Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Isomerism in the μ,μ'-diorganothiodimetallates: the structure of $[Fe(CO)_3SCF_3]_2C_4F_6$

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(Received October 12th, 1972)

SUMMARY

$[Fe(CO)_3SCF_3]_2C_4F_6$ prepared by the reaction between hexafluoro-2-butyne and $[Fe(CO)_3SCF_3]_2$ contains an Fe_2S_2 cluster with an *axial, axial* orientation of organothio substituents about the cluster.

Binuclear compounds containing two organothio bridges between two metal atoms can potentially exist as various isomers depending upon the orientation of the organo substituent with respect to the M_2S_2 cluster[1-5]. For a non-planar M_2S_2 cluster and with equivalent substituents on each metal atom three isomers (Fig. 1a,b and c) are possible but (c) (*axial, axial*) has been precluded[3] on steric grounds when a metal–metal bond is present. We now show that the *axial, axial* isomer can exist in some circumstances.

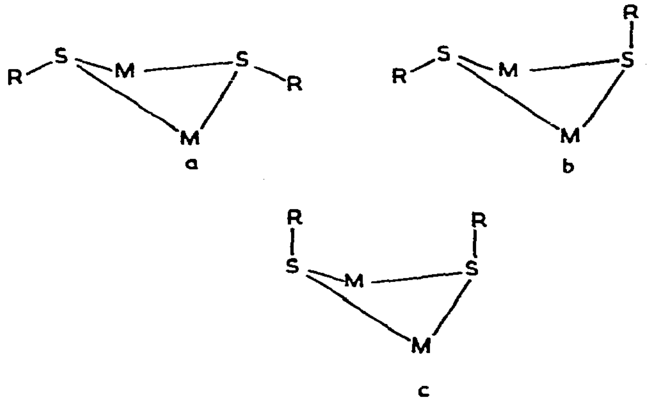

Fig. 1. Possible isomers for a non-planar M_2S_2 cluster,

$[Fe(CO)_3SCF_3]_2$[6] reacts with hexafluoro-2-butyne to give $[Fe(CO)_3SCF_3]_2C_4F_6$, the structure of which has been elucidated by X-ray crystallography.

The complex crystallises in the space group *Pnma* with $a = 10.918(4)$, $b = 12.049(2)$, $c = 15.416(4)$ Å, $Z = 4$. The analysis employed 1847 independent diffractometer intensities (Mo-K_α radiation), and least-squares adjustment of the atomic parameters converged at $R = 5.1\%$. The molecular structure with some of the principal dimensions is shown in Fig.2. The molecule has crystallographically required C_s symmetry and approximates very closely to C_{2v}. The Fe. . . .Fe distance in the Fe_2S_2-ring is 3·266(1) Å, and the Fe—S—Fe′ and S—Fe—S′ angles are 90.2(1) and 87.4(1)°. The Fe—CO bonds *trans* to sulphur have a mean length of 1.816(4) Å, while those *trans* to carbon have a mean length of 1.840(6) Å. The iron and sulphur atoms deviate by ± 0.17 Å from the mean plane of the Fe_2S_2-ring, and the fold about the Fe. . . .Fe′ line is 24°.

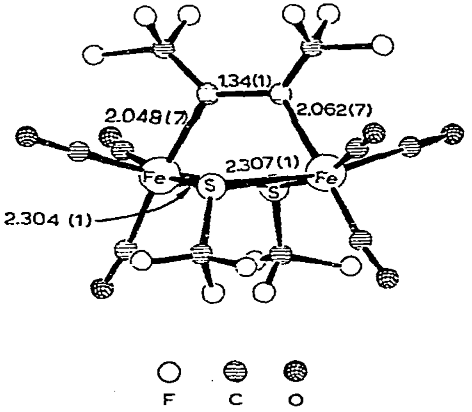

Fig.2. Molecular structure of $[Fe(CO)_3SCF_3]_2C_4F_6$.

Because of the appreciable non-planarity of the Fe_2S_2-ring, it is possible to distinguish between axial and equatorial substituents on the sulphur atoms of the ring, and the molecule shown in Fig.2 clearly corresponds to the *axial, axial* isomer (c).

It appears that the Fe—Fe distance in this compound which does not require a metal—metal bond is sufficient to allow the *axial, axial* isomer. It dissolves in methylene chloride to give a solution which by ^{19}F NMR spectroscopy contains two isomers. One of these has equivalent fluorines and by analogy with the structure of the solid is likely to have the *axial, axial* (c) structure; the other contains non-equivalent fluorines and is the *axial, equatorial* isomer (b). A dimetallated olefin has been previously described as resulting from the reaction between hexafluoro-2-butyne and methyl(triphenylphosphine) gold[7].

It is of interest that $[Fe(CO)_3SCF_3]_2$ is primarily the *anti* (b) (*axial, equatorial*) isomer. [It was previously reported as being exclusively the *anti* isomer[6] but it has now been found that the proportion of *anti* to *syn* isomers is 12/1. As this compound will contain a metal—metal bond[3] the *syn* isomer will probably be the *equatorial, equatorial* species (a).] As in previous studies[1] substitution by triphenylphosphine causes a greater favouring of the *syn* isomer. IR spectroscopy on the complexes $Fe_2(CO)_5(PPh_3)(SCF_3)_2$ and $Fe_2(CO)_4(PPh_3)_2(SCF_3)_2$ [6] (formed by the action of triphenylphosphine on $Fe_2(CO)_6(SCF_3)_2$) favours structures about the iron atoms with the phosphines *trans* to the metal–metal bond so that the phosphines are in the position giving rise to maximum steric interference with the trifluoromethyl groups. This steric interference will be greater with an *axial* than with an *equatorial* trifluoromethyl group in agreement with the observed isomer preference.

	$Fe_2(CO)_5PPh_3(SCF_3)_2$	$[Fe(CO)_2PPh_3SCF_3]_2$
Isomer ratio $\frac{Anti}{Syn}=$	$\frac{4}{1}$	$\frac{1}{1}$

We thank Dr. F.C. Wilson for helpful discussion.

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