Inorganica Chimica Acta, 35 (1979) 197–207

Iron and Ruthenium Carbonyls of 2,3,5,6-Tetrakis(methylene)bicyclo[2.2.2]octane. Crystal and Molecular Structure of $(C_{12}H_{14})Fe(CO)_3$

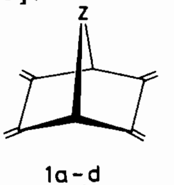
A. A. PINKERTON, G. CHAPUIS
Institute of Crystallography, Bâtiment des Sciences Physiques, Dorigny, Switzerland
P. VOGEL
Institute of Organic Chemistry, rue de la Barre 2, Lausanne, Switzerland
U. HÄNISCH, PH. NARBEL, T. BOSCHI* and R. ROULET**
Institute of Inorganic and Analytical Chemistry, Place du Château 3, University of Lausanne, Switzerland

Received October 26, 1978

The reaction of 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane (1a) with $Fe_2(CO)_9$ yields the two (η^4-1,3-diene)$Fe(CO)_3$ isomers (2: exo; 3: endo) together with two bimetallic isomers $(C_{12}H_{14})[Fe(CO)_3]_2$ (4: endo–exo; 5: diexo). The reaction of 1a with $Ru_3(CO)_{12}$ yields the endo-$(C_{12}H_{14})Ru(CO)_3$ (6) and endo, exo-$(C_{12}H_{14})[Ru(CO)_3]_2$ (7) complexes as the main products. The molecular structure of 3 has been determined by X-ray crystallography. The $Fe(CO)_3$ group is in the endo position with respect to the roof-shaped tetraene. The ligand is bound through one diene group to two basal positions of a tetragonal pyramidal $Fe(CO)_3L_2$ moiety. Hydrogen atom positions have been determined (final residual R = 0.029). The dimensions for the 1,3-butadieneirontricarbonyl system, as found in this and 41 other structures, are summarized and discussed statistically. In this study the weighted averages for all structures show the three C–C distances to be of equal length and the Fe–C (inner) distance to be shorter than the Fe–C (outer) distance. The deviations of H(Z) and H(E) atoms from the butadiene plane, as found in this and 6 other structures having an exocyclic unsubstituted 1,3-diene group, are also discussed. Neither thermal epimerization of iron nor epimerization catalyzed by H^+ were found for complexes 2 - 7 whose structures in solution were deduced from their ^1H and ^{13}C NMR data on the basis of the known structure of 3.

Introduction

The 2,3,5,6-tetrakis(methylene)bicycloalcanes 1a–d are highly reactive polyenes which have been prepared for the first time in our laboratory [1–3].



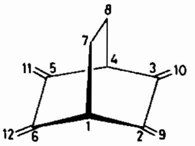
$Z = CH_2–CH_2$	1a	[1]
$Z = CH=CH$	1b	[1]
$Z = CH_2$	1c	[2]
$Z = O$	1d	[3]

1a – d

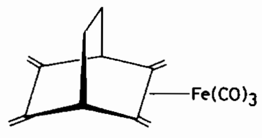
These roof-shaped molecules have two homoconjugated s-*cis*-butadiene groups and can be attacked by metal carbonyls on their exo or endo faces, thus leading to mixtures of exo and endo-$M(CO)_3$-diene complexes [4]. We report in this study the results of the reaction of 1a with iron and ruthenium carbonyls as well as the crystal structure of the endo-$(C_{12}H_{14})Fe(CO)_3$ complex (3) and a statistical comparison of the dimensions of the 1,3-butadieneirontricarbonyl system in 42 structures.

Reaction of 1a with Fe and Ru Carbonyls

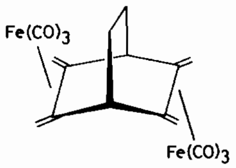
Upon treatment with $Fe_2(CO)_9$, the tetraene 1a yields the expected exo- and endo-tetrahapto-tricar-



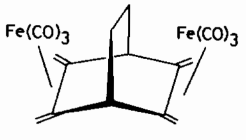
1a



2 (exo), 3 (endo)



4



5

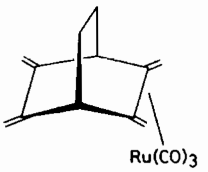
---

*Present address: Centro Chimica e Tecnologia Composti Metallorganici Elementi Transizione, Facoltà di Ingegneria, University of Padua, Italy.

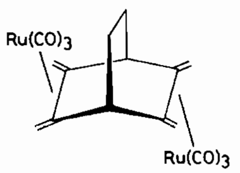
**Author to whom correspondence should be addressed.

TABLE 1. Summary of Crystal Data, Intensity Collection, and Refinement.

Formula	$(C_{12}H_{14})Fe(CO)_3$	Radiation	Mo-K_α, Nb filtered
	$C_{15}H_{14}O_3Fe$		λ = 0.71069 A
Mol. weight	297.92	μ, cm^{-1}	11.14
Dimensions, mm	0.14 × 0.22 × 0.31	Scan method	2θ–θ
Crystal class	Monoclinic	Background from	Scan profile
a, A	11.457(2)		interpretation [6]
b A	15.936(4)	$(\sin\theta/\lambda)_{max}$	0.54
c A	15.228(3)	Data collected	h, k > 0, ±l
β, deg	91.52(2)	No. of unique reflections	2198
V, A^3	2779	No. of reflections < 3σ	624
Z	8	No. of observations/No. of variables	9.6
d_{calcd}, g/cm^3	1.422		
d_{obsd}, g/cm^3	1.42(1)	Structure solution	Patterson and Fourier
F_{000}	1232	Refinement method	Block diagonal least-squares
Space group	I2/c	Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Systematic absences	h k l : h + k + l = 2n + 1	w	$1/\sigma^2$
	h 0 l : h = 2n + 1	R	0.029
	l = 2n + 1	R_w	0.027
		Goodness of fit	1.68



6



7

bonyliron complexes 2 and 3, together with the endo, exo- and the bis(exo)-bis(tricarbonyliron) isomer 4 and 5 (Scheme). The rather low global yield (54%) is due to partial polymerisation of the ligand during the synthesis. Better yields of 3 and 4 (80%) are obtained on displacing benzalacetone by 1a from (bza)$Fe(CO)_3$. The four complexes are yellow crystalline solids moderately stable (2, 3) or stable in the air (4, 5). They are thermally stable in degassed benzene up to its boiling point and no epimerization of iron could be detected in solutions containing a trace of acid (HCl). Upon treatment with $Ru_3(CO)_{12}$, 1a yields the endo-tetrahapto-tricarbonylruthenium complex 6, the endoexo-bis(tricarbonylruthenium) complex 7 and only traces of other isomers.

The molecular structure of 3 was determined to identify with certainty the stereochemistry of one tricarbonyliron isomer and to serve as a reference for the assignment of the spectroscopic data of all complexes. Highly valuable information about the geometry of the uncomplexed diene in 3 is also given by its molecular structure; this will be useful for interpreting the Diels–Alder reactivity differences observed between the free ligands 1a–d and their monometallic complexes [5].

