Inorganica Chimica Acta, 28 (1978) 123–132
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Iron and Molybdenum Carbonyls of 5,6-Dimethylene-7-Oxabicyclo[2.2.1]Hept-2-ene.
Crystal and Molecular Structure of $(C_8H_8O)Fe_2(CO)_7$ [1]

A. A. PINKERTON
Institute of Crystallography, Bâtiment des Sciences Physiques, Dorigny
P. A. CARRUPT, P. VOGEL
Institute of Organic Chemistry, rue de la Barre 2
T. BOSCHI*, NGUYEN HAI THUY and R. ROULET**
Institute of Inorganic and Analytical Chemistry, Place du Château 3, University of Lausanne, Switzerland

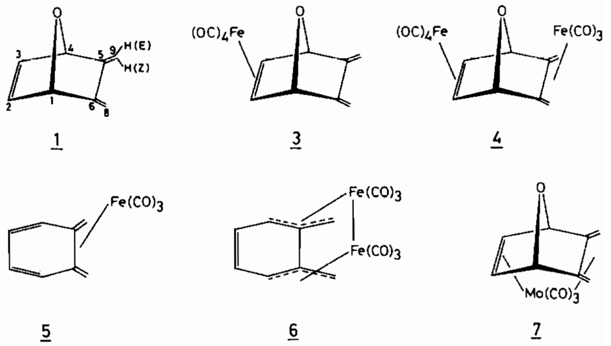
Received September 15, 1977

The photoreaction of 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene(1) with $Fe(CO)_5$ *yields initially the* dihapto-*tetracarbonyl iron complex (3), which reacts further to give a* dihapto-*tetracarbonyl*-tetrahapto-*tricarbonyl complex* $(C_8H_8O)Fe_2(CO)_7$ *(4). The molecular structure of* 4 *has been determined by X-ray crystallography. Both the* $Fe(CO)_4$ *and* $Fe(CO)_3$ *groups are in* exo *position with respect to the roof-shaped triene. The ligand is bound through its lone double bond to an equatorial position of a substituted trigonal-bipyramidal* $Fe(CO)_4L$ *moiety and through its diene group to two basal positions of a tetragonal pyramidal* $Fe(CO)_3L_2$ *moiety. Hydrogen atom positions have been determined in the last cycles (final residual* $R = 0.023$*). H(Z) atoms deviate by 39° from the diene plane away from the metal and H(E) atoms deviate by 11° towards the metal. H atoms of the lone C–C double bond deviate by 34° from the C(1)–C(2)–C(3)–C(4) plane away from the metal. The structures of complexes* 3, 4 *and* $(C_8H_8O)Mo(CO)_3$ *(7) in solution were deduced from their* ^1H *NMR data and the unknown geometries of ligands* 1 *and 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (2) were simulated by MINDO/3.*

Deoxygenation of the ligand is observed in the presence of $Fe_2(CO)_9$ *in benzene at 60 °C, giving* o-*quinodimethane complexes* 5 *and* 6, 5 *being also obtained by direct thermolysis of complex* 4.

Introduction

Polyolefins can be valuable synthons if the various unsaturated functions display selectivities or can be protected selectively. As 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene (*1*) possesses one endocyclic double bond, one exocyclic diene group and an allyl ether function, this compound is thought to become an interesting starter in the preparation of a variety of polyfunctionalised polycyclic molecules. We envisionned that the protection of the s-*cis*-butadiene group in *1* by forming a diene-$Fe(CO)_3$ complex [2] would leave the endocyclic double bond in C(2) free for electrophilic additions and substitutions and for cycloadditions with dienes [3] and dipolarophiles [4]. With this goal in mind, we have synthesised *1* (see Experimental) and have treated this ligand with iron carbonyls under various conditions. It is known that the parent ligand 5,6-dimethylene-bicyclo[2.2.1]hept-2-ene (*2*) treated with $Fe_2(CO)_9$ yields *exo*- and *endo*-$Fe(CO)_3(C_9H_{10})$ complexes [5, 6]. Strikingly, none of the expected $Fe(CO)_3$-(diene) complexes could be isolated with *1*. We wish to show that the endocyclic double bond in *1* reacts first with the iron carbonyls and leads to a stable $Fe(CO)_4$(triene) complex *3 (Scheme)*.



This compound reacts further and gives a *dihapto*-tetracarbonyl-*tetrahapto*-tricarbonyldiiron complex *4* of which an X-ray crystal structure will be given. The spectroscopic properties of complexes *3* - *7* are also

---

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

**Author to whom correspondence should be addressed.

presented together with the thermal reactivity of *3*, *4* and of the parent molybdenum complex *7*.

Reactions of *1* with Fe and Mo Carbonyls

Upon treatment with $Fe_2(CO)_9$, the 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (*2*) yields the expected *endo*- and *exo-tetrahapto*-tricarbonyliron complexes together with a mixture of cyclopentanone derivatives [5] arising from the reaction of the $\pi(2,3)$-endocyclic double bond. These results suggested the intermediacy of *dihapto*-tetracarbonyl-*tetrahapto*-tricarbonyl complexes $(C_9H_{10})Fe_2(CO)_7$ [7], but attempts to isolate them failed.

We treated the triene *1* with iron carbonyls under various conditions, and found that the *dihapto*-tetracarbonyl complex *3* is formed and can be isolated in 50% yield by treating *1* with $Fe_2(CO)_9$ in ether/pentane (36 °C, 2 days). Irradiation of *1* in pentane at −80 °C in the presence of $Fe(CO)_5$ in excess gives compounds *3* and *4* in the ratio 4/1 (global yield 30%); *3* is first formed; under these conditions, coordination of the s-*cis*-butadiene group occurs only in a subsequent step. An analogous *dihapto*-tetracarbonyl-*tetrahapto*-tricarbonyldiiron complex of 9-oxabicyclo[4.2.1]nona-2,4,7-triene has been reported; it was formed by complexation of the corresponding 2,3,4,5-η-$Fe(CO)_3$ complex [8]. Upon more drastic conditions (benzene, 60 °C, 36 h), $Fe_2(CO)_9$ brings about an oxygen atom abstraction from the ligand *1* giving the *o*-quinodimethane complexes *5* (30%) and *6* (1%). *5* has already been prepared in lower yields by treating α,α'-dibromo*ortho*xylene with $Fe_2(CO)_9$ [9], and *6* is one of the isomers obtained in the photoreaction of *5* with $Fe(CO)_5$ [10]. Treating *1* with $Mo(CO)_3(CH_3CN)_3$ gave the expected complex *7*.

Thermolysis of *3* at 95 °C (1 h) in degassed toluene leads to a mixture containing the free ligand *1* and some polymeric material (*1* is stable when treated alone in these conditions). When heated for 15 min in toluene at 95 °C, *4* was deoxygenated into *5* (50–60%). This reaction was accompanied by some polymerization and evolution of CO_2. The molybdenum carbonyl complex *7* yielded an unextractable polymeric material on thermolysis in benzene at 77 °C.

The deoxygenation of *4* finds an analogy with the formation of naphthalene by thermolysis of the benzooxanorbornadiene-$Fe(CO)_4$ complex [11]. It is not excluded that the oxygen bridge in *4* migrates and forms an epoxide intermediate that undergoes an easy deoxygenation reaction [12].

The molecular structure of *4* was determined to serve as a reference for the assignment of the spectroscopic data of all complexes and because accurate structure determinations of compounds of the type $Fe(CO)_4$(olefin) are scarce [13].

