

## Molecular Structure of Tetraethylferrole $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$ , and the Ferrole Family

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**Abstract.**  $\{\mu\text{-}[(1\text{-}4\text{-}\eta\text{:}1,4\text{-}\sigma)\text{-}1,2,3,4\text{-Tetraethyl-}1,3\text{-butadiene-}1,4\text{-diyl}]\}\text{-bis(tricarbonyliron)}(\text{Fe-Fe})$ ,  $[\text{Fe}_2\text{-}(\text{C}_{12}\text{H}_{20})(\text{CO})_6]$ ,  $M_r = 444.05$ , triclinic,  $P\bar{1}$ ,  $a = 15.534(20)$ ,  $b = 8.245(6)$ ,  $c = 8.022(6)$  Å,  $\alpha = 78.32(5)$ ,  $\beta = 88.19(4)$ ,  $\gamma = 78.14(5)^\circ$ ,  $V = 984.6(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.498$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.50$  mm<sup>-1</sup>,  $F(000) = 456$ , yellow-orange air-stable parallelepipeds elongated along  $a$ ,  $T = 291$  K, final  $R = 0.0396$  for 3765 unique observed [ $F_o > 4\sigma(F_o)$ ] reflections. One molecule consists of two non-chemically equivalent bonded Fe(CO)<sub>3</sub> moieties [ $\text{Fe-Fe} = 2.504(5)$  Å], coordinated at a tetraethyl-substituted butadiene group. The molecular structure corresponds to a ferrole system in a non-sawhorse geometry with a semibridging CO group. By comparison it is shown that the stereochemistry of the ferrole family is mainly governed by, firstly, the  $\pi_3^*$  antibonding molecular orbital localized on the butadiene moiety, secondly, the presence of a semibridging CO group and, thirdly, the electronegativity of the butadiene substituents.

**Introduction.** The X-ray structure analysis of  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$ , a ferrole derivative, was undertaken to obtain further insight into the stereochemical consequences originating from different kinds of substituents in the butadiene ligand and to contribute to the interpretation of the bonding pattern in such a system taking into account semi-empirical calculations (Thorn & Hoffmann, 1978, and references therein) and pseudopotential *ab initio* calculations (Casarin, Ajo', Vittadini, Ellis, Granozzi, Bertocello & Osella, 1987, and references therein) applied to the ferrole compound  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_4)]$ . The structural results of this study and of other known ferrole derivatives are compared

and related to results of quantum-mechanical calculations.

Such work might also be helpful to clarify the reasons for a metal-metal atom exchange of ferrole species in solution, and for the racemization of optically active ferrole derivatives.

**Experimental.**  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$  (Et = C<sub>2</sub>H<sub>5</sub>) was prepared following the method reported by Aime, Milone, Sappa, Tiripicchio & Manotti Lanfredi (1979). A yellow-orange air-stable parallelepiped approximately 0.30 × 0.15 × 0.15 mm was mounted on the end of a glass fiber. All diffraction measurements were made using a Phillips PW1100 diffractometer with Mo  $K\alpha$  graphite-monochromated radiation. Lattice and orientation parameters were obtained by least-squares treatment of 25 symmetry-related reflections. Since the standard deviations of the  $a$  parameter were found to be high, a new set of 25 related reflections was collected and the cell parameters were calculated as the mean of the two sets. Intensity data were collected by the  $\omega\text{-}2\theta$  scan method. The intensities of three standard reflections displayed random variations in the range  $\pm 3\%$ . 5852 reflections ( $h: -20 \rightarrow 20$ ,  $k: -9 \rightarrow 10$ ,  $l: 0 \rightarrow 10$ ) were processed ( $1.5 < \theta < 28^\circ$ ) and 4762 independent reflections were obtained. 3765 reflections with  $F_o > 4\sigma(F_o)$  were used in the structure refinement. The intensities were corrected for Lorentz and polarization effects and absorption corrections were made following the empirical method of North, Phillips & Mathews (1968). One Fe atom was located from a three-dimensional Patterson map and a Fourier synthesis revealed the position of the other Fe atom. A series of Fourier and difference Fourier maps revealed the positions of all non-H atoms. The struc-

