Synthesis of Styrylcycloheptatriene Derivatives *via* the Electrophilic Addition of Tropylium Ions to $[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$: *X*-Ray Crystal Structure * of Tricarbonyl(1—4-η-7-styrylcyclohepta-1,3,5-triene)iron

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The reaction between $[Fe(CO)_3(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene) and tropylium tetrafluoroborate yields $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$ (1), *X*-ray studies on which have revealed the formation of a co-ordinated styrylcycloheptatriene ligand. The C_7 ring adopts an envelope conformation (interplanar angle 138°) to which the $Fe(CO)_3$ fragment is η^4 bonded on the convex face. The atoms of the styryl substituent are all coplanar, and this plane lies approximately orthogonal to the mean plane of the C_7 ring. Crystals of $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$ are monoclinic, with space group *C2/c*, and the structure has been refined to *R* 0.063 for 1 977 reflections to $2\theta = 55°$ (Mo-K_α) at 293 K. The reaction between $[C_7H_7]^+$ and $[Fe(CO)_3(\eta^4\text{-}C_8H_7Me)]$, giving $[Fe(CO)_3\{\eta^4\text{-}C_7H_6(Me)CH{=}CHPh\}]$ in which the methyl group is located on the cycloheptatriene ring, shows that both the cot and tropylium groups undergo ring contraction during the generation of the exocyclic alkene bond of (1). Complex (1) reacts with HBF_4, giving the cycloheptadienyl complex $[Fe(CO)_3(\eta^5\text{-}C_7H_8CH{=}CHPh)][BF_4]$, and with tetracyanoethylene to give the 1,3-cyclo-adduct, 9-σ: 2—4-η-7,7,8,8-tetracyano-5-styrylbicyclo[4.2.1]nonenediyliron.

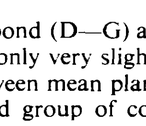
During our studies [1] of the electron-transfer properties of organo-transition metal complexes, we have shown [2] that $[Fe(CO)_3(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene) can be oxidatively dimerised by Ag^+ or $[N(C_6H_4Br\text{-}p)_3]^+$. Weaker one-electron oxidants such as $[N_2C_6H_4F\text{-}p]^+$ or the triphenylcyclopropenium ion, however, behave as electrophiles, bonding directly to the co-ordinated hydrocarbon.[3,4] The tropylium ion, $[C_7H_7]^+$, is known to function as a weak oxidant [5] or as an electrophile [6,7] towards organometallic complexes. We now give details [8] of the reaction between $[C_7H_7]^+$ and $[Fe(CO)_3(\eta^4\text{-cot})]$ which has led to the isolation, and full characterisation by *X*-ray crystallography, of $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$ (1), a complex of co-ordinated styrylcycloheptatriene. The mechanism of formation of (1) has been probed *via* a study of the reaction between $[C_7H_7]^+$ and $[Fe(CO)_3(\eta^4\text{-}C_8H_7Me)]$.

Results and Discussion

The reaction of $[Fe(CO)_3(\eta^4\text{-cot})]$ with $[C_7H_7][BF_4]$ in acetone gives a red-orange solution from which three products may be isolated by evaporating the mixture to dryness and extracting with diethyl ether. The insoluble residue contains two salts, the nature of which will be discussed below, but yellow needles of $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$ (1) are isolated from the extract by removal of the solvent, chromatography on alumina, and crystallisation from n-hexane.

Complex (1) was partially characterised by elemental analysis, i.r. spectroscopy, and the mass spectrum (Table 1) which showed a weak parent ion and the sequential loss of three carbonyl ligands. The ^1H and ^{13}C n.m.r. spectra (Table 2) showed the expected number of resonances for the $C_{15}H_{14}$ ligand, but a full assignment, particularly of unexpected peaks indicating the presence of a phenyl group, was only achieved after the structure had been fully elucidated by *X*-ray crystallography.