Crystal Structure of $(C_8H_8O)Fe_2(CO)_7$, *4*

Crystal Data

A crystal with the approximate dimensions 0.39 × 0.30 × 0.19 mm was measured with a Syntex $P2_1$ automatic four-circle diffractometer.

$C_{15}H_8O_8Fe_2$, M = 427.92, triclinic, $a = 6.728(2)$, $b = 11.356(3)$, $c = 11.809(3)$ Å, $\alpha = 65.61(2)$, $\beta = 78.33(3)$, $\gamma = 81.08(3)^\circ$, V = 802.3 Å^3, $F_{000} = 428$, $D_m = 1.767$ g cm^{-3} by floatation, Z = 2, $D_{calc.} = 1.77$ g cm^{-3}, space group $P\bar{1}$ from successful refinement, Mo-Kα X-radiation, $\lambda = 0.71069$ Å, $\mu_{Mo\text{-}K\alpha} = 18.98$ cm^{-1}.

Structure Solution

The intensities of 2125 unique reflections of which 196 were below the 3σ limit were measured using 2θ–θ scans with niobium filtered Mo radiation in one half of the reciprocal sphere (+h ±k ±l) to $(\sin\theta/\lambda)_{max} = 0.541$. The backgrounds were estimated by interpretation of the scan profile [14]. The crystal form was accurately measured by means of a special telescope mounted on the 2θ-arm of the diffractometer 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 [15]. Scattering factors for the neutral atoms were taken from Cromer and Mann [16], and anomalous dispersion coefficients for Fe from Cromer [17]. The perspective drawing was prepared by the program ORTEP [18]. The two unique iron atoms were found from the interpretation of a three dimensional Patterson map. A difference Fourier synthesis phased with these two atoms revealed all the other non-hydrogen atoms. The resulting structure was refined on the structure factors |F| by block diagonal least squares to R = 0.036. A further difference map now revealed all the hydrogen atom positions. After addition of these atoms to the model, refinement was continued to a final residual R = 0.023. The weights used were $1/\sigma^2$ where e.s.d's of the structure factors are derived from counting statistics and the variation in the intensities of the periodically measured check reflections. In the final cycles all the non-hydrogen atoms were allowed to vibrate anisotropically and the hydrogen atoms isotropically. The final positional and thermal parameters are listed in Table I. Calculated bond lengths and angles are reported in Table II and III, respectively.

The equations for several least-squares planes and some dihedral angles are presented in Table IV. A view of the molecular structure is given in Figure 1, where the numbering scheme is indicated. For the C_8H_8O moiety, the numbering scheme is identical with that used for nomenclatural purposes.

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

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	−.25618(6)	.73199(3)	.18261(3)	.0372(2)	.0223(2)	.0388(2)	.0034(2)	−.0056(2)	−.0111(2)
Fe(2)	.21867(6)	.21501(3)	.33657(3)	.0379(2)	.0202(2)	.0357(2)	.0023(2)	−.0100(2)	−.0074(2)
C(1)	−.0232(4)	.4710(2)	.3529(3)	.048(2)	.026(1)	.031(2)	.001(1)	−.010(1)	−.011(1)
C(2)	.1869(5)	.4073(3)	.3169(3)	.041(2)	.020(1)	.039(2)	−.001(1)	−.015(1)	−.006(1)
C(3)	.1710(4)	.4020(2)	.2003(3)	.034(2)	.019(1)	.033(2)	−.000(1)	−.004(1)	−.008(1)
C(4)	−.0430(4)	.4647(2)	.1747(2)	.036(2)	.023(1)	.027(1)	−.002(1)	−.006(1)	−.009(1)
C(5)	−.0235(4)	.6089(2)	.1423(2)	.028(1)	.022(1)	.032(1)	.003(1)	−.005(1)	−.009(1)
C(6)	−.0119(4)	.6127(2)	.2592(2)	.035(2)	.023(1)	.039(2)	.004(1)	−.011(1)	−.012(1)
C(8)	−.0035(5)	.7322(3)	.2677(3)	.054(2)	.029(2)	.054(2)	.004(2)	−.020(2)	−.020(2)
C(9)	−.0247(5)	.7232(3)	.0334(3)	.034(2)	.026(2)	.040(2)	−.001(1)	−.004(1)	−.008(1)
C(10)	−.2968(5)	.9063(3)	.1191(3)	.052(2)	.034(2)	.063(2)	.006(2)	−.011(2)	−.017(2)
C(11)	−.4254(5)	.6853(3)	.3291(3)	.057(2)	.042(2)	.053(2)	.004(2)	−.002(2)	−.020(2)
C(12)	−.4260(5)	.6883(3)	.1114(3)	.035(2)	.039(2)	.048(2)	.002(1)	−.003(2)	−.014(1)
C(13)	.2928(5)	.1272(3)	.4906(3)	.042(2)	.028(2)	.045(2)	.005(1)	−.008(2)	−.017(1)
C(14)	.2032(5)	.0998(3)	.2701(3)	.062(2)	.030(2)	.040(2)	.001(2)	−.012(2)	−.009(1)
C(15)	−.0454(5)	.1928(3)	.4106(3)	.048(2)	.019(1)	.044(2)	−.000(1)	−.014(2)	−.003(1)
C(16)	.4846(5)	.2316(3)	.2635(3)	.050(2)	.027(2)	.042(2)	.004(1)	−.016(2)	−.008(1)
O(1)	.1914(5)	.0260(2)	.2306(2)	.122(3)	.052(2)	.075(2)	−.010(2)	−.019(2)	−.038(1)
O(2)	−.5250(4)	.6579(3)	.0619(2)	.051(2)	.089(2)	.085(2)	−.010(1)	−.020(1)	−.041(2)
O(3)	−.3166(4)	1.0165(2)	.0778(3)	.097(2)	.025(1)	.124(2)	.008(1)	−.030(2)	−.015(1)
O(4)	−.5337(5)	.6533(3)	.4219(3)	.099(2)	.091(2)	.065(2)	−.008(2)	.032(2)	−.029(2)
O(5)	.6479(4)	.2412(2)	.2158(2)	.043(1)	.071(2)	.063(1)	−.004(1)	−.003(1)	−.022(1)
O(6)	.3395(4)	.0715(2)	.5873(2)	.071(2)	.052(1)	.040(1)	.013(1)	−.021(1)	−.013(1)
O(7)	−.1559(3)	.4254(2)	.3006(2)	.036(1)	.024(1)	.030(1)	−.0029(8)	−.0028(9)	−.0067(8)
O(8)	−.1998(4)	.1615(2)	.4677(2)	.050(2)	.037(1)	.070(2)	−.010(1)	−.003(1)	.001(1)
H(1)	−.080(4)	.455(3)	.447(2)	.037(8)					
H(2)	.297(4)	.434(3)	.331(2)	.040(9)					
H(3)	.268(4)	.420(3)	.131(2)	.030(8)					
H(4)	−.113(4)	.447(2)	.120(2)	.025(7)					
H(9E)	−.056(5)	.715(3)	−.041(3)	.06(1)					
H(9Z)	.059(5)	.775(3)	.021(3)	.032(9)					
H(8E)	−.028(5)	.736(3)	.354(3)	.047(9)					
H(8Z)	.084(4)	.792(3)	.210(3)	.041(9)					

TABLE II. Bond Lengths (Å) in *4* (the e.s.d. of the last significant digit is given in parentheses).

