\}_2\{\eta^4:\eta'^5\text{-}C_{16}H_{16}(PPh_3)\}][PF_6]_2$ (4; L′ = PPh_3)	2 081, 2 041, 2 000, 1 946	55.7 (55.4)	3.8 (3.8)
$[Fe_2(CO)_4\{P(OPh)_3\}_2\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$	2 005br, 1 955br	58.5 (59.2)	4.2 (4.1)
$[Fe_2(CO)_6(\eta^4:\eta'^4\text{-}C_{16}H_{16})]$ (5)	2 045, 1 985, 1 975 [c]	54.2 (54.1)	3.5 (3.3)

[a] In CH_2Cl_2 unless stated otherwise. [b] Calculated values in parentheses. [c] In hexane.

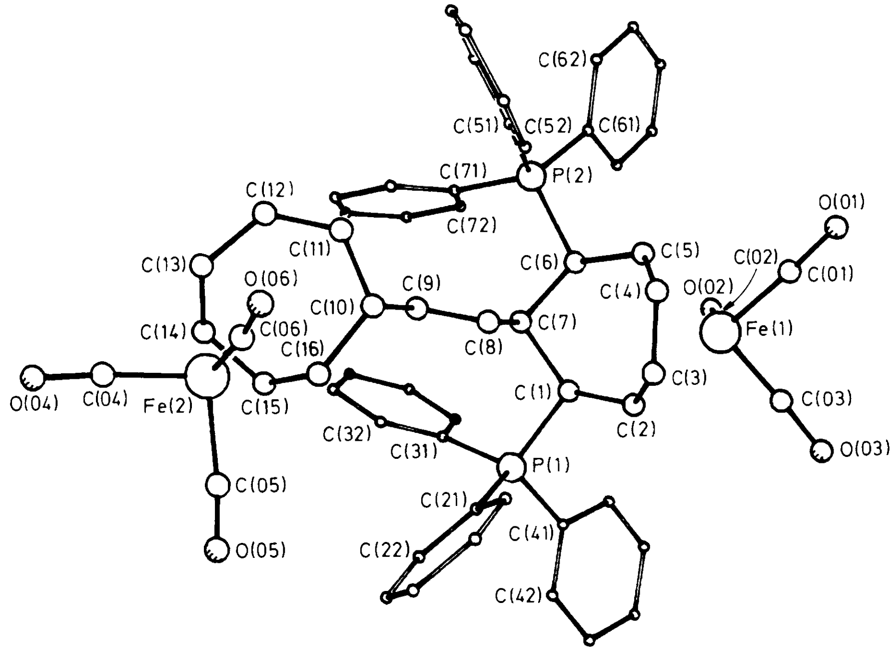


Figure 1. Molecular structure of the dication $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}]^{2+}$ showing the crystallographic numbering

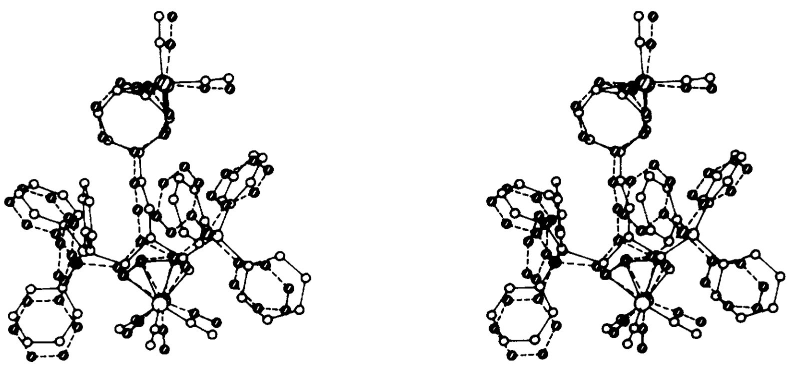


Figure 2. Stereoscopic superposition of the two dication species of (3) contained in the crystallographic asymmetric unit

Table 2. Proton, ^{13}C, and ^{31}P n.m.r. data [a]

