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Unusual Complexes formed by Reaction of Diiron Nonacarbonyl with 1-ene-3-yne Molecules

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*It is shown that $Fe_2(CO)_9$ reacts with the 1-ene-3-yne molecules $CH_2{=}C(CH_3){-}C{\equiv}CR$, R = $C(CH_3)_3$ and CH_2CH_3, to afford binuclear complexes of the type $[CH_2C(CH_3)CC(R)CO]Fe_2(CO)_6$, both of which have been characterized by X-ray crystallography. For compound **1** (R = CMe_3) the space group is $P2_1/n$ with unit cell dimensions of a = 10.025(3) Å, b = 11.168(4) Å, c = 16.482(7) Å, β = 101.94(3)°, V = 1805(1) $Å^3$, and Z = 4. The structure was refined to R_1 = 0.034 and R_2 = 0.043 using anisotropic temperature factors for all C, O and Fe atoms and isotropic ones for the 14 hydrogen atoms, and employing 1818 reflections for which $I>3\sigma(I)$. For compound **2** (R = CH_2CH_3), the space group is, again, $P2_1/n$, with a = 9.354(3) Å, b = 12.775(5) Å, c = 13.840(5) Å, β = 92.71(3)°, V = 1587(1) $Å^3$ and Z = 4. Hydrogen atoms were ignored in the refinement of this structure. The 23 C, O and Fe atoms were refined anisotropically employing 1912 reflections for which $I>3\sigma(I)$ to final discrepancy indices of R_1 = 0.049 and R_2 = 0.065. The two structures are nearly identical with an average Fe–Fe distance in the $(OC)_3Fe{-}Fe(CO)_3$ unit of 2.745 Å. The 1-ene-3-yne molecule combines with one CO group to give a five carbon chain of the type $H_2CC(CH_3)CC(R)CO$ which is a six-electron donor to the $Fe_2(CO)_6$ unit. The $H_2CC(CH_3)C$ portion serves as a allyl ligand while the CC(R)CO portion serves also as an 3-electron donor with character intermediate between allylic and C=C–CO as indicated by the bond distances. The carbon atom common to both these 3-carbon portions is of a very unusual, if not unique, type since it belongs to two nearly perpendicular 3-carbon 3-electron units and thus bridges two metal atoms.*

Introduction

In a recent communication[1] we reported that the reaction of an equimolar mixture of $Fe_2(CO)_9$ and di-*t*-butylacetylene (*t*-Bu_2C_2) produced (*t*-Bu_2C_2)$Fe_2(CO)_6$ as the main reaction product along with a very small amount of a compound which was characterized by x-ray crystallography as $(C_9H_{14}CO)Fe_2(CO)_6$, **1**. The origin of the second compound interested us for two reasons: first, this product is not one to be expected from the above reaction and, second, the binding of the $C_9H_{14}CO$ ligand to the two iron atoms has several unique features.

We describe here the synthesis and characterization of this rather unusual compound, identify its origin, and give complete details of its crystal structure. Furthermore we report the synthesis and characterization of the ethyl analog, **2**, of $(C_9H_{14}CO)Fe_2(CO)_6$ as well as details of its crystal structure.

Experimental

All operations were performed in an atmosphere of dry nitrogen. Solvents were dried over potassium–benzophenone and were distilled under nitrogen immediately prior to use. Diiron nonacarbonyl was purchased from Pressure Chemical Co., di-*t*-butylacetylene (98%) and 2-methyl-1-hexen-3-yne (99%) were purchased from Chemical Samples Co. Infrared spectra were recorded on a Perkin–Elmer 237 spectrometer. Elemental analyses were performed by Galbraith Laboratories. A sample of *t*-Bu_2C_2 was purified on a Waters Associates high pressure liquid chromatograph with re-cycle capabilities.

Synthesis of $(C_9H_{14}CO)Fe_2(CO)_6$

A mixture of 2.34 g (6.43 mmol) $Fe_2(CO)_9$ and 0.89 g (6.4 mmol) *t*-Bu_2C_2 in 40 ml hexanes was stirred for 24 hours at ambient temperature during which time the $Fe_2(CO)_9$ was consumed and the reaction solution became a very dark green due to formation of (*t*-Bu_2C_2)$Fe_2(CO)_6$.[1] The dark green solution was filtered and the filtrate was concentrated *in vacuo* to a volume of about 8 ml. This solution was then chromatographed on Florisil with hexane. After the dark green band began to move down the column, a bright orange band was observed at the top of the column. Elution with benzene caused the orange band to move rapidly down the column. The orange solution was evaporated to dryness *in vacuo,* leaving a sticky solid which was redissolved in 2 ml pentane. At –40°C this solution produced about 10 dark red–orange crystals. IR (hexane): 2060(s), 2025(vs), 1985(s), 1990(m), 1975(s) and 1780(m) cm^{-1}. *Anal.* Calcd for $C_{16}H_{14}O_7Fe_2$: C, 44.69; H, 3.28. Found: C, 44.84; H, 3.41.

Synthesis of $(C_7H_{10}CO)Fe_2(CO)_6$

A mixture of 0.64 g (1.8 mmol) $Fe_2(CO)_9$ and 0.17 g (1.8 mmol) 2-methyl-1-hexen-3-yne in 20 ml THF was stirred for 3 hours at ambient temperature. As the $Fe_2(CO)_9$ was consumed the reaction solution turned dark red in color. The deep red solution was evaporated to dryness *in vacuo,* redissolved in 5 ml benzene, and then chromatographed on Florisil (2.2 × 66 cm) with benzene. The reddish–orange chromatography band was collected and taken to dryness *in vacuo.* The compound was recrystallized in small amounts from pentane at –40°C.