Fe(1)–C(5)	2.049(3)	Fe(2)–C(2)	2.080(3)
Fe(1)–C(6)	2.062(3)	Fe(2)–C(3)	2.092(2)
Fe(1)–C(8)	2.143(4)	Fe(2)–C(13)	1.807(3)
Fe(1)–C(9)	2.127(3)	Fe(2)–C(14)	1.806(4)
Fe(1)–C(10)	1.801(3)	Fe(2)–C(15)	1.820(3)
Fe(1)–C(11)	1.789(3)	Fe(2)–C(16)	1.824(3)
Fe(1)–C(12)	1.781(4)	C(13)–O(6)	1.135(4)
C(10)–O(3)	1.137(4)	C(14)–O(1)	1.134(5)
C(11)–O(4)	1.138(4)	C(15)–O(8)	1.137(4)
C(12)–O(2)	1.136(5)	C(16)–O(5)	1.128(4)
C(5)–C(9)	1.400(3)	C(2)–C(3)	1.429(5)
C(6)–C(8)	1.412(5)	C(1)–C(2)	1.548(4)
C(5)–C(6)	1.416(4)	C(3)–C(4)	1.534(4)
C(1)–C(6)	1.534(3)	C(1)–O(7)	1.442(4)
C(4)–C(5)	1.541(4)	C(4)–O(7)	1.444(3)
C(1)–H(1)	1.04(3)	C(2)–H(2)	0.91(3)
C(3)–H(3)	0.91(2)	C(4)–H(4)	0.97(3)
C(9)–H(9E)	0.99(4)	C(8)–H(8E)	1.02(4)
C(9)–H(9Z)	0.83(3)	C(8)–H(8Z)	0.93(3)

Discussion

The structure is composed of discrete monomeric $(C_8H_8O)Fe_2(CO)_7$ 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 $(C_8H_8O)Fe(CO)_3$ moiety, with the mirror plane I (Table IV) passing through the Fe atoms, one CO group, O(7) and the midpoints of the C(2)–C(3) and C(5)–C(6) bonds.

The whole $Fe(CO)_3$ group is in the "exo" position with respect to the roof-shaped ligand; this result confirms the assignments made in the ^1H and ^{13}C NMR spectra (Table V). The average Fe–C (carbonyl)

TABLE III. Bond Angles (°) in *4* (the e.s.d. of the last significant digit is given in parentheses).

C(5)–Fe(1)–C(9)	39.1(1)	C(2)–Fe(2)–C(3)	40.0(1)
C(5)–Fe(1)–C(6)	40.3(1)	C(2)–Fe(2)–C(13)	103.4(1)
C(6)–Fe(1)–C(8)	39.2(1)	C(2)–Fe(2)–C(12)	90.2(1)
C(12)–Fe(1)–C(10)	102.3(2)	C(2)–Fe(2)–C(15)	91.7(1)
C(12)–Fe(1)–C(11)	91.5(2)	C(3)–Fe(2)–C(14)	108.3(1)
C(10)–Fe(1)–C(11)	102.7(2)	C(3)–Fe(2)–C(16)	84.2(1)
Fe(1)–C(12)–O(2)	176.0(3)	C(3)–Fe(2)–C(15)	97.4(1)
Fe(1)–C(10)–O(3)	178.0(3)	C(16)–Fe(2)–C(13)	91.0(1)
Fe(1)–C(11)–O(4)	178.5(4)	C(16)–Fe(2)–C(14)	89.7(2)
C(4)–C(5)–C(9)	135.3(3)	C(16)–Fe(2)–C(15)	178.1(1)
C(1)–C(6)–C(8)	135.3(3)	C(13)–Fe(2)–C(14)	108.5(1)
C(6)–C(5)–C(9)	120.6(3)	C(13)–Fe(2)–C(15)	88.3(1)
C(5)–C(6)–C(8)	120.4(2)	C(14)–Fe(2)–C(15)	88.8(2)
C(4)–C(5)–C(6)	104.1(2)	Fe(2)–C(16)–O(5)	178.1(4)
C(1)–C(6)–C(5)	104.2(3)	Fe(2)–C(13)–O(6)	179.6(3)
C(3)–C(4)–C(5)	102.9(2)	Fe(2)–C(14)–O(1)	178.6(2)
C(2)–C(1)–C(6)	102.6(2)	Fe(2)–C(15)–O(8)	170.1(2)
C(2)–C(3)–C(4)	104.2(2)	C(5)–C(4)–O(7)	101.1(2)
C(1)–C(2)–C(3)	103.5(3)	C(6)–C(1)–O(7)	101.2(2)
C(1)–O(7)–C(4)	97.3(2)	C(3)–C(4)–O(7)	101.7(2)
		C(2)–C(1)–O(7)	101.9(3)
H(1)–C(1)–C(2)	121(1)	H(4)–C(4)–C(3)	121(1)
H(1)–C(1)–C(6)	117(2)	H(4)–C(4)–C(5)	116(1)
H(1)–C(1)–O(7)	111(2)	H(4)–C(4)–O(7)	111(1)
H(2)–C(2)–C(1)	117(2)	H(3)–C(3)–C(4)	115(2)
H(2)–C(2)–C(3)	124(2)	H(3)–C(3)–C(2)	127(2)
C(5)–C(9)–H(9E)	116(2)	C(6)–C(8)–H(8E)	119(2)
C(5)–C(9)–H(9Z)	117(2)	C(6)–C(8)–H(8Z)	121(2)
H(9E)–C(9)–H(9Z)	117(3)	H(8E)–C(8)–H(8Z)	112(3)

TABLE IV. Least-squares Planes of *4*.

Plane	Atoms Defining Plane[a]	Equation of Mean Plane
I	Fe(1), Fe(2), O(7), C(10), O(3)	$1.541X + 4.865Y + 11.803Z = 5.358$
II	C(12), C(11), m, m′	$0.430X + 10.308Y - 0.084Z = 6.877$
III	C(5), C(6), C(9), C(8)	$6.480X - 0.450Y - 0.582Z = -0.506$
IV	C(1), C(4), C(5), C(6)	$6.429X - 0.983Y - 0.659Z = -0.847$
V	C(1), C(2), C(3), C(4)	$2.772X + 9.359Y - 0.691Z = 4.105$
VI	C(1), C(4), O(7)	$-3.029X + 8.781Y + 0.025Z = 4.215$
VII	Fe(2), C(13), C(14), O(6), O(1), m″	$6.117X + 0.457Y - 2.583Z = 0.585$
VIII	Fe(2), C(2), C(3)	$6.455X + 0.973Y - 0.921Z = 1.311$

Displacement of Atoms from Mean Plane (Å)

Plane I	Fe(1)	−0.036	Plane II	C(12)	+0.025	Plane III	C(5)	−0.003
	Fe(2)	−0.002		C(11)	−0.024		C(6)	+0.003
	C(10)	0.000		m	+0.029		C(9)	+0.001
	O(7)	+0.020		m′	−0.030		C(8)	−0.001
	O(3)	+0.018						
Plane IV	C(1)	+0.002	Plane V	C(1)	−0.004	Plane VII	Fe(2)	−0.019
	C(4)	−0.002		C(2)	+0.006		C(13)	−0.004
	C(5)	+0.003		C(3)	−0.006		C(14)	+0.006
	C(6)	−0.003		C(4)	+0.004		O(6)	+0.007
							O(1)	+0.002
							m″	+0.009

(continued on facing page)

TABLE IV. *(continued)*

Dihedral Angle between Planes (°)

I–II	89.4;	I–III	88.7;	I–IV	88.2;	I–V	88.1;	I–VI	89.8
I–VII	79.0;	I–VIII	87.1;	II–III	88.0;	III–IV	2.8;	IV–V	107.2
IV–VI	126.0;	V–VI	126.9;	V–VIII	118.7;	VII–VIII	8.2;		

