Contribution from the Aerospace Research Laboratories, ARL/LJ,
Wright-Patterson Air Force Base, Ohio 45433

Rate and Equilibrium Study of the Cis-Trans Isomerization of Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) in the Gas Phase[1a]

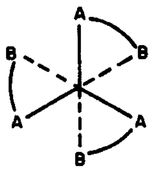
CHARLES KUTAL*[1b] and ROBERT E. SIEVERS

Received September 26, 1973

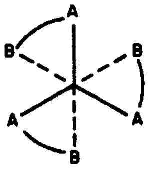
The cis-trans isomerization of Cr(tfa)$_3$ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) has been studied in the gas phase. Separation and identification of isomeric mixtures were accomplished using a gas chromatograph equipped with an electron capture detector. The system can be treated kinetically as two opposing first-order reactions, with the experimentally determined equilibrium constant, K_{eq}, agreeing with the quotient of the measured rate constants k_c (cis → trans) and k_t (trans → cis). The average observed value of K_{eq} (3.56) is slightly larger than random statistical distribution and is independent of temperature in the range 118.8-144.8°; the standard enthalpy and entropy are -0.1 ± 1.1 kcal/mol and 2.4 ± 2.8 cal/deg mol, respectively. Rate constants were determined from the initial rates of isomerization for each isomer. The activation enthalpy and entropy are 28.2 ± 1.1 kcal/mol and -5.5 ± 3.0 cal/deg mol for the cis → trans reaction and 24.6 ± 2.2 kcal/mol and -17.0 ± 5.7 cal/deg mol for the reverse process. From the magnitude of the gas-phase activation enthalpy in relation to the energy of the Cr-O bond, it is concluded that a twist mechanism is the most likely pathway for isomerization. The similarity of the gas-phase results to those for the rearrangement of various inert M(tfa)$_3$ complexes in solution suggests that solvent may not play as important a mechanistic role as previously thought.

Introduction

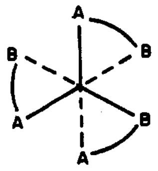
The mechanisms by which octahedral metal complexes undergo stereochemical rearrangement in solution have been the subject of numerous investigations. Perhaps the most widely studied class of compounds is the tris chelates of the type M(A-B)$_3$, where A-B represents an unsymmetrical β-diketonate ligand.[2-9] These complexes can exist as dissymmetric cis and trans isomers and thus are capable of providing considerable stereochemical information. It has generally been found that rearrangement occurs *via* an intramolecular mechanism in weakly polar solvents; on the other hand, there is some uncertainty whether stereolability results from metal-ligand bond rupture or a twist process.[2,10]



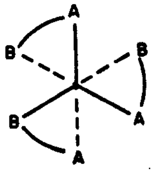
CIS-Δ



CIS-Λ



TRANS-Δ



TRANS-Λ

Most investigators have utilized three lines of evidence to support their mechanistic assignment. The first is the effect of solvent dielectric constant on the free energy of activation for rearrangement.[4,7] Although twist and bond rupture mechanisms should exhibit different sensitivities to changes in solvent, in fact the effects are usually small and no conclusive trends are evident. The magnitude of the frequency factor, A, in the Arrhenius equation is another commonly used criterion.[4,5,7,11] A twist mechanism, because of the supposed improbability of the motion involved, is associated with a small A value, while a large A value is considered evidence for bond rupture. While this generalization seems intuitively correct, some exceptions have been noted.[6,10a] More recently several systems have been reported for which the experimentally determined ratio of rates of cis-trans isomerization and inversion of configuration are compared with ratios predicted on the basis of an assumed geometry for the transition state.[5,7,12] When applied to tris β-diketonate complexes, however, these treatments have in general been unable to identify unambiguously the mechanism involved. The majority of studies conclude that bond rupture is the most likely mode for rearrangement, but the complete elimination of a twist process has not been possible. Quite probably both mechanisms are operative under the experimental conditions.

The chief obstacle to a definitive assignment of mechanism in the aforementioned studies is the ubiquitous presence of solvent molecules, whose role in the rate-determining step of the reaction is seldom known with certainty. Consequently, the activation parameters reflect not only the *intrinsic* energy needed for rearrangement but also any changes in solvation energy as well. The alternative approach of

---

* To whom correspondence should be addressed at the Department of Chemistry, The University of Georgia, Athens, Ga. 30602.