Complex	^{1}H (δ) [b]	^{13}C (p.p.m.) [c]	^{31}P (p.p.m.) [d]
(2)	3.98 [1 H, dd, $J(H^4H^3)$ 9, $J(H^4H^5)$ 6, H^4], 4.58 [1 H, dd, $J(H^5H^6)$ 9, $J(H^5H^4)$ 6, H^5], 6.09 [1 H, ddd, $J(H^7P)$ 21, $J(H^7H^1)$ 7, $J(H^7H^6)$ 2, H^7], 6.23 [1 H, dd, $J(H^3H^2)$ 7, $J(H^3H^4)$ 9, H^3], 6.71 [1 H, ddd, $J(H^6P)$ 9, $J(H^6H^5)$ 9, $J(H^6H^7)$ 2, H^6], 7.53 [3 H, m, $J(H^1H^7)$ 7, H^1 and PBu^n_3], 7.71 [1 H, m, $J(H^2H^3)$ 7, H^2], 8.24 (2 H, m, PBu^n_3), 8.46 (2 H, m, PBu^n_3), 9.04 (3 H, t, PBu^n_3) [e,f]	13.71, 19.23, 20.05, 21.19, 23.07, 25.08, 25.31 (C^1, C^2, C^8, and PBu^n_3), 33.34 [d, $J(^{13}C^{31}P)$ 35, C^7], 52.77 [d, $J(^{13}C^{31}P)$ 6, C^6], 57.06 (C^3), 87.02, 94.68 (C^4, C^5), 211.27 (CO)	37.31
(3)	2.17 (30 H, m, PPh_3), 3.50 [1 H, dd, $J(H^9H^8)$ 12, H^8], 3.92 (2 H, m, H^4, H^5), 4.22 [1 H, dd, $J(H^{15}H^{16})$ 10, $J(H^{15}H^{14})$ 7, H^{15}], 4.53 [1 H, ddd, $J(H^{13}H^{14})$ 7, $J(H^{13}H^{12})$ 5, H^{13}], 4.87 [1 H, dd, $J(H^{12}H^{11})$ 7, $J(H^{12}H^{13})$ 5, H^{12}], 5.35 [2 H, d, $J(H^2P)$ 19, $J(H^7P)$ 19, H^2, H^7], 5.60 [1 H, dd, $J(H^{16}H^{15})$ 10, $J(H^{16}H^{10})$ 4, H^{16}], 6.50 [1 H, dd, $J(H^9H^8)$ 12, $J(H^9H^{10})$ 8, H^9], 6.73 (3 H, m, H^1, H^3, H^6), 6.87 [1 H, dd, $J(H^{14}H^{15})$ 7, $J(H^{14}H^{13})$ 7, H^{14}], 7.16 [1 H, m, $J(H^{10}H^9)$ 8, $J(H^{10}H^{16})$ 4, $J(H^{10}H^{11})$ 4, H^{10}], 8.17 [1 H, dd, $J(H^{11}H^{12})$ 7, $J(H^{11}H^{10})$ 4, H^{11}]	41.77, 47.01 (C^1, C^{10}), 47.79 [d, $J(^{13}C^{31}P)$ 49], 48.82 [d, $J(^{13}C^{31}P)$ 49] (C^2, C^7), 49.20 [d, $J(^{13}C^{31}P)$ 6], 49.98 [d, $J(^{13}C^{31}P)$ 4] (C^3, C^6), 57.42, 63.14 (C^{11}, C^{14}), 87.75, 92.81, 97.20 (C^4, C^5, C^{12}, C^{13}), 118.15 [d, $J(^{13}C^{31}P)$ 81], 125.49, 126.33, 131.21, 131.75, 132.29, 135.48, 135.90, 136.87, 137.05, 137.17, 145.96 (C^8, C^9, C^{15}, C^{16}, PPh_3), 209.03, 212.10 (CO)	24.4 [d, $J(^{31}P^{31}P)$ 4, PPh_3], 26.0 [d, $J(^{31}P^{31}P)$ 4, PPh_3]
(4; L′ = PPh_3)		45.82, 46.27, 46.37, 46.74, 47.05 (C^1, C^7, C^{10}), 54.80 [d, $J(^{13}C^{31}P)$ 3.4], 55.22 [d, $J(^{13}C^{31}P)$ 3.4], 61.44 [d, $J(^{13}C^{31}P)$ 6.8], 62.31 [d, $J(^{13}C^{31}P)$ 5.1] (C^{11}, $C^{13'}$, C^{14}, $C^{16'}$), 78.4br (C^6), 86.24, 86.31, 94.68, 94.98 (C^{12}, C^{13}, $C^{14'}$, $C^{15'}$), 90.4br (C^2), 100.43, 100.80 (C^3, C^5), 103.56 (C^4) [f,g]	22.7 [d, $J(^{31}P^{31}P)$ 6, PPh_3], 143.9 [d, $J(^{31}P^{31}P)$ 6, $P(OPh_3)$], 168.9, 169.4 $[P(OPh)_3]$
(4; L′ = PBu^n_3)		43.41, 44.13, 45.0, 45.68, 46.07, 46.59 (C^1, C^7, C^{10}), 55.18 [d, $J(^{13}C^{31}P)$ 3.0], 55.56br, 61.64 [d, $J(^{13}C^{31}P)$ 87.4], 62.88 [d, $J(^{13}C^{31}P)$ 4.4] (C^{11}, $C^{13'}$, C^{14}, $C^{16'}$), 79.1br (C^6), 86.24, 95.20 (C^{12}, C^{13}, $C^{14'}$, $C^{15'}$), 91.1br (C^2), 100.47, 101.80 (C^3, C^5), 103.20 (C^4) [f]	35.5 [d, $J(^{31}P^{31}P)$ 5, PBu^n_3], 35.8 [d, $J(^{31}P^{31}P)$ 5, PBu^n_3], 144.5 [d, $J(^{31}P^{31}P)$ 5, $P(OPh_3)$], 168.8 $[P(OPh)_3]$
(5)	4.21 [1 H, dddd, $J(H^6H^7)$ 10, $J(H^6H^5)$ 7, $J(H^6H^4)$ 2, H^6 [h]], 4.64 [2 H, m, $J(H^4H^6)$, H^4, H^3], 4.80 [1 H, m, $J(H^8H^{8'})$ 15, $J(H^8H^1)$ 9, H^8 [i]], 4.97 [1 H, m, $J(H^7H^6)$ 11, H^7 [j]], 6.85 [2 H, m, $J(H^1H^8)$ 9, H^1, H^2], 6.95 [1 H, dd, $J(H^5H^6)$ 7, $J(H^5H^4)$ 7, H^5] [k]	46.59 (C^1), 55.95, 65.57 (C^2, C^5), 87.79, 95.33 (C^3, C^4), 128.48, 128.74, 134.84 (C^6—C^8), 211.53 (CO) [k]	

[a] In CD_3NO_2 unless stated otherwise. Numbering as in Scheme 2. J values in Hz. [b] 200-MHz spectra. Chemical shifts downfield from $SiMe_4$. [c] 22.56-MHz spectra, unless stated otherwise. Chemical shifts downfield from $SiMe_4$. [d] 36-MHz spectra. Chemical shifts to high frequency of H_3PO_4. [e] Resonance of H^8 obscured by PBu^n_3. [f] In [$^2H_6$]acetone. [g] 50-MHz spectrum. [h] Extra separation of 2 Hz in enantiomeric mixture. [i] Analysed as an $[AX]_2$ system. [j] Extra separation of 6 Hz in enantiomeric mixture. [k] In CD_2Cl_2.

more, the crystal structure comprises two crystallographically distinct dications which differ slightly from one another in the orientations of the carbonyl and phenyl groups. In Figure 2 is given a stereoscopic superposition of the two molecules, from which the differences between them, and their individual stereochemical relationships, can be appreciated.

