Intramolecular Rearrangement Reactions of Tris-Chelate Complexes. IV.[1] Further Investigation of the Rearrangements of Tris(α-isopropenyl- and α-isopropyltropolonato)metal(III,IV) Complexes

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Abstract: The temperature-dependent proton magnetic resonance spectra of a series of tris(α-isopropenyl- and α-isopropyltropolonato)metal(III, IV) complexes, M(α-RT)$_3$, have been investigated in order to determine if the relatively fast rates of intramolecular rearrangements and the occurrence of inversion by a twist mechanism, previously established for the Al(III) and Co(III) analogs, are general features of tropolonate systems. On the basis of line-shape changes, M(α-RT)$_3$ complexes can be classified as follows: stereochemically nonrigid complexes which attain the fast-exchange limit of inversion and/or isomerization (i) below *ca.* 0° [V(III), Mn(III), Ga(III)], (ii) below *ca.* 100° [Al(III), Co(III)], and (iii) above *ca.* 100° [Ge(IV)] and stereochemically rigid complexes [Rh(III), Ru(III)]. Spectra of Ga(α-RT)$_3$ reveal two separate kinetic processes in partially overlapping temperature intervals. Methyl averaging patterns in the low-temperature process (LTP) identify it as inversion of configuration by means of a trigonal twist. The high-temperature process (HTP) results in cis–trans isomerization; no mechanistic information could be derived from the spectra. Methyl spectra of [Ge(α-C$_3$H$_7$T)$_3$]$^+$ above 35° are similar to those of the LTP of other complexes for which the trigonal-twist mechanism has been established. Separate kinetic processes could not be observed in the isotropically shifted spectra of the V(III) and Mn(III) complexes, and only isomerization was detected. Rearrangement rates of M(α-RT)$_3$ were found in all cases to be substantially larger than those of M(tfac)$_3$ and nonfluorinated tris(β-diketonates). Metal ion dependence of rate orders in the α-RT and tfac series are similar except for the placement of V(III) and Co(III). Certain trends in rearrangement rates of ligand-invariant series of complexes are noted, and the factors which appear to favor the operation of the twist mechanism in metal tropolonate rearrangements are summarized.

Elucidation of the mechanisms of intramolecular rearrangement reactions of metal chelate complexes is a problem of continuing significance in coordination chemistry.[5] Recent studies of these reactions have primarily involved tris-chelate species of the general type M(A–B)$_3$, which may exist as cis (C) and trans (T) geometrical isomers, each of which is enantiomeric (Δ, Λ). The rearrangement reactions are isomerization (C $\rightleftharpoons$ T) and inversion ($\Delta \rightleftharpoons \Lambda$), which may occur separately or simultaneously (although not necessarily at the same rate) depending on the mechanism of the rearrangement process. Rearrangement rates frequently exhibit a significant dependence on the nature of the chelate ligand and on the size and electronic features of the coordinated metal ion. Previously, we have introduced the designations "slow" and "fast"[6,7] for complexes whose rearrangement kinetics are determined by measurement of rate of approach to equilibrium and rate of interconversion at equilibrium, respectively. Fast or stereochemically nonrigid[8] complexes have been investigated by nmr techniques.[5]

The present study is a continuation of investigations in these laboratories directed toward a satisfactory interpretation of the rearrangement rates and mechanisms of slow[6,9] and fast[1,7,9–14] tris-chelate complexes. More specifically, this work provides additional information on the rearrangement properties of tris(α-isopropenyltropolonato) and tris(α-isopropyltropolonato) complexes **1** [M(α-C$_3$H$_5$T)$_3$[15]] and **2** [M(α-C$_3$H$_7$T)$_3$], respectively. In part III[1] a permutational analysis of the rearrangement pathways of M(A–B)$_3$ complexes and the pmr-detectable methyl site exchanges of **1** and **2** were presented. Rearrangements of the Al(III) and Co(III) complexes of these types were investigated by analysis of the temperature-dependent

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[2] NSF Predoctoral Fellow, 1969–1971.

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[5] For reviews *cf.* (a) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press; (b) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971); (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 300–334.

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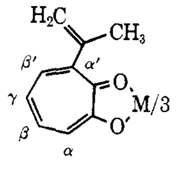
[15] The following abbreviations for ligand anions are used throughout: T, tropolonate; α-C$_3$H$_5$T, α-isopropenyltropolonate; α-C$_3$H$_7$T, α-isopropyltropolonate; α-RT, generic for α-alkyl- or -alkenyltropolonate; mhd, 5-methylhexane-2,4-dionate; pmhd, 1-phenyl-5-methylhexane-2,4-dionate; bzac, benzoylacetonate; dibm, diisobutyrylmethanide; dbm, dibenzoylmethanide; atc, acetylcamphorate; tfac, trifluoroacetylacetonate; hfac, hexafluoroacetylacetonate; RR′-dtc, N,N-disubstituted dithiocarbamate; tfd, 1,2-bis(perfluoromethyl)dithiolene; mnt, maleonitriledithiolene.



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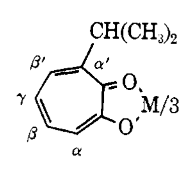

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methyl averaging patterns and rate constants and activation parameters were determined for low-temperature processes (LTP), which attained the fast-exchange limit below *ca.* 40°. By comparison of the averaging patterns of the methyl resonances of $M(\alpha\text{-}C_3H_5T)_3$ and $M(\alpha\text{-}C_3H_7T)_3$ it was possible to distinguish between mechanisms of the LTP which proceed with inversion from those which proceed without inversion. This analysis led to identification of the LTP of the cis and trans Al(III) and Co(III) complexes as inversion without isomerization. Of the eight distinguishable permutational mechanisms for a tris chelate, only one will provide the stereochemical features established for the LTP process. The simplest and most plausible physical mechanism of such permutational character is the trigonal-twist pathway, illustrated for complexes **1** and **2** in Figure 1. These studies represented the first incisive identification of the twist mechanism. Using a similar analysis, Pignolet and coworkers have very recently established the trigonal-twist mechanism for $[Fe(Me,CH_2Ph\text{-}dtc)_3]^+$[16] and $Fe(Me,CH_2Ph\text{-}dtc)_3$.[17] Previously it was shown that the trigonal twist was fully consistent with the nmr averaging patterns observed in the LTP of $Fe(R_1R_2\text{-}dtc)_2(tfd)$[11] and $Fe(R_1R_2\text{-}dtc)_2(mnt)$,[12] but it has not yet been experimentally demonstrated that these processes involve inversion of the molecular configuration.[18]

Two features of the dynamic stereochemistry of the Al(III) and Co(III) complexes **1** and **2** have stimulated further investigation of the rearrangement properties of tris(tropolonates): (i) the operation of the trigonal-twist mechanism in the LTP, (ii) the remarkable enhancement of rearrangement rates compared to those of related tris(β-diketonates). Thus, at ambient temperature the rates of inversion of $Al(\alpha\text{-}RT)_3$ are *ca.* 10^6 larger than those observed for $Al(pmhd)_3$[7] and $Al(dibm)_3$.[19] Inversion rates of $Co(\alpha\text{-}RT)_3$ are *ca.* 10^{10}–10^{11} larger than for $Co(acac)_3$,[20] $Co(mhd)_3$,[6] and $Co(bzac)_3$,[21] and the former are the first recognized examples of nonrigid Co(III) chelates. In order to ascertain if these features are general properties of tropolonate complexes, a series of complexes **1** and **2** with M = Ga(III), Ge(IV), V(III), Mn(III), and Ru(III) have been prepared and their temperature-dependent pmr spectra investigated.

