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Structural Investigations on $Fe_2(CO)_5(HC_2Bu^t)_3(CO)$

E. SAPPA, L. MILONE
Institute of Inorganic Chemistry, University of Turin, Corso Massimo d'Azeglio 48, 10125 Turin

G. D. ANDREETTI
Institute of Structural Chemistry, University of Parma, Via Massimo d'Azeglio 85, Parma, Italy
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The compound $Fe_2(CO)_5(HC_2Bu^t)_3(CO)$, obtained from $Fe_3(CO)_{12}$ and HC_2Bu^t was studied by means of X-ray, Mössbauer and ^1H nmr techniques. A comparison is made with the already known $Fe_2(CO)_5(HC_2Ph)_3(CO)$ from which the effect of the substituents of the acetylene on the structures is evidenced. Both the compounds show unusual low field absorptions at the ^1H nmr and a low temperature run also shows the fluxionality of a Bu^t group.

The compound crystallizes as orthorhombic prisms, space group Pbca; 3869 indipendent reflexions were measured and 2474 used in the crystal analysis, and the structure was refined to a R factor of 3,9%. It shows two differently surrounded iron atoms, and a complex organic moiety constituted by three acetylene molecules and a ketonic group.

Introduction

The reactions of dodecacarbonyltriiron and acetylenes HC_2R are presently reinvestigated in our laboratory. We are particularly looking for the possibilities that nmr techniques can offer to a better understanding of these reactions together with an improved picture of the bonding in the variety of bi- and tri-nuclear complexes obtained.

This report deals with some interesting features of the newly synthesized $Fe_2(CO)_5(HC_2Bu^t)_3(CO)$ (I) and with some general aspects of the $Fe_2(CO)_5(HC_2R)_3(CO)$ derivatives. Compounds of this formula have already been obtained both from bisubstituted acetylenes (C_2Me_2, C_2Et_2)[1] and monosubstituted ones (HC_2Ph)[1]. In these complexes, three acetylene molecules and a ketonic group form a complex organic moiety linked to two metal centers: an asymmetrically substituted sp^3 carbon atom, and a sp^2 carbon atom σ bonded to one iron atom and π bonded to the other one, $C[\sigma,\pi]$, are present.

Compound (I) is isostructural with $Fe_2(CO)_5(HC_2Ph)_3(CO)$ (II)[2] from which it differs for the different disposition of the ligands, as shown by ^1H nmr and X-Ray. A low-field ^1H nmr signal due to the hydrogen on $C[\sigma,\pi]$, and a temperature dependent signal due to one t-butyl group are observed.

Experimental

Compound (I) is obtained in about 2% yield by refluxing a 5:1 molar excess of 3,3-dimethyl-butyne-1 with $Fe_3(CO)_{12}$ in dehydrated n-heptane under dry nitrogen, for 25 min, together with other tri-, bi- and mono-nuclear iron derivatives[3]. The reaction mixture was purified by preparative T.L.C. (Kieselgel P.F. nach Stahl: eluent, mixtures of petroleum and ethyl ethers); the red-yellow solid obtained contains as major impurity di(t-butyl)-*p*-benzoquinone. Upon crystallization from n-heptane deep red crystals of the complex and yellow crystals of the quinone were obtained, which were manually separated. *Anal.* Calcd. C% 54.78, Fe% 21.23, H% 5.75, O% 18.24%; Found: C% 55.01, Fe% 20.79, H% 5.23, O% 18.97.

Compound (I) is diamagnetic: the measurement was carried out by Evans method[4]. Its i.r. spectrum, in CCl_4 solution, shows the following CO stretching absorptions: 2068 vs, 2022 vs(sh), 2000 vs, 1964 s, 1668 s cm^{-1}. The mass spectrum shows the parent ion: the main fragmentation pattern is, however, the loss of H_2 followed by that of six CO groups and by the fragmentation of the organic moiety; partial demolition of the organic substituent prior to the loss of CO is also observed. The abundance of mono-nuclear fragments is indicative of low stability; compound (II) decomposes in the mass spectrometer.

