# Electrochemistry and Isomerization Kinetics of Tris[(+)-3-acetylcamphorato]ruthenium(III). Circular Dichroism and Absolute Configurations of the Analogous Ruthenium(II) and Ruthenium(IV) Diastereomers

Grover W. Everett, Jr.,* and Richard R. Horn

Contribution from the Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045. Received April 27, 1973

Abstract: Electrolytic oxidation and reduction of the four diastereomers of tris[(+)-3-acetylcamphorato)-ruthenium(III) to the corresponding Ru(IV) and Ru(II) species proceed with retention of configuration. Absolute configurations may be assigned to the Ru(II) and Ru(IV) diastereomers since configurations were established for Ru(III) precursors by a previous study. Circular dichroism spectra of the Ru(II), Ru(III), and Ru(IV) diastereomers were recorded in order to establish relationships between Cotton effects and absolute configuration for these complexes. These relationships should be applicable to chiral Ru(II), Ru(III), and Ru(IV) complexes of other β-diketonate ligands. The Ru(III) diastereomers isomerize in solution at 170°. Relative isomer abundances under conditions of thermodynamic equilibrium and the 12 isomerization rate constants for the four diastereomers were measured using a high-pressure liquid chromatograph.

Recent work in this laboratory has been directed toward establishing relationships between signs of Cotton effects and absolute configuration for tris-chelate complexes of β-diketones and other ligands having planar, conjugated chelate rings.[1–4] Chiral ligands have been used in order to generate diastereomeric species which differ in absolute configuration and which can be separated chromatographically on achiral sorbents. Much of the work has involved the chiral β-diketone (+)-3-acetylcamphor, since it is easily prepared in high optical purity. A combination of nmr, CD, and X-ray powder diffraction experiments[2–4] established *relative* configurations for the four diastereomers (Δ-trans, Λ-trans, Δ-cis, and Λ-cis) of each tris((+)-3-acetylcamphorato)metal(III) complex, I,

I
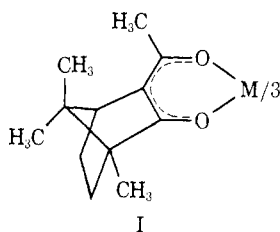
hereafter abbreviated M(atc)$_3$ where M = Co(III), Cr(III), Ru(III), and Rh(III). The absolute configurations of all 16 species were established by a single-crystal X-ray study of one diastereomer of Cr(atc)$_3$.[5]

During the course of this work Gordon, *et al.*,[6] reported the reversible one-electron reduction of tris-(trifluoroacetylacetonato)ruthenium(III) which may be carried out electrochemically or with metallic sodium. Reduction of the trans isomer takes place without isom-

erization. Earlier work by Elsbernd and Beattie[7] showed that reduction of $(-)_{350}$-[Ru(en)$_3$]$^{3+}$ to $(-)_{375}$-[Ru(en)$_3$]$^{2+}$ followed by reoxidation to $(-)_{350}$-[Ru(en)$_3$]$^{3+}$ takes place with retention of absolute configuration. These reports prompted us to investigate the redox behavior of the four diastereomers of Ru(atc)$_3$. Since absolute configurations of the initial Ru(III) diastereomers are known, reduction or oxidation to the corresponding Ru(II) or Ru(IV) species with retention of absolute configuration would permit Cotton effect configuration relationships to be established for Ru(II) and Ru(IV) β-diketonate complexes. Inasmuch as the Ru(II) complexes are expected to have a low-spin d^6 electronic configuration, it was of special interest to determine whether the signs of Cotton effects in these complexes are the same as in the diastereomers of Co(atc)$_3$ having identical absolute configurations.

Considerable effort has been made to establish the mechanisms by which tris β-diketonate complexes isomerize and racemize.[8–10] Recent studies have[11–13] involved complexes derived from unsymmetrical β-diketonate ligands, where the stereoisomers are analogous to those of Ru(atc)$_3$. Although no single mechanistic process adequately explains the kinetic data, most evidence favors a combination of bond breaking mechanisms. Investigations of slow[12] systems have necessitated at least partial resolution of enantiomeric species in order to measure racemization rates. The complexes M(atc)$_3$ potentially provide a unique opportunity for isomerization studies since (1) all four diastereomers can readily be separated in optically pure form and (2) during kinetic runs the presence and relative abundance of all four diastereomers in a mixture can be determined by routine physical methods.

(1) (a) Y. T. Chen and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **90**, 6660 (1968); (b) G. W. Everett, Jr., and Y. T. Chen, *ibid.*, **92**, 508 (1970); (c) K. S. Finney and G. W. Everett, Jr., *Inorg. Chem.*, **9**, 2540 (1970); (d) J. E. Gray and G. W. Everett, Jr., *ibid.*, **10**, 2087 (1971).

(2) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).

(3) G. W. Everett, Jr., and R. M. King, *Inorg. Chem.*, **11**, 2041 (1972).

(4) G. W. Everett, Jr., and A. Johnson, *Inorg. Chem.*, **13**, 489 (1974).

(5) W. Dew. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, **92**, 7620 (1970).

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

(7) H. Elsbernd and J. K. Beattie, *Inorg. Chem.*, **8**, 893 (1969).

(8) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971).

(9) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, **17**, 391 (1972).

(10) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 4.

(11) A. Y. Grigis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970).

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

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

The present paper describes an electrochemical and kinetic investigation of the four diastereomers of Ru-(atc)₃. Cotton effect configurational relationships for the Ru(II), -(III), and -(IV) species are discussed, and the kinetic results are analyzed in terms of possible isomerization mechanisms.

