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The X-ray Structure of $[Me_3SiC_4SiMe_3]_2Fe_2(CO)_7$: a σ–π-Type Bonding Complex between a Diacetylene and Iron Carbonyl

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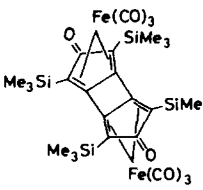
The photochemical reaction of bis-*(trimethylsilyl)butadiyne,* $Me_3SiC_4SiMe_3$, *with* $Fe(CO)_5$ *in benzene yields a product of formula* $[Me_3SiC_4SiMe_3]_2Fe_2(CO)_7$, *II. The formula and molecular structure were determined by single crystal x-ray analysis. The results correct a structure (I) previously proposed based on spectroscopic evidence. The red crystals are monoclinic, space group I2/a with* a = *21.647(6),* b = *8.924(2),* c = *19.544(8)* Å, β = *96.09(3)° and Z = 4. Anisotropic refinement of 21 independent atoms with 872 observed reflections converged at* $R = 0.062$ *and* $R_w = 0.064$.

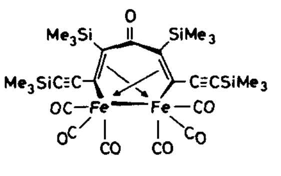
The molecule II is made up of two diacetylene ligands, an inserted CO group and an $(CO)_3Fe$–$Fe(CO)_3$ *group. The diacetylene ligands line up in a "head-to-head" arrangement and combine with the CO and iron carbonyl through reaction of one of the triple bonds. The two reactive carbon atoms from one ligand* π*-bond to one iron atom, while one of these carbon atoms* σ*-bonds to the second iron atom. The reverse occurs for the second ligand. A molecule of CO inserts and bridges between carbon atoms of each ligand substituted with* $SiMe_3$. *The other carbon atoms which* σ*-bond to the iron atoms are substituted with* $-C\equiv CSiMe_3$. *Three isomers are possible for this reaction, but II is the only one observed.*

Introduction

Conjugated diacetylenes react with transition metal carbonyls to form a variety of metal complexes and organic molecules [1–4]. With few exceptions, only one of the triple bonds is observed to participate in product formation [5]. We have noted an iron complex reported [6] resulting from the reaction of *bis*-(trimethylsilyl)butadiyne and $Fe_3(CO)_{12}$ in benzene. The product formula is reported as $[(Me_3Si)_2C_4]_2Fe_2(CO)_8$ based upon an elemental analysis and mass spectral data. Structure I was proposed based upon IR carbonyl absorption frequencies at $\nu(C\equiv O)$ cm^{-1}, 2073(m), 2047(m–s), 2018(s); $\nu(C=O)$ 1652(m), and a single p.m.r. resonance at τ 9.81(s). τ for the free ligand is reported at 9.85. The solvent medium was not reported. We sought to confirm or disprove the unusual structure I by means of X-ray analysis, and, if correct, to resolve the question of the placement of the $Fe(CO)_3$ groups since either a *cis* or *trans* isomer is possible. Our results unequivocally show that the correct structure is not I, but II.



I



II

Experimental

The compound was prepared and isolated by the method described by Pannell and Crawford [6]. All three iron carbonyls are reported to yield the product. We chose to use $Fe(CO)_5$. Red crystals were grown from a solution of hexane.

Crystal Data:
Monoclinic – Space group I2/a
$a = 21.647(6)$ Å
$b = 8.924(2)$
$c = 19.544(8)$
$\beta = 96.09(3)°$
$V = 3754(2)$ Å^3
Mol. wt. = 696.6 daltons
Formula: $C_{27}H_{36}Fe_2O_7Si_4$
Systematic absences:
hkl: h + k + l = 2n + 1
h0l: h = 2n + 1
Crystal size:
0.03 X 0.08 X 0.19 mm^3
Crystal shape: block
$D_{meas} = 1.24$ g cm^{-3}

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TABLE I. Positional and Anisotropic Thermal Parameters for $[(Me_3Si)_2C_4]_2Fe_2(CO)_7$.[a]

