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IRON AND RUTHENIUM CARBONYLS OF 6,7-DIMETHYLENE-*exo*-3-OXATRICYCLO[3.2.1.0^{2,4}]OCTANE. PROTIC ACID ADDITIONS TO AN EPOXIDE RING HOMOCONJUGATED TO A η^4-(DIENE)Fe(CO)$_3$ FUNCTION. CRYSTAL STRUCTURES OF $(C_9H_{10}O)Fe(CO)_3$ AND $(C_{10}H_{14}O_2)Fe(CO)_3$

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Summary

The reaction of the epoxydiene 6,7-dimethylene-*exo*-3-oxatricyclo-[3.2.1.0^{2,4}]octane (I) with iron and ruthenium carbonyls in various solvents yields the (η^4-1,3-diene)M(CO)$_3$ *exo* isomers (II, M = Fe; IV, M = Ru). The *endo*-Fe(CO)$_3$ isomer (III) was obtained only in small yield from the reaction of I with $Fe_2(CO)_9$ or $Fe(CO)_5$ in n-pentane. The exo configuration of II was ascertained by an X-ray crystal structure determination. It reacts cleanly and rapidly with HCl in ether giving the *exo*-2-chloro-5,6-dimethylene-*syn*-7-norbornanol-*endo*-iron tricarbonyl complex (V), while the *endo* isomer III does not react to any significant extent under the same conditions. A simple Wagner—Meerwein rearrangement can explain the formation of V from II + HCl, although participation of the (diene)Fe(CO)$_3$ moiety cannot be excluded. When treated with $HSO_3F/SO_2ClF/CD_2Cl_2$, II furnished a stable cationic complex whose ^{1}H and ^{13}C NMR spectra suggest delocalisation of the homoconjugated positive charge by the (diene)Fe(CO)$_3$ function. Quenching of the cation with methanol yielded the *exo*-2-methoxy-5,6-dimethylene-*syn*-7-norbornanol-*endo*-iron tricarbonyl complex (X) whose structure was established by single crystal X-ray diffraction.

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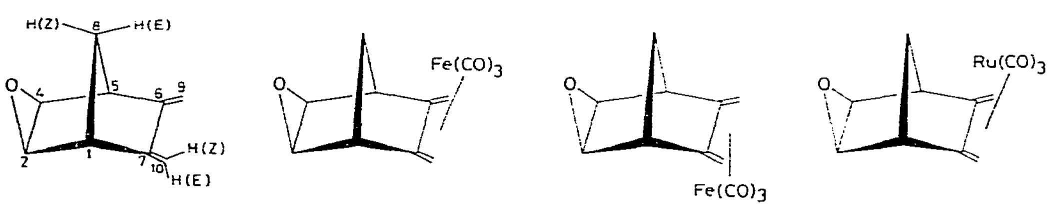
Introduction

Over the past several years the chemistry of dieneiron tricarbonyl complexes has received considerable attention and has proved to be useful in organic synthesis [1,2]. We have been interested in the effects on the physical and chemical properties of an organic function homoconjugated to a coordinated ligand [3]. We report some results of acid additions to an epoxide ring homoconjugated to a (diene)$Fe(CO)_3$ function held in a rigid geometry by the bicyclo[2.2.1]heptane skeleton. We will demonstrate that the proton promoted oxiran opening in these systems leads to a stereospecific addition-rearrangement reaction only when the $Fe(CO)_3$ group is in the *exo* position, the *endo* isomer being unreactive under the same conditions.

The high degree of stabilisation of a carbenium ion α to an organometallic substituent has been recognized for some time [4]. Little is known, however, about the effect of an organometallic substituent on the stability of a β-carbenium ion. Depending upon the geometry of the system investigated, an arenechromium tricarbonyl group has been found to accelerate [5,6] or retard [7] S_N1 solvolyses of π-complexed β-arylalkyl esters. The hydrolysis of 7-norbornadienyl tosylate is drastically retarded upon complexation of the 1,4-diene by an *endo*-$Fe(CO)_3$ group [9a], even though the iron tricarbonyl fragment is considered to be an electron-donating group [8].

Results and discussion

6,7-Dimethylene-*exo*-3-oxatricyclo[$3.2.1.0^{2,4}$]octane (I) [10] yielded the *exo*-η^4-(1,3-diene)iron tricarbonyl complex II (major product) and its *endo* isomer III (minor product) when treated with $Fe_2(CO)_9$ or $Fe(CO)_5$. Conditions



(I) (II) (III) (IV)

were found in which only II was formed in good yield (71%). When treated with (cod)$Ru(CO)_3$ [11] (cod = 1,5-cyclooctadiene) (benzene, reflux, 15 h), I yielded the *exo*-$Ru(CO)_3$ complex IV (15%); no trace of the *endo* isomer was detected. The ^{1}H and ^{13}C NMR spectral data of ligand I and its Fe and Ru complexes are reported in Table 1 and their IR, UV and mass spectral data in the experimental part. In the case of the iron tricarbonyl complexes of 2,3-dimethylenenorbornane, Steiner et al. [12] distinguished between the *exo* and *endo* isomers by comparing the corresponding values of $\Delta\delta = \delta(\text{ligand}) - \delta(\text{complex})$ for the methylene bridge protons and carbon atom. They attributed the *exo* configuration to the complex showing higher $\Delta\delta$'s for the $H(7)_{syn}$ and $H(7)_{anti}$ protons and the greater deshielding of C(7). In the present case, $\Delta\delta$ for the methylene bridge proton H(8*Z*) is smaller for II than for III (—0.28 vs. —0.45 ppm) while

TABLE 1

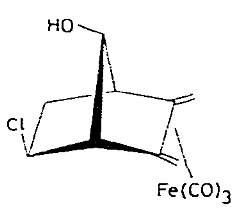
^{1}H AND ^{13}C NMR SPECTRAL DATA OF Fe AND Ru CARBONYLS OF I [a]

	I	II	III	IV
H(1), H(5)	2.95bs [b]	2.95bs	2.43m	2.84bs
H(2), H(4)	3.11bs	3.75s	3.90m	3.67s
H(8*E*)	0.99d-m; 10 [c]	1.52m; 10	1.44m; 10	1.24d; 9
H(8*Z*)	1.55d-m	1.83m	2.0m	1.72d
H(9*E*), H(10*E*)	4.92bs; <0.6 [c]	1.93d; 2.4	1.67d; 2.4	1.98d; 3.0
H(9*Z*), H(10*Z*)	5.25bs	0.50d	0.20d	0.68d
C(1), C(5)	45.5d [b]; 148 [d] [33]	42.4d; 153	43.9d; 150	42.4d; 157
C(2), C(4)	50.9d; 192 [d]	52.2d; 193	50.1d; 192	57.7d; 193
C(6), C(7)	147.0s	113.1s	109.4s	116.4s
C(8)	26.2t; 138 [d]	35.3t; 140	24.0t; 139	37.0t; 140
C(9), C(10)	103.3t; 158 [d]	34.9t; 160	32.1t; 159	27.6t; 159
CO	—	210.7s [e]	211.4s [f]	195.2 (2C) 200.3 (1C)

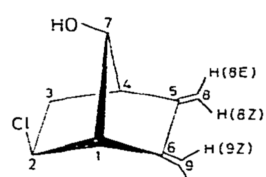
[a] In $CDCl_3$ at room temperature; ^{13}C NMR spectrum width 3750 Hz, 4096 points. [b] Chemical shifts in ppm, TMS as internal standard; s: singlet, bs: broad singlet, d: doublet, t: triplet, m: multiplet. [c] $^{2}J(ZE)$ ± 0.3 Hz. [d] ^{1}J(CH) ± 2 Hz. [e] CO exchange blocked at −40°C; δ(CO) 207.1 (2C) and 212.6 ppm (1C). [f] CO exchange blocked at −30°C; δ(CO) 209.5 (2C) and 214.7 ppm (1C).

that for C(8) is greater for II than for III (−9.1 vs. +2.2 ppm) (the numbering scheme is indicated in Fig. 1). Moreover, we have found in analogous systems [13] that the comparison of Δδ's does not permit any distinction between the two isomers. As neither the IR nor the UV and mass spectral data are helpful, we have confirmed the *exo* configuration for complex II by the determination of its crystal structure (see below).

