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

$$\begin{array}{c} & & \\ & &$$

compounds, the ligand EMe₂ 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.

In metal carbonyls, δ^{13} C shifts of the CO groups are shifted downfield by increasing the electron density at the coordination centre [5]. The inversion barrier of ER₂ 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



| (K) (\bar{s}^{-1}) (ki mol ⁻¹) (kl mol ⁻¹) (l mol ⁻¹ k ⁻¹) (kl mol ⁻¹) (kl mol ⁻¹) (ppm) 1 (¹ H) 253 ^e 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 2 (¹ H) 255 ^e 39 13.4 ± 1.0 72.3 ± 6.3 2.8 ± 20 71.4 ± 8.3 71.4 2 (¹ H) 325 ^{ed} 22.4 74.9 ± 6.3 13.4 ± 1.0 72.3 ± 6.3 2.8 ± 20 71.4 ± 8.3 71.4 3 (¹ H) 325 ^{ed} 22.4 74.9 ± 6.3 15.2 ± 1.2 86.8 ± 7.3 35.0 ± 22.3 74.9 ± 14.9 75.0 3 (¹ H) 273 ^e 362 26.8 ± 1.0 31.8 ± 0.2 24.6 ± 1.0 -106.5 ± 3.8 53.7 ± 2.0 53.5 217.65 4 (¹ H) 273 ^e 36.2 25.8 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 60.2 ± 3.3 60.0 212.45 4 (¹ H) 278 ^e 63 22.4 ± 1.6 -138.3 ± 6 60.2 ± 3.3 60.0 217.65 5 (¹ H) <th>Complex</th> <th>T_{c}</th> <th>k a</th> <th>$E_{\mathbf{A}}^{\mathbf{b}}$</th> <th>$\log A^{\rm b}$</th> <th>$\Delta H^{*b}$</th> <th>∆S*b</th> <th>∆G*b</th> <th>∆G*a</th> <th>δ CO^e</th> | Complex | T_{c} | k a | $E_{\mathbf{A}}^{\mathbf{b}}$ | $\log A^{\rm b}$ | ΔH^{*b} | ∆S*b | ∆ G*b | ∆G*a | δ CO ^e |
|--|-------------------------|------------------|--------------------|-------------------------------|---------------------------|-------------------------|--|-------------------------|------------------------|-------------------|
| 1 (^{1}H) 253°2275.5 ± 1.916.9 ± 0.473.3 ± 2.071.8 ± 7.755.1 ± 3.955.1216.892 (^{1}H) 255°3932.6 d3954.3216.8124.3216.892 (^{1}H) 325° d22.474.9 ± 6.313.4 ± 1.072.3 ± 6.32.8 ± 2071.4 ± 8.371.42 (^{1}H) 325° d22.474.9 ± 6.313.4 ± 1.072.3 ± 6.32.8 ± 2071.4 ± 8.371.43 (^{1}H) 340°2189.5 ± 7.315.2 ± 1.286.8 ± 7.335.0 ± 22.374.9 ± 14.972.74 (^{1}H) 273°36.226.8 ± 1.0-106.5 ± 3.853.7 ± 2.053.5217.655 (^{1}H) 273°53.224.6 ± 1.0-106.5 ± 3.853.7 ± 2.053.5217.655 (^{1}H) 286°6322.8 ± 1.65.9 ± 0.320.7 ± 1.6-138.3 ± 660.2 ± 3.360.0212.44aCalculated from the coalescence temperature of the methyl peaks.bObtained from accurate DNMR fit of the methyl peaks (program DNMR 2, DNM | | (Ķ) | (s ⁻¹) | (kJ mol ⁻¹) | 1 | (kJ mol ⁻¹) | (J mol ⁻¹ K ⁻¹) | (kJ mol ⁻¹) | (kJ mol ¹) | (mqq) |
| 1 (^{13}C) 255°3954.354.32 (^{14}C) 325°d22.474.9 ± 6.313.4 ± 1.072.3 ± 6.32.8 ± 2071.4 ± 8.371.42 (^{14}C) 325°d22.474.9 ± 6.313.4 ± 1.072.3 ± 6.32.8 ± 2071.4 ± 8.371.42 (^{14}C) 319d885.4 ± 1.286.8 ± 7.335.0 ± 22.374.9 ± 14.975.03 (^{14}H) 273°36226.8 ± 1.031.8 ± 0.224.6 ± 1.0-106.5 ± 3.853.7 ± 2.053.5217.654 (^{14}H) 273°56°6322.8 ± 1.631.8 ± 0.224.6 ± 1.0-106.5 ± 3.853.7 ± 2.053.5217.655 (^{14}H) 273°60.2 ± 3.350.2 ± 3.360.0212.446622.8 ± 1.65.9 ± 0.320.7 ± 1.6-138.3 ± 660.2 ± 3.360.0212.44aCalculated from the coalescence temperature of the methyl peaks. ^b Obtained from accurate DNMR fit of the methyl peaks (program DNMR 2, DNMR 5, DNM | (H ¹) 1 | 253° | 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 |