Experimental Section

Preparation of Compounds. Commercially available $GaCl_3$, $GeCl_4$, VCl_3, and $RuCl_3$ (38.6% Ru, Engelhard) were used without further purification. $H(\alpha\text{-}C_3H_5T)$,[1] $H(\alpha\text{-}C_3H_7T)$,[1] $Ga(\alpha\text{-}C_3H_7T)_3$,[10] $[Ge(\alpha\text{-}C_3H_7T)_3](PF_6)$,[10] and MnT_3[22] were prepared as previously described.

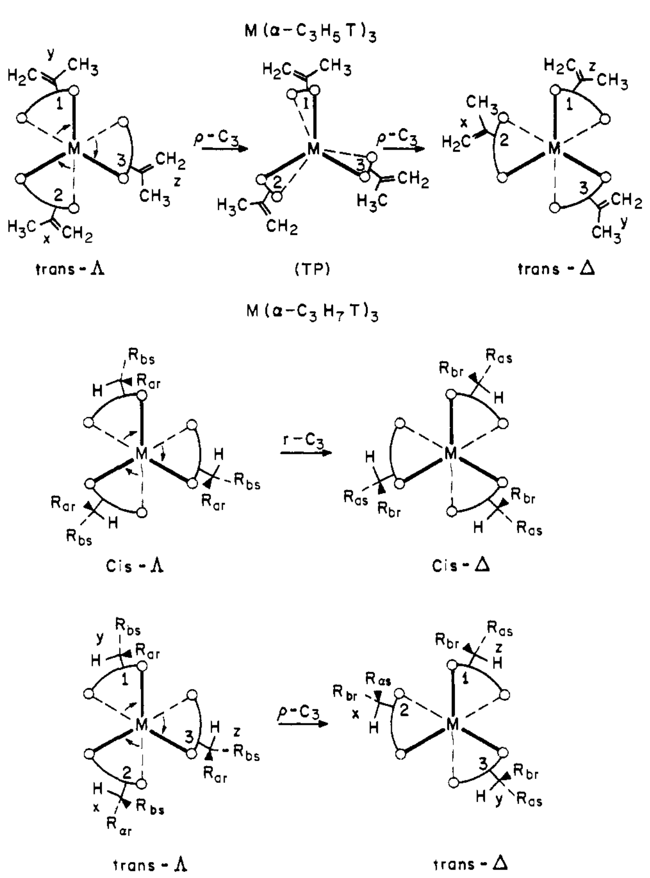

Figure 1. Illustration of isomers and site labeling (methyl groups) of tropolonate complexes. Substituent groups are labeled numerically and group magnetic environments are designated by *x*, *y*, *z*. Methyl groups of the isopropyl substituents (R = CH_3) are labeled a and b and their individual magnetic environments are arbitrarily designated by r and s. Inversions of configuration by trigonal twists about the pseudo (p-C_3) and real threefold (r-C_3) axes for trans and cis isomers, respectively, are shown. TP = idealized trigonal-prismatic transition state.

$Ga(\alpha\text{-}C_3H_5T)_3$. This complex was prepared by a method analogous to that reported for $Ga(\alpha\text{-}C_3H_7T)_3$.[10] Recrystallization from acetone–benzene gave a white powder, mp 190–192° dec. *Anal.* Calcd for $C_{30}H_{27}O_6Ga$: C, 65.13; H, 4.92. Found: C, 65.05; H, 5.15.

$[Ge(\alpha\text{-}C_3H_5T)_3]PF_6$. Preparation of this complex was similar to that reported for $[Ge(\alpha\text{-}C_3H_7T)_3]PF_6$.[10] Recrystallization from acetone–hexane gave a white powder, mp 168–170° dec. *Anal.* Calcd for $C_{30}H_{27}O_6GePF_6$: C, 51.39; H, 3.88. Found: C, 51.36; H, 4.21.

RuT_3. $RuCl_3$ (0.52 g, 2 mmol Ru), $KHCO_3$ (1.2 g, 12 mmol), and tropolone (3.0 g, 24 mmol) were mixed together and heated to ~80°. Gas was vigorously evolved. After heating for 40 hr, the mixture was cooled and extracted with dichloromethane. The brown solution was passed through a column of Woelm neutral alumina leaving a dark band at the top of the column. Volume reduction of the eluent followed by addition of hot heptane afforded dark needles. This material was recrystallized from dichloromethane–hexane and dichloromethane–ethanol and dried under vacuum at 60° to constant weight. The formula $RuT_3 \cdot HT$ was indicated by analysis. *Anal.* Calcd for $C_{28}H_{21}O_8Ru$: C, 57.34; H, 3.61. Found: C, 57.40; H, 3.68. Resonances which could be attributed to free ligand were observed in the pmr spectrum.

$Ru(\alpha\text{-}C_3H_5T)_3$. This complex was prepared by a method analogous to that used for RuT_3. Recrystallizations from ethanol–ether

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(16) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, **11**, 2843 (1972).

(17) L. H. Pignolet and M. C. Palazzotto, unpublished results; see also M. C. Palazzotto and L. H. Pignolet, *J. Chem. Soc., Chem. Commun.*, 6 (1972).

(18) The averaging patterns are also consistent with a certain permutational interchange of the two dtc rings without inversion of configuration (averaging set A_2 in Table VII, ref 1). This point has also been recognized by Musher in his analysis of $M(A\text{-}B)_3$ rearrangements: J. I. Musher, *Inorg. Chem.*, **11**, 2335 (1972).

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

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gave a dark powder, analysis of which fits the formula Ru(α-$C_3H_5T)_3 \cdot H(\alpha$-$C_3H_5T)$. *Anal.* Calcd for $C_{40}H_{37}O_8Ru$: C, 64.34; H, 4.99. Found: C, 63.87; H, 4.96. Resonances in the diamagnetic region of the pmr spectrum are consistent with the presence of free ligand.

Mn(α-$C_3H_5T)_3$. This complex was prepared by a method analogous to that reported for MnT_3.[22] Recrystallization from benzene–hexane gave a green powder, mp 130–132° dec. *Anal.* Calcd for $C_{30}H_{27}O_6Mn$: C, 66.93; H, 5.05. Found: C, 67.39; H, 4.86.

Mn(α-$C_3H_7T)_3$. Preparation of this complex was similar to that for MnT_3.[22] Recrystallization from acetone–methylcyclohexane and benzene–hexane gave a green powder, mp 162–164° dec. *Anal.* Calcd for $C_{30}H_{33}O_6Mn$: C, 66.17; H, 6.11. Found: C, 66.20; H, 6.15.

NaT. Equimolar solutions of NaOH and HT in aqueous methanol were combined. Volume reduction afforded yellow crystals.

VT_3. VCl_3 (1.2 g, 7.7 mmol) was refluxed in 150 ml of degassed acetonitrile until a clear green solution was obtained. NaT (3.3 g, 23.1 mmol) was added under nitrogen and the resultant dark slurry was stirred for 36 hr. A large amount of dark solid was filtered off and washed once with ~175 ml of dichloromethane and then with ~175 ml of hot chloroform. Volume reduction of each filtrate afforded shiny dark green crystals. The crystals from dichloromethane and chloroform were combined and dried *in vacuo*, mp ~350°. *Anal.* Calcd for $C_{21}H_{15}O_6V$: C, 60.88; H, 3.65. Found: C, 60.73; H, 3.80. Although the dry solid appears to be stable in air for brief periods, the green solutions rapidly turn brown on exposure to air.

V(α-$C_3H_7T)_3$. This complex was prepared by a method analogous to that used for VT_3. Extraction with chloroform was followed by recrystallization from chloroform–methylcyclohexane and then from acetone–methylcyclohexane. The product was obtained as a green powder, mp 92–93° (dec). *Anal.* Calcd for $C_{30}H_{33}O_6V$: C, 66.66; H, 6.15. Found: C, 66.38; H, 6.24.