Crystal Structure of $(C_{12}H_{14})Fe(CO)_3$

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

The non standard space group I2/c was chosen to allow β to be less than 120°. This setting may be derived from the standard setting C2/c by the transformation

$$\begin{pmatrix} \vec{a}_I \\ \vec{b}_I \\ \vec{c}_I \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \vec{a}_C \\ \vec{b}_C \\ \vec{c}_C \end{pmatrix}$$

The crystal was protected from the air by a sealed glass capillary. Its form was accurately measured as before [21] and used to correct the intensities for absorption. The computer programs used for the data reduction and structure analysis were taken from the 'X-RAY 72' program system [7]. Scattering factors for the neutral non-hydrogen atoms were taken from Cromer and Mann [8], for hydrogen atoms from Stewart *et al.* [9], and anomalous dispersion coefficients for Fe from Cromer [10]. The structures was solved by Patterson and Fourier methods. All hydrogen atoms were found from a difference synthesis after preliminary refinement to R = 0.073. Final refinement to R = 0.029 gave the positional and thermal parameters listed in Table II*.

---

*A list of observed and calculated structure factors is available on request.

TABLE II. Atomic Coordinates and Thermal Parameters (the e.s.d. of the last significant digit is given in parentheses). The temperature factor has the form e^{-T} when $T = 2\pi^2 \Sigma h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic atoms and $T = 8\pi^2 U \sin^2\theta/\lambda^2$ for isotropic atoms.

Atom	X	Y	Z	U11 (or U)	U22	U33	U12	U13	U23
C(1)	−0.1459(2)	0.4259(2)	0.1982(2)	0.045(2)	0.039(2)	0.062(2)	0.005(1)	−0.004(1)	−0.005(1)
C(2)	−0.1072(2)	0.3825(2)	0.2824(2)	0.033(1)	0.044(2)	0.046(2)	−0.007(1)	0.001(1)	−0.003(1)
C(3)	−0.0402(2)	0.3104(2)	0.2672(2)	0.042(1)	0.034(2)	0.050(2)	−0.007(1)	−0.001(1)	0.001(1)
C(4)	−0.0232(2)	0.2934(2)	0.1708(2)	0.052(2)	0.040(2)	0.054(2)	0.002(1)	−0.002(1)	−0.009(1)
C(5)	0.0285(2)	0.3696(2)	0.1273(2)	0.051(2)	0.058(2)	0.043(2)	−0.002(1)	−0.001(1)	0.000(1)
C(6)	−0.0415(2)	0.4452(2)	0.1436(2)	0.060(2)	0.041(2)	0.047(2)	−0.007(2)	−0.007(1)	0.004(2)
C(7)	−0.2208(3)	0.3605(2)	0.1468(2)	0.050(2)	0.066(2)	0.064(2)	0.000(2)	−0.011(2)	−0.004(2)
C(8)	−0.1485(3)	0.2808(2)	0.1312(3)	0.065(2)	0.057(2)	0.060(2)	−0.007(2)	−0.009(2)	−0.013(2)
C(9)	−0.1267(2)	0.4067(2)	0.3702(2)	0.041(1)	0.059(2)	0.061(2)	−0.004(2)	0.007(1)	−0.009(2)
C(10)	0.0038(3)	0.2648(2)	0.3407(2)	0.058(2)	0.048(2)	0.060(2)	−0.006(2)	0.002(2)	0.005(2)
C(11)	0.1230(3)	0.3657(3)	0.0794(3)	0.067(2)	0.098(3)	0.075(3)	0.007(2)	0.018(2)	0.016(2)
C(12)	−0.0211(4)	0.5217(2)	0.1137(2)	0.094(3)	0.064(3)	0.067(3)	−0.008(2)	0.003(2)	0.005(2)
C(13)	0.1907(2)	0.3694(2)	0.3028(2)	0.048(2)	0.045(2)	0.048(2)	−0.003(1)	−0.005(1)	0.000(1)
C(14)	0.0690(2)	0.5015(2)	0.3325(2)	0.041(1)	0.054(2)	0.063(2)	−0.007(1)	0.003(1)	−0.009(2)
C(15)	0.0891(2)	0.3839(2)	0.4630(2)	0.055(2)	0.073(2)	0.055(2)	−0.006(2)	0.001(1)	0.000(2)
FE(1)	0.05250(3)	0.39175(2)	0.34916(2)	0.0387(2)	0.0439(2)	0.0449(2)	−0.0032(2)	0.0005(1)	−0.0022(2)
O(1)	0.2796(2)	0.3550(1)	0.2746(1)	0.047(1)	0.090(2)	0.075(1)	0.010(1)	0.009(1)	−0.003(1)
O(2)	0.0793(2)	0.5724(1)	0.3220(2)	0.076(2)	0.047(1)	0.117(2)	−0.011(1)	0.007(1)	−0.009(1)
O(3)	0.1106(2)	0.3770(2)	0.5365(2)	0.101(2)	0.134(2)	0.049(1)	−0.008(2)	−0.005(1)	0.003(2)
H(1)	−0.188(2)	0.478(1)	0.209(1)	0.044(7)					
H(4)	0.027(2)	0.242(1)	0.161(2)	0.048(7)					
H(7E)	−0.246(2)	0.387(2)	0.094(2)	0.054(8)					
H(7Z)	−0.290(2)	0.350(2)	0.180(2)	0.067(9)					
H(8E)	−0.140(2)	0.267(2)	0.071(2)	0.08(1)					
H(8Z)	−0.185(2)	0.227(2)	0.162(2)	0.071(9)					
H(9E)	−0.158(2)	0.462(2)	0.382(2)	0.055(8)					
H(9Z)	−0.149(2)	0.366(2)	0.412(2)	0.052(8)					
H(10E)	0.064(2)	0.223(2)	0.329(2)	0.068(9)					
H(10Z)	−0.043(2)	0.258(2)	0.389(2)	0.058(9)					
H(11E)	0.169(3)	0.313(2)	0.074(2)	0.09(1)					
H(11Z)	0.157(2)	0.417(2)	0.054(2)	0.08(1)					
H(12E)	−0.071(3)	0.567(2)	0.127(2)	0.10(1)					
H(12Z)	0.049(2)	0.528(2)	0.079(2)	0.060(9)					

TABLE III. Bond Lengths (A) in *3* (the e.s.d. of the last significant digit is given in parentheses).

