Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Dynamic Stereochemistry of Tris-Chelate Complexes. III.[1] Tris(dithiocarbamato) Complexes of Ruthenium(III)

D. J. DUFFY and L. H. PIGNOLET*

The temperature-dependent pmr spectra of tris(N,N-disubstituted dithiocarbamato)ruthenium(III) complexes, Ru(RR-dtc)$_3$, have been examined in noncoordinating solvents. The complexes are stereochemically nonrigid and kinetic parameters have been determined for intramolecular metal-centered inversion and ligand-centered geometric isomerization by nmr line-broadening techniques. $\Delta G^{\ddagger}$ values for these processes are ~13 and 15.6 kcal/mol, respectively. The mechanism for metal-centered inversion and geometric isomerization has been assigned to be the trigonal twist and S$_2$C-N bond rotation, respectively. Kinetic parameters are considered in light of the solid-state structure of Ru(EtEt(dtc))$_3$ which has been determined by X-ray analysis and is reported in detail in the following paper in this journal. The nonrigid nature of the ruthenium complexes which rearrange *via* the trigonal-twist mechanism probably results from the trigonally twisted geometry found in the solid state. The kinetic parameters are compared to those of other tris-chelate complexes.

Introduction

Recently there has been much interest in the stereochemical nonrigidity of tris-chelate metal complexes.[2] Most of the experimental work has involved the use of dynamic nmr spectroscopy in measuring rates and determining mechanisms of metal-centered inversion and isomerization reactions.[2] A number of theoretical papers have also appeared in which permutational analyses have been applied to rearrangement reactions of tris-chelate metal complexes.[3-7] Four classes of tris-chelate complexes have been the subjects of most of this work: tris(β-diketonato)metal, M(R$_1$R$_2$-β-dik)$_3$;[8] tris-(α-R-tropolonato)metal, M(α-RT)$_3$;[9] bis(dithiocarbamato)-(dithiolene)metal, M(R$_1$R$_2$dtc)$_2$(S$_2$C$_2$Z$_2$);[10] tris(dithiocarbamato)metal, M(R$_1$R$_2$dtc)$_3$,[1] where R is an alkyl or aryl substituent and Z is CF$_3$ or CN.

In this laboratory we have examined the dynamic stereochemistry of a number of M(dtc)$_3$ complexes where M = V(III), Cr(III), Mn(III), Fe(III), Fe(IV), Co(III), Ga(III), In-(III), and Ru(III). Details of this work are reported in parts I and II of this series.[1b,c] A preliminary account of the Ru(III) work, which is presented in more detail here, has been published.[11] The dithiocarbamate series has permitted a rather large comparison of the effect of various metal ions on the rate and mechanism of metal-centered rearrangement. With the iron complexes alone, kinetic parameters were obtained for oxidation states II,[12] III,[13,14] and IV with spin states of $S = 0, 2; {}^1/_2, {}^5/_2;$ and 1, respectively. Most of the dtc complexes have been shown to rearrange by the trigonal-twist mechanism which was originally proposed by Bailar.[15] If the kinetic parameters for metal-centered inversion for M(dtc)$_3$ complexes are all assumed to be due to this mechanism, a relationship has been found to exist between the difference in ligand field stabilization energy for trigonal-antiprismatic, TAP, and trigonal-prismatic, TP, geometries and the activation energy for metal-centered inversion such that higher activation energies correspond to the larger values of the quantity LFSE(TAP) − LFSE(TP).[1b,c]

The dtc complexes also show another kinetic process in their variable-temperature pmr spectra. This process which causes geometrical isomerization has been assigned to S$_2$C-N bond rotation and has been examined in detail for several dtc complexes.[16]

(1) (a) Part IV: L. H. Pignolet, *Inorg. Chem.*, 13, 2051 (1974); (b) L. Que, Jr., and L. H. Pignolet, *ibid.*, 13, 351 (1974); (c) part I: M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *J. Amer. Chem. Soc.*, 95, 4537 (1973).

(2) See, for example, the following reviews: (a) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, 17, 391 (1972); (b) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, 6, 331 (1971); (c) L. H. Pignolet and G. N. La Mar in "Chemical Applications of NMR in Paramagnetic Molecules," G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N. Y., 1973, Chapter 8.

(3) M. Gielen and N. van Lautem, *Bull. Soc. Chim. Belg.*, 79, 679 (1970).

(4) J. I. Musher, *Inorg. Chem.*, 11, 2335 (1972).

(5) S. S. Eaton, J. R. Hutchinson, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 6411 (1972).

(6) W. G. Klemperer, *J. Chem. Phys.*, 56, 5478 (1972); *J. Amer. Chem. Soc.*, 94, 6940 (1972), 95, 2105 (1973); *Inorg. Chem.*, 11, 2668 (1972).

(7) S. S. Eaton and G. R. Eaton, *J. Amer. Chem. Soc.*, 95, 1825 (1973).

(8) J. R. Hutchinson, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, 10, 1004 (1971), and references cited therein.