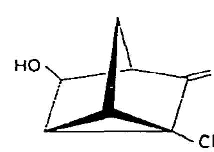
The rapid addition of gaseous HCl (ether, 0°C) to the *exo* complex II generated the stereospecifically rearranged adduct V (85%). The half-time of addition at 30°C was 2.0 ± 0.4 min (deutero-ether, molar ratio HCl/complex 2/1). In contrast, the *endo* isomer III did not react under the same conditions ($t_{1/2}$ > 8000 min) and slowly decomposed at 30°C with formation of the chlorohydrins VI



(V)



(VI)



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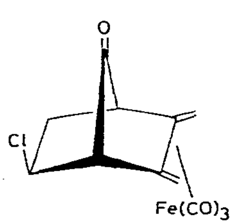


(VIII)

TABLE 2

^{1}H AND ^{13}C NMR SPECTRAL DATA [a]

	V	LIS [c]	VI	VIII	X	LIS [c]	XI
H(1)	3.22m [b], 1.4 [d]	10	3.03 [10b] [o]	3.40bs	3.10bs	15	2.87bs [o]
H(2)	4.07m, 7.5 [e]	5	4.15m	3.80m, 8.4 [e]	3.55m, 7.0 [e]	10	3.61m
H(3X)	2.70m, 4.3 [f]	12.5	2.43m	2.55m, 4.3 [f]	2.10m, 4.0 [f]	18	1.93m
H(3N)	2.30m, 14.0 [g]	5.6	2.43m	2.06m, 14.0 [g]	1.93dd, 14.0 [g]	9	1.83m
H(4)	3.14m, 4.0 [h]	10	2.93m	3.23m, 4.0 [h]	2.98bs	13	2.73m
H(7)	4.60m, 1.5 [i]	21	4.15m	—	4.40d	25	3.87m
H(8E)	1.91d, 3.1 [j]	1.6	4.92bs	2.08d, 3.0 [j]	1.86d, 3.0 [j]	4	4.83bs
H(8Z)	0.50d	1.3	5.25bs	0.66d	0.39d	2.5	5.18bs
H(9E)	1.94d, 3.1 [j]	2.4	5.05bs	2.20d, 3.0 [j]	1.96d, 3.0 [j]	3	4.96bs
H(9Z)	0.50d	1.8	5.35bs	0.78d	0.48d	2.5	5.30bs
OH	3.30m, 8.3 [k]	62		—	4.60d, 10.0 [k]	83	[n]
C(1)	53.3d [b], 155		56.0d, 150	56.0d, 157 [p]	48.8d, 152 [p]		52.9d, 152 [o]
C(2)	59.7d, 163		58.9d, 163	54.5d, 167	86.9d, 152		79.6d, 156
C(3)	41.6t, 134		39.7t, 137	42.4dd, 135, 140	38.7dd, 133, 137		35.7t, 133
C(4)	49.0d, 146		51.4d, 144	47.5d, 153	48.5d, 150		50.9d, 148
C(5)	117.0s		146.7s	114.4s	118.6s		149.0s
C(6)	112.5s		145.6s	107.7s	110.3s		145.0s
C(7)	86.7d, 163		78.7d, 157	197.8s	88.3d, 160		84.7d, 158
C(8)	33.7t, 162		103.7t, 158	34.2t, 161	33.8t, 160		102.2t, 159
C(9)	34.4t, 163		105.4t, 158	35.6t, 161	35.6t, 160		104.7t, 159
CH_3	—		—	—	57.0q, 144		56.8q, 142
CO	210.2s [l]		—	211.0s [m]	211.3s		—

[a] At room temperature, ^{1}H NMR spectra in CD_2Cl_2, ^{13}C NMR spectra in $CDCl_3$ (V—VIII) or CD_2Cl_2 (X—XI); the numbering schemes for VIII and X are indicated in Fig. 2 and 3, respectively. [b] From left to right: δ in ppm relative to TMS, multiplicity, coupling constant ($\pm$0.3 Hz for ^{1}H, $\pm$ 2 Hz for ^{13}C). [c] LIS is the slope of $(\Delta\delta - \Delta\delta_0)$ vs. [Eu(dpm)$_3$]/[complex]. [d] $J(1\text{—}7)$. [e] $J(2\text{—}3N)$; $J(2\text{—}7)$ 1.5 Hz for V. [f] $J(2\text{—}3X)$. [g] $J(XN)$; $J(3N\text{—}7)$ 1.5 Hz for V. [h] $J(3X\text{—}4)$. [i] $J(4\text{—}7)$. [j] $J(ZE)$. [k] $J(7\text{—}OH)$. [l] CO exchange blocked at -30°C: δ(CO) 204.4 (2C) and 214.8 ppm (1C). [m] CO exchange blocked at -45 C: δ(CO) 207.6, 207.8 and 213.4 ppm. [n] $\delta(CH_3)$ 3.43 for X and 3.32 ppm for XI. [o] Attributions confirmed by double resonance experiments and by LIS [Eu(dpm)$_3$]. [p] Tentative attributions bases upon comparison with V and VI.

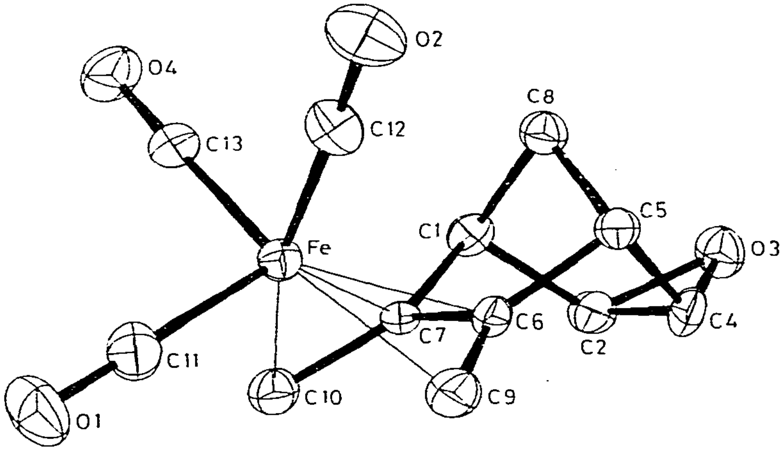
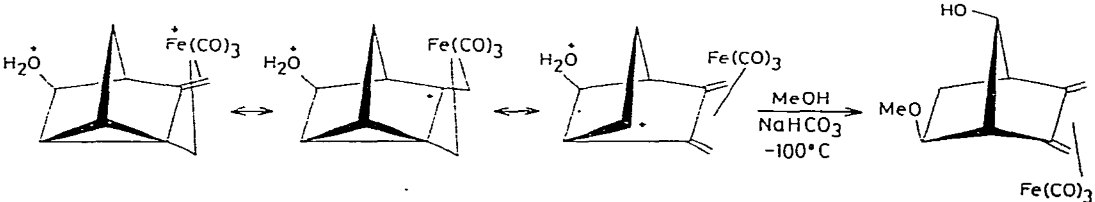


Fig. 1. A perspective view of the molecular structure of $(C_9H_{10}O)Fe(CO)_3$, (II).

and VII arising from HCl addition to the uncomplexed ligand I [10b]. DCl addition to II showed that the methylene protons H(9,10) of the dieneiron tricarbonyl groups of II (and V) did not exchange under the reaction conditions [14].

The structure of the HCl adduct V (a polycrystalline material) was deduced in the following way. Cerium(IV) oxidation of V yielded the known ligand VI (90%) [10b] while Collins oxidation [15] gave the complexed ketone VIII in low yield (5.5%). The *endo* configuration of the $Fe(CO)_3$ group in VIII was then demonstrated by a partially resolved crystal structure (see below). We assume the *exo* ⇌ *endo*-$Fe(CO)_3$ complex isomerisation does not occur under the conditions of the Collins oxidation because the *exo* complex was not detected in the reaction mixture, although it might be expected on steric grounds to be at least as stable as its *endo* isomer. The NMR parameters for V and VIII are given in Table 2, but cannot be relied upon when assigning the *exo* vs. *endo* configuration as in the case of complexes II and III.

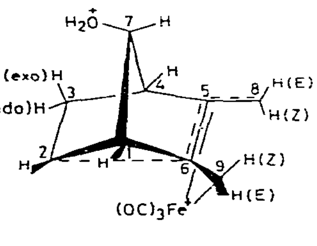
The formation of the adduct V from II + HCl may be explained by a simple Wagner—Meerwein rearrangement, although participation of the (diene)$Fe(CO)_3$ moiety cannot be excluded. When treated with $HSO_3F/SO_2ClF/CD_2Cl_2$, II furnished a cationic species stable up to −20°C. No hydrido species could be detected down to −95°C, thus if protonation of the iron or methylene carbons of the (diene)$Fe(CO)_3$ occurred, it did not lead to stable ionized Fe—H species. The ^1H and ^{13}C NMR spectral data (Table 3) suggest the structure IX ⟷ IX′ ⟷ IX″. These data are consistent with a highly delocalised cationic species involving the (diene)$Fe(CO)_3$ function as shown by the downfield shifts observed for



(IX) (IX′) (IX″) (X)

TABLE 3

^{1}H AND ^{13}C NMR PARAMETERS OF THE CATION IX IN $HSO_3F/SO_2ClF/CD_2Cl_2$ AT −55°C [a]



