Reaction of Tricarbonyliron Complexes of Some Cycloheptatrienes with Tetracyanoethylene, Sulphur Dioxide, and Protons

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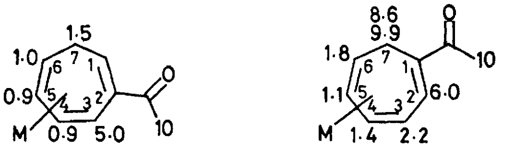
Tricarbonyl(3—6-η-cycloheptatriene)iron, (1), forms a reversible 1 : 1 adduct with sulphur dioxide. The adduct and other tricarbonyliron complexes with the σ, η^3 mode of bonding exhibit small Mössbauer quadrupole splittings. Tetracyanoethylene undergoes 1,3-addition to the unco-ordinated side of the ring of both the 1- and 2-acetyl derivatives of (1), whereas the proton adds to the co-ordinated double bond of the 2-acetyl derivative.

DESPITE the well established electrophilic chemistry of tricarbonyl(cycloheptatriene)iron (1),[1,2] it is still not clear whether electrophilic attack takes place at the co-ordinated or unco-ordinated side of the arene ring. In an effort to gain information on this point the site of addition of a proton and tetracyanoethylene (tcne) to some ring-substituted derivatives has been examined. An unexpected sulphur dioxide complex discovered in the course of this work, which exhibits unusual Mössbauer parameters, is also described.

RESULTS AND DISCUSSION

Preparation of the Complexes.—$[Fe(C_7H_8)(CO)_3]\cdot SO_2$ (2). Dissolution of $[Fe(C_7H_8)(CO)_3]$ (1) in SO_2 gave yellow needles of the adduct (2). Complex (1) is regenerated when (2) is dissolved in organic solvents.

(3—6-η-2-Acetylcycloheptatriene)tricarbonyliron (3). The 1-acetyl derivative of (1), *i.e.* (4),[1] was isomerized by Na[OMe]–MeOH to the 2-acetyl derivative (3). The structure of (3) follows from the ^1H n.m.r. spectrum and from a comparison of the n.m.r. shifts induced by $[Eu(fod)_3]$ in (3) and (4) (Scheme 1; fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate).



(3) (4)

SCHEME 1 $[Eu(fod)_3]$-induced relative ^1H n.m.r. shifts. $M = Fe(CO)_3$

2- and 5-substituted cycloheptatriene complexes. Reaction of the cycloheptadienone complex (5) with MgRX and dehydration of the alcohols produced on silica gel gave mixtures of cycloheptatriene complexes (Scheme 2). Dehydration of (6) could proceed *via* both 1,2 and 1,6 mechanisms to yield (7)—(10). The structure of the phenyl derivative was deduced with the aid of its ^1H n.m.r. spectrum. Integration of the spectrum and comparison with that of (1) revealed that substitution had removed one of the low-field resonances. This eliminates structure (10). A characteristic ten-line multiplet assigned to H^1 in the spectrum of (1) was superimposable on a multiplet at τ 4.2, which integrated for ½H. There are therefore at least two isomers present, in one of which the phenyl group is remote from H^1. This isomer can only be (8a). The other resonances due to (8a) were located by double-irradiation studies. The remaining resonances appeared to be due to one structure but it was not possible to use the spectrum to decide between (7) and (9). However, as will be shown later, the resonances are due to (7a). Dehydration of (6b) gave a product with a similar n.m.r. spectrum but the ratio of (7b) to (8b) was 1.6 : 1.