[a] m, m′ and m″ are the midpoints of the C(6)–C(8), C(5)–C(9) and C(2)–C(3) bonds, respectively.

distance of 1.79 Å is comparable with the many previously reported values (1.75–1.80 Å) [19]. Significantly longer Fe–C distances are found for the "outer" carbon atoms, C(8) and C(9), of the diene portion of the ligand than for the "inner" carbon atoms, C(5) and C(6). A similar trend has been observed in structures having an Fe atom bonded to an endocyclic 1,3-diene [19]. The orientation of the $Fe(CO)_3$ group with respect to the diene is such that one CO group lies in plane I (Table IV) over the "open" side of the C–C–C–C chain. This orientation seems thus to be independent of the diene being exo- or endocyclic. The arrangement of ligands about the Fe(1) atom is approximately tetragonal pyramidal. Four coordination sites of Fe(1) are occupied by 2 CO and the midpoints m and m′ of the exo C–C bonds, C(5)–C(9) and C(6)–C(8), m–m′–C(11)–C(12) defining the basal plane (Table IV). The diene is perpendicular to the basal plane and has three C–C bonds of equal length. The Fe atom lies 0.54 Å over the basal plane. The apex-to-base angles are 102° for the CO groups and 112° for the C–C bond midpoints m and m′. The basal angles are 92° (C(11)–Fe(1)–C(12)), 90° (C(12)–Fe(1)–m′) and 65° (m′–Fe(1)–m). The apical Fe–CO bond makes an angle of 8° with the normal to the basal plane.

The arrangement of four CO and one C–C double bond about the Fe(2) atom is approximately trigonal bipyramidal and the whole $Fe(CO)_4$ group is in the "exo" position with respect to the ligand. It is not symmetry related by the mirror plane of the rest of the molecule as the C(15)–Fe(2)–C(16) line makes an angle of 11.5° with plane I. Steric repulsion between the axial CO and O(7) is probably the cause of this deviation and of the Fe(2)–C(15)–O(8) angle being significantly smaller than 180°. The lengths of axial and equatorial Fe–CO bonds are equal within experimental errors. The midpoint m″ of the C(2)–C(3) bond and two CO lie in the equatorial plane, the C–C double bond itself making an angle of 8° with the equatorial plane. The apex-to-base angles are close to 90° and the equatorial angles are 108.5° (C(13)–Fe(2)–C(14)) and 125.7° (C(13)–Fe(2)–m″). The dihedral angle between the Fe(2)–C(2)–C(3) and C(1)–C(2)–C(3) planes is 118°. Such a deviation from perpendicularity was also observed in the case of $(C_{12}H_8)Fe(CO)_4$ [13].

The C–H bond lengths are shorter than those obtained by neutron diffraction or by spectroscopic techniques and probably reflect the difference between the positions of the nucleus of a bonded H atom and the center of gravity of its electron cloud [20].

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 I, a plane of symmetry of the $Fe(CO)_3(C_8H_8O)$ moiety which is not required crystallographically. The averaged difference in related bond angles is 2.2° (max. 5° for the two H–C–H angles, Table III). H(Z) atoms deviate by 39° from the diene plane away from the metal, whereas H(E) atoms deviate by 11° towards the metal. Analogous deviations were found in *syn*- and *anti*-substituted (1,3-butadiene)irontricarbonyl compounds and Immirzi's model [21] of C_s symmetry for the butadiene molecule bonded to $Fe(CO)_3$ appears to be valid in this case.

The mean deviation of the H atoms of the lone C–C double bond is 34° from the C(1)–C(2)–C(3)–C(4) plane away from the metal atom Fe(2) and the C(2)–C(3) bond length is significantly longer than that of a double bond. This is indicative of a carbon hybridization scheme between sp^2 and sp^3. The effect of carbon rehybridisation and H atom deviations upon ^{13}C and ^{1}H coupling constants is examined in the discussion of the spectroscopic data.

Spectroscopic Properties

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

The assignment of the NMR spectra was deduced straightforwardly from the multiplicity of the signals and by comparison of $\Delta\delta = \delta(\text{ligand } 1) - \delta(\text{complex})$ with the corresponding values for the triene *2* and its *exo*-irontricarbonyl complex [6]. Whereas ^{13}C coupling constants do not permit to differentiate a metal being in *exo* or *endo* position, proton coupling constants of H(2) give unambiguous indications about the structure of the complexes in solution. It is known that in molecules having a framework related to that of norbornane, the coupling constant of a bridge proton H(1) with H(6-*exo*) is greater (3–4 Hz for norbornene derivatives [22] and 7-oxanorbornenes [23]) than that with H(6-*endo*) (~0 Hz). We

TABLE V. ^{1}H NMR and ^{13}C NMR Spectra of Iron and Molybdenum Carbonyls of *1*[a].

	1	*3*	*4*	*5*	*7*	*8* [6][b]
H(1), H(4)	4.89 bs	4.17 bs (0.72)[c]	3.99 bs (0.90)	7.5 m	4.32 dd (0.57)[i]	3.53 (−0.23)
H(2), H(3)	6.11 t[k]	2.66 s (3.45)[l]	2.85 s (3.26)[m]		3.16 dd (2.95)	6.83 (−0.5)
H(8E), H(9E)	4.85 bs	4.79 bs (0.06)	1.66 dd (3.19)[f]	2.5 d	2.78 d (2.07)	2.25 (2.70)
H(8Z), H(9Z)	5.11 bs	5.12 bs (−0.01)	0.17 d (4.94)	0.4 d	1.47 d (3.64)	0.81 (4.36)
$\lvert {}^{2}J \rvert$ H(8E)–H(8Z)[d]	<0.6	<0.6	2.8	3.4	2.1	2.6
C(1), C(4)	82.5 d	82.3 d (0.2)	81.8 d(0.7)	129.6 d	77.8 d (4.7)	48.9 (2.1)
C(2), C(3)	135.4 d	54.9 d (80.5)	58.6 d (76.8)	133.0 d	49.5 d (85.9)	142.1 (−5.6)
C(5), C(6)	143.0 s	145.0 s (−2.0)	113.0 s (30.0)	100.5 s	85.4 s (57.6)	119.1 (29.8)
C(8), C(9)	102.3 t	103.1 t (−0.8)	34.7 t (67.6)	36.7 t	58.8 t (43.5)	39.3 (62.1)
CO	–	210.3 s[e]	211.9 s 209.8 s[g]	211.0 s[h]	226.3s[j] 218.7 s	210.8
^{1}J(C(1)–H(1))	167 ± 3	161 ± 1	172 ± 2	161 ± 2	173 ± 2	151.0
^{1}J(C(2)–H(2))	179 ± 1	171 ± 3	165 ± 2	167 ± 2	186 ± 3	175.9
^{1}J(C(8)–H(8))	160 ± 1	158 ± 1	160 ± 1	160 ± 3	164 ± 1	158.1(E) 162.2(Z)

