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Unusually High Oxidation Potentials of Di- and Trichalcogena[3]-ferrocenophanes

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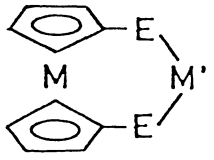
1,2,3-Trichalcogena[3]-ferrocenophanes (1: E=S , 2: E=Se) and 1,3-dithia[3]-ferrocenophane show unusually high oxidation potentials compared to non-bridged 1,1'-bis(methylthio)ferrocene and methylene-bridged [3]-ferrocenophane. The photoelectron spectrum of 1 shows that the d-electrons of Fe are attracted by sulfur bridge.

Since the discovery of novel type of fluxionality of 1,2,3-trithia[3]-ferrocenophane by Davison and Smart,1) a new field of bridged ferrocenes has been developed. The reports on the structural studies using X-ray crystallography,2) and on the activation energies for the ring inversion of trichalcogen group using variable temperature NMR3) have appeared.

Recently, the interaction between the metal atom of the metallocene moiety and the another metal atom (M') situated in the midst of the bridge has been reported by Seyferth et al.(M=Fe; E=S; M'=Pd),4) McCulloch et al.(M=Fe; E=S; M'=Pd,Pt),5) and Akabori et al.(M=Ru,Fe; E=S,Se; M'=Pd,Pt).6)



Although the cyclic voltammetry of carbon - bridged ferrocenophanes has been reported by Toma et al.7) and Kasahara et al.,8) the electrochemical and chemical reactivities of trichalcogena[3]-ferrocenophanes have not been reported.

We wish to report here unusually high electron withdrawing abilities of trithia-, triselena-, and 1,3-dithia groups in 1,2,3-trithia-, 1,2,3-triselena-, and 1,3-dithia[3]-ferrocenophanes.

1,2,3-Trithia- and 1,2,3-triselena[3]-ferrocenophanes (1:E=S3a), 2:E=Se9)), and 1,3-dithia[3]-ferrocenophane (3),10) were all prepared by the literature methods. 1,1'-Bis(methylthio)ferrocene (5) was prepared from 1 by the reduction with lithium aluminum hydride followed by the reaction with methyl iodide.

The measurement11) of redox potentials of trichalcogena[3]-ferrocenophanes and the related compounds affords the quantitative evidence for the unusually low electron donating character of 1 and 2. The $E_{1/2}$ values obtained for the compounds 1-5 and ferrocene are shown in Fig. 1. The $E_{1/2}$ value of 1 is 310 mV more positive than that of ferrocene (0.025 V). In contrast with the above result, the $E_{1/2}$ of non-bridged 1,1'-disulfide, 5, is 25 mV more negative than that of ferrocene.

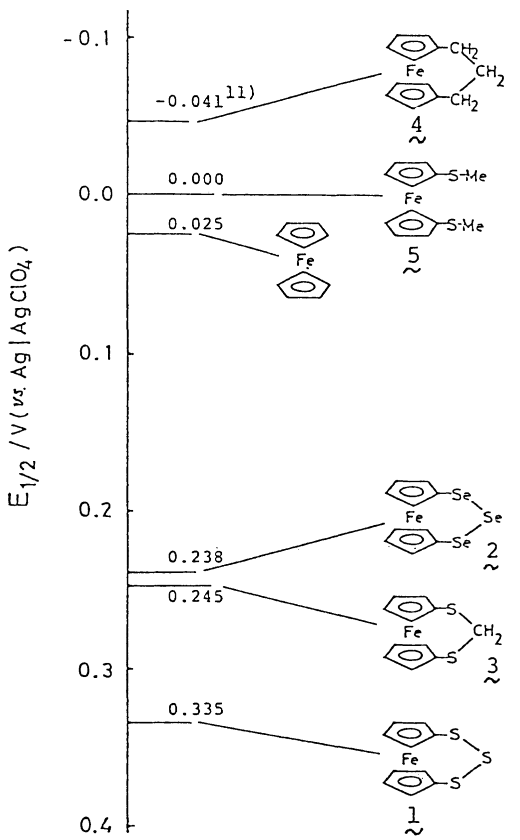


Fig.1. Oxidation potentials of bridged ferrocenes and the related compounds.

The $E_{1/2}$ value of the compound in which one of the trithia-bridge is replaced by $-CH_2-$ (3) is also more positive than that of ferrocene and the magnitude of the shift of $E_{1/2}$ from that of ferrocene (220 mV) is still large.

