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INTERMOLECULAR METAL TRANSFER REACTIONS AND METAL HYDRIDE SHIFT ISOMERIZATIONS IN (CYCLOHEPTATRIENE)TRICARBONYLIRON DERIVATIVES

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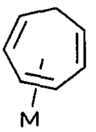
Summary

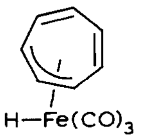
Upon heating, tricarbonyl[(3,4,5,6-η)-1-ethenyl-1,3,5-cycloheptatriene]iron derivatives $Fe(CO)_3C_7H_7CH{=}CHR$ (R = COOMe, COC_6H_4OMe-*p*) gave the corresponding hexacarbonyl di-iron complexes. Under the same conditions the phenyl derivative ($R = C_6H_5$) gave a mixture of a binuclear complex and the metal hydride shift isomer. The *anti* configuration of the binuclear complexes was established by X-ray crystallography.

Introduction

Transition metal coordinated cycloheptatrienes I and their derivatives have recently been taken as a model for numerous mechanistic studies aimed at the evaluation of metal shift isomerizations in cyclic discontinuously conjugated π complexes [1–4].


(I)

M = $Cr(CO)_3$
$Fe(CO)_3$
$Mo(CO)_3$
Rhacac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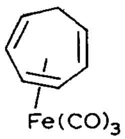
(III)

Thermally-induced metal shift isomerizations are generally presumed to be intramolecular [5] and to involve either a metal hydride intermediate [6] or a 16-electron metal coordinates species [5]. Previous evidence for the involvement of a π-allyliron hydride intermediate II in the degenerate rearrangement of 7-*exo*-d_1-

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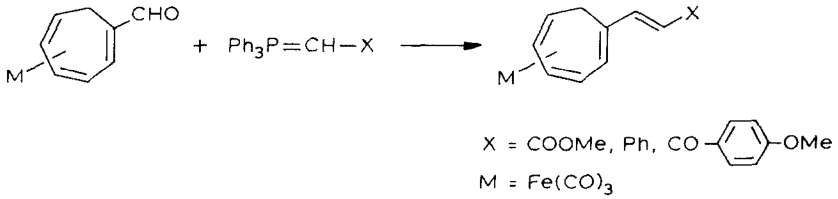
cycloheptatrienetricarbonyliron [2b] has called into question by recent NMR experiments with spin saturation transfer techniques which favor a direct 1,3 iron shift via the η^2-species III [2c,e,g]. This apparent dichotomy prompts us to report that unsymmetrical cycloheptatrienetricarbonyliron complexes IV–VI, which have extended conjugation, undergo both a facile intermolecular metal transfer [7,8] and metal hydride shift isomerizations. None of the isomers expected to be formed by a direct metal shift was detected.

Results and discussion

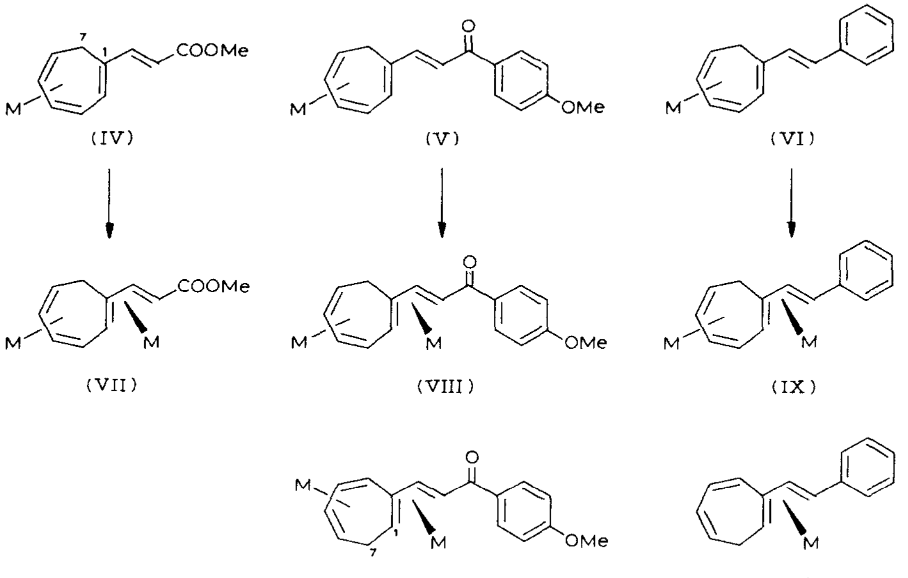
The mononuclear complexes IV–VI were prepared by a modification of the previously reported Wittig reaction [9] (eq. 1). When complexes IV and V were