[a] ^{1}H NMR spectra: in C_6D_6 at room temperature for *1–7*, in $CDCl_3$ for *8*. ^{13}C NMR spectra: in CD_2Cl_2 at room temperature for *1, 4, 5, 7,* at 0 °C for *3* (spectrum width 3750 Hz, 4096 points), in $CDCl_3$ for *8*. [b] Given for comparison; *8* is the *exo*-irontricarbonyl complex of ligand *2*, reported by Steiner *et al.* [6]. [c] 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, $\Delta\delta = \delta(\text{ligand}) - \delta(\text{complex})$. [d] Coupling constant in Hz. [e] Singlet down to −80 °C. [f] ^{4}J(H(8E)–H(1)) = 0.8 Hz. [g] From the $Fe(CO)_4$ group. [h] At −70 °C: δ(CO) = 217.1 and 207.9 ppm (intensity ratio 1:2). [i] ^{3}J(H(1)–H(2)) = 1.7 Hz, ^{4}J(H(1)–H(3)) = 1.5 Hz. [j] CO exchange blocked; the intensity ratio lower field signal/higher field signal is 2:1. [k] apparent triplet; ^{3}J(H(1)–H(2)) ≅ ^{4}J(H(1)–H(3)) ≅ 1.1 Hz (see text); ^{2}J(H(8E)–H(8Z)) ≅ 0.5 Hz; ^{4}J(H(1)–H(8E)) ≅ ^{4}J(H(1)–H(8Z)) ≅ 0.3 Hz, evaluated from line widths at half-height (resolution: 0.3 Hz). [l] ΣJ's of H(2) < 0.5 Hz; ^{2}J(H(8E)–H(8Z)) < 0.6 Hz, evaluated from line widths at half-height. [m] ^{3}J(H(1)–H(2)) + ^{4}J(H(1)–H(3)) < 0.5 Hz.

simulated the proton signals of 7-oxanorbornadiene* and the H(1–4) signals of the triene *1* respectively as an $AA'X_2X_2'$ and an AA'XX' spin system (program LAOCN IV [25]) and found ^{3}J(H(1)–H(2)) ≅ ^{4}J(H(1)–H(3)) ≅ 1.1 Hz in both cases. This value is slightly smaller than that found for ^{3}J(H(1)–H(6)) in 7-oxanorbornadiene 2,3-dicarboxylic derivatives [26]. For complex *7*, in which the metal has to occupy the *endo* position, the H(1) and H(2) resonances appear as two apparent triplets; the simulation of its H(1–4) signals as an AA'XX' system gave ^{3}J(H(1)–H(2)) ≅ ^{4}J(H(1)–H(3)) ≅ 1.7 Hz, a value greater than that of the free ligand. Thus H(2) and H(3) should be somewhat pushed toward the *exo* side of the ligand and this is the expected effect of coordination in *7*. Indeed, the crystal structure of *4* shows that H(2) and H(3) are pushed away from the $Fe(CO)_4$ group with respect to the C(1)–C(2)–C(3)–C(4) plane. The same argument can be used to show that the structure of complex *4* in the solid state is retained in solution and that the $Fe(CO)_4$ group of *3* is in the *exo* position. The H(2) resonance appears as a singlet in both *3* and *4* (width at half-height: 0.8 Hz; resolution: 0.3 Hz). The sum of coupling constants involving H(2) is smaller than 0.5 Hz, and thus ^{3}J(H(1)–H(2)) is smaller than that of the free ligand. This corresponds to H(2) and H(3) locations somewhat in the *endo* side of the roof-shaped ligand, as found in the crystal structure of complex *4*.

Discussion

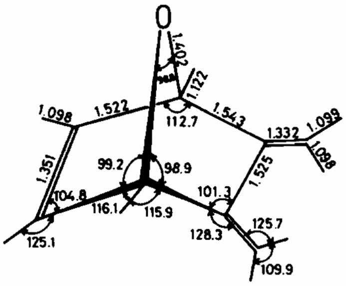
The 2,3-η-5,6-dimethylenebicyclo[2.2.1]hept-2-ene-$Fe(CO)_4$ complex could not be isolated with the stable *exo* and *endo*-irontricarbonyl complexes when the triene *2* was treated in the conditions used to generate *3* from *1* [5, 6]. It is a difficult matter to explain why *3* is formed before any *tetrahapto*tricarbonyl complex $(C_8H_8O)Fe(CO)_3$. *1* reacts more slowly than *2* with strong dienophiles [27], suggesting perhaps a reduced reactivity of the s-*cis*-butadiene group of *1* in the iron carbonyl complex formation relative to *2*. This can be ascribed to differences in electronic properties between the dienes *1* and *2* (differences between the energies and shapes of the frontier π-MO's, see Table VI). Differences in geometry and ring strain may also play a role [27]. Introduction of an ethereal bridge for the $H_2C(7)$ bridge in norbornene derivatives does not affect significantly the energy of the occupied MO involving the π electrons of the C(2)–C(3) double bond. Through space (homoconjugative) interactions

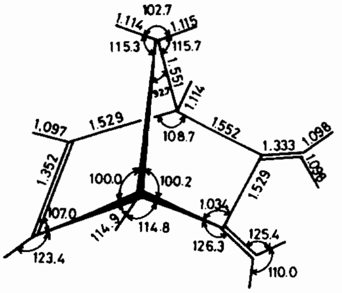
---

*We wish to thank Prof. H. Prinzbach for a sample of this material [24].

TABLE VI. MINDO/3 Results on the Minimized Geometries of *1* and *2*; MINDO/3 and EHT[a] Eigenvalues (ϵ in eV) of the Frontier Molecular Orbitals.

Bond Lengths (Å) and Angles (degree)[b]:





	Triene *1*		Triene *2*	
α[c]	2.3–2.7		0.8	
β[d]	152.4		160.0	
γ[e]	29.0		20.7	
Heat of Formation	15.7 kcal/mol		97.8 kcal/mol	
Eigenvalues:	MINDO/3	EHT	MINDO/3	EHT
HOMO's n(O)	−9.95	−13.12	–	–
π_2(diene)	−9.14	−12.46	−8.91	−12.39
π (2,3)	−9.14	−12.44	−9.02	−12.24
LUMO's π_3^*(diene)	0.95	− 8.93	1.17	− 8.84
π^*(2,3)	1.40	− 8.26	1.58	− 8.07

[a] Calculations on MINDO/3 minimized geometries. [b] Bond lengths and angles not reported may be found by symmetry with respect to the mirror plane. [c] Angle between line C(2)–H(2) and plane C(1)–C(2)–C(4). [d] Angle between lines C(1)–H(1) and C(1)–C(4). [e] Dihedral angle between lines C(1)–H(1) and C(2)–H(2).

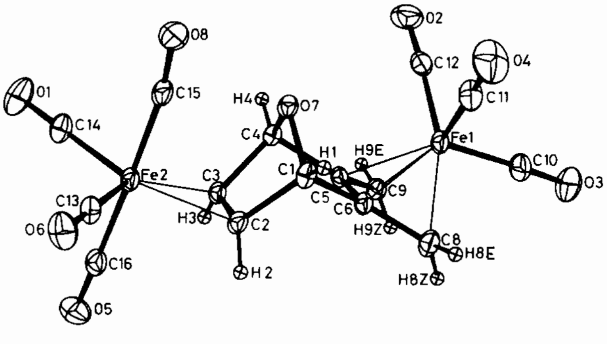
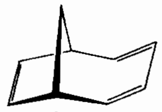
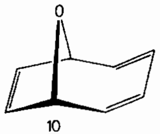


Figure 1. Perspective view of the molecular structure of $(C_8H_8O)Fe_2(CO)_7$ (*4*).

between the π double bond and the n orbitals of the oxygen bridge (which should push the π-MO to higher energies) have been found of little importance in allyl ethers [28]. The ionization potentials assigned to the endocyclic π(2,3) double bond in the PE spectra of *1* and *2* [28c] and to the π(7,8) double bond in the PE spectrum of bicyclo[4.2.1]nona-2,4,7-triene analogs *9, 10* [28e] are found slightly higher in the ethers *1, 10* than in the hydrocarbons *2, 9*. The π-MO's in *1* and *10* are stabilized relative to *2, 9* because of the greater electronegativity of oxygen relative to carbon. This stabilization arises in part from the hyperconjugative interactions between the occupied π-MO localised on C(2), C(3) in *1* and the relatively low-lying empty combination σ^*(C(1), O(7)) + σ^*(O(7), C(4)). This interaction may lead to a non-equivalent extension of the π electron density toward the *exo* face of the 7-oxanorbornene if the localized π(2, 3) MO is mixed out of phase with the perturbing σ MO's in the *exo* region and with σ MO on C(2)–C(3) in an out of phase relation to the *exo* σ MO's [31].