Pmr Spectra. Pmr spectra were obtained on Varian HA-100 and HA-220 spectrometers. Spectra of paramagnetic complexes were run in the HR mode with side bands generated by a Hewlett-Packard 200 CD wide-range oscillator and a PAR HR8 lock-in amplifier. Temperatures were measured with a thermocouple mounted in the probe which was calibrated with ethylene glycol and methanol.[23]

Results and Discussion

Mechanistic analysis of M(A–B)$_3$ complexes which rearrange on the nmr time scale is based on a comparison of the relative rates of exchange between magnetically nonequivalent sites predicted for various mechanisms[1,7] and the observed nmr averaging patterns. Isomers and site labeling for complexes **1** and **2** are shown in Figure 1. In the trans form of each complex there are three magnetic environments (x, y, z) for methyl groups due to the lack of symmetry of this isomer and one such environment in the threefold symmetric cis isomer. In addition, the methyl groups (R_a, R_b) in M(α-$C_3H_7T)_3$ are diastereotopic in the chiral cis and trans forms. The nonequivalent environments (r, s) of the methyls within each isopropyl group are readily visualized for the rotameric form shown, in which the C–H bonds are coplanar with the chelate rings. The labeling of magnetic environments is the same as that employed previously.[1] At slow exchange in the absence of accidental degeneracies the spectra of cis–trans mixtures of **1** and **2** should exhibit four methyl resonances and eight methyl spin doublets, respectively. While this signal multiplicity has been observed for several complexes of type **1**,[1,13] the spectra of Al(III) and Co(III) complexes of type **2** consist of partially overlapping doublets.[1,10]

In part III[1] the variable-temperature methyl pmr spectra of the Al(III) and Co(III) complexes **1** and **2** were analyzed in detail. Spectra of Al(α-$C_3H_5T)_3$ and Co(α-$C_3H_5T)_3$ revealed two kinetic processes occurring in partially overlapping temperature intervals. In the LTP, whose fast-exchange limit is reached at *ca.* 20–30°, two trans resonances (y, z) average while the other trans and the single cis signal remain sharp.[1,13] In the high-temperature process (HTP) all resonances average to a single peak with fast exchange reached above *ca.* 60°. Spectra of Al(α-$C_3H_7T)_3$ and Co(α-$C_3H_7T)_3$ also indicated two kinetic processes occurring in approximately the same temperature intervals[1,10] as for their α-isopropenyl analogs. In the LTP of both complexes the eight isopropyl spin doublets average in pairs to four partially superimposed doublets.[1] Complete averaging to a single doublet occurs in the HTP. Spectra of the LTP of complexes **1** serve to demonstrate rearrangement of the trans form by a specific two-site interchange, and the corresponding spectra of complexes **2** when treated by a full line-shape analysis reveal that the cis and trans isomers rearrange with inversion of configuration. Based on a permutational analysis, a trigonal twist around the r-C_3 axis (cis) or the p-C_3 axis (trans) (or its permutational equivalent), as shown in Figure 1, is the only mechanism which is consistent with the results for *both* the α-isopropenyl and α-isopropyl complexes of Al(III) and Co(III).[1] The HTP of each complex results in isomerization but no mechanistic information could be deduced from the spectra.

Variable-temperature pmr spectra of additional complexes of types **1** and **2** are considered below followed by a discussion of mechanism and relative rearrangement rates. Qualitative rate behavior and mechanistic comparisons were sought, based on examination of line-shape changes as a function of temperature.

Ga(α-$C_3H_5T)_3$ and Ga(α-$C_3H_7T)_3$. Methyl spectra of Ga(α-$C_3H_5T)_3$ at 100 MHz in dichloromethane solution were obtained between −90 and 30°. The essential spectral changes are shown in Figure 2. At −83° (slow exchange) the cis and one trans resonance are clearly resolved and the two remaining trans resonances are superimposed at higher field. As the temperature is raised two trans signals [T_3 and $T_1(T_2)$] broaden and coalesce to a single peak above *ca.* −62° (LTP). The averaged peak attains minimum line width above *ca.* −30° and then at higher temperatures coalesces with $T_2(T_1)$ and C. The temperature-dependent spectral changes are very similar to those observed for Al(α-$C_3H_5T)_3$ in dichloromethane and Co(α-$C_3H_5T)_3$ in chloroform.[1] Spectra of Ga(α-$C_3H_7T)_3$ were recorded from −80 to 30° at 100 MHz and from −50 to 22° at 220 MHz in dichloromethane. Spectra obtained under the latter conditions are given in Figure 3. The low-temperature spectra at 100 MHz are poorly resolved but do indicate that two kinetic processes are operative in the same temperature intervals as observed for the isopropenyl analog. More informative are the 220-MHz spectra in the range −50 to −24°. Based on the spectra of Ga(α-$C_3H_5T)_3$ the LTP is essentially at the fast-exchange limit in this temperature interval and the initial effects of the HTP are just discernible at −24°. The key feature of the spectra in Figure 3 is the resolution of three spin doublets at −48° with intensities 2:1:1 from low to high field. These spectra, at the fast-exchange limit of the LTP, are better resolved than those of the Al(III)

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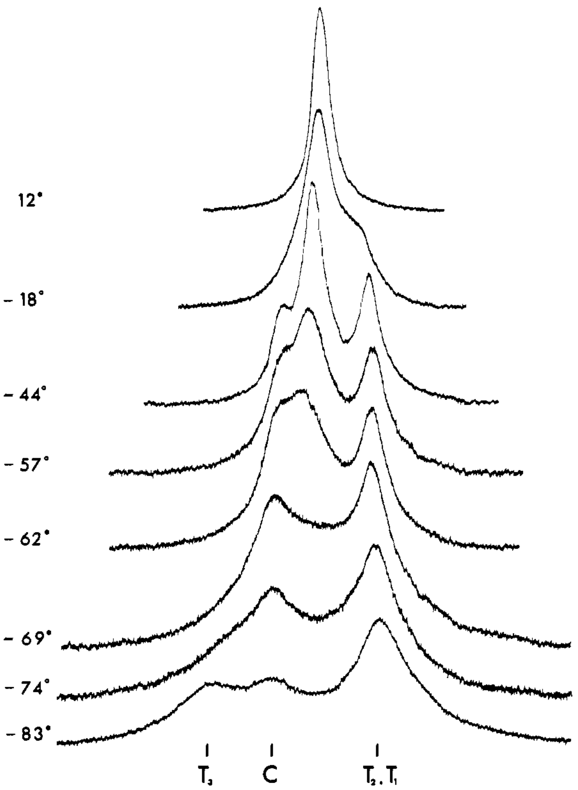

Figure 2. Methyl spectra (100 MHz) of cis (C) and trans (T) Ga(α-C_3H_5T)$_3$ in dichloromethane solution. Chemical shifts of the centers of spin doublets are T_1, T_2, 3.64; C, 3.45; T_3, 3.35 ppm upfield of dichloromethane at −83°.

and Co(III) analogs in which the features appeared as two overlapping doublets under corresponding exchange conditions.[1,10] The enhanced resolution of the Ga(α-C_3H_7T)$_3$ spectra allow the conclusion by inspection that the methyl spin doublets are averaging pairwise,[24] and obviate the use of line-shape analysis which was required to reach the same conclusion for the Al(III) and Co(III) complexes.[1]

[Ge(α-C_3H_5T)$_3$](PF$_6$) and [Ge(α-C_3H_7T)$_3$](PF$_6$). Spectra of [Ge(α-C_3H_5T)$_3$](PF$_6$) at 100 MHz in 1,1,2,2-tetrachloroethane at 30° show three methyl multiplets at 3.95, 3.98, and 4.01 ppm upfield of the solvent resonance. The central peak is of considerably greater intensity than the other two peaks. As the temperature is raised to 76° the peaks move together such that they are no longer resolved. The rather diffuse and noncharacteristic line shapes in this temperature range preclude the possibility of obtaining kinetic or mechanistic information. Chemical shift differences were smaller in other solutions (chlorobenzene, *o*-dichlorobenzene, chloroform), and investigation of this complex was discontinued.