The results of the diffraction study are summarised in Table 3, and the molecular configuration (with the crystallographic numbering) is illustrated in the Figure. The complex is identified as tricarbonyl(1—4-η-7-styrylcyclohepta-1,3,5-triene)iron. As might be expected, the atoms of the styryl group are all coplanar, so that the atom sequence C(7)—C(15) shows a root mean square deviation (r.m.s.d.) of only 0.04 Å. The C_7 ring likewise comprises two coplanar sections (r.m.s.d. 0.01 Å), the first consisting of the four atoms which are bonded to the iron atom [C(1)—C(4)], the second of the atom sequence C(4)—C(7) and C(1). This latter plane makes a dihedral angle of 97° with the plane of the styryl moiety (so that the two ring systems are approximately mutually perpendicular), while the interplanar angle in the C_7 ring is 138°. The $Fe(CO)_3$ fragment is bonded *exo* to the C_7 ring and its styryl substituent, and the Fe–C_7 bond distances show some interesting variations. The two ' outer ' bonds, Fe–C(1) and Fe–C(4), are significantly longer [2.111(4) and 2.140(5) Å] than the two ' inner ' bonds, Fe–C(2) and Fe–C(3), which are 2.067(4) and 2.047(5) Å. The corresponding C–C distances are also suggestive of a long-short-long pattern [C(1)–C(2), 1.418(6); C(2)–C(3), 1.394(6); C(3)–C(4), 1.421(8) Å]. Examples of η^4-co-ordination of the $Fe(CO)_3$ fragment to a single, substituted, C_7 ring system occur in tricarbonyliron complexes of 7-phenylcyclohepta-1,3,5-triene,[9] cycloheptatrienone,[10] and 2,4,6-triphenylcycloheptatrienone,[11] and also in $[Fe_2(CO)_6\{\eta^4{:}\eta'^4\text{-}C_7H_7CH{=}CHC_7H_7(PPh_3)_2\}]^{2+}$.[12] In all these complexes, the four atoms which are η^4 bonded to the Fe atom form a coplanar group (A—D), and the four atoms which enclose the uncomplexed double bond (D—G) are closely coplanar, with the atom A deviating only very slightly from this plane. The interplanar angles between mean planes ABCD and DEFGA for the aforementioned group of compounds are 139, 141, 139, and 140°, respectively, as compared with 138° in the title



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* *Supplementary data available* (No. SUP 23844, 18 pp.): All atom co-ordinates, complete bond lengths and angles, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Infrared spectral and analytical data

Complex	Colour	Yield (%)	M.p. (°C)	M	$\tilde{\nu}$(CO)/cm^{-1}	Analysis [a] (%) C	H	N
(1) $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$	Yellow	41	64—66	306	2 047, 1 989, 1 977	65.0 (64.7)	4.5 (4.2)	—
(6) $[Fe(CO)_3\{\eta^4\text{-}C_7H_6(Me)CH{=}CHPh\}]$	Yellow	5	60—64	318 [b]	2 048, 1 986, 1 974 [c]	65.5 (65.5)	4.6 (4.6)	—
(7) $[Fe(CO)_3(\eta^5\text{-}C_7H_8CH{=}CHPh)][BF_4]$	Pale yellow	67	—	—	2 105, 2 065, 2 053 [d]	50.5 (51.2)	3.8 (3.6)	—
(8) $[Fe(CO)_3(\sigma{:}\eta^3\text{-}C_{21}H_{14}N_4)]$	White	33	158—160 (decomp.)	434 [b]	2 070, 2 009 [d]	62.4 (62.3)	3.1 (3.0)	12.0 (12.1)

[a] Calculated values in parentheses. [b] The highest peak in the mass spectrum corresponds to the parent ion less one carbonyl ligand. [c] In n-hexane. [d] In CH_2Cl_2.

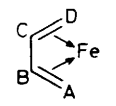
Table 2. Proton and ^{13}C n.m.r. spectral data [a]