Structure of Complex (2).—Solutions of (1) in liquid SO_2 exhibit n.m.r. spectra which are very different from those observed in normal solvents (CS_2, $CDCl_3$, *etc.*). On evaporation of these solutions pale yellow crystals are formed. Analytical data indicated the formula $[Fe(C_7H_8)(CO)_3]\cdot SO_2$. While it was not possible to observe a parent ion in the mass spectrum, abundant fragment ions due to $Fe(C_7H_8)(CO)_3$ and SO_2 occurred. Strong i.r. absorptions at 1 190 and 1 050 cm^{-1}, and the absence of any other strong bands in this region, suggest that the SO_2 group is present as an S-bonded sulphinate (*i.e.* MSO_2R not MOSOR).[3,4] The ν(MC–O) stretching bands of (2) are *ca.* 50 cm^{-1} higher than those of (1) indicating a withdrawal of electron density from iron. The ^1H n.m.r. spectrum can be assigned in terms of structure (2). In particular, the resonances at τ 3.67 (1 H) and τ 3.97 (1 H), assigned to unco-ordinated olefinic protons, were not coupled to the methylene protons (τ 8.4). The order of the remaining ^1H n.m.r. absorptions of the ring was deduced with the aid of spin-decoupling experiments. Carbon-13 n.m.r. spectra of (1) in $CDCl_3$ and liquid SO_2 (Figure) clearly demonstrate the presence of an unco-ordinated double bond in (2).

TABLE 1

Mössbauer data (mm s^{-1}) [a]

Complex	δ [b]	Δ [c]
(2)	0.14	0.67
(11)	0.11	0.83
(12)	0.10	0.62
(13)	0.12	1.36
(14)	0.12	1.97
(15)	0.25	1.59
(17)	0.13	1.44

[a] Source at room temperature, sample at −196 °C. Parameters ±0.05 mm s^{-1}. [b] Chemical shift relative to stainless steel. [c] Quadrupole splitting.

In an effort to obtain further confirmation of structure

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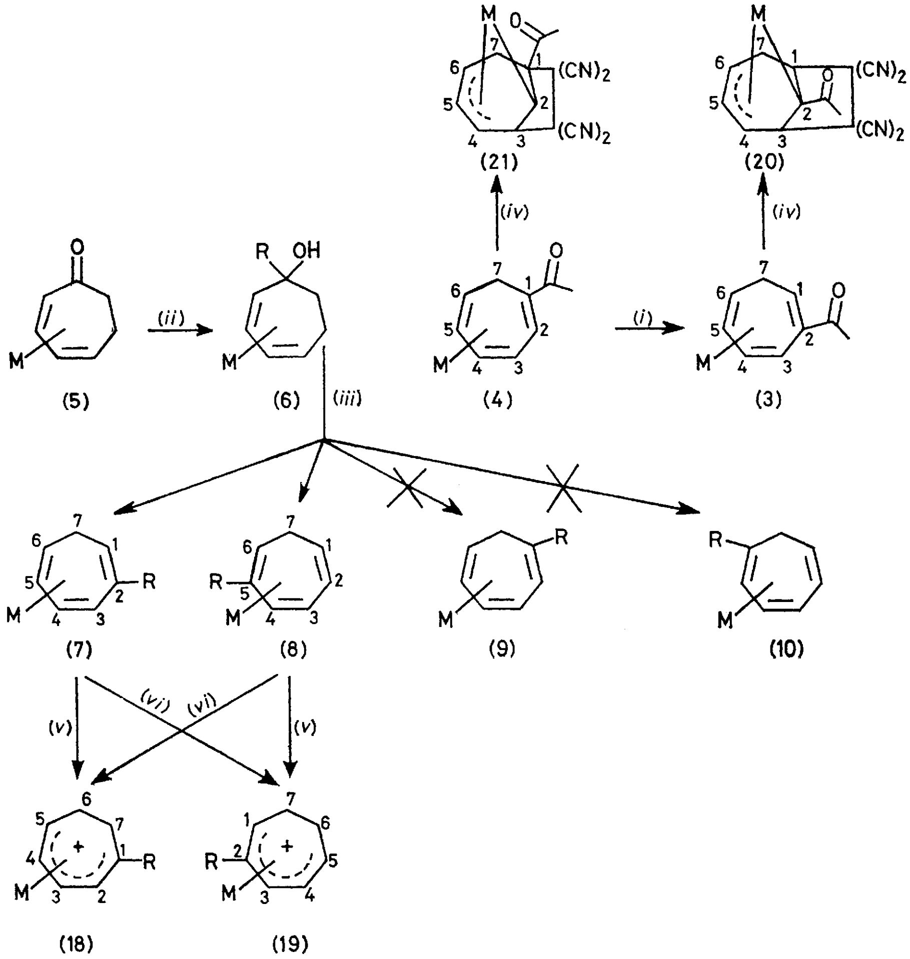
[1] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J.C.S. Dalton*, 1972, 456.