The reaction has also been repeated in hexane but complete consumption of the $Fe_2(CO)_9$ required a period of 18–24 hr. IR(hexane): 2060(s), 2025(vs), 2000(s), 1995(sh), 1975(s), and 1785(m) cm^{-1}. *Anal.* Calcd for $C_{14}H_{10}O_7Fe_2$: 41.84; H, 2.51. Found: C, 41.94; H, 3.05.

X-Ray Data Collection

A deep red–orange crystal of $(C_9H_{14}CO)Fe_2(CO)_6$ measuring approximately 0.29 × 0.23 × 0.43 mm was sealed in a glass capillary. All data were collected on a Syntex $P\bar{1}$ computer-controlled diffractometer at 21 ± 2°C using Mo-Kα radiation monochromatized with a graphite crystal. Procedures for crystal characterization, space group assignment and data collection have been previously mentioned[2] and only deviations will be described. Omega scans of several intense reflections gave peak widths at half-heights $\leqq 0.2°$.

The lattice parameters and orientation matrix used for data collection were obtained from the least-squares refinement of the diffraction geometry of fifteen high-angle reflections, $19° \leqq 2\Theta \leqq 39°$. The lattice parameters are: a = 10.025(3)Å, b = 11.168(4)Å, c = 16.482(7)Å, β = 101.94(3)°, and V = 1805(1)Å^3. The calculated density for Z = 4 and a molecular weight of 429.99 is 1.58 gm cm^{-3}.

A total of 2276 unique reflections in the range $0° < 2\Theta \leqq 45°$ were collected using the Θ–2Θ scan technique, variable scan rates from 3.0 to 24.0°/min depending upon the intensity of the reflection, and a scan range from 2Θ(Mo-Kα_1) –0.9° to 2Θ(Mo-Kα_2) +0.9°. Intensities of three standard reflections were measured after every 200 reflections and showed no significant variation during data collection. A total of 1818 reflections which had $F_o^2 > 3\sigma(F_o^2)$ (using a value of 0.07 for p in the calculation of σ) were retained as observed data and were used in all phases of the structure solution and refinement. The systematic absences, h0l (h+l $\neq$ 2n) and 0k0 (k $\neq$ 2n), uniquely determine the monoclinic space group $P2_1/n$ (a non-standard setting of $P2_1/c$).

Lorentz and polarization corrections were applied to the data[3] but no absorption correction was deemed necessary as the linear absorption coefficient is 4.2 cm^{-1}.

Solution and Refinement of the $(C_9H_{14}CO)Fe_2(CO)_6$ *Structure*

The positions of the two iron atoms were located from a three-dimensional Patterson synthesis.[3] The coordinates of both iron atoms were refined in two cycles of least-squares refinement to give discrepancy factors

$$R_1 = (\Sigma||F_o|-|F_c||/\Sigma|F_o|) = 0.378$$

$$R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{1/2} = 0.463$$

The function, $\Sigma w(|F_o|-|F_c|)^2$, where the weighting factor, w, equals $4F_o^2/\sigma(F_o^2)^2$, was minimized during least-squares refinement. Atomic scattering factors were those of Cromer and Waber.[4] Anomalous dispersion effects were included in the calculated scattering factors for the iron atoms.[5]

A difference Fourier map was then calculated which clearly revealed the positions of five terminal CO groups. Two cycles of least-squares refinement of these 12 atoms employing isotropic temperature parameters for all atoms gave $R_1 = 0.291$ and $R_2 = 0.380$. All remaining non-hydrogen atoms were found in two successive difference Fourier maps, each of which followed least-squares refinement of the atoms found up to that point. Two cycles of full-matrix least-squares refinement in which the iron atoms were refined anisotropically and the other non-hydrogen atoms were refined isotropically gave R_1 = 0.066 and R_2 = 0.096.

Following two cycles of full-matrix least-squares refinement employing anisotropic thermal parameters for all 25 non-hydrogen atoms, a difference Fourier map revealed the positions of the 14 unique hydrogen atoms. The positions of the non-hydrogen atoms were held constant and the positional and isotropic thermal parameters of the hydrogen atoms were refined in two cycles of least-squares refinement. The parameters for all atoms were then refined to convergence in four cycles of full-matrix least-squares refinement, using anisotropic thermal parameters for the 25 non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms, to R values of R_1 = 0.034 and R_2 = 0.043. During the final cycle of least-squares refinement no parameter shifted by more than 0.1σ, where σ is the estimated standard deviation of that parameter. An examination of the final calculated and observed structure factors revealed no effects of extinction, nor were any trends observed as a function of reflection number, Miller indices, or $\lambda^{-1}\sin\Theta$.

X-Ray Data Collection for $(C_7H_{10}CO)Fe_2(CO)_6$

Only deviations from the procedures outlined above will be described. A dark red–orange crystal measuring 0.20 × 0.25 × 0.18 mm was sealed in a glass capillary. Variable scan rates from 4.0° to 24.0°/min were employed in the range $0<2\Theta\leqq 45°$ and 3.0° to 24.0°/min in the $45°<2\Theta\leqq 55°$ range depending upon the intensity of the reflection. Of the 2409 unique reflections a total of 1912 had $F_o^2>3\sigma(F_o^2)$ and were subsequently used in refinement. The principal crystallographic data are as follows: Space group, $P2_1/n$; a = 9.354(3)Å, b = 12.775(5)Å, c = 13.840(5)Å, β = 92.71(3)°; V = 1587(1)Å^3. The calculated density for Z = 4 and a molecular weight of 401.93 is 1.68 gm cm^{-3}. No absorption correction was performed as the linear absorption coefficient is 4.8 cm^{-1}.

