Intramolecular Rearrangement Reactions of Tris-Chelate Complexes. III.[1,2] Analysis of the Rearrangements of Tris(α-isopropenyl- and α-isopropyltropolonato)aluminum(III) and -cobalt(III). Examples of Stereochemically Nonrigid Aluminum(III) and Cobalt(III) Complexes

S. S. Eaton,[3,4] J. R. Hutchison,[5] R. H. Holm,*[4] and E. L. Muetterties[6]

Contribution from the Departments of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139,
and Swarthmore College, Swarthmore, Pennsylvania 19081,
and the Central Research Department, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898. *Received January 27, 1972*

Abstract: Tris-chelate complexes of aluminum(III), cobalt(III), and rhodium(III) derived from α-isopropenyl- and α-isopropyltropolone have been prepared and their intramolecular rearrangement reactions studied in tetrachloroethane, chloroform, or dichloromethane solution by proton magnetic resonance. The Rh(III) complexes were found to be stereochemically rigid up to *ca.* 140°. The Al(III) and Co(III) complexes exist as cis–trans mixtures with the trans form slightly favored ($K_{\text{eq}} = T/C = 3.2$–$4.2$ at 25°). Above *ca.* -10 to 0° these complexes exhibit stereochemical nonrigidity with two distinct kinetic processes observable. The low-temperature process is one of inversion of absolute configuration ($\Delta \rightleftarrows \Lambda$) which proceeds by a trigonal-twist mechanism. Evidence for this mechanism is afforded by the averaging of two nonequivalent methyl sites of the trans isomer of the α-isopropenyl complexes **1**, while not affecting the remaining trans site or the cis isomer, and by a full line-shape analysis of the exchange-broadened methyl spectra of the cis and trans isomers of the α-isopropyl complexes **2**. Inversion reactions are characterized by $E_a = 11$–17 kcal/mol and $\Delta S^{\neq} = -16$ to $+5$ eu. The trigonal twist as opposed to a bond rupture mechanism is considered to be favored for inversion primarily by the rigid planar geometry of the tropolonate ligand. Inversion rates of the Co(III) tropolonates are *ca.* 10^{11} greater than that of Co(acac)$_3$ at 25°. These species represent the first examples of stereochemically nonrigid Co(III) complexes. The high-temperature processes of complexes **1** and **2** result in geometrical isomerization (cis $\rightleftarrows$ trans). It should not be assumed that (cis $\rightleftarrows$ trans) isomerization in these complexes also proceeds through a trigonal-twist mechanism (imaginary C_3 axes). In fact, spectra from the high-temperature processes could be simulated assuming random exchange of methyl environments. Thus there is no mechanistic information to be gleaned from the kinetic data on the (cis $\rightleftarrows$ trans) isomerization.

Determination of the mechanisms of intramolecular rearrangement reactions of chelate complexes[7] continues to be a central problem in mechanistic inorganic chemistry. Much of the recent research directed toward elucidation of mechanisms has involved tris-chelate complexes of general type M(A–B)$_3$, containing three unsymmetrical bidentate ligands. Such species can exist as cis (C) and trans (T) geometrical isomers, each of which is enantiomeric (Δ, Λ), and the possible intramolecular processes are isomerization and racemization (inversion). It is generally considered that these processes can proceed by two limiting types of pathways which are distinguished by the effective coordination number of the transition state. Nonbond rupture pathways have been variously described as Bailar[8–10] or trigonal[11] and Ray–Dutt[9,10,12] or rhombic twists, depending upon which real or artificial threefold molecular axis is used as a reference for the concerted twist motions of the chelate rings. Idealized trigonal-prismatic (TP) transition states are generated by these twists. Bond rupture pathways[1] involve five-coordinate transition states with idealized square-pyramidal (SP) or trigonal-bipyramidal (TBP) geometry and dangling axial or equatorial (basal) ligands. An idealized polyhedron implies that the positions of the ligating nuclei in an actual complex reasonably approximate the vertex positions of the polyhedron. Hence, some or all interbond angles are not defined in the idealized trigonal prism and square prism, respectively. These idealized models have been employed only to facilitate qualitative stereochemical arguments.

In order to classify chelates in terms of their rearrangement rates, we have previously introduced the designations "slow" and "fast."[1,2] Slow complexes are those whose geometrical isomers can be separated and at least partially resolved under ordinary conditions and are usually formed by nonlabile metal ions such as Cr(III), Co(III), Rh(III), and Ru(II,III). Fast or stereochemically nonrigid[13] complexes are those whose rates are too large to permit isomer separation and reso-

---

(1) Part I: J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

(2) Part II: J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, 10, 1004 (1971).

(3) NSF Predoctoral Fellow, 1969–1971.

(4) Massachusetts Institute of Technology.

(5) Swarthmore College.

(6) E. I. du Pont de Nemours and Co., Contribution No. 1904.

(7) This subject has recently been comprehensively reviewed: (a) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press. See also (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 300–334; (c) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971).

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

(9) C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).

(10) J. E. Brady, *ibid.*, **8**, 1208 (1969).

(11) R. C. Fay and T. S. Piper, *ibid.*, **3**, 348 (1964).

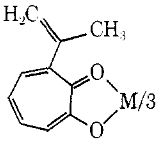
(12) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, 20, 81 (1943).

(13) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

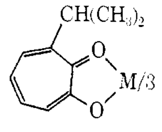
lution but do allow isomer detection and, in most cases, kinetic studies by nmr. Typical fast complexes are formed from labile ions such as Al(III), Ga(III), In(III), V(III), and high-spin Mn(III). Recent research in these laboratories has dealt with topological descriptions of the rearrangement reactions of $M(A-B)_3$[1,14] and $M(A-B)_2(A-A)$[15] complexes, formal kinetic treatment of the slow[1] and fast[2] $M(A-B)_3$ rearrangements, and rate studies of various slow [Co(III),[1] Ru(III)[16]] and fast [Al(III),[2,17,18] Ga(III),[2] Mn(III),[16] and Fe[15,19]] complexes. Despite the large body of kinetic data obtained in these and closely related[7,20,21] investigations, it has been possible in only a few cases to deduce a unique mechanism or to limit significantly the number of possible twist and bond rupture mechanisms, which are detailed elsewhere for the $M(A-B)_3$[1,2] and $M(A-B)_2$-(A-A)[15] cases. An analysis of the kinetics for the slow $M(A-B)_3$ case[1] has revealed that measurement of isomerization and racemization rates of the cis and trans isomers can lead to a determination of mechanisms if both processes involve the same transition state. Using this approach it has been shown that the octahedral β-diketonates $Co(mhd)_3$[1,22] and $Co(bzac)_3$[21] rearrange with bond rupture involving a high percentage of TBP-axial transition states. Full pmr line-shape analyses of $Al(pmhd)_3$ and $Ga(pmhd)_3$ allowed restriction of mechanisms to certain twist processes and/or a bond rupture (SP-axial) pathway.[2] Earlier a trigonal-twist mechanism for $Al(tfac)_3$ and $Ga(tfac)_3$ was shown to be incompatible with nmr results.[11]

Perhaps the most interesting fast complexes investigated to date are the bis(N,N-disubstituted dithiocarbamato)dithiolene iron complexes, $Fe(RR'\text{-dtc})_2(tfd)$[15] and $Fe(RR'\text{-dtc})_2(mnt)$.[19] The nmr averaging patterns are consistent with a "trigonal" twist (or an nmr-indistinguishable pathway, *vide infra*) around the pseudo-threefold (p-C_3) axis. In seeking a physical rationalization for this mechanism, it was observed[15,19] that the solid state structure[23] of the prototype complex $Fe(Et_2dtc)_2(tfd)$ was intermediate between the limiting trigonal-prismatic (TP, $\phi = 0°$) and trigonal-antiprismatic (TAP, $\phi = 60°$) configurations. The twist angles ϕ are defined by projection of metal-ligand vectors on a plane normal to the p-C_3 axis and for $Fe(Et_2\text{-dtc})_2(tfd)$ have the values of 33 (dtc) and 41° (tfd).[15] In these and other cases of intermediate ground-state stereochemistry, it does not appear unreasonable that rearrangements could proceed through TP transition states rather than ones generated by bond rupture.

Inasmuch as the rearrangements of these iron complexes represented the only demonstrated examples among fast complexes of the occurrence of a trigonal-twist mechanism, it was decided to investigate further the apparent correlation between intermediate ground-state structures and the operation of this mechanism. In this connection we have become interested in the rearrangement reactions of the tris chelates **1** and **2** derived from α-isopropenyl- and α-isopropyltropolone, respectively.



1



2

Two observations have drawn our attention to this group of complexes. First, the molecular parameters determined in an X-ray study of FeT_3[24] allow estimation of the twist angle as *ca.* 40°, representing a significant deviation from the TAP configuration. Second, $Al(\alpha\text{-}C_3H_7T)_3$[17] has been shown to undergo intramolecular rearrangement reactions which, while not interpreted on a mechanistic basis, were found to be qualitatively faster than those of Al(III) β-diketonates[2,11,25,26] under similar experimental conditions. Inasmuch as $Al(acac)_3$ has an essentially octahedral structure and acetylacetonate a considerably larger bite distance[27] (*ca.* 2.7–2.9 Å) than tropolonate[28] (*ca.* 2.5 Å), it appeared possible that these structural features could effect differences in rates and mechanisms of rearrangement processes.

This report details our investigation of the kinetics and rearrangement mechanisms of the complexes **1** and **2**, M = Al(III), Co(III), by total pmr line-shape analysis[2] of the temperature-dependent methyl spectra. These complexes are of the $M(A-B)_3$ type and the two trans enantiomers of the isopropenyl and all four isomers of the isopropyl complexes are illustrated in Figure 1. Methyl signals of the α substituents serve to detect the cis and trans isomers at slow exchange and to identify each provided the isomeric mixture is not statistical. In addition, the isopropyl methyl groups are diastereotopic (arbitrarily denoted by r, s) and sense the chirality of each geometrical isomer. As communicated recently,[18] pmr results are consistent with a trigonal-twist reaction pathway for all four complexes. These results demonstrate that Co(III) tropolonates are stereochemically nonrigid, thus requiring some revision of the previously proposed slow and fast categories of tris chelates.

Experimental Section

Preparation of Compounds. $Al(\alpha\text{-}C_3H_7T)_3$ was prepared as previously described.[17] α-Isopropenyltropolone was synthesized from 6,6-dimethylfulvene and dichloroketene using the reported method.[29a] α-Isopropyltropolone was obtained by hydrogenation of the isopropenyl derivative in methanol with palladium/char-

---

(14) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968).

(15) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *ibid.*, **93**, 360 (1971).

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

(17) E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **91**, 4420 (1969).

(18) S. S. Eaton and R. H. Holm, *ibid.*, **93**, 4913 (1971).

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

(20) R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, **92**, 7056 (1970).

(21) A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970).

(22) The following abbreviations for ligands are used throughout: acac, acetylacetonate; bzac, benzoylacetonate; mhd, 5-methylhexane-2,4-dionate; pmhd, 1-phenyl-5-methylhexane-2,4-dionate; tfac, trifluoroacetylacetonate; RR'-dtc, N,N-disubstituted dithiocarbamate; tfd, 1,2-bis(perfluoromethyl)dithiolene; mnt, maleonitriledithiolene; T, tropolonate; $\alpha\text{-}C_3H_5T$, α-isopropenyltropolonate; $\alpha\text{-}C_3H_7T$, α-isopropyltropolonate.

(23) D. L. Johnston, W. L. Rohrbaugh, and W. D. Horrocks, Jr., *Inorg. Chem.*, **10**, 1474 (1971).

(24) T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

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

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

(27) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(28) V. W. Day and J. L. Hoard, *ibid.*, **92**, 3627 (1970); J. J. Park, D. M. Collins, and J. L. Hoard, *ibid.*, **92**, 3636 (1970).

(29) (a) T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitihara, *Chem. Commun.*, 89 (1970); (b) Y. Kitihara, private communication.

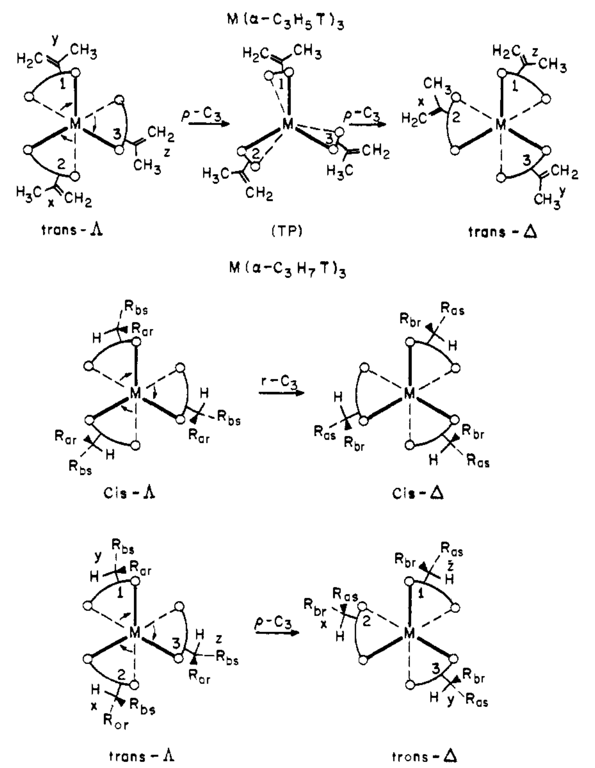


Figure 1. Upper: inversion of the trans-Λ form of M(α-C_3H_5T)[8] proceeding by a twist about the p-C_3 axis. Lower: inversion of the cis-Λ and trans-Λ forms of M(α-C_3H_7T)$_3$ (R = Me) proceeding by twists about the r-C_3 and p-C_3 axes, respectively. Substituent groups are labeled numerically and group magnetic environments are designated by *x*, *y*, *z*. Methyl groups of the isopropyl substituents are labeled a and b, and their individual magnetic environments are arbitrarily designated by r and s. The designation of environments is consistent with that employed previously.[2]

Table I. Characterization Data for Tropolonate Complexes

Complex	Mp, °C[a]	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Al(α-C_3H_5T)$_3$	175 dec	70.58	5.33	70.26	5.43
CoT_3	>300	59.73	3.58	59.37	3.61
Co(α-C_3H_5T)$_3$	>300	66.42	5.02	66.22	5.12
Co(α-C_3H_7T)$_2$	266–268 dec	62.34	5.76	62.56	5.36
Co(α-C_3H_7T)$_3$	>300	65.69	6.06	65.66	6.07
Rh(α-C_3H_5T)$_3$	197–198 dec	61.44	4.64	61.17	4.85
Rh(α-C_3H_7T)$_3$	165 dec	60.82	5.61	60.49	5.78

[a] Corrected, determined *in vacuo*.

coal.[29b] Characterization data for new complexes are given in Table I.

