Dynamic Stereochemistry of Tris-Chelate Complexes. I. Tris(dithiocarbamato) Complexes of Iron, Cobalt, and Rhodium

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Abstract: The temperature-dependent pmr spectra of tris(N,N-disubstituted dithiocarbamato)metal(III, IV) complexes, $M^{III}(dtc)_3$ and $M^{IV}(dtc)_3BF_4$, where M = Fe(III), Fe(IV), Co(III), and Rh(III) have been examined in noncoordinating solvents. Fe(II) complexes of the type $Fe(dtc)_2$(*o*-phenanthroline) have also been examined. All of the iron complexes are stereochemically nonrigid, and kinetic parameters were determined for intramolecular metal-centered rearrangement by nmr line broadening techniques. This rearrangement results in optical inversion and the trigonal twist mechanism has been proved to be the primary rearrangement pathway. This result derives directly from pmr environmental averaging patterns. $Co(dtc)_3$ is also stereochemically nonrigid but the mechanism which results in optical inversion could not be determined; however, the trigonal twist mechanism is considered the most probable by analogy with kinetic activation parameters. The $Rh(dtc)_3$ complex was rigid up to +200° in $NO_2C_6D_5$. The overall metal ion dependence on the rate of optical inversion *via* the trigonal twist mechanism is: Fe(II) ($S = 2$) > Fe(III) ($S = {}^1/_2 \rightleftarrows S = {}^5/_2$) $\sim$ Fe(IV) ($S = 1$) > Co(III) ($S = 0$) > Rh(III) ($S = 0$). Within the Fe(III) class, the rate depended on the position of the spin-state equilibrium, *i.e.*, the more high spin complexes generally rearranged faster. Trends in the rate of optical inversion are considered in light of solid-state structural parameters and electronic configuration. In particular, a consideration of ligand field stabilization energies for trigonal prismatic and trigonal antiprismatic coordination is important.

The study of intramolecular rearrangement reactions of transition metal complexes has long been a fundamental area of importance in coordination chemistry. Several reviews of this subject have been published.[1] Recently, nmr spectroscopy has been successfully applied in elucidating the mechanisms of these reactions which proceed at rates comparable to the nmr time scale for tris-chelate complexes.[2-9] Two techniques have been employed in these studies: (i) complex coalescence patterns are computer simulated for a variety of rearrangement mechanisms, and a visual comparison to the experimental spectra yields the most probable pathway(s);[6,7] (ii) coalescence patterns of well separated resonances are observed, and the rearrangement mechanism is determined from the averaging pattern directly.[2-5,8,9] Technique (ii) nearly always requires the use of paramagnetic complexes which manifest large isotropic shifts thereby magnifying small chemical shift differences.[10]

Both of these techniques require a knowledge of the possible rearrangement mechanisms as well as the detailed resonance averaging patterns which result from each reaction pathway. Recently, topological representations describing six-coordinate molecules undergoing permutational isomerization reactions have been defined.[6a,11-14] These analyses mathematically define all possible permutations. The actual configurational changes (cis ⇄ trans and Λ ⇄ Δ) and pmr observable site interchanges must be deduced from the possible permutations. If the site interchanges are unique for only one permutation, then a unique rearrangement mode can be proved for a compound when the experimental pmr averaging pattern exactly matches the predicted one. The most probable mechanism or approximate ligand motions which produce the rearrangement reaction can then be deduced. This final deduction is of course not unique and requires chemical intuition. Unique rearrangement modes have been proved in only a few cases for tris-chelate complexes: $[Fe(Me,Bz\text{-}dtc)_3]BF_4$,[2,15] $Ru(Me,Bz\text{-}dtc)_3$,[4] $M(\alpha\text{-}C_3H_5T)_3$, and $M(\alpha\text{-}C_3H_7T)_3$ where M = Al(III) and Co(III).[6] In all of these cases the rearrangement mode is A_6 (Table VII, ref 6a) or M_3' (Table I, ref 13) and the most reasonable mechanism is the trigonal twist illustrated in **1** for a trans Δ isomer. The transition state for this process is assumed to be of approximate trigonal prismatic geometry. Note that this rearrangement results in optical inversion (Λ ⇄ Δ) but not geometrical isomerization (cis ⇄ trans). The site interchanges for groups x, y, and z are $x \leftrightarrow z$, $y \leftrightarrow y$, and $z \leftrightarrow x$; there-

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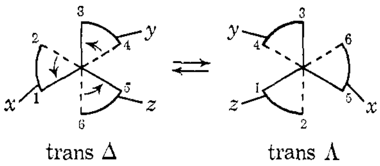
(15) Abbreviations for ligands used throughout: R,R-dtc, N,N-disubstituted dithiocarbamate where R = Me, methyl; Bz, benzyl; Ph, phenyl; *i*-Pr, isopropyl; Et, ethyl; R,R = pyr, pyrrolidyl; T, tropolonate; $\alpha\text{-}C_3H_5T$, α-isopropenyltropolonate; $\alpha\text{-}C_3H_7T$, α-isopropyltropolonate; tfd, 1,2-bis(perfluoromethyl)dithiolene; mnt; maleonitriledithiolene; acac, acetylacetonate; tfac, $CF_3COCHCOMe$; Me_2-phen, 4,7-dimethyl-1,10-phenanthroline; phen, 1,10-phenanthroline.

Table I. Magnetic Data for Tris-(dithiocarbamato) Complexes in CD_2Cl_2 Solution

Complex	Pmr shifts Temp, °C	Pmr shifts ppm[a]	μ_{eff}, BM Solid (23°)	μ_{eff}, BM CH_2Cl_2 (31°)
$Fe(Bz,Bz\text{-}dtc)_3$	−95	CH_2 −22.15, −10.60	3.38	4.03
$Fe(Me,Bz\text{-}dtc)_3$	−103	CH_3 −22.00, −21.40, −20.25, −19.50 CH_2 Figure 4	5.05	4.06[b]
$Fe(Me,\ i\text{-}Pr\text{-}dtc)_3$	−104	$N\text{-}CH_3$ −26.25, −23.70, −23.05, −22.40	2.82	4.18
$Fe(Me,Ph\text{-}dtc)_3$	−96.5	CH_3 −20.14, −16.13, −16.08, −14.38	2.81	3.33[b]
$Fe(pyr\text{-}dtc)_3$	−87	$N\text{-}CH_2$ −149.36 $\text{-}CH_2\text{-}$ −3.00	5.83	5.82[b]
$[Fe(Bz,Bz\text{-}dtc)_3]BF_4$	−100	CH_2 −76.95, −67.50	3.14	3.18
$[Fe(Me,Bz\text{-}dtc)_3]BF_4$	−110	CH_3 −141.96, −140.93, −140.38, −139.41 CH_2 Figure 1 of ref 2	3.01	3.02
$[Fe(Me,\ i\text{-}Pr\text{-}dtc)_3]BF_4$	−108	$N\text{-}CH_3$ −143.40, −142.78, −142.18, −141.71	2.89	2.83
$Fe(Et,Et\text{-}dtc)_2(phen)$	−91[e]	$N\text{-}CH_2$ −78.37, −66.57	5.33	c
$Fe(Me,Ph\text{-}dtc)_2(Me_2phen)$	−96[e]	phen–CH_3 +46.50 (1), +33.15 (2), +23.10 (1)[d]	5.43	5.21
$Co(Bz,Bz\text{-}dtc)_3$	31[f]	CH_2 AB centered at −4.86 $\delta_{AB} = 0.479, J = 15.3$ Hz	Diamagnetic	
$Rh(Bz,Bz\text{-}dtc)_3$	31[f]	CH_2 AB centered at −4.86 $\delta_{AB} = 0.521, J = 15.3$ Hz	Diamagnetic	

[a] Shifts in ppm are relative to $CHDCl_2$ internal standard. [b] $CHCl_3$ solution, ref 17. [c] Insufficient sample. [d] Numbers in parentheses are relative intensities. [e] Reference 19. [f] $CDCl_3$ solvent, shifts are in ppm relative to TMS.