Solution and Refinement of the $(C_7H_{10}CO)Fe_2(CO)_6$ Structure

The position of each iron atom was found from a three-dimensional Patterson function. Two cycles of least-squares refinement of the iron positions gave R_1 = 0.322 and R_2 = 0.409. A subsequent difference Fourier map clearly revealed the positions of all non-hydrogen atoms except C12 and C13. These two carbon positions were found from a difference-Fourier map calculated after two cycles of least-squares refinement of the initial 21 atoms. All non-hydrogen atom positions refined to convergence in three additional cycles of least-squares refinement in which isotropic thermal parameters were employed. The positional and anisotropic thermal parameters were refined to convergence in four cycles of full-matrix least-squares refinement yielding R_1 = 0.049 and R_2 = 0.065. A final difference-Fourier map exhibited no peaks greater than 0.38 e/Å^3 compared to values of 5.3 to 6.3 e/Å^3 observed for carbon atoms. The top peaks in this final map were in positions anticipated for hydrogen atoms. However, since hydrogen positions had been found in the previous structure and bond lengths and angles of the two structures are very similar, the hydrogen atoms in this second structure were not included. During the final cycle of least-squares refinement no parameter shifted by more than 0.1σ, where σ is the estimated standard deviation of that parameter. An examination of the final observed and calculated structure factors revealed no effects of extinction, nor were any trends observed as a function of reflection number, Miller indices, or $\lambda^{-1}\sin\Theta$.

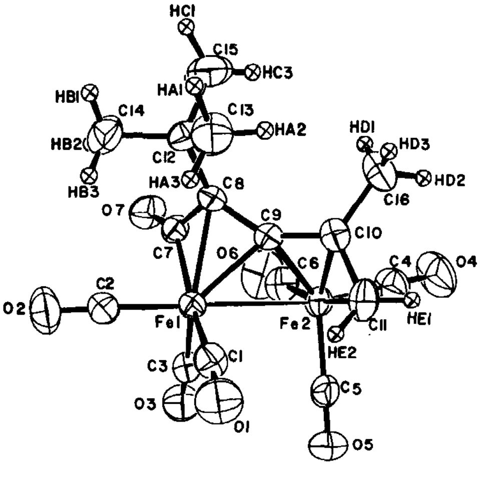

Figure 1. The molecular structure of $(C_9H_{14}CO)Fe_2(CO)_6$, **1**. Atoms are represented by their ellipsoids of thermal vibration chosen to enclose 40% of the electron density.

A table of observed and calculated structure factor amplitudes as well as tables of least squares planes are available for each structure.[6]

Results

Synthesis and Characterization

Characterization of the orange chromatography band obtained from the reaction of $Fe_2(CO)_9$ with di-*t*-butylacetylene seemed especially important since Hübel claimed that, contrary to most acetylene–iron carbonyl reactions, the reaction of a bulky acetylene with an iron carbonyl would not give complexes containing cyclic ligands due to steric hindrance. We wondered at first if the minor red–orange product might be a substance with a cyclized ligand system. Since only about 10 crystals of the complex could be isolated on a scale of 2 gm of $Fe_2(CO)_9$, the most practical way to characterize this compound was by X-ray crystallography. The X-ray structure determination[1] showed the compound to be $(C_9H_{14}CO)Fe_2(CO)_6$, **1**, with the structure shown in Figure 1.

In speculating upon the origin of the $C_9H_{14}CO$ ligand in **1**, it was first noted that the C_9H_{14} portion is formally obtainable from t-Bu_2C_2 by 1,2-elimination of methane. It did not seem likely, however, that such an elimination would really take place under the reaction conditions. A more attractive alternative was the hypothesis that 2,5,5-trimethyl-1-hexen-3-yne is present as an impurity in the t-Bu_2C_2 as purchased.[7]

To test the possibility that the reaction of a "1-ene-3-yne" with $Fe_2(CO)_9$ would produce a complex analogous to **1**, 2-methyl-1-hexen-3-yne (C_2H_5–C≡C–$C(CH_3)$=CH_2) was reacted with $Fe_2(CO)_9$. A red crystalline solid was obtained whose infrared spectrum (in the CO region) was virtually identical with that of **1**. In addition, the mass spectrum of each compound exhibited the same pattern of peaks: M^+ (not observed); $(M–nCO)^+$, n = 1–7; and $(R–C≡C–C(CH_3)=CH_2)^+$, R = t-Bu, Et. An elemental analysis of this second compound was also consistent with the formulation $(C_7H_{10}CO)Fe_2(CO)_6$.

All available data indicated that the two compounds were homologous. However, to remove any doubts the crystal structure of $(C_7H_{10}CO)Fe_2(CO)_6$ was also determined and found to be virtually identical with $(C_9H_{14}CO)Fe_2(CO)_6$ as expected.