The formation of (2) and (3) under apparently identical reaction conditions may be rationalised in terms of the mechanism shown in Scheme 2. Following the addition of one P-donor to one of the dienyl units of (1), there is competition between the ring-opening reaction, to give (4) the precursor to (3), and the direct addition of the second nucleophile, to give (2). Thus, the final product depends on the relative magnitudes of k_1 and k_2 (Scheme 2). Although kinetic studies have not been carried out for the reactions of (1) with phosphines it is well established that the nucleophilic addition of PBu^n_3 to a co-ordinated dienyl, for example to that of $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ (C_6H_7 = cyclohexadienyl)[4] is considerably faster

Table 3. Selected interatomic distances (Å) and angles (°) for $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}]^{2+}$ (3) with estimated standard deviations in parentheses *

C(1)–C(2)	1.50(3)	C(2)–C(3)	1.46(3)
C(3)–C(4)	1.45(4)	C(4)–C(5)	1.46(3)
C(5)–C(6)	1.61(3)	C(6)–C(7)	1.59(3)
C(7)–C(1)	1.61(4)	C(7)–C(8)	1.54(3)
C(8)–C(9)	1.36(4)	C(9)–C(10)	1.52(3)
C(10)–C(11)	1.43(4)	C(11)–C(12)	1.36(4)
C(12)–C(13)	1.47(4)	C(13)–C(14)	1.45(4)
C(14)–C(15)	1.43(5)	C(15)–C(16)	1.46(3)
C(16)–C(10)	1.53(3)		
Fe(1)–C(2)	2.13(2)	Fe(2)–C(13)	2.16(3)
Fe(1)–C(3)	2.08(2)	Fe(2)–C(14)	2.02(2)
Fe(1)–C(4)	2.08(3)	Fe(2)–C(15)	2.09(3)
Fe(1)–C(5)	2.08(3)	Fe(2)–C(16)	2.06(3)
Fe(1)–C(01)	1.73(2)	Fe(2)–C(04)	1.76(3)
Fe(1)–C(02)	1.80(2)	Fe(2)–C(05)	1.85(4)
Fe(1)–C(03)	1.72(3)	Fe(2)–C(06)	1.68(3)
C(01)–O(01)	1.21(3)	C(04)–O(04)	1.14(3)
C(02)–O(02)	1.15(3)	C(05)–O(05)	1.06(5)
C(03)–O(03)	1.19(4)	C(06)–O(06)	1.17(4)
C(1)–P(1)	1.84(2)	C(6)–P(2)	1.88(3)
P(1)–C(21)	1.77(1)	P(2)–C(51)	1.80(2)
P(1)–C(31)	1.78(1)	P(2)–C(61)	1.82(1)
P(1)–C(41)	1.80(2)	P(2)–C(71)	1.81(1)

C(1)–C(2)–C(3)	127(2)	C(11)–C(12)–C(13)	127(3)
C(2)–C(3)–C(4)	118(2)	C(12)–C(13)–C(14)	130(3)
C(3)–C(4)–C(5)	117(2)	C(13)–C(14)–C(15)	121(2)
C(4)–C(5)–C(6)	126(2)	C(14)–C(15)–C(16)	115(2)
C(5)–C(6)–C(7)	115(1)	C(15)–C(16)–C(10)	123(2)
C(6)–C(7)–C(1)	101(2)	C(16)–C(10)–C(11)	117(2)
C(7)–C(1)–C(2)	117(2)	C(10)–C(11)–C(12)	127(2)
C(1)–C(7)–C(8)	113(2)	C(11)–C(10)–C(9)	110(2)
C(6)–C(7)–C(8)	117(2)	C(16)–C(10)–C(9)	108(2)
C(7)–C(8)–C(9)	117(2)	C(10)–C(9)–C(8)	120(2)
C(01)–Fe(1)–C(02)	101(1)	C(04)–Fe(2)–C(05)	94(2)
C(01)–Fe(1)–C(03)	91(1)	C(04)–Fe(2)–C(06)	102(2)
C(02)–Fe(1)–C(03)	97(1)	C(05)–Fe(2)–C(06)	101(2)
C(7)–C(1)–P(1)	110(1)	C(7)–C(6)–P(2)	111(2)
C(2)–C(1)–P(1)	112(2)	C(5)–C(6)–P(2)	108(1)

* The values given in this Table refer to one molecule only of the two dications in the crystallographic asymmetric unit. All other values have been deposited.

than of PPh_3. Thus, complex (2) is presumably formed in preference to an analogue of (3) because $k_1 > k_2$. It should be noted that the syntheses of (2) and (3) are carried out at −78 °C. Whereas both k_1 and k_2 will be increased at higher temperatures their relative magnitudes clearly change; at room temperature (1) and PBu^n_3 give low yields of that isomer of $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PBu^n_3)_2\}][PF_6]_2$ [$\tilde{\nu}$(CO) = 2 065, 2 049, 2 003 (sh), and 1 989 cm^{-1} (CH_2Cl_2)] which has the same structure as (3).

In order to probe further the mechanism shown in Scheme 2, attempts were made to isolate the intermediate monophosphonium salts. Although good yields of analytically pure $[Fe_2(CO)_6\{\eta^4:\eta'^5\text{-}C_{16}H_{16}(PPh_3)\}][PF_6]_2$ were isolated from the reaction between (1; L = CO) and PPh_3 in a 1 : 1 ratio, informative n.m.r. spectra could not be obtained and no structure was assigned. The reactions of [1; L = $P(OPh)_3$] with PPh_3 and PBu^n_3 were therefore investigated.