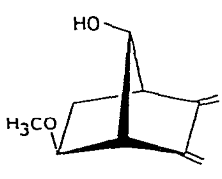
IX ↔ IX′ ↔ IX″

	δ(H) (ppm) [b]		δ(C) (ppm)	^{1}J(CH) (Hz) [e]
H(1)	2.68bs	C(1)	13.2d	175
H(2)	3.48bs	C(2)	43.1d	164
$H(3)_{exo}$	2.58bs	C(3)	56.0t	142
$H(3)_{endo}$	3.09m-d [c]	C(4)	45.8d	162
H(4)	3.96m-d [c]	C(5)	144.2s	
H(7)	5.25bs	C(6)	81.5s	
H(8E)	4.70d [d]	C(7)	84.8d	168
H(8Z)	3.31d	C(8)	78.7t	176
H(9E)	3.25d [d]	C(9)	48.2t	168
H(9Z)	1.98d	CO	200.4s (2C)	
			200.1s (1C)	

[a] $[HSO_3F]/[II]$ = 10; $[SO_2ClF]/[CD_2Cl_2]$ = 1.5 : 2 ml. [b] Internal reference: $\delta(CHDCl_2)$ 5.25 ppm; assignments were confirmed by selective decoupling experiments. [c] ^{3}J 4 Hz. [d] $^{2}J(ZE)$ 4 Hz. [e] Internal reference: $\delta(CD_2Cl_2)$ 53.6 ppm.

the diene carbons and hydrogens compared to V and X (see below) and by the relatively large ^{1}J(CH) coupling constants for C(8) and C(9). The δ(CO) 200.1 and 200.4 ppm are similar to the δ(CO) in dienyliron tricarbonyl cations [4c] and protonated dieneiron tricarbonyl complexes [14]. The doublet at δ(C) 13.2 ppm (^{1}J(CH) 175 Hz) strongly suggests a nortricyclane structure [16]. The assignments given in Table 3 are tentative; they were made with the help of selective proton decoupling of the ^{13}C NMR spectrum [17]. Further experiments (labelling, etc.) would be necessary to make them definitive.

Quenching by methanol and $NaHCO_3$ of a HSO_3F/SO_2ClF solution of IX yielded the *endo*-η^4-dieneiron tricarbonyl complex X whose structure was established by X-ray crystallography (see below). Cerium(IV) oxidation of X yielded 5,6-dimethylene-*exo*-2-methoxy-*syn*-7-norbornanol (XI). The spectro-

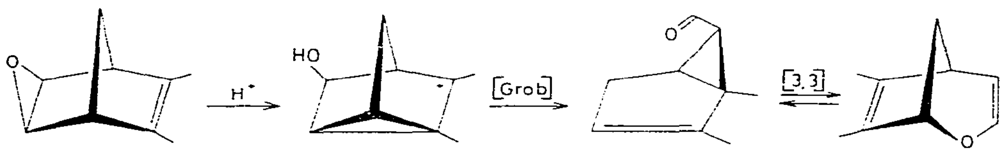


(XI)

scopic data of X (Table 2) are quite similar to those of the complexed chlorohydrin V, thus confirming this latter structure.

Several factors can be invoked to rationalise the remarkable difference in reactivity towards HCl between II and III. In the latter case, The $Fe(CO)_3$ group may retard the epoxide heterolysis because of its inductive effect [9] and/or its steric effect. The latter is probably important. Indeed, when examining the structure of X (which is also an endo complex like III), several short interatomic contacts are observed, e.g. C(11)···H(2) of 2.59 Å which is close to the sum of Van der Waals radii [18]. Assistance by solvation of the positive charge during the epoxide heterolysis should thus be more difficult in the *endo* than the *exo* case.

Further experiments are required to establish the exact role played by the dieneiron tricarbonyl function in II when generating a homoconjugated carbocationic intermediate. For the moment we recognise the importance of the sterochemistry of the $Fe(CO)_3$ group for the stabilisation of a β-carbenium ion. Finally, our results must be compared with the acid promoted rearrangement of epoxides of norbornadienes XII. In this case, the hypothetical hydroxynortricyclyl cationic intermediates XIII undergo Grob fragmentations [19] more rapidly than nucleophile quenching. The bicyclic aldehydes XIV thus formed may then equilibrate with the bicyclic ethers XV via [3,3]-sigmatropic rearrangements



(XII) (XIII) (XIV) (XV)

[20]. Our results suggest that an intermediate of type XIII or the conjugate base of IX′ generated by protonation of II does not undergo the Grob fragmentation probably because the positive charge is highly delocalised by the $Fe(CO)_3$ group (contribution of limit structure IX).

Crystal and molecular structures of $(C_9H_{10}O)Fe(CO)_3$ (II), $(C_9H_9ClO)Fe(CO)_3$ (VIII) and $(C_{10}H_{14}O_2)Fe(CO)_3$ (X)

X-ray measurements were carried out with a Syntex $P2_1$ automatic four-circle diffractometer. The crystal data and the method used are summarised in Table 4.

The crystal forms were accurately measured as before [13] and used to correct the intensities for absorption. The computer programs used for the data reduction and structure analyses of II and X were taken from the "X-RAY 72" program system [21]. Scattering factors for the neutral non-hydrogen atoms were taken from Cromer and Mann [22], for hydrogen atoms from Stewart et al. [23], and anomalous dispersion coëfficients for Fe from Cromer [24]. The structures of II and X were solved by Patterson and Fourier methods and that of VIII by direct methods (program MULTAN [26]).

Complex II: during the measurements, the intensities of the check reflections decreased to 40% of their initial values and were corrected accordingly. However the number of observed reflections and the quality of the collected data did not allow the determination of the hydrogen atom positions. The unit cell contains two crystallographically non-equivalent molecules which are referred to as A and B in subsequent tables. The final positional and thermal parameters are listed in Table 5 *, calculated bond lengths and angles in Tables 7 and 8 and the equations for several least-squares planes and some dihedral angles in Table 9. A view of the molecular structure is given in Fig. 1.

Complex VIII: Crystallisation from n-hexane (or other hydrocarbons) gave crystals of poor quality. Despite this fact, a crystal structure determination was

* Lists of observed and calculated structure factors are available on request.

TABLE 4

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND REFINEMENT

	Complex II	Complex VIII	Complex X
Formula	$C_{12}H_{10}O_4Fe$	$C_{12}H_9ClO_4Fe$	$C_{13}H_{14}O_5Fe$
Molecular weight	274.05	308.5	305.62
Dimensions (mm)	0.11 × 0.36 × 0.42	0.19 × 0.35 × 0.38	0.21 × 0.26 × 0.32
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	7.620(2)	11.505(1)	9.158(1)
b (Å)	13.950(2)	12.507(1)	12.114(2)
c (Å)	21.602(3)	35.596(3)	12.243(2)
β (°)			107.71(3)
V (Å^3)	2296	5122	1294
Z	8	16	4
d_{calcd} (g/cm^3)	1.585	1.59	1.57
d_{obsd} (g/cm^3)	1.59(1)	1.60(1)	1.57(1)
F_{000}	1040	2496	632
Space group	$P2_12_12_1$	$Pbca$	$P2_1/c$
Systematic absences	$h\ 0\ 0$: $h = 2n + 1$, $0\ k\ 0$: $k = 2n + 1$, $0\ 0\ l$: $l = 2n + 1$	$0\ k\ l$: $k = 2n + 1$, $h\ 0\ l$: $l = 2n + 1$, $h\ k\ 0$: $h = 2n + 1$	$0\ k\ 0$: $k = 2n + 1$, $h\ 0\ l$: $l = 2n + 1$, $h\ k\ l$: no conditions
Radiation	Mo-K_α(λ = 0.71069 Å), Nb filtered	same	same
μ (cm^{-1})	13.47	12.4	12.1
Scan method	2θ—θ	same	same
Background from	Scan profile interpretation [25]	same	same
(sin θ/λ_{max})	0.54	0.54	0.596
Data collected	$+h$, $+k$, $+l$	$+h$, $+k$, $+l$	$+h$, $+k$, $\pm l$
Number of unique reflections	1755	3380	2296
Number of reflections < 3σ	262	1201	578
Number of observations/ Number of variables	5.7	7.0	7.0
Structure solution	Patterson and Fourier	MULTAN [26] and Fourier	Patterson and Fourier
Refinement method	Block diagonal least-squares	same	same
Function minimised	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	same	same
w	$1/\sigma^2$	same	same
R	0.050	0.081	0.027
R_w	0.057	0.110	0.030
Goodness of fit	3.0	5.7	1.44

attempted. Solution of the structure by direct methods allows us to confirm that the iron tricarbonyl group is in the *endo* position with respect to the roof-shaped ligand and that the Cl atom is in the *exo* position (Fig. 2). The poor quality of the measurements led us to abandon further refinement at R = 0.081 when we were sure of the configuration. For this reason the molecular dimensions will not be discussed in detail.

