

21. Crystal Structure of Tricarbonyl- [2,3- η :O- σ -(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]iron

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The product of the reaction of $[\text{Fe}(\text{benzalacetone})(\text{CO})_3]$ with 7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene is tricarbonyl-[2,3- η :O- σ -(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]iron. Crystals are monoclinic, space group $P2_1/c$ with $a = 6.612(2)$, $b = 11.610(4)$, $c = 18.604(6)$ Å, and $\beta = 95.91(2)^\circ$. The coordination at the metal atom is trigonal bipyramidal. The equatorial sites are occupied by 2 CO's and by the midpoint of the endocyclic double bond of the organic ligand. The axial sites are occupied by one CO group and the O-atom of one MeO group of the $\text{C}(\text{OMe})_2$ bridge. It is an uncommon example of a d^8 metal carbonyl complex bearing an O-bonded ligand.

1. Introduction. – We have reported recently on the synthesis and reactivity of d^6 and d^8 metal carbonyl complexes of 7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene [1]. Among the 30 compounds reported in [1], we have now unambiguous indication that the iron complex **1** and the ruthenium complex **2**, originally formulated as $[\text{M}(\text{CO})_4(\eta^2\text{-olefin})]$ complexes, are in fact $[\text{M}(\text{CO})_3(\eta^2\text{:O-}\sigma\text{-olefin})]$ complexes as indicated in the *Formulae*. These are uncommon examples of d^8 metal carbonyl complexes bearing an



O-bonded ligand [2]. The elemental-analysis data reported earlier for **1** and **2** fits either formulation within experimental error. The reported mass spectra for **1** and **2** indeed showed weak peaks corresponding to an $[\text{M}(\text{CO})_4(\text{olefin})]$ molecular ion, but these have since been identified as impurity peaks. Given the correct formulation of **1** and **2**, the ¹H- and ¹³C-NMR spectra are surprisingly similar to those of **3–5** in terms of the δ_{H} and δ_{C} values for the two MeO groups. It was this similarity which gave rise to the confusion. The 3 $\nu(\text{CO})$ bands observed in the IR spectra of **1** both at 100 and 300 K were assumed to be compatible with a trigonal bipyramidal $[\text{M}(\text{CO})_4(\text{olefin})]$ complex having the olefin coordinated in an axial site with local C_{3v} symmetry. Since all previously reported $[\text{M}(\text{CO})_4(\text{olefin})]$ complexes have the olefin in the equatorial plane [3], the molecular structure of **1** was determined by X-ray analysis.

2. Crystal Structure of Complex 1. - Single crystal diffraction intensities were collected on a *Syntex P2₁* auto-diffractometer. An absorption correction based on the *Gaussian* integration method was applied. *Table 1* gives the crystallographic data and data collection procedures using the 'X-ray 72 system' of programs [4]. Atomic-scattering factors for neutral C, O, Fe [5] and H [6], and anomalous coefficients for Fe [7] were included in the structure-factor calculations. The Fe-atoms were located on the *Patterson* map and the remaining non-H-atoms were identified on successive *Fourier* maps. All H-atoms were found on a difference *Fourier* synthesis after preliminary refinement to $R = 0.055$, and were included in the structure-factor calculations. The largest peaks in the final difference synthesis were *ca.* $0.4 \text{ e}^-/\text{\AA}^3$ in the vicinity of the heavy atoms.

Atomic parameters and calculated bond lengths and angles are listed in *Tables 2-4*. A view of the molecular structure prepared by the program *ORTEP* [8] is given in the *Figure* where the numbering scheme is indicated. The geometry at the metal atom is trigonal bipyramidal. The equatorial sites are occupied by 2 CO's and the midpoint of the endocyclic double bond of the organic ligand. The axial sites are occupied by one CO group and the O-atom of one MeO group of the C(OMe)₂ bridge. The double bond at C(2),C(3) is practically in the equatorial plane, the dihedral angle between planes Fe,C(2),C(3) and a ,Fe,C(12),C(13)¹⁾ being $2.5(5)^\circ$. The 'tilt' of the olefin with respect to the equatorial plane is $108.8(5)^\circ$, as given by the dihedral angle between planes Fe,C(2),C(3) and

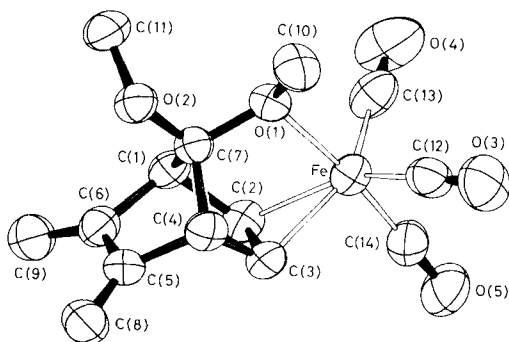


Figure. *Perspective view of the molecular structure of 1.* H-atoms are omitted for clarity.