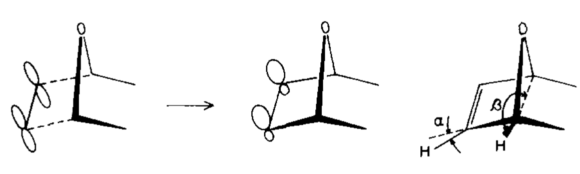


9



10

If not compensated by other electronic or steric interactions, this phenomenon must be accompanied by a change of hybridization at carbons C(2) and C(3) that modifies the angle α between the H(2)–C(2) bond and the C(1)–C(2)–C(3)–C(4) plane in the way shown below:



The coupling constants $^3J(H(1)-H(2))$ and $^4J(H(1)-H(3))$ are expected to decrease with an increasing angle α [22, 23]. The ^1H NMR spectra of 7-oxanorbornadiene, benzoxanorbornadiene [23a] and 5,6-dimethylene-7-oxanorborn-2-ene (*1*) indicate that the dihedral angle between bonds H–C(1) and H–C(2) must be larger than that in norbornadiene, benzonorbornadiene and 5,6-dimethylenenorborn-2-ene (*2*). This arises from a larger angle α and/or a smaller angle β between the H–C(1) bond and the C(1)–C(2)–C(3)–C(4) plane*. The geometries of *1* and *2* are not known. We have therefore simulated them by the MINDO/3 method [29]; they are shown in Table VI. The calculations indicate a dihedral angle between H–C(1) and H–C(2) of 29° in *1* and of 20.7° in *2*, in agreement with the measured ^3J coupling constants. The calculated geometries indicate also a deviation α of the H–C(2) bond from the C(1)–C(2)–C(3) plane of 2.3–2.7° in the ether *1*, whereas an angle α of only ~0.8° is calculated in the hydrocarbon *2*. These results point out that the change in the angle α between *1* and *2* is not the main reason for a smaller $^3J(H(1)-H(2))$ in *1* relative to *2*; the change in the angle β is more significant. They show, nevertheless, a larger deviation α in the ether *1* than in the hydrocarbon *2*. The eigenvalues of the HOMO's π_2(diene), partially localized on the diene moiety, and $\pi(2,3)$, partially localized on the endocyclic double bond C(2)–C(3), are a little lower in *1* than in *2*. The difference is, however, very small and furthermore, these two HOMO's have very similar energies (see Table VI). No dramatic differences can be noted either between the LUMO's of *1* and *2*. If the frontier MO's of *1* and *2* are the cause of the different behaviour of these trienes toward iron carbonyl complexes, it is quite probable that differences between the shapes of these MO's play a more important role than differences between their energies. Therefore, we tentatively interpret the relative ease of formation and stability of complex *3* as being due to the "enhanced" π electron density in the *exo* face of *1*. Nonequivalent HOMO extension of norbornene has been proposed by Fukui [31] as being responsible for the *exo* selectivity of the electrophilic additions to the double bond. Our hypothesis suggests that the π electron density anisotropy is more accentuated, as shown by the MINDO/3 minimized geometries of *1* and *2*, in 7-oxanorbornene derivatives than in norbornenes, probably because of the favourable $\pi \leftrightarrow \sigma^*(C(1)-O(7)) + \sigma^*(O(7)-C(4))$ hyperconjugative interaction and of the out-of-phase interactions at the n orbitals on O(7) and occupied $\sigma(C(1)-O(7)) + \sigma(O(7)-C(4))$ MO's with the π and $\sigma(C(2)-C(3))$ MO's.

IR and Mass Spectral Data

The mass spectra of complexes *3*, *4* and *7* show that deoxygenation of the ligand occurs in the gas phase only when the metal is in *exo* positon and as soon as one or several coordination sites of the metal are vacated by loss of CO.

IR spectra give little information as the ν(C=C) region is obscured by other molecular vibrations and as the ν(CO) of the $Fe(CO)_3$ group are rather insensitive to differences in geometries [6]. However, the $\bar{\nu}$(CO) of $Fe(CO)_4$(olefin) complexes were found to reflect the donor ability of the coordinated olefin [37b]. The mean value of the four ν(CO) related to the $Fe(CO)_4$ group is higher for *4* (2040 cm^{-1}) than for *3* (2032 cm^{-1}). A possible explanation for this is the higher electron density available on the C(2)–C(3) double bond in the monoiron complex *3* than in the diiron complex *4*.

Experimental

All reactions were carried out in an atmosphere of argon and all solvents were purified, dried and degassed by standard methods [32]. The melting points (uncorrected) were measured with a Tottoli apparatus; mass spectra at 70 eV with a CEC 21-490 Bell-Howell spectrometer; UV spectra in isooctane with a Carl Zeiss RPQ 20 A/C spectrophotometer; IR spectra in n-hexane and in KBr pellets with a Perkin-Elmer 577 spectrophotometer; ^1H NMR spectra with a Bruker WP-80 and a Bruker WP-60 spectrometer in the CW and the FT modes, respectively; ^{13}C-NMR spectra with a Bruker WP-60 instrument (15.08 MHz) in the FT mode and using a deuterium lock. E. Manzer (Mikrolabor ETH, Zürich) carried out the microanalyses.

5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene (*1*) was prepared according to the general procedure developed for 2,3-dimethylene-7-oxanorbornane derivatives [33]. The starting material is the Diels-Alder adduct of furan and maleic anhydride [34]. This adduct (90 mmol) was reduced by an excess of $LiAlH_4$ (180 mmol) in boiling (4 h) tetrahydrofuran (250 ml) into *exo*-5,6-bis(hydroxymethyl)-7-oxanorborn-2-ene*; yield: 83%, viscous oil; IR (film): 3300, 2950, 2900, 1450, 1040 cm^{-1}; ^1H NMR spectrum in D_2O: δ 6.6 (bs, 2H), 5.0 (bs, 2H), 3.7 (m, 4H), 2.2–1.8 (m, 2H). The crude diol (60 mmol) was esterified

---

*The replacement of the $H_2C(7)$ group by an oxygen bridge can affect the J(H,H) coupling constants because of electronic factors also. However, no significant differences have been noticed between oxanorbornane and norbornane derivatives.