Complex	^1H (δ)	^{13}C (p.p.m.)
(1) $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$	3.05 [1 H, dddd, $J(H^4H^2)$ 1, $J(H^4H^3)$ 6, $J(H^4H^5)$ 8, $J(H^4H^6)$ 1, H^4], 3.25 [2 H, m, $J(H^6H^7)$ 4, $J(H^7H^8)$ 9, H^1, H^7], 5.13 [1 H, ddd, $J(H^4H^6)$ 1, $J(H^5H^6)$ 10, $J(H^6H^7)$ 4, H^6], 5.36 [2 H, m, $J(H^2H^4)$ 1, $J(H^3H^4)$ 6, $J(H^3H^5)$ 1, H^2, H^3], 5.85 [1 H, dd, $J(H^7H^8)$ 9, $J(H^8H^9)$ 16, H^8], 5.86 [1 H, ddd, $J(H^3H^5)$ 1, $J(H^4H^5)$ 8, $J(H^5H^6)$ 10, H^5], 6.43 [1 H, d, $J(H^8H^9)$ 16, H^9], 7.30 (5 H, m, C_6H_5) [c]	46.72 (C^7), 55.39, 64.55 (C^1, C^4), 87.25, 94.95 (C^2, C^3), 126.14, 127.29, 127.77, 128.50, 128.81, 130.20, 133.84, 137.30, (C^5, C^6, C^4, C^9, C_6H_5), 210.78 (CO) [b]
(6) $[Fe(CO)_3\{\eta^4\text{-}C_7H_6(Me)CH{=}CHPh\}]$	1.49 [3 H, dd, $J(H^5Me)$ 1.4, $J(H^7Me)$ 0.8, Me], 3.02 [2 H, m, $J(H^1H^7)$ 5, $J(H^4H^5)$ 8, $J(H^7H^8)$, 9, H^4, H^7], 3.22 [1 H, m, $J(H^1H^7)$ 5, H^1], 5.32 (2 H, m, H^2, H^3), 5.72 (2 H, m, H^5, H^8), 6.45 [1 H, d, $J(H^8H^9)$ 15, H^9], 7.30 (5 H, m, C_6H_5) [c]	22.74 (Me), 50.56 (C^7), 56.80, 65.25 (C^1, C^4), 86.24, 94.10 (C^2, C^3), 124.64, 126.14, 127.24, 127.76, 128.54, 131.34, 134.71, 134.91, 137.24 (C^5, C^6, C^8, C^9, C_6H_5), 210.92 (CO) [d]
(7) $[Fe(CO)_3(\eta^5\text{-}C_7H_8CH{=}CHPh)][BF_4]$	1.30 [1 H, m, H^6 (*exo*)], 2.60 [1 H, m, H^6 (*endo*)], 4.20 (1 H, m, H^7), 4.90 (2 H, m, H^1, H^5), 5.90 (3 H, m, H^2, H^4, H^8), 6.30 [1 H, t, $J(H^2H^3)$ 8, $J(H^3H^4)$ 8, H^3], 6.60 [1 H, d, $J(H^8H^9)$ 16, H^9], 7.30 (5 H, m, C_6H_5) [b,e]	
(8) $[Fe(CO)_3(\sigma{:}\eta^3\text{-}C_{21}H_{14}N_4)]$	1.97 (1 H, m, H^5), 4.04 (1 H, dd, H^6), 4.29 (1 H, m, H^7), 4.64 [1 H, dd, $J(H^3H^4)$ 7, $J(H^4H^5)$ 9, H^4], 4.89 [1 H, dd, $J(H^1H^2)$ 9, $J(H^1H^7)$ 4, H^1], 5.08 [1 H, dd, $J(H^2H^3)$ 7, $J(H^3H^4)$ 7, H^3], 5.25 [1 H, dd, $J(H^1H^2)$ 9, $J(H^2H^3)$ 7, H^2], 6.47 [1 H, dd, $J(H^7H^8)$ 8, $J(H^8H^9)$ 16, H^8], 6.87 [1 H, d, $J(H^8H^9)$ 16, H^9], 7.37 (5 H, m, C_6H_5) [c,f]	

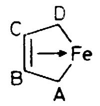
[a] In $CDCl_3$ unless stated otherwise. Numbering as in Scheme 3. J values in Hz. Chemical shifts downfield from $SiMe_4$. [b] 100-MHz spectrum. [c] 200-MHz spectrum. [d] 90-MHz spectrum. [e] In CD_3NO_2. [f] In [$^2H_6$]acetone.

compound. The precise mode of bonding between the metal and the diene moiety can be related to Hückel molecular orbital calculations [13] which suggest that the expected carbon–carbon bond lengths for the free ligand in the ground state would be A · · · B = C · · · D = 1.36; B · · · C = 1.46 Å; while for the first excited state these lengths would be A · · · B = C · · · D = 1.45; B · · · C = 1.39 Å. In the case of all the compounds mentioned above, the bonding of the iron atom to the diene unit is intermediate between the two extremes but much closer to the second. In all cases bond BC is shorter than AB or CD but longer than EF. It is therefore reasonable to regard the co-ordination state of the iron atom as approximately octahedral. The OC–Fe–CO angles are in fact slightly larger than 90° (Table 3), giving slight distortion from local C_{3v} symmetry towards a square pyramidal environment for the Fe atom, but the Fe–C–O bonds are nearly linear.*

The identification of (1) as a complex of the styrylcyclo-



Ground state



First excited state

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* A referee has pointed out that an alternative, and perhaps preferable, molecular orbital description of the bonding, can be found, for example, in J. A. Connor, L. M. R. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1974, **28**, 1193; or in M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

Table 3. Selected bond lengths (Å) and angles (°) for [Fe(CO)$_3$(η^4-C$_7$H$_7$CH=CHPh)] (1)