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fore, this mechanism results in coalescence of two of the three trans resonances. This same mechanism is suspected for the isomerization of $Fe(Me,Ph\text{-}dtc)_3$,[3,16] $Fe(Me,Ph\text{-}dtc)_2(tfd)$,[9] and $Fe(Me,Ph\text{-}dtc)_2mnt$[8] but in these cases the rearrangement mode has not been unambiguously proved.

In the present work we report the details of a pmr study on the kinetics and mechanisms of stereochemical rearrangement for $Fe^{III}(R,R'\text{-}dtc)_3$, $[Fe^{IV}(R,R'\text{-}dtc)_3]BF_4$, $Fe^{II}(R,R'\text{-}dtc)_2phen$, $Co^{III}(R,R'\text{-}dtc)_3$, and $Rh^{III}(R,R'\text{-}dtc)_3$ type complexes. Preliminary accounts of some of this work have appeared.[2-4] This work was undertaken in order to (i) unambiguously prove the rearrangement mode for the Fe(III) complexes, (ii) determine the relative rates of inversion as a function of iron spin state and oxidation state, and (iii) assess the importance of electronic configuration and ground-state geometry on inversion rates. The kinetic results in this study are the first reported for a series of iron complexes with oxidation states II, III, and IV and with spin states $S = 2$, $^1/_2 \rightleftarrows {}^5/_2$, and 1.

Experimental Section

Preparation of Compounds. All of the compounds used in this study were made according to literature preparations and were characterized by elemental analysis, pmr and infrared spectroscopy, and magnetic susceptibility (Table I).

(a) **$Fe(R,R'\text{-}dtc)_3$.**[17] Elemental analyses for R,R′ = Me,Bz, Me,Ph, and Me,*i*-Pr are given in ref 18. *Anal.* Calcd for R,R′ = Bz,Bz ($C_{45}H_{42}N_3S_6Fe$): C, 61.91; H, 4.84. Found: C, 61.78; H, 4.83.

(b) **$[Fe(R,R'\text{-}dtc)_3]BF_4$.**[19,20] Elemental analyses for R,R′ = Me,Bz, and Me,Ph are given in ref 19. *Anal.* Calcd for Bz,Bz ($C_{45}H_{42}N_3S_6FeBF_4\cdot CH_2Cl_2$): C, 52.88; H, 4.24; N, 4.02. Found: C, 52.86; H, 4.20; N, 3.94.

(c) **$Fe(R,R'\text{-}dtc)_2Me_2phen$.** Preparation and elemental analyses are reported in ref 19 for R,R′ = Et,Et and Me,Ph.

(d) **$Co(Bz,Bz\text{-}dtc)_3$ and $Rh(Bz,Bz\text{-}dtc)_3$** were prepared according to Delepine and Compin and Malatesta, respectively.[21] These preparations were carried out in absolute ethanol solvent. *Anal.* Calcd for $C_{45}H_{42}N_3S_6Co$: C, 61.77; H, 4.80. Found: C, 62.03; H, 4.53.

Pmr Measurements. All spectra were recorded on a Varian XL-100-15 nmr spectrometer equipped with a variable temperature probe. Temperatures were measured by a thermocouple mounted in an nmr tube and are accurate to ±1°. All spectra were recorded using CD_2Cl_2 or $NO_2C_6D_5$ with complex concentrations of *ca.* 0.1 *M*. Chemical shifts were measured relative to the ^2H internal lock frequency and are reported in ppm relative to either $C\mathit{H}DCl_2$ or $NO_2C_6\mathit{H}D_4$.

Magnetic Measurements. Solid moments were determined by the Faraday method. Solution moments were determined by the conventional nmr method[22] at 31° using CH_2Cl_2 solutions *ca.* 5% v/v in TMS. The TMS shifts were used in the calculation. Diamagnetic corrections were calculated from Pascal's constants.

Kinetic Analysis. Total line shape analyses, TLSA, were performed on two types of tris-chelate complexes in this study, $M(A\text{-}A')_3$ and $M(A\text{-}A)_3$. In the former, cis and trans isomers are pmr detectable at temperatures where $S_2C\text{-}N$ bond rotation is slow.[19] Four $N\text{-}CH_3$ resonances are therefore observed (*vide infra*) and are shown in Figure 1 for $Fe(Me,Ph\text{-}dtc)_3$ at −108°. As metal-centered rearrangement becomes rapid on the pmr time scale, two of the trans CH_3 resonances, T_1 and T_3, coalesce. This pattern results from a trigonal twist mechanism which inverts the configuration (*vide infra*). The coalescence was treated as a two site exchange problem and the exchange broadened line shapes were computer calculated using the Gutowsky-Holm equation.[23] The computer program superimposed the nonexchanging resonances, C and T_2, onto the exchange broadened pair (Figure 1, calculated spectra). Best fits were visually selected and are shown in Figure 1 for $Fe(Me,Ph\text{-}dtc)_3$. The cis and trans populations are nearly statistical with the cis form slightly favored at low temperatures. The line shape calculation employed here utilized a constant trans/

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(16) In ref 3 we concluded that the trigonal twist is the only reasonable mechanism for $Fe(Me,Ph\text{-}dtc)_3$, but Musher[13] has demonstrated that an alternate rearrangement mode, M_4, also satisfies the nmr data. Data presented in this paper (*vide infra*), however, provide clear evidence for our original assignment.

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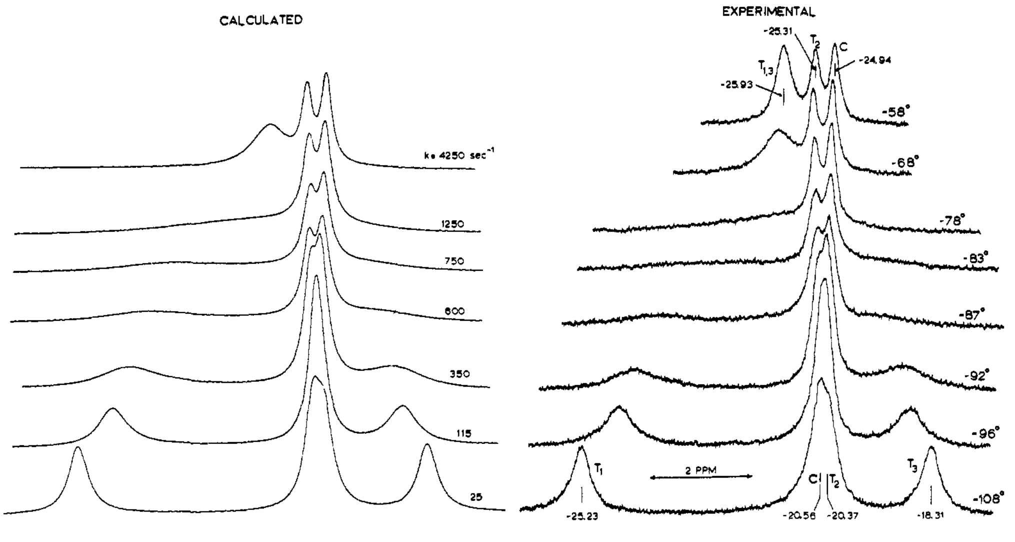

Figure 1. Observed and calculated line shapes for the N-CH$_3$ groups of Fe(Me,Ph-dtc)$_3$ in CD$_2$Cl$_2$ solution at 100 MHz. The calculated line shapes are the best fits for the two site (T$_1$ and T$_2$) exchange.