At −78 °C, equivalent quantities of [1; L = $P(OPh)_3$] and the phosphine ligand give the 1 : 1 adducts $[Fe_2(CO)_4\{P(OPh)_3\}_2(\eta^4:\eta'^5\text{-}C_{16}H_{16}L')][PF_6]_2$ (4; L′ = PBu^n_3 or PPh_3) (Tables 1 and 2). While the ^1H n.m.r. spectra were too complex to be assigned, the structures of (4) were determined by i.r., ^{13}C, and ^{31}P n.m.r. spectroscopy. The carbonyl spectra of (4) show four peaks indicative of two inequivalent $Fe(CO)_2\{P(OPh)_3\}$ groups, one cationic and one neutral. The ^{31}P n.m.r. spectrum of (4; L′ = PPh_3) shows four peaks (Table 2) which can only be assigned in terms of the structure of (4) shown in Scheme 2. By comparing the ^{31}P n.m.r. spectrum of $[Fe(CO)_2\{P(OPh)_3\}(\eta^4\text{-cot})]$ (176.0 p.p.m., [$^2H_6$]acetone) and of [1; L = $P(OPh)_3$] (147.2 p.p.m., [$^2H_6$]acetone) with that of (3) (Table 2) the doublets at 22.7 and 143.9 p.p.m. can be assigned to a phosphonium-phosphorus atom coupled to a phosphite-phosphorus bonded to a positively charged iron atom. The singlet peaks at 168.9 and 169.4 p.p.m. are in the region associated with phosphites bonded to a neutral iron atom; that there are two such peaks suggests that (4; L′ = PPh_3) exists as two isomers, (4a) and (4b), with the neutral $Fe(CO)_2\{P(OPh)_3\}$ group bonded to C^{11}—C^{14} or to $C^{13'}$—$C^{16'}$ (Scheme 2).

The ^{13}C n.m.r. spectrum of (4; L′ = PPh_3) (Table 2) is not only consistent with the cyclopropane ring-opened structure but also with the proposed isomerism. The resonances due to C^8, C^9, C^{15}, and C^{16} of isomer (4a), and the corresponding peaks for (4b), are obscured by the resonances of the P-donor phenyl groups. In addition, the peaks due to C^2—C^6 do not show the effects of the isomerism, in accord with the ^{31}P n.m.r. resonances for the phosphorus atoms associated with the cycloheptadienyl ring. However, the diene carbon atoms bonded to $Fe(CO)_2\{P(OPh)_3\}$ are ‘ doubled ’. Thus, resonances at 61.44 and 62.31, and at 54.80 and 55.22 p.p.m. which are split into doublets by ^{31}P coupling (Table 2), may be assigned to the co-ordinated outer diene carbon atoms C^{11} and C^{14} of (4a), and $C^{13'}$ and $C^{16'}$ of (4b). Similarly, the co-ordinated inner diene carbon atoms C^{12}, C^{13}, $C^{14'}$, and $C^{15'}$ give rise to peaks at 86.24, 86.31, 94.68, and 94.98 p.p.m. (unsplit by ^{31}P coupling). Although most of the phenyl carbon atoms are not assignable, those attached directly to the oxygen atoms of $P(OPh)_3$ also reveal the existence of (4a) and (4b). Thus, these carbon atoms of the phosphite attached to the cationic dienyliron centre appear as a doublet [J(PC) = 12 Hz], whereas those of the phosphite attached to the neutral dieneiron group occur as two doublets (152.27, 152.20, 152.14, and 152.07 p.p.m.).

The 1 : 1 adduct isolated from the reaction between [1; L = $P(OPh)_3$] and PBu^n_3 is structurally analogous to (4; L′ = PPh_3). The i.r. carbonyl spectrum (Table 1) is very similar, and as far as the C_{16}-hydrocarbon skeleton is concerned, the ^{13}C n.m.r. spectrum is nearly identical (Table 2). The isomerism is evidenced by the ‘ doubling ’ of the co-ordinated outer-diene resonances although the inner-diene carbon atoms show only singlet resonances at 86.24 and 95.20 p.p.m. In addition, the phosphite carbon atoms, P–O–C, occur only as two doublets at 151.03 [J(PC) = 12.5 Hz] and 152.17 [J(PC) = 7.3 Hz].

The ^{31}P n.m.r. spectrum of (4; L′ = PBu^n_3) is also a little different from that of (4; L′ = PPh_3). Despite the isomerism, evidenced by the ^{13}C n.m.r. spectrum, the ^{31}P resonance at 168.8 p.p.m., due to the $P(OPh)_3$ bonded to the diene-iron atom, is not doubled. However, the PBu^n_3 phosphorus resonance occurs as two doublets (Table 2), coupled only to the phosphite doublet resonance at 144.5 p.p.m. Bearing in mind the close similarity between the ^{13}C n.m.r. spectra of (4; L′ = PPh_3) and (4; L′ = PBu^n_3) we assume that the isomerism associated with the bonding of the $Fe(CO)_2\{P(OPh)_3\}$ group to the cycloheptatriene ring affects the chemical shift of the PBu^n_3 ligand bonded to the cycloheptadienyl ring.

The most important consequence of the isolation of (4) is the finding that cyclopropane ring-opening has occurred during the reaction of [1; L = $P(OPh)_3$] for both PPh_3 and

PBu^n_3. Obviously, the phosphite ligand will lower the susceptibility of the dienyl units of (1) to nucleophilic attack, leading to a reduction of k_1 (Scheme 2) for the addition of both PPh_3 and PBu^n_3. Presumably, k_1 is slowed relative to k_2 so that ring opening occurs before the formation of an analogue of (2). As some indication of the reduced nucleophilicity of the cationic phosphite complexes, the bis(phosphonium)salt $[Fe_2(CO)_4\{P(OPh)_3\}_2\{\eta^4{:}\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ is fully formed from [1; L = $P(OPh)_3$] and PPh_3 (1 : 2 ratio) only after 18 h.