Fe–C(1)	2.111(4)	Fe–C(2)	2.067(4)
Fe–C(3)	2.047(5)	Fe–C(4)	2.140(5)
Fe–C(16)	1.785(4)	C(16)–O(16)	1.137(4)
Fe–C(17)	1.793(4)	C(17)–O(17)	1.135(6)
Fe–C(18)	1.802(4)	C(18)–O(18)	1.139(6)
C(1)–C(2)	1.418(6)	C(2)–C(3)	1.394(6)
C(3)–C(4)	1.421(8)	C(4)–C(5)	1.474(7)
C(5)–C(6)	1.307(6)	C(6)–C(7)	1.496(6)
C(7)–C(1)	1.531(5)	C(7)–C(8)	1.511(5)
C(8)–C(9)	1.318(6)	C(9)–C(10)	1.471(6)
C(10)–C(11)	1.394(6)	C(11)–C(12)	1.382(6)
C(12)–C(13)	1.362(8)	C(13)–C(14)	1.362(8)
C(14)–C(15)	1.385(6)	C(15)–C(10)	1.376(6)
Fe–C(16)–O(16)	176.8(2)	Fe–C(17)–O(17)	178.8(4)
Fe–C(18)–O(18)	177.5(5)	C(16)–Fe–C(17)	98.8(2)
C(17)–Fe–C(18)	91.7(2)	C(16)–Fe–C(18)	100.6(2)
C(17)–Fe–C(4)	164.5(2)	C(18)–Fe–C(1)	166.7(2)
C(16)–Fe–C(2)	129.2(1)	C(16)–Fe–C(3)	132.5(2)
C(1)–C(2)–C(3)	119.4(4)	C(2)–C(3)–C(4)	120.6(4)
C(3)–C(4)–C(5)	125.4(4)	C(4)–C(5)–C(6)	128.4(5)
C(5)–C(6)–C(7)	126.8(4)	C(6)–C(7)–C(1)	116.4(3)
C(6)–C(7)–C(8)	111.1(3)	C(1)–C(7)–C(8)	109.5(3)
C(7)–C(8)–C(9)	124.8(4)	C(8)–C(9)–C(10)	128.2(4)

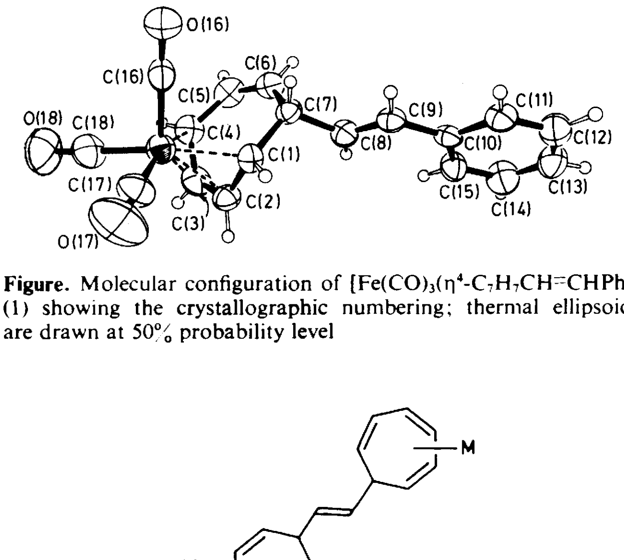
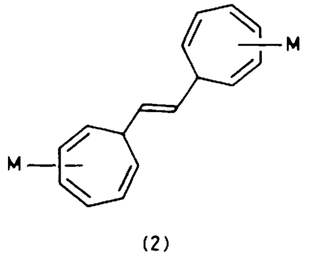


Figure. Molecular configuration of [Fe(CO)$_3$(η^4-C$_7$H$_7$CH=CHPh)] (1) showing the crystallographic numbering; thermal ellipsoids are drawn at 50% probability level

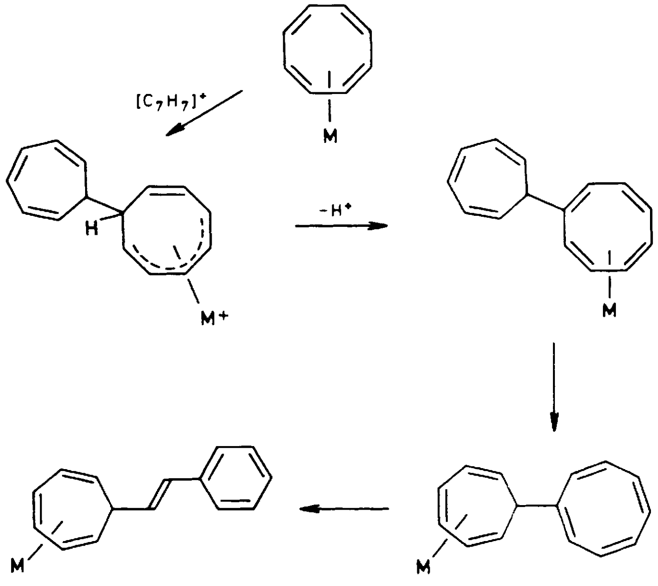


(2)

heptatriene ligand enabled the ^{1}H and ^{13}C n.m.r. spectra to be assigned fully (Table 2). While these assignments will not be discussed in detail it is notable that J(H^{8}H^9) = 16 Hz is in accord with the *trans* geometry of the exocyclic double bond, and also that the ^{13}C n.m.r. spectra of (1) and of [Fe$_2$(CO)$_6$(η^4:η'^4-C$_{16}$H$_{16}$)] (2) [12] bear striking similarities.