(1)

heated in toluene for 48 h at 90–100°C, the corresponding crystalline bis(tricarbonyliron) complexes VII and VIII were isolated in ca. 30% yield. Examination of the product mixtures by TLC at intermediate times revealed that these binuclear complexes were the primary reaction products. None of the expected shift isomers was detected. When VI was similarly treated, two crystalline complexes were isolated. The minor product was identified as the di-iron complex IX, but the major complex isolated was, unexpectedly, the metal–hydrogen shift isomer X.

Compounds VII–IX were independently prepared by reaction of the corresponding mononuclear complexes IV–VI with $Fe_2(CO)_9$. In one case however, when V



(IV) (V) (VI)

(VII) (VIII) (IX)

M = Fe(CO)$_3$ (XI) (X)

was treated with $Fe_2(CO)_9$ in toluene a second binuclear isomer XI was also obtained, albeit in low yield.

The ^{1}H NMR spectra of binuclear complexes VII–IX show three groups of characteristic signals at δ 0.3–2.1 (H(2) and H(9)), 3.0–3.6 (2H(7), H(3) and H(6)) and 5.2–5.8 ppm (H(4), H(5) and H(8)). The detailed 300 MHz ^{1}H NMR of VIII in $CDCl_3$ is as follows: δ 1.84 (d, H(9), *J* 7.8 Hz), 2.13 (d, H(2), *J* 7.5 Hz), 3.21 (bd, H(7*x*), *J* 20.3 Hz), 3.40 (m, H(6)), 3.43 (t, H(3), *J* 7.5 Hz), 3.58 (dd, H(7*x*), *J* 20.3 and 4.5 Hz), 3.86 (s, OMe), 5.27 (bt, H(4), *J* 7.5 and 5.1 Hz), 5.50 (dd, H(5), *J* 7.8 and 5.1 Hz), 5.80 (d, H(8), *J* 7.8 Hz), 6.92 and 7.33 (2d, 4H(Ar), *J* 8.7 Hz) ppm.

A similar spectrum is observed for the rearranged di-iron complex XI. It exhibits signals at δ 1.46 (d, H(1), *J* 8.4 Hz), 1.71 (d, H(9), *J* 7.8 Hz), 2.23 (bd, H(7*x*), *J* 19.0 Hz), 2.71 (m, H(7*n*)), 3.40 (m, H(6)), 3.86 (s, OMe), 3.92 (d, H(3), *J* 8.1 Hz), 5.43 (dd, H(4), *J* 8.1 and 5.0 Hz), 5.52 (m, H(5)), 6.13 (d, H(8), *J* 7.8 Hz), 6.91 and 7.34 (2d, 4H(aromatic), *J* 9.0 Hz) ppm. Notably H(3) of XI which is coupled only to H(4) appears as a doublet compared to the corresponding H(3) triplet in VIII. Also, H(7*n*), which appears as a doublet of doublets in VIII, is further split by H(1) in XI.

The ^{1}H NMR spectrum of isomer X is characterized by five low field signals (in addition to the aromatic multiplet at δ 7.26 ppm) resonating at δ 5.80 (d, H(8), *J* 9.0 Hz), 5.99 (ddd, H(6), *J* 9.8, 7.8 and 4.7 Hz, 6.20 (ddd, H(5), *J* 9.8, 5.5 and 2.3 Hz), 6.51 (dd, H(4), *J* 11.3 and 5.5 Hz) and 6.92 (d, H(3), *J* 11.3) ppm. The high field region consists of four signals at δ 1.14 (dd, H(1), *J* 9.8 and 6.7 Hz), 1.77 (m, H(7*x*), 1.87 (d, H(9), *J* 9.0 Hz) and 2.88 (ddd, H(7*n*), *J* 13.7, 7.8 and 6.7) ppm.