Fe(1)–C(2)	2.075(2)	Fe(1)–C(13)	1.787(3)
Fe(1)–C(3)	2.073(3)	Fe(1)–C(14)	1.777(3)
Fe(1)–C(9)	2.100(3)	Fe(1)–C(15)	1.777(3)
Fe(1)–C(10)	2.101(3)	C(7)–C(8)	1.538(5)
C(1)–C(2)	1.512(4)	C(4)–C(3)	1.510(4)
C(1)–C(6)	1.506(4)	C(4)–C(5)	1.512(4)
C(1)–C(7)	1.549(4)	C(4)–C(8)	1.556(4)
C(2)–C(3)	1.405(3)	C(5)–C(6)	1.471(4)
C(2)–C(9)	1.415(4)	C(5)–C(11)	1.322(5)
C(3)–C(10)	1.416(4)	C(6)–C(12)	1.325(5)
C(13)–O(1)	1.139(3)	C(14)–O(2)	1.148(4)
		C(15)–O(3)	1.145(4)
C(1)–H(1)	0.98(2)	C(4)–H(4)	1.01(2)
C(7)–H(7E)	0.95(3)	C(8)–H(8E)	0.94(3)
C(7)–H(7Z)	0.97(3)	C(8)–H(8Z)	1.07(3)
C(9)–H(9E)	0.97(3)	C(11)–H(11E)	0.99(3)
C(9)–H(9Z)	0.95(3)	C(11)–H(11Z)	0.99(3)
C(10)–H(10E)	0.98(3)	C(12)–H(12E)	0.95(3)
C(10)–H(10Z)	0.92(3)	C(12)–H(12Z)	0.98(3)

Calculated bond lengths and angles are reported in Table III and IV respectively. The equations for several least-squares planes and some dihedral angles are presented in Table V. A view of the molecular structure prepared by the program ORTEP [11] is given in Fig. 1, where the numbering scheme of the ligand is identical with that used for nomenclature purposes.

Discussion

The structure is composed of discrete monomeric $(C_{12}H_{14})Fe(CO)_3$ molecules. All intermolecular contacts are equal to or greater than the sum of normal Van der Waals radii.

There is essentially mirror symmetry for the whole molecule, with the mirror plane VII (Table V) passing through the Fe atom, one CO group and the midpoints of the bonds C(2)–C(3), C(7)–C(8) and C(5)–C(6). The whole $Fe(CO)_3$ group is in the 'endo' position with respect to the roof-shaped ligand.

TABLE IV. Bond Angles (°) in *3* (the e.s.d. of the last significant digit is given in parentheses).

C(2)–Fe(1)–C(3)	39.6(1)	C(13)–Fe(1)–C(14)	92.4(1)
C(2)–Fe(1)–C(9)	39.6(1)	C(13)–Fe(1)–C(15)	100.5(1)
C(3)–Fe(1)–C(10)	39.6(1)	C(14)–Fe(1)–C(15)	100.7(1)
Fe(1)–C(13)–O(1)	178.9(2)	Fe(1)–C(15)–O(3)	178.2(3)
Fe(1)–C(14)–O(2)	179.7(2)		
C(2)–C(1)–C(6)	110.0(2)	C(3)–C(4)–C(5)	110.2(2)
C(2)–C(1)–C(7)	105.5(2)	C(3)–C(4)–C(8)	105.0(2)
C(6)–C(1)–C(7)	107.2(2)	C(5)–C(4)–C(8)	107.5(2)
C(1)–C(2)–C(3)	112.6(2)	C(2)–C(3)–C(4)	113.0(2)
C(1)–C(2)–C(9)	128.8(2)	C(4)–C(3)–C(10)	128.6(2)
C(3)–C(2)–C(9)	118.6(2)	C(2)–C(3)–C(10)	118.3(3)
C(1)–C(6)–C(5)	111.8(2)	C(4)–C(5)–C(6)	111.2(2)
C(1)–C(6)–C(12)	121.8(3)	C(4)–C(5)–C(11)	122.6(3)
C(5)–C(6)–C(12)	126.4(3)	C(6)–C(5)–C(11)	126.1(3)
C(1)–C(7)–C(8)	109.9(2)	C(4)–C(8)–C(7)	109.2(3)
H(1)–C(1)–C(2)	113(1)	H(4)–C(4)–C(3)	112(1)
H(1)–C(1)–C(6)	109(1)	H(4)–C(4)–C(5)	111(1)
H(1)–C(1)–C(7)	113(1)	H(4)–C(4)–C(8)	111(1)
H(7E)–C(7)–H(7Z)	107(2)	H(8E)–C(8)–H(8Z)	107(2)
H(7E)–C(7)–C(1)	107(2)	H(8E)–C(8)–C(4)	107(2)
H(7E)–C(7)–C(8)	113(2)	H(8E)–C(8)–C(7)	114(2)
H(7Z)–C(7)–C(1)	108(2)	H(8Z)–C(8)–C(4)	108(1)
H(7Z)–C(7)–C(8)	113(2)	H(8Z)–C(8)–C(7)	112(1)
H(9E)–C(9)–H(9Z)	113(2)	H(10E)–C(10)–H(10Z)	119(2)
H(9E)–C(9)–C(2)	119(1)	H(10E)–C(10)–C(3)	116(2)
H(9Z)–C(9)–C(2)	120(2)	H(10Z)–C(10)–C(3)	119(2)
H(11E)–C(11)–H(11Z)	116(2)	H(12E)–C(12)–H(12Z)	123(2)
H(11E)–C(11)–C(5)	122(2)	H(12E)–C(12)–C(6)	121(2)
H(11Z)–C(11)–C(5)	121(2)	H(12Z)–C(12)–C(6)	116(2)

TABLE V. Least-squares Planes of *3*.

Plane	*Atoms Defining Plane*[a]	*Equation of Mean Plane*
I	C(1), C(2), C(3), C(4)	9.540 X + 8.809 Y + 0.146 Z = 2.389
II	C(2), C(3), C(9), C(10)	9.532 X + 8.842 Y – 0.275 Z = 2.285
III	a, b, C(13), C(14)	0.950 X – 2.392 Y + 14.964 Z = 3.835
IV	C(1), C(4), C(7), C(8)	–3.680 X – 6.099 Y + 13.316 Z = 0.575
V	C(1), C(4), C(5), C(6)	6.007 X + 2.965 Y + 12.437 Z = 2.854
VI	C(5), C(6), C(11), C(12)	6.265 X + 3.126 Y + 12.169 Z = 2.881
VII	O(3), C(15), Fe(1), c, d, e	–6.518 X + 12.821 Y + 2.824 Z = 5.594
VIII	C(1), C(5), C(6), C(12), H(12E), H(12Z)	6.035 X + 3.059 Y + 12.392 Z = 2.882
IX	C(4), C(5), C(6), C(11), H(11E), H(11Z)	6.028 X + 3.001 Y + 12.411 Z = 2.861

Displacement of Atoms from Mean Plane (Å)

Plane I	C(1)	0.000	Plane II	C(2)	–0.002	Plane III			a	–0.008
	C(2)	–0.001		C(3)	0.002				b	0.008
	C(3)	0.001		C(9)	0.001				C(13)	–0.007
	C(4)	0.000		C(10)	–0.001				C(14)	0.007
Plane IV	C(1)	0.004	Plane V	C(1)	–0.002	Plane VI			C(5)	0.002
	C(4)	–0.004		C(4)	0.002				C(6)	–0.002
	C(7)	–0.007		C(5)	–0.003				C(11)	–0.001
	C(8)	0.007		C(6)	0.003				C(12)	0.001
Plane VII	O(3)	0.034	c	–0.328		Plane VIII	C(1)	–0.003	C(12)	–0.005
	C(15)	0.055	d	0.114			C(5)	–0.002	H(12E)	–0.002
	Fe(11)	0.072	e	0.054			C(6)	0.009	H(12Z)	0.001

(continued on facing page)

TABLE V. *(continued)*

Plane IX	C(4)	0.000	C(11)	–0.037
	C(5)	0.000	H(11E)	0.020
	C(6)	0.007	H(11Z)	0.010

Dihedral Angle between Planes (°)

I–II	1.6;	I–IV	116.9;	I–V	124.5;	I–VII	88.6;	V–VIII	0.4
II–III	89.4;	II–VII	88.5;	V–VI	1.7;	IV–V	118.7;	V–IX	0.2
III–VII	90.0;	IV–VII	88.7;	V–VII	89.6;	VI–VII	89.2;	VI–VIII	1.4
								VI–IX	1.5

[a] a, b, c, d and e are the midpoints of the bonds C(2)–C(9), C(3)–C(10), C(2)–C(3), C(7)–C(8) and C(5)–C(6), respectively.