Experimental Section

Syntheses. (+)-3-Acetylcamphor was prepared as previously described.[3] The 3-trifluoromethyl derivative of this ligand, H-atc-f₃, was synthesized using Schurig's method.[14]

Ru(atc)₃ was prepared by an extensive modification of the procedure described by Wolf, et al.[15] A solution of 0.8 g (2 mM) of tris(acetylacetonato)ruthenium(III), Ru(acac)₃,[16] and 2.3 g (12 mM) of (+)-3-acetylcamphor in 25 ml of dry ethyl benzoate was placed in a 100-ml round-bottom flask equipped with a side arm, and oxygen-free nitrogen was passed over the solution for 15 min. The flask was heated to 160°, and the solution was stirred at this temperature under a stream of nitrogen for 12 hr. (Longer heating times led to extensive decomposition of both the starting materials and product.) At the end of the specified time, the system was closed and the solvent removed under vacuum at 120°. When most of the ethyl benzoate was removed, the flask was allowed to cool at room temperature. At this point it was no longer necessary to work under a nitrogen atmosphere. The residue was taken up in a minimum amount of ethanol and the solution was filtered and added dropwise to 150 ml of a rapidly stirred 2% sodium carbonate solution. The dark purple crystals (0.96 g, 70% yield based on Ru(acac)₃) were collected by filtration, washed with H₂O, and dried overnight *in vacuo* at room temperature The product was used for chromatography without further purification. This method of preparation of Ru(atc)₃ results in better yields than the method reported previously.[3]

Na[Ru(atc)₃] was synthesized in the following manner. Approximately 25–30 mg of 15% sodium amalgam[17] was placed in a spectrophotometer cell along with a 0.1–1.0 mM solution of Ru(atc)₃ in acetonitrile. The cell was tightly stoppered, sealed with Teflon tape, and shaken frequently over a 40-hr period. At the end of this time electronic absorption and circular dichroism spectra were constant and diagnostic of the Ru(II) species. The burgundy colored [Ru(atc)₃]⁻ anion is extremely air sensitive; thus the above procedure was used in order to obtain spectra in the most direct manner possible without transferring samples under inert atmosphere conditions. The sample could quantitatively be oxidized back to Ru(atc)₃ by removing the stopper and aerating the solution. No attempt was made to isolate solid Na[Ru(atc)₃].

(Ph)₄As[Ru(atc)₃] was isolated as a solid by adding tetraphenylarsonium chloride to a rapidly stirred solution of Ru(atc)₃ and sodium metal in absolute ethanol under an inert atmosphere. Minor traces of oxygen were found to oxidize the brownish red solid back to Ru(atc)₃ within a few seconds. Due to this extreme air sensitivity no attempts were made to analyze the compound.

[Ru(atc)₃]⁻ was also produced by controlled potential electrolytic reduction of Ru(atc)₃ in the presence of tetraethylammonium perchlorate in acetonitrile at a potential of −1.2 V *vs.* the saturated calomel electrode, sce. No attempt was made to isolate (C₂H₅)₄N-[Ru(atc)₃] as a solid.

[Ru(atc)₃]⁺ was synthesized by electrolytic oxidation of Ru(atc)₃ in 0.1–1.0 mM concentrations in acetonitrile at a potential of +0.95 V *vs.* sce. The complex in solution is bluish green in color; it is not affected by oxygen and is at least moderately stable to moisture. Electrolysis at +0.65 V *vs.* sce reduces the [Ru(atc)₃]⁺ species back to Ru(atc)₃. Solid [Ru(atc)₃]ClO₄ was not isolated.

Ru(atc-f₃)₃ was prepared in the following manner. Concentrated HCl (50 ml) was added to 0.26 g (1 mM) of RuCl₃·3H₂O (Alfa Inorganics), and the solution was evaporated to dryness under nitrogen. A solution of 0.190 g (3 mM) of Ba(atc-f₃)₂[14] in 50 ml of deaerated acetone was added to the residue, and the resulting mixture was allowed to reflux under nitrogen. After 2 hr the reaction mixture was cooled to room temperature. The barium chloride which

had formed was separated from the brown solution by filtration, and the solvent of the filtrate was evaporated under reduced pressure at room temperature. After the resulting oil was taken up in 15 ml of absolute ethanol and filtered, it was added dropwise to 50 ml of a rapidly stirred 2% sodium carbonate solution. The brownish red solid was collected by filtration, washed with copious amounts of water, and dried overnight *in vacuo* (yield 0.31 g or 46% based on RuCl₃·3H₂O). The product was used for chromatography without further purification.

Voltammetry. All voltammetric experiments were carried out on a controlled potential polarograph as designed by Underkofler and Shain[18] and modified by Marcus and Hawley.[19] A Mosley 7030A X-Y recorder was used to record the current-potential curves. A three-compartment cell with the compartments separated by fritted glass of medium porosity was employed throughout. In addition, the center compartment for the working electrode was equipped with two side arms for degassing the electroactive solution. The working, auxiliary, and reference electrodes were a rotating platinum electrode (rpe, 600 rpm), a platinum foil electrode, and a saturated calomel electrode (sce), respectively. For cyclic voltammetry the rpe was not rotated but used simply as a stationary platinum rod electrode. All current-potential measurements were conducted in acetonitrile purified by the method of Forcier and Olver.[20] The supporting electrolyte was recrystallized tetraethylammonium perchlorate, TEAP.

Coulometry. Controlled-potential coulometry was performed using the apparatus and conditions described in detail by DuBois, et al.[21] A three-compartment cell similar to that described above was used with the rpe replaced by a rotating platinum gauze working electrode.

Spectra. The fluorine nuclear magnetic resonance spectra were obtained on a Varian HA-100 spectrometer operating at a radiofrequency of 94.081 MHz.

All electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer, and a Cary Model 60 spectropolarimeter equipped with the Cary 6001 circular dichroism accessory was used to obtain CD data. Acetonitrile was used as the solvent in each case.

Chromatography. The diastereomers of Ru(atc)₃ and Ru(atc-f₃)₃ were quantitatively separated on 2-mm precoated preparative layer silica gel plates (Brinkmann Instruments). The developing solvent mixtures were 1:1 (by volume) heptane-ethyl ether for Ru(atc)₃ and 1:4 cyclohexane-carbon tetrachloride for the Ru-(atc-f₃)₃ complex. Approximately 250 mg of a given sample could be separated per 20 × 20 cm plate. The plates were developed by the ascending method. One development was generally sufficient to accomplish good separation between the four diastereomers of Ru(atc)₃, while five to six successive developments resulted in separation of only two bands for Ru(atc-f₃)₃.

After separation, the sorbent layer containing each band was removed from the plate, and the isomers were extracted with acetone. The solvent was removed by a rotary evaporator at room temperature. The resulting oil was dissolved in 10–15 ml of absolute ethanol and was added dropwise to 50 ml of a rapidly stirred 2% sodium carbonate solution. The crystals were collected by filtration, washed with water, and dried *in vacuo* at room temperature for at least 8 hr.