(1) (a) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1973. (b) National Research Council-Aerospace Research Laboratories Associate, 1972-1973.

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

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

(4) R. C. Fay and T. S. Piper, *Inorg. Chem.*, 3, 348 (1964).

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

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

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

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

(9) R. Fontaine, C. Pommier, and G. Guiochon, *Bull. Chim. Soc. Fr.*, 1685 (1972).

(10) It has proven possible to assign the mechanism of rearrangement for certain classes of tris chelates: (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 6411 (1972); (b) M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *ibid.*, 95, 4537 (1973), and references cited therein.

(11) D. A. Case and T. J. Pinnavaia, *Inorg. Chem.*, 10, 482 (1971).

(12) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, 6, 2022 (1967). The treatment presented in this reference refers to complexes of the type M(A-A)$_2$(B-B).

studying the reaction in the gas phase, on the other hand, eliminates this latter contribution. In the gas phase all the complications and ambiguities arising from solvation can be avoided. In cases where a compound can be studied in both solution and the gas phase, a comparison of the respective activation parameters should allow a direct assessment of the role of solvation.

We report here a study of the isomerization of *cis*- and *trans*-Cr(tfa)$_3$ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) in the gas phase. These fluorinated metal chelates were chosen because of their stability at elevated temperatures, where they possess experimentally convenient vapor pressures (~1 mm).[13] By comparing the present results with those for a series of tfa complexes in solution, one can discuss the role of solvation in the mechanism of isomerization.

Experimental Section

Preparation of Compounds. Cr(tfa)$_3$ was prepared by the method of Fay and Piper.[14] The less soluble trans isomer was obtained in 99% purity by repeated (three or four times) fractional crystallization from benzene. The cis isomer can be separated on a preparative scale from the filtrate of the first crystallization by column chromatography on alumina (Merck, acid washed) using a 7:3 v/v hexane-benzene mixture as the eluent. Although separation into distinct bands did not occur on a $^7/_8$-in. i.d. column packed to a height of 12 in., the last 25-30% of material to elute was enriched in the cis compound. By repeating the procedure on this fraction, it was possible to obtain the cis isomer ~90% pure. *Anal.* Calcd: C, 35.24; H, 2.37; Cr, 10.17. Found for trans compound: C, 35.13; H, 2.34; Cr, 9.98 (mp 153.5-155°). Found for cis compound: C, 35.48; H, 2.42; Cr, 9.55.

Analysis of Isomer Composition. The cis:trans ratio was determined by gas chromatography using a Hewlett-Packard F & M Model 810 chromatograph equipped with a 200-mCi titanium tritide electron capture detector. The operating temperatures of the instrument were as follows: injection port, 110°; column, 85°; detector, 130°. Flow rates of 90% argon-10% methane carrier gas between 60 and 100 cm^3/min were employed.

The separation of isomers was accomplished on a 16-in. glass column (4-mm i.d.) containing open-pore polyurethane prepared according to the directions of Hileman, *et al.*[15] A mixture of 3.8 ml of the isocyanate NCO-10 (Kaiser Chemical) and 4.1 ml of the polyol LA-475 (Union Carbide) dissolved in 50 ml of solvent (3:2 v/v toluene-carbon tetrachloride) was used. As shown in Figure 1, the separation of isomers is complete within 10 min. Under the experimental conditions used no isomerization occurs as the sample passes through the column. This fact was established by varying the carrier gas flow rate at a constant column temperature and noting that the isomeric purity o of a sample is independent of its retention time. At higher temperatures on other types of columns isomerization within the column has been observed, so for separations of these isomers the polyurethane columns are far superior. Since the electron capture detector response was determined experimentally to be virtually identical for both isomers, the ratio of peak areas is a direct measure of isomeric composition.

Rate and Equilibrium Studies. In order to obtain reproducible results, the glass ampoules in which the reactants were heated had to be preconditioned as follows. The inside walls of the ampoules (Kimax, ~ 30-cm^3 capacity) were soaked in No Chromix cleaning solution (Godax Labs) overnight, rinsed with distilled water and acetone, and dried at 110°. They were then filled with a 40% solution of hexamethyldisilizane (MCB Chemical) in benzene and allowed to stand overnight. After rinsing with benzene, they were dried at 110° for 2-3 hr.