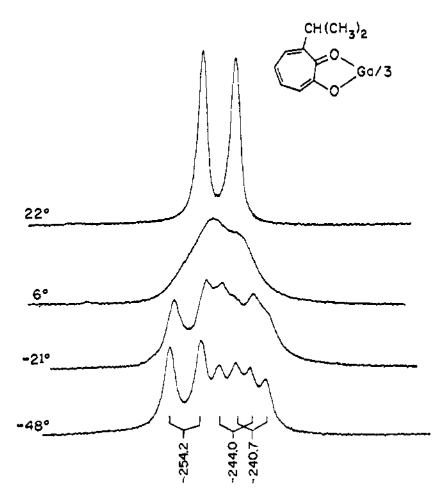

Figure 3. Methyl spectra (220 MHz) of a cis–trans mixture of Ga(α-C_3H_7T)$_3$ in dichloromethane solution. The −48° spectrum reveals the fast-exchange limit of the LTP. Chemical shifts (Hz) are downfield of TMS.

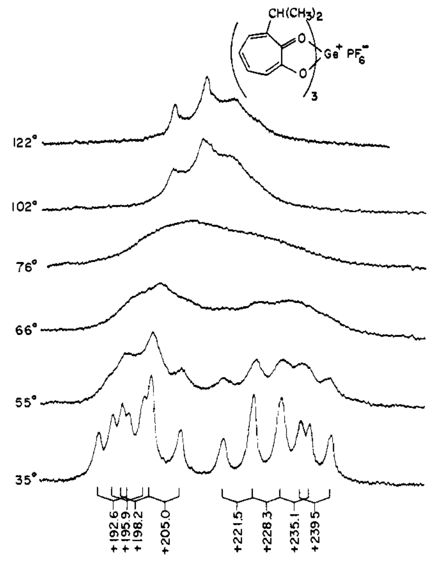

Figure 4. Methyl spectra (220 MHz) of a cis–trans mixture of [Ge(α-C_3H_7T)$_3$](PF$_6$) in *o*-dichlorobenzene solution. Chemical shifts (Hz) of the centers of spin doublets are upfield of hexamethylbenzene.

Spectra of [Ge(α-C_3H_7T)$_3$](PF$_6$) at 220 MHz in *o*-dichlorobenzene were recorded from −20 to 122°. As shown in Figure 4, the eight methyl spin doublets expected for a cis–trans mixture are clearly resolved under slow-exchange conditions (35°). All peaks have sufficiently similar intensities such that it is not possible to identify the pair of doublets from the cis isomer. Above *ca.* 45° exchange broadening occurs and at 76° a featureless broad signal is observed. At higher temperatures the spectrum sharpens to a doublet downfield of several broader partially superimposed doublets. Similar although less well resolved spectra were obtained in 1,1,2,2-tetrachloroethane (Figure 5). Spectra could not be obtained at temperatures above *ca.* 120° in either solvent due to decomposition of the sample. The observed line-shape changes are very similar to those for the LTP of Co(α-C_3H_7T)$_3$ in chloroform[1] and, to a lesser extent, of Al(α-C_3H_7T)$_3$ in tetrachloroethane.[1,10] Comparison of the Ge(IV) spectra in Figures 4 and 5 with the Co(III) and Al(III) spectra suggests that the sharper downfield doublet in the spectra of [Ge(α-C_3H_7T)$_3$]$^+$ above *ca.* 100° is the average of the two inequivalent cis environments and is partially superimposed on the incompletely averaged signals of the six trans environments.

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(24) Based on the permutational analysis[1] the signal multiplicity at fast exchange of the LTP can be 1, 2, 4, 6, or 8 doublets. The observation of three fully resolved doublets indicates that the multiplicity is 4, 6, or 8. Because all peaks are involved in the exchange process the multiplicity must be 4 with two averages superimposed in the low field signal centered at −254.2 Hz (Figure 3).

Table I. Isotropic Ring Proton Shifts of M(α-RT)$_3$ Complexes at $\sim$30° [a]

Complex	α-H	β,β'-H	γ-H
Co(α-C$_3$H$_5$T)$_3$[b,c]	−7.52	−7.34	−6.68
VT$_3$[c]	+8.1 (70)	+13.0 (30)	+17.2 (35)
V(α-C$_3$H$_7$T)$_3$[c,f]	+9.6 (70)	+12.8 (30), +14.2 (30)	+17.3 (35)
MnT$_3$[d]	+26.7 (125)	−2.0 (30)	+47.5 (30)
Mn(α-C$_3$H$_5$T)$_3$[d,f]	+25.9 (160)	−1.5 (40), −2.9 (40)	+47.0 (50)
Mn(α-C$_3$H$_7$T)$_3$[e,f]	+27.4 (160)	−1.6 (50), −5.4 (55)	+47.9 (50)
RuT$_3$[c]	+23.1 (30)	−11.5 (20)	+35.5 (45)
Ru(α-C$_3$H$_5$T)$_3$[c]	+20.1 ($\sim$30[g])	−9.6 ($\sim$20[g]), −10.2	+31.1 ($\sim$45[g])
	+22.9	−11.9, −12.4	+35.8
	+26.8	−13.7, −14.2	+40.8

[a] Shifts in ppm; line widths in Hz in parentheses. [b] Diamagnetic reference, chemical shifts relative to TMS given. [c] CDCl$_3$. [d] CD$_2$Cl$_2$. [e] CD$_3$COCD$_3$. [f] Averaged shifts for cis and trans isomers observed. [g] All signals have the same approximate line width.

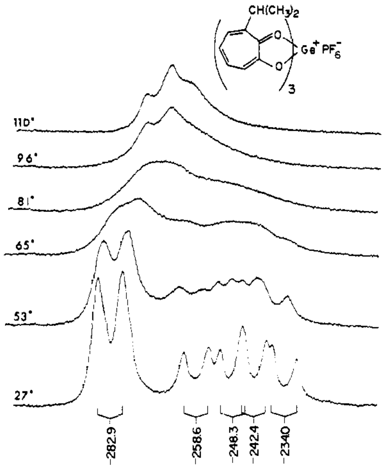

Figure 5. Methyl spectra (220 MHz) of a cis–trans mixture of [Ge(α-C$_3$H$_7$T)$_3$](PF$_6$) in 1,1,2,2-tetrachloroethane solution. Chemical shifts (Hz) of the centers of spin doublets are downfield of hexamethyldisiloxane.

Paramagnetic Complexes. In order to expand the scope of the investigation of tris(tropolonate) rearrangements, paramagnetic complexes of types **1** and/or **2** and MT$_3$, M = Ru(III), Mn(III), and V(III), were synthesized and their variable-temperature pmr spectra obtained. These metals were selected in order to allow comparison with rearrangement rate information available for their tris(β-diketonate) complexes[9] and because of their tendency to effect substantial isotropic shifts in β-diketonate[25,26] and aminotroponeiminate[27] complexes without excessive line broadening. Only MnT$_3$ has been reported previously.[22] A recent study of the tropolone complexes of V(III) led to the isolation of VT$_2$Cl from the reaction of VCl$_3$ and tropolone in *ca.* 1:7 mole ratio in the absence of base.[28] In this work VT$_3$ and V(α-C$_3$H$_7$T)$_3$ were readily prepared in acetonitrile solution by reaction of stoichiometric amounts of VCl$_3$ and the sodium tropolonate. The recrystallized Ru(III) complexes apparently contain tropolone, which was identified by its pmr spectrum. Isotropic shifts of ring protons α, β, β', and γ (**1**, **2**), referenced to diamagnetic Co(α-C$_3$H$_5$T)$_3$, are collected in Table I. Assignments of these signals are based on a comparison of relative intensities in MT$_3$ and M(α-RT)$_3$ spectra.