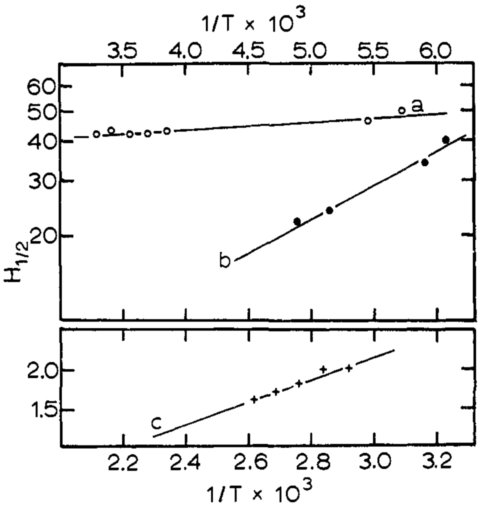

Figure 2. Ln ($H_{1/2}$) *vs.* $1/T$ plots for (a) N-CH$_2$ resonances of Fe(Bz,Bz-dtc)$_3$, (b) N-CH$_3$ resonances of Fe(Me,Ph-dtc)$_3$, and (c) N-CH$_2$ resonances of Co(Bz,Bz-dtc)$_3$.

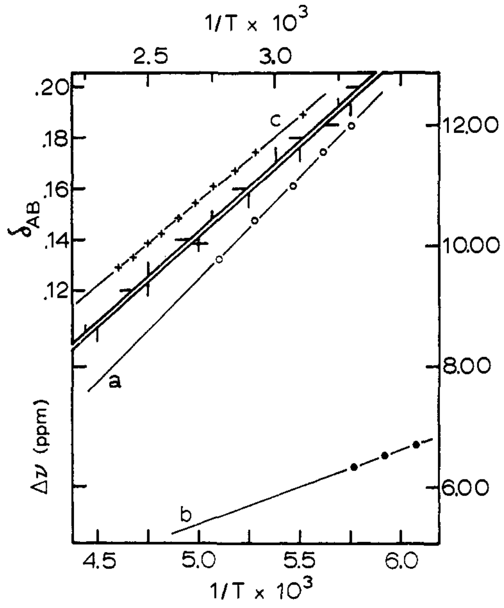

Figure 3. Observed (points) and extrapolated (lines) chemical shift separations between exchanging resonances, ΔH *vs.* $1/T$ for (a) N-CH$_2$ resonances of Fe(Bz,Bz-dtc)$_3$, (b) N-CH$_3$ resonances of Fe(Me,Ph-dtc)$_3$, and (c) N-CH$_2$ resonances of Co(Bz,Bz-dtc)$_3$.

cis ratio throughout the coalescence which was 2.45 for Fe(Me,-Ph-dtc)$_3$.[24]

For complexes of the type M(A-A)$_3$, only R,R′ = Bz,Bz was examined. Optical inversion results in a two site exchange (*vide infra*) for Fe(Bz,Bz-dtc)$_3$, where no spin-spin coupling was observed due to the paramagnetic relaxation, and in an AB exchange for Co(Bz,Bz-dtc)$_3$. Both cases were calculated with the Binsch DNMR3 computer program[25] with $J = 0$ in the former and $J = 15.3$ Hz in the latter. Best visual fits were again selected.

Line widths at half-height, $H_{1/2}$, and chemical shift separations, $\Delta\nu$, were determined in the coalescence region by linear extrapolation from slow exchange values of the plots ln $H_{1/2}$ *vs.* $1/T$ and $\Delta\nu$ *vs.* $1/T$. These extrapolations are shown in Figures 2 and 3 for all complexes examined by TLSA. Linear plots were used because of approximate linear behavior in the slow exchange region and because this procedure has previously been used for paramagnetic complexes.[8,9,19]

The rate constant for optical inversion, k (sec^{-1}), is defined as $1/\tau$ where τ is the preexchange lifetime of a proton in either environment (τ defined here equals 2τ in the Gutowsky-Holm equation[23]). Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined by least-squares fits to ln (k/T) *vs.* $1/T$ plots (Figure 4). Errors were estimated from error limits in k and T. Values of $\Delta G^{\ddagger}(t)$ in the region of exchange broadening have considerably smaller error limits (Table II).

The complexes listed in Table II which have only $\Delta G^{\ddagger}(t)$ and $\Delta H^{\ddagger}$ values reported were not analyzed by a TLSA. Rate constants, k, for Fe(Me,Bz-dtc)$_3$ and Fe(Me,*i*-Pr-dtc)$_3$ were determined by a computer fit at one temperature only near the coalescence point which is specified in Table II as t (°C). The relation $k = (k_BT/h) \cdot e^{-\Delta G^{\ddagger}/RT}$ was used to calculate $\Delta G^{\ddagger}$. $\Delta H^{\ddagger}$ values were calculated assuming $\Delta S^{\ddagger} = +3$ eu, which is the average value obtained for the tris-dtc complexes fit by a TLSA (*vida supra* and Table II). In the case of the cationic Fe(IV) complexes and Fe(pyr-dtc)$_3$, the slow exchange limit could not be completely reached and $\Delta\nu$ values at coalescence were estimated.

Results and Discussion

Magnetic Properties and Static Stereochemistry. (a) Fe(R,R′-dtc)$_3$ Complexes. These Fe(III) d^5 complexes have solid and solution magnetic moments be-

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[24] The coalescing peaks are both due to the trans isomer so no significant error results from this approximation.

[25] G. Binsch and D. A. Kleier, Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

Table II. Kinetic Parameters[a] for Intramolecular Metal-Centered Inversion for Dithiocarbamate Complexes

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (t, °C), kcal/mol
Fe(Et,Et-dtc)$_2$phen	$<7^b$		<7 (-100)
Fe(Me,Ph-dtc)$_2$Me$_2$phen	$<7^b$		<7 (-100)
Fe(Bz,Bz-dtc)$_3$	10.3 ± 1.0	4.1 ± 5.0	9.3 ± 0.2 (-54)
Fe(Me,Bz-dtc)$_3$	9.5 ± 1.5^b		8.9 ± 0.2 (-86)
Fe(Me,i-Pr-dtc)$_3$	8.3 ± 1.5^b		8.1 ± 0.2 (-96)
Fe(Me,Ph-dtc)$_3$	8.7 ± 1.0	1.7 ± 5.0	8.5 ± 0.2 (-80)
Fe(pyr-dtc)$_3$	7.6 ± 1.7^b		7.1 ± 0.3 (-103)
[Fe(Bz,Bz-dtc)$_3$]BF$_4$	8.4 ± 2.0^b		7.9 ± 0.4 (-88)
[Fe(Me,Bz-dtc)$_3$]BF$_4$	8.3 ± 2.0^b		7.8 ± 0.4 (-105)
[Fe(Me,i-Pr-dtc)$_3$]BF$_4$	8.4 ± 2.0^b		7.9 ± 0.4 (-108)
Co(Bz,Bz-dtc)$_3$	25.5 ± 1.0	4.1 ± 5.0	23.6 ± 0.2 ($+168$)
Fe(Et,Et-dtc)$_2$tfd	8.3 ± 0.6^c	-7.5 ± 3.7^c	10.0 ± 0.2 (-50)^c
Fe(Et,Et-dtc)$_2$mnt	8.6 ± 1.5^c	-3.4 ± 5.0^c	9.4 ± 0.2 (-50)^c
Fe(Me,Me-dtc)$_2$tfd	9.2 ± 0.9^c	-6.1 ± 3.9^c	10.6 ± 0.2 (-50)^c
Rh(Bz,Bz-dtc)$_3$	$>27^b$		>25.3 (200)

[a] See Experimental Section. [b] Values determined from $\Delta G^{\ddagger}(t)$ and assuming $\Delta S^{\ddagger} = 3$ eu. [c] References 8 and 9.