In a typical run (2-6) × 10^{-5} g of complex, dissolved in 3-4 drops of Nanograde benzene (Mallinckrodt), was added to each ampoule,[16] which was then flame sealed under a helium or air atmosphere. At the temperatures employed in the study, both complex and benzene exist completely in the gas phase. To ensure rapid volatilization and thus avoid an induction period, the ampoules were preheated at ~110° for 2 min (conditions which were experimentally determined to cause no significant isomerization). They were then placed in a Lauda-Brinkmann Model NB constant-temperature oil bath in which the temperature was controlled to ±0.2°. At appropriate intervals, the ampoules were removed and rapidly cooled to room temperature in a beaker of acetone. The top was broken off and ~1 ml of Nanograde benzene was added. A 0.2-0.5-μl sample was then injected into the gas chromatograph and the resultant peak areas were measured with a planimeter. Triplicate determinations were made on each peak with a precision of ±2%. Rate constants and activation parameters were obtained from a linear least-squares fit of the appropriate data to the best straight line. Most of the rate constants shown in the Results are the average of two or three independent determinations, each of which is comprised of six to eight measurements of the isomeric ratio at various times.

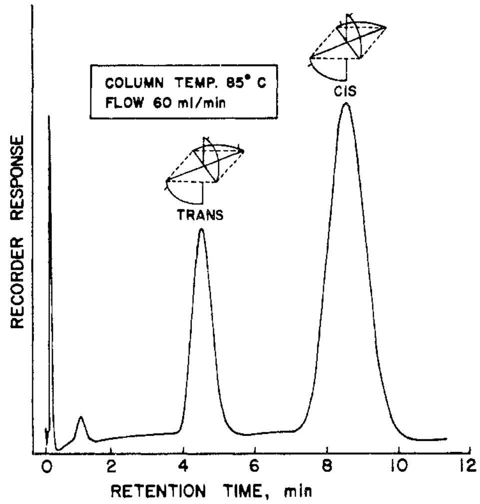


Figure 1. Gas chromatogram of a cis-trans mixture of Cr(tfa)$_3$ dissolved in benzene. (Peaks at $t < 2$ min arise from trace impurities in the solvent.)

Results

Equilibrium and Rate Studies. The cis-trans isomerization can be treated most simply as two opposing first-order reactions (*vide infra*) with forward and reverse rate constants, k_c and k_t, respectively (eq 1). The equilibrium constant, K_{eq},

$$\text{cis} \underset{k_t}{\overset{k_c}{\rightleftarrows}} \text{trans} \qquad (1)$$

can be determined directly from the measurement of the peak areas of a sample whose composition is unchanged by further heating or indirectly as the ratio, k_c/k_t (eq 2). Values

$$K_{eq} = \frac{[\text{trans}]}{[\text{cis}]} = \frac{k_c}{k_t} \qquad (2)$$

of K_{eq} obtained by the first method are listed in Table I, each representing the mean of four to nine determinations. At a given temperature K_{eq} is independent of the initial isomeric composition, a result which is required by the scheme in eq 1. Within experimental uncertainty, K_{eq} is also independent of temperature over the range studied. Values of $\Delta H°$ and $\Delta S°$ were determined from the slope and intercept, respectively, of a plot of ln K_{eq} *vs.* $1/T$, and are included in Table I.

As shown in eq 3 for the cis isomer, the rate law which

---

[13] W. R. Wolf, R. E. Sievers, and G. H. Brown, *Inorg. Chem.*, 11, 1995 (1972).

[14] R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, 85, 500 (1963).

[15] F. D. Hileman, R. E. Sievers, G. G. Hess, and W. D. Ross, *Anal. Chem.*, 45, 1126 (1973).

[16] When solid samples are heated, considerable scatter in the kinetic data results. This is probably due to the longer (and mass-dependent) time required for the complex to sublime into the gas phase compared to the rapid volatilization of the solution. In any event, the rate of isomerization is independent of the concentration of benzene (in range (1.7-3.4) × 10^{-3} g/cm^3).