Al(α-C_3H_5T)$_3$. This complex was prepared by a method analogous to that reported for Al(α-C_3H_7T)$_3$.[17] Recrystallization from methanol gave small cream-colored crystals.

Co(α-C_3H_5T)$_3$. Sodium tris(carbonato)cobaltate(III) monohydrate (1.3 g, 3.6 mmol) was added to 1.5 g (9.3 mmol) of α-isopropenyltropolone dissolved in 15 ml of 60% v/v acetone–water followed by dropwise addition of 0.6 ml of concentrated nitric acid. The solution was refluxed for 15 min, cooled, and extracted with 75 ml of chloroform. After removal of solvent the resulting oil was dissolved in *ca.* 5 ml of acetone and passed through a column (2.5 × 10 cm) of Merck alumina. The rapidly moving green band was collected and the solvent removed. The residue was recrystallized from toluene–heptane yielding 0.95 g (58%) of dark green microcrystals.

Co(α-C_3H_7T)$_3$. Preparation of this complex was similar to the procedure for the isopropenyl analog. The oil obtained after the chromatography was triturated with pentane to give a green powder. Two recrystallizations from benzene–heptane afforded a green noncrystalline solid.

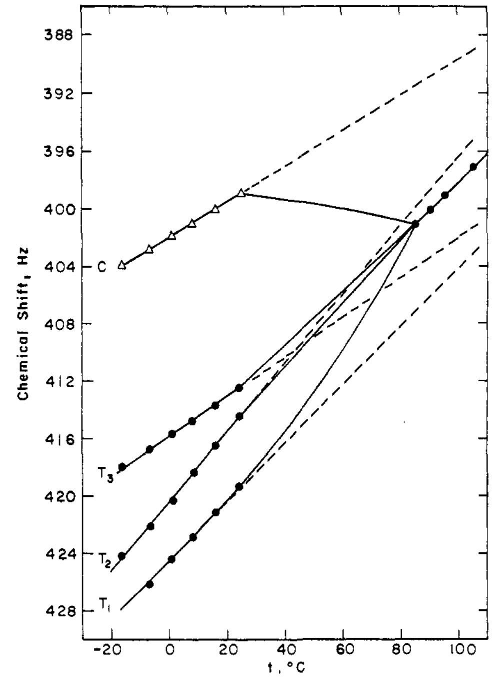


Figure 2. Temperature dependencies of the methyl chemical shifts of cis (C) and trans (T) Al(α-C_3H_5T)$_3$ in 1,1,2,2-tetrachloroethane solution at 100 MHz. The shifts of the center of each methyl spin multiplet are plotted in hertz upfield from the solvent resonance.

CoT_3. This compound was prepared by a procedure analogous to those for the substituted complexes. It was purified by Soxhlet extraction with toluene and obtained as green microcrystals.

Co(α-C_3H_7T)$_2$. Preparation of this compound was similar to that reported for anhydrous CoT_2.[30] Recrystallization from benzene–heptane yielded a red-brown powder which could not be eluted from alumina with acetone or chloroform.

Rh(α-C_3H_5T)$_3$ and Rh(α-C_3H_7T)$_3$. These compounds were prepared by a method analogous to that reported for Rh(acac)$_3$.[31] Recrystallization from benzene–hexane gave the pure complexes as yellow powders. RhT_3 has been described earlier.[32]

Pmr Spectra. Spectra of the complexes were obtained using either a Varian HA-100 or HA-220 spectrometer equipped with a variable temperature probe and operated at power levels well below saturation. For spectra obtained at 100 MHz temperatures were measured with a thermocouple mounted in the probe which was calibrated with methanol and ethylene glycol after each set of spectra using the frequency difference *vs.* temperature data of Van Geet.[33] Temperatures are considered accurate to ±1°. For 220-MHz spectra temperatures were obtained from the same calibrants and have an uncertainty of ±2°. Chemical shifts of resolved peaks are considered accurate to ±0.2 Hz. 1,1,2,2-Tetrachloroethane was purified by distillation from P_2O_5 under nitrogen. Chloroform was passed through an alumina column and stored under nitrogen. Deuterated solvents were used as received. All solutions were prepared under nitrogen immediately before use. The majority of solutions examined over a temperature range did not contain TMS and chemical shifts were referenced to either dichloromethane or tetrachloroethane, whose resonances are 5.30 and 6.00 ppm, respectively, downfield of TMS at ~29°. The concentration of solutions was *ca.* 0.25 *M* at 25°.

Kinetic Analysis. Rates of intramolecular rearrangements of the aluminum(III) and cobalt(III) complexes were determined by visual comparison of observed and calculated pmr line shapes of the isopropyl and isopropenyl methyl signals over temperature intervals encompassing the slow- and fast-exchange limits. Kinetic analyses were carried out using 220-MHz spectra of Al(α-C_3H_7T)$_3$ and 100-MHz spectra of the three other complexes. The complexes usually displayed two kinetic processes which could be analyzed separately.

---

(30) F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, **82**, 2979 (1960).

(31) F. P. Dwyer and A. Sargeson, *ibid.*, **75**, 984 (1953).

(32) E. L. Muetterties and C. M. Wright, *ibid.*, **87**, 4706 (1965).

(33) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

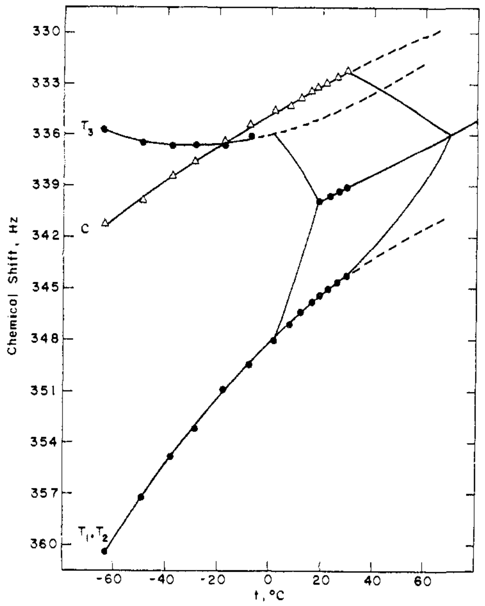


Figure 3. Temperature dependencies of the methyl chemical shifts of cis (C) and trans (T) Al(α-C_3H_7T)$_3$ in dichloromethane solution at 100 MHz. The shifts of the center of each methyl spin multiplet are plotted in hertz upfield from the solvent resonance.

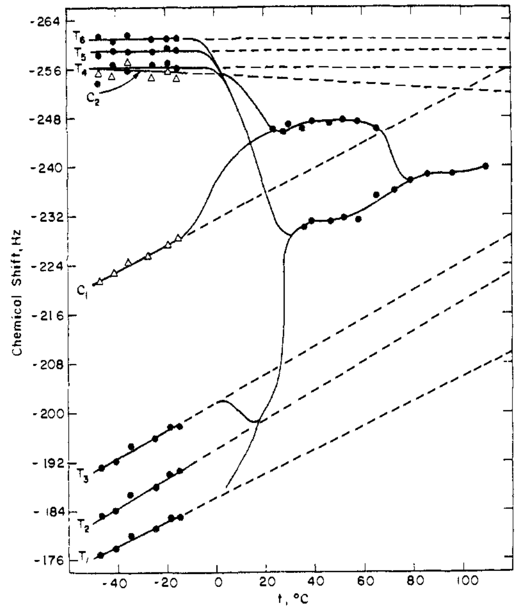


Figure 5. Temperature dependencies of the methyl chemical shifts of cis (C) and trans (T) Al(α-C_3H_7T)$_3$ in 1,1,2,2-tetrachloroethane solution at 220 MHz. The shifts of the low-field component of each methyl spin doublet (J = 7.0 Hz) are plotted in hertz downfield from hexamethyldisiloxane.

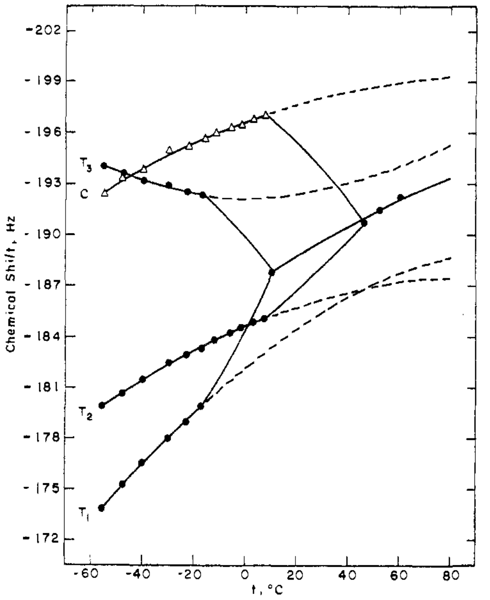


Figure 4. Temperature dependencies of the methyl chemical shifts of cis (C) and trans (T) Co(α-C_3H_7T)$_3$ in deuteriochloroform solution at 100 MHz. The shifts of the center of each methyl spin multiplet are plotted in hertz downfield from TMS.

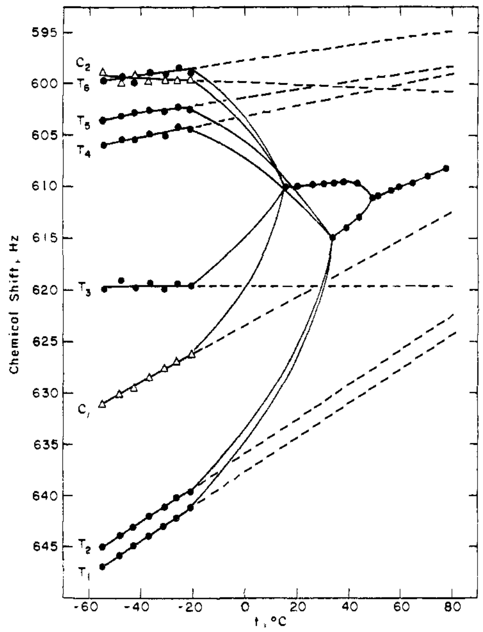


Figure 6. Temperature dependencies of the methyl chemical shifts of cis (C) and trans (T) Co(α-C_3H_7T)$_3$ in chloroform solution at 100 MHz. The shifts of the low-field component of each methyl spin doublet (J = 6.9 Hz) are plotted in hertz upfield from the solvent resonance.

As discussed below the low-temperature process (LTP) and the high-temperature process (HTP) involve inversion and geometrical isomerization, respectively. Simulated spectra were calculated by total line-shape analysis using a modification[34] of the Whitesides–Lisle EXCNMR computer program.[35] The use of this program in a study of the rearrangements of M(pmhd)$_3$ complexes is described in detail elsewhere.[2] Input at each temperature consists of chemical shifts, line widths, and relative intensities of all methyl peaks in the absence of exchange, and the kinetic exchange matrix.

(a) M(α-C_3H_7T)$_3$. Temperature dependencies of methyl chemical shifts are shown in Figures 2–6. Except for Al(α-C_3H_7T)$_3$ in dichloromethane the one cis and three trans resonances are resolved under slow-exchange conditions (<*ca.* −25°). In each case the cis signal could be identified by its lower intensity, signifying a nonstatistical mixture of isomers. Slow-exchange chemical shifts were determined by a combination of direct measurements and computer simulation of overlapping signals. Chemical shifts used in analysis of the rearrangement processes were obtained by extrapolation, indicated by the dashed lines in the figures. Linear extrapolation was used for Al(α-C_3H_7T)$_3$ in tetrachloroethane (Figure 2) since the extrapolated average agreed within 0.5 Hz of the observed average chemical shift at fast exchange. For Co(α-C_3H_7T)$_3$ in deuteriochloroform (Figure 4) a smooth nonlinear extrapolation of signals C and T_2 was assumed. Because signals T_1 and T_3 begin to average at *ca.* −20°, their extrapolated shifts were chosen to

---

(34) J. Krieger, Ph.D. Thesis, MIT, 1971.

(35) G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967); J. S. Lisle, S.B. Thesis, MIT, 1968.