$Fe_2(CO)_5(HC_2Ph)_3(CO)$ (II) was obtained following the literature reports[1].

The analyses of the compounds were performed by means of an F. & M. 187 C, H, N, Analyzer and Atomic Absorption Spectrophotometer Perkin–Elmer 303; the i.r. spectra were obtained on a Beckmann IR-12 and the pmr spectra either on a JEOL C60 HL or on a

JEOL NM-100 PS. The mass spectrum was registred on an Hitachi–Perkin Elmer RMU-6H*.

X-Ray Crystal and Molecular Analysis

The compound crystallizes as orthorhombic prism elongated along [100] and showing the forms: {010}, {021} and {100}. The space group, determined from the systematic absences is *Pbca*. The unit cell parameters were determined from the least-squares fit to $(\Theta,\chi,\Phi)_{hkl}$ values of 18 reflections measured on a Siemens single-crystal diffractometer at room temperature, to be $a = 14.12(1)$, $b = 19.99(1)$, $c = 17.38(1)$ Å; $V = 4905.7$ Å^3; $Z = 8$; $D_x = 1.46$, D_m (floatation) $= 1.45$ g cm^{-3}; $\mu = 12.8$ cm^{-1} (Mo Kα). The intensity data were collected up to $\Theta = 29°$ (corresponding to the complete copper sphere data), using the ω–2Θ scan method (Mo *K*α). 3869 independent reflections were measured and 2474 were used in the crystal analysis, having considered as "unobserved" the reflections whose intensities were less than twice $[\sigma^2(I)\ (0.01 \times I)^2]^{1/2}$, where I is the relative intensity and $\sigma^2(I)$ its variance. The statistical factor $\Sigma 0.7979\sigma(F_o)/\Sigma|F_o|$, taken as a measure of the precision in the data was 3.9%. The volume of the crystal used for data collection was 5.3×10^{-2} mm^3 and the absorption effects were taken in account by gaussian integration[6]. Transmission factors ranged from 0.810 to 0.640.

Structure Determination and Refinement

The position of the heavy atoms has been determined by direct methods. All the other atoms have been located by Fourier techniques. The refinement was carried out by means of cycles of block-diagonal least-squares using at the beginning isotropic and then anisotropic thermal parameters. At R = 7.2% a difference synthesis was computed and it revealed significant residual peaks of about 0.5 e Å^{-3} over a background of ± 0.3 e Å^3, which could be interpreted as being due to hydrogen atoms. The methyl hydrogen atoms peaks were slightly smeared but well resolved. Three more least-squares cycles were computed including the hydrogen atoms with isotropic thermal parameters held constant at 5.5 Å^2. The resulting value of R was 0.050. At this stage weights derived from a plot of ΔF versus $|F_o|$ were introduced and two more cycles dropped the R factor to 0.047 [goodness of fit $= \Sigma w\Delta F^2/(m-n) = 1.14$]. The atomic scattering factors were those of Cromer and Waber (1965)[7] for Fe^{3+} (the oxidation state of Fe has been deduced from the Mössbauer spectrum), O, C and those of Stewart, Davidson and Simpson (1965)[8] for H. The positional and thermal parameters are listed in Table I, together with the arbitrary numbering scheme. Bond distances and angles are given in Table II. In Figure 1 the structure is represented.

All the calculations have been performed on the C.D.C. 6600 computer of the Centro di Çalcolo Elettronico Interuniversitario dell'Italia Nord Orientale, Casalecchio, Bologna.

^{1}H Nmr Spectra

The ^{1}H nmr spectra for compounds (I) and (II) are reported in Table III (in the annexed Scheme, the different disposition of the substituents in the compounds is evidenced). The appearance in the ^{1}H nmr spectrum of (II) of three singlets for the three hydrogen atoms clearly indicates that they are not on adjacent carbon atoms in agreement with the known structure[2]. The chemical shift of H_1 ($\tau = -1.80$) is noteworthy. Such low field values for H bonded to sp^2 carbon in organometallic complexes of transition elements are quite unusual.