Table I. Thermodynamic Parameters for the Cis-Trans Equilibrium of $Cr(tfa)_3$ in the Gas Phase

T, °C	K_{eq}[a]	T, °C	K_{eq}[a]
118.8	3.57 ± 0.13[b]	137.5	3.67 ± 0.16
127.7	3.52 ± 0.16	144.8	3.49 ± 0.11

$\Delta H° = -0.1 \pm 1.1$ kcal/mol; $\Delta S° = 2.4 \pm 2.8$ cal/deg mol

[a] [Trans]/[cis]. [b] Error limits represent the mean deviation of four to nine determinations.

$$-d[\text{cis}]/dt = k_c[\text{cis}] - k_t[\text{trans}] \qquad (3)$$

describes the kinetics of isomerization is comprised of two terms representing the opposing reactions. During the initial portion of the reaction, however, the first term will dominate and the system can be treated kinetically as a simple first-order process. Under these conditions k_c (or k_t for the trans isomer) is obtained from the initial slope of the plot of ln P_c (or P_t) *vs.* time, where P is the per cent composition.[17] Results at several temperatures are listed in Table II, along with the activation parameters determined from the usual Arrhenius plot. Both k_c and k_t are independent of initial concentration in the range $(0.7\text{-}2) \times 10^{-6}$ g/cm^3, an observation which confirms that isomerization is a first-order intramolecular[18] process. In addition the ratio k_c/k_t is reasonably close to the directly determined value of K_{eq}, taking into account the larger error inherent in the kinetic measurements.

Interaction of $Cr(tfa)_3$ with Glass Surfaces. Results obtained early in the study were frequently irreproducible and seemingly spurious. Typically, the apparent rate of isomerization was much larger than expected for an inert complex. In addition, the amount of complex in a sealed ampoule (as determined by the combined peak areas) diminished upon continued heating.[19] Both problems were particularly noticeable at low complex concentrations. Although we were unable to determine the exact details experimentally, the difficulty was traced to the interaction of $Cr(tfa)_3$ with the glass walls. To eliminate this effect, the walls of the ampoules were silanized with a benzene solution of hexamethyldisilizane. As depicted in Figure 2, potentially reactive surface O-H groups were replaced by $O\text{-}Si(CH_3)_3$ linkages. This type of treatment is very frequently successfully employed to inactive siliceous solid supports in gas chromatography columns.

The fact that k_c and k_t are independent of complex concentration in the range $(0.7\text{-}2) \times 10^{-6}$ g/cm^3 indicates that wall effects have been minimized under these conditions. Below this range, however, k_c increases, which suggests a small residual interaction. Also, k_c appears to be smaller in the presence of air. This retardation could be indicative of a poisoning of remaining active sites by oxygen or water vapor. In any event it is interesting to note that the cis isomer, which has a higher dipole moment, appears to be more sensitive to interaction with glass surfaces than the trans isomer.

Discussion

Previous studies of the stereochemical rearrangements of tris β-diketonate complexes have been complicated by the uncertain role of solvent in the mechanistic sequence. In contrast, the experimental conditions employed in the present investigation avoid solute-solvent interactions. Consequently, the gas-phase results are representative of the *intrinsic* thermodynamic and kinetic properties of *cis*- and *trans*-$Cr(tfa)_3$. Table III summarizes these results and includes, for comparison, an extensive compilation of data for various $M(tfa)_3$ complexes in solution.

Table II. Rate Constants and Activation Parameters for the Cis-Trans Isomerization of $Cr(tfa)_3$ in the Gas Phase

	Trans → cis	Cis → trans	
T, °C	10^5k_t, sec^{-1}	10^5k_c, sec^{-1}	k_c/k_t
118.8	1.23 ± 0.04[a]	3.71 ± 0.19	3.0
127.7	2.05 ± 0.20	8.12 ± 0.50	4.0
137.5	4.63 ± 0.13	21.2	4.6
144.8	9.20 ± 0.76	36.6	4.0

	Value	
Parameter	Trans → cis	Cis → trans
ln A	21.2 ± 2.9	27.0 ± 1.5
E_a,[b] kcal/mol	25.4 ± 2.3	29.0 ± 1.2
$\Delta H^\ddagger$, kcal/mol	24.6 ± 2.2	28.2 ± 1.1
$\Delta S^\ddagger$, cal/deg mol	−17.0 ± 5.7	−5.5 ± 3.0

[a] Where given, error limits for rate constants represent mean deviations of two or more determinations. [b] Error limits estimated according to the procedure of S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 94.