As final proof that **1** originated from the reaction between $Fe_2(CO)_9$ and the impurity and not from the reaction of *t*-Bu_2C_2 and $Fe_2(CO)_9$, a sample of the *t*-Bu_2C_2 was chromatographed on a high pressure liquid chromatograph to eliminate impurities. The purified sample of *t*-Bu_2C_2 was reacted with $Fe_2(CO)_9$ as before. Chromatography of the reaction product did not produce the orange band as previously seen. This observation proves that **1** is produced by the reaction of the 1-ene-3-yne impurity with $Fe_2(CO)_9$ and not by the reaction of *t*-Bu_2C_2 itself with $Fe_2(CO)_9$.

Structures of the Compounds

The atomic positional parameters of $(C_9H_{14}CO)Fe_2(CO)_6$ are given in Tables I and II and the thermal parameters in Tables II and III. The structure of $(C_9H_{14}CO)Fe_2(CO)_6$ is shown in Figure 1 along with the labelling scheme. Table IV contains the atomic positional parameters of $(C_7H_{10}CO)Fe_2(CO)_6$ while Table V contains the thermal parameters. The structure and labelling scheme are shown in Figure 2. No unusual intermolecular contacts were observed in either crystal.

TABLE I. Atomic Positional Parameters for $(C_9H_{14}CO)Fe_2(CO)_6$[a].

	x	y	z
Fe1	0.4363(1)	0.2152(1)	0.2497(1)
Fe2	0.6126(1)	0.1686(1)	0.1467(1)
O1	0.5726(4)	0.4404(3)	0.3172(2)
O2	0.2508(4)	0.2315(3)	0.3647(2)
O3	0.6047(3)	0.0422(3)	0.3582(2)
O4	0.7533(4)	0.0949(4)	0.0163(2)
O5	0.8552(4)	0.1755(4)	0.2823(2)
O6	0.5315(4)	–0.0820(3)	0.1538(3)
O7	0.2459(3)	0.0130(3)	0.1874(2)
C1	0.5204(5)	0.3571(4)	0.2876(3)
C2	0.3219(5)	0.2287(4)	0.3193(3)
C3	0.5417(4)	0.1105(4)	0.3152(3)
C4	0.7000(5)	0.1253(5)	0.0672(3)
C5	0.7621(5)	0.1726(4)	0.2301(3)
C6	0.5597(5)	0.0164(5)	0.1519(3)
C7	0.3054(4)	0.1053(4)	0.1852(2)
C8	0.2990(4)	0.2089(3)	0.1313(2)
C9	0.4295(4)	0.2417(3)	0.1259(2)
C10	0.5045(4)	0.3071(4)	0.0778(3)
C11	0.6301(5)	0.3536(4)	0.1204(3)
C12	0.1656(4)	0.2760(4)	0.0976(3)
C13	0.1933(6)	0.4095(5)	0.0858(4)
C14	0.0655(5)	0.2628(6)	0.1553(4)
C15	0.1046(6)	0.2170(6)	0.0132(4)
C16	0.4664(6)	0.3086(5)	–0.0155(3)

[a] The numbers in parentheses are estimated standard deviations in the last significant digits.

TABLE II. Atomic Positional and Thermal Parameters for Hydrogen Atoms in $(C_9H_{14}CO)Fe_2(CO)_6$[a].

	x	y	z	B_{iso}[b]
HA1	0.160(5)	0.452(5)	0.062(3)	3.8(12)
HA2	0.251(5)	0.418(4)	0.045(3)	2.7(10)
HA3	0.227(4)	0.448(4)	0.143(3)	1.7(10)
HB1	–0.013(5)	0.296(4)	0.130(3)	1.4(9)
HB2	0.058(5)	0.167(4)	0.169(3)	2.8(10)
HB3	0.105(5)	0.312(4)	0.206(3)	1.7(9)
HC1	0.007(6)	0.252(4)	–0.006(3)	3.3(11)
HC2	0.091(5)	0.132(5)	0.025(3)	2.7(11)
HC3	0.161(6)	0.228(5)	–0.018(4)	4.1(15)
HD1	0.415(4)	0.241(3)	–0.039(2)	1.5(10)
HD2	0.535(5)	0.302(4)	–0.045(3)	2.4(11)
HD3	0.436(5)	0.391(5)	–0.031(3)	3.5(12)
HE1	0.688(4)	0.374(3)	0.086(2)	0.8(8)
HE2	0.634(5)	0.394(4)	0.174(3)	2.1(9)

[a] The numbers in parentheses are estimated standard deviations in the last significant digits. [b] Isotropic thermal parameters in Å^2.

The labelling schemes for the two molecules are identical insofar as possible to facilitate comparisons. In addition, bond lengths of both molecules have been tabulated together in Table VI and their bond angles are listed together in Table VII.

In the subsequent discussion whenever it is necessary to compare bond lengths or angles of these two structures with those of other complexes, the numbers will be given in the order: $(C_9H_{14}CO)Fe_2(CO)_6$; $(C_7H_{10}CO)Fe_2(CO)_6$.

Discussion

The most striking aspect of these structures is the relationship of the skeleton of five carbon atoms to the two iron atoms. These five atoms donate a total of six electrons to the iron atoms. To achieve an inert gas electronic configuration each iron atom must acquire three more electrons. In each structure a total of three electrons is donated to Fe(1) by the C7–C8–C9 portion of the 5-carbon chain and Fe(2) receives three electrons from the C9–C10–C11 portion. In other words, the atom C9 is common to both 3-atom, 3-electron portions of the chain.