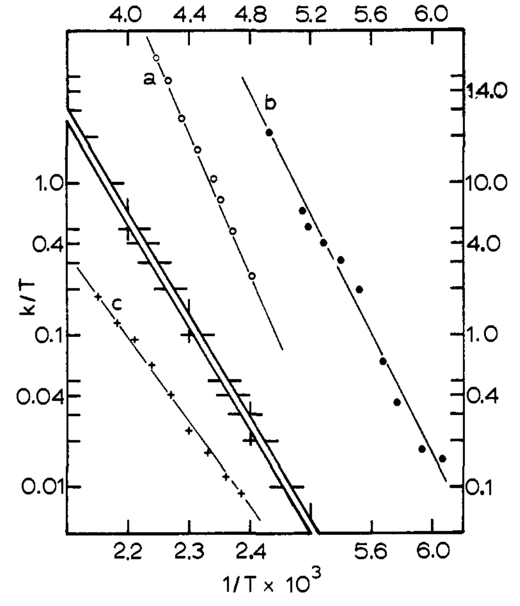


Figure 4. Eyring plots for metal-centered inversion for (a) Fe(Bz,Bz-dtc)$_3$, (b) Fe(Me,Ph-dtc)$_3$, and (c) Co(Bz,Bz-dtc)$_3$.

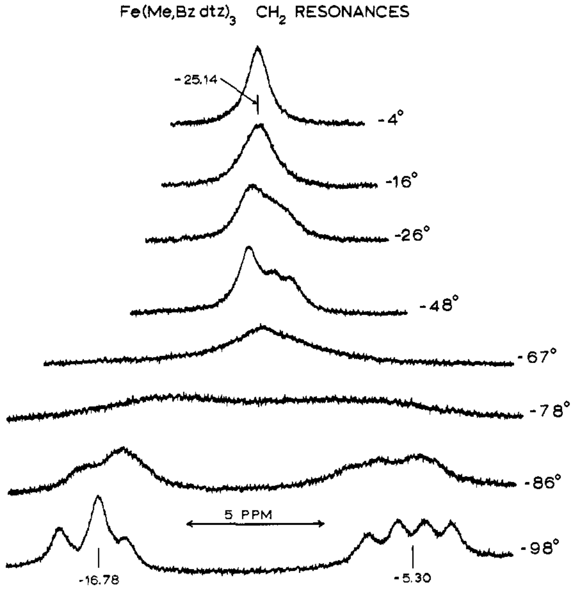
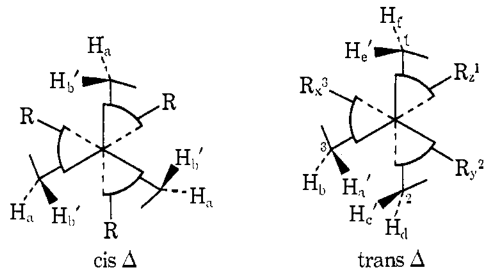


Figure 5. Temperature-dependent pmr traces of the N–CH$_2$ resonances for Fe(Me,Bz-dtc)$_3$. The spectra were recorded using CD$_2$Cl$_2$ solvent at 100 MHz.

tween *ca.* 2.0 and 5.9 BM which has been interpreted in terms of a $^2T_{2g}$–$^6A_{1g}$ spin-state equilibrium.[17,26] Temperature-dependent magnetic susceptibility[27] and pmr[28] studies show non-Curie behavior which is also consistent with this interpretation.[29] Most authors agree that the $S = {}^1/_2 \rightleftarrows S = {}^5/_2$ spin-state equilibrium is the correct explanation for these observations. The complexes examined here have solution magnetic moments from 5.82 (R,R′ = pyr) to 3.47 BM (R,R = Me,Ph) and thus illustrate different positions of the $S = {}^1/_2 \rightleftarrows S = {}^5/_2$ equilibrium. Recently, however, some doubt has been cast on this theory because the temperature-dependent Mössbauer quadrupole splittings are not in agreement with the $^2T_{2g}$–$^6A_{1g}$ equilibrium.[30] Thus, the true description remains open.

These complexes possess tris-chelate coordination with approximate D_3 symmetry.[18] They can therefore be represented by **2** which shows the cis and trans



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isomers of Δ optical configuration for Fe(Me,Bz-dtc)$_3$.[31] In the limit of slow isomerization and optical inversion, four methyl and eight methylene resonances should be observed. Figures 1 and 5 show these reso-

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(31) In **2**, R refers to the methyl group and H refers to the methylene protons. Numbers and primes refer to substituent groups while letters refer to magnetic environments.

nances at −108 and −98° for Fe(Me,Ph-dtc)$_3$ and Fe(Me,Bz-dtc)$_3$, respectively. In the case of Fe(Bz,Bz-dtc)$_3$ and Fe(pyr-dtc)$_3$, the methylene resonances are magnetically nonequivalent because of the asymmetry around the metal center.[32] At low temperatures where optical inversion is slow, two resonances are observed in these complexes (Table I).

(b) [Fe(R,R′-dtc)$_3$]BF$_4$ Complexes. These Fe(IV) complexes are low-spin d^4 (S = 1) with solid and solution magnetic moments of *ca.* 3.0 BM (Table I). Mössbauer spectra of several symmetrically substituted analogs provide further evidence for this magnetic description.[20] The variable temperature pmr shows large isotropic shifts which manifest linear $1/T$ behavior.[21] These complexes are of the tris-chelate type,[2] M(A–A′)$_3^+$ or M(A–A)$_3^+$, and their stereochemical description is identical with that of the Fe(III) complexes (*vide supra*). [Fe(Me,Bz-dtc)$_3$]BF$_4$ shows eight methylene and four methyl resonances at −110° (Figures 1 and 2, ref 2) which demonstrates that both geometrical isomerization and optical inversion are slow on the pmr time scale at this temperature. In [Fe(Bz,Bz-dtc)$_3$]BF$_4$, two broad methylene resonances are observed at −100° (Table I) which is consistent with slow optical inversion.

(c) Fe(R,R′-dtc)$_2$L Where L = phen or Me$_2$phen. These Fe(II) tris-chelate complexes[19] are high spin d^6 (S = 2) with solid and solution magnetic moments of *ca.* 5.4 BM (Table I). The pmr shifts show linear $1/T$ behavior from −105° to +30°.[19] In cases where R,R′ = Et,Et all four methylene protons in each dtc ligand are magnetically nonequivalent if S$_2$C–N bond rotation and metal centered isomerization are slow (see arguments presented in ref 8, 9, and 19). The pmr of Fe(Et,Et-dtc)$_2$phen shows only two N–CH$_2$ resonances at −91° (Table I); therefore, one of these processes is fast. Complexes where R,R′ = Me,Ph have three geometric isomers (II of ref 19) and should exhibit four N–CH$_3$ and four phen–CH$_3$ resonances in the limit of slow isomerization and inversion (see arguments presented in ref 8, 9, and 19). The pmr spectrum of Fe(Me,Ph-dtc)$_2$Me$_2$phen at −96° (Table I) shows three phen–CH$_3$ resonances with populations *ca.* 2:1:1. This result requires that S$_2$C–N bond rotation is slow and metal-centered isomerization is fast.[34] We extend this conclusion to the diethyl analog.