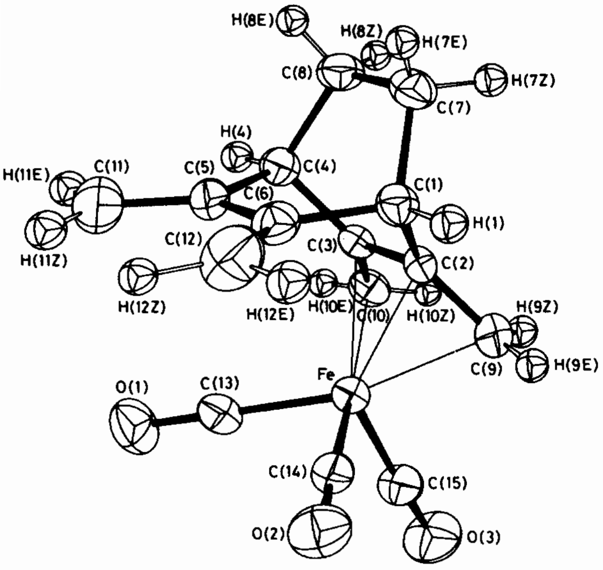


Fig. 1. Perspective view of the molecular structure of $(C_{12}H_{14})Fe(CO)_3$ (endo isomer, *3*).

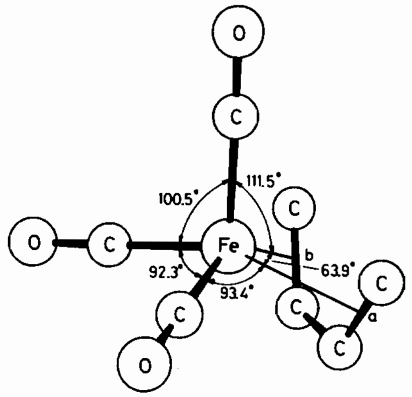


Fig. 2. Iron coordination polyhedron in *3*.

The arrangement of ligands about the iron atom is approximately tetragonal pyramidal (Fig. 2). Four coordination sites are occupied by 2 CO and the midpoints a and b of the exo C–C bonds of one s-*cis*-butadiene system, a-b-C(13)–C(14) defining the basal

TABLE VI. Comparison of (1,3-diene)$Fe(CO)_3$ Structures. Fe–C and C–C Distances.

Complex		Δ_1(Fe–C)[a]	Δ_2(C–C)[b]	Reference
$C_4H_4Ph_2Fe(CO)_3$		0.098(9)	0.010(12)	[13]
$[C_5H_7N_2Fe(CO)_3]^+$		0.120(2)	0.029(4)	[14]
$C_6H_6COFe(CO)_3$		0.075(10)	0.043(16)	[15]
$C_6H_7CNFe(CO)_3$	A	0.04(3)	0.08(4)	[16]
	B	0.04(3)	0.01(2)	[16]
$C_6H_8O_2Fe(CO)_3$	A	0.075(7)	0.011(12)	[17]
	B	0.086(7)	0.018(12)	[17]
$C_6H_8SO_2Fe(CO)_3$		0.012(4)	0.011(7)	[18]
$C_7H_{12}OFe(CO)_3$	A	0.067(4)	–0.004(7)	[19]
	B	0.080(4)	–0.010(8)	[19]
$C_8H_8Fe(CO)_3$		0.13(1)	0.00(2)	[20]
$C_8H_8[Fe(CO)_3]_2$	Fe_1	0.06(3)	0.003(5)	[20]
	Fe_2	0.12(3)	0.05(5)	[20]
$C_8H_8OFe_2(CO)_7$		0.077(3)	–0.013(5)	[21]

(continued overleaf)

TABLE VI. *(continued)*

Complex		Δ_1(Fe–C)[a]	Δ_2(C–C)[b]	Reference
$C_8H_8Br_2Fe(CO)_3$		0.077(9)	0.017(19)	[22]
$[C_8H_9Fe(CO)_3]_2$		0.056(3)	0.012(5)	[23]
$C_8H_9NOFe(CO)_3$		0.117(9)	0.067(15)	[24]
$C_8H_9NO_2Fe(CO)_3$		0.073(9)	0.013(16)	[25]
$C_8H_{11}NO_2Fe(CO)_3$		0.058(4)	0.001(9)	[26]
$C_9H_{10}OFe(CO)_3$		0.07(1)	0.006(4)	[27]
$C_9H_{12}[Fe(CO)_3]_2$		0.005(10)	0.00(2)	[28]
$(C_{10}H_8)_2Fe_4(CO)_{10}$		0.087(6)	0.068(11)	[29]
$C_{10}H_{10}[Fe(CO)_3]_2$		0.059(15)	0.06(3)	[30]
$C_{10}H_{10}CO[Fe(CO)_3]_2$		0.101(14)	–	[31]
$C_{10}H_{10}OFe(CO)_3$[c]		0.024(6)	0.023(7)	[32]
$C_{10}H_{10}O[Fe(CO)_3]_2$[c]	Fe_1	0.087(4)	−0.012(6)	[33]
	Fe_2	0.080(4)	−0.003(6)	[33]
$C_{10}H_{12}Fe(CO)_3$		0.070(6)	0.015(10)	[34]
$C_{10}H_{12}[Fe(CO)_3]_2$		0.071(11)	0.035(20)	[35]
$C_{10}H_{13}NO_3Fe(CO)_3$		0.072(4)	0.025(7)	[36]
$C_{10}H_{14}O_2Fe(CO)_3$[c]		0.009(3)	0.006(4)	[27]
$C_{11}H_{14}Fe(CO)_3$		0.083(2)	0.004(5)	[12]
$C_{12}H_{10}OFe_2(CO)_5$		0.049(3)	0.041(6)	[37]
$C_{12}H_{12}[Fe(CO)_3]_2$	Fe_1	0.073(3)	0.034(5)	[38]
	Fe_2	0.082(2)	0.016(5)	[38]
$C_{12}H_{12}Fe(CO)_3$[c]		0.038(2)	0.025(4)	[5]
$C_{12}H_{12}[Fe(CO)_3]_2$[c]	Fe_1	0.012(8)	0.028(12)	[39]
	Fe_2	0.023(7)	0.017(11)	[39]
$C_{12}H_{12}O[Fe(CO)_3]_2$		0.056(5)	0.017(7)	[40]
$C_{12}H_{14}Fe(CO)_3$		0.028(3)	0.010(4)	this work
$C_{12}H_{16}Fe(CO)_3$		0.106(10)	0.03(2)	[41]
$C_{13}H_{12}OFe(CO)_3$		0.045(6)	−0.018(10)	[42]
$C_{13}H_{16}N_2O_2Fe(CO)_3$		0.078(2)	0.006(4)	[43]
$C_{13}H_{17}N_2Fe(CO)_3$		0.086(2)	0.019(4)	[43]
$C_{14}H_{20}O_2Fe(CO)_3$		0.043(3)	0.017(6)	[44]
$C_{16}H_{14}[Fe(CO)_3]_2$	Fe_1	0.125(20)	0.00(4)	[45]
	Fe_2	0.09(2)	0.02(3)	[45]
$C_{16}H_{16}Fe(CO)_3$		0.05(2)	0.03(2)	[46]
$C_{16}H_{16}Fe(CO)_3$		0.093(15)	0.02(3)	[47]
$C_{20}H_{30}OFe(CO)_3$		0.08(1)	0.07(2)	[48]