RuT$_3$ and Ru(α-C$_3$H$_5$T)$_3$. The spectrum of RuT$_3$ in deuteriochloroform consists of three signals with intensities 2:2:1 from low to high field. Signs of the isotropic shifts alternate, being positive for α-H and γ-H and negative for β-H. A similar pattern is found with Ru(α-C$_3$H$_5$T)$_3$. In deuteriochloroform or nitrobenzene-d_5 solutions of this complex three signals of apparently equal intensity were observed for each of the ring protons, consistent with the presence of the trans isomer. An additional relatively weak α-H resonance with an isotropic shift of +23.7 ppm at 30° was observed in chloroform and is attributed to the cis isomer. The expected β,β'- and γ-H cis signals were not located and are presumably obscured by the more intense trans resonances. The intensity of the cis feature did not appear to change after heating a nitrobenzene solution between 120 and 170° for several hours. From considerations based on the 28 kcal/mol[9] activation energy for T $\rightarrow$ C isomerization of Ru(tfac)$_3$ and on the rate enhancement for M(α-RT)$_3$ compared to M(tfac)$_3$ and other tris(β-diketonates) (*vide infra*), it is presumed that the solution attained C $\rightleftharpoons$ T equilibrium during this period. The nmr spectra in nitrobenzene and deuteriochloroform up to 170 and 90°, respectively, gave no evidence of exchange broadening. These observations indicate that Ru(α-C$_3$H$_5$T)$_3$ is stereochemically rigid on the nmr time scale. Methyl spectra of this complex were broad and poorly resolved and provided no information concerning isomer distribution or isomerization.

MnT$_3$ and Mn(α-RT)$_3$. Spectra of MnT$_3$ at 100 MHz in dichloromethane-d_2 were recorded from −32 to 41°. The positive isotropic shifts of α- and γ-H show $1/T$ dependence; the negative β-H isotropic shifts were too small to obtain accurate temperature-dependent data. Mn(α-C$_3$H$_5$T)$_3$ was examined under the same conditions from −80 to 31°. Based on a comparison with Mn(α-C$_3$H$_7$T)$_3$ the resonances of the isopropenyl group are assigned as follows: CH$_3$, −2.85; CH$_2$, −1.10, −6.80 ppm (downfield of TMS at 30°). As the temperature is decreased below *ca.* 0° all resonances broaden, but the increase in line width is much less for the isopropenyl signals. At −47° the γ-H signals appear as two overlapping features, the α-H signal is a broad unresolved band, and the β,β'-H signals consist of four broad poorly resolved resonances at 9–14 ppm downfield of TMS which partially overlap with one of the methylene signals. This overlap precludes an analysis of the averaging patterns of the β protons. Upon a further decrease in temperature each methylene resonance splits into two peaks,

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(25) D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965).

(26) A. Johnson and G. W. Everett, Jr., *ibid.*, **94**, 1419 (1972).

(27) D. R. Eaton, W. R. McClellan, and J. F. Weiher, *Inorg. Chem.*, **7**, 2040 (1968).

(28) J. B. White and J. Selbin, *J. Inorg. Nucl. Chem.*, **32**, 2434 (1970).

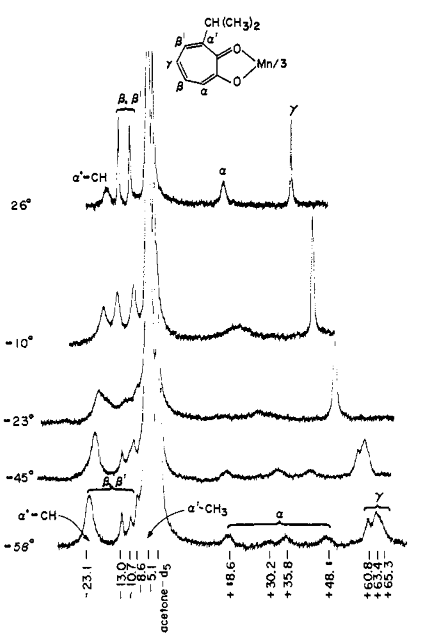


Figure 6. Complete 100-MHz pmr spectra of Mn(α-C_3H_7T)$_3$ in acetone-d_6 solution. Chemical shifts at $-58°$ are in ppm from TMS.

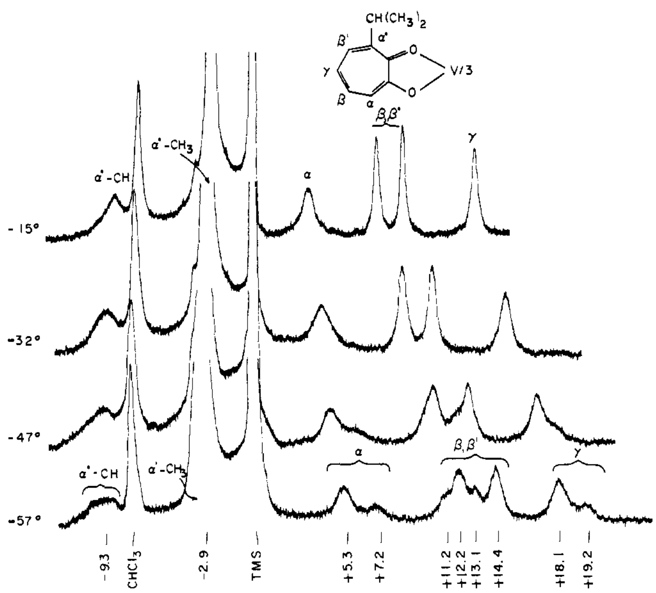


Figure 7. Complete 100-MHz pmr spectra of V(α-C_3H_7T)$_3$ in deuteriochloroform solution. Chemical shifts at $-57°$ are in ppm from TMS.

further obscuring the β,β'-H signals; there was no improved separation of the α-H and γ-H features. The spectra do reveal the existence of one or more kinetic processes in the interval -70 to $-10°$, with the fast-exchange limit reached near *ca.* 0°. However, because of the complexity of the spectra no mechanistic information could be obtained.

Spectra of Mn(α-C_3H_7T)$_3$ were recorded at 100 MHz in acetone-d_6 solution from -73 to 26°. The essential spectral features are displayed in Figure 6. As the temperature is decreased below *ca.* 0° the α-, β,β'-, and γ-H resonances broaden and split into multiple peaks. The behavior is clearest for α-H. At the slow-exchange limit ($-58°$) three equally intense signals due to the trans form and a less intense signal (at +30.2 ppm), assigned to the cis isomer, are clearly resolved. All four α-H signals appear to average simultaneously as the temperature is increased. Thus there is no evidence for a separate LTP or a specific averaging of trans sites.

VT_3 and V(α-C_3H_7T)$_3$. The spectrum of VT_3 in deuteriochloroform contains three signals with positive isotropic shifts and relative intensities 2:2:1 from low to high field. Spectra of V(α-C_3H_7T)$_3$ in the same solvent were recorded from -57 to 62° (*cf.* Figure 7). Temperature dependencies of ring proton shifts exhibit $1/T$ behavior in the fast-exchange region (above *ca.* $-32°$). Below this temperature the ring proton resonances broaden and then split into two resolved components at *ca.* $-57°$. Spectra at lower temperatures could not be obtained in deuteriochloroform. The low-temperature signal multiplicity does not provide adequate information to determine whether there is only one kinetic process or whether $-57°$ is the fast-exchange limit for a lower temperature process. To investigate this matter further, spectra were measured in two other solvents. In dichloromethane-d_2 solution the shift differences between slow-exchange peaks were sufficiently small that at temperatures down to $-75°$ the four ring proton resonances merely broadened and no increase in multiplicity could be discerned. Spectra in acetone-d_6 solution from -30 to 12° were similar to those in deuteriochloroform. At temperatures between -30 and $-82°$ the splittings between nonequivalent ring proton signals were so large that considerable overlap occurred, preventing identification of the actual number of resonances. Therefore, it was not possible to determine whether there was a second lower temperature process. Throughout the slow and exchange-broadened regions in deuteriochloroform the methyl resonance appeared as a broad unresolved feature.