(9) S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 95, 1116 (1973), and references cited therein.

(10) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *Inorg. Chem.*, 11, 99 (1972).

(11) L. H. Pignolet, D. J. Duffy, and L. Que, Jr., *J. Amer. Chem. Soc.*, 95, 295 (1973).

(12) Iron(II) was studied in complexes of the type Fe(dtc)$_2$(L) where L = *o*-phenanthroline or bipyridyl.[1b]

(13) Tris(dithiocarbamato) complexes of iron(III) possess the well-studied spin-state equilibrium ${}^6A_{1g} \rightleftarrows {}^2T_{2g}$. The position of this equilibrium can be varied by changing the N substituent.[14]

(14) R. L. Martin and A. H. White, *Transition Metal Chem.*, 4, 113 (1968).

(15) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 8, 165 (1958).

Table I. Magnetic Data for Tris(RR'dtc)Ru III Complexes

RR'	Temp, °C	Pmr Shifts		μ_{eff}, BM (solid, 23°)
		Ppm		
EtEt	−94	N-CH$_2$[a]	−34.12, −15.43	1.86
	+44	N-CH$_2$[a]	−13.55	
BzBz	−45	N-CH$_2$[b]	−35.73, −4.68	1.80
	+57	N-CH$_2$[b]	−12.44	
MeBz	−57	N-CH$_3$[b,c]	C = −31.81; T = −35.44, −35.05, −29.59	1.88
	+58	N-CH$_3$[b]	−18.22	
MePh	−58	N-CH$_3$[b,c]	C = −32.08; T = −44.96, −36.68, −23.98	1.78
	+60	N-CH$_3$[b]	−19.09	

[a] Shifts are relative to CHDCl$_2$ internal reference in CD$_2$Cl$_2$ solution.　[b] Shifts are relative to CHCl$_3$ internal reference in CDCl$_3$ solution.　[c] C = cis and T = trans.

Ru(MeBz(dtc))$_3$[17] has been shown to be stereochemically nonrigid on the pmr time scale with $\Delta F^{\ddagger}(10°) \cong 13$ kcal/mol for metal-centered inversion.[11] This result was surprising because all other tris-chelate complexes of Ru(III) which have been examined to date are stereochemically rigid. For example, Ru(α-C$_3$H$_5$T)$_3$ does not show dynamic pmr behavior in nitrobenzene solution even at 170°[9] and Ru(CH$_3$CF$_3$-β-dik)$_3$ has been found to have an activation energy for trans → cis isomerization of 28 kcal/mol[18] which places it too in the rigid category.

The present work was undertaken in order to characterize further the kinetics and mechanism of metal-centered and ligand-centered rearrangement for Ru(dtc)$_3$ complexes. In addition, a single-crystal X-ray structure determination was performed on Ru(EtEt(dtc))$_3$. The details of the structure determination are reported in part IV.[1a] The crystal structure was determined to permit a comparison of solid-state parameters with those of other tris-chelate complexes with the hope of explaining the nonrigid nature of Ru(dtc)$_3$. Several papers have appeared[1,5,9,19] in which various solid-state parameters of tris-chelate complexes have been related to activation energies for optical inversion. An attempt will be made in this paper to assess the importance of these effects.

Experimental Section

Preparation of Compounds, Ru(RR'dtc)$_3$. All of the compounds used in this study were prepared according to Malatesta[20] except as outlined below and were characterized by elemental analysis, pmr, infrared, and magnetic susceptibility (Table I). RuCl$_3$·nH$_2$O was purchased from Research Organic/Inorganic Chemical Corp. and was purified by twice stirring the solid with a concentrated HCl-ethanol solution and evaporating to dryness with heat under a stream of nitrogen. The product was dissolved in absolute ethanol and treated with a stoichiometric amount of NaRRdtc. The solid product was purified by column chromatography using silica gel and benzene eluent. The purified solids were then recrystalized or oiled out from CH$_2$Cl$_2$-heptane solution by slow evaporation. If the entire procedure is carried out under a nitrogen atmosphere, chromatography is unnecessary. For RR' = EtEt, BzBz, MeBz, MePh: mp 241-243°, 209-210°, oil, 218-220°; $10^3\chi_m^{uncor}$ (solid, 23°) = 1.149, 0.8361, 1.102, 0.9913 cgsu/mol, respectively. *Anal.* Calcd for C$_{15}$H$_{30}$N$_3$S$_6$Ru (RR' = EtEt): C, 33.00; H, 5.54. Found: C, 33.07; H, 5.53. Calcd for C$_{45}$H$_{42}$N$_3$S$_6$Ru (RR' = BzBz): C, 58.86; H, 4.61; N, 4.68. Found: C, 58.87; H, 4.89; N, 4.70. Calcd for C$_{27}$H$_{30}$N$_3$S$_6$Ru (RR' = MeBz): C, 47.00; H, 4.38; N, 6.09. Found: C, 46.81; H, 4.12; N, 5.95. Calcd for C$_{24}$H$_{24}$N$_3$S$_6$Ru (RR' = MePh): C, 44.49; H, 3.73; N, 6.49. Found: C, 44.28; H, 3.89; N, 6.46.