[a] The diene is formally designated by $C_1{=}C_2{-}C_3{=}C_4$; Δ_1 is the difference in Å between the weighted average of ($Fe{-}C_1$) and ($Fe{-}C_4$) and the weighted average of ($Fe{-}C_2$) and ($Fe{-}C_3$). [b] Δ_2 is the difference in Å between the weighted average of ($C_1{-}C_2$) and ($C_3{-}C_4$) and $C_2{-}C_3$). The statistical formulas used here are the same as those used by Cotton *et al.* [12].:

$$\text{weighted estimate} = \sum_{i=1}^{N} (d_i/\sigma_i^2) / \sum_{i=1}^{N} (1/\sigma_i^2)$$

$$\text{e.s.d. for weighted estimate} = [1/\sum_{i=1}^{N} (1/\sigma_i^2)]^{1/2}$$

$$\text{e.s.d. on a difference} = [\sigma_1^2 + \sigma_2^2]^{1/2}$$

Here d_i is the ith distance with an esd σ_i and N is the number of distances to be averaged.

[c] Hereafter are listed the full names of complexes whose structure reports are still to be published. $C_9H_{10}OFe(CO)_3$: tetrahapto-6,7-bis(methylene)-exo-3-oxatricyclo[3.2.1.0^{2,4}]octane-exo-irontricarbonyl. $C_{10}H_{10}OFe(CO)_3$: tetrahapto-2,3,5,6-tetrakis-(methylene)-7-oxabicyclo[2.2.1]heptane-endo-irontricarbonyl. $C_{10}H_{10}O[Fe(CO)_3]_2$: bis(tetrahapto)-2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane-bis(exo-irontricarbonyl). $C_{10}H_{14}O_2Fe(CO)_3$: tetrahapto-5,6-bis(methylene)-exo-2-methoxy-syn-7-norbornanol-endo-irontricarbonyl. $C_{12}H_{12}Fe(CO)_3$: tetrahapto-5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene-exo-irontricarbonyl. $C_{12}H_{12}[Fe(CO)_3]_2$: bis(tetrahapto)-5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene-endo, exo-bis(irontricarbonyl).

TABLE VII. Comparison of (1,3-diene)Fe(CO)$_3$ Structures. Dihedral Angles at Terminal Carbon Atoms.[a]

Complex		α(H(E))[b]	α(H(Z))[c]	Reference
$C_8H_8OFe_2(CO)_7$		10	46	[21]
		14	42	
$C_{10}H_{10}OFe(CO)_3$		12	44	[32]
		13	42	
$C_{10}H_{10}O[Fe(CO)_3]_2$	Fe(1)	12	43	[33]
		17	40	
	Fe(2)	16	34	
		17	39	
$C_{10}H_{14}O_2Fe(CO)_3$		11	42	[27]
		13	45	
$C_{12}H_{12}Fe(CO)_3$		16	43	[5]
		17	41	
$C_{12}H_{12}[Fe(CO)_3]_2$	Fe(1)	13	49	[39]
		13	37	
	Fe(2)	9	42	
		18	41	
$C_{12}H_{14}Fe(CO)_3$		14	39	this work
		13	44	

[a] The list includes only 1,3-diene complexes having unsubstituted terminal carbon atoms and H atom positions available. [b] The diene is designated by $C_1{=}C_2{-}C_3{=}C_4$; α(H(E)) is the dihedral angle in degree between the planes defined by C_1–C_2–C_3–C_4 and H(E)–C_1–C_2 (or H(E)–C_4–C_3), respectively. [c] α(H(Z)) is the dihedral angle between the planes defined by C_1–C_2–C_3–C_4 and H(Z)–C_1–C_2 (or H(Z)–C_4–C_3), respectively.

plane (Table V). The apex-to-base angles are 100° for the carbonyl groups and 112° for the C–C bond midpoints. The basal angles are 92, 93 and 64°, the small angle being that subtended by the two outer C–C bonds of the diene. The diene 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 'inner' carbon atoms, C(2) and C(3), of the complexed diene are equidistant at 2.073(3) from the Fe atom. Significantly longer distances of 2.100(3) and 2.101(3) Å are found for the terminal carbon atoms, C(9) and C(10), of the diene. This feature has been discussed by Cotton *et al.* in 1973 [12] on the basis of 13, (1,3-diene)Fe(CO)$_3$ structures. We have extended this comparison to 42 structures (Table VI) using the same statistical formulas as in the previous compilation by Cotton *et al.* Table VI deals with molecules in which the butadiene residue is endo-or exocyclic and includes the more recent structures. The weighted average of the weighted estimates of Δ_1 is 0.069(28) Å and is thus significantly greater than zero (the formula used to calculate its e.s.'d is $[\sum_{i=1}^{N} w_i(\Delta_i - \bar{\Delta})^2/\sum_{i=1}^{N} w_i]^{1/2}$ with $w_i = 1/\sigma_i^2$).

The second feature of the (1,3-diene)Fe(CO)$_3$ grouping, also reviewed by Cotton *et al.* [12] is the difference Δ_2, between the average of the "outer" or terminal C–C distances and the 'inner' C–C distance. The extended comparison of Δ_2 values is also reported in Table VI. The weighted average of the weighted estimates of Δ_2 is 0.013(16) Å which is not significantly greater than zero. Cotton's conclusions are thus confirmed by this extended compilation. Three complexes listed in Table VI, $C_{10}H_{10}OFe(CO)_3$ [32], $C_{12}H_{12}Fe(CO)_3$ [5] and $C_{12}H_{14}Fe(CO)_3$ (this work), are good candidates for comparing C–C distances in free and bonded *cis*-butadiene systems as each compound contains one bonded and one free unsubstituted 1,3-diene group. The terminal C–C averaged distances are 1.405(4), 1.421(3) and 1.416(3) Å respectively for the bonded diene, and 1.323(5), 1.324(4) and 1.324(3) Å for the free diene. The corresponding 'inner' C–C distances are 1.382(5), 1.396(4) and 1.405(3) (bonded diene), and 1.467(6), 1.484(4) and 1.471(4) Å (free diene). In these three structures, complexation causes the terminal C–C bonds to become longer by 0.063(7), 0.097(4) and 0.092(5) respectively, whereas the 'inner' C–C bond becomes shorter by 0.046(9), 0.088(6) and 0.066(5) Å.