Synthesis of $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{16})]$ (5).—The reaction between (2) and $NaBH_4$ in tetrahydrofuran (thf) results in phosphine substitution by hydride ion and the isolation of $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$, identical to the complex formed from (1; L = CO) and $NaBH_4$ [1] (Scheme 1). By contrast, the reaction of (3) with $[BH_4]^-$ results in reduction and the formation of yellow, crystalline $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{16})]$ (5) (Table 1), ^1H and ^{13}C n.m.r. studies on which (Table 2) reveal the presence of the co-ordinated *trans*-di(cycloheptatrienyl)ethylene ligand. The ^1H n.m.r. spectrum of (5) not only confirms the retention of the *trans*-exocyclic double bond when (3) is reduced, [$J(H^8H^{8'})$ = 15 Hz] but also shows the effects of the chirality at bridgehead carbon atoms C^8 and $C^{8'}$. A careful examination of the 200-MHz spectrum apparently showed an additional coupling of 6 Hz for H^7, not expected for the assigned structure. However, the 100-MHz spectrum showed the separation reduced to 3 Hz, thereby identifying a chemical shift difference due to the presence of two diastereoisomers. A freshly crystallised sample of (5), from n-heptane at −20 °C, has a ^1H n.m.r. spectrum due to only one such isomer, but equilibration slowly occurs in CD_2Cl_2.

Conclusions

The synthesis of (5) from (1), in an overall yield of 17%, represents a novel route for the conversion of cyclo-octatetraene to a cycloheptatriene derivative, in effect a carbon extrusion reaction; a similar process yields $[Fe(CO)_3(\eta^4\text{-styrylcycloheptatriene})]$ [5] from $[Fe(CO)_3(\eta^4\text{-cot})]$ and the tropylium ion, $[C_7H_7]^+$. That stereo- and regio-specific C–C bond formation and cleavage *via* one-electron transfer is not restricted to $[Fe(CO)_3(\eta^4\text{-cot})]$ and (1) has recently been demonstrated in the oxidative cyclopropane ring-opening reactions of, for example, $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{18})]$.[6]

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Where appropriate, reactions were monitored by i.r. spectroscopy; unless stated otherwise the complexes are moderately air-stable in the solid state, and dissolve in polar solvents such as CH_2Cl_2 and acetone to give solutions which slowly decompose in air. The complexes $[Fe_2(CO)_4L_2(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})][PF_6]_2$ [L = CO or $P(OPh)_3$] were prepared by the published method.[1] Infrared spectra were recorded on Perkin-Elmer PE 257 or 457 spectrophotometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on a JEOL FX 200 spectrometer and ^{13}C n.m.r. spectra on JEOL FX 200 or FX 90Q instruments; both were calibrated against $SiMe_4$ as internal reference. ^{31}P N.m.r. spectra were recorded on a JEOL FX 90Q instrument using H_3PO_4 as external reference. Mass spectra were recorded on a A.E.I. MS 902 instrument.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

Synthesis of $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{16}(PBu^n_3)_2\}][PF_6]_2$ (2).—To a cold (−93 °C), stirred solution of complex (1) (0.57 g, 0.74 mmol) in acetone (50 cm^3) was added dropwise a solution of PBu^n_3 (0.30 g, 1.48 mmol) in acetone (2 cm^3). The mixture was then warmed to room temperature, over a period of 30 min, and the pale yellow solution evaporated to dryness. Recrystallisation of the residue from CH_2Cl_2–diethyl ether gave the *product* as a pale yellow solid, yield 0.47 g (53%).

The complexes $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ (3) (bright yellow, 85%), $[Fe_2(CO)_6(\eta^4{:}\eta'^5\text{-}C_{16}H_{16}L')][PF_6]_2$ (L′ = PPh_3, yellow-brown, 68%; L′ = PBu^n_3, pale yellow, 16%), $[Fe_2(CO)_4\{P(OPh)_3\}_2(\eta^4{:}\eta'^5\text{-}C_{16}H_{16}L')][PF_6]_2$ [in CH_2Cl_2, (4) L′ = PPh_3, yellow, 39%; (4) L′ = PBu^n_3, bright yellow, 64%], and $[Fe_2(CO)_4\{P(OPh)_3\}_2(\eta^4{:}\eta'^4\text{-}C_{16}H_{16}L'_2)][PF_6]_2$ (in CH_2Cl_2, at room temperature, L′ = PPh_3, bright yellow, 67%; L′ = PBu^n_3, pale yellow, 31%, recrystallised from diethyl ether–n-hexane) were prepared similarly, but with the modifications noted. In addition, where difficulty was encountered in obtaining solid samples, the following procedure was adopted. After dissolving the residue in CH_2Cl_2, diethyl ether was carefully added to deposit small quantities of an impure oil. Decantation of the mother-liquors, and addition of more diethyl ether, gave the pure solid.

μ-[1—4-η:1′—4′-η-trans-*Bis(cyclohepta*-1,3,5-*trien*-7-*yl)ethylene*]-*bis(tricarbonyliron)*, $[Fe_2(CO)_6(\eta^4{:}\eta'^4\text{-}C_{16}H_{16})]$ (5).—To a stirred, cooled (−78 °C) solution of (3) (1.64 g, 1.26 mmol) in thf (120 cm^3) was added an excess of $NaBH_4$ (0.95 g, 25.1 mmol). After 2.5 h the orange-yellow solution was evaporated to dryness, and the residue dissolved in CH_2Cl_2 (9 cm^3). Chromatography on a silica–hexane column (40 × 3 cm) and elution with hexane–diethyl ether (10 : 1) gave a pale yellow band. Evaporation to dryness and recrystallisation from n-hexane at −78 °C gave the product as *yellow crystals*, yield 0.13 g (22%, m.p. 128—130 °C). The complex is moderately soluble in n-hexane and very soluble in more polar solvents.