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 CDCl$_3$ or CD$_2$Cl$_2$ with complex concentrations *ca.* 0.1 *M*. Chemical shifts were measured relative to either C*H*Cl$_3$ or C*H*DCl$_2$ internal reference and are reported in ppm where downfield shifts have negative values.

Magnetic Measurements. Solid-phase moments were determined by the Faraday method. Diamagnetic corrections were calculated from Pascal's constants.

Kinetic Analysis. Total line shape analyses, TLSA, were performed for Ru(BzBz(dtc))$_3$ and Ru(EtEt(dtc))$_3$. These complexes possess diastereotopic N-CH$_2$ protons which give two separate resonances in the limit of slow optical inversion (*vide infra*). Spin-spin coupling is not observed due to the paramagnetic broadening. Coalescence of these two resonances results from metal-centered inversion. A simple two-site exchange was used and exchange-broadened line shapes were computer calculated using the rigorous Gutowsky-Holm equation.[21] Best fits were visually selected and are shown in Figure 1 for Ru(EtEt(dtc))$_3$.

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 of ln $H_{1/2}$ *vs.* $1/T$ and $\Delta\nu$ *vs.* $1/T$. These plots are shown in Figures 2 and 3. This procedure has been previously applied for paramagnetic complexes.[2,16,22]

The rate constant for optical inversion, k (sec^{-1}), is defined as τ^{-1} where τ is the preexchange lifetime of a proton in either environment (τ used here equals 2τ in the Gutowsky-Holm equation[21]). 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). The usual assumption of unity for the transmission coefficient in the Eyring equation was made. Errors were estimated from error limits in k and T. Values of $\Delta G^{\ddagger}$ in the region of coalescence have small errors and are therefore best used for comparative purposes.[23]

Kinetic parameters are listed in Table II. The complexes which have only $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ values reported were not subjected to a total line shape fit. Rate constants for Ru(MeBz(dtc))$_3$ and Ru(MePh(dtc))$_3$ were determined by a computer fit using the Binsch DNMR3 program[24] at or near the coalescence temperature only. The relation $k = (k_B T/h)$ exp($-\Delta G^{\ddagger}/RT$) was used to calculate $\Delta G^{\ddagger}$. These unsymmetrically substituted complexes have cis and trans isomers which are pmr detectable below *ca.* 40° where S,C-N bond rotation is slow on the pmr time scale. Optical inversion results in coalescence of two of the four N-CH$_3$ environments. Details of the line shape fit have been published for analogous iron complexes.[1b,c]

A high-temperature kinetic process which results in cis-trans isomerization is also observed for the unsymmetrically substituted complexes. Unfortunately, the coalescence due to this process overlaps with the line-broadening region of the low-temperature process thus preventing a total line shape fit. A computer fit was performed, however, near the coalescence point of Ru(MePh(dtc))$_3$ using the Binsch DNMR3[24] computer program and assuming a 3:1 trans:cis population ratio. The detailed procedure of this fit has been reported for analogous iron complexes.[16]

Results and Discussion

Magnetic and Pmr Properties. Ru(dtc)$_3$ complexes are

(16) B. L. Edgar, D. J. Duffy, M. C. Palazzotto, and L. H. Pignolet, *J. Amer. Chem. Soc.*, **95**, 1125 (1973).

(17) Abbreviations used throughout: Me = methyl, Bz = benzyl, Ph = phenyl, Et = ethyl, and Pyr = pyrrolidyl.

(18) J. G. Gordon, II, M. J. O'Connor, and R. H. Holm., *Inorg. Chim. Acta*, **5**, 381 (1971).

(19) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).

(20) L. Malatesta, *Gazz. Chim. Ital.*, **68**, 195 (1938); *Chem. Abstr.*, **32**, 7364 (1938).

(21) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(22) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971), and references cited therein.