For $C_{12}H_{14}Fe(CO)_3$, the reliability of hydrogen atom positions obtained from the least-squares refinement may be judged by considering the pairs of H atoms related by plane VII (Table V), a plane of symmetry of the molecule which is not required crystallographically. The averaged difference in related bond angles is 2.2° (max. 7° for one H–C–H angle, Table IV). H(Z) atoms deviate from the diene plane away from the metal, whereas H(E) atoms deviate towards the metal. These deviations are listed in Table VII for seven (1,3-diene)Fe(CO)$_3$ structures. The mean

TABLE VIII. ^{1}H NMR and ^{13}C NMR Spectra of Iron and Ruthenium Carbonyls of 1a.[a]

	1a	*2*	*3*	*4*	*5*	*6*	*7*
H(1), H(4)	3.10bs	3.30bs(–0.20)[b]	3.30bs(–0.20)	3.53bs(–0.43)	3.53bs(–0.43)	3.18bs(–0.08)	3.40bs(–0.30)
H(7), H(8)	1.80m	1.78m (0.02)[d]	2.00m (–0.20)	2.20bs(–0.40)	2.18bs(–0.38)	1.94m(–0.14)[d]	2.05m (–0.25)
H(9E), H(10E)	4.91bs	1.90d (3.01)	1.91d (3.00)	1.93d (2.98)	2.03d (2.88)	1.86d (3.05)	1.89d (3.02)
H(9Z), H(10Z)	5.31bs	0.32d (4.99)	0.31d (5.00)	0.31d (5.00)	0.37d (4.94)	0.42d (4.89)	0.47d (4.84)
H(11E), H(12E)	4.91	5.11s (–0.20)	4.80s (0.11)	2.13d (2.78)	2.03	4.69s (0.22)	2.15d (2.76)
H(11Z), H(12Z)	5.31	5.53s (–0.22)	5.19s (0.12)	0.54d (4.77)	0.37	5.08s (0.23)	0.75d (4.56)
^{2}J(H(7E)–H(7Z))[c]	1.4						
$\|^2J\|$H(9E)–H(9Z)	<1	2.4	2.5	3.1	2.7	2.7	2.8
$\|^2J\|$H(11E)–H(11Z)	<1	<0.6	<0.6	2.5	2.7	<0.6	3.0
C(1), C(4)	48.0d	45.1d(2.9)[b]	45.0d(3.0)	42.0d(6.0)		45.5d(2.5)	42.9d(5.1)
C(2), C(3)	146.8s	111.8s(35.0)	108.1s(38.7)	106.8s(40.0)		112.1s(34.7)	108.9s(37.9)
C(5), C(6)		146.1s(0.7)	147.2s(–0.4)	113.5s(33.3)		148.6s(–1.8)	117.7s(29.1)
C(7), C(8)	26.8t	29.9t(–3.1)	27.0t(–0.2)	30.3t(–3.5)		26.8t(0)	31.2t(–4.4)
C(9), C(10)	103.7t	36.5t(67.2)[e]	36.3t(67.4)	36.3t(67.4)		29.3t(74.4)	28.5t(75.2)
C(11), C(12)		105.4t(–1.7)[e]	102.6t(1.1)	38.4t(65.3)		102.2t(1.5)	31.3t(72.4)
CO	–	211.7s(3C)	211.6s(3C)	211.0s(3C)		196.1s(2C) 201.9s(1C)	195.4s(4C) 200.6s(2C)
^{1}J(C(1)–H(1))[c]	137 ± 1	144 ± 1	144 ± 1	143 ± 1		146 ± 2	145 ± 1
^{1}J(C(7)–H(7))	133 ± 2	134 ± 2	135 ± 2	131 ± 2		135 ± 1	132 ± 2
^{1}J(C(9)–H(9))		160 ± 1[e]	160 ± 1	162 ± 1		159 ± 1	160 ± 1
^{1}J(C11)–H(11))	158 ± 1	159 ± 1[e]	163 ± 2	161 ± 1		156 ± 3	159 ± 1

[a] ^{1}H NMR spectra in $CDCl_3$ at 30 °C, ^{13}C NMR spectra in CD_2Cl_2 at 30 °C (spectrum width 3750 Hz, 4096 points). [b] From left to right: δ (in ppm relative to TMS), multiplicity (*s: singlet*, bs: *broad singlet*, d: *doublet*, t: *triplet*, *m: multiplet*) *and, in parentheses*, $\Delta\delta = \delta$*(ligand)* – δ*(complex)*. [c] *Coupling constant in Hz.* [d] *These protons do not present* any clear A_2B_2 pattern (of a $A_2B_2X_2$ spin system), but instead a broad multiplet superposed in parts by the H(9E) doublet. For comparison, the exo- and endo-isomers of 5,6-bis-(methylene)bicyclo[2.2.2]oct-2-ene-irontricarbonyl reported by Steiner *et al.* [49] also present H(7E) and H(7Z) multiplets centered at 1.73 and 1.78 ppm respectively. [e] For *1a–7*, J(C–H(Z)) ≅ J(C–H(E)).

deviations of H(Z) and H(E) atoms from the diene plane are 42(4) and 14(3)° respectively (the formula used to calculate the e.s.d's is $[\sum_{i=1}^{N}(\alpha_i - \bar{\alpha})^2/(N - 1)]^{1/2}$).

Spectroscopic Properties

The ^1H and ^{13}C NMR spectral data of ligand 1a and its Fe and Ru complexes are reported in Table VIII and their IR, UV and mass spectral data in the experimental part.

The relative intensities of the fragmentation peaks found in the mass spectra of irontricarbonyl complexes of some bicyclic 1,3-dienes were used by Steiner *et al.* [49] to distinguish between exo- and endo-isomers. In the present case, the method has proved fruitless as does the comparison of the IR spectra.

The assignments of the NMR spectra were deduced from the multiplicity of the signals and by comparison of $\Delta\delta = \delta$(ligand) – δ(complex) with the corresponding values for the diene 2,3-bis(methylene)bicyclo[2.2.2]octane and its irontricarbonyl complex [49]. The ^{13}C NMR spectra are temperature independent except for the fast intramolecular CO exchange which is blocked at about –40 °C in the case of the iron complexes. It was hoped that the signals of the H(7E, 8E) and H(7Z, 8Z) would be differentiated because of the metal. Unfortunately, this is not the case; these signals appear as a broad singlet in the ^1H-NMR spectrum of *4,5* and as a multiplet in *2,3,6,7* (in $CDCl_3$, acetone, benzene). Thus the attribution of the exo configuration in solution to complex *2* relies on its crystal structure. This argument is conclusive as *2* and *3* do not epimerize thermally in benzene or dichloromethane. Complex *5* must be the diexo isomer as the equivalence of the protons 11, 12 and also 9, 10 require a C_{2v} symmetry (the diendo isomer cannot be formed for steric reasons). The ^1H and ^{13}C NMR spectra show that the mirror plane defined by C(1), C(4), C(7), C(8) is absent in complexes *4* and *7* which must then be the endo, exo isomers. The attribution of the endo configuration to the ruthenium complex *6* remains tentative as it relies solely on the comparison of $\Delta\delta_C$'s: whenever a metal is present in the exo position (complexes, *2, 4* and *7*), the resonance of C(7) and C(8) shifts to lower field by 3–4 ppm whereas for *3* (endo-Fe) and *6*, the chemical shifts remain practically unchanged with respect to that of the free ligand.