Table II. Thermodynamic Data for the Cis ⇌ Trans Equilibria of $M(\alpha\text{-RT})_3$ Complexes

Complex[a]	Solvent	$\Delta H°$,[b] kcal/mol	$\Delta S°$,[b] eu	$\Delta G°_{298}$,[b] kcal/mol	$K_{eq}^{298°} = T/C$[c]
$Al(\alpha\text{-}C_3H_5T)_3$[d]	$C_2H_2Cl_4$	-1.7 ± 0.2	-2.7 ± 0.3	-0.9 ± 0.1	4.2 ± 0.2
$Al(\alpha\text{-}C_3H_5T)_3$[e]	CH_2Cl_2	-0.20 ± 0.02	$+2.2 \pm 0.2$	-0.8 ± 0.1	4.0 ± 0.2
$Al(\alpha\text{-}C_3H_7T)_3$[f]	$C_2H_2Cl_4$	0.0 ± 0.5	$+2.9 \pm 0.5$	-0.9 ± 0.5	3.2 ± 0.5
$Co(\alpha\text{-}C_3H_5T)_3$[g]	$CDCl_3$	-0.8 ± 0.08	-0.3 ± 0.05	-0.7 ± 0.1	3.3 ± 0.1
$Co(\alpha\text{-}C_3H_7T)_3$[h]	$CHCl_3$	-0.94 ± 0.40	-0.2 ± 0.4	-0.9 ± 0.5	4.2 ± 0.5

[a] Temperature ranges and numbers of temperatures at which spectra were simulated in order to obtain temperature dependence of K_{eq} are given in footnotes *d–h*. [b] Errors were determined graphically from maximum and minimum slopes. [c] Estimated maximum error given. [d] −35 to +30°, 15. [e] −63 to +25°, 12. [f] −55 to −20°, 6. [g] −56 to +20°, 14. [h] −55 to −20°, 8.

agree with the fully averaged values at higher temperatures as determined by line-shape analysis. The weighted average of the extrapolated shifts agreed to within 0.5 Hz of the observed fast-exchange shift. A similar procedure was followed for $Al(\alpha\text{-}C_3H_5T)_3$ in dichloromethane (Figure 3). The degeneracy of the T_1, T_2 shifts observed from −60 to −5° was assumed to be maintained throughout the exchange region. The form of the T_3 shift extrapolation was determined from the shifts of the T_2 signal and the observed positions of the average T_2, T_3 shifts (LTP). In the slow-exchange region line widths of resolved signals of each complex were found to be the same (*e.g.*, 2.8 Hz at −24° for Co(III) in $CDCl_3$, 2.5 Hz (−29°) for Al(III) in CH_2Cl_2). In analyzing the LTP the line width at each temperature of the nonexchange-broadened resonances (the cis and one trans signal) was used as the nonexchanging line width of the two trans signals which underwent exchange. For the HTP (*ca.* 30–80°) line widths of all four signals were interpolated between the slow- and fast-exchange values (Al(III), 2.9–1.0 Hz; Co(III), 1.5–1.0 Hz). Due to spin coupling the isopropenyl methyl resonances are the X portion of an $AA'X_3$ pattern and appear as four partially resolved lines of relative intensities 1.0:1.0:0.80:0.75 (low to high field) based on line-shape analysis of spectra obtained at the slow- and fast-exchange limits. Relative populations of isomers were determined by simulation of slow-exchange spectra and yielded the thermodynamic data given in Table II. These data were used to calculate relative populations in the exchange region. Using EXCNMR line shapes were computed for one component of each methyl resonance (C_1, T_1, T_2, T_3) and plotted (Calcomp) by superimposing four such patterns spaced and weighted as described.

(b) $M(\alpha\text{-}C_3H_7T)_3$. The slow-exchange spectra of these complexes revealed less than the eight methyl spin doublets arising from the diastereotopic nature of the methyl groups in the chiral C and T isomers (*vide infra*). These spectra were resolved into eight Lorentzian doublets by a nonlinear least-squares computer program.[36] In the calculations the coupling constants J_{H-Me} were fixed at 7.0 (Al) and 6.9 Hz (Co). The six trans doublets ($T_1, \ldots, T_6$) were assumed to have the same intensity and line widths; a similar assumption was made for the two cis doublets (C_1, C_2). Chemical shifts of each of the eight doublets were treated as independent parameters in the calculations. By this procedure the slow-exchange shifts were determined and are shown in Figures 5 and 6 together with shifts extrapolated through the intermediate exchange region. Linear extrapolations were made in all cases, resulting in agreement within 0.5 (Co(III)) and 2.0 Hz (Al(III)) of the observed fast-exchange shifts. For $Co(\alpha\text{-}C_3H_7T)_3$ the line widths for both the LTP and HTP were obtained by interpolation between the slow- and fast-exchange values of 2.9 and 0.95 Hz, respectively, assuming a temperature dependence similar to that previously observed for isopropyl chelate ring substituents.[37] For $Al(\alpha\text{-}C_3H_7T)_3$ the fast-exchange line width of 3.0 Hz was used throughout the exchange region inasmuch as the line width of the TMS reference peak was constant over that temperature range. Upfield components of the methyl doublets of the Co(III) complex were found to have an intensity 0.95 times that of the low-field component. For the Al(III) complex at 220 MHz the two components were of equal intensity. Relative populations of isomers were determined by the nonlinear least squares; thermodynamic data are entered in Table II. Methyl line shapes were calculated by superpositions of two lines separated by the values of J_{H-Me}. Further discussion of line-shape calculations for the isopropyl and isopropenyl complexes is given in the text and the Appendix.

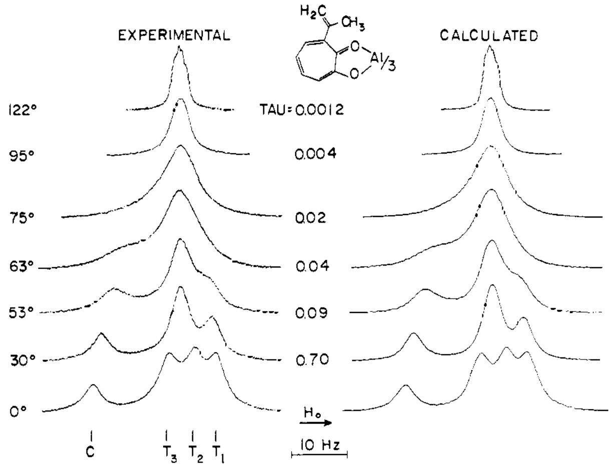


Figure 7. Experimental methyl spectra (100 MHz) of cis (C) and trans (T) $Al(\alpha\text{-}C_3H_5T)_3$ in 1,1,2,2-tetrachloroethane and spectra calculated for random exchange. τ values are in seconds.

Ligand Exchange. It has been shown previously that the rate of ligand exchange between $H(\alpha\text{-}C_3H_7T)$ and $Al(\alpha\text{-}C_3H_7T)_3$ in tetrachloroethane is slow compared to rates of intramolecular averaging of inequivalent methyl groups.[17] Similarly, in a deuteriochloroform solution of $H(\alpha\text{-}C_3H_5T)$ and $Co(\alpha\text{-}C_3H_5T)_3$ two sharp methyl signals are observed under fast-exchange conditions (80°). Further, when $Co(\alpha\text{-}C_3H_5T)_3$ and $Co(\alpha\text{-}C_3H_7T)_3$ are mixed in deuteriochloroform, the pmr spectrum at ambient temperature and at 80° is a superposition of the spectra of the two complexes recorded separately. After several hours of heating at 70° new signals are observed and are assigned to mixed ligand species. These observations demonstrate that the rates of ligand exchange for the aluminum(III) and cobalt(III) complexes are markedly slower than those of their low- and high-temperature processes, which therefore must be intramolecular.

Cobalt(II) Catalysis. In order to determine if the observed kinetic behavior of the $Co(\alpha\text{-RT})_3$ complexes was affected by Co(II) contamination, several experiments were performed. The most likely Co(II) impurity in preparations of $Co(\alpha\text{-RT})_3$ is considered to be $Co(\alpha\text{-RT})_2$. However, as described above, the Co(III) complexes were purified by chromatography under conditions such that Co(II) species were not eluted. Further, addition of up to 20 mol% of $Co(\alpha\text{-}C_3H_7T)_2$ to a deuteriochloroform solution of $Co(\alpha\text{-}C_3H_7T)_3$ at ambient temperature (intermediate exchange conditions) produced no detectable effect on the line shapes of the Co(III) complex. Solutions of $Co(\alpha\text{-RT})_3$ were also exposed to sunlight for several days. Line shapes were found to be the same as those for freshly prepared solutions, indicating the absence of photocatalytic effects such as have been observed in the racemization of $[Co(C_2O_4)_3]^{3-}$ [7b] and the decomposition of $Co(acac)_3$.[38] These results signify that labile Co(II) species, *e.g.*, $Co(\alpha\text{-RT})_3^-$, are not involved in the rearrangement reactions. Because the fastest bimolecular rate constant reported for Co(II)–Co(III) electron transfer is 1.1 M^{-1} sec^{-1} ($(Co(phen)_3)^{2+,3+}$ at 0°[39]), the presence of such a species in small amounts is unlikely to account for the observed kinetic behavior of $Co(\alpha\text{-RT})_3$ (*vide infra*).

---

(36) "Biomedical Computer Programs," UCLA Health Sciences Computing Facility, X Series Supplement, 1969, p 177, BMDX-55.

(37) S. S. Eaton and R. H. Holm, *Inorg. Chem.*, 10, 1446 (1971).

(38) N. Filipescu and H. Way, *ibid.*, 8, 1863 (1969).

(39) Reference 7b, pp 475–476.

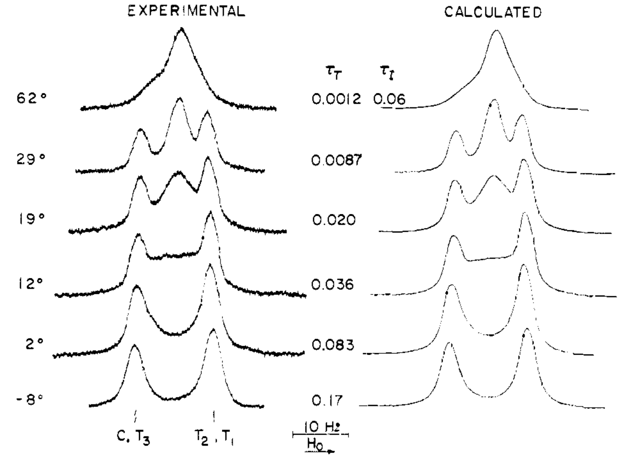


Figure 8. Experimental methyl spectra (100 MHz) of cis (C) and trans (T) Al(α-C_3H_5T)$_3$ in dichloromethane solution, and spectra calculated for inversion (LTP, p-C_3 twist) of the trans isomer below 30°. The spectrum at 62° shows the beginning of isomerization (HTP). τ values are in seconds: τ_T, inversion of T; τ_I, C → T isomerization.

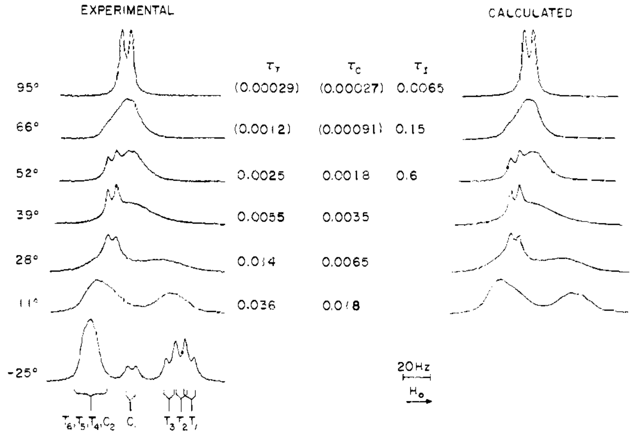


Figure 10. Experimental methyl spectra (220 MHz) of cis (C) and trans (T) Al(α-C_3H_7T)$_3$ in 1,1,2,2-tetrachloroethane solution, and spectra calculated for inversion (LTP, r-C_3 twist (C), p-C_3 twist (T)) below 40° with a random isomerization process (HTP) superimposed above 40°. τ values are in seconds; τ_T, inversion of T; τ_C, inversion of C; τ_I, C → T isomerization. Extrapolated values are in parentheses.

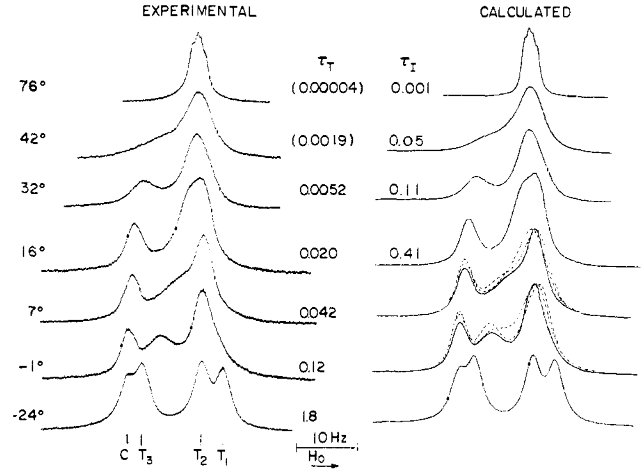


Figure 9. Experimental methyl spectra (100 MHz) of cis (C) and trans (T) Co(α-C_3H_5T)$_3$ in chloroform solution, and spectra calculated for inversion (LTP, p-C_3 twist) below 20° with a random isomerization process (HTP) superimposed above 20°. Spectra calculated using different τ values for an exchange process involving all three trans sites are indicated by the broken lines. τ values are in seconds; τ_T, inversion of T; τ_I, C → T isomerization. Extrapolated values are in parentheses.

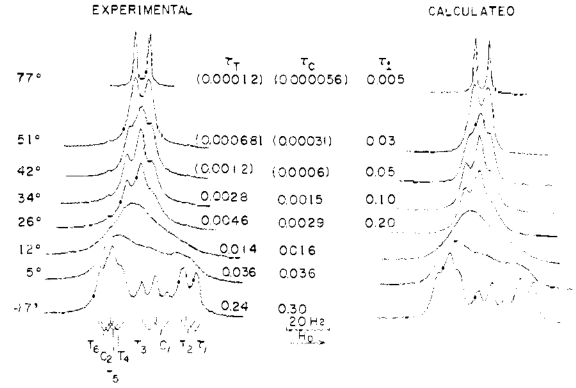


Figure 11. Experimental methyl spectra (100 MHz) of cis (C) and trans (T) Co(α-C_3H_7T)$_3$ in deuteriochloroform solution, and spectra calculated for inversion (LTP, r-C_3 twist (C), p-C_3 twist (T)) below 20° with a random isomerization process (HTP) superimposed above 20°. τ values are in seconds; τ_T inversion of T; τ_C, inversion of C; τ_I, C → T isomerization. Extrapolated values are in parentheses.