(23) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

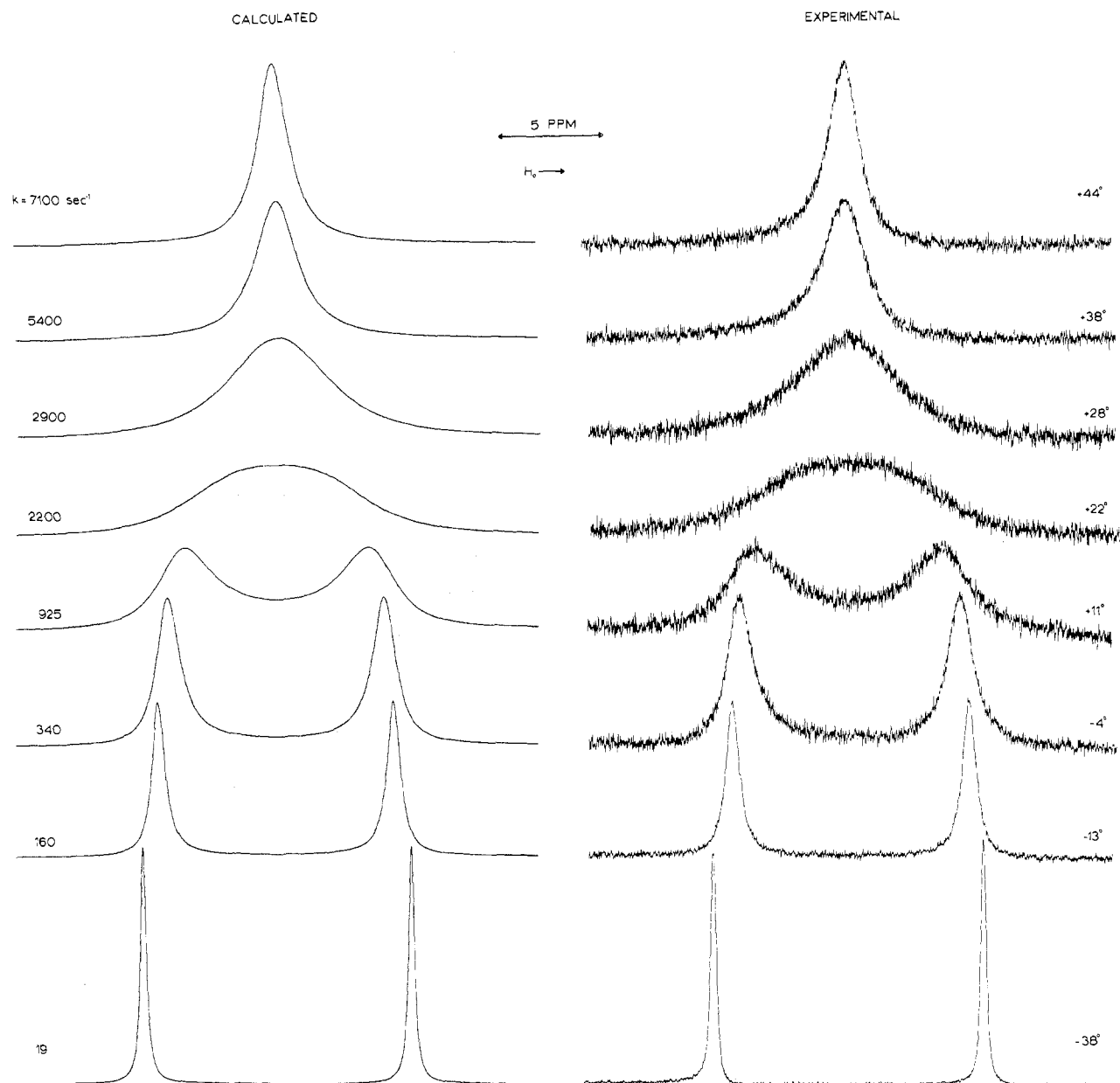(24) G. Binsch and D. A. Kleier, Department of Chemistry, University of Notre Dame, Notre Dame, Ind. 46556.

Figure 1. Experimental and calculated pmr traces for the $N\text{-}CH_2$ groups of $Ru(EtEt(dtc))_3$ in $CDCl_3$ solution recorded at 100 MHz.

Table II. Kinetic Parameters[a] for Intramolecular Metal-Centered Inversion for Tris(dithiocarbamate) Complexes of Ruthenium(III)

Complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol $(T, °C)$
$Ru(EtEt(dtc))_3$	10.3 ± 1	-8 ± 5	12.8 ± 0.2 (22)
$Ru(BzBz(dtc))_3$	11.6 ± 1	-7 ± 5	13.8 ± 0.2 (42)
$Ru(MeBz(dtc))_3$	11.1^{b}		13.3 ± 0.2 (15)
$Ru(MePh(dtc))_3$	10.1^{b}		12.1 ± 0.2 (9)

[a] See Experimental Section. $CDCl_3$ solutions were used except for $Ru(EtEt(dtc))_3$ in which case CD_2Cl_2 solution was used. [b] Values determined from $\Delta G^{\ddagger}(T)$ and assuming $\Delta S^{\ddagger} = -7.5$ eu.

low-spin d^5 in solid state and in CH_2Cl_2 solution. The pmr spectra consist of isotropically shifted resonances[2c,25] with line widths at half-height which are significantly narrower than those of the analogous iron(III) complexes. The temperature dependence of the pmr shifts shows linear behavior *vs.* $1/T$ over the temperature range −95 to +70°.[26] Al-

though high-temperature magnetic measurements have not been made, there is no evidence to suggest that a higher spin state of Ru(III) is populated as has been observed in the analogous iron(III) complexes.[14]

The dibenzyl and diethyl N substituents give symmetrical tris-chelate complexes which have C_3 symmetry. The methylene protons in these ligands are in diastereotopic environments[27] and therefore serve as probes for metal-centered inversion.[1,28] At temperatures where optical inversion is slow on the pmr time scale two well-separated resonances are observed. This is illustrated in the −38° spectrum of Figure 1 which shows the pmr traces for the $N\text{-}CH_2$ resonances of $Ru(EtEt(dtc))_3$ at several temperatures. As the temperature is increased, the two resonances broaden and coalesce into a single line at *ca.* +22°. The $N\text{-}CH_2$ resonances of Fe-$(BzBz(dtc))_3$ show the same behavior. The kinetic process

(25) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).
(26) This statement is only true for resonances not involved in exchange broadening or averaging (*vide infra*).