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
Fe	0.2267(1)	0.2843(2)	0.0566(1)	0.0484(12)	0.0836(17)	0.0619(13)	0.0024(13)	0.0099(9)	−0.0041(14)
Si1	0.3076(2)	0.0357(6)	0.1382(2)	0.0892(32)	0.1002(39)	0.0591(26)	0.0111(28)	−0.0105(23)	0.0059(28)
Si2	0.4959(2)	0.3542(8)	0.1312(3)	0.0708(36)	0.2034(71)	0.1571(56)	−0.0443(41)	−0.0398(35)	0.0541(51)
C1	0.1865(8)	0.4620(24)	0.0351(9)	0.0718(110)	0.0879(161)	0.1000(128)	0.0131(114)	0.0309(92)	−0.0136(125)
O1	0.1609(6)	0.5694(15)	0.0242(7)	0.1102(104)	0.0762(99)	0.1527(118)	0.0231(82)	0.0210(83)	0.0013(89)
C2	0.1694(8)	0.1992(18)	0.1045(8)	0.0685(98)	0.0888(128)	0.0690(100)	0.0057(101)	0.0094(79)	0.0120(94)
O2	0.1320(6)	0.1416(15)	0.1290(7)	0.0829(80)	0.1385(107)	0.1382(103)	−0.0091(77)	0.0412(78)	0.0206(89)
C3	0.2704(8)	0.3756(23)	0.1286(10)	0.0797(123)	0.1142(149)	0.0909(135)	0.0009(116)	0.0102(104)	−0.0048(127)
O3	0.2959(6)	0.4466(17)	0.1734(7)	0.1034(97)	0.1518(137)	0.1219(105)	0.0080(87)	0.0099(81)	−0.0525(96)
C4	0.2500	−0.0103(31)	0.0	0.0565(121)	0.0689(170)	0.0626(146)	0.0	0.0043(110)	0.0
O4	0.2500	−0.1468(20)	0.0	0.1270(137)	0.0615(116)	0.0711(98)	0.0	−0.0049(86)	0.0
C5	0.2818(6)	0.0794(18)	0.0585(6)	0.0623(91)	0.1024(128)	0.0359(77)	0.0051(99)	−0.0093(66)	−0.0127(92)
C6	0.3130(6)	0.2056(17)	0.0339(6)	0.0655(97)	0.0727(104)	0.0490(77)	0.0010(94)	0.0180(71)	−0.0116(84)
C7	0.3702(6)	0.2512(18)	0.0637(6)	0.0229(70)	0.1097(143)	0.0754(90)	−0.0260(93)	−0.0106(68)	0.0024(101)
C8	0.4191(7)	0.2888(20)	0.0872(7)	0.0684(103)	0.1240(142)	0.0661(88)	0.0079(110)	0.0057(81)	−0.0075(99)
C9	0.3314(9)	0.0860(21)	0.2161(8)	0.1373(149)	0.1350(170)	0.0631(97)	−0.0021(133)	−0.0120(92)	−0.0054(108)
C10	0.2401(9)	−0.1559(20)	0.1585(8)	0.1307(153)	0.1143(160)	0.0853(123)	−0.0289(121)	−0.0072(114)	0.0364(108)
C11	0.2763(9)	−0.1512(22)	0.1192(9)	0.1402(165)	0.1376(164)	0.1054(132)	0.0570(134)	−0.0374(119)	−0.0059(126)
C12	0.5508(10)	0.2028(35)	0.0953(24)	0.0801(144)	0.2219(298)	0.5589(649)	0.0240(180)	0.0319(259)	0.1239(366)
C13	0.5179(10)	0.5406(29)	0.1039(12)	0.1244(164)	0.1918(248)	0.1821(207)	0.0022(151)	−0.0692(166)	0.0262(190)
C14	0.4828(14)	0.3809(41)	0.2337(15)	0.1882(272)	0.3881(532)	0.1911(260)	0.0298(202)	−0.1262(314)	−0.0456(288)

[a] The anisotropic temperature factors (A^2) are introduced into the structure factor expression in the form: $T = \exp\{-[2\pi^2(U11h^2a^{*2} + U22k^2b^{*2} + U33l^2c^{*2} + 2U12hka^*b^* + 2U13kla^*c^* + 2U23klb^*c^*)]\}$.