Results and Discussion

Slow-Exchange Spectra and Structural Equilibria. Temperature-dependent methyl spectra of complexes **1** and **2** are given in Figures 7-11. The spectrum at the lowest temperature in each figure is appropriate to the slow-exchange limit. Chemical shifts at slow exchange are shown in Figures 2-6. In the absence of exchange an isomeric mixture of M(α-C_3H_5T)$_3$ can exhibit a total of four methyl signals due to the C_3 and C_1 symmetries of the cis and trans forms, respectively. Spectra in tetrachloroethane and deuteriochloroform clearly reveal four signals, with the less intense cis resonance appearing downfield of the three equally intense trans features. Slow-exchange spectra of Al(α-C_3H_5T)$_3$ in dichloromethane exhibit only two resolved resonances (Figure 8). Their unequal intensities require that the cis signal occur in the downfield resonance. Interpretation of the M(α-C_3H_7T)$_3$ spectra at slow exchange is less straightforward. Chirality of the cis and trans isomers renders the methyls of each isopropyl group diastereotopic. As shown in Figure 1, the nonequivalence of methyl groups a and b is readily apparent if each isopropyl substituent is oriented such that its C-H bond is coplanar with the chelate ring. Magnetic environments are arbitrarily designated by r and s.[2] Hence an isomeric mixture generates a total of eight methyl spin doublets. The spectra in Figures 10 and 11 reveal eight to nine resolved or overlapping signals out of the maximum of 16. Assignment of the spectrum of Al(α-C_3H_7T)$_3$ in tetrachloroethane (Figure 10) follows that given elsewhere.[17] The doublet C_1 is readily assigned from its relatively low intensity. The other cis doublet (C_2) was located in the broad downfield resonance on the basis of a nonlinear least-squares analysis of the intensity distribution using Lorentzian line shapes. Signal assignments for Co(α-C_3H_7T)$_3$ were facilitated by examination of the slow-exchange 220-MHz spectrum. The two upfield features in the

100-MHz spectrum (Figure 11) were found to be split into two equally intense spin doublets (T_1, T_2). The overlapping doublets C_1 and T_3 were clearly resolved, with the former less intense than the latter. These results place C_2 in the low-field feature as shown. This assignment was fully consistent with a least-squares analysis of the intensities.

Using the above assignments simulation of the slow-exchange spectra allowed determination of the temperature dependence of the equilibrium constants for the isomerization reaction $C \rightleftharpoons T$. Values of K_{eq} at 25° and thermodynamic quantities for this reaction are collected in Table II. Isomer distributions are nonstatistical and reveal a small preferential stability of the trans form. With one exception thermodynamic values are comparable with those characterizing the isomerization of tris(β-diketonato) Al(III) and Co(III) complexes in weakly polar solvents.[16] The enthalpy change for $Al(\alpha\text{-}C_3H_5T)_3$ is considerably larger than reported values for similar complexes and contrasts with $\Delta H^\circ \sim 0$ for its isopropyl analog. The source of this difference is unclear.

Kinetics and Mechanism of Rearrangement Processes. The possible twist and bond rupture mechanisms and kinetic treatment appropriate to an analysis of the rearrangements of complexes **1** and **2** are given in detail in parts I[1] and II.[2] To supplement these mechanistic considerations, a permutational analysis of the rearrangements of an $M(A\text{-}B)_3$ complex is presented in the Appendix. Definitions of microscopic rate constants and the general forms of the kinetic exchange matrices used in the investigation of the rearrangements of $M(pmhd)_3$ by full line-shape analysis[2,40] are the same as those employed here. The exchange matrix for the isopropenyl methyl groups is easily obtained from that appropriate to isopropyl methyl environmental interchange by removing the distinction between r and s environments and is identical with that for the β protons of cis and trans $M(pmhd)_3$.[2] As the results presented below indicate, the methyl spectra of the LTP and HTP of each of the complexes arise from inversion and isomerization, respectively. The LTP averaging pattern of the isopropenyl complexes can be seen visually to be consistent with a twist mechanism (A_6) or a mechanism (A_2) which does not effect inversion at the metal center (see Appendix). Line-shape analysis of the LTP of the isopropyl complexes shows the averaging to be consistent with a trigonal twist (A_6) or a mechanism (A_5) which inverts at the metal without exchanging the sites x, y, z of the trans isomer. Due to the close similarity between the isopropyl and isopropenyl complexes it seems reasonable to assume that the rearrangement mechanism is the same for both, which leaves the trigonal twist (A_6) as the sole mechanism which is consistent with all the spectra. The necessarily detailed arguments which establish the trigonal-twist pathway for the LTP of the isopropyl complexes are presented in the Appendix. The sections immediately following describe the exchange-broadened spectra and kinetic data obtained by line-shape analysis and compare and contrast the kinetic and mechanistic behavior of tropolonate complexes with that of other tris chelates.

As shown in Figure 1, the three inequivalent methyl and isopropyl sites of the trans isomers are designated by x, y, and z. These sites in the cis forms are identical. Trigonal twists about the p-C_3 axis of trans $M(\alpha\text{-}C_3H_5T)_3$ and $M(\alpha\text{-}C_3H_7T)_3$ or about the true or real (r-C_3) threefold axis of cis $M(\alpha\text{-}C_3H_7T)_3$ are illustrated. Three other axes which bisect opposite triangular faces of idealized octahedral configurations of the cis and trans isomers are termed imaginary (i-C_3) threefold axes.[1,2] Twist motions about these axes correspond to rhombic twists.

(a) $M(\alpha\text{-}C_3H_5T)_3$. The temperature-dependent spectra of $Al(\alpha\text{-}C_3H_5T)_3$ in tetrachloroethane (Figure 7) reveal that all four methyl signals undergo essentially simultaneous exchange broadening and shifting. The uncertainty in the temperature dependence of the small chemical shift difference between signals T_2 and T_3 (Figure 2) makes it difficult to determine whether these signals coalesce due to chemical exchange or chemical shift degeneracy between 0 and 30°. Only one broad feature is observed above 75°, which sharpens in the fast-exchange limit to a spin multiplet due to coupling of the methylene and methyl protons. These spectra can be simulated on the basis of a cis–trans isomerization. Assuming as previously[2] that rotations about the three i-C_3 axes of each isomer are equally probable and that all metal–ligand bonds rupture with equal probability,[41] exchange matrices are generated which differ only in the four matrix elements related to interconversion of the trans sites y and z ($y \rightarrow y$, $y \rightarrow z$, $z \rightarrow z$, $z \rightarrow y$). The matrices afford very similar line shapes, making the exchange an apparently random process. Assuming that T_2 and T_3 have averaged or have degenerate shifts, the spectra from 30 to 110° can be accurately simulated with either assumption using τ values for random exchange which agree within 10%. Hence, the spectra of this complex in tetrachloroethane permit detection of only one kinetic process and provide no evidence as to its mechanism.

In contrast to the behavior in tetrachloroethane, the spectra of $Al(\alpha\text{-}C_3H_5T)_3$ in dichloromethane (Figure 8) reveal two averaging processes and afford evidence for the mechanism of the LTP. Between 0 and 30° one signal from each of the two composite slow-exchange resonances broadens and coalesces. Relative intensities of the three resultant signals at 29° reveal that the cis and one trans signal are unaffected, requiring an exchange process which averages two trans sites without involving the cis isomer. By 62° all resonances are markedly broadened due to the onset of isomerization. Satisfactory spectra above 62° could not be obtained due to the low boiling point of the solvent.

The spectra of $Co(\alpha\text{-}C_3H_5T)_3$ in deuteriochloroform (Figure 9) span the slow- and fast-exchange limits and immediately reveal that this complex must be cate-

---

(40) The element corresponding to the environmental change $T_{yr} \rightarrow T_{ys}$ in matrix 3 of ref 2 should be 0 rather than $^1/_8$. The correct matrix element was used in the line-shape calculations reported therein.

(41) These assumptions are also made in the analysis of the HTP of all other systems. The assumption of equal probability of bond rupture implies that the two inequivalent M–O bonds of the cis form and the six inequivalent M–O bonds of the trans form have essentially equal strengths. While not subject to experimental verification, this assumption is considered reasonable so long as coordinated tropolonate possesses a resonance delocalized structure as found in FeT_3,[24] ThT_4, SnT_3Cl, and $SnT_3(OH)$,[28] and NaT.[42a] Evidence for C–C bond-length alternation and different C–O and M–O bond lengths has been found only for CuT_2, where the existence of these features has been attributed to crystal-packing effects.[42b]

(42) (a) R. Shiono, *Acta Crystallogr.*, **14**, 42 (1961); Y. Sasada and I. Nitta, *ibid.*, **9**, 205 (1956); (b) W. M. Macintyre, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc., Ser. A*, **289**, 161 (1967).

gorized as fast. Two kinetic processes are clearly evident. Below *ca.* 20° the averaging pattern is the same as for Al(α-C_3H_5T)$_3$ in dichloromethane. The trans component (T_3) of the low-field pair of slow-exchange resonances averages with the upfield component (T_1) of the pair of signals occurring at higher field while not affecting the remaining cis and trans signals. The fast-exchange limit is reached at *ca.* 20°. In the 16° spectrum the coalesced feature occurs as a shoulder on the upfield resonance (T_2). At higher temperatures all signals average due to cis–trans isomerization (HTP) and the fast-exchange spectrum (76°) reveals a single methyl spin multiplet. Spectra at intermediate temperatures are similar to those above *ca.* 60° for Al(α-C_3H_5T)$_3$ in tetrachloroethane (Figure 7).

The averaging patterns for the LTP of Al(α-C_3H_5T)$_3$ in dichloromethane and Co(α-C_3H_5T)$_3$ in deuteriochloroform are consistent with inversion of the trans isomers by a trigonal twist about the p-C_3 axis. As shown in Figure 1, this mechanism results in inversion *without* isomerization and effects the following site interchanges for methyl groups 1, 2, and 3.

$$\mathrm{T\Lambda}\begin{Bmatrix}1 - y\\ 2 - x\\ 3 - z\end{Bmatrix} \rightleftharpoons \begin{Bmatrix}1 - z\\ 2 - x\\ 3 - y\end{Bmatrix}\mathrm{T\Delta}$$

The signals labeled T_2 in Figures 7 and 8 are associated with environment x. The cis isomers are presumably undergoing a similar, but pmr-undetectable, inversion at comparable rates. Our previous analysis[2] of the twist processes for trans isomers has shown that rotations about i-C_3 axes lead either to formation of the cis isomer or to interchanges involving all three sites, both of which are contrary to observation. The possibility of three-site interchange of the trans form was further investigated by line-shape calculation. Simulated line shapes corresponding to the −1 and 7° exchange-broadened spectra of Co(α-C_3H_5T)$_3$ are shown in Figure 9. These spectra were calculated with those values of τ_T (defined below) which produced the best fits with the experimental spectra. The simulated spectra clearly do not adequately match the experimental line shapes whereas those calculated for two-site interchange accurately reproduce the observed spectra. Bond-rupture mechanisms for the LTP of both complexes can be excluded on the basis of site interchanges generated by either TBP or SP transition states.[43] If all bonds of the trans form are broken with equal probability, the cis isomer is necessarily formed. If the fortuitous event that only those bonds are ruptured which produce transition states yielding exclusively the trans isomer is entertained, the consequences are as follows. (i) No SP transition state can generate products which only average two sites. Further, the operation of SP-primary and -secondary mechanisms[2] leads to cis and trans products. (ii) While TBP transition states which generate products with one type of two-site interchange can be produced by rupture of a specific bond, a corollary requirement is that only the axial or equatorial form of the transition state be of kinetic consequence. Highly discriminate bond rupture, as well as the additional requirement of (ii), is considered to be physically unrealistic. On the basis of these considerations and others presented in the Appendix, a trigonal twist is concluded to be the predominant mechanism for the LTP of M(α-C_3H_5T)$_3$ complexes.

(b) M(α-C_3H_7T)$_3$. The temperature-dependent spectra of Al(α-C_3H_7T)$_3$ in tetrachloroethane and Co(α-C_3H_7T)$_3$ in chloroform are displayed in Figures 10 and 11, respectively. The latter complex, like its isopropenyl analog, is stereochemically nonrigid. Cis and trans spin doublets are numbered sequentially from high to low field. The pattern of signal averaging is similar for the two complexes.[44] The methyl doublets first merge into two broad features of unequal intensity. At higher temperatures in the intermediate exchange region these features coalesce to a broad resonance with two relatively sharp signals superimposed on the low-field side. Further increase in temperature results in a single broad resonance (Al) or an unsymmetrical set of three resonances (Co), both of which pass to one sharp spin doublet in the limit of fast exchange. The experimental spectra were analyzed in terms of two kinetic processes. At temperatures below *ca.* 40° for Al(α-C_3H_7T)$_3$ and below *ca.* 30° for Co(α-C_3H_7T)$_3$, the spectra of each complex (LTP) could be accurately simulated by line-shape analysis on the basis of r-C_3 and p-C_3 twists for the cis and trans isomers, respectively. For the cis form the twist results in the following environmental interchanges for methyl groups a and b.

$$\mathrm{C\Lambda}\begin{Bmatrix}\mathrm{a - r}\\ \mathrm{b - s}\end{Bmatrix} \rightleftharpoons \begin{Bmatrix}\mathrm{a - s}\\ \mathrm{b - r}\end{Bmatrix}\mathrm{C\Delta}$$

For the trans form the interchanges are the same as for the isopropenyl complexes with an additional r $\rightleftharpoons$ s interconversion for each methyl group. In the higher temperature region the spectra could be satisfactorily interpreted in terms of cis–trans isomerization (HTP) with random site interchange. Comparison of the calculated and experimental spectra (Figures 10 and 11) reveals satisfactory agreement. None of the bond rupture or other twist mechanisms recently analyzed[1,2] for M(A–B)$_3$ complexes, when assumed for the LTP of either complex, gave calculated spectra which agreed with the observed line shapes over the full exchange-broadened regions. Details of the line-shape calculations and elimination of other mechanisms are discussed in the Appendix.