All high-pressure liquid chromatography was conducted on a Nester & Faust Series 1210 liquid chromatograph with a NFLC-250 ultraviolet detector operating at 366 mμ. The Ru(atc)₃ isomers were separated on a silica gel column by a 15% (by volume) mixture of tetrahydrofuran in *n*-hexane at a flow rate of 0.4 ml/min. Retention times were 10 min for Δ-trans, 11 min for Λ-trans, 13 min for Λ-cis, and 23 min for Δ-cis.

Isomerization Studies. Rates of isomerization of the four diastereomers of Ru(atc)₃ were determined in the following manner. Spectroquality methylcyclohexane was distilled over P₂O₅ under a dry nitrogen atmosphere, and 0.02 M solutions of each of the four diastereomers of Ru(atc)₃ were prepared in this solvent. Twenty 30-μl aliquots of each solution were transferred into 2-mm diameter capillary tubes, and the 80 tubes were sealed in a flame. The tubes were then immersed in an oil bath maintained at 170°. Preliminary work had shown isomerization rates for the cis diastere-

(14) V. Schurig, *Inorg. Chem.*, **11**, 736 (1972).
(15) L. Wolf, E. Butter, and H. Weinelt, *Z. Anorg. Allg. Chem.*, **306**, 87 (1960).
(16) A. Johnson and G. W. Everett, Jr., *J. Amer. Chem. Soc.*, **94**, 1419 (1972).
(17) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1030.

(18) W. L. Underkofler and I. Shain, *Anal. Chem.*, **35**, 1778 (1963).
(19) M. F. Marcus and M. D. Hawley, *J. Electroanal. Chem.*, **18**, 175 (1968).
(20) G. A. Forcier and J. W. Olver, *Anal. Chem.*, **37**, 1447 (1965).
(21) D. W. DuBois, R. T. Iwamoto, and J. Kleinberg, *Inorg. Chem.*, **8**, 815 (1969).

omers to be greater than those of the trans isomers. Thus tubes containing cis isomers were removed from the oil bath at 15-min intervals over a 6-hr period. Tubes containing trans isomers were removed at 1-hr intervals over a 12-hr period. The relative abundances of the four diastereomers in these solutions after thermal isomerization could be determined by liquid chromatography. Each tube was broken open, and 1–2 μl of the methylcyclohexane solution was injected into the chromatograph. Chromatography was performed as described above. Signal integration was achieved using a planimeter.

The relative abundances of the diastereomers under equilibrium conditions were determined in a similar manner. Solutions of each diastereomer were heated at 170° until no further change in relative signal areas could be detected (4–14 days). Relative equilibrium abundances thus obtained beginning with a given diastereomer are in good agreement with those obtained from the other diastereomers.

Results and Discussion

Electrochemistry. Voltammograms using the rpe were recorded for all four diastereomers of Ru(atc)₃ in acetonitrile solution under an inert atmosphere as described in the Experimental Section. The oxidation and reduction of each diastereomer are characterized by well-defined, one-electron waves with $E_{1/2}$ values of +0.8 and −1.0 V, respectively, vs. sce. These half-wave potentials are the same within error for all four diastereomers.

Patterson and Holm[22] have recently shown that the reduction half-wave potentials for a series of tris(β-diketonato)ruthenium(III) complexes depend markedly on the nature of the ligand substituents. A good correlation between Hammett substituent constants and $E_{1/2}$ values was found. The reduction $E_{1/2}$ observed for Ru(atc)₃ is close to that reported[22] for tris(dipivaloyl-methanato)ruthenium(III) (−1.04 V vs. sce in dimethylformamide), indicating a similar electron-releasing ability for the two ligands. For Ru(atc-f₃)₃, where the acetylmethyl group has been replaced by a trifluoromethyl group, the oxidation and reduction $E_{1/2}$ values are +1.5 and −0.3 V, respectively, vs. sce. These results are consistent with the expected shift of potentials toward more positive values in the presence of the electron-withdrawing CF₃ group. The substituent effect on the oxidation potential found here is much more pronounced than those reported[22] for other β-diketonate complexes of ruthenium(III) in dimethylformamide solution.

Cyclic voltammograms were recorded for each Ru(atc)₃ diastereomer in acetonitrile solution under an inert atmosphere using sweep rates (v) between 2 and 20 V/min. At potentials more negative than −1.8 V or more positive than +1.6 V, the voltammograms show evidence of decomposition of the complex. Within these limits, however, the potential can be cycled many times with no observable change in the voltammogram (see Figure 1). The oxidation process (Ru(III) $\rightleftarrows$ Ru(IV)) is nearly reversible[23] with $E_p{}^a - E_p{}^c$ values ranging from 60 mV to a maximum of 95 mV over the four diastereomers. Also $i_p/v^{1/2}$ is constant, and $i_p{}^a/i_p{}^c$ is unity and independent of v within error over the 2–20 V/min range investigated. Fast electron transfer is expected both for oxidation and reduction of low-spin
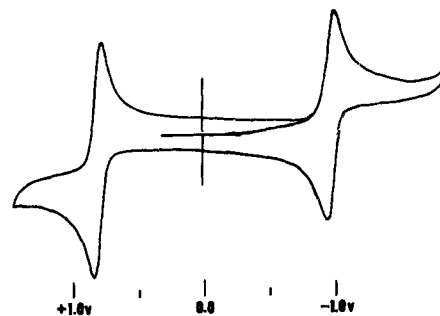

Figure 1. Cyclic voltammogram of Δ-trans-Ru(atc)₃ in acetonitrile solution at 25°. Supporting electrolyte is TEAP (0.1 M); scan rate is 9 V/min.

octahedral Ru(III) complexes, since electrons can be added to or removed from the t₂g orbitals. These orbitals are sterically more accessible than the eg orbitals, and electron changes within the t₂g set require less reorganization energy than changes within the eg orbitals.[24] Cyclic voltammetry of the Ru(atc)₃ diastereomers at negative potentials reveals $E_p{}^a - E_p{}^c$ values ranging from 80 to 105 mV with the notable exception of the Δ-cis isomer for which the separation varies from 140 to 185 mV, increasing linearly with v. These results indicate the charge transfer process for the Ru(III)/Ru(II) couple is not in general as rapid as is the case for the Ru(III)/Ru(IV) couple, and the former is best classified as a quasireversible couple at the scan rates employed in this study.

Only one diastereomer of Ru(atc-f₃)₃ was obtained in optically pure form (vide infra). Cyclic voltammetry of the isomer tentatively assigned the Δ-trans configuration shows near reversibility for both the Ru(III)/Ru(II) and the Ru(III)/Ru(IV) couples. Peak separations are 80 and 65 mV, respectively.