Crystal Structure Determination of $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2\cdot0.5C_6H_5Me$ (3).—Crystals of (3) grow as clear yellow striated rhombs from methylene chloride–toluene at −20 °C. Diffracted intensities were recorded at 220 K for a crystal of dimensions 0.40 × 0.48 × 0.50 mm mounted in a Lindemann capillary tube under solvent and sealed in with low-temperature epoxy resin. Of the 22 019 independent reflections measured for $2.9 \leqslant 2\theta \leqslant 55^\circ$ on a Nicolet $P2_1m$ diffractometer, only 6 436 had $I \geqslant 2.0\sigma(I)$, reflecting very poor crystal quality. These were used in the solution and refinement of the structure. Two check reflections ($7\bar{2}\bar{3}$ and $\bar{6}04$) were remeasured every 48 reflections and showed some 12% decay in intensity over 604 h of exposure to *X*-rays. Corrections were applied for Lorentz, polarisation, anomalous dispersion, and crystal decay, but not for *X*-ray absorption, effects.

Crystal data. $C_{58}H_{46}F_{12}Fe_2O_6P_4\cdot0.5C_7H_8$, M = 1 347.6, monoclinic, a = 26.795(13), b = 19.699(25), c = 26.297(23) Å, β = 116.37(6)°, U = 12 436(21) Å^3, D_m not measured, Z = 8, D_c = 1.44 g cm^{-3}, $F(000)$ = 5 496, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 6.5 cm^{-1}.

The structure was solved by heavy-atom methods, and was refined by blocked-cascade least squares with anisotropic thermal parameters for Fe, F, P, and carbonyl [except C(01)] atoms. Because of the size of the structure (which comprises two dication species, four $[PF_6]^-$ counter ions, and two half-molecules of toluene per asymmetric unit) no hydrogen atoms were included in the model. The phenyl groups of the triphenylphosphine ligands were constrained to idealised geometry, as also were the two half-molecules of toluene

Table 4. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for $[Fe_2(CO)_6\{\eta^4:\eta'^4\text{-}C_{16}H_{16}(PPh_3)_2\}][PF_6]_2$ (3) *