(27) K. Mislow and M. Rabin, *Top. Stereochem.*, **1**, 1 (1965).
(28) Optical inversion in tris-chelate complexes is the interconversion of Λ and Δ isomers. This process has been described in ref 1b and 1c.
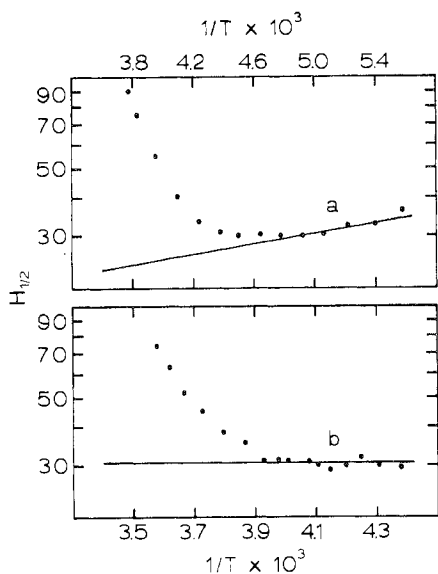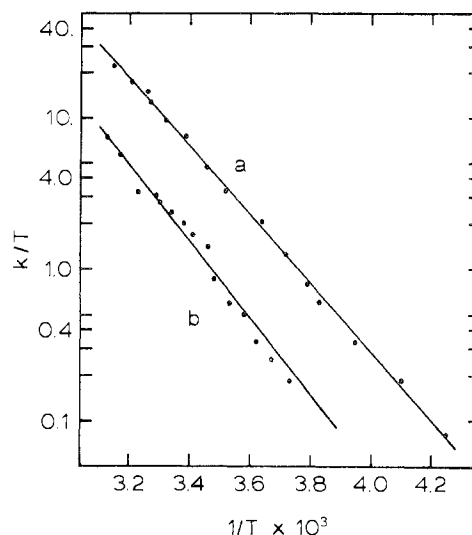
Figure 2. ln $(H_{1/2})$ vs. $1/T$ plots for N-CH_2 resonances of (a) $Ru(EtEt(dtc))_3$ and (b) $Ru(BzBz(dtc))_3$.
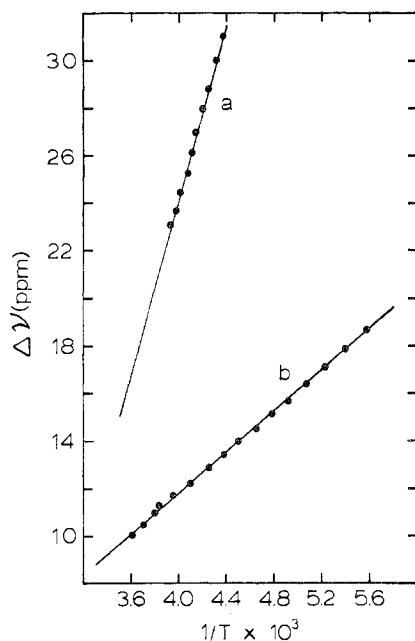
Figure 3. Observed (points) and extrapolated (lines) chemical shift separations between exchanging N-CH_2 environments: $\Delta\nu$ vs. $1/T$ for (a) $Ru(BzBz(dtc))_3$ and (b) $Ru(EtEt(dtc))_3$.

Figure 4. Eyring plots for metal-centered inversion for (a) $Ru(EtEt(dtc))_3$ and (b) $Ru(BzBz(dtc))_3$.

which causes this interchange of the diastereotopic environments is intramolecular (*vide infra*) and results in metal-centered inversion. A computer line shape calculation (Figure 1) confirms that the coalescence results from a kinetic exchange process and that metal-centered inversion is indeed fast on the pmr time scale at temperatures greater than +38°.

The unsymmetrically substituted complexes have the additional feature of cis and trans geometric isomers. The pmr spectra are therefore more complex but are entirely consistent with the results from the symmetrically substituted complexes. The pmr spectra recorded at various temperatures of $Ru(MeBz(dtc))_3$ have been published in a preliminary communication of this work[11] and reveal four N-CH_3 resonances below −13° which coalesce into three resonances at *ca.* +20°. Careful integration of the spectra shows that two of the trans N-CH_3 environments are interchanged while the cis and other trans environments are un-

affected by the process. Geometric isomerization cannot cause this result; however, several metal-centered rearrangements can (*vide infra*). The coalescence pattern of the N-CH_2 resonances[11] shows that metal-centered inversion must accompany this process and therefore is consistent with the results from the symmetrically substituted complexes (*vide supra*). At higher temperatures (>40°) S_2C-N bond rotation becomes fast on the pmr time scale and causes coalescence of all remaining N-CH_3 and N-CH_2 environments. Pmr spectra at various temperatures of $Ru(MePh$-$(dtc))_3$ are in agreement with the above observations.