*We wish to thank Prof. Dr. W. R. Roth for a detailed prescription of the preparation of this material [3].

by paramethylbenzenesulfonyl chloride (240 mmol) in anhydrous pyridine (300 ml) at 0 °C (3 days). The crude ester (bis-tosylate) was washed three times with ice-cold water, dried over P_4O_{10}, washed three times with ether and finally recrystallised in $CHCl_3$/pentane (1:1). Yield: 65%; m.p.: 150–151 °C; IR (KBr): 2950, 1600, 1350, 1170, 950 cm^{-1}; ^1H NMR ($CDCl_3$): 7.75–7.35 (m, 8H), 6.33 (bs, 2H), 4.75 (bs, 2H), 4.1 (m, 4H), 2.5 (s, 6H), 1.66 (bs, 2H). The bis-tosylate (10 mmol) eliminated two equivalents of paramethylbenzenesulfonic acid by treatment in anhydrous DMSO (80 ml) containing freshly sublimed t-butOK (50 mmol) at 0 °C, under nitrogen (7 h). The triene *1* was extracted with pentane and purified by distillation under reduced pressure. Yield: 50%, colourless oil, b.p.: 30 °C/1 Torr; IR spectrum (film): 2950, 1290, 1000, 880, 800; UV, ^1H NMR and ^{13}C NMR spectra, see Table V and [35]; mass spectrum: m/e$^+$ [amu] (% base peak): 120 (10, *1*$^+$), 103(5), 91(100), 68(80), 65(30), 45(25).

Reaction of 1 *with Fe and Mo Carbonyls*

a) $Fe_2(CO)_9$ (10 g) and *1* (4.6 g) were heated at 36 °C in pentane/ether (1:1, 200 ml) for 2 days. 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 × 3 cm column packed with Florisil using n-hexane/5 v% ether as eluent; the first fraction of eluate contained $Fe(CO)_5$, the second a trace of complex *5* and the third yielded complex *3* after recrystallisation from n-pentane and sublimation. Yield: 50%.

b) $Fe(CO)_5$ (11.7 g) and *1* (1.4 g) were irradiated in n-pentane (200 ml) at –80 °C for 6 h (high pressure Hg lamp HPK 125; pyrex vessel). After evaporation to a small volume, the reaction mixture was chromatographed on a 80 × 2 cm column packed with Florisil. Elution of two yellow bands with n-hexane/5 v% ether brought down compounds *3* and *4* in the ratio 4/1. Global yield: 30% after fractional sublimation. Samples of the reaction mixture taken in the first 25% of the reaction revealed by IR and TLC that the first complex to be formed was *3*. Irradiation for a longer period of time (10 h) provoked the partial conversion of *3* and *4* into *5*.

3: yellow crystals unstable in air; m.p.: 47–48 °C. *Anal.* Found: C, 49.54; H, 2.74; $C_{12}H_8FeO_5$ Calcd.: C, 50.04; H, 2.80%. Mass spectrum (peaks corresponding to ^{56}Fe, (M^+–O) is designated by N^+): 288 (1; M^+), 272 (<1; N^+), 260 (4; M^+–CO), 244 (1; N^+–CO), 232 (30; M^+–2CO), 204 (28; M^+–3CO), 176 (9; M^+–4CO), 163 (9), 161 (9), 160 (3; N^+ – 4CO), 148 (14; M^+–3CO–Fe), 56 (100; Fe^+). IR spectrum: 2097, 2032, 2017 and 1984 (ν(CO)), 3005 (ν(C–H)), 1070 cm^{-1} (δ(C–O–C)). UV spectrum: λ_{max} in nm (ϵ in l mol^{-1} cm^{-1}): 265sh (8800), 219 (34100).

4: yellow crystals stable in air; the monocrystal used in the X-ray structure determination was obtained by slow cooling of a n-hexane solution at –20 °C under argon; m.p. 114–115 °C. *Anal.* Found: C, 42.12; H, 1.93; $C_{15}H_8Fe_2O_8$ Calcd.: C, 42.10; H, 1.88%. Mass spectrum (M^+–$Fe(CO)_4$ is designated by P^+): 428 (1; M^+), 400 (6; M^+–CO), 372 (23; M^+–2CO), 344 (14; M^+–3CO), 328 (0.1; N^+–3CO), 316 (3; M^+–4CO), 300 (0.3; N^+–4CO), 288 (9; M^+–5CO), 272 (3; N^+–5CO), 260 (17; M^+–6CO), 244 (7; N^+–6CO), 232 (100; P^+–CO), 216 (8; P^+–O–CO), 204 (25; P^+–2CO), 188 (7; P^+–O–2CO), 176 (10; P^+–3CO), 160 (26; P^+–O–3CO), 148 (7), 146 (9), 132 (7), 128 (24), 112 (5), 104 (5), 103 (3), 91 (4), 56 (25; Fe^+). IR spectrum: 2103, 2040, 2028 and 1991 cm^{-1} (ν(CO) of $Fe(CO)_4$), 2061 (A′(1)), 1986 (A′ (2)) and 1979 cm^{-1} (A″) (ν(CO) of $Fe(CO)_3$, assigned after Adams [3]), 3012 (ν(C–H), 1068 cm^{-1} (δ(C–O–C)). UV spectrum: 258sh (20100), 217 (55000).

c) $Fe_2(CO)_9$ (2 g) and *1* (0.2 g) were heated in benzene (100 ml) at 60 °C for 36 h. The $Fe_3(CO)_{12}$ formed was decomposed as in reaction (a). After filtration and removal of solvent, the residue was taken up in hexane and chromatographed on a 80 × 2 cm column packed with Florisil. Elution with n-hexane revealed a yellow band followed by a small red band. The first band yielded complex *5* (30%); the red eluate was rechromatographed on neutral alumina, activity grade I, using n-hexane as eluent and yielded *6* (1%).

5: *Anal.* Found: C, 53.68; H, 3.27; $C_{11}H_8FeO_3$ Calcd.: C, 54.14; H, 3.30%. Mass spectrum: 244 (30; M^+), 216 (46; M^+–CO), 188 (38; M^+–2CO), 160 (100:, M^+–3CO), 132 (47), 56 (40; Fe^+). Its IR spectrum in n-hexane and its ^1H NMR spectrum in CCl_4 are identical to those of *o*-quinodimethanetricarbonyliron reported and partially characterised by Roth *et al.* [9]. ^{13}C NMR (see Table V).

6: *Anal.* Found: C, 43.77; H, 2.36; $C_{14}H_8Fe_2O_6$ Calcd.: 43.80; H, 2.10%. Mass spectrum: 384 (2; M^+), 356 (26; M^+–CO), 328 (40; M^+–2CO), 300 (34; M^+–3CO), 272 (41; M^+–4CO), 244 (100; M^+–5CO), 216 (61; M^+–6CO), 188 (9), 160(31), 112 (30; Fe_2^+), 56 (22; Fe^+). Its m.p., IR and ^1H NMR spectra are identical to those of bis(*trihapto*)-*o*-quinodimethanehexacarbonyldiiron reported by Rae Victor *et al.* [10].

d) A solution of $Mo(CO)_6$ (5 g) in acetonitrile (300 ml) was refluxed for 14 h. After distilling the solvent off, $Mo(CO)_3(CH_3CN)_3$ [37] was taken up in pentane/ether/THF (2:2:1) (200 ml) containing *1* (1 g). The reaction mixture was kept overnight at 30 °C and then evaporated to dryness. The brownish residue was taken up in hexane and chromatographed on a 80 × 2 cm column packed with Florisil. Elution with n-hexane revealed only one red band which yielded *7* (45%).

7: red crystals, stable in air; m.p. 84–85 °C. *Anal.* Found: C, 44.05; H, 2.60; $C_{11}H_8MoO_4$ Calcd.: C, 44.02; H, 2.68%. Mass spectrum (peaks corresponding to ^{96}Mo): 300 (45; M^+), 272 (22; M^+–CO), 244 (30; M^+–2CO), 216 (100; M^+-3CO), 188 (69), 160 (18), 96 (16). IR spectrum: 2005, 1945 and 1919 cm^{-1} (ν(CO)), 1010 cm^{-1} (δ(C–O–C)). UV spectrum: 317 (11100), 215 (29500).