The ^{1}H nmr spectra of (I) show two doublets for H_2 and H_3 (J = 5.3 Hz) therefore suggesting a bonding different from that of (II) of the acetylene molecules in the organic moiety. Moreover the different substituent strongly influences the chemical shift of H_1 with an upfield shift (about 2 ppm) when the substituent is the electron donor Bu^t. The three absorptions at τ 8.18, 8.64, 9.10 are assigned to the three Bu^t groups; the first two low field sharp absorptions can be associated with the Bu^t close to the sp^2 carbons on ground of the chemical shift for the Bu^t in related systems.[9] The broad signal at τ 9.10 splits into three singlets (1:1:1) at –40° C with a coalescence temperature of –12° C and is associated to the Bu^t bonded to the asymmetrically substituted sp^3 carbon.

Results and Discussion

From the reaction of $Fe_3(CO)_{12}$ with HC_2Bu^t and HC_2Ph one only out of the eight conceivable isomeric forms with the same skeleton has been obtained in appreciable yield for the $Fe_2(CO)_5(HC_2R)_3(CO)$ derivatives. If we compare this with the number of isomers obtained for other tri- and bi-nuclear products of the same reaction[3], $Fe_2(CO)_5(HC_2R)_3(CO)$ show that a highly selective mechanism is operating in their formation, in which the nature of the substituent is effective in determining the isomer obtained.

Compound (I) could be obtained neither from the $Fe_3(CO)_8(HC_2Bu^t)_2$ (CO bridge-bonded isomers) and $Fe_2(CO)_6(HC_2Bu^t)_2$ compounds, nor from the $Fe_2(CO)_6(HC_2Bu^t)_2(CO)$[3] under conditions comparable with those of the original preparation and even in excess of ligand and under a CO atmosphere.

We therefore suggest that the tri-acetylenic derivatives are formed either by already polymerized acety-

* A. Mössbauer investigation shows that in compound (I) two non-equivalent iron atoms are present, in good agreement with the X-ray results and with the values reported for iron organic compounds[5].

TABLE I. Fractional Coordinates (× 10^4) and Thermal Parameters (× 10^2 Å^2) with e.s.d.'s.[a]