The C9–C10–C11 portion of the carbon skeleton can be satisfactorily described as a slightly distorted η^3-allyl group donating three electrons to Fe(2). The C9–C10 and C10–C11 bond lengths, which are equal within experimental error (Table VI), are but slightly longer than the carbon–carbon distances observed in various other compounds containing $(\eta^3\text{-allyl})Fe(CO)_3$ groups, where mean distances of 1.401,[2,8] 1.390,[9]

TABLE III. Thermal Parameters of $(C_9H_{14}CO)Fe_2(CO)_6$[a].

	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}[c]
Fe1	2.65(3)	2.49(3)	2.26(2)	0.05(2)	0.51(2)	–0.11(2)	2.46
Fe2	2.69(3)	3.07(3)	2.94(2)	0.26(2)	0.79(2)	–0.26(2)	2.83
O1	6.9(2)	4.7(2)	6.0(2)	–2.0(2)	1.3(2)	–2.0(2)	5.3
O2	5.8(2)	6.9(2)	4.7(2)	0.4(2)	2.9(2)	–0.2(2)	5.1
O3	5.0(2)	5.1(2)	4.7(2)	1.5(2)	0.6(1)	1.7(1)	4.7
O4	7.6(2)	9.6(3)	4.8(2)	3.4(2)	3.0(2)	0.1(2)	6.0
O5	4.1(2)	8.2(2)	4.0(2)	–0.4(2)	–0.3(1)	–0.3(2)	5.2
O6	8.3(3)	2.8(2)	9.5(3)	0.0(2)	2.9(2)	–1.3(2)	5.7
O7	4.3(2)	3.4(2)	5.1(2)	–1.3(1)	0.5(1)	0.1(1)	4.1
C1	4.0(2)	3.5(2)	3.2(2)	–0.1(2)	0.9(2)	–0.1(2)	3.5
C2	3.6(2)	3.4(2)	2.7(2)	0.2(2)	0.7(2)	0.0(2)	3.2
C3	3.4(2)	3.4(2)	3.1(2)	0.0(2)	1.0(2)	0.1(2)	3.2
C4	4.5(2)	5.3(3)	3.5(2)	1.4(2)	1.0(2)	–0.1(2)	4.2
C5	3.4(2)	4.4(2)	3.5(2)	–0.4(2)	1.3(2)	–0.7(2)	3.6
C6	4.3(2)	3.5(2)	4.3(2)	0.8(2)	1.2(2)	–0.8(2)	3.8
C7	2.5(2)	3.1(2)	3.0(2)	–0.2(2)	0.6(1)	–0.2(2)	2.8
C8	2.9(2)	2.7(2)	1.9(2)	–0.1(1)	0.2(1)	–0.1(1)	2.5
C9	2.7(2)	2.2(2)	2.4(2)	0.4(1)	0.5(1)	0.0(1)	2.4
C10	3.5(2)	2.7(2)	3.2(2)	0.4(2)	1.1(2)	0.2(2)	3.0
C11	4.2(2)	3.3(2)	4.6(2)	–0.6(2)	2.0(2)	0.2(2)	3.7
C12	2.6(2)	4.3(2)	3.3(2)	0.5(2)	0.2(2)	0.1(2)	3.3
C13	4.7(2)	3.8(2)	5.1(3)	1.2(2)	1.1(2)	1.0(2)	4.3
C14	3.1(2)	5.9(3)	5.2(3)	1.0(2)	1.2(2)	0.8(2)	4.4
C15	4.1(2)	7.4(3)	4.4(3)	0.9(2)	–0.8(2)	–0.9(2)	5.1
C16	5.6(3)	4.7(2)	3.2(2)	0.7(2)	1.7(2)	0.6(2)	4.1

[a] The numbers in parentheses are estimated standard deviations in the last significant digits. [b] The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement by $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

TABLE IV. Atomic Positional Parameters for $(C_7H_{10}CO)Fe_2(CO)_6$[a].

	x	y	z
Fe1	–0.0784(1)	0.0967(11)	0.2810(1)
Fe2	0.1293(1)	0.2098(1)	0.1888(1)
O1	0.0346(6)	–0.1125(5)	0.2089(4)
O2	–0.3190(7)	–0.0164(6)	0.3631(5)
O3	0.0939(7)	0.1149(5)	0.4620(4)
O4	0.3060(8)	0.3576(6)	0.0812(5)
O5	0.3568(7)	0.0775(6)	0.2821(5)
O6	0.1070(7)	0.3749(5)	0.3395(4)
O7	–0.2219(6)	0.2962(5)	0.3582(4)
C1	–0.0082(8)	–0.0306(6)	0.2317(5)
C2	–0.2250(8)	0.0265(7)	0.3318(6)
C3	0.0299(8)	0.1077(7)	0.3909(5)
C4	0.2393(9)	0.2994(7)	0.1242(6)
C5	0.2695(9)	0.1288(7)	0.2450(6)
C6	0.1106(8)	0.3098(7)	0.2813(5)
C7	–0.1807(7)	0.2340(6)	0.2993(5)
C8	–0.2042(7)	0.2105(5)	0.1972(5)
C9	–0.0742(7)	0.1857(5)	0.1578(4)
C10	–0.0091(7)	0.1819(6)	0.0680(4)
C11	0.1068(7)	0.1081(6)	0.0624(5)
C12	–0.3542(7)	0.1948(7)	0.1499(6)
C13	–0.3702(9)	0.0947(8)	0.0858(6)
C14	–0.0459(9)	0.2664(8)	–0.0100(5)

[a] The numbers in parentheses are estimated standard deviations in the last significant digits.