Schemes 1 and 2 show two possible mechanisms for the formation of (1). The first step in the reaction, common to both proposals, has ample precedent, with electrophilic addition of H$^+$ [14] or [CPh$_3$]$^+$ [15] to [Fe(CO)$_3$(η^4-cot)] giving derivatives of tricarbonyl(η^5-cyclo-octa-2,4,6-trien-1-yl)iron, and with tropylium ions adding to the co-ordinated ring of ferrocene [6] or tricarbonyl(η^4-cycloheptatriene)iron.[7]

The subsequent steps in the two mechanisms are, however,

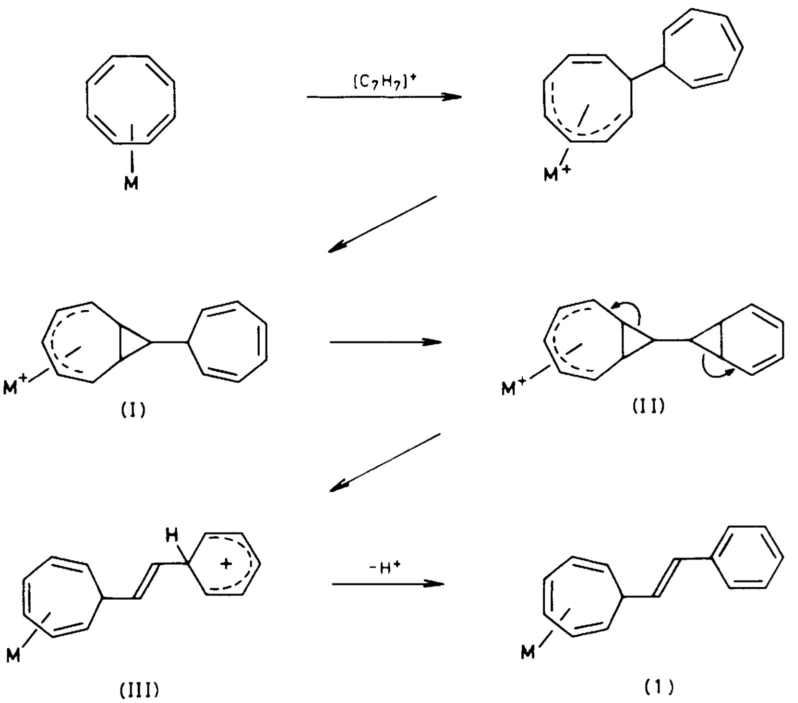


Scheme 1. M = Fe(CO)$_3$

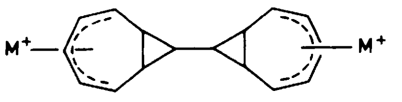
very different. Scheme 1 involves deprotonation, metal migration from the eight- to the seven-membered ring, and isomerisation of the cyclo-octatetraenyl group to the styryl moiety; the last reaction is reminiscent of the conversion of cot to styrene under u.v. light.[16] In Scheme 2, electrocyclic ring closure, observed [14] during the room temperature protonation of [Fe(CO)$_3$(η^4-cot)], gives a bicyclo[5.1.0]octadienyl complex (I) which undergoes further isomerisation to the norcaradiene derivative (II); electron-withdrawing substituents, R, on the CHR group of substituted cycloheptatrienes C$_7$H$_7$R are known [17] to stabilise the norcaradiene valence tautomer. Having generated the two cyclopropane groups in (II), a ring-opening reaction occurs which is entirely similar to that observed when PPh$_3$ is added to [Fe$_2$(CO)$_6$(η^5:η'^5-C$_{16}$H$_{16}$)]$^{2+}$ (3),[12] and when either [Fe$_2$(CO)$_6$(η^4:η'^4-C$_{16}$H$_{16}$)] (4) or [Fe$_2$(CO)$_6$(η^4:η'^4-C$_{16}$H$_{18}$)] (5) is oxidised [18] by ferrocenium ions. Complex (1) then results from the spontaneous deprotonation of (III).