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	1879(1)	1517(0)	760(1)	343(4)	231(3)	286(3)	16(3)	−53(3)	0(3)
Fe(2)	2676(1)	421(0)	992(1)	333(4)	239(3)	303(3)	24(3)	6(3)	−9(3)
O(1)	2359(4)	2940(3)	574(3)	717(31)	325(18)	669(27)	−78(22)	−48(27)	40(19)
O(2)	1524(5)	1444(3)	−907(3)	924(38)	642(26)	373(22)	−244(28)	−204(24)	65(20)
O(3)	−146(4)	1772(3)	1012(4)	540(30)	638(28)	850(35)	246(25)	−1(27)	89(27)
O(4)	2838(5)	−112(3)	−565(3)	931(41)	648(26)	480(26)	36(27)	82(26)	−219(22)
O(5)	3554(5)	−793(3)	1592(3)	822(36)	399(22)	767(33)	189(25)	−82(29)	61(22)
O(6)	615(4)	914(3)	2632(3)	533(26)	528(23)	527(27)	−99(22)	243(22)	−121(20)
C(1)	2220(5)	2378(3)	699(4)	396(32)	406(27)	383(29)	11(26)	−94(27)	−19(24)
C(2)	1702(6)	1479(3)	−258(4)	574(42)	295(25)	439(31)	−54(28)	−79(30)	24(24)
C(3)	640(6)	1683(3)	923(4)	624(43)	332(29)	442(35)	122(29)	−145(32)	68(24)
C(4)	2784(5)	95(4)	46(4)	422(37)	338(26)	483(32)	38(27)	−3(28)	−66(25)
C(5)	3190(6)	−310(4)	1355(4)	433(35)	428(30)	423(30)	−59(29)	32(29)	−79(24)
C(6)	1335(5)	585(3)	802(4)	298(28)	300(24)	375(29)	47(21)	−21(24)	−37(21)
C(7)	1240(5)	318(3)	1546(4)	362(30)	268(23)	343(27)	34(24)	−16(23)	−23(20)
C(8)	1218(5)	887(3)	2136(4)	383(31)	330(27)	393(30)	44(25)	−66(26)	0(22)
C(9)	1998(5)	1382(3)	1989(3)	406(31)	236(23)	320(26)	−23(23)	17(24)	17(18)
C(10)	2892(5)	966(3)	2012(4)	455(35)	297(23)	270(25)	−12(24)	−85(24)	20(19)
C(11)	3613(5)	1069(3)	1497(4)	374(31)	317(25)	333(27)	−6(25)	15(25)	12(22)
C(12)	3344(5)	1273(3)	758(4)	395(32)	273(23)	372(27)	32(22)	−36(25)	−40(21)
C(13)	701(5)	−332(3)	1716(4)	446(35)	265(24)	497(33)	−50(27)	104(29)	−1(24)
C(14)	2031(6)	1991(3)	2574(4)	606(43)	355(26)	358(28)	−85(29)	30(29)	−124(23)
C(15)	4149(5)	1503(4)	203(4)	499(37)	464(30)	321(30)	−8(31)	18(27)	−14(25)
C(16)	867(6)	−864(4)	1098(5)	637(39)	301(29)	760(47)	−37(31)	−30(40)	−59(30)
C(17)	−348(6)	−197(4)	1728(5)	481(41)	509(36)	642(43)	−139(32)	137(34)	−169(31)
C(18)	986(7)	−606(4)	2514(6)	616(46)	428(32)	770(48)	−113(34)	45(41)	140(34)
C(19)	1145(6)	2434(4)	2492(5)	638(44)	502(33)	525(38)	103(36)	2(36)	−178(31)
C(20)	2078(6)	1724(4)	3403(4)	786(53)	455(31)	328(29)	−106(35)	−7(32)	−125(25)
C(21)	2935(7)	2413(4)	2450(4)	928(58)	397(29)	446(34)	−215(38)	81(38)	−140(26)
C(22)	4608(6)	2130(4)	532(5)	538(42)	515(36)	561(40)	−178(33)	22(34)	16(31)
C(23)	4900(6)	960(4)	160(5)	637(47)	491(38)	723(49)	57(35)	336(41)	12(34)
C(24)	3808(6)	1667(4)	−601(4)	663(46)	562(37)	351(32)	−131(35)	58(31)	18(27)

Fractional Coordinates (× 10^3) for Hydrogens

	x	y	z		x	y	z
H(1)	082(5)	035(3)	033(4)	H(16)	159(5)	134(3)	350(4)
H(2)	299(5)	067(4)	255(5)	H(17)	272(5)	148(4)	352(5)
H(3)	442(5)	099(4)	155(4)	H(18)	218(5)	206(5)	371(4)
H(4)	059(4)	−130(3)	123(4)	H(19)	266(5)	284(3)	277(4)
H(5)	131(5)	−098(3)	124(4)	H(20)	344(6)	196(4)	251(5)
H(6)	078(5)	−067(3)	063(4)	H(21)	321(5)	269(4)	194(4)
H(7)	−058(5)	−013(3)	117(4)	H(22)	416(5)	252(4)	052(4)
H(8)	−057(5)	011(3)	204(4)	H(23)	469(5)	200(5)	098(4)
H(9)	−072(5)	−065(3)	196(4)	H(24)	519(5)	236(3)	034(4)
H(10)	156(5)	−072(3)	253(5)	H(25)	463(6)	053(4)	−006(4)
H(11)	064(6)	−105(4)	248(4)	H(26)	522(5)	084(3)	065(4)
H(12)	098(5)	−017(3)	296(4)	H(27)	535(6)	108(4)	−018(4)
H(13)	116(5)	272(3)	302(4)	H(28)	435(5)	178(3)	−097(5)
H(14)	038(6)	215(3)	253(5)	H(29)	332(5)	132(4)	−081(4)
H(15)	098(5)	262(4)	203(4)	H(30)	343(5)	211(3)	−077(4)