Experimental

All reactions were carried out in an atmosphere of argon and all solvents were purified, dried and degassed by standard methods [50]. The melting points (uncorrected) were measured with a Tottoli apparatus; mass spectra at 70 eV 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; ^1H and ^{13}C (15.08 MHz) NMR spectra with a Bruker WP-60 spectrometer in the FT mode and using a deuterium lock. E. Manzer (Mikrolabor, ETH Zürich) carried out the microanalyses.

The preparation of 2,3,5,6-tetramethylenebicyclo-[2.2.2]octane (1a) has been described elsewhere [1].

Reaction of 1a with Fe and Ru Carbonyls

$Fe(CO)_3$(benzalacetone) [51] (0.55 g) and 1a (0.22 g) were heated at 70 °C in benzene (100 ml) for 6 h and then stirred at room temperature for 15 h. After filtration and removal of solvent, the residue was taken up in n-hexane and chromatographed on a 40 × 2 cm column packed with Florisil using n-hexane as eluent. After recrystallisation from n-pentane at –25 °C, the first fraction of eluate yielded complex 3 (58%) and the second fraction of eluate yielded complex 4. Overall yield 80%.

3: yellow crystals moderately stable in air; m.p.: 85–86 °C. The crystal used in the X-ray measurements was obtained by slow sublimation: a 15 × 1 cm glass tube containing the polycrystalline material was purged with argon, sealed under 10^{-3} torr and dipped in a thermostatted bath at 39 °C for a few days. The X-ray beam decomposed the complex in the presence of air, thus the crystal used was protected from O_2 by a sealed glass capillary. *Anal.* Found: C, 60.53; H, 4.77; $C_{15}H_{14}O_3Fe$ Calcd.: C, 60.43; H, 4.73%. Mass spectrum (peaks corresponding to ^{56}Fe): 298 (0.4; M^+), 270 (3; M^+ – CO), 242 (5; M^+ – 2CO), 214 (15; M^+ – 3CO), 186 (2), 162 (9), 141 (5), 84 (25), 56 (100; Fe^+). IR spectrum: ν(CO) 2060 (A'(1)), 1981 (A'(2)) and 1975 cm^{-1} (A'') (assigned following Adams [52]). UV spectrum: λ_{max} in nm (ϵ in l mol^{-1} cm^{-1}): 294sh (5555), 251sh (8571), 242sh (11110), 221 (16670).

4: yellow crystals stable in air; m.p.: 91–93 °C. *Anal.* Found: C, 50.08; H, 3.60; $C_{18}H_{14}O_6Fe_2$ Calcd.: C, 49.36; H, 3.22%. Mass spectrum: 438 (0.1; M^+), 410 (2; M^+ – CO), 382 (5; M^+ – 2CO), 354 (2; M^+ – 3CO), 326 (1; M^+ – 4CO), 298 (7; M^+ – 5CO), 270 (9; M^+ – 6CO), 243 (3), 214 (11), 186 (3), 162 (16), 84 (17), 56 (100). IR spectrum: ν(CO) 2061, 2058, 1985, 1983, 1974 and 1966 cm^{-1}. UV spectrum: 294sh (4444), 220 (32780).

$Fe_2(CO)_9$ (5 g) and 1a (1 g) were heated under reflux in pentane/ether (1:1, 400 ml) for 25 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 n-hexane and chromatographed on a 70 × 2 cm column packed with Florisil using n-hexane as eluent.

The successive fractions of eluate yielded after recrystallisation from n-pentane at –25 °C the complexes 2 (8%), 3(33%), 4 (12%) and 5 (1%). Overall yield 54%.

2: yellow crystals; m.p. 78–80 °C. *Anal.* Found: C, 60.58; H, 4.85; $C_{15}H_{14}O_3Fe$ Calcd.: C, 60.43; H, 4.73%. Mass spectrum: 298 (7; M^+), 270 (43; M^+ – CO), 242 (50; M^+ – 2CO), 214 (100; M^+ – 3CO), 177 (17), 162 (24), 149 (63), 71 (60), 69 (72), 56 (57). IR spectrum: ν(CO) 2058, 1981 and 1967 cm^{-1}. UV spectrum: 300 (2941), 261sh (7647), 252sh (11180), 219 (19900).

5: yellow crystals; m.p. 151–153 °C. *Anal.* Found: C, 50.14; H, 3.51; $C_{18}H_{14}O_6Fe_2$ Calcd.: C, 49.36; H, 3.22%. Mass spectrum: 438 (8; M^+), 410 (49; M^+ – CO), 382 (64; M^+ – 2CO), 354 (41; M^+ – 3CO), 326 (27; M^+ – 4CO), 298 (57; M^+ – 5CO), 270 (79; M^+ – 6CO), 242 (19), 214 (43), 177 (36), 162 (43), 159 (100), 112 (28), 56 (63). IR spectrum: ν(CO) 2055, 1986 and 1971 cm^{-1}. UV spectrum: 330sh (4285), 224 (43100).

$Ru_3(CO)_{12}$ (1.8 g) and 1a (0.7 g) were heated at 100 °C in toluene (130 ml) for 37 h. After filtration of excess $Ru_3(CO)_{12}$ (0.47 g) and removal of solvent, the residue was taken up in n-hexane/10v% ether and chromatographed on a 70 × 2 cm column packed with Florisil using n-hexane/10v% ether as eluent for the removal of the first yellow band and n-hexane/50v% ether for the elution of a second yellow band. After recrystallisation from n-hexane, the fractions of eluate yielded the complexes 6 (12%) and 7 (14%).

6: yellow crystals; m.p. 77–78 °C. *Anal.* Found: C, 52.34; H, 4.18; $C_{15}H_{14}O_3Ru$ Calcd.: C, 52.47; H, 4.11%. Mass spectrum (peaks corresponding to ^{101}Ru, isotopic abundance 17%): 343 (2; M^+), 315 (39; M^+ – CO), 287 (32; M^+ – 2CO), 259 (100; M^+ – 3CO), 101 (11). IR spectrum: ν(CO) 2072 (A′(1)), 1993 (A′(2)) and 1987 cm^{-1} (A″). UV spectrum: 280sh (2978), 262sh (6382), 250 (8830), 241 (9148), 234sh (8723), 214 (9574).

7: yellow crystals; m.p. 127–129 °C. *Anal.* Found: C, 41.42; H, 2.78; $C_{18}H_{14}O_6Ru_2$ Calcd.: C, 40.91; H, 2.67%. Mass spectrum: 528 (0.8; M^+), 500 (5; M^+ – CO), 472 (2; M^+ – 2CO), 444 (3; M^+ – 3CO), 416 (16; M^+ – 4CO), 388 (9; M^+ – 5CO), 360 (10; M^+ – 6CO), 178 (30), 149 (100), 101 (4). IR spectrum: ν(CO) 2079, 2072, 1997, 1993, 1988 and 1982 cm^{-1}. UV spectrum: 282sh (5694), 213 (16900).