The preexchange lifetime τ (sec) employed in the calculations of the line shapes shown in Figures 7–11 refers to the following processes.

$$\mathrm{C\Delta} \xrightarrow{k_C} \mathrm{C\Lambda} \quad \tau_C = 1/k_C \tag{1}$$

$$\mathrm{T\Delta} \xrightarrow{k_T} \mathrm{T\Lambda} \quad \tau_T = 1/k_T \tag{2}$$

$$\mathrm{C\Delta(C\Lambda)} \xrightarrow{k_1} \mathrm{T\Delta(T\Lambda)} \tag{3}$$

$$\mathrm{C\Delta(C\Lambda)} \xrightarrow{k_2} \mathrm{T\Lambda(T\Delta)} \tag{4}$$

$$k_1 = k_1 + k_2,\ \tau_I = 1/(k_1 + k_2)$$

k_I and τ_I are the rate constant and preexchange lifetime for isomerization. No mechanistic information could be deduced for the HTP of any of the complexes. Exchange matrices corresponding to various isomerization mechanisms[2] were tested, but the resultant calculated spectra fit the experimental line shapes adequately, albeit with slightly different τ values. Line shapes

---

(43) See Tables V, VI, and VII of ref 2.

(44) Spectra of Al(α-C_3H_7T)$_3$ in tetrachloroethane at several temperatures other than those shown in Figure 10 are given in ref 17.

Table III. Kinetic Parameters for the Intramolecular Rearrangements of Tropolonate Complexes

Compound	Process	$\Delta G^{\ddagger}_{298°}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	log A	$k_{298°}$, sec^{-1}
Al(α-C_3H_5T)$_3$[a]	C → T[b]	17.5 ± 1.4	16.2 ± 1.0	−4.3 ± 3.2	16.9 ± 1.1	12.3 ± 0.6	1.0
	TΔ → TΛ[c]	14.9 ± 1.2	12.6 ± 1.4	−7.4 ± 4.8	13.2 ± 1.4	11.6 ± 0.7	80
Al(α-C_3H_7T)$_3$[b]	CΔ → CΛ[d]	14.6 ± 5.0	10.0 ± 3.6	−16 ± 12	10.5 ± 3.6	9.9 ± 2.6	120
	TΔ → TΛ[d]	14.9 ± 2.8	11.7 ± 2.0	−11 ± 7	12.3 ± 2.0	10.8 ± 1.4	75
	C → T[e]	18.7 ± 5.3	25.1 ± 4.0	21 ± 12	25.8 ± 4.0	18.0 ± 2.7	0.04
Co(α-C_3H_5T)$_3$[a,f]	TΔ → TΛ	14.3 ± 0.7	16.2 ± 1.1	5.4 ± 3.9	16.7 ± 0.9	14.4 ± 0.6	100
	C → T	16.5 ± 1.0	14.9 ± 1.2	−5.3 ± 3.7	15.5 ± 1.1	12.1 ± 0.5	4.0
Co(α-C_3H_7T)$_3$[a,g]	CΔ → CΛ	14.3 ± 1.5	13.7 ± 1.1	−2.1 ± 3.5	14.3 ± 1.0	12.7 ± 0.6	210
	TΔ → TΛ	14.1 ± 1.8	15.6 ± 1.4	4.8 ± 3.9	16.1 ± 1.3	14.3 ± 0.6	350
	C → T	16.6 ± 1.6	15.0 ± 1.3	−5.1 ± 4.2	15.7 ± 1.4	12.1 ± 0.5	5.0

[a] Error estimates calculated as three times the standard deviation in the least-squares lines for τ values accurate to ±10%. [b] $C_2H_2Cl_4$. [c] CH_2Cl_2. [d] Error estimates calculated as three times the standard deviation in the least-squares lines for τ values accurate to ±15%. [e] Error estimates calculated as three times the standard deviation in the least-squares lines for τ values uncertain from ±30 to ±75% at the low- and high-temperature ends of the isomerization region, respectively. [f] $CDCl_3$. [g] $CHCl_3$.

for the HTP of each complex were calculated on the basis of random-site interchange. Least-squares plots of the Arrhenius equation, $k = 1/\tau = A \exp(E_a/RT)$, for the intramolecular rearrangements of the four complexes are given in Figures 12 and 13. τ values were also fit to the Eyring equation, $k = 1/\tau = (kT/h) \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$. Rate constants at 25° and activation parameters are summarized in Table III.

Rh(α-C_3H_5T)$_3$ and Rh(α-C_3H_7T)$_3$. The stereochemically nonrigid behavior of Co(α-RT)$_3$, which is unprecedented among Co(III) complexes, led to an investigation of the temperature-dependent 100-MHz methyl spectra of their Rh(III) analogs. At ambient temperatures Rh(α-C_3H_5T)$_3$ in deuteriochloroform displayed three resolved but overlapping signals at 1.87, 1.90, and 1.93 ppm downfield of TMS. Measurements at temperatures up to 73° indicated a small temperature dependence of the chemical shifts but provided no evidence of exchange broadening. Similar results were obtained in chlorobenzene from 27 to 144°. The ambient temperature spectrum of Rh(α-C_3H_7T)$_3$ in tetrachloroethane revealed a large spin doublet at 4.73 ppm and three partiallly resolved doublets centered at 4.91, 4.95, and 4.99 upfield of the solvent resonance. Chemical shifts were found to be somewhat temperature dependent, and at 146°, the highest temperature of observation, some 13 methyl signals were resolved. These results clearly show that the fast behavior of the Co(III) complexes does not extend to the corresponding Rh(III) species.

Kinetic and Mechanistic Comparisons. Rate constants and activation energies for the rearrangements of other Al(III) and Co(III) tris chelates are given in Table IV. The data refer to inversion and/or isomerization of the slow Co(III) complexes and environmental interchange of methyl or perfluoromethyl groups of the fast Al(III) complexes. Comparison of kinetic results among the tropolonates or among the various complexes in Tables III and IV is not as precise as might be desired due to differences in solvents and the lack of full sets of activation parameters for a number of the complexes in Table IV. However, several useful comparisons can be made. As earlier qualitative results[17] indicated, rearrangements of Al(III) tropolonates are considerably faster than those of nonfluorinated Al(III) β-diketonates but comparable to rates for complexes containing perfluoromethyl groups.[16] Much more striking and significant are the remarkable differences in rates between the tropolonates and other Co(III) complexes. As one example, *trans*-Co(α-C_3H_5T)$_3$ inverts *ca.* 10^{11} times more rapidly than Co(acac)$_3$ in weakly polar media at 25°. Because the activation parameters of the latter[20] are quite similar to those for simultaneous inversion and isomerization of Co(mhd)$_3$[1] and Co(bzac)$_3$[21] in the same solvent (chlorobenzene), it is probable that Co(acac)$_3$ inverts primarily by means of a bond-rupture pathway. The relatively rigid nature of the Rh(III) tropolonates compared with the nonrigidity of their Co(III) analogs correlates with the relative inversion rates of Rh(acac)$_3$ and Co(acac)$_3$. The activation energy of the former is at least *ca.* 9 kcal/mol greater than that of Co(acac)$_3$.[20] A similar difference for the tropolonates could place the range of dynamic behavior above the highest temperature of the pmr observations if preexponential factors for the Co(III) and Rh(III) complexes are similar. Another and more relevant guide to the relative rigidities of cobalt and rhodium tropolonates is found in fluxional molecules of the type H_2ML_4 and MHL_4 where the re-

Table IV. Rearrangement Rates and Activation Energies for Al(III) and Co(III) Tris-Chelate Complexes

Compound[a]	E_a, kcal/mol	$k_{298°}$, sec^{-1}	Ref
Al(pmhd)$_3$	28–30	4×10^{-4}	2
Al(tfac)$_3$	24		11
Al(dibm)$_3$	15 (19[d])		26
Al(acac)(hfac)$_2$	19–21	0.8–1.5	*b*
Al(acac)$_2$(hfac)	18	80	*b*
Al(acac)$_2$(bzbz)	22	2×10^{-3}	*b*
Co(acac)$_3$	35	8×10^{-10} [c]	20
Co(mhd)$_3$	31–33	$\sim 10^{-9}$ [c]	1
Co(bzac)$_3$	32–33	$\sim 10^{-9}$ [c]	21
Co(tfac)$_3$	31	$\sim 10^{-8}$ [c]	11
Co(S_2CO-1-bornyl)$_3$		4×10^{-5} (60°)	*e*
Co(S_2CO-*l*-menthyl)$_3$	~20	4×10^{-7}	*f*
[Co($S_2COCH_2CH_2SO_3$)$_3$]$^{3-}$ [g]	27	$\sim 10^{-5}$	*h*
[Co(C_2O_4)$_3$]$^{3-}$ [g]		2×10^{-5}	53

[a] dibm = diisobutyrylmethanide; bzbz = dibenzoymethanide; hfac = hexafluoroacetylacetonate. [b] D. A. Case and T. J. Pinnavaia, *Inorg. Chem.*, **10,** 482 (1971). [c] Extrapolated value. [d] More precise value as quoted in ref 7a. [e] H. Krebs and R. Rasche, *Naturwissenschaften*, **41,** 63 (1954). [f] H. Krebs and W. Schumaker, *Z. Anorg. Allg. Chem.*, **344,** 187 (1966). [g] Aqueous solution. [h] H. Krebs, J. Diewold, H. Arlitt, and J. A. Wagner, *Z. Anorg. Allg. Chem.*, **287,** 98 (1956).

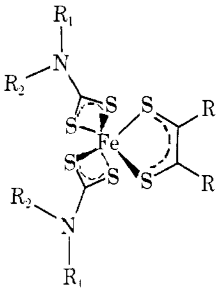
Table V. Structural Data[a] for Selected Tris-Chelate Complexes

Complex	Angle, deg: Twist (ϕ)	Angle, deg: Bite	Distance, Å: Metal–ligand	Distance, Å: Bite	Ref
$Fe(Et_2dtc)_2(tfd)$	33,[b] 41[c]	75[b], 88[c]	2.31,[b] 2.20[c]	2.80,[b] 3.05[c]	23
$Fe(MePhdtc)_3$	40	(76)[d]	2.30, 2.33	(2.90)[d]	*e*
FeT_3	40	78	2.01	2.52	24
$Fe(phen)_3{}^{2+}$	~56	83		2.61	*f*
$Fe(acac)_3$	~60[k,l]	87	1.99	2.89	*g*
$Co(Et_2dtc)_3$	43	76	2.26	2.79	*h*
$Co(S_2COEt)_3$	42	76	2.28	2.81	*i*
CoT_3	~55	86	1.88	2.55	47
$Co(C_2O_4)_3{}^{3-}$	54	84	1.92	2.86	*j*
$Co(acac)_3$	~60[k]	97	1.90	2.85	27
$Al(acac)_3$	~60[k]	92	1.89	2.72	27

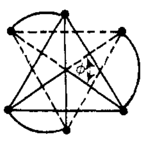
[a] Average values given. [b] Et_2dtc. [c] tfd. [d] Approximate value in $Fe(S_2COEt)_3$ ($\phi = 41°$), which has doublet ground state: B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970). [e] P. C. Healy and A. H. White, *ibid.*, 1446 (1971). [f] Data calculated from atomic coordinates supplied by Professor D. Templeton and Dr. A. Zalkin for antimonyl-*d*-tartrate salt. [g] J. Iball and C. H. Morgan, *Acta Crystallogr.*, **23**, 239 (1967). [h] S. Merlino, *Acta Crystallogr., Sect. B*, **24**, 1441(1968); T. Brennan and I. Bernal, *J. Phys. Chem.*, **73**, 443 (1969). [i] S. Merlino, *Acta Crystallogr., Sect. B*, **25**, 2270 (1969). [j] K. R. Butler and M. Snow, *J. Chem. Soc. A*, 565 (1971); *Chem. Commun.*, 550 (1971). [k] Approximate octahedral structure implied by structural data; exact values unknown. [l] A value of 54° has been published.[50]

arrangement barriers[45] increase uniformly within a specific transition metal group in going from first to second to third row elements. The relative difference in $\Delta G^{\neq}$ value for first and second row transition metals found for these series would be sufficient to account for the observed data on the tropolonates.

As mentioned at the outset, the principal motivation for undertaking the present study has been to investigate any relation between ground-state structures (established in the crystalline phase) and rearrangement mechanisms. Structural data for a number of tris-chelate complexes, some of which are the same as, or analogous to, complexes for which kinetic data are available (Table IV), are set out in Table V. An apparent structure-mechanism correlation has been found for the fast complexes **3** (R_1, R_2 = alkyl, Ph: R = CF_3, CN) whose structural parameter of interest is the twist angle, defined generally by **4**. The LTP of these complexes is one of inversion by a p-C_3 twist.[15,19] A representative member of the series, $Fe(Et_2dtc)_2(tfd)$, has a structure intermediate between the TP and TAP limits.[23] A second correlation between intermediate stereochemistry and mechanism is afforded by the current work of Palazzotto and Pignolet.[46] Below *ca.* −40° $Fe(MePhdtc)_3$ ($\phi = 40°$) exists as cis and trans isomers due to slow rotation about the C–N bonds. The same averaging pattern of methyl signals of the trans form as for $M(\alpha\text{-}C_3H_5T)_3$ has been observed. A similar relationship between operation of a trigonal-twist mechanism and intermediate stereochemistry does not obtain for the Co(III) tropolonates. A structural investigation of $CoT_3 \cdot CHCl_3$ reveals a near-TAP stereochemistry[47] ($\phi = 55°$) rather than the intermediate stereochemistry found for the Fe(III) analog.[48] Provided solid-state and solution structures are the same, the small displacement from the TAP limit is unlikely to be the principal structural feature accounting for the twist mechanism and the stereochemical nonrigidity.[48] The results in Tables IV and V reveal other cases where intermediate stereochemistry, assessed by the structural parameter ϕ, does not lead to fast kinetic behavior. Twist angles of CoT_3 and $Co(C_2O_4)_3{}^{3-}$ are essentially identical, yet the rate constant for uncatalyzed inversion of the latter[53] clearly places it in the slow category. Tris(dithiocarbamato)- and tris(xanthato)-Co(III) complexes have considerably smaller twist angles. Kinetic studies of xanthate complexes and pmr results[54] for several N,N-disubstituted dithiocarbamate



3



4

---

(45) (a) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971); (b) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *ibid.*, **93**, 1797 (1971).