In a similar manner, cyclic voltammetry of one diastereomer each of the cobalt(III) and chromium(III) complexes of (+)-acetylcamphor, Co(atc)₃ and Cr-(atc)₃, was investigated. However, these both exhibited irreversible behavior, and no further electrochemistry on these complexes was attempted.

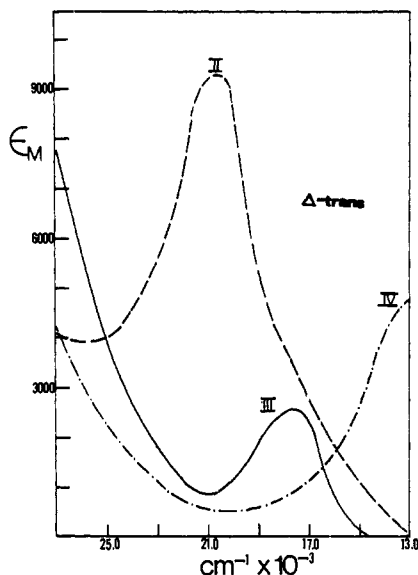**Ruthenium(II) Complexes.** Diastereomers of [Ru-(atc)₃]⁻ were prepared in the presence of several cations by reduction of the corresponding diastereomers of Ru(atc)₃ electrolytically or with sodium. Exposure of the Ru(II) complexes to air results in immediate oxidation of the Ru(III) complexes. (Ph)₄As[Ru(atc)₃] was isolated as a brownish red solid which was not further characterized due to its extreme air sensitivity. The CD spectrum of each diastereomer of Ru(atc)₃ in acetonitrile solution[25] was recorded just prior to reduction to the Ru(II) isomer in the spectrophotometer cell. After the CD spectrum of the Ru(II) complex was recorded, the Ru(III) complex was regenerated by aerating the solution. A comparison of CD and absorption spectra of each Ru(III) isomer taken before and after the reduction process revealed no change in overall sign and contour, and band maxima were diminished by only ~3% after the redox cycle. Also the initial and regenerated Ru(III) species showed identical chromatographic behavior on thin-layer strips of silica gel.

(22) G. S. Patterson and R. H. Holm, *Inorg. Chem.*, 11, 2285 (1972).

(23) Diagnostic criteria for reversible, quasireversible, and irreversible charge transfer processes as measured by the cyclic voltammetric response are summarized by E. R. Brown and R. F. Large in "Physical Methods of Chemistry, Part IIA, Electrochemical Methods," A. Weissberger and B. W. Rossiter, Ed., Wiley-Interscience, New York, N. Y., 1971, Chapter VI.

(24) Reference 10, Chapter 6.

(25) CD spectra of the Ru(III) diastereomers in acetonitrile solution are essentially identical with those reported earlier in cyclohexane solution.[3]

Figure 2. Absorption spectra of Δ-trans diastereomers of [Ru-(atc)₃]⁻, Ru(atc)₃, and [Ru(atc)₃]⁺ in acetonitrile solution. Numbers in the figure denote oxidation states of ruthenium.

Figure 3. Circular dichroism spectra of Δ-trans diastereomers of [Ru(atc)₃]⁻, Ru(atc)₃, and [Ru(atc)₃]⁺ in acetonitrile solution. Numbers in the figure denote oxidation states of ruthenium.

Thus it is concluded that no isomerization occurs during reduction and that the Ru(II) diastereomers have the same absolute configurations as their Ru(III) precursors. The kinetic inertness of octahedral Ru-(III) and Ru(II) may be attributed to the crystal field activation energy involved in forming a five-coordinate transition state during isomerization.[26] Also the observed retention of configuration during reduction (and oxidation, *vide infra*) of Ru(III) is consistent with the fact that electron transfer involves the t_{2g} metal orbitals which are essentially nonbonding.

In principle, CD spectra of the [Ru(atc)₃]⁻ diastereomers in the ligand field region should bear qualitative similarity to those of the corresponding diastereomers of Co(atc)₃, since both ions have the low-spin d⁶ electronic configuration. In a trigonal d⁶ complex the low-energy ligand field transition ($^1A_{1g} \rightarrow {}^1T_{1g}$ in the O_h point group) is split into transitions of ^1A and ^1E symmetry. The transition of ^1E symmetry in Co(atc)₃ occurs at higher energy than the ^1A transition, and their Cotton effects have opposite signs.[2] A positive Cotton effect for the ^1E transition is diagnostic of the Λ configuration for Co(atc)₃. Unfortunately the low-energy absorption band for [Ru(atc)₃]⁻, which occurs ∼4000 cm⁻¹ toward higher energy than the low-energy band for Co(atc)₃, has an $E_M \cong 9000$ (see Figure 2) and cannot be assigned to a pure ligand field transition. Absorption spectra of the four [Ru(atc)₃]⁻ diastereomers are identical.

It is readily seen from Figures 3–6 that all four Ru(II) diastereomers show two CD bands of opposite sign and nearly equal intensity centered about the wavelength of the low-energy absorption band. On going from low to high energy, a positive CD followed by a negative CD is found for the two isomers having the Δ configuration; the signs of these CD's are reversed for the Λ isomers. Although these bands do not arise from pure d–d transitions, it is interesting and perhaps significant that the signs of Cotton effects match those of the diastereomers of Co(atc)₃ having the same absolute con-

(26) Reference 10, Chapter 3.
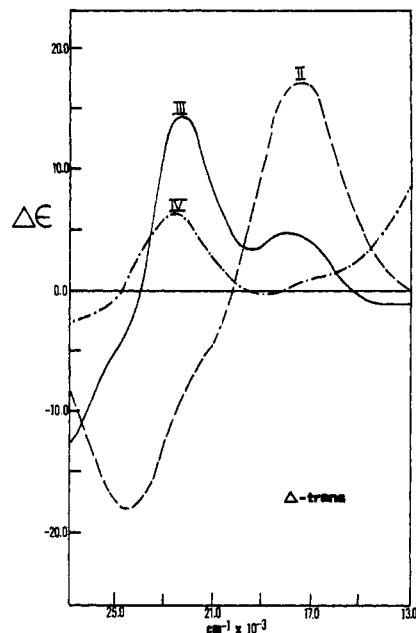
figurations.[2] The energy order of the ^1A and ^1E transitions in [Co(en)₃]³⁺ is the reverse of that found for Co(atc)₃. In view of the fact that this reversal may occur also for Ru(II), it is of interest to note that the signs of Cotton effects for the Λ isomers of [Ru(atc)₃]⁻ are the reverse of those found by Elsbernd and Beattie[7] for Λ-[Ru(en)₃]²⁺. However, the low-energy absorption band for the latter complex has an ϵ_M value (∼120) more in line with that expected for a d–d transition than is the case for [Ru(atc)₃]⁻, and further speculation regarding the significance of the CD bands for [Ru-(atc)₃]⁻ is not justifiable at this time. From a simple empirical viewpoint, the CD curves presented in Figures 3–6 should be useful for assigning absolute configurations to Ru(II) complexes of other β-diketonate ligands.