| 2 (¹ H) 325^{cd} 22.4 74.9 ± 6.3 13.4 ± 1.0 72.3 ± 6.3 2.8 ± 20 71.4 ± 8.3 71.4 ± 2.7 72.7 2 (¹ C) 319 ^d 8 72.7 72.7 72.7 72.1 15.0 15.0 ± 21 89.5 ± 7.3 15.2 ± 1.2 86.8 ± 7.3 35.0 ± 22.3 74.9 ± 14.9 75.0 72.7 4 (¹ H) 273 ^c 362 26.8 ± 1.0 31.8 ± 0.2 24.6 ± 1.0 -106.5 ± 3.8 53.7 ± 2.0 53.5 217.65 5 (¹ H) 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 2 Cloulated from the coalescence temperature of the methyl peaks. ^b Obtained from accurate DNMR fit of the methyl peaks (program DNMR 2, DNMR 2, DNMR 2, DNMR 2, DNMR 1, DNMR 2, DNM | 1 (¹³ C) | 255 ^c | 39 | | | | | | 54.3 | |
| 2 (^{14}C) 319 ^d 8 72.7 72.7 72.9 35.0 ± 22.3 74.9 ± 14.9 75.0 75.0 217.65 (¹ H) 273 ^c 36.2 26.8 ± 1.0 31.8 ± 0.2 24.6 ± 1.0 -106.5 ± 3.8 53.7 ± 2.0 53.5 217.65 (¹ H) 273 ^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 (¹ H) 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 (¹ H) 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 (¹ H) 286 ^c 60.2 ± 3.6 50.0 53.5 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 60.0 212.46 (¹ H) 286 ^c 60.2 ± 3.6 50.0 53.5 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 60.0 212.46 (¹ H) 286 ^c 63 22.8 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 60.0 212.46 (¹ H) 286 ^c 63 20.2 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 60.0 212.46 (¹ H) 286 ^c 63 20.2 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 60.0 212.46 (¹ H) 286 ^c 63 20.2 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 50.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 1.6 50.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 63 20.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 60.2 ± 3.3 50.0 212.46 (¹ H) 286 ^c 60.2 ± 3.3 50.0 200 ^c 70.0 50.0 200 ^c 70.0 50.0 50.0 200 ^c 70.0 50.0 50.0 50.0 50.0 50.0 50.0 50.0 | (H1) 2 | 325°d | 22.4 | 74.9 ± 6.3 | 13.4 ± 1.0 | 72.3 ± 6.3 | 2.8 ± 2 0 | 71.4 ± 8.3 | 71.4 | |
| 3 (H) 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 (H) 273^{c} 362 26.8 ± 1.0 31.8 ± 0.2 24.6 ± 1.0 -106.5 ± 3.8 53.7 ± 2.0 53.5 217.6^{c} 5 (H) 286^{c} 63 22.8 ± 1.6 5.9 ± 0.3 20.7 ± 1.6 -138.3 ± 6 60.2 ± 3.3 60.0 212.4^{c} ^a Calculated from the coalescence temperature of the methyl peaks. ^b Obtained from accurate DNMR fit of the methyl peaks (program DNMR 2, | 2 (¹³ C) | 319d | 8 | | | | | | 72.7 | |
| 4 $^{(H)}$ 273° 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 $^{(H)}$ 286° 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 ARHEN 1). | (H ₁) E | 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 | |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | 4 (¹ H) | 273° | 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 |
| ^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). | 5 (¹ H) | 286° | 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 coales | scence temperat | ure of the methyl pe | aks. ^b Obtaine | ed from accurate DN | WR fit of the methyl pe | aks (program DNMF | 2, DNMR 5 and Al | RRHEN 1). |

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

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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