Inorganica Chimica Acta, 37 (1979) L541
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[3]-Ferrocenophanes with Group VI Elements as Bridging Atoms

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Received July 27, 1979

As part of a general study [1, 2] on ferrocenophanes we were interested in synthesising ferrocenophanes where all the bridging atoms are elements other than carbon. The number of known compounds of this type is low, but the novel fluxional compound (I) (Table I) has been reported [3, 4]. We have now extended the range of [3]-ferrocenophanes with Group VI elements in a bridging position, by including selenium and tellurium as part of the bridge, thus making available a range of compounds containing heterotrichalcogen chains (III, IV and V), which is an uncommon structural grouping (Fig. 1).

TABLE I. Physical Properties of some [3]-Ferrocenophanes.

Compound	X[a]	Y[a]	Z[a]	Colour	^{1}H nmr, δ/ppm[b]
I	S	S	S	orange	4.06(t), 4.30(t)
II	Se	Se	Se	red-orange	4,11(t), 4.31(t)
III	S	Se	S	dark-red	4.07(t), 4.31(t)
IV	Se	S	Se	orange	4.11(t), 4.35(t)
V	S	Te	S	bronze	4.09(t), 4.24(t)

[a] See Fig. 1 for explanation of letters. [b] High temperature limiting spectra, $d_5$nitrobenzene solution; δ(TMS) = 0; t = triplet.

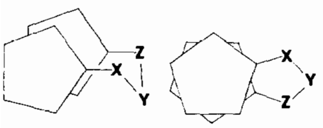

Fig. 1. Limiting conformations of [3]-ferrocenophanes.

All the [3]-ferrocenophanes are air-stable crystalline solids, soluble in organic solvents and give satisfactory analytical results. In the mass spectrometer all the compounds show parent ions and the stepwise loss of the Group VI atoms as predominant peaks. In solution the molecules are all fluxional. At room temperature the ^{1}H n.m.r. spectra consist of several complex multiplets, the broadness of the signals varying amongst the compounds, indicating the differing degrees of fluxionality at that temperature. Detailed studies of the fluxional process are being made separately [5] but qualitative observations of the spectra indicate an order of activation energies, $S_3 > S_2Se > Se_2S > Se_3 > S_2Te$. The high temperature limiting ^{1}H n.m.r. spectra of these compounds consists of two unsymmetrical triplets (Table I), similar to that found for $1,1^1$-disubstituted ferrocenes. In the solid state, I has been shown [4] to have an eclipsed structure, and it is probable that these new [3]-ferrocenophanes will also have eclipsed structures.

II was prepared from $1,1^1$-dilithioferrocene and selenium in boiling hexane; $(C_5H_5FeC_5H_4)_2Se$ and $(C_5H_5FeC_5H_4)_2Se_2$ were isolated as minor products. III was prepared by reaction of the disodium salt of $1,1^1$-ferrocenedithiol with selenium, and V was prepared by reaction of the dithiol with tellurium tetrachloride. IV was prepared by reaction of $1,1^1$ferrocenediselenol with sulphur dichloride. Attempts to prepare 1,2,3-tritelluro-[3]ferrocenophane (X = Y = Z = Te) have failed, but further work is in progress synthesising unsymmetrical chain compounds.

Acknowledgements

R.E.H. thanks the S.R.C. for a maintenance grant.

References

1 A. G. Osborne and R. H. Whiteley, *J. Organometal. Chem., 101*, C27 (1975).
2 H. Stoeckli-Evans, A. G. Osborne and R. H. Whiteley, *Helv. Chim. Acta, 59*, 2402 (1976).
3 A. Davison and J. C. Smart, *J. Organometal. Chem., 19*, P7 (1969).
4 B. R. Davis and I. Bernal, *J. Cryst. Mol. Struct., 2*, 107 (1972).
5 E. W. Abel, M. Booth and K. G. Orrell, personal communication.