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Pyramidal Inversion in Cyclopentadienyliron Derivatives of Dimethyl Chalcogenides

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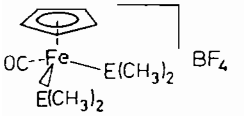
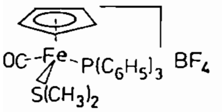
Pyramidal inversion about the donor atom of organochalcogen ligands has been the subject of numerous investigations in the past two decades [1]. The symmetry required for the application of dynamic NMR spectroscopy was achieved by the use of ligands containing prochiral substituents for the most part. This may be the reason that quantitative data for tellurium compounds are almost completely absent from the literature, such ligands being difficult to prepare.

Recently, we have described the synthesis of the cations $[C_5H_5Fe(CO)(EMe_2)_2]^+$ (**1**–**3**) [2]. In these compounds, the ligand EMe_2 acts as a prochiral group itself in an ion of suitable symmetry [3] and therefore may be used for the observation of pyramidal inversion by DNMR spectroscopy. Table I shows the expected increase of ΔG^+ values going from the sulfide complex **1** to its heavier analogues **2** and **3**. As indicated by coalescence temperatures in the complexes $PtI_2(E(C_2H_5)_2)_2$ (E = S, Se, Te) [4], the difference between selenium and tellurium inversion energy in **2** and **3** is small compared with the ΔG^+ difference in **1** and **2**.



	E
1	S
2	Se
3	Te

In metal carbonyls, $\delta^{13}C$ shifts of the CO groups are shifted downfield by increasing the electron density at the coordination centre [5]. The inversion barrier of ER_2 ligands is also thought to be influenced by the electron density at the coordination centre [1]. For this reason we have substituted one dimethyl sulfide ligand in **1** for other ligands; the inversion energies of the resulting complexes **4** and **5** are also



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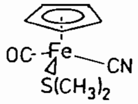

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TABLE I. Arrhenius and Activation Parameters of Ligand Atomic Inversion for the Complexes **1**–**5**

Complex	T_c (K)	k_c[a] (s^{-1})	E_A[b] (kJ mol^{-1})	log A[b]	ΔH^*[b] (kJ mol^{-1})	ΔS^*[b] (J mol^{-1} K^{-1})	ΔG^*[b] (kJ mol^{-1})	ΔG^*[a] (kJ mol^{-1})	δ CO[e] (ppm)
1 (^1H)	253[c]	22	75.5 ± 1.9	16.9 ± 0.4	73.3 ± 2.0	71.8 ± 7.7	55.1 ± 3.9	55.1	216.89
1 (^{13}C)	255[c]	39						54.3	
2 (^1H)	325[c,d]	22.4	74.9 ± 6.3	13.4 ± 1.0	72.3 ± 6.3	2.8 ± 20	71.4 ± 8.3	71.4	
2 (^{13}C)	319[d]	8						72.7	
3 (^1H)	340[d]	21	89.5 ± 7.3	15.2 ± 1.2	86.8 ± 7.3	35.0 ± 22.3	74.9 ± 14.9	75.0	
4 (^1H)	273[c]	362	26.8 ± 1.0	31.8 ± 0.2	24.6 ± 1.0	−106.5 ± 3.8	53.7 ± 2.0	53.5	217.69
5 (^1H)	286[c]	63	22.8 ± 1.6	5.9 ± 0.3	20.7 ± 1.6	−138.3 ± 6	60.2 ± 3.3	60.0	212.46

[a] Calculated from the coalescence temperature of the methyl peaks. [b] Obtained from accurate DNMR fit of the methyl peaks (program DNMR 2, DNMR 5 and ARRHEN 1). [c] $(CD_3)_2CO$, *ca.* 5% solution; no change could be detected up to 10%. [d] CD_3NO_2, *ca.* 5% solution; no change could be detected up to 10%. [e] $(CD_3)_2CO$ at 300 K.

given in Table I completed by ^{13}C NMR shift data. In fact, the sulfide inversion energy in **1**, **4** and **5** increases with increasing ^{13}C NMR carbonyl shifts (*i.e.* with decreasing electron density at the iron atom) which parallels the results obtained for pyramidal nitrogen inversion, the barrier being increased here by strongly electronegative substituents.

To confirm this correlation investigation of an enhanced series of $C_5H_5Fe(CO)(SMe_2)L^+$ complexes is in progress.

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References

1 E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem.*, *32*, 1 (1984).
2 N. Kuhn and H. Schumann, *J. Organomet. Chem.*, *276*, 55 (1984).
3 W. B. Jennings, *Chem. Rev.*, *75*, 307 (1975).
4 R. J. Cross, Th. Green and R. Keat, *J. Chem. Soc., Chem. Commun.*, 207 (1974); *J. Chem. Soc., Dalton Trans.*, 1150 (1976).
5 B. E. Mann and B. F. Taylor, '^{13}C NMR Data of Organometallic Compounds', Academic Press, London, 1981.