Table 1. *Crystal Data of 1, Intensity Collection, and Refinement*

Formula	C ₁₄ H ₁₄ O ₅ Fe	Min. and max. transmission	0.869 and 0.912
Molecular mass	318.1	Scan type	$\theta(\text{crystal}) - 2\theta(\text{counter})$
Dimensions [mm]	0.21 × 0.14 × 0.63	Scan width	$[2\theta(K\alpha_2) + 1.0] - [2\theta(K\alpha_1) - 1.0]^\circ$
Crystal system	Monoclinic	Scan speed	Variable (2 to 10°/min)
Space group	<i>P</i> 2 ₁ / <i>c</i>	($\sin \theta/\lambda$) _{max}	0.54
<i>a</i> [Å]	6.612(2)	Background from	Scan profile interpretation [9]
<i>b</i> [Å]	11.610(4)	Standard reflections	3, measured after each
<i>c</i> [Å]	18.604(6)		97 reflections
β [°]	95.91(2)	2θ limits [°]	(0,0,8; 1,5,1; 3,0,0)
<i>V</i> [Å ³]	1420.7(7)	Data collected	± <i>h</i> , ± <i>k</i> , ± <i>l</i>
<i>Z</i>	4	No. of unique reflections	1869
<i>d</i> _{obs} [g cm ⁻³]	1.48(2)	No. of reflections (<i>I</i> > 3σ)	1247
<i>d</i> _{calc} [g cm ⁻³]	1.49	Solution method	<i>Patterson</i> and <i>Fourier</i>
μ [cm ⁻¹]	11.06	Refinement method	Block-diagonal least-squares
Radiation	Mo-K α , Nb-filtered	Function minimised	$\sum w(F_o - F_c)^2$
Systematic absences	<i>h</i> 0 <i>l</i> : <i>l</i> = 2 <i>n</i> + 1 (0 0 <i>l</i> : <i>l</i> = 2 <i>n</i> + 1) 0 <i>k</i> 0: <i>k</i> = 2 <i>n</i> + 1	<i>w</i>	1/ σ^2
<i>F</i> ₀₀₀	656	<i>R</i>	0.031
		<i>R</i> _w	0.027
		Goodness of fit	1.51

¹⁾ *a* is the midpoint of the C(2),C(3) bond.

Table 2. List of Atomic Parameters for Complex 1^{a)}

Atom	x	y	z	U_{eq}
Fe	0.20406(7)	0.29315(4)	0.41586(3)	0.0489(3)
O(1)	0.0799(3)	0.2271(2)	0.3196(1)	0.0445(1)
O(2)	0.0486(3)	0.0523(2)	0.2585(1)	0.0491(1)
O(3)	-0.1680(4)	0.3857(3)	0.4682(2)	0.086(1)
O(4)	0.3923(5)	0.4805(3)	0.3397(2)	0.101(1)
O(5)	0.4107(4)	0.3571(3)	0.5539(2)	0.090(1)
C(1)	0.0902(5)	0.0472(3)	0.3893(2)	0.047(1)
C(2)	0.2163(5)	0.1219(3)	0.4433(2)	0.053(1)
C(3)	0.3909(5)	0.1549(3)	0.4098(2)	0.048(1)
C(4)	0.3670(5)	0.0982(3)	0.3361(2)	0.044(1)
C(5)	0.3912(5)	-0.0298(3)	0.3487(2)	0.051(1)
C(6)	0.2099(5)	-0.0635(3)	0.3845(2)	0.049(1)
C(7)	0.1361(4)	0.1065(3)	0.3198(2)	0.042(1)
C(8)	0.5423(7)	-0.0961(5)	0.3323(2)	0.067(2)
C(9)	0.1608(7)	-0.1653(4)	0.4075(2)	0.068(2)
C(10)	-0.1341(6)	0.2492(5)	0.2967(3)	0.062(2)
C(11)	0.1278(8)	0.0881(5)	0.1923(2)	0.062(2)
C(12)	-0.0286(6)	0.3468(3)	0.4449(2)	0.057(1)
C(13)	0.3200(6)	0.4065(4)	0.3688(2)	0.062(2)
C(14)	0.3291(5)	0.3331(3)	0.4981(2)	0.061(2)
H(1)	-0.044(4)	0.038(2)	0.397(1)	0.036(8)
H(2)	0.216(5)	0.109(3)	0.487(2)	0.05(1)
H(3)	0.514(4)	0.159(2)	0.435(2)	0.043(9)
H(4)	0.442(4)	0.132(2)	0.304(2)	0.036(8)
H(5)	0.649(5)	-0.061(3)	0.310(2)	0.06(1)
H(6)	0.539(5)	-0.175(4)	0.347(2)	0.08(1)
H(7)	0.250(5)	-0.235(4)	0.402(2)	0.07(1)
H(8)	0.034(5)	-0.182(3)	0.428(2)	0.07(1)
H(9)	-0.145(5)	0.327(4)	0.296(2)	0.07(1)
H(10)	-0.161(5)	0.213(3)	0.251(2)	0.08(1)
H(11)	-0.208(4)	0.224(3)	0.336(2)	0.06(1)
H(12)	0.123(6)	0.167(4)	0.189(2)	0.10(2)
H(13)	0.036(6)	0.059(3)	0.153(2)	0.09(1)
H(14)	0.264(6)	0.058(4)	0.190(2)	0.09(1)

^{a)} For numbering, see the *Figure*.