(d) M(Bz,Bz-dtc)$_3$, M = Co or Rh. The Co(III) complex is low-spin d^6 (S = 0). Its ground-state solid geometry[35] is very similar to that of the Fe(III) tris-dtc complexes[30] and therefore this complex is subject to the same stereochemistry. The 25° pmr spectrum of the methylene group consists of an AB pattern (Table I).[4] Hence, optical inversion is slow at this temperature. The Rh(III) compound shows a 31° pmr spectrum which is nearly identical with that of the Co(III) compound. The stereochemistry is presumably similar. Further evidence for a similar geometry is provided by nearly superimposable solution infrared spectra.

Dynamic Pmr Spectra. All of the complexes examined in this study are nonrigid on the pmr time scale except for Rh(Bz,Bz-dtc)$_3$. The M(R,R′-dtc)$_3$-type complexes possess two separate kinetic processes which are shown for the methylene protons of Fe(Me,Bz-dtc)$_3$ in Figure 5. Variable temperature pmr spectra are shown for Fe(Me,Ph-dtc)$_3$ and [Fe(Me,Bz-dtc)$_3$]BF$_4$ in ref 3 and 2, respectively. The higher temperature coalescence (*ca.* −26° in Figure 5) is cis–trans isomerization which results from S$_2$C–N bond rotation.[2,19] Arguments leading to this assignment are given in ref 19. The lower temperature coalescence (*ca.* −78° in Figure 5) results from metal-centered rearrangement (*vide infra*).[2,3] In Figure 1 this coalescence is shown for the methyl protons of Fe(Me,Ph-dtc)$_3$. The high-temperature kinetic process (S$_2$C–N bond rotation) has been thoroughly discussed for these complexes in ref 19 and will not be commented on further. The metal-centered process is of interest here and will be discussed below.

Complexes of the type M(R,R-dtc)$_3$, where R = benzyl or R,R = (CH$_2$)$_4$, show only one kinetic process (see Figure 2 of ref 4). The coalescence for the methylene protons is either a simple two-site exchange in the case of paramagnetic Fe(III) and -(IV) compounds or a complex AB exchange for the diamagnetic Co(III) compound. The collapse of the AB spectrum for Co(Bz,Bz-dtc)$_3$ is a true kinetic coalescence rather than a temperature-dependent accidental moving together of the two resonances. This is verified by the successful line shape fit. Further, a simulated set of spectra where δ_{AB} goes to zero yields an entirely different pattern. Also, Rh(Bz,Bz-dtc)$_3$ shows a nearly identical δ_{AB} *vs.* $1/T$ plot except no coalescence is observed up to +200°. This coalescence is a direct result of optical inversion which averages the diastereotopic methylene environments (see detailed arguments in ref 4 and 36).[37] Slow S$_2$C–N bond rotation has no effect on the methylene resonances because geometric isomers are not possible.

Complexes of the type Fe(R,R′-dtc)$_2$L where L = phen or Me$_2$phen and R,R′ = methyl,phenyl or ethyl,ethyl show only one kinetic process which results from

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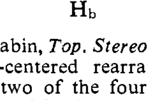
[32] This is the well known diastereotopic relationship[33] which renders H$_a$ and H$_b$ nonequivalent in the moiety



[33] K. Mislow and M. Rabin, *Top. Stereochem.*, 1, 1 (1965).

[34] Only certain metal-centered rearrangement mechanisms will lead to averaging of only two of the four resonances (*vide infra*).[8,9] Fe(Me,Ph-dtc)$_2$Me$_2$bipy where Me$_2$bipy is 4,4′-dimethyl-2,2′-bipyridine shows the exact same pmr pattern at −97°.[19] This provides further evidence that metal-centered rearrangement is fast on the pmr time scale at this temperature and argues against accidental degeneracy of two lines.

[35] S. Merlino, *Acta Crystallogr., Sect. B*, **24**, 1441 (1968); T. Brennan and I. Bernal, *J. Phys. Chem.*, 73, 443 (1969).

[36] B. Jurado and C. S. Springer, Jr., *Chem. Commun.*, 85 (1971).

[37] Recently, Golding, *et al.*,[38] reported that certain M(i-Pr,i-Pr-dtc)$_n$ complexes where n = 2 or 3 show a splitting of the isopropyl methyl group at low temperatures. They interpret this in terms of hindered rotation about the S$_2$CN(–CH(CH$_3$)$_2$)$_2$ bonds. Steric hindrance leading to slow exchange was only observed for large bulky N-substituents like isopropyl ($E_a \approx 5$ kcal/mol). They did not find such a splitting for benzyl or ethyl substituents. We have noted similar steric hindrance in Fe(i-Pr,i-Pr-dtc)$_3$ which precluded this compound from our study. Smaller N-substituents such as R,R = benzyl,(CH$_2$)$_4$ and R,R′ = methyl,benzyl, methyl,isopropyl, and methyl,phenyl do not show pmr slow rotations about the S$_2$CN–C bond at temperatures at low as −100°. In Co(Bz,Bz-dtc)$_3$, the AB pattern is observed at −100° with no sign of further kinetic broadening. Further, the kinetic processes examined in this study have $\Delta H^{\ddagger}$ values greater than 8 kcal/mol and as high as 26 kcal/mol for Co(Bz,Bz-dtc)$_3$. Therefore, the pmr spectra of complexes in this study are not affected by this hindered rotation.

[38] R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, **11**, 2435 (1972).

$S_2C{-}N$ bond rotation.[19] The low-temperature kinetic process (metal-centered rearrangement) is fast on the pmr time scale even at $-100°$ (*vide supra*) so only an upper limit to $\Delta G^{\ddagger}$ can be determined (Table II).

Mechanism of Metal-Centered Rearrangement. Detailed descriptions of the possible intramolecular metal-centered rearrangement reactions of tris-chelate complexes have been reported and no further discussion is needed here.[1,7,9a,39] Permutational analyses which list all possible ligand interchanges have also been carried out.[6a,11–14] In light of the results presented in these papers, $[Fe(Me,Bz\text{-}dtc)_3]BF_4$ has been shown to isomerize by a trigonal twist mechanism which is illustrated for the trans Δ isomer in **1** (see ref 2 for details).[40] This mechanistic assignment was made from direct pmr results (method (ii) in the introductory section).[2,40] The other Fe(IV) complexes listed in Table II (R,R′ = Me,*i*-Pr and Me,Ph) show the same methyl group averaging pattern which was found for the Me,Bz complex. This pattern, *i.e.*, the averaging of only two of the methyl resonances from the trans isomer while the other trans resonance and the cis resonance are unaffected, is derived from **1**, site interchanges $x \leftrightarrow z$, $y \leftrightarrow y$, and $z \leftrightarrow x$ for the trans isomer. This strongly suggests the same rearrangement mechanism although it is not absolute proof. The coalescence of the two resonances in $[Fe(Bz,Bz\text{-}dtc)_3]BF_4$ is also most probably due to this same mechanism. All of the Fe(IV) complexes have nearly identical $\Delta G^{\ddagger}$ values (Table II) which provides further support for the same mechanistic assignment.

The rearrangement mode of the $Fe(R,R'\text{-}dtc)_3$ complexes has not been previously determined. Only the Me,Ph complex has been examined[3] in detail and the trigonal twist mechanism was favored but not proved. The methyl coalescence pattern for this complex is shown in Figure 1. At $-108°$ all four resonances from the cis (C) and trans (T_1, T_2, and T_3) isomers are evident. The C resonance is assigned because the T/C ratio is slightly less than statistical. As the temperature is increased two of the trans resonances, T_1 and T_3, broaden and coalesce (coalescence at *ca.* $-83°$). The other methyl lines, T_2 and C, are not affected by this kinetic process which is complete on the pmr time scale at *ca.* $-58°$. This kinetic process does not cause cis–trans isomerization but scrambles two of the three trans methyl environments. The observed averaging pattern can result from two different rearrangement modes, A_6 of ref 6a or M_3' of ref 13 (identical permutations), or M_4'[13] (identical with mode A_2).[6a] The former mode requires that optical inversion accompanies environmental averaging of T_1 and T_3 whereas in the latter, optical inversion does not occur.[41] All of the $Fe(Me,R\text{-}dtc)_3$ complexes possess this same methyl averaging pattern.