In order to establish unequivocally the structure of the binuclear complexes, and in particular the *anti* stereochemistry of the two $Fe(CO)_3$ groups, an X-ray diffraction study was carried out on IX, for which a suitable crystal was available. The X-ray study (Fig. 1) revealed that the presence of a second $Fe(CO)_3$ group did not alter the typically bent conformation of the cycloheptatriene ring observed in mononuclear systems [10]. This conformation prevents the coplanarity of the tetraene moiety. Thus, the two diene-$Fe(CO)_3$ groups appear in the ^{1}H NMR spectrum as two regular nonconjugated systems. The significant downfield shift (ca. 1.0 ppm) observed for both methylene protons (2H(7)) may be attributed to the *anti* configuration of the two $Fe(CO)_3$ groups.

The facile metal transfer reactions in IV–VI coupled with the metal hydride shift isomerization observed in VI demonstrate that these reactions compete favorably with the direct 1,3-metal shift isomerization established for other cyclohep-

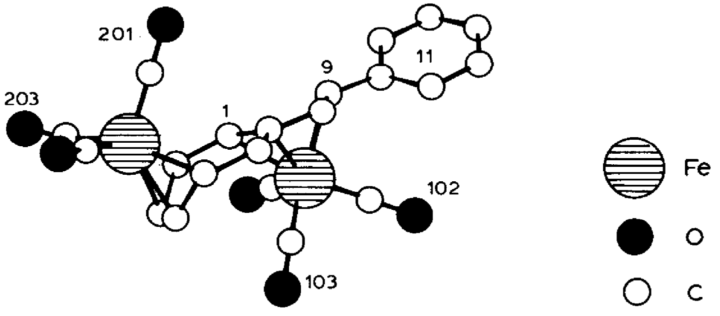
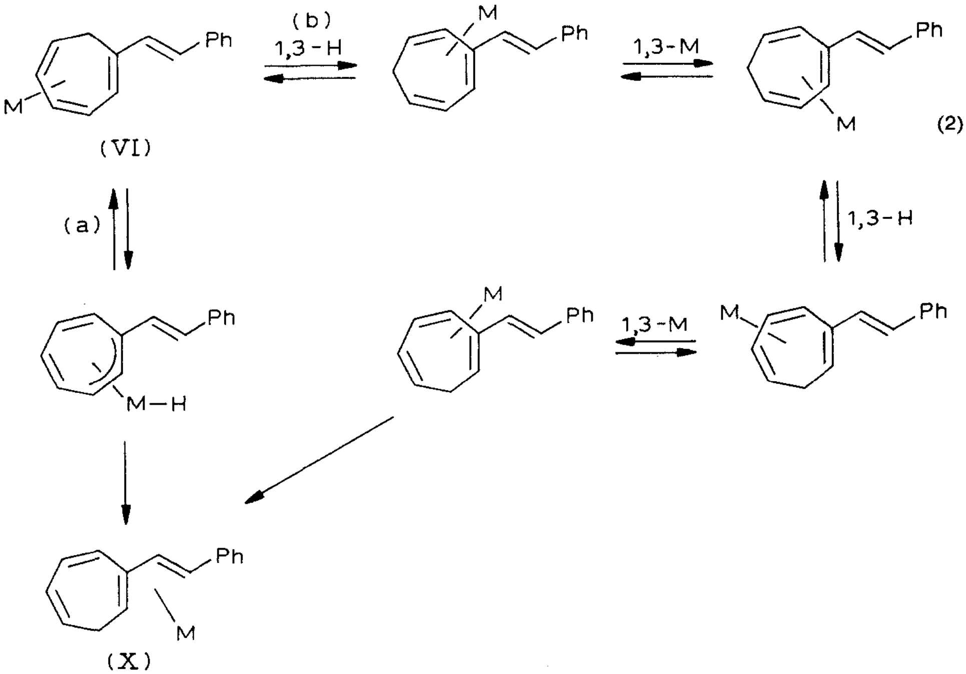


Fig. 1. Molecular structure of $[Fe_2(CO)_6(\eta^4{:}\ \eta^4\text{-}C_7H_7\text{-}1\text{-}CH{=}CHPh)]$ (IX).

tatrienetricarbonyliron complexes [2]. That metal transfer is favored over hydrogen migration in IV and V but not in VI suggests that electron-withdrawing groups facilitate intermolecular metal–olefin bonding over intramolecular hydrogen abstraction.