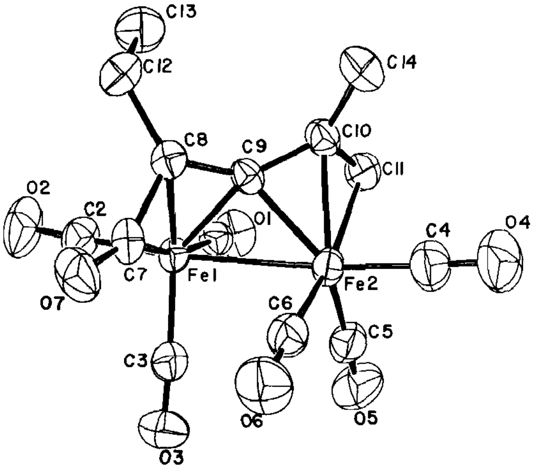

Figure 2. The molecular structure of $(C_7H_{10}CO)Fe_2(CO)_6$, 2. Atoms are represented by their ellipsoids of thermal vibration chosen to enclose 40% of the electron density.

1.36[10] have been found. The C9–C10–C11 angles found here (115.9(4)°; 115.7(6)°) are somewhat smaller than those found in some other (η^3-allyl)Fe$(CO)_3$ systems (121–124°) but should not be considered anomalous since there are also η^3-allyl–metal

TABLE V. Thermal Parameters of $(C_7H_{10}CO)Fe_2(CO)_6$[a].

	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}[c]
Fe1	2.66(4)	2.77(4)	2.66(3)	–0.03(3)	0.43(4)	0.21(5)	2.67
Fe2	2.67(4)	3.07(4)	3.00(4)	0.52(4)	0.69(4)	–0.32(6)	2.82
O1	6.1(3)	3.0(3)	5.8(3)	0.7(2)	1.0(3)	–0.5(2)	4.6
O2	4.8(3)	7.0(4)	8.4(4)	–0.7(3)	2.4(3)	3.1(3)	5.7
O3	5.7(3)	6.6(4)	3.7(3)	–0.3(3)	–1.0(2)	–0.1(3)	5.1
O4	8.4(4)	7.8(4)	5.7(3)	–4.3(4)	1.3(3)	0.9(3)	6.2
O5	4.3(3)	6.6(4)	7.2(4)	1.1(3)	–0.7(3)	–0.2(3)	5.8
O6	7.2(4)	5.0(3)	5.4(3)	–1.2(3)	1.0(3)	–2.1(3)	5.4
O7	5.4(3)	5.2(3)	3.8(2)	1.5(2)	1.4(2)	–0.8(2)	4.3
C1	3.5(3)	3.2(2)	3.0(3)	–0.4(3)	0.1(2)	0.2(3)	3.2
C2	3.7(3)	4.0(4)	4.5(4)	–0.4(3)	0.5(3)	1.3(3)	3.9
C3	3.5(3)	3.8(4)	3.6(3)	0.1(3)	0.5(3)	–0.1(3)	3.6
C4	5.1(4)	4.9(4)	4.1(4)	–1.2(4)	1.0(3)	0.1(3)	4.5
C5	3.3(4)	4.7(4)	4.5(4)	–0.3(3)	0.6(3)	–0.4(3)	4.1
C6	3.7(3)	3.9(4)	3.8(3)	–0.9(3)	0.5(3)	–0.3(3)	3.7
C7	3.0(3)	3.1(3)	3.4(3)	0.2(2)	1.1(2)	0.3(3)	3.0
C8	3.0(3)	2.4(3)	3.0(3)	0.3(2)	0.4(2)	0.1(2)	2.7
C9	3.3(3)	2.4(3)	2.1(2)	–0.2(2)	0.4(2)	–0.2(2)	2.5
C10	3.5(3)	3.3(3)	2.6(3)	–0.6(3)	0.4(2)	–0.3(2)	3.0
C11	3.4(3)	4.3(4)	2.9(3)	0.3(3)	0.6(2)	–0.7(3)	3.4
C12	2.8(3)	4.4(4)	4.6(4)	0.2(3)	–0.1(3)	0.0(3)	3.8
C13	5.1(4)	5.9(5)	4.9(4)	–1.1(4)	–0.6(3)	–1.3(4)	5.1
C14	5.3(4)	4.4(4)	3.0(3)	0.0(3)	0.5(3)	0.8(3)	4.0

[a] The numbers in parentheses are estimated standard deviations in the last significant digits. [b] The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement by $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

systems with even smaller angles, as for example $[(\eta^5\text{-}C_5H_5)Ni(\eta^3\text{-}C_3H_4)\text{-}]_2$[11] where the angle is 111.5(4)°. The three Fe–C distances in each set (1.972(4), 2.085(4), 2.126(5); 1.954(7), 2.093(7), 2.151(7)) lack the long–short–long symmetry usually found in (η^3-allyl)M systems (as in the compounds already mentioned[2,8–10] where typical values are 2.15, 2.05, 2.15) but the irregularities are not surprising when the very unsymmetrical situation in which the allyl moiety finds itself is noted. Actually, it is only the short Fe–C distance at one end which is unusual and that involves the unprecedented type of carbon atom, C9, which is bonded to two metal atoms. The fact that C16 in **1** and C14 in **2**, which are the methyl carbon atoms attached to C10, are not significantly out of the plane defined by C9–C10–C11 is consistent with the designation of this three atom sequence as an allylic group.

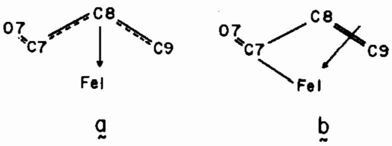

Figure 3. Extreme representations of the interaction of the C7–C8–C9 chain with Fe1.