Table 3. Bond Lengths (Å) in 1^{a)}

Fe–C(2)	2.052(4)	C(4)–C(7)	1.523(4)
Fe–C(3)	2.036(4)	C(5)–C(6)	1.482(5)
Fe–O(1)	2.041(2)	C(5)–C(8)	1.323(6)
Fe–C(12)	1.794(4)	C(6)–C(9)	1.309(6)
Fe–C(13)	1.796(4)	C(7)–O(1)	1.448(4)
Fe–C(14)	1.727(4)	C(7)–O(2)	1.377(4)
C(1)–C(2)	1.512(5)	C(10)–O(1)	1.458(4)
C(1)–C(6)	1.517(5)	C(11)–O(2)	1.448(5)
C(1)–C(7)	1.523(5)	C(12)–O(3)	1.151(5)
C(2)–C(3)	1.420(5)	C(13)–O(4)	1.146(6)
C(3)–C(4)	1.515(5)	C(14)–O(5)	1.153(5)
C(4)–C(5)	1.510(5)		

^{a)} The e.s.d. of the last significant digit is given in parentheses.

Table 4. Bond Angles (°) in 1^a)

C(2)–C(1)–C(6)	105.6(3)	O(1)–C(7)–O(2)	110.7(3)
C(2)–C(1)–C(7)	99.2(3)	C(10)–O(1)–C(7)	114.3(3)
C(6)–C(1)–C(7)	100.5(3)	C(11)–O(2)–C(7)	114.5(3)
C(1)–C(2)–C(3)	106.3(3)	C(7)–O(1)–Fe	106.3(2)
C(2)–C(3)–C(4)	105.5(3)	O(3)–C(12)–Fe	174.3(3)
C(3)–C(4)–C(5)	106.6(3)	O(4)–C(13)–Fe	178.5(4)
C(3)–C(4)–C(7)	99.3(3)	O(5)–C(14)–Fe	178.2(4)
C(5)–C(4)–C(7)	100.4(3)	O(1)–Fe–C(12)	96.6(1)
C(4)–C(5)–C(6)	104.6(3)	O(1)–Fe–C(13)	90.0(1)
C(4)–C(5)–C(8)	127.4(4)	O(1)–Fe–C(14)	172.4(1)
C(6)–C(5)–C(8)	128.0(4)	C(12)–Fe–C(13)	108.3(2)
C(1)–C(6)–C(5)	104.7(3)	C(12)–Fe–C(14)	89.2(2)
C(1)–C(6)–C(9)	126.6(4)	C(13)–Fe–C(14)	92.7(2)
C(5)–C(6)–C(9)	128.6(4)		

^a) The e.s.d. of the last significant digit is given in parentheses.

C(1), C(2), C(3), C(4). As expected, the H-atoms at C(2) and C(3) are pushed away from the metal by *ca.* 30° with respect to plane C(1), C(2), C(3), C(4). Coordination at O(1) does not significantly distort the bicyclic skeleton (see Table 4). The torsion angles C(11)–O(2)–C(7)–O(1) and C(10)–O(1)–C(7)–O(2) are 68(2) and 43(2)°, respectively, the smaller values being probably due to repulsion between the Me group and the Fe-atom. No structures of comparable d⁸ metal carbonyl were found in the *Cambridge Data Files*. However, the structure of tetracarbonyl(7,7-dimethoxynorborn-2-ene)chromium shows another example in which the alkoxynorbornene acts as a bidentate ligand [9].

Given the correct formulation of **1**, the two diiron isomers of the ligand 7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene reported in [1] should be formulated as hexacarbonyl-*cis*-μ-[(1*R*,2*S*,3*R*,4*S*,5*R*,6*S*)-2,3-η : O-σ : C,5,6, C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]diiron and hexacarbonyl-*trans*-μ-[(1*R*,2*S*,3*R*,4*S*,5*S*,6*R*)-2,3-η : O-σ : C,5,6, C-η-(7,7-dimethoxy-5,6-dimethylidenebicyclo[2.2.1]hept-2-ene)]diiron.

A variable temperature and pressure NMR study of the fluxional behaviour of **1** and **2** is under study.

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Supplementary Material. Lists of observed and calculated structure factors, thermal parameters, bond lengths and angles involving H-atoms, and least-square planes are available on request from R. R.

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