[2] M. Green, S. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

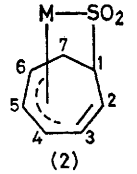
[3] A. Wojcicki and J. P. Bibler, *J. Amer. Chem. Soc.*, 1966, **88**, 4862.

[4] A. Wojcicki and J. E. Thomasson, *J. Amer. Chem. Soc.*, 1968, **90**, 2709.

(2) the ^{57}Fe Mössbauer spectrum was recorded. This, together with spectra of other complexes [(11)–(15)], some of which have the σ,η^3 mode of bonding proposed for (2), is given in Table 1. Published Mössbauer spectra of normal (*i.e.* conjugated) diene- and dienium-tricarbonyliron complexes all contain large quadrupole splittings which are not markedly dependent on the nature of the olefin.[5-7] In contrast, the results for σ,η^3 systems display much smaller splittings. More extensive data will be required before it is clear whether this is general for the latter mode of bonding. However, the present data support structure (2).



SCHEME 2 M = Fe(CO)$_3$, R = Ph (a) or C_6H_4Me-*p* (b). (*i*) Na[OMe]–MeOH; (*ii*) MgRX; (*iii*) silica gel, toluene; (*iv*) tcne; (*v*) protonation of an unco-ordinated double bond; (*vi*) protonation of a co-ordinated double bond



(2)

Other tricarbonyliron complexes, including (11) and (12) (see Experimental section), were tested for the reaction with SO$_2$, but all except one exhibited normal ^{1}H n.m.r. spectra. The ^{1}H n.m.r. spectrum of (12) is not well resolved in the alkyl region.[8] Its ^{13}C n.m.r. spectrum was obtained in SO$_2$ solution, but it did not show the significant chemical-shift changes expected for an SO$_2$-insertion product. The exception was the mixture of (7b) and (8b). The resonances due to (8b) were unchanged in SO$_2$, but those expected for (7b) were replaced by a set easily assigned to a 2-substituted derivative of (2). The (7b) : (8b) ratio of 1.6 : 1 was also preserved. This rules out a fluxional nature for the (7b)–(8b) system.[9]

Reversible SO$_2$ insertion is quite rare.[10] Perhaps

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[5] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[6] D. V. Banthorpe, H. Fitton, and J. Lewis, *J.C.S. Perkin I*, 1973, 2051.

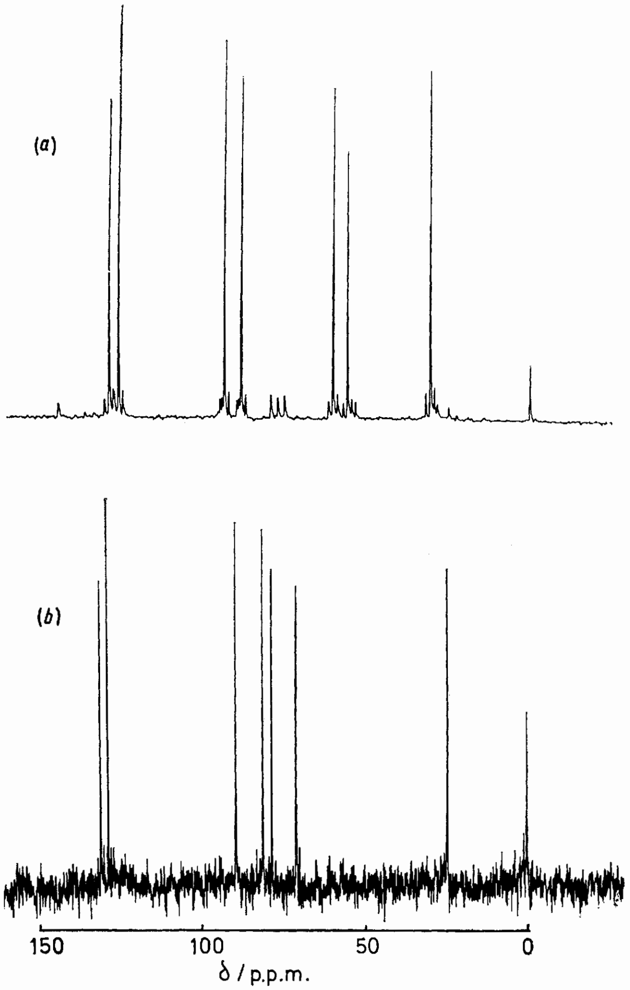
[7] R. L. Collins and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 2332.