Figure 5 shows the coalescence pattern of the methylene resonances in $Fe(Me,Bz\text{-}dtc)_3$. In the limit of slow isomerization, eight resonances should be observed (**2**). Seven are clearly visible in the $-98°$ spectrum. As the temperature is increased, all of the CH_2 lines broaden and simultaneously coalesce into three resolvable resonances at $-48°$. The high temperature coalescence ($> -48°$) is due to $S_2C{-}N$ bond rotation (*vide supra*). The low-temperature coalescence pattern is only consistent with rearrangement mode A_6 or M_3' because all diastereotopic pairs are averaged. Mode M_4' or A_2 is unambiguously eliminated.[42] Hence, the trigonal twist pathway which is the most reasonable one for this mode is the primary rearrangement mechanism for this complex. All other mechanisms including the numerous bond rupture types are eliminated by the pmr data directly. All of the Fe(III) complexes have very similar $\Delta G^{\ddagger}$ values (Table II) so we assign this mechanism to these complexes also.

Complexes of the type $Fe(R,R'\text{-}dtc)_2L$ where L = phen or Me_2phen do not yield detailed mechanistic information because the rate of metal-centered rearrangement is fast on the pmr time scale at all accessible temperatures.[19] However, the observed $-95°$ spectrum does contain some mechanistic implications. The multiplicity of the $N{-}CH_2$ and phen–CH_3 peaks in the R,R′ = Et,Et and Me,Ph complexes, respectively (Table I), strongly suggests the trigonal twist mechanism. In fact, the $N{-}CH_2$ and CF_3 coalescence patterns in $Fe(Et,Et\text{-}dtc)_2$tfd and $Fe(Me,Ph\text{-}dtc)_2$tfd, respectively, show very similar spectra when metal-centered rearrangement is fast and $S_2C{-}N$ bond rotation is slow.[8,9] The rearrangement mode in these complexes has also been assigned as a trigonal twist.[8,9,43]

No mechanistic information can be obtained from the dynamic pmr of $Co(Bz,Bz\text{-}dtc)_3$ which is shown from 120 to 194° in ref 4. Unfortunately, the analogous Me,Bz complex does not lend itself to the same analysis because $S_2C{-}N$ bond rotation is fast at these temperatures. However, $\Delta S^{\ddagger}$ for $Co(Bz,Bz\text{-}dtc)_3$ (Table II) is very similar to the values obtained for tris-dtc complexes which isomerize *via* the trigonal twist mechanism. This suggests a similar pathway.

Ligand Exchange. The metal-centered rearrangements discussed above are intramolecular because in all cases ligand exchange is slower than isomerization. Reaction 1 was performed for M = Fe(III), Fe(IV), and Co(III).

$$M(RR\text{-}dtc)_3 + M(R'R'\text{-}dtc)_3 \rightleftharpoons M(RR\text{-}dtc)_2(R'R'\text{-}dtc)_1 + M(RR\text{-}dtc)_1(R'R'\text{-}dtc)_2 \quad (1)$$

With Fe(III) and Fe(IV), mixed complexes appeared immediately and usually reached equilibrium within several minutes. Mixed complex resonances did not coalesce at temperatures well above isomerization

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(39) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

(40) The pmr averaging patterns of the methyl and methylene resonances are shown in Figures 1 and 2, respectively, of ref 2. The trigonal twist averaging patterns are derived in detail in ref 2 also. The pmr spectra can only lead to a determination of the rearrangement mode. In this case the A_6[6a] or the M_3'[13] mode is uniquely determined and the trigonal twist is considered the most reasonable pathway which is consistent with this mode.

(41) Rearrangement mode A_6 or M_3' is best described by the trigonal twist mechanism shown in **1**. Note that the *X* and *Z* environments of the trans isomer are averaged whereas *Y* is not. Mode A_2 or M_4' is best described by a mechanism in which each chelate ring twists 180° about an axis defined by a line which passes through the metal and the midpoint of the chelate backbone. An approximate hexagonal planar transition state is envisioned.

(42) The detailed analysis leading to this conclusion is presented in ref 2. The conclusion can be qualitatively reached, however, because M_4' does not lead to optical inversion while A_6 or M_3' does. The fact that all eight CH_2 resonances coalesce requires that diastereotopic pairs are being averaged. This can only result from optical inversion.

(43) These complexes are subject to the ambiguity pointed out by Musher[13] in that the pmr experiment cannot distinguish between rearrangement mode M_3' or M_4' (*vide supra*). Analogy to the Me,Bz complexes (*vide supra*) suggests, however, that these compounds do indeed isomerize *via* mode M_3', *i.e.*, the trigonal twist mechanism.

averaging. Reaction 1 for Co(III) did not proceed to a pmr detectable extent at +195° even after several hours. These experiments demonstrate the intramolecularity of the isomerization reactions.

It is possible that the metal-centered rearrangement is accelerated by dtc ligand oxidation to thiuram disulfide and corresponding metal reduction. This is especially possible in the Fe(IV) complexes.[44] For all of the complexes studied here, addition of thiuram disulfide does not affect the pmr of the complex throughout the entire temperature range. The resonances of the thiuram disulfide are clearly visible in their usual positions in these mixtures at temperatures where isomerization is fast.

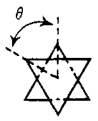
Kinetics of Metal-Centered Rearrangement. Kinetic parameters for optical inversion were determined by TLSA or by a computer calculation near the coalescence point (see Experimental Section). The results are listed in Table II. The $\Delta G^{\ddagger}$ values at or near coalescence are the most accurate.[45] The average $\Delta S^{\ddagger}$ value for $M(dtc)_3$ complexes is *ca.* 3 eu. This is consistent with the near zero or slightly negative $\Delta S^{\ddagger}$ values (−8 to 5 eu) usually obtained for a trigonal twist mechanism in weakly polar media.[1c,6a,8,9,46] These values should be compared with the larger positive $\Delta S^{\ddagger}$ values (7 to 10 eu) usually obtained with bond rupture mechanisms in weakly polar media.[47,48] However, $\Delta S^{\ddagger}$ values alone are not sufficient to establish a mechanism. $\Delta H^{\ddagger}$ values were calculated from the equation $\Delta H^{\ddagger} = \Delta G^{\ddagger} + T\Delta S^{\ddagger}$. In cases where $\Delta S^{\ddagger}$ was not directly measured, a value of 3 eu was assumed.[49] The trends in $\Delta H^{\ddagger}$ parallel the trends in $\Delta G^{\ddagger}(t)$.