Ligand Exchange. The intramolecular nature of the line-shape changes described for Mn(III) and V(III) complexes has been verified by ligand-exchange experiments. The spectrum of an approximately equimolar mixture of Mn(α-C_3H_5T)$_3$ and Mn(α-C_3H_7T)$_3$ in acetone-d_6 at ambient temperature shows five α-H and five γ-H signals. For either Mn(α-C_3H_5T)$_3$ or Mn(α-C_3H_7T)$_3$ (Figure 6) at this temperature the nonequivalent cis and trans environments are fully averaged. The observation of more than two α-H and γ-H resonances indicates that intermolecular ligand exchange between the various Mn(α-C_3H_5T)$_x$(α-C_3H_7T)$_{3-x}$ species is slow on the pmr time scale, and that the averaging processes observed for Mn(α-RT)$_3$ at and below *ca.* 30° are intramolecular. Similarly, the spectrum of a mixture of VT_3 and V(α-C_3H_7T)$_3$ in deuteriochloroform at ambient temperature reveals 11 signals in the region associated with ring proton resonances (Figure 7). Although these signals have not been assigned, the observation of more than seven resonances (2α, β', 2β, 2γ) ensures that intermolecular ligand exchange is slow and that the exchange-broadened spectra of V(α-C_3H_7T)$_3$ result from an intramolecular process. The presence of separate cis and trans signals in the LTP of Ga(α-C_3H_5T)$_3$ demonstrates the intramolecularity of that process.

Rearrangement Mechanisms. The preceding considerations of the variable-temperature pmr spectra reveal that clearcut mechanistic information is available only for the Ga(α-RT)$_3$ complexes. The observed averaging patterns in the LTP of both complexes are entirely consistent with a trigonal-twist mechanism as depicted in Figure 1. The averaging of two of the three methyl signals in *trans*-Ga(α-C_3H_5T)$_3$, without simultaneously affecting the remaining trans and the cis resonance, is interpretable in terms of the site interchange (1) which has been observed for the related Al-

$$\mathrm{T\Lambda}\left\{\begin{matrix}1-y\\2-x\\3-z\end{matrix}\right\} \rightleftharpoons \mathrm{T\Delta}\left\{\begin{matrix}1-z\\2-x\\3-y\end{matrix}\right\} \tag{1}$$

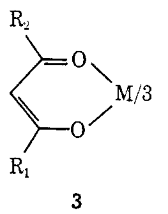
(III) and Co(III) complexes.[1] The $\mathrm{C\Lambda} \rightleftharpoons \mathrm{C\Delta}$ inversion of the α-isopropenyl complexes is undetectable by pmr. The pairwise averaging of eight methyl doublets to four in the spectra of Ga(α-C_3H_7T)$_3$ is concordant with the site interchanges (2) and (3) in which the two cis and six

$$\mathrm{C\Lambda}\left\{\begin{matrix}\mathrm{a}-\mathrm{r}\\\mathrm{b}-\mathrm{s}\end{matrix}\right\} \rightleftharpoons \mathrm{C\Delta}\left\{\begin{matrix}\mathrm{a}-\mathrm{s}\\\mathrm{b}-\mathrm{r}\end{matrix}\right\} \tag{2}$$

$$\mathrm{T\Lambda}\left\{\begin{matrix}1-y\mathrm{r}\\1-y\mathrm{s}\\2-x\mathrm{r}\\2-x\mathrm{s}\\3-z\mathrm{r}\\3-z\mathrm{s}\end{matrix}\right\} \rightleftharpoons \mathrm{T\Delta}\left\{\begin{matrix}1-z\mathrm{s}\\1-z\mathrm{r}\\2-x\mathrm{s}\\2-x\mathrm{r}\\3-y\mathrm{s}\\3-y\mathrm{r}\end{matrix}\right\} \tag{3}$$

trans doublets are averaged to one and three doublets, respectively, at fast exchange. The results for both complexes conform only to averaging set A_6 in the permutational analysis presented previously,[1] which corresponds to inversion without isomerization and averages trans sites y and z. The most satisfactory physical conception of the site interchanges is, in our view, the trigonal twist.[29] Based on the similarities in line shapes of the LTP of the Al(III) and Co(III) complexes **2** and those in the exchange-broadened region of [Ge(α-C_3H_7T)$_3$]$^+$ (Figures 4 and 5), the rearrangement mechanism of the latter is provisionally assigned as a trigonal twist. The evidence for this mechanism is clearly less complete than for other systems where it was possible to observe site averaging patterns for both the α-isopropenyl and α-isopropyl complexes.

Relative Rearrangement Rates. The most significant kinetic feature of the intramolecular rearrangements of the complexes **1** and **2** is the unexpectedly low barriers and consequently high rates of rearrangement, which are most profitably compared with similar data for the tris(β-diketonates) **3**. These complexes contain the



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M–O_6 core in common with the tropolonates and, being uncharged, have been studied in weakly polar media as have the tropolonates. The relative rate enhancement is most dramatically illustrated by Co(α-RT)$_3$,[30] which, as mentioned above, inverts $\sim 10^{11}$ times faster than does Co(acac)$_3$[20] and $\sim 10^9$ times faster than Co(tfac)$_3$ isomerizes[32] (both comparisons at 25°).

For the metal tropolonates described in this paper, the rates for inversion and isomerization are consistently higher than for diketonate complexes **3**. Although the data do not allow a quantitative evaluation, the substantial rate or barrier differences are in evidence from qualitative or approximate comparisons. For example, approximate coalescence temperatures for inversion in Ga(α-RT)$_3$ and the estimated stereoisomerization barrier[33] are substantially lower than for analogous diketonate analogs (*cf.* Table II). Whereas all vanadium(III) β-diketonates[9,34–36] as well as related salicylaldehydato complexes[37] exhibit limiting slow-exchange spectra at ambient temperatures, the tropolone chelate, V(α-C_3H_7T)$_3$, is at the fast-exchange limit below 0°. The specific comparison between V(tfac)$_3$ and V(α-C_3H_7T)$_3$ is rather convincing on the point of rate enhancement. There is no exchange broadening in the pmr spectrum of the former up to 100°,[9,38] whereas there is coalesence of the α-H and γ-H signals of the tropolonate at $\sim -40°$ (estimated $\Delta G_{233}^{\ddagger}$ is 11 kcal/mol). There is then 140° or more difference in coalescence temperatures.[39,40] Similar relations hold for manganese(III) with coalescence temperature differentials in the 80–100° range.[39,41] Data are not available for a comparison based on a

Table II. Coalescence Temperatures and Stereoisomerization Barriers

	Coalescence temp, °C	$\Delta G,^{\ddagger}$ kcal/mol
Ga(α-RT)$_3$	−65, −15	10 (−65°)
Ga(acac)$_2$(hfac)[a]	−26	15.3
Ga(tfac)$_3$[32]	62	20.8
Ga(acac)$_2$(dbm)[a]	80	20.2
Ga(pmhd)$_3$[7]	80	20.1–20.5

[a] T. J. Pinnavaia, J. M. Sebeson, and D. A. Case, *Inorg. Chem.*, **8**, 644 (1969); D A. Case and T. J. Pinnavaia, *ibid.*, **10**, 482 (1971).

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(29) We emphasize here, as we have done elsewhere,[1,14] that the pmr observations on nonrigid tris(tropolonates) furnish no direct evidence for the absence of bond breaking. However, it can be asserted that no five-coordinate transition states (trigonal bipyramidal, square pyramidal) of the types previously considered, which have predictable kinetic consequences,[7] can be of significance in the pmr-detectable rearrangements of the Al(III), Ga(III), and Co(III) complexes.