Complex X: All hydrogen atoms were found from a difference synthesis after preliminary refinement to R = 0.051. The final positional and thermal parameters are listed in Table 6, calculated bond lengths and angles in Tables 10 and 11 and the equations for several least-squares planes and some dihedral angles in Table 12. A view of the molecular structure prepared by the program ORTEP [27] is given in Fig. 3. All numbering schemes of the ligands are identical with those used for nomenclature purposes.

TABLE 5

POSITIONAL AND THERMAL PARAMETERS FOR II[a]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(A)[b]	0.0992(2)	0.2629(1)	0.22841(7)	0.0330(7)	0.0413(8)	0.0353(8)	0.0016(7)	0.0003(8)	−0.0005(8)
C(1A)	0.338(1)	0.0872(7)	0.1760(5)	0.049(7)	0.044(7)	0.035(7)	0.005(6)	0.003(6)	−0.005(6)
C(2A)	0.490(1)	0.0389(8)	0.2119(5)	0.037(7)	0.056(8)	0.046(8)	0.009(6)	0.005(6)	0.004(6)
C(4A)	0.598(1)	0.1162(8)	0.2348(6)	0.027(6)	0.057(7)	0.069(9)	0.004(6)	0.000(7)	0.009(7)
C(5A)	0.509(1)	0.2101(8)	0.2104(5)	0.032(6)	0.058(7)	0.035(7)	−0.011(6)	−0.002(5)	0.004(6)
C(6A)	0.346(1)	0.2098(7)	0.2510(5)	0.034(6)	0.037(7)	0.047(7)	0.002(5)	−0.010(5)	0.009(6)
C(7A)	0.238(1)	0.1367(7)	0.2309(5)	0.033(6)	0.036(6)	0.030(6)	0.000(5)	0.003(5)	0.014(6)
C(8A)	0.436(2)	0.1746(7)	0.1478(5)	0.049(7)	0.040(6)	0.043(7)	−0.006(6)	0.001(6)	0.000(5)
C(9A)	0.071(1)	0.1176(7)	0.2595(5)	0.040(7)	0.040(6)	0.060(7)	0.005(6)	0.004(6)	0.018(5)
C(10A)	0.289(2)	0.2691(9)	0.3016(5)	0.045(7)	0.067(8)	0.045(7)	0.002(7)	−0.011(6)	−0.007(7)
C(11A)	−0.070(2)	0.3065(9)	0.2786(6)	0.052(8)	0.078(9)	0.044(8)	0.002(7)	0.000(8)	−0.005(7)
C(12A)	0.174(2)	0.3724(9)	0.1964(5)	0.050(8)	0.046(7)	0.049(8)	−0.002(6)	0.012(6)	−0.017(6)
C(13A)	−0.022(2)	0.2332(8)	0.1598(6)	0.052(7)	0.054(7)	0.045(8)	−0.005(6)	−0.005(6)	0.000(7)
O(1A)	−0.180(1)	0.3349(7)	0.3088(4)	0.069(7)	0.129(9)	0.065(7)	0.017(7)	0.030(6)	−0.019(6)
O(2A)	0.219(1)	0.4444(6)	0.1745(4)	0.087(7)	0.061(6)	0.076(7)	−0.011(6)	0.020(6)	0.002(5)
O(3A)	0.660(1)	0.0526(6)	0.1867(4)	0.044(5)	0.063(5)	0.070(6)	0.017(4)	0.007(5)	0.003(5)
O(4A)	−0.096(1)	0.2176(6)	0.1154(4)	0.076(6)	0.083(6)	0.053(5)	−0.004(6)	−0.017(5)	−0.013(5)
Fe(B)	0.0530(2)	0.0186(1)	−0.04119(7)	0.0411(8)	0.0335(7)	0.0386(8)	−0.0017(8)	−0.0089(8)	0.0023(8)
C(1B)	0.295(2)	−0.1510(7)	0.0180(5)	0.037(6)	0.031(6)	0.050(8)	0.010(5)	−0.010(6)	0.001(5)
C(2B)	0.444(2)	−0.1337(7)	0.0661(5)	0.034(7)	0.035(6)	0.066(8)	0.012(6)	−0.005(6)	0.003(6)
C(4B)	0.550(1)	−0.0564(7)	0.0421(5)	0.028(5)	0.042(6)	0.047(7)	0.010(5)	0.003(6)	−0.002(6)
C(5B)	0.466(1)	−0.0305(8)	−0.0216(5)	0.032(6)	0.048(6)	0.051(7)	0.013(6)	0.003(6)	0.000(6)
C(6B)	0.294(1)	0.0175(8)	0.0031(4)	0.037(6)	0.046(7)	0.027(6)	−0.007(6)	−0.012(5)	0.003(6)
C(7B)	0.189(1)	−0.0572(7)	0.0267(5)	0.035(6)	0.037(6)	0.025(6)	−0.007(5)	−0.008(5)	0.001(5)
C(8B)	0.395(1)	−0.1284(7)	−0.0443(5)	0.046(7)	0.037(6)	0.047(7)	0.002(5)	0.007(7)	−0.012(6)
C(9B)	0.019(1)	−0.0366(8)	0.0523(5)	0.031(6)	0.065(7)	0.037(7)	0.002(5)	−0.009(5)	0.020(6)
C(10B)	0.232(2)	0.1139(7)	0.0051(6)	0.042(7)	0.032(7)	0.069(9)	−0.003(6)	−0.024(7)	0.001(6)
C(11B)	−0.120(2)	0.1025(8)	−0.0321(6)	0.061(8)	0.036(7)	0.061(8)	−0.004(6)	−0.025(7)	0.010(6)
C(12B)	−0.061(2)	−0.0825(7)	−0.0744(5)	0.047(7)	0.030(6)	0.039(7)	0.008(6)	−0.007(6)	0.006(5)
C(13B)	0.142(2)	0.0502(7)	−0.1149(6)	0.076(9)	0.043(7)	0.043(8)	−0.005(6)	−0.013(7)	0.003(6)
O(1B)	−0.236(1)	0.1558(6)	−0.0273(4)	0.075(7)	0.052(6)	0.088(7)	0.022(5)	−0.008(6)	0.001(5)
O(2B)	−0.131(1)	−0.1426(5)	−0.0961(4)	0.086(7)	0.040(5)	0.073(6)	−0.024(5)	−0.013(5)	−0.010(5)
O(3B)	0.620(1)	−0.1528(5)	0.0446(4)	0.040(5)	0.071(6)	0.060(6)	0.014(4)	−0.002(4)	−0.005(5)
O(4B)	0.205(1)	0.0709(6)	−0.1614(4)	0.105(8)	0.069(6)	0.046(6)	−0.011(6)	0.008(6)	0.013(5)

[a] The temperature factor has the form e^{-T} where $T = 2\pi^2\Sigma h_i h_j U_{ij} a_i^{\star} a_j^{\star}$. [b] A and B refer to the two crystallographically non-equivalent molecules.

TABLE 6

POSITIONAL AND THERMAL PARAMETERS FOR X[a]