[a] Temperature factors are of the form exp − 1/4 ($b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl$) where $b_{11} = a^{*2} B_{11}$, $b_{12} = a^*b^* B_{12}$, *etc.*

TABLE II. Bond Distances and Angles (e.s.d.'s on the last digit).

Fe(1)–Fe(2)	=	2.496(2)	C(6)–C(7)	=	1.405(9)
Fe(1)–C(1)	=	1.790(6)	C(7)–C(13)	=	1.535(9)
Fe(1)–C(2)	=	1.789(7)	C(7)–C(8)	=	1.532(9)
Fe(1)–C(3)	=	1.803(9)	C(8)–O(6)	=	1.213(9)
Fe(1)–C(6)	=	2.017(6)	C(8)–C(9)	=	1.503(9)
Fe(1)–C(9)	=	2.160(6)	C(9)–C(14)	=	1.587(9)
Fe(1)–C(12)	=	2.125(7)	C(9)–C(10)	=	1.512(10)
Fe(2)–C(4)	=	1.775(7)	C(10)–C(11)	=	1.371(10)
Fe(2)–C(5)	=	1.749(8)	C(11)–C(12)	=	1.400(10)
Fe(2)–C(6)	=	1.950(7)	C(12)–C(15)	=	1.560(10)
Fe(2)–C(7)	=	2.254(7)	C(13)–C(16)	=	1.530(11)
Fe(2)–C(10)	=	2.103(7)	C(13)–C(17)	=	1.506(11)
Fe(2)–C(11)	=	2.049(7)	C(13)–C(18)	=	1.545(12)
Fe(2)–C(12)	=	1.989(6)	C(14)–C(19)	=	1.539(11)
C(1)–O(1)	=	1.111(9)	C(14)–C(20)	=	1.538(10)
C(2)–O(2)	=	1.158(9)	C(14)–C(21)	=	1.545(12)
C(3)–O(3)	=	1.135(10)	C(15)–C(22)	=	1.523(11)
C(4)–O(4)	=	1.142(9)	C(15)–C(23)	=	1.519(11)
C(5)–O(5)	=	1.169(10)	C(15)–C(24)	=	1.514(10)
Fe(2)–Fe(1)–C(3)	=	125.0(6)°	C(4)–Fe(2)–C(12)	=	94.8(6)°
Fe(2)–Fe(1)–C(6)	=	49.8(2)	C(5)–Fe(2)–C(6)	=	127.2(9)
Fe(2)–Fe(1)–C(1)	=	137.1(7)	C(5)–Fe(2)–C(7)	=	98.2(6)
Fe(2)–Fe(1)–C(12)	=	50.2(2)	C(5)–Fe(2)–C(10)	=	93.9(6)
Fe(2)–Fe(1)–C(2)	=	100.7(4)	C(5)–Fe(2)–C(11)	=	96.1(6)
Fe(2)–Fe(1)–C(9)	=	72.2(2)	C(5)–Fe(2)–C(12)	=	126.3(9)
C(3)–Fe(1)–C(6)	=	78.2(4)	C(6)–Fe(2)–C(10)	=	101.3(6)
C(3)–Fe(1)–C(1)	=	95.4(6)	C(6)–Fe(2)–C(11)	=	126.4(9)
C(3)–Fe(1)–C(12)	=	170.7(9)	C(6)–Fe(2)–C(12)	=	106.4(6)
C(3)–Fe(1)–C(2)	=	91.6(6)	C(7)–Fe(2)–C(10)	=	79.5(4)