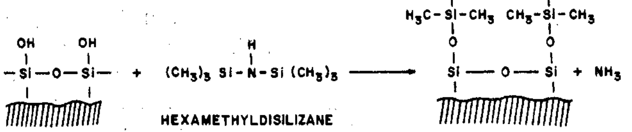


Figure 2. The effect of silanization on a glass surface.

The equilibrium studies indicate that *cis*- and *trans*-$Cr(tfa)_3$ are of comparable stability ($\Delta H° \cong 0$) in the gas phase, with K_{eq} slightly larger than expected on statistical grounds. This is perhaps not surprising, since the isomers differ only in the position of peripheral CF_3 groups and there is no interaction with the environment. By comparison, $M(tfa)_3$ complexes in weakly polar solvents generally exhibit values of $K_{eq} > 4$. The value reported by Fontaine, *et al.*,[9] for $Cr(tfa)_3$ in 1,2,4-trimethylbenzene appears to be unusually large in relation to the gas-phase result, with the preference for the trans isomer residing mainly in the entropy term. No explanation for this apparent discrepancy is evident.

The gas-phase isomerization of *trans*-$Cr(tfa)_3$ possesses a lower enthalpy of activation but a more negative entropy of activation than the corresponding cis isomer. A similar compensation of activation parameters between isomers has been noted for the Cr(III) complexes in 1,2,4-trimethylbenzene and $Ru(tfa)_3$ in *sym*-$C_2H_2Cl_4$. Of more significance, however, are the absolute values of the activation parameters in the gas phase and solution. For $Cr(tfa)_3$ the presence of solvent lowers $\Delta H^\ddagger$ by 3-5 kcal/mol but results in a more negative $\Delta S^\ddagger$. While there is thus some influence of solvent on the isomerization process, the effect (at least for $\Delta H^\ddagger$) is not particularly large. Likewise, a comparison of the gas-phase results with those for the inert Co(III) and Ru(III) complexes in solution reveals a similarity in $\Delta H^\ddagger$ and, for the latter complex, in $\Delta S^\ddagger$ as well. Although the amount of data presently available is limited, it would appear that the role of solvent in the mechanism of rearrangement, while not entirely negligible, may not be as important as previously imagined.

The assignment of mechanism in the gas phase is intrinsically more straightforward than in solution. In solution much of the energy needed for bond rupture is most likely provided

---

(17) Since $k_c/k_t > 3$, the initial rate approximation is valid over a larger composition range for the cis isomer. Consequently, the values of k_c are considered to be more accurate.

(18) For energetic reasons cited later, we discount an intermolecular mechanism involving the complete dissociation of a tfa ligand.

(19) For example, the peak area dropped by a factor of 50 on heating a sample of the trans isomer for 2400 sec at 127.7°.

Table III. Comparison of Equilibrium and Rate Parameters for Various M(tfa)$_3$ Complexes

M	Solvent	K_{eq}[a]	$\Delta H°$, kcal/mol	$\Delta S°$, cal/deg mol	$\Delta H^{\ddagger}$, kcal/mol Trans → cis	$\Delta H^{\ddagger}$, kcal/mol Cis → trans	$\Delta S^{\ddagger}$, cal/deg mol Trans → cis	$\Delta S^{\ddagger}$, cal/deg mol Cis → trans
Al[b]	CDCl$_3$	4.5	−0.24 ± 0.19	+2.2 ± 0.6	23.5 ± 1.8[c]			
Ga[b]	CDCl$_3$	4.7	−0.47 ± 0.22	+1.5 ± 0.7	20.8 ± 1.6[c]			
V[d]	CDCl$_3$	6.1	−1.4 ± 0.3	−1.0 ± 1.0				
Mn[d]	CDCl$_3$	4.4	−1.1 ± 0.4	−0.7 ± 1.2				
Co[b]	CDCl$_3$	4.1 (79°)	−0.34 ± 0.71	+1.8 ± 2.4		30.7 ± 0.6		8.6 ± 1.7
Ru[d]	*sym*-C$_2$H$_2$Cl$_4$	4.9 (150°)	−1.1 ± 0.6	+0.6 ± 1.4	27.3 ± 1.1	32.1 ± 0.8	−23 ± 3	−7.5 ± 2.0
Cr[e]	TMB	7.2 (120°)	−1.5 ± 1.3	+8 ± 3	21.3 ± 0.6	23 ± 2	−27 ± 1	−19 ± 2
Cr	None (gas phase)	3.5 (127.7°)	−0.1 ± 1.1	+2.4 ± 2.8	24.6 ± 2.2	28.2 ± 1.1	−17.0 ± 5.7	−5.5 ± 3.0