Comparison of the $\Delta G^{\ddagger}(t)$ and $\Delta H^{\ddagger}$ values for these tris-chelate complexes yields the following order for the rate of optical inversion *via* the trigonal twist mechanism: Fe(II) hs > Fe(III) ls $\rightleftarrows$ hs ~ Fe(IV) ls ≫ Co(III) ls > Rh(III) ls (hs = high spin and ls = low spin). This order is in part consistent with results for $M(tfac)_3$[15] complexes where Fe(III) hs ≫ Co(III) ls > Rh(III) ls.[50] These complexes presumably racemize by a bond rupture mechanism, however.[50] Our results are the first reported for tris-chelate complexes of Fe(IV) and Fe(II) hs. Studies on $Fe(phen)_3^{2+}$ which is a Fe(II) ls complex indicate that intramolecular optical inversion is slow, $E_a \sim 29$ kcal/mol, and proceeds by a trigonal twist mechanism.[51]

The Fe(III) tris-dtc complexes possess a ls $\rightleftarrows$ hs equilibrium (*vide supra*). The 31° solution magnetic moments are listed in Table I. A one to one correlation between μ_{eff} and $\Delta H^{\ddagger}$ does not exist; however, there is a trend which suggests that the lower $\Delta H^{\ddagger}$ or $\Delta G^{\ddagger}$ values correspond to the higher per cent hs. For example, $Fe(pyr\text{-}dtc)_3$ and $Fe(Me,Ph\text{-}dtc)_3$ are *ca.* 97 and 35% hs, respectively, and have $\Delta H^{\ddagger} = 7.6$ and 8.7 kcal/mol. Comparison of the more accurate $\Delta G^{\ddagger}$ values shows that this is outside of experimental error. The other three Fe(III) compounds do follow the same trend but the Me,Ph analog has a $\Delta H^{\ddagger}$ which is too low. A similar trend with spin-state population has been observed with $Fe(dtc)_2$dithiolene complexes which possess a $S = 0 \rightleftarrows S = 1$ spin-state equilibrium.[8]

The $[Fe(dtc)_3]^+$ complexes have $\Delta H^{\ddagger}$ values which are almost identical with those of $Fe(dtc)_3$. This surprising result implies that there is little effect on the rate of optical inversion upon varying the formal oxidation state of iron from III to IV. The presence of the Fe(III) spin-state equilibrium prevents a direct comparison of spin state, however. The $Fe(dtc)_2$phen complexes, on the other hand, undergo optical inversion at a rate which is faster than that observed for Fe(III) or -(IV). These Fe(II) complexes have an $S = 2$ ground state. It is not known what effect the phen ligand has compared to dtc; therefore meaningful comparisons are not possible without further investigation of other Fe(II) tris-chelate complexes. The most important observation is that these three classes of compounds all isomerize *via* the trigonal twist mechanism.

Relation of Structure to Kinetics and Mechanism. Kepert[52] has recently shown that a relation exists between the bite distance of a bidentate chelate where the metal donor distance is defined as unity and the geometry of the coordination core for a tris-chelate complex, such that small bite ligands favor distortions toward trigonal prismatic coordination. The twist angle, θ, is defined in **3** where trigonal prismatic (TP) and trigonal antiprismatic (TAP or O_h) coordination geometry have θ = 0 and 60°, respectively. The small bite distance of the dtc ligand forces the complex to be distorted toward TP, *i.e.*, θ < 60°. Kepert also showed that the summation of ligand–ligand repulsion energies is minimized for small bite distances when θ is significantly less than 60°. Structural data on $Fe(pyr\text{-}dtc)_3$ and $Fe(Me,Ph\text{-}dtc)_3$ give bite distances of 1.21 and 1.22 Å where the Fe–S distance is unity and θ values of 38.6 and 40.4°, respectively.[30,52] Hence, the Me,Ph complex is less distorted toward TP geometry. Healy and White[18] have pointed out the trend that the metal donor distance increases and θ decreases as the $Fe(dtc)_3$ complex is more high spin (see Table I). We find that isomerization rates *via* the trigonal twist mechanism are generally faster for the more high spin complexes.[53] This argument assumes that the nature of



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[44] This mechanism has been suggested by J. P. Fackler, Jr.

[45] G. Binsch, *Top. Stereochem.*, 3, 97 (1968).

[46] P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, 20, 81 (1943).

[47] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, 92, 5319 (1970).

[48] A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 92, 7061 (1970).

[49] All kinetic comparisons are valid if similar $\Delta S^{\ddagger}$ values are found. The iron complexes isomerize by the trigonal twist mechanism (*vide supra*) in CD_2Cl_2 solution and are expected to have very similar values of $\Delta S^{\ddagger}$. Hence, $\Delta S^{\ddagger} = 4.1$, 1.7, and 4.1 eu for the three TLSA cases.

[50] (a) J. G. Gordon, II, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, 5, 381 (1971); (b) R. C. Fay and T. S. Piper, *Inorg. Chem.*, 3, 348 (1964).

[51] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 76, 3807 (1954); P. Dowley, K. Garbett, and R. D. Gillard, *Inorg. Chim. Acta*, 1, 278 (1967).

[52] D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

[53] Solid-state structural parameters are averages over the hs and ls states. The trends in θ and Fe–S bond length do indeed imply that the hs state is expanded and more distorted toward TP geometry. However, the spin-state equilibrium is presumably a much faster process than metal-centered rearrangement;[54] hence during the lifetime of an optical isomer many spin-state changes will have occurred. So even a compound which is only 10% hs has ample opportunity to invert *via* the hs state. Recently, however, the concept of a spin-state equilibrium for these complexes has been questioned.[30] If the ground state is described as a mixed spin state[55] as has recently been suggested,[30] our kinetic comparison is indeed meaningful.

the dtc N substituent affects $\Delta G^{\ddagger}$ for optical inversion only by perturbing the spin-state equilibrium. Of course, the nature of the substituent can also affect the rate by steric or solvent interaction. No trends are apparent from such considerations, however.

It has been suggested that the trigonal twist mechanism is favored in complexes which are distorted toward TP geometry.[8,9] Indeed, all of the M(dtc)$_3$ complexes are distorted in this way.[18,35] Kepert's[52] ligand–ligand repulsion calculations also show that the barrier to optical inversion *via* the trigonal twist mechanism is lower for small bite ligands than for large bite ligands. We find $\Delta H^{\ddagger}$ for Co(dtc)$_3$ to be *ca.* 10 kcal/mol lower than for Co(acac)$_3$.[56] The bite distances defined for a metal donor distance of unity are 1.23 and 1.50 Å for Co(Et,Et-dtc)$_3$[35] and Co(acac)$_3$,[57] respectively. The corresponding twist angles, θ, are 43.6 and ~60°, respectively. Co(acac)$_3$ presumably racemizes *via* a bond rupture pathway by analogy to tris(benzoylacetonato)cobalt(III)[48] and tris(5-methylhexane-2,4-dionato)cobalt(III)[47] for which a bond rupture mechanism has been determined. The rearrangement mechanism of Co(Bz,Bz-dtc)$_3$ is not known but the activation parameters suggest the trigonal twist mechanism. This would also be consistent with the solid-state distortion toward TP geometry. Solid-state distortions do not always lead to the correct prediction of relative rate, however. Tris(α-R-tropolonato)cobalt(III) has a bite distance of 1.35 Å (see previous definition) and a twist angle of θ = 55.0°.[6a] $\Delta H^{\ddagger}$ for optical inversion *via* the trigonal twist mechanism is only *ca.* 15 kcal/mol.[5,6a] These complexes clearly do not fit a simple ground-state geometry argument and require a more sophisticated understanding of electronic excited states.[58]

Stiefel and Brown[59] recently pointed out that the solid-state distortions, found in tris-dtc complexes are not entirely toward trigonal prismatic geometry. Known trigonal prismatic complexes have a side to height ratio of ~1.00 as observed with the trigonal prismatic tris-dithiolene complexes of Re, Mo, and V.[60] The tris-dtc complexes have side/height ratios of *ca.* 1.4 which indicates a highly compressed structure. Stiefel and Brown[59] state that this compressed structure suggests a racemization pathway involving a distorted hexagonal transition state. Rearrangement mode A$_2$ or M$_4'$ could occur *via* this transition state. The pmr data, however, unambiguously eliminates all modes which utilize a distorted hexagonal planar transition state (*vide supra*).

