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Preliminary communication

THE STRUCTURE AND VARIABLE TEMPERATURE ^{13}C NMR SPECTRA OF μ,μ'-(1,3-DITHIOLATOCYCLOHEPTA-4,6-DIENE)HEXACARBONYLDIIRON(I)

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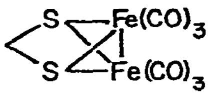
Summary

μ,μ'-(1,3-Dithiolatocyclohepta-4,6-diene)hexacarbonyldiiron(I) was prepared by the reaction of 2,3,4-trithiabicyclo[4,3,1]deca-6.8-diene with $Fe_2(CO)_9$ The carbonyls undergo rapid site exchange within each $Fe(CO)_3$ group but there is no exchange of carbonyls between the two different $Fe(CO)_3$ moieties The novel bicyclic nature of the bridging ligand results in a short iron—iron bond distance and a long sulfur—sulfur distance as compared to other members of this class.

Complexes of the type $[(RS)(CO)_3Fe]_2$ have been of interest since their preparation more than 40 years ago [1]. Unbridged examples exist as a mixture of isomers which differ in the relative geometry of the R groups, i e , axial—axial, equatorial—equatorial, and axial—equatorial [2]. The $Fe(CO)_3$ groups of such complexes are stereochemically non-rigid with rapid interconversion of axial and basal carbonyl positions [3], however, it remains uncertain whether carbonyl exchange between the two $Fe(CO)_3$ units occurs All complexes reported to date, both bridged and unbridged, have been symmetrical so that the $Fe(CO)_3$ residues are spectroscopically identical Substitution of one carbonyl group removes the symmetry of the system and in the cases studied there is no exchange of carbonyl ligands between the $Fe(CO)_3$ and $Fe(CO)_2L$ groups [4,5] However, the effects on stereochemical lability of such a change are notoriously difficult to predict [5] Extrapolation of results from these $Fe_2(CO)_5L$ type complexes to the parent hexacarbonyl compounds is somewhat hazardous.

We have reported a decarbasulfurization type of reaction between sulfur-containing cyclic olefins and $Fe_2(CO)_9$ whereby the novel bridged complex 1 may be prepared from 2 and $Fe_2(CO)_9$ [6] The isolation of the title complex 3 from the reaction of 4 with $Fe_2(CO)_9$ was briefly mentioned Complex 3 is of particular interest since it is, to our knowledge, the first unsymmetrical example in this class.

Treatment of 4 [7] with excess $Fe_2(CO)_9$ in THF for 2 hours results in a complex mixture of compounds. Column chromatography of the reaction mixture on alumina produces 3 upon elution with n-hexane. The complex can be isolated as dark red crystals (m.p. 122°C) from n-hexane (yield 17—25%), satisfactory elemental analyses were obtained for C, H and S; infrared (n-hexane) ν(CO): 2075m, 2036s, 2005s, 1995s, 1982w cm^{-1}, ^1H NMR (CD_2Cl_2) 1.30 (H_a,m), 3.53(H_b,(br)s), 6.28 ppm (H_c and H_d, (br)s); the parent ion (*m/e* 436) was observed in the mass spectrum followed by sequential loss of 6 carbonyl ligands. The identity of other products is still under investigation.



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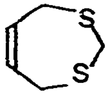

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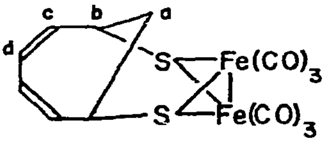

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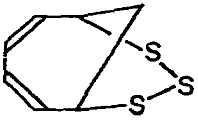

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The ^{13}C NMR spectrum of 3 in the carbonyl region shows two single peaks at room temperature (208.7, 207.4 ppm in CD_2Cl_2) consistent with rapid site exchange within each $Fe(CO)_3$ residue but with no exchange of carbonyl ligands between the two different $Fe(CO)_3$ groups. The complex decomposes in DMSO-d_6 at about 120°C, however, the two singlets are invariant up to 95°C in toluene-d_8. This proves that inter-iron carbonyl exchange does not occur rapidly for the $[(RS)(CO)_3Fe]_2$ class of complex. Upon cooling, the carbonyl bands begin to broaden at −8°C, coalesce at about −35°C and appear as four sharp peaks, in the approximate ratio 2/2/1/1 (209.7, 207.4, 205.7, 204.7 ppm), at −80°C. The low temperature study is consistent with the gradual slowing of the site exchange process within each $Fe(CO)_3$ group as the temperature is lowered until a limiting spectrum of two peaks (2/1) is observed for both unique $Fe(CO)_3$ residues. The four peaks due to the carbons of the C_7H_8 ring do not change between −80 to 95°C.

Crystals of 3 are monoclinic: space group $P2_1/n$, a 12.981(1), b 13.294(1), c 9.583(1) Å, β 98.46(1)°, $Z = 4$. Data collection by the stationary crystal—stationary counter method (graphite monochromatized Ag-K_β radiation) yielded 1053 symmetry independent reflections having $I > 2\sigma(I)$. Direct methods were used to solve the structure. Least-squares refinement employing anisotropic thermal parameters for all non-hydrogen atoms has resulted in a conventional unweighted residual of 5.2%.