[8] A. J. Deeming, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 2093.

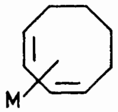
[9] J. Takats and L. K. K. Li Shing Man, *J. Organometallic Chem.*, 1976, **117**, C107.

[10] A. Wojcicki, *Accounts Chem. Res.*, 1971, **4**, 344.

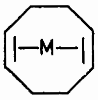
complex (16) reported by Kaesz *et al.*, which also contains an *endo*-SO_2 group, is related to (2).[11] However, unlike (2), (16) requires BF_3 for reaction, it is an *O*-sulphinate, and it is air sensitive. The reaction of unco-ordinated cycloheptatriene with SO_2 has been investigated.[12] Like tcne,[13] SO_2 is thought to react *via* the norcaradiene structure. The product is phenylmethanesulphinic acid.[12] The norcaradiene structure has neither been observed nor proposed for reactions of complex (1) with tcne [14] or SO_2.



Carbon-13 n.m.r. spectrum of complex (1) in $CDCl_3$ (*a*) and SO_2 solutions (*b*)



(13)



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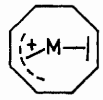
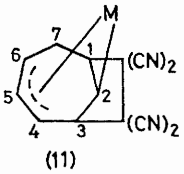
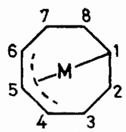


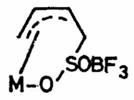
(15)



(11)

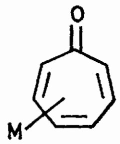


(12)



(16)

The Site of Electrophilic Attack in $[Fe(C_7H_7R)(CO)_3]$ *Complexes.*—Previous studies have established that attack of both proton and tcne on (1) leads to *exo* products probably *via* an *exo* mechanism.[1,2] Whether these reactions involve initial attack at the co-ordinated or unco-ordinated sides of the ring has not been established. In a related system, (17), these two modes of attack have been distinguished using a selectively deuteriated derivative. The proton adds to the co-ordinated double bond [15] and tcne adds to the unco-ordinated double bond.[14] Selective deuteriation of (1) has not been achieved. A difficulty here is that if the symmetrical tricarbonyl(cycloheptadienium)iron cation is an intermediate in an attempt to selectively incorporate ^2H into (1) then selective deuteriation will not be achieved. It was hoped that the availability of a range of derivatives would allow some conclusions to be drawn with respect to (1).



(17)

Protonation Studies.—Hydrogen-1 n.m.r. spectra clearly show that the 2-acyl derivatives of (1) all add protons at the co-ordinated double bond. This is in line with the results reported [15] for (17), and it is suggested that the site of addition observed here is also due to the electron-withdrawing effect of the carbonyl group. (The 1-acetyl complex adds a proton to the unco-ordinated double bond *via* an O-protonation mechanism.[1] A similar mechanism is not possible for the 2-acyl derivatives.)