(30) Recently evidence has been presented for the stereochemical nonrigidity of another Co(III) chelate. The sexadentate species [Co(py$_3$tame)]$^{3+}$ exhibits an exchange-broadened pmr spectrum above *ca.* 100° in DMSO which has been interpreted in terms of inversion *via* a trigonal twist.[31]

(31) S. O. Wandiga, J. E. Sarneski, and F. L. Urbach, *Inorg. Chem.*, **11**, 1349 (1972).

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

(33) Using the Gutowsky–Holm approximation: J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 223.

(34) G. W. Everett, Jr., and A. Johnson, *J. Amer. Chem. Soc.*, **94**, 6397 (1972).

(35) (a) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967); (b) Y. T. Chen and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968); (c) G. W. Everett, Jr., and Y. T. Chen, *ibid.*, **92**, 508 (1970).

(36) D. R. Eaton and K. L. Chua, *Can. J. Chem.*, **49**, 56 (1971).

(37) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *J. Amer. Chem. Soc.*, **89**, 6472 (1967).

(38) While the V(III) complexes **3** do not rearrange at a perceptible rate on the nmr time scale, they do belong to the fast category. Cis and trans forms of only one complex, V(bzac)$_3$, have been separated (fractional sublimation) and these give identical isomer ratios in fresh solutions.[9]

(39) Coalescence temperatures for paramagnetic species cannot be compared as precisely as for diamagnetic complexes due to the larger variations in slow-exchange chemical shifts and to the effects of paramagnetism on the temperature dependence of the shifts.

(40) The α-H and γ-H signals in V(α-C_3H_7T)$_3$ are separated by 1–2 ppm at −57° (Figure 7). Although the slow-exchange methyl chemical shift difference in V(tfac)$_3$[9] is about ten times greater than ring proton shift differences in V(α-C_3H_7T)$_3$ under comparable conditions, this effect could at most account for an approximate 25° variation in coalescence temperatures if $\Delta G_T^{\ddagger}$ values were the same.

(41) The α-H coalescence temperature of Mn(α-C_3H_7T)$_3$ is $\sim -15°$, whereas the methyl coalescence temperatures of Mn(tfac)$_3$ and Mn(bzac) are 70 and 80°, respectively. Mn(+atc)$_3$ exhibits a spectrum at *ca.* 30° that is at or near the slow-exchange limit.[34]

Table III. Relative Rearrangement Rates of M–O$_6$ Complexes (**1–3**) in Weakly Polar Media

Ligand	Process	Rate order: M [k,[a] sec^{-1} (°C); E_a, kcal/mol]	Ref
α-RT[b]	Inv	Ga [$\sim 10^2$ ($-65°$)] > Co [10^2, 17] $\gtrsim$ Al [80, 13] > Ge > Si, Rh, Ru	1, 13, *c*, *h*
	Isom	V $\sim$ Mn $\sim$ Ga > Co[d] [4.0, 16] $\gtrsim$ Al[d] [1.0, 17] > Ge > Si, Rh, Ru	1, 13, *c*, *h*
tfac	Isom	Fe, In [>36 ($-57°$), <14] > Mn [$\sim 10^3$ (70°)] > Ga [38 (62°), 21] > Al [34 (103°), 24] > V > Co[d] [5×10^{-8}, 31] > Ru[2×10^{-12}, 33] > Rh [$<10^{-8}$ (163°), >42]	9, 32
bzac	Isom	Mn[8×10^2 (80°)] > V > Co[d] [5×10^{-9}, 33]	9, 21
pmhd	Isom + inv	Sc > Ga[e] [$\sim$8, 20] > Al[e] [$\sim 10^{-4}$, $\sim$29]	7
acac	Inv	Co [8×10^{-10}, 35] $\gtrsim$ Cr [2×10^{-11}, 35] > Ru [$<3 \times 10^{-6}$ (135°), >39] $\gtrsim$ Rh [$<2 \times 10^{-6}$ (165°), >42]	20
acac–hfac[f]	Site ex	Ga [8×10^2, 15] > Al [80, 18]	43
acac-dbm[g]	Site ex	Ga [8×10^{-2}, 20] > Al [2×10^{-3}, 22]	43

[a] Measured or extrapolated value at 25° unless otherwise noted. [b] Data for R = C_3H_5 complexes. [c] This work. [d] C → T; T → C kinetic parameters are similar. [e] Calculated using average values of the kinetic data obtained by line shape analysis. [f] M(acac)$_2$(hfac). [g] M(acac)$_2$(dbm). [h] T. Ito, N. Tanaka, I. Hanazaki, and S. Nakagura, *Inorg. Nucl. Chem. Lett.*, **5**, 781 (1969).

germanium center. All ruthenium(III) complexes of classes **1**, **2**, and **3**[9,20] are stereochemically rigid, a behavior consistently observed for chelates based on second-row transition metals[1,9,20,32] with one recent exception.[42]

In order to compare in more detail the relative rearrangement rates of tris(tropolonate) and tris(β-diketonate) complexes, reference is made to Table III. This table contains rate constants and activation energies, where available, for inversion, isomerization, and site exchange and indicates the order of increasing rearrangement rates as a function of metal for various ligands. In addition, rate order as a function of ligand with invariant metal may be obtained from the data. The rate orders given in the table and below were deduced from a combination of known or estimated rate constants and coalescence temperatures. A more extensive body of kinetic results is available elsewhere.[5a] Although all systems were not investigated in the same medium, it is considered unlikely that differences among the weakly polar solvents usually employed would significantly affect the rate orders.

Ligand kinetic series (4) is fully consistent with the data for complexes of Al(III), Ga(III), V(III), Mn(III), and Co(III). The substantially larger rearrangement

$$\alpha\text{-RT} > \text{tfac} > \text{bzac} \sim \text{acac} \sim \text{pmhd} \sim \text{mhd} \quad (4)$$

rates for the tropolonates are additionally emphasized when compared to those for fluorinated β-diketonates. The rate-accelerating influence of CF_3 groups is now well documented.[5b,43–45] Therefore, it is particularly striking that rearrangement rates for the tropolonates are substantially larger than for fluorinated β-diketonates. In the Al(III) and Ga(III) cases, rates become comparable to isomerization rates of the tropolonates only when at least one hfac ligand is present. Inversion of Al(α-RT)$_3$[1] also proceeds at rates comparable to site exchange in Al(acac)$_2$(hfac), but the inversion of Ga(α-RT)$_3$ is substantially faster than site exchange in Ga(acac)$_2$(hfac).[43] It is not known whether site exchange in M(acac)$_2$(hfac) proceeds with inversion of configuration. Like Co(tfac)$_3$, Co(tfac)$_2$(acac) is stereochemically rigid up to at least 115°.[44b] The fast-exchange limit for isomerization (HTP) of Co(α-RT)$_3$ is reached at *ca.* 70–80°.[1] From the results at hand it is concluded that rate enhancement of tris(tropolonate) compared to M(tfac)$_3$ and nonfluorinated tris(β-diketonate) complexes is a general phenomenon.

There is a consistent dependency in rearrangement rates for the chelates based on the character of the central metal ions. A qualitative grouping of M(α-RT)$_3$ is as follows: nonrigid complexes which attain the fast-exchange limit of inversion and/or isomerization (i) below *ca.* 0° [V(III), Mn(III), and Ga(III)], (ii) below *ca.* 100° [Al(III) and Co(III)], (iii) above *ca.* 100° [Ge(IV)], (iv) rigid or slow complexes [Si(IV), Rh(III), Ru(III)]. No rate order can be given for the complexes in group (i). The classification of Si(IV) species as rigid is based on the resolution of [SiT$_3$]$^+$ [46] and the partial separation of [Si(α-C_3H_7T)$_3$]$^+$ into cis and trans forms.[10] It is observed that, except for the placement of V(III) and Co(III), the rate orders in the α-RT and tfac series are similar. Rates in general parallel activation energies (Table III) or activation enthalpies, where known, except for several M(α-RT)$_3$ complexes. Most preexponential factors are smaller for Al(III) than Co(III) tropolonates,[1] thereby leading to comparable or slightly lower rates for the former despite their smaller activation energies.