Ruthenium(IV) Complexes. The [Ru(atc)₃]⁺ complexes were prepared by controlled potential electrolytic oxidation of the individual Ru(atc)₃ diastereomers in acetonitrile solution. The number of coulombs required to complete the oxidation is very nearly that expected based on the number of moles of complex present. This is good evidence that the one-electron oxidation proceeds without any complicating side reactions. Following the recording of their CD and visible electronic absorption spectra, the cationic complexes were reduced electrolytically back to their Ru(III) analogs, and absorption and CD spectra were recorded again. These spectra are qualitatively the same as those recorded before the oxidation process, indicating that isomerization does not occur to a large extent. However, the band intensities in both CD and absorption spectra are reduced by an average of 10% after the redox cycle. Similarly, coulometry indicated only an ∼85% average recovery of the initial Ru(atc)₃ complexes. Products of the redox cycle were chromatographed on silica gel strips along with samples of unreacted Ru(atc)₃ diastereomers. The latter experiment revealed that some decomposition of [Ru(atc)₃]⁺ occurs during the time required to record the CD and absorp-

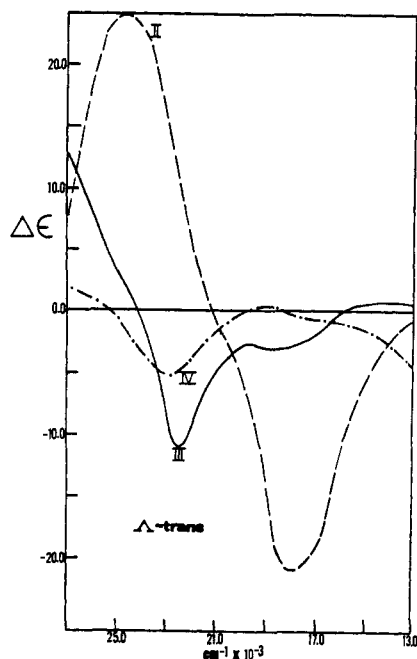**Figure 4.** Circular dichroism spectra of Λ-trans diastereomers of [Ru(atc)₃]⁻, Ru(atc)₃, and [Ru(atc)₃]⁺ in acetonitrile solution. Numbers in the figure denote oxidation states of ruthenium.

Figure 5. Circular dichroism spectra of Λ-cis diastereomers of [Ru(atc)₃]⁻, Ru(atc)₃, and [Ru(atc)₃]⁺ in acetonitrile solution. Numbers in the figure denote oxidation states of ruthenium.

tion spectra (45–60 min), but no detectable isomerization occurs during this time.[27] Thus it may be concluded that the process Ru(atc)₃ ⇌ [Ru(atc)₃]⁺ proceeds with complete retention of configuration.

Visible absorption spectra of the four [Ru(atc)₃]⁺ diastereomers are identical except for slight differences in ϵ_M values. A representative spectrum is shown in Figure 2; the low-energy band maximizes around 11,000 cm⁻¹ (ϵ_M 6000). The Cary 60 instrument is unable to record CD spectra below 13,000 cm⁻¹; thus, it was not possible to record all of the CD associated with the low-energy transition. Cotton effects for the two Δ diastereomers are qualitatively the same in the visible region and are opposite in sign to those of the two Λ isomers. No previous Cotton effect configuration relationship has been established for tris-bidentate complexes of d⁴ ions, primarily as a result of the fact that most are high spin and labile. The kinetic inertness of [Ru(atc)₃]⁺ may be attributed to its low-spin electronic configuration.[26] In view of the high ϵ_M value found for the 11,000-cm⁻¹ transition, there is some question about its origin and the origin of the CD bands throughout the visible region. However, the CD spectra presented in Figures 3–6 should serve to diagnose absolute configurations of other Ru(IV) β-diketonate complexes.

Ru(atc-f₃)₃. This complex was prepared in hopes that its isomerization kinetics could be investigated by ¹⁹F nmr. Several fluorinated β-diketonate complexes have been shown to isomerize more readily than their protonated analogs.[28] However, attempts to separate the four diastereomers of Ru(atc-f₃)₃ by thin-layer

(27) When Ru(atc)₃ is oxidized electrolytically to [Ru(atc)₃]⁺ and then immediately reduced electrolytically, the recovery of Ru(atc)₃ is quantitative as indicated by absorption, CD, and coulometric data.

(28) A summary of references may be found in a recent publication: S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **95**, 1116 (1973).
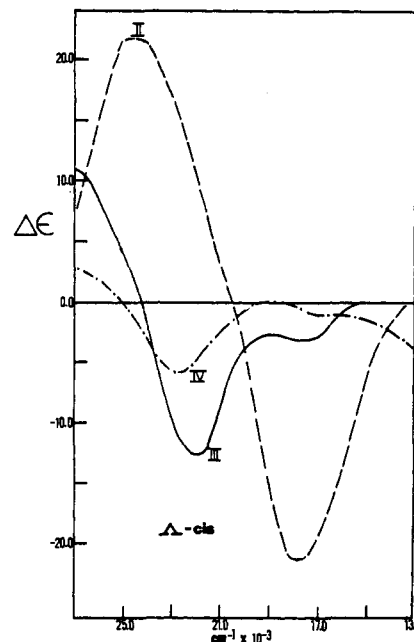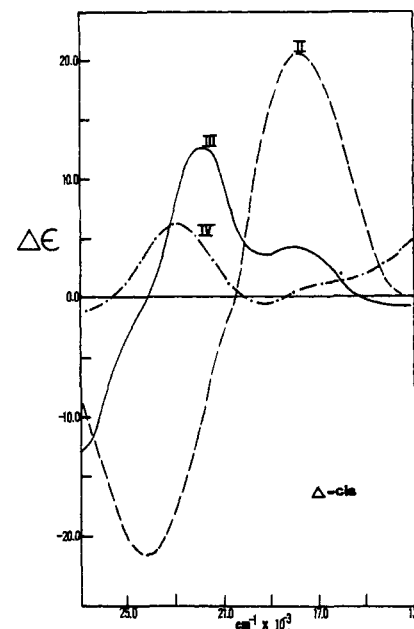
Figure 6. Circular dichroism spectra of Δ-cis diastereomers of [Ru(atc)₃]⁻, Ru(atc)₃, and [Ru(atc)₃]⁺ in acetonitrile solution. Numbers in the figure denote oxidation states of ruthenium.