Atom	X	Y	Z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.3809(3)	0.5544(2)	0.1538(2)	0.028(1)	0.035(1)	0.031(1)	0.002(1)	0.012(1)	0.004(1)
C(2)	0.3517(3)	0.4316(2)	0.1765(2)	0.027(1)	0.031(1)	0.041(1)	0.003(1)	0.012(1)	−0.003(1)
C(3)	0.4213(3)	0.4211(2)	0.3074(2)	0.034(1)	0.034(1)	0.043(1)	0.006(1)	0.013(1)	0.008(1)
C(4)	0.4796(3)	0.5380(2)	0.3464(2)	0.025(1)	0.044(1)	0.032(1)	0.001(1)	0.002(1)	0.000(1)
C(5)	0.3478(3)	0.6188(2)	0.3256(2)	0.025(1)	0.028(1)	0.038(1)	−0.005(1)	0.008(1)	−0.005(1)
C(6)	0.2865(3)	0.6298(2)	0.2056(2)	0.026(1)	0.027(1)	0.041(1)	−0.003(1)	0.010(1)	0.003(1)
C(7)	0.5383(3)	0.5730(2)	0.2453(2)	0.024(1)	0.038(2)	0.050(2)	−0.003(1)	0.014(1)	−0.002(1)
C(8)	0.2820(3)	0.6807(2)	0.3970(2)	0.034(1)	0.041(2)	0.046(2)	−0.002(1)	0.011(1)	−0.010(1)
C(9)	0.1614(3)	0.7019(2)	0.1588(2)	0.038(1)	0.030(1)	0.048(2)	0.003(1)	0.012(1)	0.005(1)
C(10)	0.3514(4)	0.3276(3)	0.0112(2)	0.052(2)	0.056(2)	0.044(2)	0.008(2)	0.016(2)	−0.010(1)
C(11)	−0.0033(3)	0.5053(2)	0.1638(2)	0.027(1)	0.039(1)	0.047(1)	0.006(1)	0.013(1)	−0.001(1)
C(12)	0.1097(3)	0.4879(2)	0.3798(2)	0.037(1)	0.048(2)	0.047(2)	0.000(1)	0.017(1)	−0.003(1)
C(13)	−0.0399(3)	0.6770(2)	0.2922(2)	0.034(1)	0.038(1)	0.062(2)	−0.006(1)	0.014(1)	−0.010(1)
Fe(1)	0.11004(3)	0.59140(3)	0.27577(3)	0.0236(1)	0.0307(2)	0.0393(2)	−0.0002(2)	0.0104(1)	−0.0047(2)
O(1)	0.6629(2)	0.5116(2)	0.2324(2)	0.026(1)	0.060(1)	0.066(1)	0.003(1)	0.018(1)	−0.006(1)
O(2)	0.4344(2)	0.3582(1)	0.1248(1)	0.037(1)	0.044(1)	0.046(1)	0.0108(8)	0.0113(8)	−0.0098(8)
O(3)	−0.0818(2)	0.4503(2)	0.0941(2)	0.041(1)	0.061(1)	0.064(1)	−0.005(1)	0.001(1)	−0.024(1)
O(4)	0.1056(3)	0.4226(2)	0.4461(2)	0.081(2)	0.073(1)	0.077(1)	0.003(1)	0.040(1)	0.027(1)
O(5)	−0.1350(2)	0.7334(2)	0.3020(2)	0.051(1)	0.053(1)	0.136(2)	0.011(1)	0.041(1)	−0.023(1)
H(1)	0.372(2)	0.570(2)	0.076(2)	0.025(6)					
H(2)	0.244(3)	0.412(2)	0.149(2)	0.027(6)					
H(3N)	0.347(3)	0.396(2)	0.339(2)	0.048(7)					
H(3X)	0.507(3)	0.370(2)	0.324(2)	0.026(6)					
H(4)	0.556(3)	0.541(2)	0.419(2)	0.042(7)					
H(7)	0.568(3)	0.647(2)	0.253(2)	0.032(6)					
H(8E)	0.306(3)	0.664(2)	0.479(2)	0.041(7)					
H(8Z)	0.257(3)	0.752(2)	0.377(2)	0.048(8)					
H(9E)	0.108(3)	0.697(2)	0.077(2)	0.041(7)					
H(9Z)	0.163(3)	0.775(2)	0.192(2)	0.041(7)					
H(10)	0.634(3)	0.457(2)	0.204(2)	0.05(1)					
H(100)	0.250(4)	0.296(2)	0.003(2)	0.08(1)					
H(101)	0.325(4)	0.394(3)	−0.038(3)	0.10(1)					
H(102)	0.417(3)	0.281(2)	−0.010(2)	0.062(9)					

[a] The temperature factor has the form e^{-T} where $T = 2\pi^2 \Sigma h_i h_j U_{ij} a_i^{\star} a_j^{\star}$ for anisotropic atoms and $T = 8\pi^2 U \sin^2\theta/\lambda^2$ for isotropic atoms.

TABLE 7

DISTANCES FOR $(C_9H_{10}O)Fe(CO)_3$ (II)

Atoms	Distance (Å)	
	Molecule A [a]	Molecule B
Fe—C(6)	2.08(1)	2.06(1)
Fe—C(7)	2.07(1)	2.08(1)
Fe—C(9)	2.14(1)	2.17(1)
Fe—C(10)	2.15(1)	2.14(1)
Fe—C(11)	1.77(1)	1.78(1)
Fe—C(12)	1.75(1)	1.75(1)
Fe—C(13)	1.79(1)	1.79(1)
C(11)—O(1)	1.16(2)	1.15(2)
C(12)—O(2)	1.17(2)	1.18(2)
C(13)—O(4)	1.13(2)	1.12(2)
C(1)—C(2)	1.57(2)	1.55(2)
C(1)—C(7)	1.55(1)	1.55(1)
C(1)—C(8)	1.56(2)	1.59(1)
C(2)—C(4)	1.45(2)	1.44(2)
C(4)—C(5)	1.56(2)	1.56(1)
C(5)—C(6)	1.52(1)	1.56(1)
C(5)—C(8)	1.57(2)	1.55(1)
C(6)—C(7)	1.41(1)	1.42(1)
C(6)—C(10)	1.44(2)	1.42(2)
C(7)—C(9)	1.43(2)	1.43(1)
C(2)—O(3)	1.43(1)	1.45(1)
C(4)—O(3)	1.45(2)	1.44(1)

[a] A and B are the two crystallographically non-equivalent molecules.

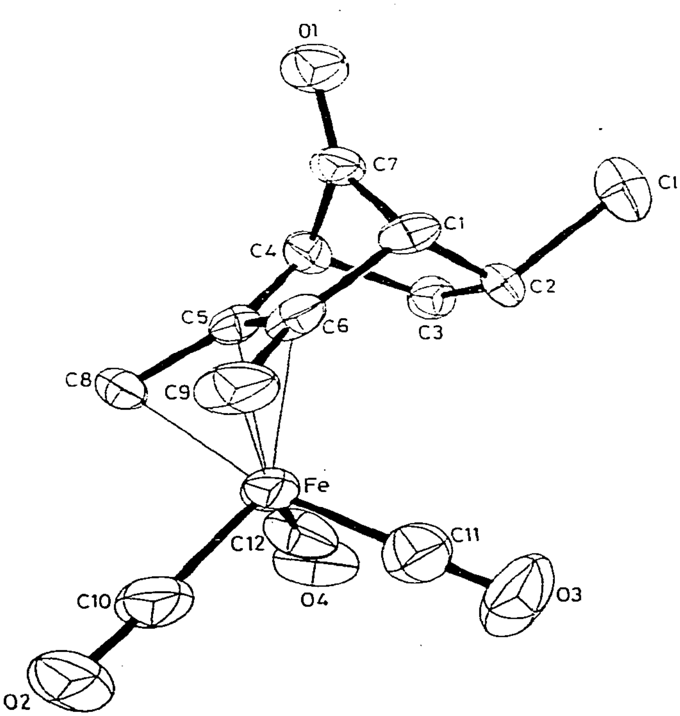


Fig. 2. A perspective view of the molecular structure of $(C_9H_9ClO)Fe(CO)_3$ (VIII).

TABLE 8

BOND ANGLES FOR $(C_9H_{10}O)Fe(CO)_3$ (II)

Atoms	Angle (°)	
	Molecule A	Molecule B
C(11)—Fe—C(12)	100.0(6)	101.4(6)
C(11)—Fe—C(13)	102.2(6)	101.8(6)
C(12)—Fe—C(13)	91.9(6)	91.2(6)
Fe—C(11)—O(1)	179.1(12)	179.4(12)
Fe—C(12)—O(2)	178.1(12)	177.3(13)
Fe—C(13)—O(4)	177.5(12)	178.5(11)
C(2)—C(1)—C(7)	99.4(9)	100.2(8)
C(2)—C(1)—C(8)	100.4(9)	101.3(8)
C(7)—C(1)—C(8)	101.2(9)	100.6(8)
C(1)—C(2)—C(4)	105.6(9)	106.0(8)
C(2)—C(4)—C(5)	105.6(9)	105.8(9)
C(4)—C(5)—C(6)	99.5(8)	98.6(7)
C(4)—C(5)—C(8)	100.5(9)	102.1(7)
C(6)—C(5)—C(8)	101.7(9)	100.8(7)
C(5)—C(6)—C(7)	107.1(9)	106.2(9)
C(5)—C(6)—C(9)	132.7(10)	133.9(9)
C(7)—C(6)—C(9)	120.1(10)	119.8(10)
C(1)—C(7)—C(6)	106.5(9)	106.5(9)
C(1)—C(7)—C(10)	132.5(10)	133.6(9)
C(6)—C(7)—C(10)	121.0(10)	119.9(10)
C(1)—C(8)—C(5)	94.5(8)	94.1(7)
C(1)—C(2)—O(3)	115.2(9)	115.4(9)
C(4)—C(2)—O(3)	60.2(8)	59.6(7)
C(2)—C(4)—O(3)	59.2(7)	60.6(7)
C(5)—C(4)—O(3)	115.0(9)	113.8(9)
C(2)—O(3)—C(4)	60.5(8)	59.8(7)
C(7)—Fe—C(10)	39.7(4)	39.2(4)
C(6)—Fe—C(7)	39.7(4)	40.0(4)
C(6)—Fe—C(9)	39.6(4)	39.6(4)

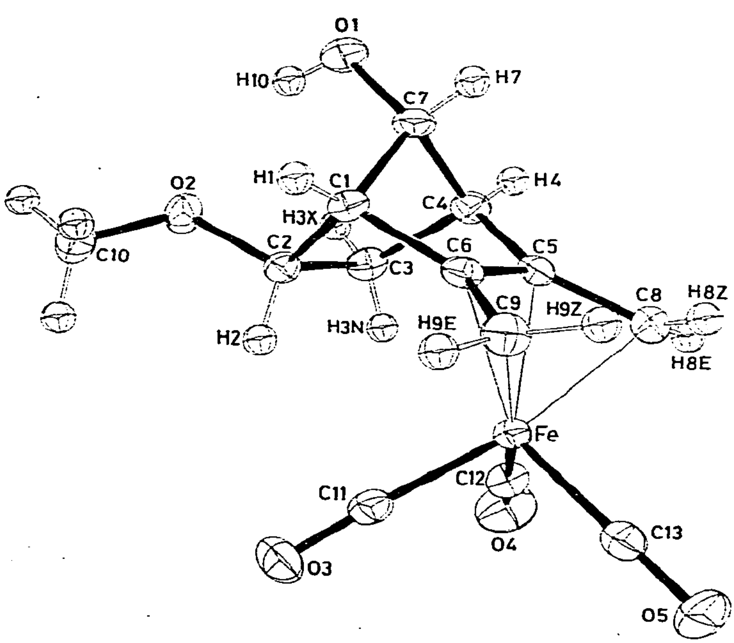


Fig. 3. A perspective view of the molecular structure of $(C_{10}H_{14}O_2)Fe(CO)_3$, (X).