C(3)–Fe(1)–C(9)	=	86.7(5)	C(7)–Fe(2)–C(11)	=	117.1(7)
C(6)–Fe(1)–C(1)	=	173.1(9)	C(7)–Fe(2)–C(12)	=	126.3(8)
C(6)–Fe(1)–C(12)	=	99.1(5)	C(10)–Fe(2)–C(11)	=	38.5(3)
C(6)–Fe(1)–C(2)	=	86.8(5)	C(10)–Fe(2)–C(12)	=	70.1(4)
C(6)–Fe(1)–C(9)	=	83.0(4)	C(11)–Fe(2)–C(12)	=	40.5(3)
C(1)–Fe(1)–C(12)	=	87.6(5)	Fe(1)–C(1)–O(1)	=	170.6(7)
C(1)–Fe(1)–C(2)	=	91.1(5)	Fe(1)–C(2)–O(2)	=	175.4(7)
C(1)–Fe(1)–C(9)	=	99.1(5)	Fe(1)–C(3)–O(3)	=	178.0(7)
C(12)–Fe(1)–C(2)	=	97.2(6)	Fe(2)–C(4)–O(4)	=	178.9(8)
C(12)–Fe(1)–C(9)	=	84.1(4)	Fe(2)–C(5)–O(5)	=	178.4(9)
C(2)–Fe(1)–C(9)	=	169.8(9)	Fe(1)–C(6)–C(7)	=	114.9(7)
Fe(1)–Fe(2)–C(4)	=	102.2(4)	Fe(1)–C(6)–H(1)	=	125.0(6)
Fe(1)–Fe(2)–C(5)	=	168.1(5)	Fe(1)–C(9)–C(8)	=	101.2(6)
Fe(1)–Fe(2)–C(6)	=	52.2(2)	Fe(1)–C(9)–C(10)	=	99.2(5)
Fe(1)–Fe(2)–C(7)	=	75.1(2)	Fe(1)–C(12)–C(11)	=	109.2(7)
Fe(1)–Fe(2)–C(10)	=	75.3(3)	Fe(1)–C(12)–C(15)	=	130.0(10)
Fe(1)–Fe(2)–C(11)	=	78.8(3)	Fe(2)–C(6)–C(7)	=	82.7(5)
Fe(1)–Fe(2)–C(12)	=	55.2(2)	Fe(2)–C(7)–C(6)	=	59.1(4)
C(4)–Fe(2)–C(5)	=	89.5(6)	Fe(2)–C(12)–C(15)	=	136.4(12)
C(4)–Fe(2)–C(6)	=	89.3(5)	Fe(2)–C(12)–C(11)	=	72.0(4)
C(4)–Fe(2)–C(7)	=	116.1(7)	Fe(2)–C(11)–C(12)	=	67.4(4)
C(4)–Fe(2)–C(10)	=	163.4(8)	Fe(2)–C(11)–C(10)	=	72.9(4)
C(4)–Fe(2)–C(11)	=	125.0(9)	Fe(2)–C(10)–H(2)	=	117.0(7)
Fe(2)–C(10)–C(9)	=	98.1(5)	C(7)–C(13)–C(16)	=	112.2(10)
Fe(2)–C(10)–C(11)	=	68.6(4)	C(7)–C(13)–C(17)	=	109.8(10)
C(7)–C(6)–H(1)	=	115.0(6)	C(7)–C(13)–C(18)	=	110.1(11)
C(6)–C(7)–C(13)	=	123.1(12)	C(16)–C(13)–C(17)	=	106.6(10)
C(6)–C(7)–C(8)	=	109.6(10)	C(16)–C(13)–C(18)	=	110.1(12)
C(8)–C(7)–C(13)	=	119.3(11)	C(17)–C(13)–C(18)	=	107.9(12)
C(7)–C(8)–C(9)	=	111.1(9)	C(9)–C(14)–C(19)	=	111.0(10)

TABLE II. (Cont.)