The unusually large shift of $E_{1/2}$ value towards the positive side by bridging is not observed in the carbon bridged [3]-ferrocenophane. The $E_{1/2}$ value of methylene bridged [3]-ferrocenophane was reported[8)] to be 0.363 V (vs. SCE) which corresponds to -0.041 V vs. Ag | $AgClO_4$ (0.1 mol dm^{-3} in CH_3CN).[11)] The shift of $E_{1/2}$ value from that of ferrocene is negative in this case. Kasahara et al.[8)] have observed no unusual electrochemical behavior accompanied by bridging the two cyclopentadienyl ring with carbon chain. Based on the $E_{1/2}$ value of [3]-ferrocenophane and the reported $E_{1/4}$ value of 1,1'-diethylferrocene[12)] (0.194 V vs. SCE in CH_3CN corresponds to -0.088 V vs. Ag | $AgClO_4$), the shift of $E_{1/2}$ value from non-bridged 1,1'-diethylferrocene to bridged [3]-ferrocenophane is positive but the magnitude of the shift is only 47 mV. Compared to this value, the positive shift of $E_{1/2}$ value from 1,1'-bis(methylthio)ferrocene to 1,2,3-trithia[3]-ferrocenophane is unusually large (335 mV).

These results indicate that the inhibition of the free rotation of the two cyclopentadienyl rings by bridging causes the interaction between sulfur atoms in the bridge and iron. A similar positive shift of $E_{1/2}$ can also be observed in 1,2,3-triselena[3]-ferrocenophane.

The HeI photoelectron spectra[13)] of 1 can afford more direct evidence for the electron withdrawing effect of -S-S-S- group in 1 (Fig.2). The first (vertical) IP (7.30 eV) due to the Fe 3d orbitals in 1 is higher than that in ferrocene itself (6.86 eV), while the second IP (8.52 eV) due to the lone pair orbitals of S in 1 is lower than that in non-bridged compounds, such as $(CH_3)_2S$ (8.72 eV).[14)]

These results suggest that the electrons in ferrocene moiety in 1 is strongly attracted by -S-S-S- bridge. These results agreed with the suggestion of Good et al.$^{15)}$ that extensive d-electron delocalization occurs through tri-sulfur bridge and this bridge has partial multiple bonding and electron delocalization within the bridge.

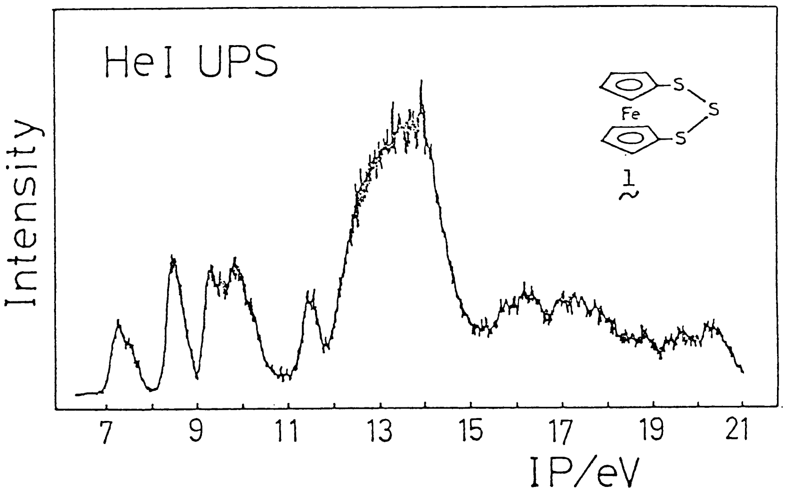


Fig.2. He I Photoelectron spectrum of 1.

It has been known that ferrocene forms a charge transfer (CT) complex with CCl_4. The CT absorption was observed in the non-bridged 1,1'-bis(methylthio)ferrocene-CCl_4 system, whereas the systems which contain trichalcogen atom-bridged ferrocenophanes and CCl_4 do not show CT absorption. These results also support the electrochemical data obtained above.

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Kasahara et al. The calculation was done ; i) by taking the difference of $E_{1/2}$ value of [3]-ferrocenophane from that of ferrocene obtained by Kasahara et al. and ii) by adding the difference obtained in (i) to the $E_{1/2}$ value of ferrocene obtained by us (0.025 V).

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13) The photoelectron spectra were measured using the apparatus already described elsewhere(Y.Harada, K.Ohno, and H.Mutoh, J. Chem. Phys., 79, 3251 (1983)). To obtain gas-phase spectra, the sample of **1** was heated up to 210 °C in a sample tube attached to the ionization chamber of the spectrometer.

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