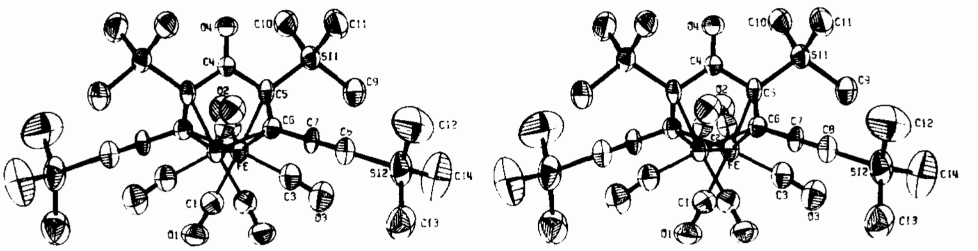

Fig. 1. A stereographic view of the molecular structure of $[Me_3SiC_4SiMe_3]_2Fe_2(CO)_7$.

$D_{calc} = 1.23$ g cm^{-3}
$\mu = 8.8$ cm^{-1} (MoKα = 0.71069 Å)

Intensities were collected on a quarter-circle manual General Electric XRD-7 diffractometer equipped with a pulse-height discriminator, NaI scintillation counter and balanced Zr/Y filters. The take-off angle from the X-ray tube was set at 5.0°. Peak height counts were recorded for 10 seconds for each filter. A set of five reflections was measured periodically to monitor crystal alignment and decomposition. No corrections were necessary. The intensity data were converted to structure factors (F_o) after applying a background correction for the scatter of MoKα photons and a linear absorption correction. The absorption factor was determined as a function of the diffractometer angle phi (ϕ) at chi (χ) = 90.00°. The maximum and minimum transmission factors are 0.97 and 0.85 respectively. A total of 1928 independent reflections was measured of which 872 were considered to be significantly above background having $[I_{Zr} - 2\sigma(I)_{Zr}] - [I_Y + 2\sigma(I)_Y] > 80$ counts, where I_{Zr} and I_Y are measured counts for designated filters and $\sigma(I)_{Zr}$ and $\sigma(I)_Y$ are the usual standard deviations from counting statistics. A weight w was assigned to each reflection where $w = {}^1/\sigma^2(F_o)$ and $\sigma(F_o) = \frac{1}{2}\{(LP)^{-1} [I_{Zr} + I_Y]/(I_{Zr} - I_Y)\}^{1/2}$. (LP) is the Lorentz-polarization factor.

The structure was solved by the heavy atom method. Atomic coordinates and temperature parameters were refined by full-matrix least squares calculations. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is the weight and F_o and F_c are observed and calculated structure amplitudes respectively. The final agreement indices are R = 0.062 and $R_w = 0.064$ where $R = \Sigma|F_o - |F_c||/\Sigma F_o$ and $R_w = [\Sigma w|F_o - |F_c||^2]^{1/2}$. If all the data are included in the refinement (N = 1928), the agreement indices are R = 0.157 and $R_w = 0.138$. The final structure parameters reported in Table I are the results of the refinement using the limited data set (N = 872). A final difference map showed no structural features. The largest residual peak was 0.4 e Å^{-3} located near the iron atom. Hydrogen atom positions could not be determined from the difference map, and the scattering contribution of hydrogen was not included in the calculations. All atoms were refined with anisotropic temperature factors. Most of the calculations were done using the SHELX X-ray program system [7]. A table of the observed and calculated structure factors has been deposited with the editor.

The structure was also refined in the non-centrosymmetric group Ia. Two molecular fragments were refined separately to break the two-fold molecular symmetry required by the centrosymmetric space group. This was followed by refinement of the entire structure. There were large correlations between atom parameters previously related by the two-fold axis and the chemical sense of the bond distances and angles rapidly deteriorated. Space group I2/a is thus confirmed as correct by the successful completion of the refinement.