Clearly, it is impossible to prove unequivocally every step in either mechanism. However, the fundamental difference between the two, namely that the first (Scheme 1) requires metal migration whereas the second (Scheme 2) does not, has enabled us to reject the former. The reaction of [Fe(CO)$_3$(η^4-C$_8$H$_7$Me)] with [C$_7$H$_7$][BF$_4$] proceeds similarly to that of [Fe(CO)$_3$(η^4-cot)], giving a low yield of [Fe(CO)$_3${η^4-C$_7$H$_6$(Me)CH=CHPh}] (6). The ^{1}H and ^{13}C n.m.r. spectra of (1) and (6) (Table 2) are very similar, indicating the same C$_{15}$ skeleton, but the proton spectrum of (6) clearly shows the methyl substituent at C^6; the methyl group is coupled to both H^5 and H^7, and the resonance due to H^6 is absent. Thus, the mechanism of formation of (1) involves the contraction of both the eight- and seven-membered rings rather than intramolecular metal migration.

As noted above, the reaction between [Fe(CO)$_3$(η^4-cot)] and [C$_7$H$_7$][BF$_4$] gives not only (1) but also two salts insoluble in diethyl ether. Although these salts are inseparable they are readily characterised by ^{1}H n.m.r. spectroscopy as [Fe(CO)$_3$(η^5-C$_8$H$_9$)][BF$_4$] and [Fe(CO)$_3$(η^5-C$_7$H$_8$CH=CHPh)][BF$_4$] (7). The former is the product of the room-temperature protonation of [Fe(CO)$_3$(η^3-cot)],[14] and the latter may be synthesised independently by reacting (1) with HBF$_4$. Com-



Scheme 2. M = Fe(CO)$_3$



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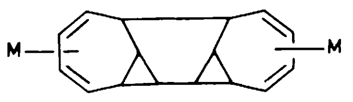

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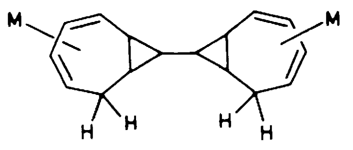


(5)

plex (7) is unambiguously characterised as a cycloheptadienyl derivative by the data given in Tables 1 and 2. The ^{1}H n.m.r. spectrum is similar to that of $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$, the protonated form of tricarbonyl(η^4-cycloheptatriene)iron, and the coupling constant $J(H^8H^9)$ = 16 Hz shows that the *trans* exocyclic double bond is retained.

The formation of (1), (7), and $[Fe(CO)_3(\eta^5\text{-}C_8H_9)]^+$ in the reaction between $[Fe(CO)_3(\eta^4\text{-cot})]$ and $[C_7H_7]^+$ is simply rationalised in terms of equations (i)—(iii); protons evolved in the formation of (1) will act as electrophiles towards both $[Fe(CO)_3(\eta^4\text{-cot})]$ and (1). Clearly, reactions (ii) and (iii) lead to a reduction in the yield of (1). Accordingly, the reaction between $[Fe(CO)_3(\eta^4\text{-cot})]$ and $[C_7H_7]^+$ was carried out in the presence of pyridine as a base, and the yield of (1) was increased from 24 to 41%.

$$[Fe(CO)_3(\eta^4\text{-cot})] + [C_7H_7]^+ \longrightarrow (1) + H^+ \tag{i}$$

$$[Fe(CO)_3(\eta^4\text{-cot})] + H^+ \longrightarrow [Fe(CO)_3(\eta^5\text{-}C_8H_9)]^+ \tag{ii}$$

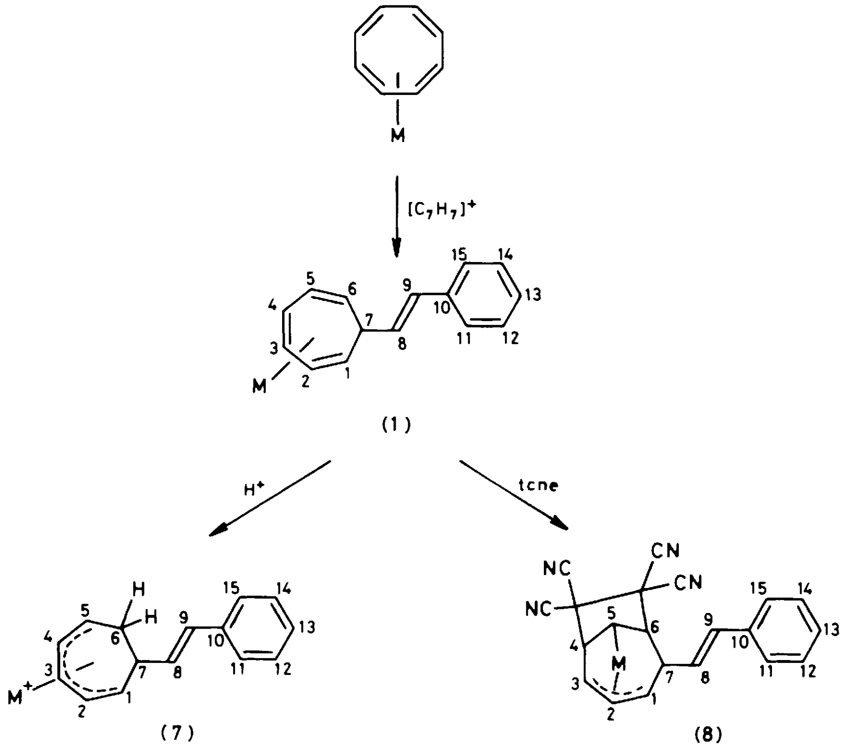
$$(1) + H^+ \longrightarrow (7) \tag{iii}$$