The mixtures of the 2- and 5-substituted complexes provide a more interesting but more complex case. Protonation of the (7b)–(8b) mixture will give rise to a mixture of (18b) and (19b) (Scheme 2). Since it has been shown above that the (7b)–(8b) system is not fluxional and that the ratio of the components is 1.6 : 1 (not 1 : 1), the result of different protonation mechanisms can be predicted and tested as follows. If (7b) and (8b) both protonate at their unco-ordinated double bonds [(*v*) in Scheme 2] then the ratio of (18b) : (19b) will be the same as that (1.6 : 1) of (7b) : (8b). However, if protonation

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[11] M. R. Churchill, J. Wormald, D. A. T. Young, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 7201.

[12] Y. E. Rhodes, *Diss. Abs.*, 1964, **25**, 845.

[13] G. H. Wahl, *J. Org. Chem.*, 1968, **33**, 2158.

[14] M. Green, S. M. Heathcock, T. W. Turney, and D. M. P. Mingos, *J.C.S. Dalton*, 1977, 204.

[15] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349.

of the co-ordinated double bonds of (7b) and (8b) takes place [(*vi*) in Scheme 2] then the ratio of (18b) : (19b) should be 1 : 1.6 or 0.6 : 1. There are two other possible results, (7b) (*v*) and (8b) (*vi*) and (7b) (*vi*) and (8b) (*v*), which should yield pure samples of (18b) and (19b) respectively. (A completely non-specific or random reaction is considered to be unlikely.)

On treatment with CF_3CO_2H both (7b) and (8b) are protonated. The ^1H n.m.r. spectrum shows the presence of (18b) and (19b) in the ratio 1.6 : 1. Thus (7b) and (8b) protonate at their unco-ordinated double bonds. Since the presence of the *p*-tolyl group on either the unco-ordinated double bond of (7b) or the co-ordinated double bond of (8b) does not appear to influence the site of addition, it is tentatively suggested that, in the absence of an aromatic substituent as in (1), protonation will also take place at the unco-ordinated double bond.

Addition of tcne to (3) *and* (4).—The effect of acetyl substitution on tcne addition was examined. Complexes (3) and (4) readily undergo addition of tcne. The ^1H n.m.r. spectra of the products (20) and (21), which correlate well with the published spectrum of (11),[2] clearly show that tcne adds to the unco-ordinated side of the arene ring in both cases (Table 2 and Scheme 2).

TABLE 2

Hydrogen-1 n.m.r. data (τ)

Complex	H^1	H^2	H^3	H^4	H^5	H^6	H^7	Me
(2)	6.22	3.97	3.67	5.02	5.02	4.70	7.54, 8.4	
(7b) in SO_2	5.8		3.6	(4.6—5.0)			7.44, 8.2	7.72
(11)	6.1	8.31	5.5	4.84	4.84	5.20	6.82, 7.58	
(20)	5.61		5.04	4.64	4.64	4.79	6.52, 7.25	7.66
(21)		7.9	5.43	4.85	4.85	5.17	7.13	7.49

Since acetyl substitution would be expected to decrease the rate of electrophilic attack and to direct addition to the co-ordinated side of the arene ring, the present results are somewhat surprising. It is interesting that the C=O group in complex (17) also fails to direct tcne to the co-ordinated side of the arene ring.[14] Since the expected directing effect of the acetyl group is not in fact the most important one, these results suggest that (1) will also add tcne at its unco-ordinated double bond.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra (τ units) were recorded on Varian HA-100 or JEOL MH-100 spectrometers. Proton-decoupled ^{13}C n.m.r. spectra (p.p.m. downfield from $SiMe_4$) were obtained on a JEOL FX-60 spectrometer. Mass spectra were recorded on an MS 12, and Mössbauer spectra on a J. and P. Engineering 256-channel constant-acceleration spectrometer.