In three M(α-RT)$_3$ complexes [Al(III), Ga(III), Co(III)] two distinct kinetic processes have been found. Only one process could be detected for [Ge(α-RT)$_3$]$^+$ within the temperature range attainable without decomposition. Spectra of the V(III) and Mn(III) complexes clearly revealed only one process (isomerization), but the existence of a lower temperature process cannot be ruled out. Sufficient information is not available at this time to explain fully the different rearrangement rates within the tropolonate series or the occurrence of the twist mechanism in the LTP which have been detected. In the following sections are discussed those factors which are recognized as pertinent to the relative rearrangement rates for various complexes and which may contribute to low barriers for trigonal twisting in the tropolonates.

The kinetic results for the tropolonates conform to certain regularities, noted earlier,[7,9] in metal ion dependence of rearrangement rates. The collective rate data for the d^{0,10} complexes **1–3** reveal the metal kinetic series (5), in which the Shannon–Prewitt ionic radii[47]

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(42) Stereochemical nonrigidity has been observed for several tris(dithiocarbamato)Ru(III) complexes: L. H. Pignolet, D. J. Duffy, and L. Que, Jr., *J. Amer. Chem. Soc.*, **95**, 295 (1973).

(43) (a) T. J. Pinnavaia, J. M. Sebeson, and D. A. Case, *Inorg. Chem.*, **8**, 644 (1969); (b) D. A. Case and T. J. Pinnavaia, *ibid.*, **10**, 482 (1971).

(44) (a) J. J. Fortman and R. E. Sievers, *ibid.*, **6**, 2022 (1967); (b) R. A. Palmer, R. C. Fay, and T. S. Piper, *ibid.*, **3**, 875 (1964).

(45) J. J. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, **92**, 7342 (1970); M. Elder, J. G. Evans, and W. A. Graham, *ibid.*, **91**, 1245 (1969).

(46) T. Ito, N. Tanaka, I. Hanazaki, and S. Nakagura, *Inorg. Nucl. Chem. Lett.*, **5**, 781 (1969).

(Å) are given in parentheses. The dependence of rate

$$\mathrm{In^{3+}}\ (0.79),\ \mathrm{Sc^{3+}}\ (0.73) \gg \mathrm{Ga^{3+}}\ (0.62) > \mathrm{Al^{3+}}\ (0.53) \qquad (5)$$

on ionic size also extends to bis(β-diketonato)M^{IV}X$_2$ complexes[48–50] [X = halide, O(Mo(VI))[50]], leading to the rate order (6). Of these species only Ge(dpm)$_2$Cl$_2$[49]

$$\mathrm{Zr^{4+}}\ (0.72),\ \mathrm{Hf^{4+}}\ (0.71) \gg \mathrm{Ti^{4+}}\ (0.61) > \mathrm{Mo^{6+}}\ (0.60) > \mathrm{Ge^{4+}}\ (0.54) \qquad (6)$$

does not show exchange broadening at temperatures up to *ca.* 40°. Pinnavaia and Clements[50] have proposed a more extensive rate order by combining series (5) and (6). Decreasing intramolecular lability with decreasing ionic radius is clearly evident in the orders (5) and (6) and, despite several apparent exceptions[51] to this trend, ionic size must be considered the dominant parameter determining relative rearrangement rates in series of $d^{0,10}$ complexes with invariant ligands. In contrast, rates for d^2–d^6 complexes show no correlation with ionic radius. Further, the rate orders Fe^{3+} (0.65) > Ru^{3+} (0.70) and Co^{3+} (0.53) > Rh^{3+} (0.67) are the reverse of those found in descending the Ti, Al, and Si vertical groups. These orders appear to be of some generality since they are also found in the complexes H$_2$ML$_4$[53] (M = Fe, Ru) and HML$_4$[54] (M = Co, Rh, Ir; L = phosphine, phosphite), whose principal rearrangement pathways are not possible for tris chelates.

The origin of rearrangement barriers in the metal ion series above remains unclear. *The problem of assessing these barriers is compounded by the lack of any definite mechanistic information for fast bis- and tris(β-diketonates).* Detailed line-shape analysis of M(pmhd)$_3$ [M = Al(III), Ga(III)] led to the exclusion of certain mechanisms but did not allow a clear distinction between (a) a combination of twists about the real and imaginary C_3 axes, and (b) several bond-rupture pathways.[7] A similar situation holds for M(β-diketonato)$_2$X$_2$.[43,50,55] Co(mhd)$_3$,[6] Co(bzac)$_3$,[21] and, presumably, Co(acac)$_3$[20] rearrange primarily through a bond-rupture pathway. Other than noting for β-diketonates an inverse relation between bond energies[56] and rates for the $d^{0,10}$ and d^6 cases and a rough correspondence between M–O stretching force constants[57] and rates for d^{3-6} complexes, we have been unable to discern any satisfactory interrelationship between structural and electronic properties and rearrangement rates.

The findings that Co(α-RT)$_3$ and Co(III) β-diketonates rearrange by twist and bond-rupture pathways, respectively, suggest that rate differences for complexes of other metal ions may be due to similar mechanistic differences. It is, however, a rather demanding task to delineate the factors that so distinguish the tropolonate chelates with respect to rearrangement rates and possibly to mechanistic pathway. How and why is the potential energy surface between ground state and an excited state, that probably resembles a trigonal prism, so substantially altered in the tropolonates? With the present state of knowledge, we can only summarize those features of tropolonates that appear to favor the twist mechanism, for which the transition state is an idealized trigonal prism (TP, Figure 1).[58] (i) The rigid, planar nature of the tropolonate ligand should tend to suppress a bond rupture mechanism since more energy, in the form of M–O or M–O–C bond deformations, would be required to remove one end of the ligand from bonding distance to the metal than in the case of the internally flexible β-diketonates. (ii) The relatively short bite distance of the tropolonate ligand (*ca.* 2.5 Å[14]) leads to polyhedron radius to polyhedron edge ratios which are close to the ideal value of 0.76 given by Day and Hoard[59] for TP geometry. The following ratios have been calculated assuming bite and M–O distances are the same in the TP as in the ground-state trigonal antiprismatic (TAP) configuration: CoT$_3$, 0.74;[1] Co(acac)$_3$, 0.66;[60] AlT$_3$, 0.76;[14] Al(acac)$_3$, 0.69;[60] GaT$_3$, 0.78 (estimated); MnT$_3$, ~0.78.[61] (iii) Ligand electrostatic repulsion energy differences in TP and TAP geometries decrease with increasing ratio of M–O to bite distance;[62] these energy differences are smaller in the tropolonates.

In addition, the twist angle in AlT$_3$[14] is 49°, not the 60° value for an idealized M–O$_6$ octahedra. This change from the octahedral toward the trigonal-prismatic parameter may have a favorable effect on the energetics for a twisting about an r-C_3 or p-C_3 axis. The corresponding angle in CoT$_3$[1] is ~55° and, as for the Al(α-RT)$_3$ complexes, this structural feature alone is insufficient to explain the fast rates and the operation of a twist mechanism. Other factors such as d-electron effects and solvation may also contribute to the rearrangement barriers but cannot be adequately assessed at present. Lastly, it is observed that all complexes for which the trigonal twist is considered the most probable rearrangement pathway are stereochemically nonrigid. Further research on slow complexes is required to establish whether or not this mechanism is confined to reactions with relatively low barriers.

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