Mechanism for Metal-Centered Inversion. The primary metal-centered rearrangement mechanism can be deduced from the coalescence pattern of the unsymmetrically substituted complexes. This is best accomplished by considering the several permutational analysis schemes for tris-chelate rearrangements which have been published.[3-7] The following discussion makes use of the scheme by Eaton and Eaton.[7] The exchange averaging which is evident in the pmr spectra results from intramolecular processes (*vide infra*) and therefore is suitable to analysis by this permutational scheme. The low-temperature coalescence involves the averaging of two trans environments without affecting the cis or the remaining trans resonances (see Figure 1 in ref 11). This pattern is consistent with only rearrangement modes A_6 and A_2.[7] Only the former mode requires optical inversion which indeed has been shown to occur by the simultaneous coalescence of all four diastereotopic N-CH_2 pairs in $Ru(MeBz(dtc))_3$[11] and by the coalescence shown in Figure 1 for $Ru(EtEt(dtc))_3$. Hence, A_6 is the primary rearrangement mode for the low-temperature process. This mode is unambiguously established for $Ru(MeBz(dtc))_3$ which is the only complex where the diastereotopic probe is present in an unsymmetrically substituted ligand. The other Ru(III) complexes in this study all show nonrigidity not only with very similar activation parameters (Table II) but also with coalescence patterns which are entirely consistent with rearrangement mode A_6. It is therefore concluded that the four complexes in this study all rearrange by mode A_6 which is illustrated in (1) for the trans Δ isomer. Numbers label the N-CH_3 groups and letters designate the three environments. The permutation ($x \rightleftarrows z$) is clearly evident. The most reasonable physical motion which gives this rearrangement mode is the trigonal or Bailar twist.

trans Δ   trans Λ

$$(1)$$
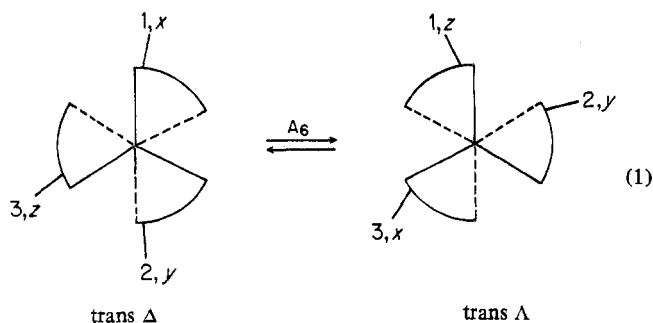
This mechanism is best envisioned as a twisting motion of one triangular face with respect to the other about the pseudo-C_3 symmetry axis. A trigonal-prismatic transition state has been suggested for this mechanism.[1b,c,9,10]

Ligand Exchange. Experiments were performed by mixing equimolar amounts of Ru(MeBz(dtc))₃ and Ru(MePh-(dtc))₃ in CDCl₃ solution and looking for mixed-ligand complexes by pmr. No new resonances appeared after several hours at 60° which indicates that ligand exchange is very slow or that mixed complexes are not thermodynamically stable. The latter is unlikely because similar experiments with M(dtc)₃ complexes of Fe(III), Ga(III), In(III), and V(III) all gave significant amounts of the mixed complexes. The observation that ligand exchange is slower than the pmr time scale proves that inversion and geometric isomerization are intramolecular in nature.

Pmr spectra of Ru(dtc)₃ complexes were also recorded in the presence of their respective thiuram disulfides to test if ligand oxidation and subsequent thiuram disulfide exchange occurred. The addition of the thiuram disulfide had no effect on the complexed dtc ligand resonances.

Kinetics of Metal-Centered Inversion. Kinetic parameters for metal-centered inversion were determined by TLSA or by computer simulation near the coalescence point (see Experimental Section). Results are listed in Table II. The average entropy of activation, $\Delta S^{\ddagger}$, is −7.5 eu which is consistent with the near-zero or slightly negative values usually obtained for a trigonal-twist mechanism in weakly polar media.[1b,c,2a,5,10,29] The low values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are surprising for tris-chelate complexes of ruthenium(III) because all other such compounds studied are rigid on the nmr time scale. For example, Ru(α-C₃H₅T)₃ is rigid even at 170°[9] and Ru(CH₃CF₃-β-dik)₃ has an activation energy for trans to cis isomerization of 28 kcal/mol.[18] It is not fully understood why the Ru(dtc)₃ complexes rearrange with such low activation energies; however, some considerations are offered in the following sections.