Table 1. *Positional parameters and equivalent isotropic thermal parameters ( $U_{eq} \times 10^2$ ) and their standard deviations for  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Fe(1)	0.21743 (4)	0.39284 (7)	0.14482 (7)	3.28 (2)
Fe(2)	0.21798 (4)	0.15468 (7)	-0.00585 (7)	3.12 (2)
<b>Butadiene moiety</b>				
C(1)	0.3191 (3)	0.2113 (5)	0.1233 (5)	3.6 (2)
C(2)	0.3094 (3)	0.0432 (5)	0.1994 (5)	3.6 (2)
C(3)	0.2218 (3)	0.0357 (5)	0.2580 (5)	3.4 (2)
C(4)	0.1625 (3)	0.1953 (5)	0.2290 (5)	3.2 (2)
<b>Carbonyl groups bonded to Fe(1)</b>				
C(5)	0.2675 (3)	0.5572 (6)	0.0173 (6)	4.5 (2)
O(5)	0.2965 (3)	0.6625 (5)	-0.0609 (5)	7.2 (2)
C(6)	0.1144 (3)	0.5421 (5)	0.1424 (6)	4.5 (2)
O(6)	0.0507 (0)	0.6400 (0)	0.1433 (0)	6.9 (2)
C(7)	0.2550 (3)	0.3945 (6)	0.3496 (6)	4.6 (2)
O(7)	0.2815 (3)	0.3913 (6)	0.4810 (5)	7.6 (2)
<b>Carbonyl groups bonded to Fe(2)</b>				
C(8)	0.2935 (3)	0.0862 (6)	-0.1617 (6)	4.6 (2)
O(8)	0.3440 (3)	0.0401 (6)	-0.2567 (5)	7.2 (2)
C(9)	0.1383 (3)	0.0417 (6)	-0.0563 (5)	4.4 (2)
O(9)	0.0894 (3)	-0.0306 (5)	-0.0911 (5)	7.1 (2)
C(10)	0.1669 (3)	0.3543 (5)	-0.1325 (5)	4.0 (2)
O(10)	0.1320 (3)	0.4641 (4)	-0.2359 (4)	5.7 (2)
<b>Ethyl groups</b>				
C(11)	0.4073 (3)	0.2445 (8)	0.0532 (7)	5.3 (2)
C(12)	0.4578 (4)	0.3113 (11)	0.1763 (10)	7.3 (3)
C(13)	0.3819 (4)	-0.1115 (7)	0.2132 (7)	5.2 (2)
C(14)	0.4394 (5)	-0.1475 (11)	0.3716 (10)	7.8 (3)
C(15)	0.1940 (4)	-0.1285 (6)	0.3369 (6)	4.6 (2)
C(16)	0.2077 (6)	-0.1759 (9)	0.5292 (7)	7.5 (3)
C(17)	0.0677 (3)	0.2108 (7)	0.2817 (6)	4.4 (2)
C(18)	0.0523 (5)	0.2574 (10)	0.4573 (7)	6.2 (3)

ture was refined by full-matrix least-squares method using the *SHELX76* package of programs (Sheldrick, 1976),  $w = 1$ . At the beginning, displacement parameters were anisotropic for Fe atoms only, but, when the conventional residual  $R$  reached 0.08, all non-H atoms were assigned anisotropic displacement parameters, this brought  $R$  to 0.049. At this point a Fourier synthesis showed the positions of all the H atoms. A final least-squares cycle including isotropic H atoms (315 variables) yielded  $R = 0.040$ . Four reflections (200, 110, 001 and  $\bar{4}11$ ) are probably affected by extinction effects.  $\Delta/\sigma = 0.068$  and the final difference Fourier synthesis revealed peaks of  $0.5 \text{ e \AA}^{-3}$ , 0.85 to 0.95  $\text{\AA}$  from the Fe atoms. Scattering factors are those incorporated in the *SHELX* package. The final atomic coordinates are listed in Table 1.\*