There is considerable ambiguity about how best to describe the interaction of the C7–C8–C9 chain with Fe1. Two simple, extreme views are presented as **a** and **b** (Figure 3). In **a** the C7–C8–C9 chain is represented as an η^3-allyl unit with O7 (rather than two univalent groups) attached to the terminal atom, C7. In **b** we have a σ-bond to C7 and a metal–olefin bond of the η^2 type to C8–C9. However, the observed bond lengths are not fully consistent with either of these representations. The C7–C8 distance (1.452(6)Å, 1.449(9)Å) is considerably longer (by more than 7σ than the C8–C9 distance (1.379(6)Å; 1.389(8)Å). In fact the former is some 0.04Å longer and the latter some 0.04Å shorter than the usual C–C distance (*ca.* 1.41Å) for an η^3-allyl group. Also, the Fe–C distances deviate from a short–long–short pattern in such a way that the C7–Fe1 distance (1.945(4)Å; 1.961(7)Å) is by far the shortest of the three. It is evident that the actual structure deviates from **a** in the direction of **b** and from **b** in the direction of **a**, although **b** may be a slightly better approximation.

Though coordination of unsaturated carbon–carbon bonds are well documented and, indeed, very common entities in organometallic chemistry, the two structures here are (to the best of our knowledge) the only ones known in which one carbon atom (*i.e.* C9) is common to two unsaturated carbon–carbon systems which are bound to two different metals. The two 3-carbon units

TABLE VI. Bond Lengths in $(C_9H_{14}CO)Fe_2(CO)_6$ and $(C_7H_{10}CO)Fe_2(CO)_6$[a].

	C_9H_{14}	C_7H_{10}
Fe1–Fe2	2.742(1)	2.751(1)
Fe1–C1	1.842(5)	1.839(8)
–C2	1.788(5)	1.790(8)
–C3	1.783(5)	1.791(8)
Fe2–C4	1.788(5)	1.776(8)
–C5	1.813(5)	1.794(8)
–C6	1.788(5)	1.789(8)
Fe1–C7	1.945(4)	1.961(7)
–C8	2.144(4)	2.133(6)
–C9	2.049(4)	2.027(6)
Fe2–C9	1.972(4)	1.954(7)
–C10	2.085(4)	2.093(7)
–C11	2.126(5)	2.151(7)
C7–C8	1.452(6)	1.499(9)
C8–C9	1.379(6)	1.389(8)
C9–C10	1.405(6)	1.411(8)
C10–C11	1.408(6)	1.418(10)
C8–C12	1.533(6)	1.533(9)
C12–C13	1.535(7)	1.519(12)
C12–C14	1.526(7)	–
–C15	1.546(7)	–
C10–C16	1.506(6)	–
C10–C14	–	1.525(10)
C–O(ave)[b]	1.134	1.134
C_7–O_7	1.195(5)	1.194(8)
C11–HE1	0.92(4)	
–HE2	0.98(5)	
C13–HA1	1.00(5)	
–HA2	0.98(5)	
–HA3	1.02(5)	
C14–HB1	0.89(4)	
–HB2	1.10(5)	
–HB3	1.01(5)	
C15–HC1	1.04(6)	
–HC2	0.99(5)	
–HC3	0.84(6)	
C16–HD1	0.95(4)	
–HD2	0.92(5)	
–HD3	0.98(5)	

[a] The numbers in parentheses are estimated standard deviations in the last significant digits. [b] Terminal carbonyls.

TABLE VII. Bond Angles in $(C_9H_{14}CO)_6$ and $(C_7H_{10}CO)Fe_2(CO)_6$[a].

	C_9H_{14}	C_7H_{10}
Fe2–Fe1–C1	93.7(1)	89.1(3)
–C2	173.8(2)	174.7(3)
–C3	82.7(1)	88.4(2)
C1–Fe1–C2	91.1(2)	91.7(3)
–C3	100.8(2)	100.4(3)
C2–Fe1–C3	92.6(2)	96.7(3)
Fe1–Fe2–C4	169.1(1)	170.0(3)
–C5	93.7(1)	92.1(3)
–C6	85.2(1)	85.4(2)
C4–Fe2–C5	96.2(2)	97.6(4)
–C6	88.5(2)	90.8(4)
C5–Fe2–C6	101.2(2)	99.4(4)
C7–Fe1–C1	159.7(2)	164.5(3)
–C2	87.4(2)	88.6(3)
–C3	99.5(2)	94.9(3)
C11–Fe2–C4	92.3(2)	89.2(3)
–C5	92.3(2)	94.2(3)
–C6	166.3(2)	166.3(3)
Dihedral-I[b]	10.9	4.7
M–C–O(ave)[c]	177.1	177.2
Fe–C7–O7	144.3(3)	144.4(6)
C8–C7–O7	138.3(4)	138.9(7)
C7–C8–C9	109.1(3)	109.4(6)
C8–C9–C10	143.1(4)	140.9(6)
C9–C10–C11	115.9(4)	115.7(6)
Fe1–C9–C8	74.6(2)	74.7(4)
–C10	136.6(3)	138.5(5)
–Fe2	86.0(1)	87.4(3)
Fe2–C9–C8	137.7(3)	137.9(5)
Fe2–C9–C10	74.2(2)	75.0(4)
Fe1–Fe2–C9	48.2(1)	47.4(1)
Fe2–Fe1–C9	45.8(1)	45.2(2)
Dihedral–II[d]	54.1	55.0
C10–C11–HE1	114(3)	
–HE2	119(3)	
HE1–C11–HE2	121(4)	
C12–C13–HA1	110(3)	
–HA2	109(3)	
–HA3	109(3)	
HA1–C13–HA2	106(4)	
–HA3	105(4)	
HA2–C13–HA3	117(4)	
C12–C14–HB1	108(4)	
–HB2	107(3)	
–HB3	106(3)	
HB1–C14–HB2	108(4)	
–HB3	114(4)	
HB2–C14–HB2	113(4)	
C12–C15–HC1	107(3)	
–HC2	106(3)	
–HC3	107(4)	
HC1–C15–HC2	106(4)	
–HC3	117(5)	
HC2–C15–C3	113(5)	
C10–C16–HD1	114(3)	
–HD2	118(3)	
–HD3	106(3)	
HD1–C16–HD2	98(4)	
–HD3	122(4)	
HD2–C16–HD3	100(4)	