The structure exhibits the typical butterfly Fe_2S_2 core with the C_7H_8 group double-bridging the two sulfur atoms. One $Fe(CO)_3$ group lies under the diene

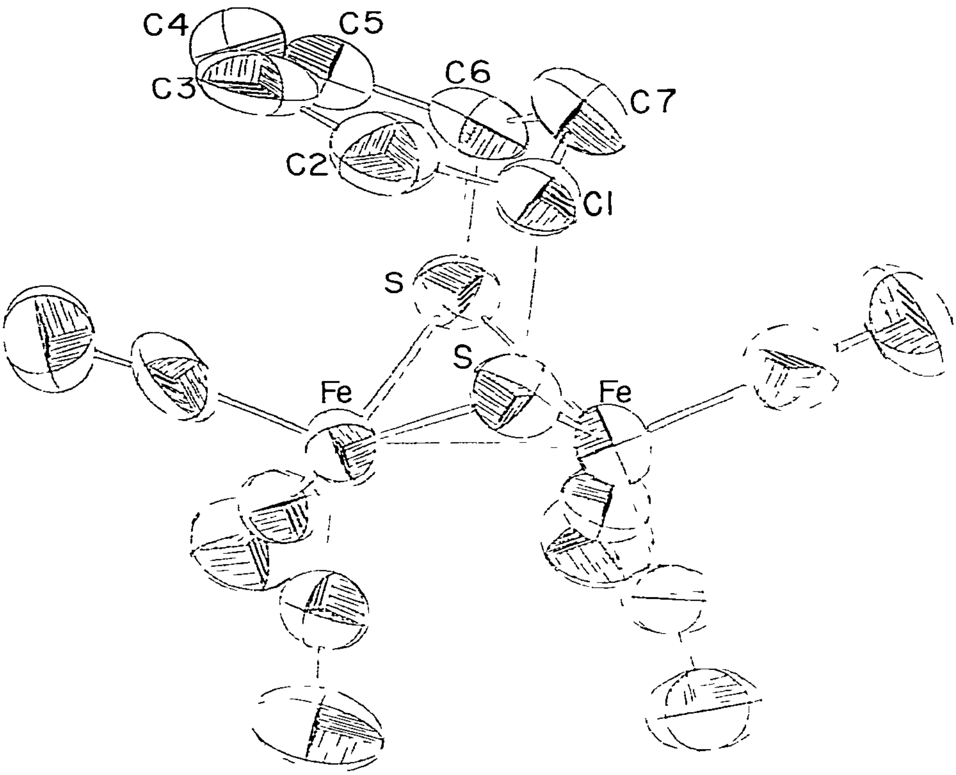


Fig 1 An ORTEP drawing of μ,μ'-(1 3-dithiolatocyclohepta-4 6-diene)hexacarbonyldiiron(I) which illustrates the different environments of the two $Fe(CO)_3$ groups

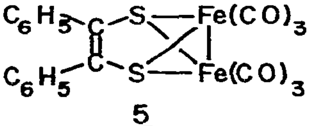
part of the ring while the other lies under the methylene group (Fig 1), the molecule possessing effective C_S symmetry The crystal structures of the bridged complexes 1 [6] and $[(C_6H_5CS)(CO)_3Fe]_2$ (5) [8], the unbridged $[(RS)(CO)_3Fe]$ where R = C_2H_5 [2] and C_6H_5 [9], as well as $[(S)(CO)_3Fe]_2$ which contains an S_2 ligand [10], have been reported The shortest S—S distance occurs in the latter compound, as expected, whereas in 3 the non-bonded S—S distance and S—Fe—S angles of 3 027(6) Å and 84 5(1)°, respectively, are the largest observed for this class of complex and approach the values expected for a planar Fe_2S_2 core. The C(1)—C(6) separation at the mercapto-bridgehead is 2 61(2) Å which results in a C(6)—C(7)—C(1) angle which is significantly distorted (118 5(1 7)°) from the expected tetrahedral geometry The methylene fragment is slightly bent away from its nearest $Fe(CO)_3$ residue (S—C—C(7) 114 9(1 0)°) while the diene portion of the ring lies closer to the remaining $Fe(CO)_3$ group (S—C—C (diene) 105.6(1.0)°) Thus the cycloheptadiene ligand exhibits a large degree of flexibility in its bonding mode

The Fe—Fe distance in 3 is very close to that in 1 which is the shortest observed to date (Table 1). Unlike 1 where short S—S and Fe—Fe distances are found, the double bridging in 3 leads to a long S—S distance and a short Fe—Fe one In complex 5 the S—S approach is intermediate between that observed in 1 and 3, whereas the Fe—Fe bond length is the longest of the three bridged species

TABLE 1

A COMPARISON OF SELECTED BOND LENGTHS (Å) AND ANGLES (deg) IN SOME BRIDGED AND UNBRIDGED [(RS)(CO)$_3$Fe]$_2$ COMPLEXES

	S—Fe—S	S—S	Fe—Fe
[(S)(CO)$_3$Fe]$_2$	53 5(1)	2 007(5)	2 552(2)
$CH_2S_2(CO)_6Fe_2$ (1)	72 45(4)	2 673(2)	2 485(1)
[(C_6H_5CS)(CO)$_3$Fe]$_2$ (5)	78 70(15)	2 876(7)	2 507(5)
[(C_6H_5)S(CO)$_3$Fe]$_2$	79 80(7)	2 910(5)	2 516(2)
[(C_2H_5)S(CO)$_3$Fe]$_2$	81 0(3)	2 932(14)	2 537(10)
$C_7H_8S_2(CO)_6Fe_2$ (3)	84 5(1)	3 027(6)	2 497(4)



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Thus the iron—iron and sulfur—sulfur distances seem unrelated Molecular orbital calculations on [X(CO)$_3$Fe]$_2$ dimers [11] postulate the existence of a bent M—M bond The vibrational spectra of these complexes are being studied to see whether a correlation exists between the Fe—Fe stretching frequency and the molecular structure [12], as well as to probe any differences in the bonding involving the axial and basal carbonyl ligands [13]

Acknowledgements

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