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53337 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The molecular structure of  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$  ( $\text{Et} = \text{C}_2\text{H}_5$ ) is shown in Figs. 1 and 2. The atomic arrangement contains an Fe(1) atom, covalently bonded to a tetraethyl substituted butadiene group thereby forming a ferracyclopentadiene ring, and a second Fe(2) atom  $\pi$ -bonded to the same heterocyclic ring. This ferrole system exhibits a non-sawhorse geometry (Fig. 3) resulting from a sawhorse structure by rotation of the Fe(2)-tris(carbonyl) fragment  $\pi$ -bonded to the butadiene moiety through an angle of  $60^\circ$  around its threefold axis (Thorn & Hoffmann, 1978). This brings one [CO(10)] of the three CO groups in to a semibridging position between the two Fe atoms. The ligand CO(10) and Fe(1) and Fe(2) atoms are situated on a pseudo-mirror plane which is perpendicular to the butadiene moiety and bisects the C(2)—C(3) bond.

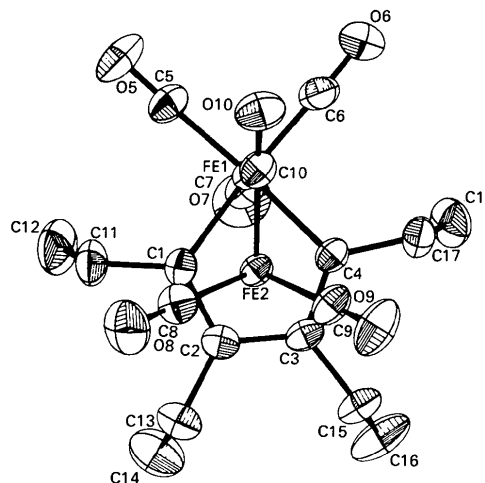


Fig. 1. ORTEP (Johnson, 1965) view of  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$  with numbering scheme for non-H atoms projected on the butadiene mean plane. The molecular pseudo-mirror plane is perpendicular to the figure.

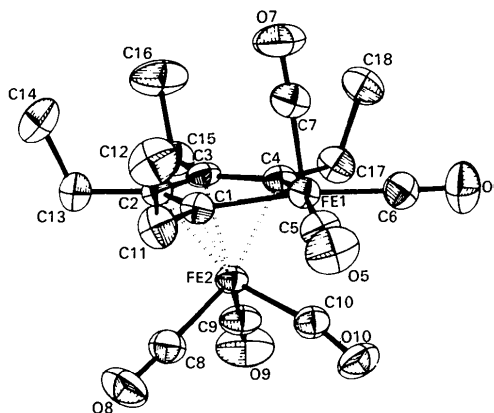


Fig. 2. Perspective view of  $[\text{Fe}_2(\text{CO})_6(\text{C}_4\text{Et}_4)]$  showing the  $\pi$  interaction between the  $\text{Fe}(\text{CO})_3$  group and the butadiene moiety.

Bond distances and angles of the title substance are reported in Table 2. Table 3 summarizes some bonding parameters for related ferrole derivatives having various substituents in the butadiene ligand formally considered as a dianion: columns I (title complex), II (Dettlaf & Weiss, 1976), III (Riley & Davis, 1975), IV (Epstein & Dahl, 1970), V (Bennett, Graham, Smith & Stewart, 1973), VI (Hock & Mills, 1961) and VII (Chin & Bau, 1973). In column VIII (Aime *et al.*, 1979) the same data for a sawhorse derivative are shown. Column IX contains the Mulliken overlap population of [Fe<sub>2</sub>(CO)<sub>6</sub>(C<sub>4</sub>H<sub>4</sub>)] as calculated using a pseudopotential *ab initio* method (Casarin *et al.*, 1987).