We note that X is the only metal–hydrogen shift isomer isolated out of nine possible isomers of VI. Since any rearrangement involving the migration of hydrogen is likely to involve a tropylium metal hydride II it is conceivable that the mechanism includes a one step 1,5 hydrogen shift, e.g. via the metal hydride intermediate shown in eq. 2a. However, if we assume a fast equilibrium between the isomers, an alternative stepwise mechanism may be invoked consisting of consecutive 1,3 hydrogen and 1,3 metal shifts (eq. 2b). Preference for 1,3 over 1,5 hydrogen migration in tricarbonyliron complexes has been previously noted [6].

Thus we conclude that bimolecular processes and hydrogen shift isomerizations in cycloheptatrienetricarbonyliron complexes are no less efficient than direct metal migrations. Whether migration of hydrogen proceeds via a specific or random mechanism must await further investigation.



(2)

Experimental

General

^{1}H NMR spectra were recorded on Varian Model HA-100 and 300 MHz Brucker WX spectrometers, with TMS as internal standard. IR spectra were recorded on a Perkin–Elmer Model-257 spectrometer. Mass spectra were determined with a GC/MS Finnigan Model 4000 spectrometer using an EI source, with ionization energy of 70 eV, unless otherwise stated. Column chromatographic separations were performed under a slight positive nitrogen pressure using Merck Kieselgel 60.

Elemental analyses were determined at the analytical laboratories of the Hebrew University, Jerusalem. All reactions were conducted under nitrogen.

[Fe(CO)$_3$(η^4-C$_7$H$_7$-1-CH=CHCOOMe)] (IV) [9]

A solution of 2.6 g (10 mmol) 1-formylcycloheptatrienetricarbonyliron [11], 4.0 g (12 mmol) triphenyl(carbomethoxymethylene)phosphorane [12] and 250 mg benzoic acid in 80 ml CH_2Cl_2 was kept at room temperature for 3 days. The solvent was removed and the residual brown oil chromatographed (hexane elution) to give 1.6 g (50% yield) of IV, m.p. 101°C (hexane); *m/e* 288 ($M-$ CO), 260, 232, 176; IR (Nujol) 2020, 1980, 1950, 1705 cm^{-1}, Anal: Found C, 53.16; H, 3.80. $C_{14}H_{12}FeO_5$ calcd.: C, 53.07; H, 3.73%. The ^{1}H NMR spectrum was identical to that reported previously [9].

[Fe(CO)$_3$(η^4-C$_7$H$_7$-1-CH=CHCOC$_6$H$_4$-4'-OMe)] (V)

This was made in similar fashion by reaction of 1-formylcycloheptatrienetricarbonyliron and triphenyl(4-methoxybenzoylmethylene)phosphorane [13], for two weeks at room temperature, in 18% yield; m.p. 147°C (CH_2Cl_2/hexane); *m/e* 364 ($M-$ CO), 336, 308, 352; IR (Nujol) 2045, 1975, 1640 cm^{-1}. Anal.: Found C, 61.44; H, 4.15. $C_{20}H_{16}FeO_5$ calcd.: C, 61.20; H, 4.08%. ^{1}H NMR ($CDCl_3$): δ 2.52 (dd, 2H, *J* 20 and 5 Hz), 3.13 (t, 1H, *J* 9 Hz), 3.43 (m, 1H), 3.80 (s, OMe), 5.40 (m, 2H), 6.38 (d, 1H, *J* 8 Hz), 6.7 (d, 1H, *J* 16 Hz), 7.18 (d, 1H, *J* 16 Hz), 6.87, 7.87 (m, 4H, aromatic) ppm.

[Fe$_2$(CO)$_6$(η^4:η^4-C$_7$H$_7$-1-CH=CHCOOMe)] (VII)

(a) By thermal reaction. A solution of 200 mg (0.6 mmol) of IV in 10 ml of dry toluene was heated at 90–100°C for 48 h. The mixture was filtered and the solvent removed under vacuum. Chromatography afforded 80 mg (27% yield) of crystalline VII, m.p. 152°C (pentane).