chromatography using a variety of solvents and solvent mixtures were unsuccessful. No more than two chromatographic bands were observed in any instance. The reddish brown crystalline product (A) isolated from the more rapidly eluted band gave a satisfactory elemental analysis. ¹⁹F nmr shows this to be a trans isomer, and the CD spectrum of A is very similar to that of Λ-*trans*-Ru(atc)₃. The oily product (B) extracted from the second chromatographic band failed to give a satisfactory elemental analysis. Cotton effects in the CD spectrum of B are weaker than and opposite in sign to those of A, and ¹⁹F nmr of B indicates the presence of a trans isomer and at least one cis isomer.

The electrochemical behavior of A, which is presumed to have the Λ-trans configuration, is described above. Kinetic experiments were not performed for this complex, since only one pure diastereomer was obtained.

Isomerization Studies. The tendency of Ru(III) complexes to be inert to isomerization is well known[29] and is consistent with the predictions of crystal field theory.[26] In an earlier publication[3] it was reported that no isomerization of Ru(atc)$_3$ could be detected by nmr after heating a carbon tetrachloride solution at 60° for 5 days. More recent efforts, however, at temperatures of 120° or higher have shown that isomerization does occur accompanied by some decomposition. Thermal decomposition has been reported previously for other Ru(III) β-diketonate complexes.[6,30] Since the four isomers of Ru(atc)$_3$ are diastereomers and have distinctly different physical properties, the kinetics of cis $\rightleftarrows$ trans and $\Delta \rightleftarrows \Lambda$ interconversions may be investigated without the problems encountered in resolving enantiomeric species. Assuming that isomerization is an intramolecular process for Ru(atc)$_3$, as has been shown to be the case for tris-β-diketonate complexes of other metal ions,[11-13] 12 microscopic rate constants are necessary to describe all possible interconversions among diastereomers. These rate constants are defined in eq 1.

$$\begin{array}{ccc}
\Delta\text{-cis} & \xrightleftharpoons{k_4} & \Lambda\text{-cis} \\
k_8 \Big\updownarrow k_2 & \begin{matrix} k_3 & k_1 & k_9 \\ & \times & \\ k_{12} & & k_6 \\ & k_{10} & \end{matrix} & k_{11} \Big\updownarrow k_5 \\
\Delta\text{-trans} & \xrightleftharpoons{k_7} & \Lambda\text{-trans}
\end{array} \quad (1)$$
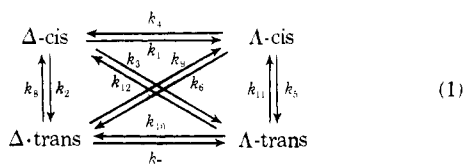
Preliminary experiments using the Nester–Faust liquid chromatograph showed that the four diastereomers of Ru(atc)$_3$ could be separated under the conditions described in the Experimental Section. The wavelength of the detector is at one of the absorption maxima ($\epsilon_M \approx 10^4$) of the complex, and extremely small quantities of material are easily detected. In a typical experiment ca. 10^{-8} mol of an isomeric mixture of Ru(atc)$_3$ was injected onto the column. Kinetic runs were carried out at 170° in methylcyclohexane using capillary tubes as described in the Experimental Section. The relative concentrations of initial isomer and isomerization products for a given sample removed from the oil bath at time t were determined by integration of the signals from the uv detector on the chromatograph.

A temperature of 170° proved convenient for the kinetic experiments, since measurable isomerization occurs within a few hours. The extent of decomposition proved to be minimal when the solvent is carefully dried as described in the Experimental Section. The occurrence of some decomposition during kinetic runs is demonstrated by the presence of a broad signal near the end of the chromatograms for samples heated several hours. Also for kinetic runs beginning with pure cis isomers, a narrow chromatographic signal between signals due to the two trans isomers grows with time. Neither of these decomposition product signals

interferes significantly with those being measured, however.

Thermodynamic equilibrium is attained for the cis isomers after heating solutions for 4–5 days at 170°. A heating period of at least 2 weeks is required for the two trans isomers. Good agreement is found among the relative isomer abundances at equilibrium obtained starting with each of the individual isomers. Averages of the values obtained are Δ-cis = 0.019 ± 0.006, Λ-cis = 0.20 ± 0.01, Δ-trans = 0.35 ± 0.01, and Λ-trans = 0.44 ± 0.02. Error limits are standard deviations from the mean. This same order of relative abundances is found[2] for the cobalt(III) and chromium-(III) complexes of (+)-3-acetylcamphor and is attributed to a stereoselective influence of the chiral ligands. Recent work by King and Everett shows that stereoselectivity for the labile V(III) complex is strongly solvent dependent.[31]

Kinetic data were treated in the following manner. The assumptions were made (1) that isomerization of Ru(atc)$_3$ follows first-order kinetics, (2) that for short heating periods the concentration of the initial isomer in each run does not change significantly as a result of isomerization, and (3) that further isomerization of products is negligible for short t. This permits simple integration of the first-order rate expression describing the growth of the chromatographic signal arising from a given product. A plot of (concentration of product at time t)/(concentration of initial isomer), $[P_i]/[I]$, vs. t should be linear and pass through the origin. The rate constant for the formation of the product isomer is the slope of this line.