$[Fe(C_7H_8)(CO)_3]\cdot SO_2$ (2).—Complex (1) was dissolved in liquid SO_2. Evaporation of the solvent gave the product as yellow needles. I.r. (Nujol mull): ν(MC-O) at 2 090 and 2 020 cm^{-1}; ν(SO_2) at 1 190 and 1 050 cm^{-1}. N.m.r. in SO_2–$SiMe_4$: ^1H, τ 3.67(m, 1 H, H^3), 3.97(t, *J* 9, 1 H, H^2), 4.70(m, 1 H, H^6), 5.02(m, 2 H, H^4 and H^5), 6.22(t, *J* 6, ^1H, H^1), 7.54(d of t, *J* 16 and 6, H^7), and 8.4(d, *J* 16 Hz, 1 H, $H^{7'}$); ^{13}C, 206.9 $[Fe(CO)_3]$, 129.5 and 131.8 (C^2 and C^3), 72.0, 79.4, 82.2, and 90.5 (C^1, C^4, C^5, and C^6), and 25.7 p.p.m. (C^7) (Found: C, 40.7; H, 2.9. $C_{10}H_8FeO_5S$ requires C, 40.5; H, 2.7%). Complexes (3), (4), (11), and (12), tricarbonyliron complexes of penta-1,3-diene, cyclohexa-1,3-diene, cyclo-octatetraene, and 7-*p*-tolylmethylenecyclohepta-1,3,5-triene, and cyclopentadienylrhodium(I) complexes of cycloheptatriene and cycloocta-1,3,5-triene gave normal spectra in SO_2 solution Carbon-13 n.m.r. spectra of complex (12): in $CDCl_3$–$SiMe_4$, 216.0 $[Fe(CO)_3]$, 93.8 (C^5), 88.6 (C^4 and C^6), 51.8 (C^1), 51.2 (C^3 and C^7) *, 27.4 (C^2 and C^8) *; in SO_2–$SiMe_4$, 215.6 $[Fe(CO)_3]$, 94.1 (C^5), 89.1 (C^4 and C^6), 51.9 (C^1), 51.3 (C^3 and C^7) *, and 27.3 p.p.m (C^2 and C^8) *.

(3—6-η-2-*Acetylcyclohepta*-1,3,5-*triene*)*tricarbonyliron* (3).—Sodium (1.2 g) was dissolved in absolute methanol (30 cm^3). The 1-acetyl complex, (4), was added with constant stirring. After 0.5 h at 25 °C the reaction mixture was poured into diethyl ether (50 cm^3)–water (100 cm^3) and treated with dilute HCl until the aqueous layer was clear. The organic layer was washed with sodium hydrogencarbonate solution (100 cm^2) and water (3 × 100 cm^3) and dried ($Mg[SO_4]$). Evaporation of the solvent gave a yellow oil which was chromatographed on silica gel using 10% ethyl acetate in toluene as eluant. The orange band which developed was evaporated to give the product as an orange oil (2.4 g, 80%). I.r. in n-heptane solution: ν(MC-O) at 2 058, 1 993, and 1 984; ν(C=O) at 1 674 cm^{-1}. Hydrogen-1 n.m.r. in $CDCl_3$–$SiMe_4$: τ 3.63(m, 1 H, H^1), 4.69(m, 2 H, H^4 and H^5), 6.07(m, 1 H, H^3), 6.77(m, 1 H, H^6), 7.46(m, 2 H, H^7), and 7.78(s, 3 H, Me) (Found: C, 52.8; H, 3.7. $C_{12}H_{10}FeO_4$ requires C, 52.5; H, 3.6%).

Protonation of Complex (3).—Hydrogen-1 n.m.r. spectrum of (3) in CF_3CO_2H–$CDCl_3$–$SiMe_4$, structure (19): τ 2.35(d, *J* 6 Hz, 1 H, H^3), 3.98(m, 1 H, H^4), 4.76(m, 2 H, H^1 and H^5), 7.0—8.3(m, 4 H, H^6 and H^7), and 7.31(s, 3 H, Me). When this solution was poured into OEt_2–HPF_6 the $[PF_6]^-$ salt was obtained (Found: C, 34.5; H, 2.5. $C_{12}H_{11}F_6PO_4P$ requires C, 34.4; H, 2.6%). The low-field resonance at τ 2.35 is a doublet. This confirms structure (19). The 1-formyl and 1-ethoxycarbonyl complexes were isomerized in a similar manner and were protonated at their co-ordinated double bonds.