C(7)–C(8)–O(6)	=	121.5(12)	C(9)–C(14)–C(20)	=	109.6(9)
C(9)–C(8)–O(6)	=	127.3(14)	C(9)–C(14)–C(21)	=	110.7(10)
C(8)–C(9)–C(10)	=	104.2(9)	C(19)–C(14)–C(20)	=	108.8(11)
C(8)–C(9)–C(14)	=	114.7(10)	C(19)–C(14)–C(21)	=	110.1(12)
C(10)–C(9)–C(14)	=	112.4(10)	C(20)–C(14)–C(21)	=	106.5(11)
C(9)–C(10)–C(11)	=	121.3(13)	C(12)–C(15)–C(22)	=	108.7(10)
C(9)–C(10)–H(2)	=	115.0(7)	C(12)–C(15)–C(23)	=	109.2(11)
C(11)–C(10)–H(2)	=	122.0(8)	C(12)–C(15)–C(24)	=	113.8(11)
C(10)–C(11)–C(12)	=	116.2(12)	C(22)–C(15)–C(23)	=	108.0(11)
C(10)–C(11)–H(3)	=	131.0(9)	C(22)–C(15)–C(24)	=	107.7(10)
C(12)–C(11)–H(3)	=	113.0(6)	C(23)–C(15)–C(24)	=	109.4(11)
C(11)–C(12)–C(15)	=	117.1(12)			

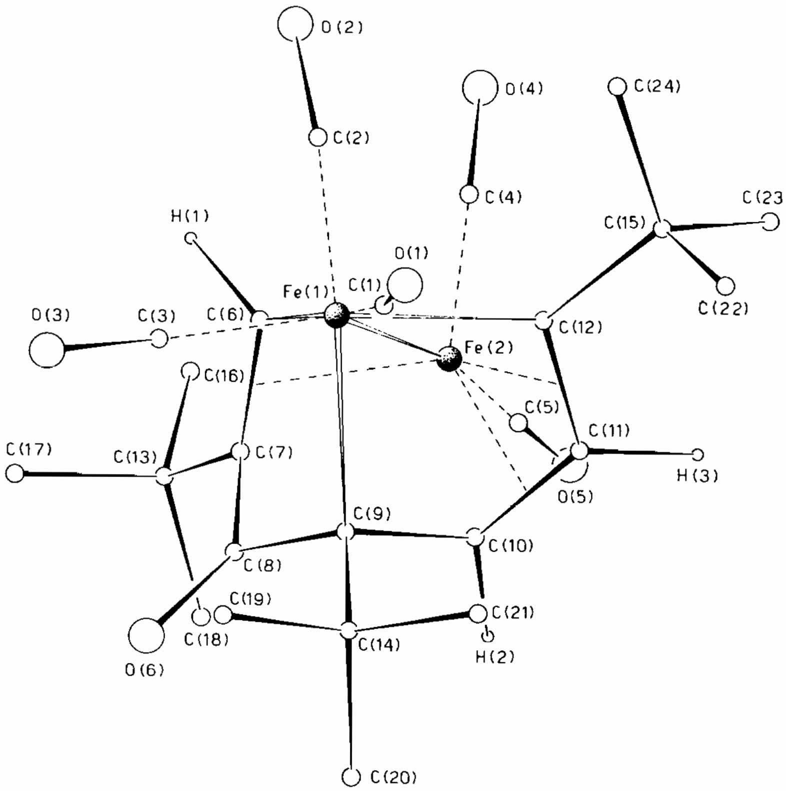


Figure 1. Structure of $Fe_2(CO)_5(HC_2Bu^t)_3(CO)$.