Kinetic parameters for metal-centered inversion have now been determined for a number of tris-chelate complexes containing dithiocarbamate ligands. The following order for the rate of inversion is established:[1b,c] Fe(II)ₕₛ, V(III), Ga(III), In(III) > Fe(III)ₕₛ $\gtrsim$ Fe(III)ₗₛ, Fe(IV)ₗₛ > Mn(III) > Ru(III)ₗₛ >> Co(III)ₗₛ > Rh(III)ₗₛ with Cr(III) faster than Ru(III)ₗₛ but only a lower limit has been established (hs = high spin; ls = low spin). All of these complexes with the exception of Co(III), Rh(III), and Cr(III) have been shown to rearrange *via* the trigonal-twist mechanism and Co(III) has activation parameters which strongly suggest the same mechanism. Studies[30,31] on Fe(o-phen)₃²⁺, which is a Fe(II)ₗₛ

complex, show that metal-centered inversion *via* the trigonal-twist mechanism is slower than for Co(dtc)₃ complexes. This complex which does not have dtc ligands is perhaps inappropriate in the above list but it does show that Fe(II)ₗₛ is greatly different from Fe(II)ₕₛ with respect to rate of optical inversion. Recent results in this laboratory[32] with several tris-chelate complexes containing dtc ligands have confirmed that Fe(II)ₗₛ is indeed stereochemically rigid with respect to metal-centered inversion.

Geometric Isomerization. The unsymmetrically substituted tris(dithiocarbamato)complexes of ruthenium(III) show a high-temperature kinetic process in their variable-temperature pmr spectra which are characterized by the simultaneous coalescence of the remaining three N-methyl resonances (*vide supra*). This averaging results from geometric isomerization. Several intramolecular mechanisms can cause geometric isomerization. The most obvious one is S₂C-N bond rotation which has been invoked to account for the analogous high-temperature process in M(dtc)₃ complexes of Fe(III),[16] Fe(IV),[16] V(III),[1b] and Mn(III)[1b] and for the low-temperature process in Co(III).[1c] Various metal-centered rearrangement reactions can also result in geometric isomerization, especially reactions of the bond rupture variety.[2] Several arguments can be made which favor the S₂C-N bond rotation mechanism. With other M(dtc)₃ complexes definite trends exist which relate the higher barriers for geometric isomerization to the larger infrared frequencies of the S₂C-N stretch. Reasonable inductive effect arguments have also been successfully applied which relate the barrier to S₂C-N bond rotation to the rate of geometric isomerization in tris-chelate dtc complexes of Fe(II), -(III), and -(IV).[16] The free energy of activation, $\Delta G^{\ddagger}$, was determined for geometric isomerization in Ru(MePh(dtc))₃ by an approximate computer simulation near the point of maximum exchange broadening (see Experimental Section). At 50° $\Delta G^{\ddagger} = 15.6$ kcal/mol. Table III lists values of $\Delta G^{\ddagger}$ for geometric isomerization and the average S₂C-N bond distances which have been crystallographically determined for several M(dtc)₃ complexes. Although the standard deviations are rather large which weakens the comparison, a definite trend exists which suggests that geometric isomerization results from S₂C-N bond rotation. A detailed discussion of S₂C-N bond rotation in all of the M(dtc)₃ complexes will be published.[32]

Structural Parameters and Their Relation to Dynamics. The crystal structure of Ru(EtEt(dtc))₃ has been determined and the results are presented in part IV of this series.[1a] Various angles and distances which best describe the geometry of the RuS₆ core are defined in Figure 2 and listed in Table III of part IV. Ru(EtEt(dtc))₃ is typical of other M(dtc)₃ complexes in that it has $\sim D_3$ symmetry with a geometry which is intermediate between trigonal antiprismatic (TAP) and trigonal prismatic (TP). The twist and the pitch angles, ϕ and ψ, are 38.1 and 27.8°, respectively.[1a] The coordination geometry is very similar to that found in hs Fe(EtEt(dtc))₃ and Fe(Pyr(dtc))₃ which are among the most twisted (toward TP) M(dtc)₃ complexes. The various structural parameters of the MS₆ core for a number of M(dtc)₃ complexes are listed in Table III of part IV.

Kepert[19] has shown *via* interligand repulsion calculations that the bite angle, α, is of prime importance in determining the most stable solid-state geometry.[33] These calculations

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(33) Kepert actually used the quantity *b* which is the ligand bite distance defined for a metal–ligand distance of unity. The parameter *b* uniquely determines α by the relation $b = 2 \sin (\alpha/2)$.

Table III. Barriers to Geometric Isomerization and C–N Bond Distances for Several Complexes Containing dtc Ligands

Complex	$\Delta G^{\ddagger}$, kcal/mol (T, °C)	S_2C–N bond length,[a] Å	Ref of structure determination
Ru(MePh(dtc))$_3$	15.6 ± 0.3 (50)	1.30 (2)	b
Fe(MePh(dtc))$_2$S$_2$C$_2$(CF$_3$)$_2$	14.9 ± 0.2 (25)[10]	1.30 (1)	c
Fe(MePh(dtc))$_3$	12.0 ± 0.3 (−38)[1c]	1.32–1.34	d
Mn(MePh(dtc))$_3$	11.8 ± 0.3 (−19)[1b]	1.35 (3)	e

[a] Bond lengths are reported for the analogous EtEt(dtc) complex. [b] Reference 1a. [c] D. L. Johnston, W. L. Rohrbaugh, and W. D. Horrocks, Jr., *Inorg. Chem.*, 10, 1474 (1971). [d] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972). [e] P. C. Healy and A. H. White, *ibid.*, 1883 (1972).