[a] The numbers in parentheses are estimated standard deviations in the last significant digits. [b] Dihedral–I is the angle between plane defined by Fe1, C1, and C3, and the plane defined by Fe2, C5, C6. [c] Terminal carbonyl. [d] Dihedral–II is the angle between the least-squares plane of C7, C8, C9, and C12 and the least-squares plane of either C9, C10, and C16 (**1**), or C9, C10, C11, and C14 (**2**).[6]

TABLE VIII. Mean Planes for $(C_9H_{14}CO)Fe_2(CO)_6$ and $(C_7H_{10}CO)Fe_2(CO)_6$[a].

Plane I

(C7, C8, C9, C12): $0.06x-0.57y-0.82z+2.95=0$[b]

(C7, C8, C9, C12): $0.05x+0.96y-0.36z-1.60=0$[b]

Deviations of Atoms from the Plane

	C7	C8	C9	C12
$C_9H_{14}CO$	0.01	–0.04	0.01	0.01
$C_7H_{10}CO$	0.02	–0.06	0.02	0.02

Plane II

(C9, C10, C11, C16): $0.52x-0.85y-0.08z+10.47=0$[b]

(C9, C10, C11, C14): $-0.65x-0.66y-0.39z+1.81=0$[c]

Deviations of Atoms from the Plane

	C9	C10	C11	C16/C14
$C_9H_{14}CO$	–0.02	0.06	–0.02	–0.02
$C_7H_{10}CO$	–0.02	0.06	–0.02	–0.02

Plane III[d]

(Fe1, C1, C3): $0.74x-0.08y-0.67z+0.27=0$[b]

(Fe1, C1, C3): $0.70x-10.52y-0.48z+1.90=0$[c]

Plane IV[d]

(Fe2, C5, C6): $0.72x-0.26y-0.64z-2.04=0$[b]

(Fe2, C5, C6): $0.70x+0.57y-0.42z-1.14=0$[c]

[a] Equations are of the form $Ax+By+Cz+D=0$ where x, y, and z are fractional coordinates. [b] $(C_9H_{14}CO)Fe_2(CO)_6$. [c] $(C_7H_{10}CO)Fe_2(CO)_6$. [d] By definition three points define a plane so all deviations are exactly zero.

which have C9 in common define planes which make a dihedral angle of 54.1°, 55.5°. Thus, the π systems of these two units are by no means orthogonal, although there is a definite interruption of the continuity of the $p\pi$–$p\pi$ interactions at C9.

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Supplementary Material Available

Copies of the observed and calculated structure factors for both structures and the equations for least squares planes are available from F.A.C. upon request.

References

1 F.A. Cotton, J.D. Jamerson and B.R. Stults, *J. Organometal. Chem., 94,* C53 (1975).

2 F.A. Cotton, B.A. Frenz, G. Deganello and A. Shaver, *ibid., 50,* 227 (1973).

3 The following computer programs were used: DATARED, a data reduction program by Frenz; NUCLS, a least-squares program by Doedens and Ibers, FOURIER, a crystallographic Fourier summation program by Dellaca and Robinson based on Zalkin's FORDAP; SADIAN, a program for calculating atomic distances and angles; ORFE, a function and error program by Busing, Martin and Levy as modified by Johnson and Thiessen; ORFLSE, a full-matrix least-squares refinement, a highly modified version of Busing, Martin and Levy's original ORFLS; MPLANE, least-squares mean-plane calculation program from L. Dahl's laboratory; PRTOUT, structure factor table program by V. Day, and ORTEP, a plotting program by Johnson.

4 D.T. Cromer and J.T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.3.1.

5 D.T. Cromer and D. Liberman, *J. Chem. Phys., 53,* 1891 (1970).

6 See paragraph at end of paper concerning supplementary material.

7 K. Greenlee of Chemical Samples Co. confirmed that $H_2C{=}C(CH_3)C{\equiv}CC(CH_3)_3$ is very possibly an impurity in the t-Bu_2C_2 supplied but noted that he had no proof of its presence.

8 F.A. Cotton, B.G. DeBoer and T.J. Marks, *J. Am. Chem. Soc., 93,* 5069 (1971).

9 F.A. Cotton and J.M. Troup, *J. Organometal. Chem., 76,* 81 (1974).

10 F.A. Cotton, B.A. Frenz and J.M. Troup, *J. Organometal. Chem., 61,* 337 (1973).

11 A.E. Smith, *Inorg. Chem., 11,* 165 (1972).