Discussion

The structures are composed of discrete monomeric molecules and all intermolecular contacts are equal to or greater than the sum of normal Van der Waals radii.

$(C_9H_{10}O)Fe(CO)_3$ (II): there is essentially mirror symmetry for the whole molecule, with mirror plane I (Table 9) passing through the Fe atom, one CO group, C(8) and O(3). The $Fe(CO)_3$ group is in the *exo* position position and the epoxide ring has the same *exo* configuration as in the free ligand, the latter being based on NMR arguments [10]. Apart from the *cis*-butadiene system, coordination to Fe does not significantly affect the rest of the carbon skeleton as the plane defined by C(1), C(5) and C(8) bisects the dihedral angle between planes III and IV (Table 9).

$(C_{10}H_{14}O_2)Fe(CO)_2$ (X): the most interesting result for this derivative of II is

TABLE 9

WEIGHTED LEAST—SQUARES PLANES FOR $(C_9H_{10}O)Fe(CO)_3$ (II)

Plane	atoms defining plane [a]		Equation of mean plane
I	O(1), C(11), Fe, C(8), O(3)	A. [b]	$4.459X + 10.498Y + 6.529Z = 4.723$
		B.	$4.358X + 10.119Y + -8.273Z = 0.779$
II	C(7), C(6), C(9), C(10)	A.	$3.337X - 8.621Y + 14.103Z = 2.880$
		B.	$3.186X + 1.872Y + 19.421Z = 1.014$
III	C(1), C(5), C(6), C(7)	A.	$0.450X - 0.624Y + 0.898Z = 1.015$
		B.	$0.419X + 0.134Y + 0.898Z = 1.015$
IV	C(1), C(2), C(4), C(5)	A.	$-0.540X + 0.052Y + 0.840Z = 1.882$
		B.	$-0.574X + 0.679Y + 0.458Z = -2.541$
V	*m*, *m*′, C(12), C(13)	A.	$-5.220X + 3.352Y + 14.856Z = 3.256$
		B.	$-5.411X + 9.354Y + 4.639Z = -0.802$

Displacement of atoms from mean plane (Å)

		A	B			A	B
plane I	Fe	−0.028	−0.018	plane II	C(7)	−0.002	+0.001
	C(11)	+0.003	+0.004		C(6)	+0.002	−0.001
	O(3)	+0.012	+0.006		C(9)	−0.001	0.000
	C(8)	+0.014	+0.009		C(10)	+0.001	0.000
	O(1)	−0.002	+0.001				
plane III	C(1)	0.000	−0.002	plane IV	C(1)	+0.001	+0.006
	C(7)	−0.001	+0.002		C(2)	−0.001	−0.006
	C(6)	+0.001	−0.001		C(4)	+0.001	+0.009
	C(5)	0.000	+0.001		C(5)	−0.002	−0.009
plane V	*m*	+0.001	−0.012				
	m′	−0.001	+0.012				
	C(12)	+0.001	+0.009				
	C(13)	−0.001	−0.009				

Dihedral angle between planes, deg.

I—II	89.1(A)	88.9(B)	I—III	89.4(A)	89.5(B)	I—IV	88.2(A)	89.2(B)
I—V	89.5(A)	89.8(B)	II—III	1.0(A)	0.3(B)	II—V	90.0(A)	89.0(B)
III—IV	105.3(A)	105.2(B)	III—VI [c]	129.3(A)	126.9(B)	IV—VI	125.4(A)	128.1(B)

[a] *m* and *m*′ are the midpoints of the C(2)—C(9) and C(3)—C(8) bonds, respectively. [b] A and B are the two crystallographically non-equivalent molecules. [c] Plane VI is defined by atoms C(1), C(8) and C(5).

TABLE 10

DISTANCES FOR $(C_{10}H_{14}O_2)Fe(CO)_3$ (X)

Atoms	Distance (Å)	Atoms	Distance (Å)
Fe—C(5)	2.101(2)	C(10)—O(2)	1.417(3)
Fe—C(6)	2.101(3)	C(11)—O(3)	1.147(3)
Fe—C(8)	2.105(3)	C(12)—O(4)	1.143(3)
Fe—C(9)	2.115(3)	C(13)—O(5)	1.142(3)
Fe—C(11)	1.783(2)	C(1)—H(1)	0.95(2)
Fe—C(12)	1.788(3)	C(2)—H(2)	0.97(2)
Fe—C(13)	1.780(3)	C(3)—H(3*X*)	0.97(2)
C(1)—C(2)	1.552(3)	C(3)—H(3*N*)	0.93(3)
C(1)—C(6)	1.552(4)	C(4)—H(4)	0.95(2)
C(1)—C(7)	1.549(3)	C(7)—H(7)	0.93(2)
C(2)—C(3)	1.539(3)	C(8)—H(8*E*)	0.97(3)
C(2)—O(2)	1.433(3)	C(8)—H(8*Z*)	0.91(3)
C(3)—C(4)	1.537(3)	C(9)—H(9*E*)	0.97(2)
C(4)—C(5)	1.515(3)	C(9)—H(9*Z*)	0.97(2)
C(4)—C(7)	1.551(4)	C(10)—H(100)	0.97(3)
C(5)—C(6)	1.411(3)	C(10)—H(101)	0.99(3)
C(5)—C(8)	1.418(4)	C(10)—H(102)	0.92(3)
C(6)—C(9)	1.416(3)	O(1)—H(10)	0.75(2)
C(7)—O(1)	1.410(3)	O(2)···H(10)	2.16(1)
C(11)···H(2)	2.59(2)	C(12)···H(3*N*)	2.63(2)

TABLE 11

BOND ANGLES FOR $(C_{10}H_{14}O_2)Fe(CO)_3$ (X)

Atoms	Angle (°)	Atoms	Angle (°)
C(5)—Fe—C(6)	39.2(1)	H(1)—C(1)—C(2)	114(1)
C(5)—Fe—C(8)	39.4(1)	H(1)—C(1)—C(6)	114(1)
C(6)—Fe—C(9)	39.3(1)	H(1)—C(1)—C(7)	118(1)
C(11)—Fe—C(12)	90.6(1)	H(2)—C(2)—C(1)	113(1)
C(11)—Fe—C(13)	97.9(1)	H(2)—C(2)—C(3)	113(1)
C(12)—Fe—C(13)	99.1(1)	H(2)—C(2)—O(2)	108(1)
C(2)—C(1)—C(6)	110.5(2)	H(3X)—C(3)—C(2)	109(1)
C(2)—C(1)—C(7)	100.5(1)	H(3*X*)—C(3)—C(4)	110(1)
C(6)—C(1)—C(7)	97.6(1)	H(3*X*)—C(3)—H(3*N*)	110(2)
C(1)—C(2)—C(3)	103.0(1)	H(3*N*)—C(3)—C(2)	110(1)
C(1)—C(2)—O(2)	111.9(2)	H(3*N*)—C(3)—C(4)	114(1)
C(3)—C(2)—O(2)	107.5(2)	H(4)—C(4)—C(3)	114(1)
C(2)—C(3)—C(4)	104.0(2)	H(4)—C(4)—C(5)	117(2)
C(3)—C(4)—C(5)	111.1(2)	H(4)—C(4)—C(7)	114(2)
C(3)—C(4)—C(7)	100.1(2)	H(7)—C(7)—C(1)	113(1)
C(5)—C(4)—C(7)	98.1(2)	H(7)—C(7)—C(4)	110(1)
C(4)—C(5)—C(6)	106.3(2)	H(7)—C(7)—O(1)	107(1)
C(4)—C(5)—C(8)	134.8(2)	H(8*E*)—C(8)—H(8*Z*)	115(2)
C(6)—C(5)—C(8)	118.9(2)	H(8*E*)—C(8)—C(5)	121(1)
C(1)—C(6)—C(5)	106.3(2)	H(8*Z*)—C(8)—C(5)	117(2)
C(1)—C(6)—C(9)	133.9(2)	H(9*E*)—C(9)—H(9*Z*)	115(2)
C(5)—C(6)—C(9)	119.7(2)	H(9*E*)—C(9)—C(6)	118(1)
C(1)—C(7)—C(4)	93.7(2)	H(9*Z*)—C(9)—C(6)	119(1)
C(1)—C(7)—O(1)	116.6(2)	H(100)—C(10)—O(2)	115(1)
C(4)—C(7)—O(1)	115.7(2)	H(101)—C(10)—O(2)	109(2)
Fe—C(11)—O(3)	176.7(3)	H(102)—C(10)—O(2)	104(1)
Fe—C(12)—O(4)	178.2(3)	H(100)—C(10)—H(101)	102(3)
Fe—C(13)—O(5)	178.7(3)	H(100)—C(10)—H(102)	114(3)
C(2)—O(2)—C(10)	113.4(2)	H(101)—C(10)—H(102)	113(3)
O(2)···H(10)—O(1)	145(3)	H(10)—O(1)—C(7)	134(2)