Table IV. Crystallographic Parameters of the MS$_6$ Core and Kinetic Parameters for Metal-Centered Inversion of Several M(dtc)$_3$ Complexes

Complex	$\Delta H^{\ddagger}$, kcal/mol (±1)	Angles[b] of MS$_6$ core, deg α	ϕ^{c}	ψ	Ref of structure determination
In(Pyr(dtc))$_3$	≪8.6[a]	69.4	32.8	25.3	d
Fe(Pyr(dtc))$_3$	7.6[1c]	74.4	37.4	26.5	e
Fe(MePh(dtc))$_3$	8.7	75.1	40.7	28.9	e
Ru(EtEt(dtc))$_3$	10.3	73.0	38.1	27.8	f
Mn(EtEt(dtc))$_3$	11.0[a]	72.8	40.2	29.9	g
Co(EtEt(dtc))$_3$	23.6[a]	76.2	43.7	30.7	h

[a] $\Delta H^{\ddagger}$ determined for the analogous BzBz(dtc) complex.[1] [b] Average values calculated from the crystallographic coordinates given in the appropriate reference. [c] Values differ slightly from those reported elsewhere due to the method of calculation; however, these values are correct for relative comparison. [d] P. J. Hauser, J. Bordner, and A. F. Schreiner, *Inorg. Chem.*, 12, 1347 (1973). [e] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972). [f] Reference 1a. [g] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972). [h] S. Merlino, *Acta Crystallogr., Sect. B*, 24, 1441 (1968).

also show that the activation energy for metal-centered inversion *via* a TP transition state is related to α such that the smaller values of α lead to lower activation energies. In this laboratory we have determined the barrier to metal-centered inversion for a number of M(dtc)$_3$ complexes which have also been the subjects of X-ray investigations. Results of these studies should provide an opportunity to apply the findings of Kepert's calculation. Of course electronic effects of the metal ion are ignored in this comparison. Table IV lists $\Delta H^{\ddagger}$, α, ϕ, and ψ for these compounds. Although some of the $\Delta H^{\ddagger}$ values are within experimental error, an overall relation exists. The higher $\Delta H^{\ddagger}$ values in general correspond to the less twisted (toward TP) complexes; however, the magnitude of the differences in angular parameters is hardly sufficient to account for the much greater $\Delta H^{\ddagger}$ value found for Co(III). Electronic effects must be invoked in this case. A complete analysis of the kinetic parameters for metal-centered inversion in light of ligand field stabilization energy effects has been made.[1c] This analysis does account for the large differences in $\Delta H^{\ddagger}$ values; however, it fails to explain some of the smaller differences. It is clear that a complete understanding of all the parameters which affect the rate of metal-centered inversion is beyond reach at this time; however, a consideration of both ligand field stabilization effects and solid-state structural parameters does explain the gross differences for M(dtc)$_3$ complexes. Unfortunately this is the only series of complexes which is large enough to permit the above analyses.

The structural parameters for M(dtc)$_3$ complexes all show a MS$_6$ geometry which is intermediate between TAP and TP. Most of these complexes have also been shown to enantiomerize *via* the trigonal-twist mechanism which presumably involves a TP transition state. It is tempting to conclude that the trigonal-twist mechanism is the lowest energy pathway due to the small bite angle and rigid nature of the

dtc ligand. It is the small bite angle which causes the small values for ϕ and ψ (*vide supra*). A comparison to tris-chelate complexes of other ligands bears this out. Most of the tris(β-diketonate) complexes have approximately O_h geometry and values of α, ϕ, and ψ are commonly 90, 60 and 35°, respectively. All tris(β-diketonate) complexes which have been examined have been found to enantiomerize *via* bond rupture pathways.[8,34,35] The tris(α-R-tropolonate) complexes on the other hand have smaller bite angles (α, ϕ, and ψ are 82.6, 48.1, and 31.0°, respectively, for tris(tropolonato)aluminum(III)[36]) and rearrange *via* the trigonal-twist mechanism.[9]

In all cases except one the M(dtc)$_3$ complexes enantiomerize faster than analogous M(β-dik)$_3$ and M(α-RT)$_3$ complexes regardless of mechanism. The exception is with Co(α-RT)$_3$ complexes which rearrange ~10^7 times faster than Co(dtc)$_3$ complexes.[9] No explanation has been put forth for this observation. The other M(dtc)$_3$ complexes most likely rearrange faster because of their smaller bite angles and hence greater twist toward TP geometry.

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