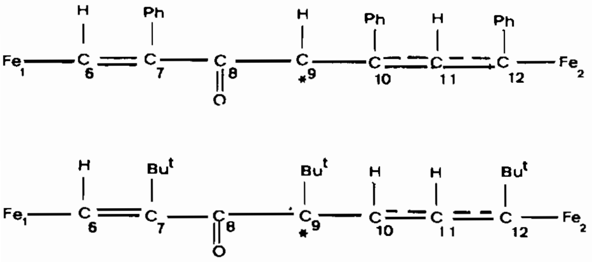
lenes or by "oriented" polymerization on the cluster, rather than by stepwise CO substitution on the above carbonyl–acetylenic derivatives; compounds such as $Fe_2(CO)_5(Me_2NCHC_3H_5CHC_5H_4)$[10] and (1-diphenyl-methylene-3-phenyl-indene)$Fe_2(CO)_5$[11] obtained from complex organic molecules and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ respectively, are indeed known, as well as tri- and tetra-acetylene substitutcd trimetallic compounds of Iron and Ruthenium at present investigated in our laboratory[3].

The iron–iron distance found for (I) is in good agreement with the known values for other binuclear iron compounds, with the only significant exceptions of $Fe_2(CO)_6(C_2H_2)_3$ "deep-red isomer"[12] and $Fe_2(CO)_5(Me_2NCHC_5H_3CHC_5H_4)$[10] in which two non-equivalent iron atoms are present with a bond length of 2.679 and 2.739 Å respectively; in the opinion of the Authors, this is due to the existence of only one carbon atom bridge between the metals[12], whereas in (I) at least two carbons are directly involved.

TABLE III. ^{1}H Nmr Spectra (τ) of $Fe_2(CO)_5(HC_2R)_3(CO)$ at 25° C. CCl_4 Solutions.

$R = Bu^t$	$R = Ph$
0.01 s (H_1)	–1.80 s (H_1)
4.0 d (H_2)	2.60 m (15 H)
6.33 d (H_3)	5.50 s (H_2)
8.18 s (9 H)	7.75 s (H_3)
8.64 s (9 H)	
9.10 s (9 H) broad	

Scheme showing the substitution of the organic moieties of $Fe_2(CO)_5(HC_2R)_3(CO)$ ($R = Bu^t$, Ph), and the numbering of the skeleton carbon atoms:



In Table IV the most significant bond lengths are reported for (I) and (II): the same general trend is observed in the compounds. For the t-butyl derivative, however, an elongation of the σ M–C bonds and a shortening in the multiple C–C as well as in the π M–C bonds is observed, which is in good agreement with the electron-donor properties of the substituent. In particular, the Fe(1)–C(9) distance is greater than the reported value for the covalent Fe–C(sp^3) bond[13].

TABLE IV. Comparison between the Most Significant Bonding Distances in $Fe_2(CO)_5(HC_2R)_3(CO)$.

Bond	$R = Bu^t$	$R = Ph$
Fe(1)–Fe(2)	2.496(2)	2.501(3)
Fe(1)–C(6)	2.017(6)	2.006(11)
Fe(1)–C(12)	2.125(7)	2.088(13)
Fe(1)–C(9)	2.160(6)	2.097(10)
Fe(2)–C(12)	1.989(6)	1.975(11)
Fe(2)–C(11)	2.049(7)	2.108(11)
Fe(2)–C(10)	2.103(7)	2.203(11)
C(6)–C(7)	1.405(9)	1.419(15)
C(11)–C(12)	1.400(10)	1.407(15)
C(10)–C(11)	1.371(10)	1.425(16)

The lengthening of the σ M–C bonds, and the corresponding shortening of the C–C and π M–C bonds, indicative of a lesser σ donation from the metal and a greater π retrodonation from the ligand, indicate that the inductive effects of the substituents on the acetylenes play a role in the determining the bond lengths.

The bond angles are of the order of magnitude expected from the hybridization of the carbon atoms; C(6)–C(7)–C(8) is the only remarkable exception, probably due to steric interaction between the two halves of the organic moiety.

The chemical shift of H_1 in both compounds is quite interesting for its low field position. This is quite unusual if compared with the upfield shift observed for an H on a sp^2 carbon in π complexes of transition elements. To our knowledge the only examples so far known[14] are for systems in which, as in our case, the low-field absorption is associated to an H on a sp^2 C[σ,π].

Further work is in progress in our laboratory to look for wider explanation of the reasons for these absorptions.

Acknowledgments

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