TABLE 12

LEAST-SQUARES PLANES FOR $(C_{10}H_{14}O_2)Fe(CO)_3$ (X)

Plane	Atoms defining the plane [a]	Equation of mean plane
I	Fe, C(7), C(13), O(5), *n*	$0.750X - 0.822Y + 11.291Z = 2.711$
II	C(11), C(12), *m*, *m'*	$-6.381X + 8.563Y + 4.018Z = 5.005$
III	C(5), C(6), C(8), C(9)	$6.072X + 9.066Y - 2.270Z = 6.982$
IV	C(1), C(4), C(5), C(6)	$6.006X + 9.144Y - 2.279Y = 7.008$
V	H(1), C(1), C(7), C(4), H(4)	$-2.734X + 11.480Y + 2.427Z = 5.704$

Displacement of atoms from mean plane (Å)

Plane I		Plane II [b]		Plane IV		Plane V	
Fe	−0.001	C(11)	0.001	C(1)	−0.002	H(1)	0.007
C(7)	−0.008	C(12)	−0.001	C(4)	0.002	C(1)	−0.007
C(13)	0.002	*m*	0.001	C(5)	−0.003	C(7)	−0.003
O(5)	−0.005	*m'*	−0.001	C(6)	0.003	C(4)	0.002
n	0.012					H(4)	0.002

Dihedral angle between planes (°) [c]

I—II	89.0	II—III	86.0	III—IX	45	V—X	121.2
I—III	88.8	III—IV	0.6	IV—V	121.4	V—XI	122.4
I—IV	89.0	III—VI	13	IV—X	117.4	X—XI	1.2
I—V	88.6	III—VII	42	IV—XI	116.3		
I—X	89	III—VIII	11				
I—XI	89						

[a] *n*, *m* and *m'* are the midpoints of the bonds C(5)—C(6), C(5)—C(8) and C(6)—C(9), respectively. [b] Plane III: same displacements. [c] Plane VI is defined by C(5), C(8), H(8*E*); VII by C(5), C(8), H(8*Z*); VIII by C(6), C(9), H(9*E*); IX by C(6), C(9), H(9*Z*); X by C(2), C(3), C(4); XI by C(1), C(2), C(3).

that the $Fe(CO)_3$ group is now in the *endo* position with respect to the roof-shaped ligand. The methoxy group is in the *exo* position and is linked intramolecularly to the hydroxyl group, the O(2)···H(10) distance of 2.16(1) Å being typical for a hydrogen bond [28]. The *cis*-butadiene carbon chain is planar but H(7) atoms deviate from the diene plane away from the metal by 42 and 45° (for H(8*Z*) and H(9*Z*), respectively), whereas H(*E*) atoms deviate by 11 and 13° towards the metal. Similar deviations have been found and discussed elsewhere [29] for several *exo*-1,3-dieneiron tricarbonyl complexes.

The following features are common to the three structures: the arrangement of ligands about the iron atom is approximately tetragonal pyramidal. Four coordination sites are occupied by 2 CO and the midpoints of the outer C—C bonds of the *cis*-butadiene system. The apex-to-base angles are ca. 100° for the carbonyl groups and 111° for the C—C bond midpoints. The basal angles are 92, 94 and 64°, the small angle being that subtended by the two outer C—C bonds of the diene. The diene plane is perpendicular to the basal plane and the Fe atom lies 0.5 Å over it. The apical Fe—CO bond makes an angle of 8° with the normal to the basal plane. The sum of angles at each inner carbon atom of the bonded diene is 360.0(5)° and the difference Δ_2 between the average of the outer C—C distances and the inner C—C distance is not significantly greater than zero (0.006(4) Å for II and X). We have shown recently [13] from a comparison of Δ_2 values extended to 42 (1,3-diene)$Fe(CO)_3$ structures that, on the average, the three C—C distances have indeed to be considered as equal.

Experimental

All reactions were carried out in an argon atmosphere and the solvents were dried and degassed by standard methods [30]. Mass spectra at 70 eV were measured with a Hewlett—Packard GC-MS 5980; UV spectra in isooctane with a Beckman Acta V spectrophotometer; IR spectra in n-hexane with a Perkin—Elmer 577 spectrophotometer; ^{1}H (60 MHz) and ^{13}C (15.08 MHz; spectral width 3750 Hz, 4096 points) NMR spectra with a Bruker WP-60 spectrometer operating in the FT mode and using a deuterium lock. E. Manzer (Mikrolabor, ETH Zurich) carried out the microanalyses.

The preparation of 6,7-dimethylene-*exo*-3-oxatricyclo[3.2.1.0^{2,4}]octane I) has been described elsewhere [10]

Reaction of I with iron and ruthenium carbonyls. (a) $Fe_2(CO)_9$ (13 g, 35.7 mmol) and I (3.2 g, 23.8 mmol) were heated under reflux in THF/n-hexane (1/1, 250 ml) for 24 h. Acid alumina, activity grade I was then added to decompose the $Fe_3(CO)_{12}$ formed. After filtration and removal of solvent, the residue was taken up in THF and chromatographed on a 80 × 2 cm column packed with Florisil using THF/n-hexane (1/1) as eluent. The first fraction of eluate contained $Fe(CO)_5$ and the second yielded complex II after recrystallisation from n-pentane at −25°C (4.1 g; 15 mmol). Yield 63%. The same reaction in methanol gave II with a better yield (71%).

II: Yellow air stable crystals. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of an n-hexane solution at 0°C under argon. M.p. 102—103°C. Anal. Found: C, 52.49; H, 3.76. $C_{12}H_{10}O_4Fe$ calcd.: C, 52.59; H, 3.67%. Mass spectrum: 274 (1.5; M^+), 246 (12; $M^+ - CO$), 218 (27; $M^+ - 2\ CO$), 190 (37; $M^+ - 3\ CO$), 160 (17), 134 (15; 1^+), 105 (14), 91 (21), 84 (26), 56 (100%; Fe^+). IR spectrum: ν(CO) 2060 (A′(a)), 1983 (A′(2)), 1971 cm^{-1} (A″) (assigned according to Adams [31]), ν(C—O—C) 851 cm^{-1}. UV spectrum, λ_{max} in nm (ϵ in l mol^{-1} cm^{-1}): 289 (2405), 220 (14700).

(b) The reaction of $Fe_2(CO)_9$ (5 g, 13.7 mmol) and I (0.85 g, 6.3 mmol) in n-pentane (250 ml, room temperature, 3 days) yielded after chromatography and fractional crystallisation the complexes II (*exo*) and III (*endo*-isomer). Yields 8 and 1%.

III: Pale yellow air stable crystals. M.p. 124—125°C. Anal. Found: C, 52.48; H, 3.79. $C_{12}H_{10}O_4Fe$ calcd.: C, 52.59; H, 3.67%. Mass spectrum: 274 (8; M^+), 246 (61; $M^+ - CO$), 218 (100; $M^+ - 2\ CO$), 190 (11; $M^+ - 3\ CO$), 164 (99), 91 (62), 56 (26%; Fe^+). IR: ν(CO) 2059 (A′(1)), 1980 (A′(2)), 1968 cm^{-1} (A″). UV: 287 (2280), 220 (15400).

Irradiation (high pressure Hg lamp HPK 125; pyrex vessel) of I (16.4 mmol) and $Fe(CO)_5$ (82 mmol) in n-pentane (200 ml) at −70°C resulted mainly in the polymerisation of the ligand. The reaction of I with $Fe(CO)_3$(bza) [32] was unsuccessful as the diene did not displace benzalacetone (bza) from the complex to any significant extent.