Experimental plots for ten of the 12 rate constants are linear up to a $[P_i]/[I]$ ratio of around 0.2 (corresponding to ~ 2.5 and ~ 12 hr heating periods for cis and trans isomers, respectively) and pass through the origin. The plots generally show curvature beyond this point. The slope of the line obtained from a least-squares fit of the data points in the linear region of each plot is taken as the rate constant. Error limits shown in Table I are the average of deviations of $[P_i]/[I]t$ from the slope of the least-squares line. Two of the rate

Table I. Rate Constants for Isomerization of Ru(atc)$_3$ Diastereomers[a]

Initial isomer	Rate constant (sec^{-1})[b]
Δ-cis	$k_1 = 5.3 \pm 0.8 \times 10^{-6} \, (2.0 \pm 1.0 \times 10^{-5})^c$
	$k_2 = 2.1 \pm 0.2 \times 10^{-5}$
	$k_3 = 1.1 \pm 0.2 \times 10^{-5}$
Λ-cis	$k_4 = 1.9 \pm 0.3 \times 10^{-6}$
	$k_5 = 3.1 \pm 0.6 \times 10^{-5}$
	$k_6 = 3.1 \pm 0.3 \times 10^{-5}$
Δ-trans	$k_7 = 4.4 \pm 0.6 \times 10^{-6}$
	$k_8{}^d = 1.1 \pm 0.5 \times 10^{-6}$
	$k_9 = 2.2 \pm 0.3 \times 10^{-6} \, (1.8 \pm 0.3 \times 10^{-5})^c$
Λ-trans	$k_{10} = 2.8 \pm 0.3 \times 10^{-6}$
	$k_{11} = 4.7 \pm 0.3 \times 10^{-6} \, (1.4 \pm 0.4 \times 10^{-5})^c$
	$k_{12}{}^d = 4.4 \pm 2.4 \times 10^{-7}$

[a] In methylcyclohexane solution at 170°. [b] Error limits shown are deviations of $[P_i]/[I]t$ from the slope of the least-squares line or a combination of these errors and those contained in the equilibrium data. [c] "Corrected" value using relative isomer abundances at equilibrium. [d] Calculated using relative isomer abundances at equilibrium.

(29) A few exceptions to this rule have recently been reported: L. H. Pignolet, D. J. Duffy, and L. Que, Jr., J. Amer. Chem. Soc., **95**, 295 (1973).

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

(31) R. M. King and G. W. Everett, Jr., Inorg. Chim. Acta, **7**, 43 (1973).

constants, k_8 and k_{12}, are relatively small, and only approximate values could be determined from the chromatograms. More accurate values for these were determined using the equilibrium diastereomer abundances and assuming the values for k_2 and k_3 are accurately known, e.g., $k_8 = k_2[\Delta\text{-cis}_{eq}]/[\Delta\text{-trans}_{eq}]$.

The ratio of rate constants for each isomerization and its reverse in eq 1 should equal the ratio of equilibrium abundances of the corresponding isomers. This holds for the Δ-trans $\rightleftharpoons$ Δ-cis and Λ-trans $\rightleftharpoons$ Δ-cis interconversions, since this relationship was assumed in calculating k_8 and k_{12}. Also k_{10}/k_7 and $[\Delta\text{-trans}_{eq}]/[\Lambda\text{-trans}_{eq}]$ agree just within the limits of error. However the agreement between kinetic and equilibrium data is poor for any process involving the Λ-cis isomer. The implication is that the observed values for k_1, k_9, and k_{11} are too small or that k_4, k_6, and k_5 are too large.[32]

The rate constants obtained as described above should be regarded as "apparent" rate constants, for they are not necessarily rate constants for the simple transformations indicated by straight lines in eq 1. For example, the observed rates could contain contributions from two- or three-step routes in eq 1. k_1 is assumed to be the rate constant for formation of Λ-cis from Δ-cis, but if k_3 and k_{11} were large relative to k_1, formation of Λ-cis via Λ-trans would be significant. Under these circumstances the observed value for k_1 would be too large. It can be shown in this case that the product $k_3 k_{11} t^2/2$ must be comparable to $k_1 t$ for this two-step route to be significant. Analogous relationships apply to other two-step routes, and thus any significant contributions from two-step (or three-step) processes for short t would produce curvature in the plots of $[P_i]/[I]$ vs. t. This has not been observed for short t in any case.

Of the three initial assumptions made in treating the kinetic data, (3) is most likely to be invalid in certain instances. If the rate constant for further isomerization or decomposition of a product isomer is significantly larger than the k of its formation, the product will be consumed at a nonnegligible rate, even at short t, and the observed k of formation will be too small. Observed values for k_5 and k_6 are appreciably larger than all others. Both of these involve isomerization of the Λ-cis isomer, and isomerization of Λ-cis during formation from Δ-cis, Δ-trans, and Λ-trans could be significant, leading to observed values for k_1, k_9, and k_{11} which are too small. However, it seems unlikely that the magnitude of apparent error in these rate constants could result solely from further isomerization of Λ-cis. If this were the case, one would expect appreciable curvature in the plots of $[P_i]/[I]$ vs. t.

If any isomer were undergoing continuous decomposition, all isomers would eventually be consumed, and thermodynamic equilibrium would not be attained.[33] On the other hand if rapid decomposition of a product isomer occurs through reaction with a trace impurity (such as water) in the solvent, the initial rate of decomposition would be rapid but would decrease as the impurity is consumed. The rate law followed by

(32) The probability of gross errors in the measured isomer abundances at equilibrium is small, since complicating factors such as those potentially present in the kinetic experiments are absent.

(33) Beginning with the Λ-cis isomer, thermodynamic equilibrium was reached after heating for 5 days at 170°. Continued heating of this solution for 2 additional weeks produced no significant change in the relative isomer abundances.

Table II. Comparison of Experimental and Statistical Rate Constant Ratios for Twist and Bond Rupture Mechanisms for Ru(atc)$_3$[a]

Mechanism or transition state	Δ-Cis $\frac{(k_1 + k_3)}{(k_2 + k_3)}$	$\frac{k_1}{(k_2 + k_3)}$	$\frac{k_2}{(k_1 + k_3)}$	Λ-Cis $\frac{(k_4 + k_6)}{(k_5 + k_6)}$	$\frac{k_4}{(k_6 + k_5)}$	$\frac{k_5}{(k_6 + k_4)}$	Δ-Trans $\frac{(k_7 + k_9)}{(k_8 + k_9)}$	$\frac{k_7}{(k_8 + k_9)}$	$\frac{k_8}{(k_7 + k_9)}$	Λ-Trans $\frac{(k_{10} + k_{12})}{(k_{11} + k_{12})}$	$\frac{k_{10}}{(k_{11} + k_{12})}$	$\frac{k_{11}}{(k_{10} + k_{12})}$
a Trigonal twist	∞	∞	0	∞	∞	0	∞	∞	0	0	∞	∞
b Rhombic twist	1.33	0.33	0	1.33	0	0	3	2	0	0	2	3
c Combined twist[b]	0	0	∞	0	0.33	∞	4	3	0	0	3	4
d TBP equatorial	1	0	0	1	0	0	0	0	∞	∞	0	0
e TBP axial, SP basal	0	0	1	0	0	1	3	2	0	0	2	3
f Combined TBP[b]	0.5	0.5	0.5	0.5	0.5	0.5	1.5	1	0.33	0.33	1	1.5
g SP axial primary process	1	0	0	1	0.08	0	3	2.5	0.17	0.17	2.5	3
h SP axial secondary process	1	0	0	1	0	0	3	2	0	0	2	3
i SP axial combined processes[b]	0.67	0.08	0.62	0.67	0.08	0.62	2	1.4	0.21	0.21	1.4	2
Exptl	0.97	0.62	0.68	0.53	0.03	0.94	1.17	0.23	0.05	4.32	0.19	0.22