The calculations reveal that the C atoms of the C<sub>4</sub>H<sub>4</sub> moiety carry a strong negative charge: C(1), C(4) -0.60 and C(2), C(3) -0.40 e respectively, electrons being formally donated by the two Fe atoms [Fe(1) charge = +1.04, Fe(2) = +1.06 e]. In such a way there is a high electron occupation of the HOMO† in [Fe<sub>2</sub>(CO)<sub>6</sub>(C<sub>4</sub>H<sub>4</sub>)], mainly constituted by a π<sub>3</sub>\* antibonding orbital of the butadiene moiety, causing C—C bond lengths to be equalized. From this fact it can be suggested that two different charge redistribution mechanisms (namely, π delocalization and metal-induced σ, π rehybridization) are effective in obtaining a bond-length equalization within the butadiene chain. Furthermore, when the butadiene moiety carries π acceptors or electronegative substituents which withdraw electrons from the ring, the π<sub>3</sub>\* orbital becomes less populated so that alternating single and double bonds are partially restored. In fact, the C(2)—C(3) distance (Table 3) is always the longest one, in particular when R<sub>1</sub> and R<sub>4</sub> are C<sub>6</sub>H<sub>5</sub> (columns III, IV) or OH (columns VI, VIII) groups.

The Fe(1)—C(1) and Fe(1)—C(4) bond lengths are 1.970 (5) and 1.981 (6) Å and both are shorter than the single Fe—CH<sub>3</sub> bond of 2.079 (5) Å in [Fe(CO)<sub>2</sub>CH<sub>3</sub>(Ph<sub>3</sub>BNC){P(CH<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (Ginderow, 1980). This finding agrees with a qualitative explanation (Astier, Daron, Jeannin & Rigault, 1983) that in addition to a σ bond, a partial π bond between symmetry-related metal orbitals of the Fe(1) atom and the butadiene group might be responsible for the bond shortening. The latter view is in accordance with the following features: (a) the deviation of the metal(1) atom from the butadiene plane is lower when the π interaction is stronger [the deviation of Fe(1) is 0.250 (2) Å, confirming the strong π interaction]; in [Ru(CO)<sub>3</sub>Si(CH<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>2</sub>Ph<sub>2</sub>)], containing a dimethylsilacyclopentadienyl ring, the Si atom, which cannot give such π bonds, lies 0.72 Å above the butadiene plane (Muir, Walker, Abel, Blackmore & Whitley, 1975); (b) the significant lengthening of

Table 2. Selected bond distances (Å) and angles (°) in [Fe(CO)<sub>6</sub>(C<sub>4</sub>Et<sub>4</sub>)]

Fe(1)—Fe(2)	2.504 (5)		
Metal—carbon σ bond		Metal—carbonyl bond	
Fe(1)—C(1)	1.970 (6)	Fe(1)—C(5)	1.819 (6)
Fe(1)—C(4)	1.981 (6)	Fe(1)—C(6)	1.805 (6)
Metal—carbon π bond		Fe(1)—C(7)	1.764 (7)
Fe(2)—C(1)	2.088 (6)	Fe(1)—C(10)	2.483 (7)
Fe(2)—C(2)	2.138 (6)	Fe(2)—C(8)	1.783 (6)
Fe(2)—C(3)	2.142 (6)	Fe(2)—C(9)	1.795 (7)
Fe(2)—C(4)	2.107 (6)	Fe(2)—C(10)	1.791 (5)
Butadiene moiety and ethyl groups		Carbonyl groups	
C(1)—C(2)	1.434 (6)	C(5)—O(5)	1.128 (7)
C(2)—C(3)	1.434 (7)	C(6)—O(6)	1.142 (7)
C(3)—C(4)	1.424 (6)	C(7)—O(7)	1.136 (7)
C(1)—C(11)	1.520 (8)	C(8)—O(8)	1.139 (7)
C(11)—C(12)	1.530 (12)	C(9)—O(9)	1.129 (8)
C(2)—C(13)	1.506 (7)	C(10)—O(10)	1.151 (5)
C(13)—C(14)	1.521 (10)		
C(3)—C(15)	1.515 (7)		
C(15)—C(16)	1.524 (8)		
C(4)—C(17)	1.506 (8)		
C(17)—C(18)	1.533 (9)		
C(1)—Fe(1)—C(4)	81.2 (3)	Fe(1)—C(7)—O(7)	177.7 (7)
C(1)—Fe(1)—C(5)	93.4 (4)	Fe(2)—C(8)—O(8)	177.5 (6)
C(1)—Fe(1)—C(6)	170.2 (4)	Fe(2)—C(9)—O(9)	178.4 (6)
C(4)—Fe(1)—C(5)	165.7 (4)	Fe(1)—C(1)—C(2)	115.6 (5)
C(1)—Fe(1)—C(7)	89.6 (4)	Fe(1)—C(4)—C(3)	115.0 (5)
C(4)—Fe(1)—C(7)	92.9 (3)	C(1)—C(2)—C(3)	112.9 (6)
C(10)—Fe(1)—C(7)	173.3 (4)	C(2)—C(3)—C(4)	114.0 (6)
C(8)—Fe(2)—C(9)	93.3 (4)	C(1)—C(11)—C(12)	112.5 (6)
C(8)—Fe(2)—C(10)	97.4 (4)	C(2)—C(13)—C(14)	114.1 (6)
C(9)—Fe(2)—C(10)	95.3 (4)	C(3)—C(15)—C(16)	112.9 (6)
Fe(1)—C(5)—O(5)	178.0 (7)	C(4)—C(17)—C(18)	112.3 (6)
Fe(1)—C(6)—O(6)	177.6 (7)		
Semi-bridging carbonyl			
Fe(2)—C(10)—O(10)	166.9 (6)		