(b) By reaction with $Fe_2(CO)_9$. A mixture of 144 mg (0.45 mmol) of IV and 780 mg (2.2 mmol) $Fe_2(CO)_9$ in 10 ml of dry toluene was refluxed for 17 h, filtered and the solvent removed under vacuum. The residue was purified by chromatography and recrystallization from hexane to give 120 mg (57% yield) of VII. *m/e* 456 (M), 428, 400, 372, 344, 316, 288, 232. IR (Nujol): 2040, 1980, 1705 cm^{-1}. Anal.: Found C, 44.55; H, 2.63. $C_{17}H_{12}Fe_2O_3$ calcd.: C, 44.74; H, 2.63%. ^{1}H NMR ($CDCl_3$): δ 0.90 (d, 1H, *J* 8 Hz), 1.78 (d, 1H, *J* 8 Hz), 3.1–3.5 (m, 4H), 3.62 (s, 3H), 5.24 (dd, 1H, *J* 7 and 5 Hz), 5.48 (m, 1H obscured), 5.52 (d, 1H, *J* 8 Hz) ppm.

[Fe$_2$(CO)$_6$(η^4: η^4-C$_7$H$_7$-1-CH=CHCOC$_6$H$_4$-4'-OMe)] (VIII)

Complex VIII was similarly prepared from V by thermal reaction, in 30% yield; m.p. 145–146°C (hexane). *m/e* 504 ($M-$ CO), 476, 448, 420, 392, 364, 308, 252. IR ($CHCl_3$): 2050, 1980, 1640 cm^{-1}. Anal.: Found C, 52.01; H, 3.14. $C_{23}H_{16}Fe_2O_8$ calcd.: C, 51.88, H, 3.01%. ^{1}H NMR spectrum see text.

The reaction of V with $Fe_2(CO)_9$ carried out as above gave VIII in 37% yield and its isomeric [Fe$_2$(CO)$_6$(η^4: η^4-C$_7$H$_7$-2-CH=CHCOC$_6$H$_4$-4'-OMe)] (XI) in 8% yield (pentane); m.p. 185°C (dec.). *m/e* CI(CH_4) 533 ($M+1$), 505, 477, 449, 421, 393, 309, 253. IR ($CHCl_3$): 2050, 1980, 1640 cm^{-1}. ^{1}H NMR spectrum see text.

$[Fe_2(CO)_6(\eta^4\text{: }\eta^4\text{-}C_7H_7\text{-}1\text{-}CH{=}CHPh)]$ (IX)

Complex IX was similarly prepared, from VI [9] and excess $Fe_2(CO)_9$, in 64% yield; m.p. 163–164°C (hexane). *m/e* 446 (M − CO), 418, 390, 362, 334, 306, 250, 194. IR (KBr): 2150, 2135, 1990, 1975, 1960, 1955 cm^{-1}. Anal.: Found C, 53.12; H, 2.78. $C_{21}H_{14}Fe_2O_6$ calcd.: C, 53.16; H, 2.95%. ^1H NMR ($CDCl_3$): δ 1.80 (d, 1H, J 7.4 Hz), 1.90 (d, 1H, J 9.0 Hz), 3.22 (bd, 1H, J 20.0 Hz), 3.38 (dd, 1H, J 7.8 and 4.3 Hz), 3.44 (t, 1H, J 7.4 Hz), 3.58 (dd, 1H, J 20.0 and 4.3 Hz), 5.28 (dd, 1H, J 7.4 and 5.1 Hz), 5.48 (dd, 1H, J 7.8 and 5.1 Hz), 5.50 (d, 1H, J 9.0 Hz), 7.18 (m, 5H) ppm.

$[Fe(CO)_3(\eta^4\text{-}C_7H_7\text{-}2\text{-}CH{=}CHPh)]$ (X)

A solution of 68 mg of VI in 10 ml of dry toluene was heated at 100°C for 48 h. TLC showed the presence of two new products in addition to starting material. The mixture was filtered and separated by chromatography (hexane). Complex X, the first to be eluted, was recrystallized from cold pentane to give 15 mg (25% yield); m.p. 79°C. *m/e* (EI, 15 eV): 334 (M), 306, 278, 250, 194, 179, 172. IR ($CHCl_3$) 2050, 1990, 1975 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.14 (dd, 1H, J 9.8 and 6.7 Hz), 1.77 (m, 1H), 1.87, (d, 1H, J 9.0 Hz) 2.88 (ddd, 1H, J 13.7, 7.8 and 6.7 Hz) 5.80 (d, 1H, J 9.0 Hz), 5.99 (ddd, 1H, J 9.8, 7.8 and 4.7 Hz), 6.20 (ddd, 1H, J 9.8, 5.5 and 2.3 Hz), 6.51 (dd, 1H, J 11.3 and 5.5 Hz), 6.92 (d, 1H, J 11.3 Hz), 7.26 (m, 5H) ppm. The second compound eluted (10 mg) was starting material VI. Finally, 5 mg (12% yield) of the binuclear complex IX were collected and identified spectroscopically as above.