The Complexes $[Fe(C_7H_7R)(CO)_3]$ (7) *and* (8) (R = Ph *or* C_6H_4Me-*p*).—A diethyl ether solution of the cycloheptadienone complex (5) [16] at −40 °C was treated with a ten-fold excess of the Grignard reagent MgRX and stirred at −40 °C for 0.5 h. Ammonium chloride solution was added to the cold solution with constant stirring until hydrolysis was complete. The organic layer was washed with water (2 × 100 cm^3) and dried ($Mg[SO_4]$). Evaporation of the solvent gave the alcohol (6) which was dehydrated on silica gel–toluene. Chromatography of the products on silica gel–toluene gave the triene mixture (7)–(8) in *ca.* 60% yield. (7a)–(8a): I.r. of liquid film, ν(MC–O) at 2 050 and 1 980 cm^{-1}. Hydrogen-1 n.m.r. in $CDCl_3$–$SiMe_4$: (8a), τ 2.72(m, 5 H, aryl), 4.2(m, 1 H, H^1), 4.5(d of d, 8 and 2 Hz, H^2), 4.82(part of, H^4), 6.35(m, 1 H, H^6), 7.08(t, *J* 8 Hz, H^3), 7.54(part of, H^7). (7a), 2.72(m, 5 H, aryl), 4.82(part of, H^1 and H^4 and H^5), 6.75(m, 2 H, H^3 and H^6), and 7.54 (part of, H^7) (Found: C, 62.8; H, 3.95. $C_{16}H_{12}FeO_3$ requires C, 62.4; H, 3.9%). (7b)–(8b): I.r. of liquid film, ν(MC–O) at 2 050 and 1 980 cm^{-1}. Hydrogen-1 n.m.r.

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* These assignments could be reversed.

[16] A. W. Parkins, Ph.D. Thesis, University of London, 1969.

spectra in $CDCl_3$–$SiMe_4$: (8b), τ 2.80(m, 4 H, aryl), 4.14(m, 1 H, H^1), 4.4(d of d, 8 × 2 Hz, H^2), 4.70(m, part of, H^4), 6.24(m, 1 H, H^6), 7.0(t, *J* 8 Hz, H^3), 7.54(m, part of, H^7), and 7.62(s, 3 H, Me); (7b), 2.80(m, 4 H, aryl), 4.70(m, part of H^1 and H^4 and H^5), 6.66(m, 2 H, H^3 and H^6), 7.45(m, part of, H^7), and 7.68(s, 3 H, Me) (Found: C, 63.2; H, 4.3. $C_{17}H_{14}FeO_3$ requires C, 63.5; H, 4.4%).

Protonation of (7a)–(8a).—Protonation led to (18a) and (19a). In (18a) the lowest-field resonance (excluding aryl H), H^3, is a triplet and H^2 a doublet. These absorptions, together with those of H^4 and H^5, were located by spin decoupling. The lowest-field resonance of (19a) should be a doublet, H^3. However, this was obscured by the aromatic absorption. The resonance H^4 in (19a) was cleanly resolved and decoupled on irradiation of the aromatic peak. Hydrogen-1 n.m.r. spectra of (7a)–(8a) in $CDCl_3$–CF_3CO_2H–$SiMe_4$: (18a), τ 2.5 (m, part of, 5 H, aryl), 3.0(t, *J* 6, 1 H, H^3), 3.5(d, *J* 6 Hz, 1 H, H^2), 4.3(m, 1 H, H^4), 5.3(m, aryl and H^3 part of, H^1 and H^5), and 6.5—8.5(m, part of, H^6 and H^7); (19a), 2.5(m, part of, aryl and H^3), 4.11(m, 1 H, H^4), 5.3(m, part of, H^1 and H^5), and 6.5—8.5(m, part of, H^6 and H^7). The ratio of (18a) : (19a) was 1 : 1. The $[PF_6]^-$ salt was obtained on addition of HPF_6–OEt_2 (Found: C, 42.8; H, 3.1. $C_6H_{13}F_6FeO_3P$ requires C, 42.3, H, 2.9%).