the Fe(1)—CO distances of the two carbonyl groups *trans* to the butadiene ligand [Fe(1)—C(5) = 1.819 (4), Fe(1)—C(6) = 1.805 (4) Å] compared with the *cis* carbonyl group [Fe(1)—C(7) = 1.764 (5) Å]; (c) the Fe(1)—C(1) and Fe(1)—C(4) distances in the present complex are shorter than those found for [Fe(CO)<sub>4</sub>(CO)<sub>2</sub>(C<sub>2</sub>Et<sub>2</sub>)] [mean value 2.009 (5) Å (Aime *et al.*, 1979)], in which the butadiene fragment does not exhibit delocalization. These authors suggested some π interaction for these Fe—C bonds, also in accordance with the low-field resonance in the <sup>13</sup>C spectra; such data agree with the lower *trans* effect on the carbonyl groups in respect to those of (1); (d) the shortening in respect to our mean value [1.975 (6) Å] of these Fe—C distances (Table 3, columns V and VI) when butadiene brings strongly electronegative substituents. This bond shortening due to electronegative effects appears hardly justifiable in the presence of a pure Fe—C σ bond.

In all the ferrole derivatives the four Fe(2)—C π bonds are not equal. In fact, Fe(2)—C(1) and Fe(2)—C(4) distances are shorter by 0.03–0.06 Å with respect to Fe(2)—C(2) and Fe(2)—C(3). Only for the sawhorse ferrole (column VIII) is the situa-

† The molecular orbital symbols are those used commonly in the theoretical papers reported in the references.

Table 3. Bond distances (Å) and angles (°) in symmetrical ferrole derivatives [Fe<sub>2</sub>(CO)<sub>6</sub>(C<sub>4</sub>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>)]