Atom	*x*	*y*	*z*
Fe(1)	0.073 01(14)	0.372 2(2)	0.069 82(14)
Fe(2)	0.079 09(14)	0.085 8(2)	0.376 53(15)
P(1)	0.097 3(3)	0.136 2(4)	0.121 0(3)
P(2)	−0.085 4(3)	0.299 8(4)	0.091 1(3)
C(01)	0.062 0(10)	0.458 8(11)	0.064 8(10)
O(01)	0.056 2(8)	0.519 6(9)	0.065 7(7)
C(02)	0.025 0(10)	0.345 5(11)	−0.000 5(12)
O(02)	−0.007 5(8)	0.327 7(10)	−0.044 6(8)
C(03)	0.129 6(10)	0.381 9(11)	0.056 3(10)
O(03)	0.169 4(7)	0.387 2(9)	0.047 7(7)
C(04)	0.071 6(11)	0.034 3(13)	0.427 3(10)
O(04)	0.069 1(7)	−0.000 1(8)	0.460 6(7)
C(05)	0.150(2)	0.053(2)	0.394(2)
O(05)	0.191 6(11)	0.037(2)	0.407 7(14)
C(06)	0.095 2(14)	0.161 5(15)	0.409 1(15)
O(06)	0.105 1(10)	0.213 5(12)	0.433 3(10)
C(1)	0.061 9(9)	0.218 5(11)	0.098 3(9)
C(2)	0.102 2(10)	0.276 2(12)	0.109 7(10)
C(3)	0.114 1(10)	0.331 1(12)	0.150 8(10)
C(4)	0.068 1(11)	0.373 7(12)	0.146 7(10)
C(5)	0.013 6(9)	0.360 9(10)	0.099 8(9)
C(6)	−0.018 7(9)	0.289 2(11)	0.085 1(9)
C(7)	0.016 3(9)	0.226 9(11)	0.122 0(9)
C(8)	0.041 9(9)	0.233 9(11)	0.186 9(9)
C(9)	0.021 0(10)	0.193 3(11)	0.214 6(10)
C(10)	0.043 9(10)	0.197 4(12)	0.278 7(10)
C(11)	0.001 2(11)	0.216 9(13)	0.294 2(11)
C(12)	−0.022 0(11)	0.177 7(13)	0.320 5(11)
C(13)	−0.009 5(11)	0.105 8(13)	0.337 1(11)
C(14)	0.008 4(11)	0.051 5(12)	0.311 6(11)
C(15)	0.047 9(11)	0.064 2(13)	0.290 0(11)
C(16)	0.074 8(10)	0.130 9(12)	0.303 9(10)
C(21)	0.146 6(6)	0.127 7(8)	0.192 7(5)
C(22)	0.162 8(6)	0.062 0(8)	0.213 1(5)
C(23)	0.203 2(6)	0.051 9(8)	0.268 8(5)
C(24)	0.227 3(6)	0.107 5(8)	0.304 1(5)
C(25)	0.211 1(6)	0.173 2(8)	0.283 7(5)
C(26)	0.170 7(6)	0.183 3(8)	0.228 0(5)
C(31)	0.042 2(5)	0.077 1(7)	0.106 6(6)
C(32)	0.032 4(5)	0.053 3(7)	0.151 4(6)
C(33)	−0.015 5(5)	0.015 6(7)	0.140 1(6)
C(34)	−0.053 5(5)	0.001 7(7)	0.084 2(6)
C(35)	−0.043 7(5)	0.025 5(7)	0.039 5(6)
C(36)	0.004 2(5)	0.063 2(7)	0.050 7(6)
C(41)	0.128 6(8)	0.123 8(10)	0.073 4(7)
C(42)	0.178 2(8)	0.087 1(10)	0.094 2(7)
C(43)	0.204 8(8)	0.076 0(10)	0.059 8(7)
C(44)	0.181 8(8)	0.101 8(10)	0.004 7(7)
C(45)	0.132 2(8)	0.138 6(10)	−0.016 0(7)
C(46)	0.105 6(8)	0.149 6(10)	0.018 3(7)
C(51)	−0.082 4(7)	0.339 8(8)	0.153 9(6)
C(52)	−0.032 5(7)	0.362 6(8)	0.197 6(6)
C(53)	−0.032 0(7)	0.391 0(8)	0.246 4(6)
C(54)	−0.081 5(7)	0.396 6(8)	0.251 4(6)
C(55)	−0.131 4(7)	0.373 8(8)	0.207 7(6)
C(56)	−0.131 9(7)	0.345 4(8)	0.158 9(6)
C(61)	−0.128 4(7)	0.347 3(8)	0.027 0(6)
C(62)	−0.166 7(7)	0.394 7(8)	0.028 1(6)
C(63)	−0.203 7(7)	0.426 2(8)	−0.022 0(6)
C(64)	−0.202 5(7)	0.410 5(8)	−0.073 2(6)
C(65)	−0.164 2(7)	0.363 2(8)	−0.074 2(6)
C(66)	−0.127 2(7)	0.331 6(8)	−0.024 1(6)
C(71)	−0.116 6(7)	0.216 8(6)	0.085 1(7)
C(72)	−0.140 4(7)	0.184 3(6)	0.032 5(7)
C(73)	−0.164 0(7)	0.120 0(6)	0.027 5(7)
C(74)	−0.163 7(7)	0.088 3(6)	0.075 1(7)
C(75)	−0.139 8(7)	0.120 8(6)	0.127 6(7)
C(76)	−0.116 2(7)	0.185 1(6)	0.132 6(7)
P(3)	0.090 6(4)	0.661 4(5)	0.600 3(4)
F(31)	0.128 7(6)	0.637 3(10)	0.663 8(7)
F(32)	0.067 2(12)	0.590 2(10)	0.584 3(10)
F(33)	0.137 4(9)	0.653(2)	0.584 5(9)
F(34)	0.043 7(10)	0.679 3(13)	0.616 1(10)
F(35)	0.054 1(6)	0.688 3(8)	0.536 8(7)
F(36)	0.107 2(11)	0.738 2(12)	0.615 9(9)
P(4)	0.144 8(4)	0.408 8(5)	0.313 4(4)
F(41)	0.116 1(11)	0.410(2)	0.349 5(11)
F(42)	0.106 4(9)	0.354 9(10)	0.276 8(9)
F(43)	0.185 3(11)	0.466 8(12)	0.345 7(11)
F(44)	0.184 4(12)	0.360 0(12)	0.358 6(10)
F(45)	0.172 5(14)	0.410(2)	0.274 7(13)
F(46)	0.103 9(10)	0.458 4(11)	0.272 4(10)
Fe(1′)	0.489 49(14)	0.265 0(2)	0.494 5(2)
Fe(2′)	0.694 06(15)	0.602 7(2)	0.770 9(2)
P(2′)	0.567 1(3)	0.195 9(4)	0.685 4(3)
P(1′)	0.673 3(3)	0.355 5(4)	0.582 6(3)
C(03′)	0.467 1(10)	0.291(2)	0.426 9(14)
O(03′)	0.450 9(8)	0.308 2(11)	0.377 9(10)
C(02′)	0.522 8(10)	0.187 5(13)	0.488 4(13)
O(02′)	0.540 7(9)	0.140 1(11)	0.480 5(10)
C(01′)	0.421 5(13)	0.227(2)	0.476(2)
O(01′)	0.379 7(10)	0.208 1(13)	0.461 7(10)
C(06′)	0.619 0(14)	0.620(2)	0.757(2)
O(06′)	0.580 9(9)	0.632 5(12)	0.756 1(10)
C(04′)	0.729 0(9)	0.670 7(14)	0.814 4(12)
O(04′)	0.754 2(9)	0.715 4(11)	0.846 6(10)
C(05′)	0.694 0(14)	0.647(2)	0.713 8(14)
O(05′)	0.691 7(10)	0.679 6(12)	0.676 4(10)
C(6′)	0.566 5(11)	0.238 0(12)	0.624 5(10)
C(5′)	0.508 0(10)	0.258 7(12)	0.581 5(10)
C(4′)	0.488 3(11)	0.326 2(13)	0.558 6(11)
C(3′)	0.514 9(10)	0.359 6(11)	0.529 5(9)
C(2′)	0.560 6(10)	0.327 4(11)	0.528 1(10)
C(1′)	0.613 5(10)	0.301 4(12)	0.578 3(10)
C(7′)	0.611 0(10)	0.294 7(12)	0.636 8(10)
C(8′)	0.603 7(10)	0.360 5(12)	0.662 7(10)
C(9′)	0.642 4(9)	0.389 1(11)	0.707 9(10)
C(10′)	0.634 7(10)	0.459 4(12)	0.730 3(10)
C(11′)	0.638 0(10)	0.448 3(12)	0.787 8(10)
C(12′)	0.670 8(10)	0.483 0(12)	0.837 5(10)
C(13′)	0.713 1(11)	0.536 3(13)	0.842 6(11)
C(14′)	0.752 9(10)	0.531 9(12)	0.815 1(11)
C(15′)	0.732 9(12)	0.518 2(14)	0.760 1(12)
C(16′)	0.671 8(11)	0.509 7(12)	0.721 4(11)
C(51′)	0.543 4(7)	0.243 7(9)	0.727 4(8)
C(52′)	0.512 6(7)	0.303 4(9)	0.708 3(8)
C(53′)	0.495 1(7)	0.338 6(9)	0.743 6(8)
C(54′)	0.508 4(7)	0.314 1(9)	0.797 8(8)
C(55′)	0.539 1(7)	0.254 5(9)	0.816 9(8)
C(56′)	0.556 6(7)	0.219 2(9)	0.781 7(8)
C(61′)	0.524 8(7)	0.122 0(8)	0.659 7(9)
C(62′)	0.499 4(7)	0.093 3(8)	0.689 7(9)
C(63′)	0.466 7(7)	0.035 1(8)	0.669 7(9)
C(64′)	0.459 5(7)	0.005 7(8)	0.618 6(9)
C(65′)	0.485 0(7)	0.034 5(8)	0.587 6(9)
C(66′)	0.517 6(7)	0.092 6(8)	0.607 6(9)
C(71′)	0.636 1(6)	0.169 7(9)	0.731 0(7)
C(72′)	0.650 9(6)	0.102 4(9)	0.727 9(7)
C(73′)	0.704 0(6)	0.079 2(9)	0.764 8(7)
C(74′)	0.742 1(6)	0.123 1(9)	0.804 8(7)
C(75′)	0.727 3(6)	0.190 3(9)	0.807 8(7)
C(76′)	0.674 3(6)	0.213 6(9)	0.770 9(7)
C(21′)	0.659 9(7)	0.444 7(7)	0.572 9(7)
C(22′)	0.698 4(7)	0.483 4(7)	0.563 3(7)
C(23′)	0.692 1(7)	0.553 7(7)	0.557 5(7)
C(24′)	0.647 4(7)	0.585 3(7)	0.561 5(7)
C(25′)	0.608 8(7)	0.546 5(7)	0.571 1(7)
C(26′)	0.615 1(7)	0.476 2(7)	0.576 8(7)
C(41′)	0.686 8(7)	0.325 6(9)	0.525 0(6)
C(46′)	0.712 1(7)	0.262 7(9)	0.528 7(6)