X-ray structure determination of $C_{15}H_{14}[Fe(CO)_3]_2$

anti-Hexacarbonyl[μ-[(1,2,8,9-η:3,4,5,6-η)-1-(*trans*-phenylethenyl)-1,3,5-cycloheptatriene]]di-iron (IX) forms red prismatic crystals elongated along the *a* axis. Preliminary unit cell parameters and space group information were determined from precession photographs. Refined cell parameters were obtained by the least-squares refinement of the θ values of some twenty reflections measured on a Hilger and Watts Y290 automated four-circle diffractometer. Intensity data were also collected on this instrument using Zr-filtered Mo-radiation and the $\omega/2\theta$ step-scanning method. The scan width was chosen to be 0.64° with a step-size of 0.01° and a count time of 1 s per step. The integrated intensity for each reflection was obtained with a "moving window" technique [14] in which 48 steps were taken as the peak and the remaining 16 as background. Four reference reflections were measured after every 50 reflections in order to monitor any gradual variations in experimental conditions. The sums of the intensities of the reference reflections were used to scale the observed intensities by interpolation between groups of reference reflections.

Intensity data were collected for the (h, $\pm k$, $\pm l$) reflections over the range $1° \leqq \theta \leqq 15°$ and for the (h, k, $\pm l$) reflections over the range $15° \leqq \theta \leqq 30°$ to give a total of 7089 measurements. Merging of these data sets yielded 5660 independent reflections of which 3134 had $I \geqq 3\sigma(I)$ and were thereby classified as significant; the overall residual for the 1038 reflections measured more than once (2264 measurements) was 1.4% Lorentz and polarisation corrections were applied to all reflections and empirical absorption corrections were obtained by the method of North et al. [15] using several h,0,0 reflections.

Crystal data. $C_{21}H_{14}O_6Fe_2$, $M = 474.0$. Monoclinic, a 7.742(1), b 17.744(2), c

14.184(1) Å, β 92.451(5)°, D_c 1.62 g cm^{-3}, $Z = 4$. μ(Mo-K_α) 15.7 cm^{-1}. Space group $P2_1/c$ (No. 14).

The structure was solved by the heavy atom method. Atomic coordinates for the iron atoms were obtained from a three-dimensional Patterson synthesis and the remaining non-hydrogen atoms located by the iterative Fourier synthesis technique. The structure was refined by the method of least-squares using only the significant reflections and initially with all atoms treated isotropically. Hydrogen atoms were placed in calculated positions assuming a C–H bond length of 1.0 Å and further refinement proceeded by a partial full-matrix technique in which the non-hydrogen atoms were treated anisotropically but no more than 17 atoms were refined in any one cycle; an overall scale factor was refined in each cycle to give a maximum number of variable parameters of 154. The refinement was terminated when all shifts were less than the corresponding estimated standard deviations to give a final R value of 0.069 (for 3134 h,k,l). The weighting scheme $\omega = [1 - \exp(-20\sin^2\theta/\lambda^2)]/(20 + |F_0| + 0.001\,|F_0|^2)$ if $|F_0| \geqq 10$ else $\omega = 0.001$ was used to make

TABLE 1

FRACTIONAL ATOMIC COORDINATES OF THE NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES. $\bar{U}$ IS A SPHERICAL ISOTROPIC THERMAL PARAMETER, (Å^2), DERIVED FROM THE ANISOTROPIC PARAMETERS USING THE EXPRESSION $\bar{U} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$