Acknowledgements

The authors wish to thank the Swiss National Science Foundation (grants FN 2.780.77 and 2.891.77) for financial support. We are grateful also to Mme Sonney for preparing a pure sample of 1a and to Mr. Serra for recording the mass spectra. We thank Prof. D. Schwarzenbach for making the Syntex $P2_1$ diffractometer available to us.

References

1 A. Chollet, M. Wismer and P. Vogel, *Tetrahedron Lett.*, 4271 (1976).
2 A. Florey and P. Vogel, *Helv. Chim. Acta, 58,* 1488 (1975).
3 P. Vogel and A. Florey, *Helv. Chim. Acta, 57,* 200 (1974).
4 T. Boschi, Ph. Narbel, P. Vogel and R. Roulet, *J. Organometal. Chem., 133,* C39 (1977).
5 Ph. Narbel, T. Boschi, R. Roulet, P. Vogel, A. A. Pinkerton and D. Schwarzenbach, *Inorg. Chim. Acta,* to be published.
6 a) H. Blessing, P. Coppens and P. Becker, *J. Appl. Cryst., 7,* 488 (1972).
b) D. Schwarzenbach, 'TWOTHLEH', a Syntex $P2_1$ data collection program including scan profile interpretation.
7 J. M. Stewart, F. A. Kundell and J. C. Baldwin, "X-RAY 72" system, version of June 1972, Technical Report TR-192 of the Computing Science Center, University of Maryland (as modified by D. Schwarzenbach).
8 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).
9 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Phys. Chem., 42,* 3175 (1965).
10 D. T. Cromer, *Acta Cryst., 18,* 17 (1965).
11 C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory (1971).
12 F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle and J. M. Troup, *J. Am. Chem. Soc., 95,* 4522 (1973).
13 A. de Cian, P. M. L'Huillier and R. Weiss, *Bull. Soc. Chim. Fr.,* 451 (1973).
14 A. J. Carty, N. J. Taylor and C. R. Jablonski, *Inorg. Chem., 15,* 1169 (1976).
15 R. P. Dodge, *J. Am. Chem. Soc., 86,* 5429 (1964).
16 B. F. G. Johnson, J. Lewis, D. G. Parker, P. R. Raithby and G. M. Sheldrick, *J. Organometal. Chem., 150,* 115 (1978).
17 R. Eiss, *Inorg. Chem., 9,* 1650 (1970).
18 K. Hoffmann and E. Weiss, *J. Organometal. Chem., 128,* 389 (1977).
19 P. E. Riley and R. E. Davis, *Acta Cryst., B32,* 381 (1976).
20 B. Dickens and W. N. Lipscomb, *J. Chem. Phys., 37,* 2084 (1962).
21 A. A. Pinkerton, P. A. Carrupt, P. Vogel, T. Boschi, Nguyen Hai Thuy and R. Roulet, *Inorg. Chim. Acta, 28,* 123 (1978).
22 P. Skarstad, P. Janse-van Vuuren, J. Meinwald and R. R. Hughes, *J. Chem. Soc. Perkins Trans. II,* 88 (1975).
23 F. A. Cotton and J. M. Troup, *J. Organometal. Chem., 77,* 83 (1974).
24 M. G. Waite and G. A. Sim, *J. Chem. Soc. A,* 1009 (1971).
25 S. M. Johnson and I. C. Paul, *J. Chem. Soc. B,* 1783 (1970).
26 A. de Cian, P. M. L'Huillier and R. Weiss, *Bul. Soc. Chim. Fr.,* 457 (1973).
27 A. A. Pinkerton, D. Schwarzenbach, P. Vogel, T. Boschi, J. Wenger, Nguyen Hai Thuy and R. Roulet, to be published.
28 N. Yasuda, Y. Kai, N. Yasuoka, N. Kasai and M. Kakudo, *Chem. Commun.,* 157 (1972).
29 M. R. Churchill and P. H. Bird, *Inorg. Chem., 8,* 1941 (1969).

30 G. N. Schrauzer, P. Glockner, K. I. G. Reid and I. C. Paul, *J. Am. Chem. Soc., 92,* 4479 (1970).

31 A. H. J-Wang, I. C. Paul and R. Aumann, *J. Organometal. Chem., 69,* 301 (1974).

32 A. A. Pinkerton, D. Schwarzenbach, P. Vogel, E. Meier, T. Boschi and R. Roulet, *Inorg. Chim. Acta,* to be published.

33 E. Meier, T. Boschi, R. Roulet, P. Vogel, A. A. Pinkerton and D. Schwarzenbach, *Inorg. Chim. Acta,* to be published.

34 F. A. Cotton and J. M. Troup, *J. Organometal. Chem., 77,* 369 (1974).

35 F. A. Cotton, B. A. Frenz and J. M. Troup, *J. Organo-Metal. Chem., 61,* 337 (1973).

36 D. I. Woodhouse, G. A. Sim and J. G. Sime, *J. Chem. Soc. Dalton,* 1331 (1974).

37 R. M. Moriarty, K. N. Chen, M. R. Churchill and S. W. Y. Chang, *J. Am. Chem. Soc., 96,* 3661 (1974).

38 G. I. Birnbaum, *J. Am. Chem. Soc., 94,* 2455 (1972).

39 Ph. Narbel, J. Wenger, T. Boschi, R. Roulet, P. Vogel, A. A. Pinkerton and D. Schwarzenbach, to be published.

40 K. Birnbaum, *Acta Cryst., B28,* 161 (1972).

41 F. A. Cotton, V. W. Day and K. I. Hardcastle, *J. Organometal. Chem., 92,* 369 (1975).

42 G. G. Cash and R. C. Pettersen, *Inorg. Chem., 17,* 650 (1978).

43 A. Immirzi, *J. Organometal. Chem., 76,* 65 (1974).

44 R. E. Ireland, G. G. Brown, R. H. Stanford and T. C. McKenzie, *J. Org. Chem., 39,* 51 (1974).

45 A. Eisenstadt, J. M. Guss and R. Mason, *J. Organometal. Chem., 80,* 245 (1974).

46 A. Robson and M. R. Truter, *J. Chem. Soc. A,* 794 (1968).

47 K. I. G. Reid and I. C. Paul, *J. Chem. Soc. Dalton,* 1106 (1970).

48 R. Mason and G. B. Robertson, *J. Chem. Soc. A,* 1229 (1970).

49 U. Steiner, H.-J. Hansen, K. Bachmann and W. von Philipsborn, *Helv. Chim. Acta, 60,* 643 (1977).

50 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, London (1966); D. F. Schriver, 'The Manipulation of Air-Sensitive Compounds', McGraw–Hill, New York (1969).

51 J. A. S. Howell, B. F. G. Johnson, P. L. Josty and J. Lewis, *J. Organometal. Chem., 39,* 329 (1972).

52 D. M. Adams, 'Metal–Ligand and Related Vibrations', E. Arnold, London (1967).