Results and Discussion

The stereographic view of the refined molecular structure in Fig. 1 clearly shows how the original chemical components combine together to yield the metal complex. A crystallographic two-fold axis contains the C4–O4 atoms and the midpoint of the iron–iron bond. Table II lists the pertinent bond distances and angles along with their estimated standard deviations in parentheses. The C5–C6 triple bond of the original diacetylene ligand has been reduced to intermediate double/single bond character (1.42 Å). These two carbon atoms π-bond to one iron atom while one of them (C6) σ-bonds to the other iron atom. The two-fold axis reverses the bonding of the iron atoms with the other diacetylene ligand. A carbonyl group (C4–O4) inserts between C5 and its symmetry-related atom C5′.

The molecule is one of three possible isomers, although the other two were not observed as reaction products. Two *bis*(trimethylsilyl)diacetylene ligands line up in a 'head-to-head' manner and the equivalent triple bond from each molecule reacts with the iron carbonyl. The other triple bond remains intact and is part of the substituent group attached to the carbon atom σ bonded to an iron atom.

TABLE II. Interatomic Distances and Angles for $[(Me_3Si)_2C_4]_2Fe_2(CO)_7$.[a]

Distances (Å)			
Fe–Fe	2.528(3)	C5–C6	1.42(2)
Fe–C1	1.84(2)	C6–C7	1.37(2)
Fe–C2	1.80(2)	C7–C8	1.16(2)
Fe–C3	1.81(2)	C5–Si1	1.90(1)
Fe–C5	2.18(1)	Si1–C9	1.90(2)
Fe–C6	2.09(1)	Si1–C10	1.89(2)
Fe–C6′	2.01(1)	Si1–C11	1.88(2)
C1–O1	1.12(2)	C8–Si2	1.88(2)
C2–O2	1.11(2)	Si2–C12	1.98(3)
C3–O3	1.17(2)	Si2–C13	1.83(2)
C4–C5	1.50(2)	Si2–C14	2.07(3)
C4–O4	1.22(2)		
Angles (°)			
Iron Coordination[b]			
Fe′–Fe–C1	91.3(7)°	C2–Fe–C3	96.8(7)°
Fe′–Fe–C2	144.8(6)	C2–Fe–C5	92.5(6)
Fe′–Fe–C3	117.2(6)	C2–Fe–C6	130.6(6)
Fe′–Fe–C5	75.3(6)	C2–Fe–C6′	93.3(7)
Fe′–Fe–C6	50.5(5)	C2–Fe–Mid	111.1(7)
Fe′–Fe–C6′	53.3(5)	C3–Fe–C5	97.1(7)
Fe′–Fe–Mid	62.2(7)	C3–Fe–C6	84.9(6)
C1–Fe–C2	98.5(7)	C3–Fe–C6′	169.7(8)
C1–Fe–C3	89.1(8)	C3–Fe–Mid	91.2(6)
C1–Fe–C5	166.6(6)	C5–Fe–C6	38.9(5)
C1–Fe–C6	130.9(6)	C5–Fe–C6′	90.2(7)
C1–Fe–C6′	87.3(6)	C6′–Fe–Mid	87.1(6)
C1–Fe–Mid	150.1(7)		
Ligand groups			
Fe–C1–O1	177.3(1.6)	C5–C6–C7	122.0(1.3)
Fe–C2–O2	174.1(1.5)	C6–C7–C8	178.1(1.4)
Fe–C3–O3	173.8(1.7)	C7–C8–Si2	175.7(1.3)
C5–C4–O4	122.2(1.0)	C5–Si1–C9	112.3(7)
C5–C4–C5′	115.6(1.0)	C5–Si1–C10	108.2(7)
Fe–C5–C4	103.2(1.0)	C5–Si1–C11	107.8(7)
Fe–C5–C6	67.0(8)	C9–Si1–C10	107.8(8)
Fe–C5–Si1	125.5(6)	C9–Si1–C11	108.6(8)
C4–C5–C6	111.1(1.2)	C10–Si1–C11	112.1(9)
C4–C5–Si1	114.0(1.2)	C8–Si2–C12	99.3(1.2)
C6–C5–Si1	126.6(1.0)	C8–Si2–C13	113.2(9)
Fe–C6–Fe′	76.2(6)	C8–Si2–C14	105.9(9)
Fe–C6–C5	74.1(7)	C12–Si2–C13	109.4(1.3)
Fe–C6–C7	126.6(1.0)	C12–Si2–C14	124.9(1.7)
Fe′–C6–C5	113.6(7)	C13–Si2–C14	104.2(1.3)
Fe′–C6–C7	123.5(7)		

[a] Primed numbers (′) refer to atoms generated by the two-fold axis of symmetry passing through O4, C4 and the mid-point of the iron–iron bond. [b] Mid = midpoint of the C5–C6 bond.