Table 4 (*continued*)

Atom	x	y	z
C(45′)	0.720 4(7)	0.238 6(9)	0.483 2(6)
C(44′)	0.703 4(7)	0.277 4(9)	0.433 9(6)
C(43′)	0.678 1(7)	0.340 3(9)	0.430 2(6)
C(42′)	0.669 8(7)	0.364 4(9)	0.475 8(6)
C(31′)	0.732 6(6)	0.337 2(8)	0.649 4(5)
C(36′)	0.745 0(6)	0.271 1(8)	0.670 5(5)
C(35′)	0.789 0(6)	0.259 4(8)	0.723 9(5)
C(34′)	0.820 5(6)	0.313 8(8)	0.756 3(5)
C(33′)	0.808 0(6)	0.379 8(8)	0.735 3(5)
C(32′)	0.764 0(6)	0.391 5(8)	0.681 8(5)
P(3′)	0.463 7(4)	0.518 6(5)	0.618 8(4)
F(31′)	0.454 3(9)	0.590 1(13)	0.595 8(15)
F(32′)	0.472 6(11)	0.446 1(11)	0.633 8(14)
F(33′)	0.495 0(13)	0.529(2)	0.678 1(13)
F(34′)	0.428(2)	0.501 3(2)	0.562 0(11)
F(35′)	0.409 9(13)	0.526(2)	0.627(2)
F(36′)	0.514 9(13)	0.513(2)	0.612(2)
P(4′)	0.318 6(5)	0.576 2(6)	0.915 8(6)
F(41′)	0.291 8(11)	0.505 8(13)	0.913(2)
F(42′)	0.267 6(9)	0.609 2(13)	0.914 8(13)
F(43′)	0.347 6(13)	0.578(3)	0.977 0(12)
F(44′)	0.370 4(13)	0.545 1(13)	0.915(3)
F(45′)	0.285 8(14)	0.576(3)	0.850 6(14)
F(46′)	0.343 7(8)	0.644 9(10)	0.909 0(11)
C(91)	0.331 6(12)	0.350 6(13)	0.747 4(13)
C(92)	0.321 7(12)	0.368 6(13)	0.692 5(13)
C(93)	0.350 2(12)	0.423 2(13)	0.683 8(13)
C(94)	0.388 5(12)	0.459 8(13)	0.730 1(13)
C(95)	0.398 4(12)	0.441 8(13)	0.785 1(13)
C(96)	0.369 9(12)	0.387 2(13)	0.793 7(13)
C(97)	0.385(3)	0.372(3)	0.849(3)
C(85)	0.300 6(13)	0.323 1(15)	0.024 6(13)
C(86)	0.286 3(13)	0.256 2(15)	0.006 5(13)
C(81)	0.316 5(13)	0.202 6(15)	0.041 1(13)
C(82)	0.361 0(13)	0.215 8(15)	0.093 9(13)
C(83)	0.375 4(13)	0.282 7(15)	0.112 0(13)
C(84)	0.345 1(13)	0.336 3(15)	0.077 4(13)

* Primes are used to indicate atoms of the second molecular species in the crystallographic asymmetric unit.

(solvent) incorporated into the crystal. One of these solvent molecules was well defined, but the other showed positional disorder of the methyl group which was consequently omitted from the refinement. Individual weights were ascribed according to the sheme $w = [\sigma^2(F_o) + 0.002\,2|F_o|^2]^{-1}$. Scattering factors and corrections for anomalous dispersion were from ref. 7. A final electron-density difference synthesis showed no peaks >1.2 or <-1.2 e Å^{-3}, the largest peaks being in the vicinity of the disordered solvent molecule. Refinement converged at $R = 0.142$, $R' = 0.136$, and the high values can be ascribed to poor crystal quality. There can be little doubt about the correctness of the structure, however, as there are no unexplained peaks in the final difference map, the refinement was stable, and the structure formed is both chemically reasonable and in agreement with the spectroscopic data. All computations were carried out in the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[8] Final atom co-ordinates for (3) are listed in Table 4.

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