Protonation of (7b)–(8b).—Hydrogen-1 n.m.r. of (7b)–(8b) in $CDCl_3$–CF_3CO_2H–$SiMe_4$: (18b), τ 2.5(m, part of, aryl), 2.9(t, *J* 6, 1 H, H^3), 3.4(d, *J* 6 Hz, 1 H, H^2), 4.2(m, 1 H, H^4), 5.3(m, part of, H^5), 6.5—8.5(m, part of H^6 and H^7), and 7.6(s, 3 H, Me); (19b), 2.5(m, part of, aryl and H^3), 4.0(m, 1 H, H^4), 5.3(m, part of, H^1 and H^5), 6.5—8.5(m, part of, H^6 and H^7), and 7.7(s, 3 H, Me). The ratio of (18b) : (19b) was 1.6 : 1. Hydrogen-1 n.m.r. spectrum of (7b)–(8b) in SO_2–$SiMe_4$: (2b), structure (2) with H^2 = *p*-tolyl, τ 2.8(m, part of, aryl), 3.6(d, *J* 10, H^3), 4.6—5.0(m, part of, H^4 and H^5 and H^6), 5.8(d, *J* 6, H^1), 7.52(m, part of, H^7), 7.72(s, 3 H, Me), and 8.2(d, *J* 16, 1 H, $H^{7'}$); (8b), 2.8(m, part of, aryl), 4.1(m, 1 H, H^1), 4.32(d of d, *J* 8 and 2, 1 H, H^2), 4.6—5.0(m, part of, H^4), 6.2(m, 1 H, H^6), 6.9(t, *J* 7 Hz, 1 H, H^3), 7.52(m, part of, H^7 and $H^{7'}$), and 7.68(s, 3 H, Me). The ratio of (2b) : (8b) was 1.6 : 1.

Reactions of Tetracyanoethylene.—With complex (3). The method used to prepare (20) was similar to that reported for (11).[2] The product was recrystallized from toluene–n-hexane as white crystals. I.r. (Nujol mull): ν(CN) at 2 260; ν(MC–O) at 2 090 and 2 020; ν(C=O) at 1 740 cm^{-1}. Hydrogen-1 n.m.r. spectrum in $(CD_3)_2CO$: τ 4.64(m, 2H, H^4 and H^5), 4.79(m, 1 H, H^6), 5.08(m, 1 H, H^3), 5.61(d, *J* 12, 1 H, H^1), 6.52(m, 1 H, H^7), 7.25(d, *J* 16 Hz, 1 H, $H^{7'}$), and 7.66(s, 3 H, Me) (Found: C, 53.0; H, 2.75; N, 13.9. $C_{18}H_{10}FeN_4O_4$ requires C, 53.7; H, 2.5; N, 13.9%).

With complex (4). Complex (21) was obtained by the method described for (20). Recrystallization from toluene–n-hexane gave the product as white needles. I.r. (Nujol mull): ν(CN) at 2 260; ν(MC–O) at 2 093 and 2 040; ν(C=O) at 1 760 cm^{-1}. Hydrogen-1 n.m.r. spectrum in $(CD_3)_2CO$: τ 4.85(m, 2 H, H^4 and H^5), 5.17(t, *J* 8, 1 H, H^6), 5.43(t, *J* 8 Hz, 1 H, H^3), 6.85(m, 2 H, H^7), 7.46(s, 3 H, Me), and 7.9 (H^2, overlapped with solvent). Spin-decoupling experiments confirmed the position of H^2 (Found: C, 53.75; H, 2.70; N, 13.85. $C_{18}H_{10}FeN_4O_4$ requires C, 53.7; H, 2.70; N, 13.85%).

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