Atom	x	y	z	$\bar{U}$
Fe(1)	0.11743(12)	0.34488(5)	0.43375(6)	0.0356
Fe(2)	0.23612(12)	0.48378(6)	0.14117(6)	0.0407
C(1)	0.2567(8)	0.3769(3)	0.3094(4)	0.0411
C(2)	0.1721(9)	0.3829(3)	0.2158(4)	0.0465
C(3)	0.0218(8)	0.4272(4)	0.1851(4)	0.0484
C(4)	0.0110(9)	0.5024(5)	0.2104(5)	0.0581
C(5)	0.1462(9)	0.5370(4)	0.2654(4)	0.0484
C(6)	0.2106(9)	0.5126(3)	0.3612(5)	0.0483
C(7)	0.2625(7)	0.4330(3)	0.3782(4)	0.0373
C(8)	0.3251(8)	0.4118(3)	0.4731(4)	0.0369
C(9)	0.3832(8)	0.3367(4)	0.4869(4)	0.0417
C(10)	0.4416(7)	0.3113(3)	0.5838(4)	0.0396
C(11)	0.3995(9)	0.3464(4)	0.6659(4)	0.0501
C(12)	0.4770(10)	0.3235(4)	0.7535(4)	0.0505
C(13)	0.5859(9)	0.2634(5)	0.7578(5)	0.0605
C(14)	0.6305(10)	0.2272(5)	0.6749(6)	0.0630
C(15)	0.5506(9)	0.2487(4)	0.5871(5)	0.0585
C(101)	0.0901(8)	0.2534(4)	0.3792(4)	0.0500
O(101)	0.0674(10)	0.1984(4)	0.3396(5)	0.0748
C(102)	0.0446(8)	0.3222(4)	0.5466(4)	0.0530
O(102)	−0.0054(9)	0.3020(5)	0.6191(4)	0.0723
C(103)	−0.0826(8)	0.3893(4)	0.4021(4)	0.0522
O(103)	−0.2184(9)	0.4138(5)	0.3879(6)	0.0845
C(201)	0.4580(8)	0.4863(4)	0.1861(5)	0.0517
O(201)	0.5930(8)	0.4837(4)	0.2150(6)	0.0711
C(202)	0.2220(8)	0.5708(4)	0.0746(4)	0.0519
O(202)	0.2162(11)	0.6231(4)	0.0324(5)	0.0838
C(203)	0.2622(11)	0.4315(5)	0.0357(5)	0.0687
O(203)	0.2890(14)	0.3989(6)	−0.0307(5)	0.0920

TABLE 2(a)

INTRAMOLECULAR BOND LENGTHS (Å)

Fe(1)–C(1)	2.181(5)	C(4)–C(5)	1.418(10)
Fe(1)–C(7)	2.098(6)	C(5)–C(6)	1.491(9)
Fe(1)–C(8)	2.057(6)	C(6)–C(7)	1.485(8)
Fe(1)–C(9)	2.165(6)	C(7)–C(8)	1.460(7)
Fe(1)–C(101)	1.806(6)	C(8)–C(9)	1.417(8)
Fe(1)–C(102)	1.766(7)	C(9)–C(10)	1.496(8)
Fe(1)–C(103)	1.778(6)	C(10)–C(11)	1.372(9)
Fe(2)–C(2)	2.147(6)	C(10)–C(15)	1.395(8)
Fe(2)–C(3)	2.058(6)	C(11)–C(12)	1.415(8)
Fe(2)–C(4)	2.062(7)	C(12)–C(13)	1.360(10)
Fe(2)–C(5)	2.141(6)	C(13)–C(14)	1.396(11)
Fe(2)–C(201)	1.807(6)	C(14)–C(15)	1.418(10)
Fe(2)–C(202)	1.811(7)	C(101)–O(101)	1.136(8)
Fe(2)–C(203)	1.778(8)	C(102)–O(102)	1.171(8)
C(1)–C(2)	1.460(8)	C(103)–O(103)	1.148(9)
C(1)–C(7)	1.392(8)	C(201)–O(201)	1.106(8)
C(2)–C(3)	1.455(9)	C(202)–O(202)	1.104(8)
C(3)–C(4)	1.384(11)	C(203)–O(203)	1.131(10)

TABLE 2(b)

INTERMOLECULAR BOND ANGLES (°)

