Evidence for a Trigonal Twist Mechanism in the Intramolecular Rearrangement of Tris-(*N*-methyl-*N*-phenyldithiocarbamato)iron(III)

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Summary The variable temperature ^{1}H n.m.r. of the title complex in CD_2Cl_2 solution shows the occurrence of two independent stereochemical processes with approximate coalescence lifetimes of $1{\cdot}3 \times 10^{-2}$ s ($-37°$) and $9{\cdot}2 \times 10^{-4}$ s ($-83°$); the lower temperature process is assigned as a non-bond rupture trigonal twist motion about the pseudo-C_3 axis.

RECENTLY many publications have appeared assigning mechanisms to intramolecular rearrangements of tris-chelates *via* variable temperature n.m.r. and polarimetry techniques. These include studies on tris-(β-diketonate) complexes of Co$^{\text{III}}$,[1–3] Al$^{\text{III}}$,[1,4–7] and Ga$^{\text{III}}$;[7,8] bis-(*NN*-disubstituted-dithiocarbamate)dithiolene complexes of iron, Fe(R^1,R^2-dtc)$_2S_2C_2Z_2$ where $Z = CF_3$ or CN;[9,10] and tris-(tropolonato) complexes of Al$^{\text{III}}$[11,12] and Co$^{\text{III}}$.[12] Only in the cases of Fe(R^1,R^2-dtc)$_2S_2S_2Z_2$ containing a FeS_6 core and tris-(α-C_3H_7-tropolonato)Co$^{\text{III}}$ containing a CoO_6 core do the n.m.r. data directly support the assignment of mechanism without the use of kinetic arguments. We report the first such direct mechanistic determination for an unsymmetrically substituted tris-chelate of iron(III).

Tris-(*N*-methyl-*N*-phenyldithiocarbamato)iron(III), Fe(Me,Ph-dtc)$_3$, was prepared by standard means[13] and characterized by ^{1}H n.m.r.[14] and elemental analysis. The 100 MHz ^{1}H n.m.r. spectrum of the methyl region in CD_2Cl_2 solution is shown in Figure 1. At —89° and below, four distinct methyl resonances, 1—4, are observed and are assigned to the *cis*,C,(1 signal) and *trans*,T,(3 signals) isomers. Resonances 2 and 3 become nearly degenerate at

$-93°$. As the temperature is increased, peaks 1 and 4 coalesce while 2 and 3 are unaffected up to $-50°$ (low temperature process, LTP). Increased temperatures coalesce all the resonances to one sharp line at $-10°$ (high temperature process, HTP). Coalescence lifetimes of exchanging sites, τ_a (s), were calculated using the equation, $\tau_a = \sqrt{2}/\pi(\Delta\nu)$, where $\Delta\nu$ is the chemical shift separation in Hz,[15] and are $9{\cdot}2 \times 10^{-4}$ at $-83°$ (LTP) and $1{\cdot}3 \times 10^{-2}$ at $-37°$ (HTP).

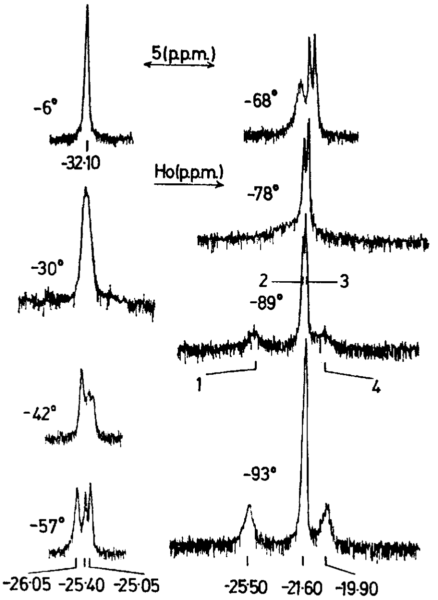

FIGURE. *The proton dynamic n.m.r. of the methyl region of Fe(methyl, phenyl-dtc)*$_3$ *in* CD_2Cl_2 *solution at* 100 *MHz.*

The kinetic processes are intramolecular in origin because ligand exchange between Fe(Me,phenyl-dtc)$_3$ and other tris(disubstituted-dtc)Fe^{III} complexes is slow at temperatures where isomerization is fast on the n.m.r. time scale. The LTP cannot be S_2C–N bond rotation because this motion would interconvert the C and T isomers resulting in simultaneous collapse of all four methyl resonances; indeed, any mechanism resulting in C$\leftrightarrow$T interconversion will not account for the LTP. Resonances 1 and 4 must be due to the T isomer while 2 and 3 cannot be uniquely defined because the relative C and T populations are nearly statistical. The LTP requires a mechanism which (i) averages two of the T resonances while leaving the third unaffected and (ii) does not interconvert C and T isomers.

The only mechanism which satisfies the above conditions is a non-bond rupture trigonal twist motion about the pseudo-C_3 axis of the T isomer (or real C_3 axis of the C) proceeding through an idealized trigonal prismatic transition state (see Figure 7 of ref.7).† This conclusion is reached by considering the analysis of isomerization mechanisms for M(A–B)$_3$ complexes.[2,7] All bond-rupture pathways *via* five-co-ordinate transition states can be eliminated because in order to satisfy (i) and (ii) only highly specific bonds must break in T with no similar bond breaking in C. Twists about the imaginary C_3 axes of C and T will also not accommodate the data. We conclude that the trigonal twist is the primary isomerization pathway for the LTP. This analysis has recently been put forth by Eaton and Holm for tris-(α-C_3H_5-tropolonato)Co^{III}.[12]

The HTP is either S_2C–N bond rotation or a mixture of other isomerization mechanisms. The latter is considered more likely because the barrier to bond rotation is expected to be much higher than observed.‡

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† This mechanism must be considered the primary pathway and any operationally equivalent motion will satisfy the conditions It is assumed that an equivalent motion is occurring in the C isomer, *i.e.*, twisting about the real C_3 axis.

‡ Compare to Fe(methyl,phenyl-dtc)$_2S_2C_2(CF_3)_2$ where the lifetime for S_2C–N bond rotation at $-37°$ is 8·6 s, ref. 9.

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