One further reaction of (1) was investigated, namely that with tetracyanoethylene (tcne). Despite the presence of the exocyclic alkene bond, (1) behaves as a simple cycloheptatriene derivative, undergoing 1,3-cycloaddition to give $[Fe(CO)_3(\sigma{:}\eta^3\text{-}C_{21}H_{14}N_4)]$ (8). The structure shown in Scheme 3, deduced from the proton-decoupled ^{1}H n.m.r. spectrum, is similar to that of the tcne adduct of tricarbonyl(η^4-cycloheptatriene)iron;[7] once again, the coupling between H^8 and H^9 (J = 16 Hz) reveals the retention of the *trans* olefinic bond.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless stated otherwise the complexes are air-stable solids which dissolve in polar solvents such as CH_2Cl_2 or acetone; the solutions slowly decompose in air. The compounds $[Fe(CO)_3(\eta^4\text{-}C_8H_7R)]$ (R = H [19] or Me [14]) and $[C_7H_7][BF_4]$,[20] were prepared by published methods, and tetracyanoethylene was purchased from the Aldrich Chemical Company Ltd. Infrared spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on JEOL FX 200 or PS 100 spectrometers, and ^{13}C n.m.r. spectra on JEOL FX 90Q or PFT 100 instruments; both were calibrated against $SiMe_4$ as internal reference. Mass spectra were recorded on an 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.



Scheme 3. M = $Fe(CO)_3$

Table 4. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for $[Fe(CO)_3(\eta^4$-$C_7H_7CH=CHPh)]$ (1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	0.105 65(2)	0.752 10(12)	0.238 26(3)	C(12)	0.394 5(3)	0.075 6(9)	0.510 0(3)
C(16)	0.068 8(2)	0.626 4(8)	0.292 1(3)	C(13)	0.436 2(2)	0.218 2(10)	0.511 9(3)
O(16)	0.047 60(14)	0.544 4(6)	0.328 4(2)	C(14)	0.424 9(2)	0.415 0(9)	0.483 0(3)
C(17)	0.097 8(2)	0.546 0(8)	0.176 7(3)	C(15)	0.372 2(2)	0.471 9(8)	0.451 5(3)
O(17)	0.093 6(2)	0.413 9(6)	0.138 4(2)	H(1)	0.190 4(14)	0.474(6)	0.275 1(15)
C(18)	0.052 2(2)	0.912 8(8)	0.188 7(3)	H(2)	0.206 3(13)	0.751(7)	0.213(2)
O(18)	0.017 29(15)	1.013 0(7)	0.159 0(2)	H(3)	0.163 4(15)	1.093(7)	0.221(2)
C(1)	0.180 2(2)	0.620 1(8)	0.290 7(2)	H(4)	0.107(2)	1.149(7)	0.290(2)
C(2)	0.189 2(2)	0.789 4(7)	0.248 7(2)	H(5)	0.139 0(14)	1.088(6)	0.393 7(15)
C(3)	0.164 1(3)	0.988 8(8)	0.252 0(3)	H(6)	0.187(2)	0.810(7)	0.444(2)
C(4)	0.132 0(3)	1.026 6(8)	0.299 0(3)	H(7)	0.172 2(12)	0.498(5)	0.378 3(14)
C(5)	0.149 1(2)	0.980 3(7)	0.369 7(3)	H(8)	0.276 0(13)	0.677(5)	0.387 4(14)
C(6)	0.176 0(2)	0.813 2(8)	0.398 3(3)	H(9)	0.247(2)	0.287(7)	0.427(2)
C(7)	0.193 0(2)	0.618 1(7)	0.365 7(2)	H(11)	0.312 5(14)	0.031(6)	0.478(2)
C(8)	0.253 0(2)	0.568 7(7)	0.391 4(2)	H(12)	0.400(2)	−0.063(7)	0.529(2)
C(9)	0.272 2(2)	0.386 8(8)	0.420 1(2)	H(13)	0.470(2)	0.178(8)	0.535(3)
C(10)	0.329 5(2)	0.330 7(7)	0.449 6(2)	H(14)	0.449(2)	0.505(7)	0.482(2)
C(11)	0.341 5(2)	0.129 6(8)	0.479 2(2)	H(15)	0.364 2(14)	0.605(6)	0.434(2)