(46) M. C. Palazzotto and L. H. Pignolet, *J. Chem. Soc., Chem. Commun.*, 6 (1972).

(47) A. P. Gaughan and R. Eisenberg, private communication. The data in Table V were obtained at a stage of refinement with $R = 11\%$. Crystalline samples of $Co(\alpha\text{-}C_3H_5T)_3$ or $Co(\alpha\text{-}C_3H_7T)_3$ suitable for X-ray studies could not be obtained.

(48) It is noted that there is no unique relationship between ϕ and the metal–ligand distance r even with a fixed bite distance d. The following relationship, in which s is the length of an edge of a triangular face, is readily derived[49] for complexes of minimal D_3 symmetry: $d^2 = 4r^2 - (4/3)s^2 \cos^2 \phi/2$. For the rigid tropolonate ligand d is essentially constant. If r is changed in going from one metal ion to another, compensating changes must occur in s and/or ϕ. If d and s are held constant the change in r of 0.13 Å (2.01–1.88 Å) on passing from FeT_3 to CoT_3 would require that ϕ increase from *ca.* 40° to *ca.* 80°. Actually, s decreases by *ca.* 0.2 Å as ϕ increases to 55° in CoT_3. Aluminum(III) and cobalt(III) have comparable six-coordinate ionic radii[51] and presumably have comparable twist angles in their tropolonates if metal ion size differences and d-electron effects dominate the geometry.[52] Gallium(III) has a radius similar to high-spin iron(III) and may have a twist angle of 40–50°. $Ga(\alpha\text{-}C_3H_7T)_3$ is less rigid than its aluminum analog.[17] On the other hand, $Rh(\alpha\text{-}RT)_3$, which could have a smaller twist angle than $Co(\alpha\text{-}TR)_3$ due to the larger size of the metal ion, is far more rigid than the latter.

(49) An equivalent expression has been derived independently.[50]

(50) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972).

(51) J. P. Jesson and E. L. Muetterties, "Chemist's Guide," Marcel Dekker, New York, N. Y., 1969.

(52) Angular overlap calculations show that the electronic energy of the low-spin d^6 configuration is minimized in the 50–56° ϕ region for complexes having bite angles of 70–85°, thereby indicating a possible electronic contribution to the observed geometry of CoT_3. These calculations are discussed elsewhere: E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, in press.

(53) J. A. Broomhead, I. Lauder, and P. Nimmu, *J. Chem. Soc. A*, 645 (1971).

(54) T. H. Siddall, III, *Inorg. Nucl. Chem. Lett.*, 7, 545 (1971).

complexes, which indicate slow C–N bond rotation and chiral structures at room temperature, demonstrate that these complexes are also of the slow type. While the rate increases of 10^1–10^4 compared to the Co(III) β-diketonates are presumably significant, attempts to relate structural parameters of these slow complexes to comparative kinetic properties must await establishment of their rearrangement mechanisms. These considerations reveal that, although twist angles substantially less than 60° are apparently associated with the trigonal-twist and stereochemical nonrigidity in several instances, they are not necessarily reliable indicators of these properties, particularly for Co(III) complexes. The effect of twist angle on the rearrangements of Al(III) tropolonates cannot be assessed at present due to the lack of structural information.[54a]

Further comparisons of kinetic and mechanistic properties are restricted to tropolonate and β-diketonate complexes, which contain the $M–O_6$ core and have been investigated in weakly polar media. The data in Table V show that these complexes have very similar M–O distances but differ significantly in bite distances and angles. A further important difference between the two types of complexes is the ligand structures. The tropolonate ion is a rigid planar unit. Consequently, any bond-rupture process producing a five-coordinate transition state of kinetic significance (*vide infra*) would require deformation of the M–O–C angle of the intact bond of the same tropolonate ligand. In contrast, β-diketonate ligands have the possibility of internal bond rotation after rupture of an M–O bond, allowing removal of one end of the ligand from the immediate vicinity of the metal ion. In this sense tropolonate can be likened to *o*-phenanthroline. $Fe(phen)_3^{2+}$ has essentially the same twist angle as CoT_3 and a slightly larger bite distance (Table V). Ligand exchange of the former is much slower than inversion.[7a,b,55] The rigid geometry of the phen ligand may not allow it to act as an effective monodentate necessary for a bond-rupture pathway, and a trigonal-twist mechanism has been proposed.[55] The same structural feature is postulated to be operative in the tropolonates, thereby suppressing a bond-rupture mechanism in the LTP of the Al(III) and Co(III) complexes. Considering next the relative stabilities of the TP transition states for tris(β-diketonates) and tris(tropolonates), the following widths (s) and heights (h) have been estimated assuming the same bite distances and angles as in the ground-state structures: $Co(acac)_3$, $s = 2.16$ Å, $h = 2.85$ Å; CoT_3, $s = 2.36$ Å, $h = 2.55$ Å. From these data the ratios s/h are 0.76 and 0.93 for the trigonal-prismatic intermediates derived from $Co(acac)_3$ and CoT_3, respectively. The latter is much closer than the former to the values cited for stable trigonal-prismatic complexes.[50] The ratios of polyhedron radius to polyhedron edge length are 0.66 for $Co(acac)_3$ and 0.74 for CoT_3. The latter is quite close to the value of 0.76 calculated by Day and Hoard[28] for a stable trigonal-prismatic arrangement of six identical ligands and found for a number of dithiolene and diselenetene complexes which possess this geometry.[56] The smaller value of s for $Co(acac)_3$ suggests larger O···O interactions along the triangular edges and a consequent destabilization of the trigonal prism. These data suggest that the potential energy surface as a function of the twist angle is relatively higher and lower at 60 and 0°, respectively, for tris(tropolonato)metal complexes than for the acetylacetonato analogs. Hence the trigonal-prismatic state in the stereoisomeric form with tropolonate ligands only spanning edges of rectangular faces would appear to be more readily accessible than the trigonal-prismatic state for either stereoisomeric form with acetylacetonate ligands or the trigonal-prismatic state in the stereoisomeric form with tropolonate ligands spanning edges of rectangular and triangular faces. This is of course consistent with the twist mechanism proposed for the LTP or inversion process in the tropolonates. The strikingly low barrier to rearrangements in cobalt tropolonates may be partly a consequence of the rigid character of the tropolone ion. Assessment of the relative stabilities of MT_3 and $M(acac)_3$ TP transition states is, however, speculative, especially in view of possible changes in spin multiplicity of CoT_3 throughout the inversion process.[57] Further experiments are required in order to define the effects of bite distances and angles and ligand rigidity on rearrangement rates and mechanisms of $M–O_6$ complexes.[58] In particular, the source of the much larger differential rate increase for inversion of Co(III) tropolonates and β-diketonates, compared to the corresponding Al(III) complexes, remains to be elucidated.

"Twist-with-Rupture" Mechanism. The trigonal-twist mechanism as it is generally conceived involves concerted twist motions of the three chelate rings around an r-C_3 or p-C_3 axis. The TP transition state formed in this way may generate product enantiomer or initial enantiomer by continuation or reversal of the twist motion (*cf.* Figure 1), without actual metal–ligand bond rupture. While this conception is entirely reasonable, another interpretation of the twist mechanism is indicated by the sequence **5**–**8** for a trans isomer. Bond rupture generates, *e.g.*, **6**, which twists or "pseudorotates" the starred vertices giving **7**. Bond formation generates the inverted isomer **8**. Such a process requires that the conversion **6** → **7** be fast compared to any reorientation of the dangling ligand. Entity **6** has the geometry of a SP-basal transition state (kinetically equivalent to TBP-axial[1]) which can yield both CΔ and TΔ products by attack of the dangling end at the starred positions.[1,2] The "twist-with-rupture" sequence

---

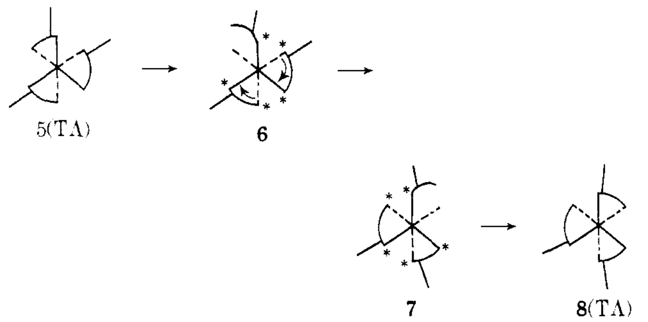
[54a] NOTE ADDED IN PROOF. The twist angle of crystalline AlT_3 has been determined to be 49°: E. L. Muettertries and L. J. Guggenberger, *J. Amer. Chem. Soc.*, in press. As for $Co(\alpha\text{-}RT)_3$, this structural feature itself is insufficient to explain the fast rates and the twist mechanism of $Al(\alpha\text{-}RT)_3$

(55) P. Dowley, K. Garbett, and R. D. Gillard, *Inorg. Chim. Acta*, **1**, 278 (1967).

(56) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970); C. G. Pierpont and R. Eisenberg, *J. Chem. Soc. A*, 2285 (1971). Ratios of 0.75–0.77 have been calculated from the reported structural data. In addition to regular TP structures, an example of irregular TP stereochemistry has recently been reported. The structural parameters for $Er(dpm)_3$ indicate ratios of s/h ranging from 1.09 to 1.25 for various edges and a ratio of metal–ligand bond distance to bite distance of 0.83: J. P. R. de Villiers and J. C. A. Boeyens, *Acta Crystallogr., Sect. B*, **28**, 2335 (1971).

(57) It has been suggested previously that Fe(II) in $Fe(phen)_3^{2+}$ is excited to a high-spin state prior to twisting.[7b] The large $\Delta S^{\ddagger}$ value (+21 eu) considered consistent with this suggestion was not found for the inversion reactions of $Co(\alpha\text{-}RT)_3$ (Table III). However, the Fe(II) and Co(III) complexes were studied in different solvents.

(58) Attempts to prepare complexes from the enolate anion (estimated bite distance 2.8 Å) of 3-methylcyclopentene-1,2-dione [G. Singh, *J. Amer. Chem. Soc.*, 78, 6109 (1956)] have thus far proven unsuccessful. A cobalt derivative of this anion was expected to be stereochemically more rigid than the tropolone analogs.



is presented only to indicate that observation of pmr site interchanges consistent with a trigonal twist does not nessarily require a non-bond-breaking rearrangement pathway. The above sequence and the conventional visualization of the twist mechanism in Figure 1 are limiting representations of the same overall transformation, inversion without isomerization, and are not subject to direct experimental differentation in the present study or in other cases[15,19,46] where nmr data are sensibly compatible only with a trigonal twist.

Activation Parameters for the Trigonal Twist. The proposal[12] that small frequency factors and corresponding negative entropies of activation are associated with twist mechanisms has received considerable attention.[7a] Some support for this proposal is obtained from kinetic data for the inversion of the complexes **3** for which log $A \sim 12$ and $\Delta S^{\ne}$ ranges from *ca.* -3 to -8 eu.[15,19] Bond-rupture processes for Co(III) β-diketonates are characterized by log $A \sim 14$–16 and positive $\Delta S^{\ne}$ values.[1,21] Kinetic parameters for four of the six inversion reactions studied (Table III) are characterized by negative activation entropies and values of log A from 10 to 13. However, the remaining two reactions have positive $\Delta S^{\ne}$ values and log $A \sim 14$. In view of these results and the relatively large uncertainties in $\Delta S^{\ne}$ values obtained by line-shape analysis, further data for demonstrated twist processes in a number of different solvents must be accumulated before any generally valid correlation between activation parameters and mechanisms can be accepted.[59]

Appendix

A. Kinetic Analysis of M(α-C_3H_7T)$_3$. Tris(α-isopropyltropolonato)metal(III) complexes are of the M(A–B)$_3$ type and contain diastereotopic methyl groups (r, s). In an isomeric mixture there are eight magnetically nonequivalent environments (*cf.* Figure 1) designated as C_r, C_s, T_{xr}, . . . , T_{zs}. Rearrangement mechanisms fall into two categories. Type 1 mechanisms effect either inversion or isomerization: (1a) TBP-equatorial transition states (isomerization without inversion); (1b) trigonal twists about r-C_3 and p-C_3 axes (inversion without isomerization). Kinetic-exchange matrices for these mechanisms can be factored into block-diagonal form with exchange occurring only within certain groups of sites and not between them. For mechanism 1a, matrix I ($k = K_{eq}/3$), there are two 4 × 4 blocks of nonzero elements, one block comprising the r environments and the other the s environments. For mechanism 1b, matrix II,[62] there are four 2 × 2 blocks of nonzero elements corresponding to the pairwise interchanges $T_{xr} \rightleftharpoons T_{xs}$, $T_{ys} \rightleftharpoons T_{zr}$, $T_{yr} \rightleftharpoons T_{zs}$, and $C_r \rightleftharpoons C_s$. Nmr spectra of molecules with large chemical shift differences at slow exchange which rearrange by these mechanisms are predicted to broaden and then reveal two (type 1a) or four (type 2a) separate features, in the absence of accidental degeneracy of averaged resonances, as the temperature is raised. If the separate features subsequently broaden and coalesce, an additional kinetic process must be involved. Type 2 mechanisms (TBP-axial, SP-basal, and SP-axial) effect inversion and isomerization at comparable rates. Exchange matrices for these mechanisms cannot be factored and exchange between any two sites occurs directly or *via* two other sites at most. The matrix for the TBP-axial process (III, $k = K_{eq}/3$) is given as an example. Once the spectrum has reached maximum exchange broadening, it will collapse to a single feature at higher temperatures. Hence, if the temperature-dependent nmr spectrum passes through a range where the sharp slow-exchange features are lost, and subsequently more than one distinct feature emerges, the exchange process must proceed by a type 1 mechanism. The spectra of Al(α-C_3H_7T)$_3$ (Figure 10) and Co(α-C_3H_7T)$_3$ (Figure 11) reveal this type of behavior. In order to analyze these spectra in terms of mechanism, assignments of the methyl spin doublets to specific magnetic environments are required. Resolution of the slow-exchange spectra into eight doublets and assignments of signals to cis and trans isomers are discussed in the Experimental Section and the text. As discussed previously,[2] there are 360 kinetically distinguishable ways to assign the doublets C_1, C_2, T_1, $\cdots$, T_6 (reduced from the maximum of 720 because reversal of all r and s labels does not yield a distinguishable assignment).