[a] See text for a summary of assumptions made in constructing this table. [b] Combined mechanisms assume equal probability of their component mechanisms.

the decomposition reaction is unknown, but it is conceivable that a plot of observed $[P_t]/[I]$ vs. t might appear roughly linear, assuming the normal scatter of data points. The slope of this line may be considerably smaller than it would be in the absence of decomposition. There is some evidence that traces of water in the solvent are responsible for the decomposition of Ru(atc)$_3$ at elevated temperatures. Decomposition during kinetic runs, as detected by chromatography, is minimized by using rigorously dry solvent, capillary tubes, and syringes. However, since the concentration of the product isomers at short t is only of the order of 10^{-3} M, the relative molar concentration of traces of moisture could be significant.

Although the reasons for the disparity in kinetic and thermodynamic data involving the Λ-cis isomer cannot be pinpointed at this time, the rate constants k_1, k_9, and k_{11} may be corrected using the more reliable thermodynamic data and observed values of k_4, k_5, and k_6. "Corrected" values for k_1, k_9, and k_{11} are listed in Table I along with the observed values. A check on the validity of the entire set of rate constants is possible. It can be shown that as a result of the principle of microscopic reversibility, products of rate constants around any of the four triangles and the rectangle in eq 1 in a clockwise direction must equal the corresponding products in a counterclockwise direction.[34] This is seen to be true to a good approximation in each case, although k_7 and k_{10} are the only rate constants independent of the thermodynamic data.[35]

The kinetic results show a definite trend favoring formation of Λ isomers from Δ isomers and trans isomers from cis isomers. There is not general agreement among the relative order of these rate constants and those obtained for analogous isomerizations of tris β-diketonate complexes of cobalt(III).[11,12,36] Stereoselective effects are seen in the fact that ratios of rate constants for interconversions which must have equal rate constants for enantiomeric species[11,12] deviate significantly from 1.0 for these diastereomeric species. For instance, $k_2/k_5 = 0.68$, $k_3/k_6 = 0.35$, $k_4/k_1 = 0.095$, and $k_{10}/k_7 = 0.64$.

Two basic processes are generally considered in deducing the mechanism of isomerization of trisbidentate complexes. These are (1) twisting motions in which no bonds are broken and which have idealized transition states resulting from rotation of ligands about real, pseudo, or imaginary threefold axes[37] and (2) processes in which one metal-to-ligand bond is broken. The latter have several idealized transition states, usually referred to as square pyramidal with axial or basal dangling ligands (SP axial or SP basal) and trigonal bipyramidal with axial or equatorial dangling ligands (TBP axial or TBP equatorial). Kinetic data do not permit a distinction between processes which

involve TBP axial and SP basal transition states.[12] The products which may be formed from these transition states have been described in detail by others, and the relative values of rate constants for each mechanism have been worked out for tris complexes of unsymmetrical bidentate ligands.[11,12] We extended these results to apply to complexes such as Ru(atc)$_3$ where 12 measurable rate constants exist.

All twist mechanisms require at least one k to be zero for each diastereomer; thus twist mechanisms cannot be solely responsible for the isomerization of Ru(atc)$_3$. Similarly, at least one k must be zero for each diastereomer if isomerization occurs solely through the TBP equatorial, the TBP axial, or the SP basal transition states. If a SP axial transition state is considered in which primary and secondary processes[12] are weighted equally both in formation of the transition state and rearrangement to products, all 12 k's should be nonzero. The same is true if the primary process alone is assumed. In order to aid in determining whether a given mechanism can account for the experimental results for each diastereomer, Table II was constructed. For each diastereomer the left-hand column in Table II gives the ratio of the statistically expected rates of formation of inversion ($\Delta \rightleftharpoons \Lambda$) products to the overall rate of formation of rearrangement (cis $\rightleftharpoons$ trans) products. The center column in each case gives the ratio of the rate of inversion without rearrangement to the rates of all other processes, and the right-hand column gives the ratio of the rate of rearrangement without inversion to the rates of all other processes. Experimental values of these ratios are presented in the bottom row of Table II.

For the Δ-cis and Λ-cis isomers, the experimental data show reasonably good fits to mechanisms g and f, respectively. No single mechanism fits the data for the trans isomers, however. Table II was constructed using the statistical proportions of isomerization products predicted from a given transition state, assuming (1) that any metal–ligand bond is broken with equal probability for a given diastereomer in forming the transition state and (2) that no stereoselectivity occurs in formation of products. Either or both these assumptions are potentially invalid for complexes of sterically stringent chiral ligands. Also error limits (neglecting indeterminate errors) for the rate constants range from 10 to 50%. Thus a more detailed interpretation of the data directed at deducing relative contributions of several mechanistic processes would not be meaningful. The kinetics of isomerization of Co(atc)$_3$ are currently under investigation by Springer.[36]

(34) I. Amdur and G. G. Hammes, "Chemical Kinetics: Principles and Selected Topics," McGraw-Hill, New York, N. Y., 1966, pp 16–17.
(35) $k_1k_6k_8/k_2k_9k_4 = 0.95$, $k_2k_7k_{12}/k_8k_3k_{10} = 1.2$, $k_9k_5k_{10}/k_7k_{11}k_6 = 0.82$, $k_3k_{11}k_4/k_1k_5k_{12} = 1.07$, $k_1k_5k_{10}k_8/k_2k_7k_{11}k_4 = 0.78$.
(36) C. S. Springer, Jr., *J. Amer. Chem. Soc.*, **95**, 1459 (1973).
(37) C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).