Tricarbonyl(1—4-η-7-*styrylcyclohepta*-1,3,5-*triene*)*iron*, $[Fe(CO)_3(\eta^4$-$C_7H_7CH=CHPh)]$ (1).—A solution of $[C_7H_7][BF_4]$ (1.4 g, 7.9 mmol) in acetone (200 cm^3) was added to a stirred, cooled (−23 °C) mixture of $[Fe(CO)_3(\eta^4$-cot)] (2.0 g, 8.2 mmol) and pyridine (0.3 cm^3) in acetone (15 cm^3). After 7 h the resulting orange solution was evaporated to dryness and the residue extracted with diethyl ether (100 cm^3). Evaporation of the extract to *ca.* 10 cm^3 and chromatography on an alumina–n-hexane column gave a yellow band which was eluted with n-hexane–diethyl ether (10 : 1) as a bright yellow solution. On evaporation of the eluate to low volume, and cooling to −78 °C, the *product* was obtained as yellow needles, yield 1.11 g (41%). The complex $[Fe(CO)_3\{\eta^4$-$C_7H_6(Me)CH=CHPh\}]$ (6) was prepared similarly.

Complexes (1) and (6) are soluble in all common organic solvents.

Tricarbonyl(1—5-η-7-*styrylcyclohepta*-2,4-*dien*-1-*yl*)*iron Tetrafluoroborate*, $[Fe(CO)_3(\eta^5$-$C_7H_8CH=CHPh)][BF_4]$ (7).—An excess (*ca.* 0.3 cm^3) of an aqueous solution of HBF_4 (40% w/w) was added to a stirred solution of $[Fe(CO)_3(\eta^4$-$C_7H_7CH=CHPh)]$ (1) (0.19 g, 0.57 mmol) in diethyl ether (15 cm^3). After 15 min the yellow solution was evaporated to dryness, and the residue recrystallised from acetone–n-hexane to give *the product* as a pale yellow solid, yield 0.16 g (67%).

The complex is soluble in acetone but only slightly so in CH_2Cl_2.

1,3-*Cycloaddition Reaction of* (1) *with Tetracyanoethylene*; *Synthesis of* $[Fe(CO)_3(\sigma{:}\eta^3\text{-}C_{21}H_{14}N_4)]$ (8).—Tetracyanoethylene (0.09 g, 0.70 mmol) was added to $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$ (1) (0.24 g, 0.72 mmol) in CH_2Cl_2 (25 cm^3). After stirring for 5 h the yellow solution was filtered, and n-hexane added to precipitate a white solid which was recrystallised from CH_2Cl_2–n-hexane, yield 0.11 g (33%).

Crystal Structure Determination of $[Fe(CO)_3(\eta^4\text{-}C_7H_7CH{=}CHPh)]$ (1).—Crystals of (1) grow as thin needles elongated along *b*, from heptane at −20 °C. Intensities were measured at 293 K in the range $2.9 \leqslant 2\theta \leqslant 55°$ from a crystal fragment of dimensions 0.35 × 0.15 × 0.15 mm cut from a larger crystal. Two check reflections ($\bar{1}\ 3\ \bar{3}$ and $1\ \bar{3}\ 3$) were remeasured every 50 reflections and showed no significant variation during the 106 h of exposure to *X*-rays. Of the total 3 524 independent intensities, only 1 977 satisfied the criterion $I > 1.5\sigma(I)$; these were used in the solution and refinement of the structure. The data were corrected for Lorentz and polarisation effects but not for *X*-ray absorption [$\mu(\text{Mo-}K_\alpha) = 9.3\ cm^{-1}$].

Crystal data. $C_{18}H_{14}FeO_3$, $M = 333.8$, monoclinic, $a = 25.035(8)$, $b = 6.195(2)$, $c = 20.938(12)$ Å, $\beta = 102.69(4)°$, $U = 3\ 168(3)$ Å^3, D_m not measured, $Z = 8$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\ 376$, space group $C2/c$ (no. 15), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, $\mu(\text{Mo-}K_\alpha) = 9.3\ cm^{-1}$.

The structure was solved by conventional heavy-atom methods and refined by blocked-cascade least squares. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically (and all were located by electron density difference methods). Weights were ascribed according to the scheme $w = [\sigma^2(F_0) + 0.0001|F_0|^2]^{-1}$, and refinement converged at *R* 0.063, *R′* 0.046. Scattering factors were from ref. 21, and the computational work was carried out within the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[22] The final atom co-ordinates are listed in Table 4.

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