	I	II	III*	IV	V†	VI	VII	VIII‡	IX
Fe(1)—Fe(2)	2.504 (5)	2.515 (1)	2.504 (1)	2.494 (5)	2.500 (3)	2.484 (2)	2.462 (3)	2.544 (3)	0.00
C(1)—C(2)	1.434 (6)	1.368 (9)	1.427 (9)	1.370 (19)		1.424 (10)	1.414 (19)	1.411 (6)	1.06
C(2)—C(3)	1.434 (7)	1.412 (9)	1.439 (10)	1.421 (19)		1.430 (10)	1.429 (21)	1.436 (6)	1.02
C(3)—C(4)	1.424 (6)	1.405 (9)	1.418 (9)	1.393 (18)		1.413 (10)	1.404 (17)	1.419 (6)	1.06
Metal—C $\sigma$ bond									
Fe(1)—C(1)	1.970 (6)	1.953 (5)	1.958 (7)	1.990 (15)		1.948 (8)	1.935 (13)	1.935 (5)	0.59
Fe(1)—C(4)	1.981 (6)	1.938 (6)	1.981 (7)	1.978 (16)	1.92 (2)	1.943 (8)	1.987 (14)	1.930 (5)	0.59
Metal—C $\pi$ bond									
Fe(2)—C(1)	2.088 (6)	2.080 (4)	2.103 (8)	2.065 (16)	2.13 (2)	2.111 (8)	2.087 (14)	2.161 (4)	0.16
Fe(2)—C(4)	2.107 (6)	2.082 (7)	2.086 (8)	2.074 (16)		2.121 (8)	2.066 (12)	2.205 (5)	0.16
Fe(2)—C(2)	2.138 (6)	2.111 (7)	2.131 (8)	2.098 (16)		2.150 (8)	2.172 (12)	2.095 (5)	0.00
Fe(2)—C(3)	2.142 (6)	2.112 (7)	2.148 (8)	2.109 (15)	2.19 (2)	2.142 (8)	2.189 (13)	2.100 (4)	0.00
Ferracyclopentadiene ring									
$\alpha$	115.6 (5)	117.5 (5)	116.8 (5)	113.6 (11)		117.0 (5)	116.5 (10)	118.5 (3)	
$\beta$	112.9 (6)	113.0 (7)	112.6 (6)	115.5 (14)		111.0 (5)	114.4 (11)	111.1 (3)	
$\gamma$	114.0 (6)	112.5 (7)	113.1 (6)	114.1 (15)		114.0 (5)	110.9 (12)	112.7 (3)	
$\delta$	115.0 (5)	116.6 (6)	115.9 (5)	113.8 (11)		116.0 (5)	117.1 (11)	117.4 (3)	
Semibridging C—O group (non-sawhorse structure)									
Fe(1)—CO	2.483 (7)	2.508 (4)	2.374 (9)	2.388 (20)		2.484 (8)	2.321 (19)		0.01
C—O	1.151 (5)	1.146 (9)	1.162 (11)	1.207 (18)		1.171 (10)	not reported		1.04
Fe(2)—C—O	166.9 (6)	167.3 (7)	162.1 (8)	166.4 (17)		168.0 (7)	161.9 (28)		

(I) R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> = C<sub>2</sub>H<sub>5</sub>; (II) R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> = H; (III) R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> = C<sub>6</sub>H<sub>5</sub>; (IV) R<sub>1</sub>, R<sub>4</sub> = C<sub>6</sub>H<sub>5</sub>, R<sub>2</sub>, R<sub>3</sub> = C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; (V) R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> = O—SiO<sub>3</sub>; (VI) R<sub>1</sub>, R<sub>4</sub> = OH, R<sub>2</sub>, R<sub>3</sub> = CH<sub>3</sub>; (VII) R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> = cyclic —CH<sub>2</sub>—CH<sub>2</sub>—; (IX) Mulliken overlap populations of the ferrole (II).

\* Structure determination at  $-40^\circ$ .

† This column shows only the bond distances reported by the authors, the atomic fractional coordinates were not published.

‡ This column reports the parameters of a sawhorse structure.

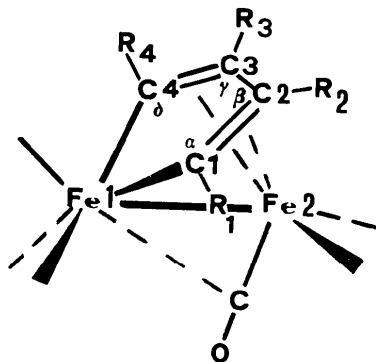


Fig. 3. Structural scheme of non-sawhorse ferrole derivatives. R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> substituents are shown in Table 3.

tion reversed; this indicates that the semibridging CO group reduces the Fe(2)—C(1) and Fe(2)—C(4) distances and the Fe—Fe distance from 2.544 (VIII) to 2.504 Å (I).

The features of the semibridging CO group agree with those previously discussed (Thorn & Hoffmann, 1978; Casarin *et al.*, 1987).

Intermolecular distances in the title compound do not indicate interactions greater than van der Waals forces.

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