TABLE III. Mass Spectral Analyses of $[(Me_3Si)_2C_4]_2Fe_2(CO)_7$.

Mass fragment, m/e (relative abundance)		*Assignment*
Pettersen & Cash	Pannell & Crawford	
	724(1)	
	694(15)	
	666(2)	
	638(8)	
612(25)	610(78)	$M^+ - 3(CO)$
584(0.6)	582(2)	$M^+ - 4(CO)$
556(1.3)	554(20)	$M^+ - 5(CO)$
528(100)[a]	526(72)	$M^+ - 6(CO)$
	498(8)	
472(60)	470(100)	$[(Me_3SiC_4SiMe_3)_2FeCO]^+$
416(2.6)	416(32)	$[(Me_3SiC_4SiMe_3)_2CO]^+$
	398(26)	
306(14)	306(32)	$[(Me_3SiC_4SiMe_3)Fe(CO)_2]^+$
	262(28)	
250(8)		$[(Me_3SiC_4SiMe_3)(CO)_2]^+$ or $[(Me_3SiC_4SiMe_3)Fe]^+$
179(4)	179(12)	$[Me_2SiC_4SiMe_3]^+$
73(40)	73(68)	Me_3Si^+

[a] The size of the ^{54}Fe satellite at m/e 526 indicates that the fragment at m/e 528 is $M^+ - 6(CO)$ and not $M^+ - Fe(CO)_4$.

Careful inspection of Fig. 1 indicates a possible steric effect influencing the formation of this isomer. If the trimethylsilyl group was attached to C6 instead of C5, the present configuration of the atoms Si2, C12–C14, leads to close contacts of 2.26 Å and 2.05 Å between C13 and O1′ and C1′ respectively. This steric effect may indeed be the primary factor influencing the formation of this isomer. On the other hand, studies of other diacetylene–metal carbonyl reactions in this laboratory and elsewhere have revealed highly nonstatistical isomer distributions for which neither steric nor electronic considerations provide a ready explanation [8, 9].

There does not appear to be any unusual strain in the molecule. The coordination about each iron atom can be considered as a distorted octahedron if the midpoint of the C5–C6 bond is taken as one of the six octahedral sites. (see Table II for angles). The crystal packing is normal and there are no unusually short intermolecular contacts, the two shortest contacts being 3.25 Å between O4 and O1 related by a unit cell translation on y, and 3.53 Å between C12 and O1 related by the symmetry operation ½ + x, 1 – y, z applied to the O1 coordinates.

A mass spectrometric analysis was done on II using a Hewlett-Packard model HP-5980A quadrupole mass spectrometer. The purpose was to verify that compound II is indeed the same as that reported by Pannell and Crawford [6]. Table III summarizes our data obtained at 70 eV and compares it to that reported previously [6]. We conclude that our compound is identical, but that the heavier mass assignments previously reported are low by two mass units.

We did not attempt to assign mass fragments to peaks observed previously, but not observed by us. A p.m.r. spectrum of II in CCl_4 yielded two resonances at τ 9.79 and 9.81.

Similar X-ray structures have been reported for monoacetylene complexes with iron carbonyls. Acetylene reacts with $Fe_3(CO)_{12}$ to yield $(C_2H_3)_3$-$Fe_2(CO)_6$ [10]. The X-ray structure shows this molecule is also a σ–π-type of complex where an Fe_2-$(CO)_6$ moiety bonds to two acetylene ligands [11]. The third acetylene converts to an ethylene bridge and occupies the same position as the bridge carbonyl in II. The reaction of dimethylacetylene and Fe_2-$(CO)_9$ in petroleum ether yields $[Me_2C_2]_2\ Fe_2(CO)_7$ [12]. The X-ray structure shows this compound to be identical to II except for the substituents on the acetylenic carbon atoms bonding to the iron atoms. For both reactions and structures mentioned in comparison here, isomer formation is not possible.

Acknowledgement

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