Al(α-C_3H_7T)$_3$. Slow-exchange chemical shifts of doublets T_4, T_5, T_6 cover an interval of *ca.* 4 Hz (Figure 5). If their shifts were identical permutation of environment labels among them would not be distinguishable kinetically, reducing the maximum number of nonequivalent assignment schemes to 360/3! = 60. (Although the chemical shifts of these doublets are not degenerate, 60 remains a practical maximum because it has been found that permutation of labels among the doublets has only a small effect on the appearance of the simulated spectra.) This maximum was further reduced for some of the mechanisms considered because of identical rates of exchange between several pairs of environments. The kinetically distinguishable assignment schemes for each mechanism were selected by a computer program which set up the matrices of exchange coefficients for the eight doublets for each of the 60 different assignment schemes and selected those with identical matrices. (Identical matrices will yield identical simulated spectra.) The number of distinguishable assignment schemes for each of the mechanisms is listed in Table VI. Spectra were simulated for several τ values for each of these assignment schemes for every mechanism.

---

(59) Parameters for the rearrangements of Ti(acac)$_2$X$_2$ (log $A \sim 8$–10, $\Delta S^{\ne} = -14$ to -22 eu) are consistent with the above proposal if the postulated twist mechanism[60] is accepted. Recent results[61] have confirmed the large negative activation entropies and have led to the postulation of a mechanism different from the (previously unproven[60]) twist pathway.

(60) D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).

(61) J. F. Harrod and K. Taylor, *Chem. Commun.*, 696 (1971).

(62) Because the rates of twisting about the r-C_3 and p-C_3 axes need not be, and were found not to be, equal (*cf.* Table III), the τ values were varied independently ($\tau_c = \tau_T/a$).

Matrix I

$$\begin{array}{ccccccccc} & \mathrm{T}_{xr} & \mathrm{T}_{yr} & \mathrm{T}_{zr} & \mathrm{C}_{r} & \mathrm{T}_{xs} & \mathrm{T}_{ys} & \mathrm{T}_{zs} & \mathrm{C}_{s} \\ \mathrm{T}_{xr} & -1 & 1/3 & 1/3 & 1/3 & & & & \\ \mathrm{T}_{yr} & 1/3 & -2/3 & 0 & 1/3 & & 0 & & \\ \mathrm{T}_{zr} & 1/3 & 0 & -2/3 & 1/3 & & & & \\ \mathrm{C}_{r} & k/3 & k/3 & k/3 & -k & & & & \\ \mathrm{T}_{xs} & & & & & -1 & 1/3 & 1/3 & 1/3 \\ \mathrm{T}_{ys} & & & & & 1/3 & -2/3 & 0 & 1/3 \\ \mathrm{T}_{zs} & & 0 & & & 1/3 & 0 & -2/3 & 1/3 \\ \mathrm{C}_{s} & & & & & k/3 & k/3 & k/3 & -k \end{array}\ \frac{1}{\tau}$$

Matrix II

$$\begin{array}{ccccccccc} & \mathrm{T}_{xr} & \mathrm{T}_{xs} & \mathrm{T}_{yr} & \mathrm{T}_{zs} & \mathrm{T}_{ys} & \mathrm{T}_{zr} & \mathrm{C}_{r} & \mathrm{C}_{s} \\ \mathrm{T}_{xr} & -1 & 1 & & & & & & \\ \mathrm{T}_{xs} & 1 & -1 & & & & & & \\ \mathrm{T}_{yr} & & & -1 & 1 & & 0 & & \\ \mathrm{T}_{zs} & & & 1 & -1 & & & & \\ \mathrm{T}_{ys} & & & & & -1 & 1 & & \\ \mathrm{T}_{zr} & & 0 & & & 1 & -1 & & \\ \mathrm{C}_{r} & & & & & & & -a & a \\ \mathrm{C}_{s} & & & & & & & a & -a \end{array}\ \frac{1}{\tau_{\mathrm{T}}}$$

Matrix III

$$\begin{array}{ccccccccc} & \mathrm{T}_{xr} & \mathrm{T}_{xs} & \mathrm{T}_{yr} & \mathrm{T}_{ys} & \mathrm{T}_{zr} & \mathrm{T}_{zs} & \mathrm{C}_{r} & \mathrm{C}_{s} \\ \mathrm{T}_{xr} & -1 & 0 & 0 & 1/3 & 0 & 1/3 & 0 & 1/3 \\ \mathrm{T}_{xs} & 0 & -1 & 1/3 & 0 & 1/3 & 0 & 1/3 & 0 \\ \mathrm{T}_{yr} & 0 & 1/3 & -1 & 1/3 & 0 & 0 & 0 & 1/3 \\ \mathrm{T}_{ys} & 1/3 & 0 & 1/3 & -1 & 0 & 0 & 1/3 & 0 \\ \mathrm{T}_{zr} & 0 & 1/3 & 0 & 0 & -1 & 1/3 & 0 & 1/3 \\ \mathrm{T}_{zs} & 1/3 & 0 & 0 & 0 & 1/3 & -1 & 1/3 & 0 \\ \mathrm{C}_{r} & 0 & k/3 & 0 & k/3 & 0 & k/3 & -k & 0 \\ \mathrm{C}_{s} & k/3 & 0 & k/3 & 0 & k/3 & 0 & 0 & -k \end{array}\ \frac{1}{\tau}$$

Table VI. Nonequivalent Assignment Schemes for Different Intramolecular Rearrangement Mechanisms

Mechanisms[a]	No. of nonequiv assignments schemes
Nonbond breaking	
Rotation about r-C_3 and p-C_3 axes	4
Rotation about i-C_3 axes with equal probability	20
Admixtures of both	60
Bond breaking	
TBP-axial	20
TBP-equatorial	42
1:1 admixture of TBP-axial and TBP-equatorial	12
SP-axial (primary process only)	12
SP-axial (1:1 admixture of primary and secondary processes)	20

[a] For a description of mechanisms, *cf.* ref 1 and 2.

(i) **LTP.** Of the two type 1 mechanisms TBP-equatorial processes were eliminated by line-shape analysis. Simulated spectra were inconsistent with the experimental spectra between 2 and 39° for all assignment schemes. However, spectra simulated on the basis of a trigonal-twist mechanism (1b) match well the observed spectra, as shown in Figure 10, with the sharp downfield doublet assigned to the cis isomer. Of the four nonequivalent assignment schemes (assuming T_4, T_5, T_6 degeneracy), only the scheme which averages each trans doublet in the high-field peak with a doublet in the low-field peak was consistent. Because the doublets T_4, T_5, and T_6 are not precisely degenerate, the pairing of doublets could be done in six different ways. Simulated spectra for different pairings showed small differences which affected the τ values but did not affect the overall validity of the mechanism. The assignment scheme which best reproduced the experimental spectra averaged the following pairs of doublets: T_1–T_6, T_2–T_5, T_3–T_4, and C_1–C_2. The error limits for the rate constants and activation parameters reflect the effect of uncertainty in assignment upon the rate constants. Due to difficulties with instrumental phase and uncertainties in temperatures at the extremes of the exchange process, the thermodynamic parameters are considerably more uncertain for $\mathrm{Al}(\alpha\text{-}\mathrm{C_3H_7T})_3$ than for the other $\mathrm{M}(\alpha\text{-}\mathrm{RT})_3$ complexes studied, although the mechanistic arguments are not affected.

(ii) **HTP.** The spectra above 39° reflect the effects of an isomerization process. Spectra were simulated for this region (Figure 10) by extrapolating inversion rates of cis and trans (Figure 12) and superimposing the various isomerization mechanisms. Matrices for these mechanisms gave nearly identical spectra for the same values of τ_{I}, thereby precluding any mechanistic conclusions about the process.

$\mathrm{Co}(\alpha\text{-}\mathrm{C_3H_7T})_3$. As for $\mathrm{Al}(\alpha\text{-}\mathrm{C_3H_7T})_3$, the spectra of $\mathrm{Co}(\alpha\text{-}\mathrm{C_3H_7T})_3$ (Figure 11) are characteristic of a type 1

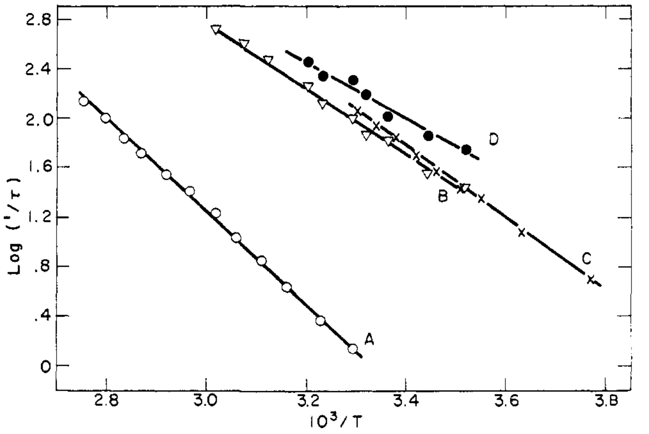


Figure 12. Arrhenius plots for intramolecular rearrangements of Al(III) complexes. Al(α-$C_3H_5T)_3$ in tetrachloroethane: A, C–T isomerization. Al(α-$C_3H_5T)_3$ in dichloromethane: C, inversion of trans. Al(α-$C_3H_7T)_3$ in tetrachloroethane: B, inversion of trans; D, inversion of cis.

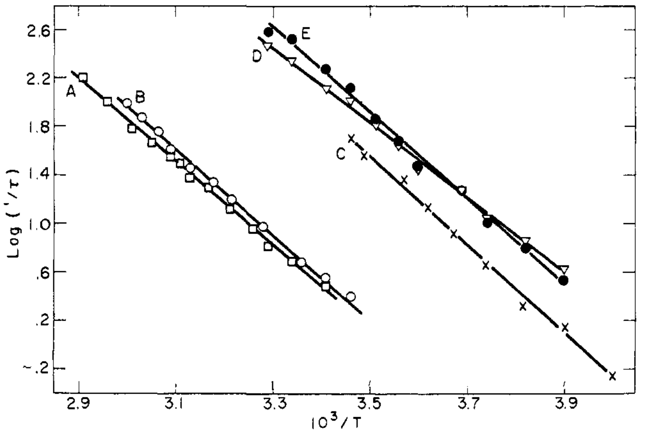


Figure 13. Arrhenius plots for intramolecular rearrangements of Co(III) complexes. Co(α-$C_3H_5T)_3$ in deuteriochloroform: B, C–T isomerization; C, inversion of trans. Co(α-$C_3H_7T)_3$ in chloroform: A, C–T isomerization; D, inversion of trans; E, inversion of cis.

mechanism at low temperatures and a second process occurring at higher temperatures.

(i) LTP. As discussed above, only type 1 mechanisms are consistent with the qualitative features of the spectra from −16 to +26° (Figure 14).[63] Considering first the trigonal twist, the pairs of trans resonances can be assigned on the basis of their averaged chemical shifts in the temperature range 26–39° (Figure 6), where the LTP is nearly complete but the effects of the HTP are just beginning. There remains the ambiguity that the pairings $T_1 \leftrightarrow T_5$, $T_2 \leftrightarrow T_4$, $T_3 \leftrightarrow T_6$ are indistinguishable on the basis of line-shape calculations from $T_1 \leftrightarrow T_4$, $T_2 \leftrightarrow T_5$, $T_3 \leftrightarrow T_6$ and produce calculated spectra in close agreement with the observed spectra below *ca.* 26° (Figure 11). No other pairings have the required averaged shifts. Beginning at 26° the HTP must also be taken into account (*vide infra*). For the TBP-equatorial mechanism the resonances are divided into two groups, each including a cis doublet. Any combination of resonances can be rejected unless it has one group which averages to the chemical shift of the sharp downfield feature. This requirement leaves two combinations: (a) (T_1, T_2, T_6, C_2)(T_3, T_4, T_5, C_1) and (b) (T_2, T_5, T_6, C_1)(T_1, T_3, T_4, C_2). Since the assignment of cis is known by intensity and interchanging the assignments of *y* and *z* within a group does not affect the calculated spectra, only the assignment of the *x* site must be varied. For combination b no assignment of *x* gives a sharper doublet downfield than upfield in the temperature interval 20–33°. For combination a only one assignment gives reasonable agreement of calculated and observed spectra at 26°: $T_6 = T_{xr}$; T_1, $T_2 = T_{yr}$, T_{zr}; $C_2 = C_r$; $T_4 = T_{xs}$; T_3, $T_5 = T_{ys}$, T_{zs}; $C_1 = C_s$ (interchange of all r and s labels has no effect on the exchange matrices). However, as shown in Figure 14, this assignment generates spectra in the initial exchange region, −11 to +8°, which do not agree with the observed spectra. C_1 averages much too rapidly with T_3. Thus no assignment scheme for TBP-equatorial gives calculated spectra which agree with the observed spectra over the full range, −17 to 26°, of the LTP.