C(1)–Fe(1)–O(7)	37.9(2)	C(5)–Fe(2)–C(202)	92.2(3)
C(7)–Fe(1)–C(8)	41.1(2)	C(5)–Fe(2)–C(203)	167.0(3)
C(8)–Fe(1)–C(9)	39.1(2)	C(201)–Fe(2)–C(202)	101.4(3)
C(1)–Fe(1)–C(101)	86.6(3)	C(201)–Fe(2)–C(203)	99.7(3)
C(1)–Fe(1)–C(102)	168.5(3)	C(202)–Fe(2)–C(203)	90.7(3)
C(1)–Fe(1)–C(103)	97.8(3)	C(2)–C(1)–C(7)	125.8(5)
C(7)–Fe(1)–C(101)	124.3(3)	C(1)–C(2)–C(3)	129.3(6)
C(7)–Fe(1)–C(102)	135.0(3)	C(2)–C(3)–C(4)	119.9(5)
C(7)–Fe(1)–C(103)	92.8(3)	C(3)–C(4)–C(5)	120.5(6)
C(8)–Fe(1)–C(101)	135.3(3)	C(4)–C(5)–C(6)	125.9(6)
C(8)–Fe(1)–C(102)	99.3(3)	C(5)–C(6)–C(7)	120.0(5)
C(8)–Fe(1)–C(103)	118.3(3)	C(1)–C(7)–C(6)	124.5(5)
C(9)–Fe(1)–C(101)	100.4(3)	C(1)–C(7)–C(8)	117.5(5)
C(9)–Fe(1)–C(102)	90.3(3)	C(6)–C(7)–C(8)	118.1(5)
C(9)–Fe(1)–C(103)	157.2(3)	C(7)–C(8)–C(9)	117.4(5)
C(101)–Fe(1)–C(102)	98.5(3)	C(8)–C(9)–C(10)	119.5(5)
C(101)–Fe(1)–C(103)	101.9(3)	C(9)–C(10)–C(11)	124.5(5)
C(102)–Fe(1)–C(103)	91.2(3)	C(9)–C(10)–C(15)	115.5(6)
C(2)–Fe(2)–C(3)	40.1(3)	C(11)–C(10)–C(15)	119.8(6)
C(3)–Fe(2)–C(4)	39.3(3)	C(10)–C(11)–C(12)	120.5(6)
C(4)–Fe(2)–C(5)	39.4(3)	C(11)–C(12)–C(13)	120.2(6)
C(2)–Fe(2)–C(201)	94.7(3)	C(12)–C(13)–C(14)	119.9(6)
C(2)–Fe(2)–C(202)	163.2(2)	C(13)–C(14)–C(15)	120.1(7)
C(2)–Fe(2)–C(203)	90.9(3)	C(10)–C(15)–C(14)	119.0(7)
C(3)–Fe(2)–C(201)	132.2(3)	Fe(1)–C(101)–O(101)	175.2(6)
C(3)–Fe(2)–C(202)	122.8(3)	Fe(1)–C(102)–O(102)	175.2(7)
C(3)–Fe(2)–C(203)	92.0(3)	Fe(1)–C(103)–O(103)	173.6(7)
C(4)–Fe(2)–C(201)	129.6(3)	Fe(2)–C(201)–O(201)	176.1(7)
C(4)–Fe(2)–C(202)	94.5(3)	Fe(2)–C(202)–O(202)	178.3(7)
C(4)–Fe(2)–C(203)	127.7(3)	Fe(2)–C(203)–O(203)	175.9(9)
C(5)–Fe(2)–C(201)	92.1(3)		

the average values of $\Sigma\omega\Delta^2$ constant when analysed in terms of batches of increasing $|F_0|$ and sin θ/λ. A final difference Fourier synthesis indicated the correctness of the refinement and structure factor calculations for the insignificant reflections revealed no outstanding discrepancies. Throughout the structure factor calculations the atomic scattering factors listed by Hanson et al. [16] were used.

In the crystal structure of IX the iron atom bonded to the diene moiety of the cycloheptatriene ring lies 1.603(9) Å out of the plane defined by the four ring carbon atoms whereas the remaining iron atom lies 1.663(9) Å out of the plane defined by the second diene moiety. The dihedral angle between these two planes is 43.3(6)°. The phenyl ring is inclined at a dihedral angle of 24.4(8)° to the exocyclic diene plane.

All computer calculations were carried out on the CDC computers at the University of London Computer Centre using the Birkbeck College crystallographic program library. The least-squares program is a modified version of that originally coded by D.W.J. Cruickshank and J.G.F. Smith. Tables of observed and calculated structure factors, anisotropic thermal parameters and calculated hydrogen atom coordinates can be obtained from P.F. Lindley.

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