Another possible rationale for the trigonal twist mechanism is weak S···S interligand interactions which would presumably stabilize a TP transition state. This interaction has been postulated as being partly responsible for the stability of the TP coordination of tris-dithiolene complexes of Re, Mo, and V.[60] This same interaction has also been put forth to explain the stabilization of the cis form of tris(β-thioketonates) of V(III) and Co(III).[50]

Relation of Electronic Structure to Kinetics. Structural arguments alone cannot account for the relative rates of optical inversion. The ground-state geometries of Fe(Me,Ph-dtc)$_3$ and Co(Et,Et-dtc)$_3$ are very similar (bite distance, θ = 1.22, 40.4, and 1.23 Å, 43.6°, respectively) whereas $\Delta H^{\ddagger}$ for optical inversion is 8.7 and 25.5 kcal/mol, respectively. Clearly, any explanation for these barriers must be based on electronic configuration arguments. Recent interest in trigonal prismatic coordination has yielded several ligand field calculations which give the variation of the energies of the d orbitals as a function of the twist angle, θ.[61] The results of these calculations allow an estimation of the relative ligand field stabilization energies, LFSE, for TP and TAP geometries. ΔLFSE values can be obtained where ΔLFSE = TAP(LFSE) − TP(LFSE) and are shown in Table III. These values were determined from Gillum's calculation;[61a] however, the more sophisticated calculation of Larsen, *et al.*,[61b] yields very similar results. The activation energy for the trigonal twist mechanism should be related to ΔLFSE.[62] The results in Table III do support this assumption. Fe(II) ls and Co(III) ls do indeed have the largest $\Delta H^{\ddagger}$ values which correspond to the largest ΔLFSE. Fe(II) hs also is consistent because ΔLFSE is zero (the lowest value obtained) and $\Delta H^{\ddagger}$ is the smallest. The Fe(III) complexes possess a ls ⇄ hs equilibrium so it is difficult to assign a ΔLFSE value. A trend is observed, however, in which the hs complexes have lower values of $\Delta H^{\ddagger}$ than the ls compounds (*vide supra*). This is consistent with the ΔLFSE values. The Fe(IV) complexes have a ΔLFSE which is between hs and ls Fe(III). The $\Delta H^{\ddagger}$ values for Fe(IV) are close to the average value for the Fe(III) complexes.

Table III. ΔLFSE[a] Values for Various d Configurations

Metal Ion	d configuration TAP	d configuration TP	ΔLFSE (*Dq*)	$\Delta H^{\ddagger}$, kcal/mol for optical inversion[b]
Fe(II), ls	t_{2g}^6	$a_1' e'^4$	13.6	~29
Fe(II), hs	$t_{2g}^4 e_g^2$	$a_1'^2 e'^2 e''^2$	0	<7.5
Fe(III), ls	t_{2g}^5	$a_1'^2 e'^3$	10.2	7.6–10.3[c]
Fe(III), hs	$t_{2g}^3 e_g^2$	$a_1' e'^2 e''^2$	0	
Fe(IV), ls	t_{2g}^4	$a_1'^2 e'^2$	6.8	8.4
Co(III), ls	t_{2g}^6	$a_1'^2 e'^4$	13.6	25.5
Rh(III), ls	t_{2g}^6	$a_1'^2 e'^4$	13.6	>27

[a] ΔLFSE = TAP(LFSE) − TP(LFSE). [b] All values are for M(dtc)$_3$ complexes except for Fe(II), ls, which is for Fe(phen)$_3^{2+}$, ref 51, and Fe(II), hs, which is for Fe(dtc)$_2$phen. All of these complexes are assumed to racemize *via* the trigonal twist mechanism. [c] Values are for various positions of ls ⇄ hs equilibrium.

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(54) Recent experiments indicate that spin-state lifetimes are of the order of 10^{-7} sec for bis(hydrotris(pyrazolyl)borate)iron(II): J. K. Beattie, Proceedings of the XIVth International Conference on Coordination Chemistry, Toronto, Canada, June 1972, p 507.

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This oversimplified model seems qualitatively correct for these complexes and recent work in this laboratory on tris-dtc complexes of V(III) and Mn(III) is also qualitatively consistent.[63] This model also requires that all of the complexes invert by the trigonal twist mechanism. This pathway has not been proved for the Co(III) and Rh(III) tris-dtc complexes but is the most likely mechanism (*vide supra*).

The observation that Co(dtc)$_3$ inverts faster than Rh(dtc)$_3$ is consistent with the general trend found for transition metals, *i.e.*, the rate of metal-centered rearrangement decreases on descending a group. Work in this laboratory has recently yielded the result that Fe(dtc)$_3$ complexes racemize faster than the Ru(dtc)$_3$ analogs, and both by the trigonal twist mechanism.[2,64] This trend is consistent with the order in rate of isomerization found for H_2ML_4[65] and $HM(PF_3)_4^-$[66] type complexes where L = phosphine or phosphite and where Fe > Ru and Co > Rh > Ir, respectively. Other examples of this order in rate are for M(tfac)$_3$ complexes where Co(III) > Rh(III)[50b] and Fe(III) > Ru(III);[50a] and for M(α-RT)$_3$ where Co(III) > Rh(III).[5] In cases where the trigonal twist mechanism is operative, the ΔLFSE argument can be applied. The size of ΔLFSE depends on *Dq*. Larger ligand field strengths will increase ΔLFSE and hence raise the activation energy. The value of *Dq* for the same ligand increases on descending a group. This same argument also applies for bone rupture mechanisms because the LFSE for TAP coordination increases on descending a group; hence the TAP complex becomes more stable. This behavior contrasts with the isomerization rates found for tris-β-diketonate complexes[7,50b] and tris-α-R-tropolonate complexes[5] of group IIIA metal ions. For these complexes the rate of isomerization increases in the order Al < Ga < In, and Al < Ga, respectively. Ligand field effects are absent here and the order parallels the order in metal ionic radius $Al^{3+} < Ga^{3+} < In^{3+}$.[5] The β-diketonate complexes presumably isomerize *via* a bond rupture mechanism[7,50b] whereas the α-RT complexes invert by a trigonal twist pathway.[5]

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Molecular Structures of Porphyrin Complexes in Solution. An ^{1}H Nuclear Magnetic Resonance Spectroscopic Investigation of the Interaction between 2,4,7-Trinitrofluorenone and Nickel(II) and Cobalt(II) Mesoporphyrin IX Dimethyl Esters

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Abstract: Complexes (1 : 1) formed between cobalt(II) and nickel(II) mesoporphyrin IX dimethyl ester and 2,4,7-trinitrofluorenone in $CDCl_3$ have been investigated by ^{1}H nmr spectroscopy. The chemical shifts of the trinitrofluorenone resonances are linearly dependent on the concentration of both cobalt(II) and nickel(II) porphyrins, and the shifts in the fully formed complexes and formation constants have been calculated. It is concluded that the shifts are caused by the ring current in the case of nickel(II) porphyrin and the ring current plus the dipolar interaction for the paramagnetic cobalt(II) porphyrin. By using the ratios of the dipolar shifts and assuming the ring current effect with cobalt(II) porphyrin is equal to that with nickel(II) porphyrin, the possible solution structures for the molecular complex have been calculated by computer methods. One family has the planes of the two components parallel at 4.0 ± 0.2 Å with complete overlap of the porphyrin and nitroarene.

Recently, there has been[2] considerable interest in the use of lanthanides as "shift reagents" though perhaps the most important aspect[3] of such work is the ability to derive detailed geometric information of the structures of lanthanide complexes in solution, making use of the assumption, justifiable in many instances, that the shift is caused primarily by the dipolar contribution.[4] In a brief communication,[5] we reported the use of cobalt(II) mesoporphyrin IX dimethyl ester to perturb the ^{1}H nmr spectrum of 1,3,5-

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