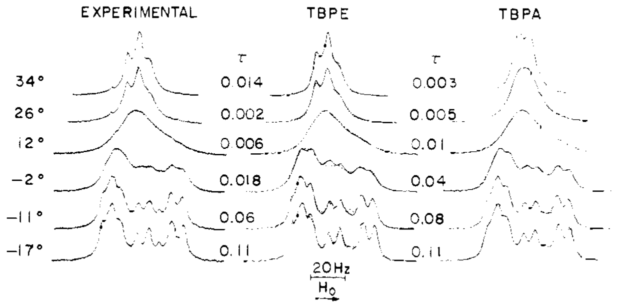


Figure 14. Experimental methyl spectra (100 MHz) of an isomeric mixture of Co(α-$C_3H_7T)_3$ in chloroform solution and spectra calculated assuming trigonal-bipyramidal equatorial (TBPE) and axial (TBPA) transition states. The dotted lines indicate the best fit obtained for a trigonal twist as the LTP of both isomers (see also Figure 11). τ values are in seconds.

(ii) HTP. Provided the pair T_3, T_6 is assigned to the *x* environment, any isomerization mechanism superimposed on the twist process gives satisfactory agreement between the calculated and observed spectra from 26 to 70°. The spectra in Figure 11 were calculated for a random process.

Summary. Line-shape analysis of the methyl spectra of Al(α-$C_3H_7T)_3$ and Co(α-$C_3H_7T)_3$ indicates that the LTP (inversion without isomerization) occurs by a trigonal twist with the rotation around the p-C_3 axis of the trans and the r-C_3 axis of the cis isomer. Spectra of each complex at higher temperatures can be adequately simulated by superimposing upon the LTP cis-trans isomerization (HTP) with random site interchange.

B. Permutational Analysis of M(A–B)$_3$ Rearrangements. The foregoing analysis of rearrangement mechanisms has been based largely on examination of nmr averaging patterns arising from processes involving transition states whose geometries and means of formation (concerted twists, bond rupture) are considered physically reasonable.[1,2] Thus, there is no assurance that every feasible rearrangement has been considered. A complete analysis of all rearrangements has been

---

[63] The spectra below *ca.* 12° can be simulated with varying degrees of agreement for mechanisms of type 2. However, as τ is decreased below the value which adequately reproduces the 12° spectrum, mechanisms of this type generate spectra which sharpen to a single doublet. This behavior is incompatible with the experimental spectra, as shown in Figure 14.

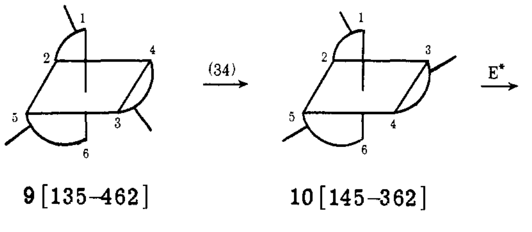
Table VII. Permutational Analysis of $M(A\text{-}B)_3$ Nmr Spectra

Operation	Resulting isomer[a]	Averaging set	Net configurational change	Net site interchanges (trans)
E	[135–462]	A_1	None	None
(12)(34)(56)	[153–642]	A_2	None	(*yz*)
(12)	[164–532]	A_3	Cis → trans	(*xy*), (*xz*)
(34)	[145–362]		Trans → $^1/_3$ cis + $^2/_3$ trans	
(56)	[136–452]			
(12)(34)	[163–542]	A_4	Cis → trans	(*xzy*), (*xyz*)
(34)(56)	[146–352]		Trans → $^1/_3$ cis + $^2/_3$ trans	
(12)(56)	[154–632]			
*E**	[153–264]	A_5	$\Lambda \rightleftharpoons \Delta$	(rs)
(12)(34)(56)*	[135–246]	A_6	$\Lambda \rightleftharpoons \Delta$	(*yz*), (rs)
(12)*	[146–235]	A_7	$\Lambda \rightleftharpoons \Delta$	
(34)*	[154–263]		Cis → trans	(*xy*), (*xz*)
(56)*	[163–254]		Trans → $^1/_3$ cis + $^2/_3$ trans	(rs)
(12)(34)*	[136–245]	A_8	$\Lambda \rightleftharpoons \Delta$	
(34)(56)*	[164–253]		Cis → trans	(*xyz*,) (*xzy*)
(12)(56)*	[145–236]		Trans → $^1/_3$ cis + $^2/_3$ trans	(rs)

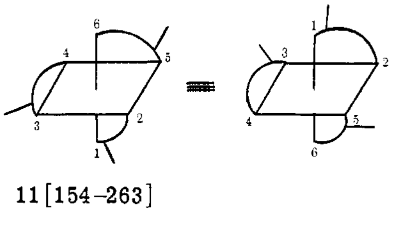
[a] Isomers resulting from performing the indicated operations on [135–462] are given as examples. Columns 3, 4, and 5 summarize net effects of operations on all 16 isomers.

carried out[64] using the molecular symmetry groups for nonrigid molecules introduced by Longuet-Higgins.[65] An analysis of this problem has also been performed by Musher[66] using a different approach. For the $M(A\text{-}B)_3$ case the set of all permutations and permutation–inversions of the six ligating nuclei is a group of order 384 which factors into a group of order 16 (consisting of the rearrangements) and a group of order 24 (which can be regarded as consisting of the rigid-body rotations of the molecule). The group of order 16, which is of primary interest here, is an Abelian group so that each operation is in a separate class. These 16 operations constitute the complete group of rearrangements of stereochemically nonrigid tris-chelate complexes. It is important to note that the 16 rearrangements are expressed as permutations; *i.e.*, they describe only the net change and not the pathway by which the atoms move from initial to final positions. The nmr site averaging for each operation is presented in Table VII and compared below with the results discussed above. Trans sites are defined as in Figure 1.

The notation is illustrated in **9** for the cis isomer [135–462]. As the complex is viewed down the r-C_3 (or p-C_3) axis with the triangular face containing vertex 1 upward, the labels are given clockwise for this face starting with 1 and similarly for the lower face starting with the vertex to the right of 1. Square brackets denote isomers and parentheses denote permutations. The permutation (34) is illustrated by **9** → **10** and takes cis to trans. The conversion **10** → **11** is effected by *E**, the inversion of all ligands through the metal center. The operation which takes **9** to **11** is the permutation–inversion (34)*. The effect of the 16 operations on [135–462] is given in Table VII. Because all 16 isomers generated in this fashion contribute to the pmr spectra, the net effect of each rearrangement on the pmr spectra is derived by summing the changes in ligand environments produced by a particular operation. These results are compiled in Table VII. Permutations which give the same net averaging pattern for the sites *x*, *y*, *z*, r, and s are placed together in averaging sets A_i, although the permutations within each set may have different effects on different isomers.



9 [135–462]   **10** [145–362]



11 [154–263]

The following correspondences can be made between the various physical mechanisms considered previously[1,2,43] and the permutations derived here: i-C_3 twists, A_8; TBP-axial, A_7; TBP-equatorial, A_3; SP-axial, $A_3 + A_6 + A_8$. Because permutations A_3, A_4, A_7, and A_8 effect cis–trans isomerization, they cannot be contributing significantly to the site averaging observed in the LTP of $M(\alpha\text{-RT})_3$ complexes. A_5 results in inversion at the metal center but does not average any of the *x*, *y*, *z* sites in trans. Thus, it cannot account for the observed two-site averaging (*yz*) of $M(\alpha\text{-}C_3H_5T)_3$ but is consistent with the pairwise averaging (rs) of $M(\alpha\text{-}C_3H_7T)_3$. A_2 results in neither inversion nor isomerization but does interchange sites *y* and *z*. Although it is consistent with the LTP of $M(\alpha\text{-}C_3H_5T)_3$, it would have no effect on C_r, C_s, T_{xr}, T_{xs} and therefore is inconsistent with the LTP of $M(\alpha\text{-}C_3H_7T)_3$. Because it is unreasonable that the closely related isopropenyl and isopropyl complexes would rearrange by different pathways, A_2 and A_5 are rejected as significant rearrangement processes. The only permutation which is consistent with the low-temperature pmr spectra of *both* $M(\alpha\text{-}C_3H_5T)_3$ and $M(\alpha\text{-}C_3H_7T)_3$ is A_6, which effects

---

(64) S. S. Eaton and G. R. Eaton, unpublished results.
(65) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).
(66) J. I. Musher, results submitted for publication.

inversion without isomerization and averages trans sites *y* and *z*. The trigonal twist (Figure 1) is one physical conception of this permutation.[67]

Musher[66] has pointed out that permutation A_2, as well as A_6, is compatible with the pmr-averaging patterns of $Fe(R_1R_2dtc)_2(tfd)$[15] (**3**) and $Fe(R_1R_2dtc)_3$.[46] Pignolet[68] has recently obtained evidence that the LTP of the latter complexes proceeds with inversion of configuration, thereby revealing that A_2 is not a significant process. It has recently been suggested that the complexes **3** rearrange *via* a distorted hexagonal-planar structure.[50] If for the tropolonate complexes a similar transition state is entertained, rotation of the ligands through a coplanar arrangement to positions roughly perpendicular to the original ones gives as the net result A_5. If the rotation is continued, effectively a trigonal twist, the net result is A_2. Since neither A_2 nor A_5 is consistent with the averaging patterns of both types of tropolonate complexes, a planar transition state is not involved in the LTP of these complexes.

Acknowledgments. Research at MIT was supported by Grant GP-18978X from the National Science Foundation. The calculation of the $Al(\alpha\text{-}C_3H_7T)_3$ spectra carried out by J. R. H. at Swarthmore College was performed using the computer facilities of Haverford College. We are indebted to Dr. G. R. Eaton for suggesting the use of nonrigid point groups and for collaboration in the permutational analysis. R. H. H. acknowledges a useful discussion with Dr. J. I. Musher. We thank Dr. Serpone for a copy of ref 7a and Dr. R. Eisenberg for communicating experimental results prior to publication. The assistance of Mr. F. W. Barney in obtaining the 220-MHz proton spectra is gratefully acknowledged.

(67) The product isomer, resulting from a permutation or permutation–inversion, can be drawn in 24 rotated forms. Comparison of the starting isomer with each of the orientations of the product can suggest ligand motions required to effect the observed site averaging. For A_6 physical mechanisms other than the trigonal twist appear to require greater ligand motion or highly selective bond rupture and formation and thus are considered less plausible than the trigonal twist.

(68) L. H. Pignolet, private communication.

Blue Chloroammine Complexes of Ruthenium

E. E. Mercer* and L. W. Gray

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received February 19, 1972*

Abstract: The preparation, characterization, and some reactions of the blue complex formed from $Ru(NH_3)_6Cl_2$ and HCl are described. The complex was identified as $Ru_2Cl_3(NH_3)_6^{2+}$, a mixed oxidation state complex, and is formed by the reaction $4Ru(NH_3)_6^{2+} + 14H^+ + 6Cl^- \rightarrow 2Ru_2Cl_3(NH_3)_6^{2+} + H_2 + 12NH_4^+$. The blue cation decomposes to *cis*-$RuCl_3(NH_3)_3$ in the presence of oxygen. This, combined with spectral data, suggests that there is a triple chloride bridge between the two metal atoms.

The formation of intense blue solutions by the action of reducing agents on hydrochloric acid solutions of ruthenium has been the subject of considerable interest since first reported by Claus[1] in 1846. Recently we have identified the blue species in these solutions as ruthenium(II,III) dimers[2] which have the general formula $Ru_2Cl_{3+n}^{(2-n)+}$. In that study we noted that the formation of the blue complexes was always preceded by reduction of the metal to $Ru(H_2O)_6^{2+}$, followed by an oxidation to form the final product.

There have been several reports in the literature on the formation of blue solutions when hydrochloric acid is added to ruthenium(II) complexes containing nitrogen donor ligands. The simplest of these ligands is ammonia. Endicott and Taube[3] reported some qualitative observation on this reaction. Later Lever and Powell[4] isolated a blue solid. On the basis of chemical analysis they formulated the complex as $Ru(NH_3)_3Cl_2(H_2O)^+$, a ruthenium(III) complex. When our work was near completion, Bottomley and Tong[5] reported the characterization of a blue solid formed from the same reaction as $[Ru_2Cl_4(H_2O)(NH_3)_6]Cl$. In this report they have correctly identified this as a mixed oxidation state complex of ruthenium(II,III).

Experimental Section

Analyses. Ruthenium was determined spectrophotometrically[6] as RuO_4^{2-}.

Chloride determinations were made by two methods, both involving gravimetric determinations as AgCl. The first method has been reported previously.[2] In the second method, the chloride was separated from the ruthenium by distillation of HCl from a sulfuric acid solution of the compound. The distillate was collected in 2 *M* NaOH, and after acidification with nitric acid, the chloride was precipitated by addition of $AgNO_3$ solution.

Nitrogen was determined by either the Kjeldahl or Dumas method. Tin and zinc were measured polarographically. It was necessary to remove the ruthenium from solution by hydrogen reduction before the zinc determination was performed.

Reagents. Ruthenium chloride hydrate (~38% Ru) was obtained from Engelhard Industries. This was converted to $Ru(NH_3)_6Cl_2$ as reported by Allen and Senoff.[7] Ion exchange resins used were Dowex 50 × 8, 200–400 mesh (H^+ form), and Dowex 1 × 8, 100–200 mesh (Cl^- form). The cation resin was always washed with 6 *M* HCl to remove iron impurities, and washed free of acid with water prior to use.

All other chemicals were reagent grade and were used without further purification.

---

(1) C. Claus, *Justus Liebigs Ann. Chem.*, **59**, 283 (1846).

(2) E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, **10**, 2755 (1971).

(3) J. F. Endicott and H. Taube, *ibid.*, **4**, 437 (1965).

(4) F. M. Lever and A. R. Powell, *J. Chem. Soc. A*, 1477 (1969).

(5) F. Bottomley and S. B. Tong, *Can. J. Chem.*, **49**, 3739 (1971).

(6) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5037 (1961).

(7) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).