(c) (cod)$Ru(CO)_3$ [11] (0.55 g, 1.87 mmol; cod = 1,5-cyclooctadiene) and I (0.5 g, 3.7 mmol) were heated under reflux in benzene (250 ml) for 15 h. After filtration and removal of solvent, the residue was taken up in diethyl ether and chromatographed on a 40 × 2 cm column packed with Florisil using n-hexane/ether (10/1) as eluent. The first fraction of yellow eluate contained a small amount of an unidentified product and the second fraction yielded complex IV after recrystallisation from n-pentane at −25°C (0.18 g, 0.56 mmol). Yield 15%.

IV: Pale yellow crystals. M.p. 105—106°C. Anal. Found: C, 45.18; H, 3.19. $C_{12}H_{10}O_4Ru$ calcd.: C, 45.14; H, 3.15%. Mass spectrum (peaks corresponding to ^{102}Ru): 320 (7; M^+), 292 (65; M^+ − CO), 264 (37; M^+ − 2 CO), 236 (100; M^+ − 3 CO), 204 (78), 102 (22; Ru^+). IR: ν(CO) 2076, 1995, 1982 cm^{-1}. UV: 272 (2706), 240 (sh) (4130), 220 (6500).

The reaction of I with $Ru_3(CO)_{12}$ in refluxing toluene gave a lower yield of complex IV.

Reaction of II with acids. (a) Gaseous HCl was bubbled for 5 min through a solution of II (0.8 g, 2.92 mmol) in diethyl ether (200 ml) at 0°C. The solution was then flushed with argon, neutralised with aqueous $NaHCO_3$ and the product extracted with diethyl ether. The extract was dried over $MgSO_4$ and chromatographed on a 40 × 2 cm column packed with Florisil. Elution with n-hexane/ether (10/1) brought down a single yellow band which yielded complex (0.77 g, 2.48 mmol) after recrystallisation in n-pentane at −25°C. Yield 85%. When carrying out the same reaction in dichloromethane, extensive decomposition was observed with formation of VI.

V: Pale yellow needles. M.p. 103—104°C. Anal. Found: C, 46.52; H, 3.47; Cl, 11.42. $C_{12}H_{11}ClO_4Fe$ calcd.: C, 46.41; H, 3.57; Cl, 11.41%. Mass spectrum: 310 (8; M^+), 282 (72; M^+ − CO), 254 (100; M^+ − 2 CO), 226 (62; M^+ − 3 CO), 190 (21), 162 (18), 56 (45%; Fe^+). IR: ν(CO) 2063 (A′(1)), 1987 (A′(2)), 1972 cm^{-1} (A″); ν(OH) 3555 cm^{-1} (in CCl_4). UV: 304 (1897), 220 (13000).

Elimination of the metal was obtained by oxidation of complex V (0.3 g, 0.97 mmol) in acetone (60 ml) with ammonium hexanitratocerate(IV) (1.98 mmol) for 30 min at room temperature. After removal of solvent, the ether extracts yielded ligand VI as a colorless oil. Its characteristics were identical to those reported by Vogel et al. [10b] for *exo*-2-chloro-5,6-dimethylene-*syn*-7-norbornanol (see Table 2 for its ^1H and ^{13}C NMR parameters in $CDCl_3$).

The ^1H NMR spectrum of a solution of II and HCl (molar ratio 1/2) in deuterated ether showed that the formation of V was essentially complete after 15 min at 30 ± 1°C. Under the same conditions, the endo isomer III did not react and slowly decomposed with formation of VI and VII [10b]. By contrast, the ruthenium complex IV (*exo*) reacted rapidly but the formed complex decomposed liberating an organic product whose ^1H NMR spectrum was identical to that of VI.

Reaction of II with DCl. (b) DCl (ca. 70 mmol) was transferred on a vacuum line into a frozen solution of II (1.8 mmol) in diethyl ether (60 ml) and the solution warmed to 0°C for 30 min. After filtration, the solvent and excess DCl were pumped off and CD_2Cl_2 distilled in. The resulting solution showed an ^1H NMR spectrum identical to that of V (Table 2), except for the disappearance of the hydroxyl resonance at 3.3 ppm and the loss of the related coupling constant J(H(7), OH). The isolated product showed bands at 2063, 1987, 1972 cm^{-1} (ν(CO)) and a band at 2640 cm^{-1} (in CCl_4) attributable to ν(OD); upon standing in air, the band at 2640 cm^{-1} decreased in intensity and a broad absorption band appeared around 3550 cm^{-1} (ν(OH)). After recrystallisation from (wet) pentane, a pale yellow complex was obtained (yield 80%) whose analytical and spectral data were identical to those of V.

Reaction of II with HSO_3F. (c) A mixture of CD_2Cl_2 and SO_2ClF (dried over P_4O_{10}) (1/1.5, 2 ml) was transferred on a vacuum line to a 10 mm NMR tube containing complex II (0.18 g). Pure SO_2ClF (ca. 1 ml) was then condensed into the upper part of the NMR tube and HSO_3F added under nitrogen ([HSO_3F]/[II] ca. 10/1) in such a manner as to keep it frozen in the upper part of the tube which was then sealed under vacuum. The upper part of the tube was gently warmed keeping the lower part at −110°C in order to allow slow mixing of the two solutions. The ^1H and ^{13}C NMR spectra of the resulting carbocation are described in Table 3.

The carbocation solution was vigorously mixed at −100°C with a saturated solution of $NaHCO_3$ in methanol. After removal of the solvent, the residue was extracted with diethyl ether/water and the ether extract washed with aqueous $NaHCO_3$, then water and dried over $MgSO_4$. After removal of solvent, the residue was taken up in diethyl ether and chromatographed on a 40 × 2 cm column packed with Florisil. Elution with n-hexane/ether (9/1) brought down one yellow band containing complex X which was recrystallised from n-pentane at −25°C (0.157 g, yield 78%).

X: Pale yellow crystals; single crystals were obtained by slow evaporation under argon of an n-hexane solution at 0°C. The crystal used for the X-ray measurements was protected from the air by a sealed glass capillary. M.p. 85–86°C. Anal. Found: C, 51.16; H, 4.61. $C_{13}H_{14}O_5Fe$ calcd.: C, 51.01; H, 4.61%. MS: 306 (9; M^+), 278 (68; $M^+ - CO$), 250 (100; $M^+ - 2\ CO$), 222 (48; $M^+ - 3\ CO$). IR: ν(CO) 2060, 1983, 1965 cm^{-1} (in hexane); ν(OH) 3485, $\nu(OCH_3)$ 1100 cm^{-1} (in CCl_4). UV: 310 (2010).

The organic ligand *exo*-2-methoxy-5,6-dimethylene-*syn*-7-norbornanol (XI) was obtained by oxidizing complex X (0.3 g, 0.98 mmol) in acetone (60 ml) with $(NH_4)_2Ce(NO_3)_6$ (3.2 mmol) for 30 min at room temperature. After removal of solvent, the residue was taken up in ether, washed with water, dried over $MgSO_4$ and filtered over Florisil. Distillation of the solvent left XI as a colourless oil (0.145 g). Yield 89%.

XI: Anal. Found: C, 71.52; H, 7.81. $C_{10}H_{14}O_2$ calcd.: C, 72.26; H, 8.49%. mass spectrum: 166 (4; M^+), 148 (9), 134 (38), 117 (10), 106 (39), 105 (91), 91 (100), 79 (32), 77 (31), 65 (14), 61 (20). IR (CCl_4): ν(OH) 3475, $\nu(OCH_3)$ 1083 cm^{-1}.

Oxidation of complex V to a norbornanone-7 complex (VIII). A solution of V (0.8 g, 2.57 mmol) in dichloromethane (5 ml) was added to a solution of CrO_3 (3.28 g, 33 mmol) and pyridine (5.2 g, 66 mmol) in dichloromethane (60 ml) and stirred for 9 days at room temperature. After removal of solvent, the residue was extracted with ether. The combined extracts were filtered, washed with 5% HCl, aqueous $NaHCO_3$, then water, dried over $MgSO_4$ and evaporated to dryness. The oily residue was chromatographed on silica gel with n-hexane/ether (20/1) as eluent. The first yellow band yielded the expected complex VIII after recrystallisation from n-pentane at −25°C (0.044 g, yield 5.5%.

VIII: yellow air stable crystals. M.p. 74–76°C. Anal. Found: C, 47.67; H, 2.99; Cl, 11.20. $C_{12}H_9ClO_4Fe$ calcd.: C, 46.72; H, 2.94; Cl, 11.49%. Mass spectrum: 308 (5; M^+), 280 (58; $M^+ - CO$), 252 (91; $M^+ - 2\ CO$), 224 (27; $M^+ - 3$

CO), 188 (91), 56 (100; Fe^+). IR: ν(CO) 2059, 1985, 1970 cm^{-1}; ν(C=O) 1800 cm^{-1}. UV: 273 (4250), 220 (10600).

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