Acknowledgements

The authors wish to thank the Swiss National Science Foundation (grants FN 2.548.76 and 2.648.76) for financial support. We are grateful also to Mr. Serra for recording the mass spectra and to Mr. R. Favez for help in recording the NMR spectra. We thank Prof. D. Schwarzenbach for making the Syntex P2$_1$ diffractometer available to us. We wish to thank Prof. P.-E. Bonzon for generous computer (CYBER-7326, NOS/BE) time.

References

1 T. Boschi, P. Vogel and R. Roulet, *J. Organometal. Chem., 133,* C36 (1977).

2 B. F. G. Johnson, J. Lewis and G. L. P. Randall, *Chem. Commun.,* 1273 (1969); B. F. G. Johnson, J. Lewis, A. W. Parkins and G. L. P. Randall, *ibid.,* 595 (1969); C. H. DePuy, R. N. Greene and T. E. Schroer, *ibid.,* 1225 (1968); C. H. DePuy and C. H. Jablonski, *Tetrahedron Lett.,* 3989 (1969); B. J. H. Cowles, B. F. G. Johnson, J. Lewis and A. W. Parkins, *J. Chem. Soc. Dalton,* 1768 (1972).

3 W. R. Roth, H. Humbert, G. Wegener, G. Erker and H. D. Exner, *Chem. Ber., 108,* 1655 (1975).

4 R. Huisgen, *J. Org. Chemistry, 41,* 403 (1976); M. Franck- Neumann and D. Martina, *Tetrahedron Lett.,* 1759 (1975).

5 U. Steiner and H.-J. Hansen, *Helv. Chim. Acta, 60,* 191 (1977).

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

7 E. Weissberger and G. Page, *J. Am. Chem. Soc., 99,* 147 (1977); E. Weissberger and P. Laszlo, *Acc. Chem. Res., 9,* 209 (1976).

8 R. Aumann and H. Averbeck, *J. Organometal. Chem., 85,* C4 (1975).

9 W. R. Roth and J. D. Meier, *Tetrahedron Lett.,* 2053 (1967).

10 R. Victor and R. Ben-Shoshan, *J. Organometal. Chem., 80,* C1 (1974).

11 L. Lombardo, D. Wege, and S. P. Wilkinson, *Aust. J. Chem., 27,* 143 (1974); see also: R. W. Ashworth and G. A. Berchtold, *J. Am. Chem. Soc., 99,* 5200 (1977).

12 R. Aumann, H. Averbeck and C. Krüger, *Chem. Ber., 108,* 3336 (1975).

13 F. A. Cotton and P. Lahuerta, *Inorg. Chem., 14,* 116 (1975); C. Krüger, *J. Organometal. Chem., 22,* 697 (1970).

14 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.

15 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).

16 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).

17 D. T. Cromer, *Acta Cryst., 18,* 17 (1965).

18 C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory (1971).

19 F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle and J. M. Troup, *J. Am. Chem. Soc., 95,* 4522 (1973) and references therein.

20 A. Halgren, R. G. Anderson, D. S. Jones and W. N. Lipscomb, *Chem. Phys. Lett., 8,* 547 (1971).

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

22 H. Joela, *Org. Magn. Reson., 9,* 338 (1977) and ref. cited therein; R. Gassend, Y. Limousin and J. C. Maire, *ibid., 6,* 259 (1974); M. C. Thorpe and W. C. Coburn, Jr., *J. Org. Chemistry, 34,* 2576 (1969); Y. F. Shealy and J. D. Clayton, *J. Am. Chem. Soc., 91,* 3075 (1969); E. I. Snyder and B. Franzus, *ibid., 86,* 1166 (1964); J. Meinwald and Y. C. Meinwald, *ibid., 85,* 2514 (1963); K. Tori, K. Kitahonoki, Y. Takano, H. Tanida and T. Tsuji, *Tetrahedron Lett.,* 559 (1964); S. E. Masar and H. Krieger, *Suomen Kemistilehti, B42,* 1 (1969); J. Paasivirta, *ibid., B44,* 131 (1971).

23 a) R. Caple, D. K. Harris and S. C. Kuo, *J. Org. Chemistry, 38,* 381 (1973); b) T. A. Eggelte, H. de Koning and H. O. Huisman, *Tetrahedron, 29,* 2445, 2491 (1973); W. L. Nelson and D. R. Allen, *J. Heterocyclic Chemistry, 9,* 561 (1972); L. F. Fieser and M. J. Haddadin, *Can. J. Chem., 43,* 1599 (1965); A. W. McCulloch, D. G. Smith and A. G. McInnes, *ibid., 52,* 143, 1013 (1974).

24 H. Prinzbach and H. Babsch, *Angew. Chem., 87,* 772 (1975).

25 J. A. Musso and A. Isaia, NMR-LAOCN-4A, QCPE Program, No. 232.

26 P. Vogel, B. Willhalm and H. Prinzbach, *Helv. Chim. Acta, 52,* 584 (1969); H. Prinzbach, P. Vogel and W. Auge, *Chimia, 21,* 469 (1967); A. W. McCulloch, D. G. Smith and A. G. McInnes, *Can. J. Chem., 51,* 4125 (1973).

27 M. Hardy, P. A. Carrupt and P. Vogel, *Helv. Chim. Acta, 59,* 1685 (1976); P. Vogel, *Chimia, 31,* 53 (1977).

28 a) A. B. Bain, J. C. Bünzli, D. C. Frost and L. Weiler, *J. Am. Chem. Soc., 95,* 291 (1973); b) B. J. M. Neijzen, R. F. Schmitz, G. W. Klumpp and C. A. De Lange, *Tetrahedron, 31,* 873 (1975); c) H.-U. Pfeffer, M. Klessinger, G. Erker and W. R. Roth, *Chem. Ber., 108,* 2923 (1975); d) R. S. Brown, *Can. J. Chem., 54,* 805 (1976); e) H. Schmidt, A. Schweig, A. G. Anastassiou and J. C. Wetzel, *Tetrahedron, 32,* 2239 (1976); P. Bischof, R. Gleiter and E. Heilbronner, *Helv. Chim. Acta, 53,* 1425 (1970).

29 M. J. S. Dewar, *Science, 187,* 1037 (1975); *190,* 591 (1975); *Chem. in Britain, 11,* 97 (1975); R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc., 97,* 1285 (1975).

30 R. Hoffmann, *J. Chem. Phys., 39,* 1397 (1963); R. Hoffmann, S. Swaminathan, B. G. Odell, R. Gleiter, *J. Am. Chem. Soc., 92,* 7091 (1970); A. B. Anderson, *J. Chem. Phys., 62,* 1187 (1975).

31 S. Inagahi, H. Fumimoto and K. Fukui, *J. Am. Chem. Soc., 98,* 4054 (1976).

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

33 V. Gergely, Z. Akhavin and P. Vogel, *Helv. Chim. Acta, 58,* 871 (1975).

34 O. Diels and K. Alder, *Ber. Deut. Chem. Ges., 62,* 554 (1929).

35 D. Quarroz, J. M. Sonney, A. Chollet, A. Florey and P. Vogel, *Org. Magn. Reson., 9,* 611 (1977): see ref. 27.

36 a) D. M. Adams, "Metal–Ligand and Related Vibrations", Arnold, London (1967); b) M. Bigorgne, *J. Organometal. Chem., 127,* 55 (1977).

37 J. M. Graham and M. Kilner, *J. Organometal. Chem., 77,* 247 (1974).