[a] [Trans]/[cis]; value refers to 25° unless noted otherwise. [b] Data from ref 14. [c] Value refers to E_a determined from the nmr coalescence behavior; see ref 4 for assumptions employed. [d] Data from ref 8. [e] Data from ref 9; TMB = 1, 2, 4-trimethylbenzene.

by solvation of the incipient charge separation in the transition state. Such compensation is, of course, absent in the gas phase, so that the energy ($\Delta H^{\ddagger}$) required to break a metal-ligand bond should be nearly the coordinate bond energy. Although the energy of a single Cr-O bond in M(tfa)$_3$ complexes has not been determined, a value of 55 kcal/mol has been reported as a realistic measure of the average energy needed to break this bond in Cr(acac)$_3$ (acac is the anion of 2,4-pentanedione).[20,21] Due to the electron-withdrawing CF$_3$ groups, the energy will probably be less in the analogous tfa complex.[22-24] However, the difference is probably no more than a few kilocalories per mole[25,26] and almost certainly is much less than the ~30-kcal/mol discrepancy with the $\Delta H^{\ddagger}$ values found for the gas-phase isomerization. It is thus reasonable to discount a bond-rupture mechanism on energetic grounds. A twist process, on the other hand, generates less charge separation and is therefore less dependent on solvation in its transition state. On the basis of the low activation enthalpy (relative to the Cr-O bond energy) and the negative activation entropy,[27] a twist appears to be the most likely pathway for rearrangement. The similarity in the gas-phase and solution activation parameters noted earlier suggests that a twist process may also be operative in solution. If solvent is involved in the rate-determining step, its influence appears to be minimal.

In concluding the discussion of mechanism, it might be useful to consider the difference between a bond-rupture and twist process in more detail. Some ambiguity can arise over what is meant by bond rupture; we have chosen to define it operationally as the energy needed to break the metal-oxygen bond in the gas phase. On this basis our data discount the "complete" rupture of the Cr-O bond in Cr(tfa)$_3$ as the major cause of isomerization. The twist-with-rupture mechanism discussed by Eaton, *et al*,[10a] is likewise eliminated. A twist process, on the other hand, involves distortion of all or most of the bonds in the complex. The requisite atomic motion, and any resultant charge redistribution, are discriminated against to a lesser extent by the lack of solvation than would be the case in a bond-rupture process.

Finally, it has been observed that most of the complexes for which a twist mechanism is considered the most probable rearrangement pathway are stereochemically nonrigid.[28] The results of the present study indicate that a non-bond-rupture process is also possible for an inert complex. Future work will be directed toward obtaining gas-phase kinetic and equilibrium data for other inert tris-chelate complexes.

Acknowledgment. The authors thank Dr. J. J. Brooks, Dr. K. J. Eisentraut, and Mr. W. D. Ross for technical advice and Dr. J. A. Cunningham for supplying the least-squares program. C. K. acknowledges the support of the National Research Council.

Registry No. *trans*-Cr(tfa)$_3$, 21496-96-8; *cis*-Cr(tfa)$_3$, 21496-95-7.

---

(20) J. O. Hill and R. J. Irving, *J. Chem. Soc. A*, 1413 (1967).

(21) J. L. Wood and M. M. Jones, *Inorg. Chem.*, 3, 1553 (1964). The 55-kcal/mol energy reported in this reference (as well as in ref 20) refers to the homolytic cleavage of the Cr-O bond.

(22) Bond weakening caused by the presence of CF$_3$ groups is consistent with the observations that (a) the rearrangement rates of M(tfa)$_3$ complexes are almost always faster than their nonfluorinated analogs,[8] (b) the metal-oxygen stretching frequency decreases with increasing fluorination of the β-diketonate ligand,[23] and (c) the formation constants of Ni^{2+} and Cu^{2+} with tfa are smaller than with acac.[24]

(23) R. D. Hancock and D. A. Thornton, *J. Mol. Struct.*, 377 (1969).

(24) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, 75, 457 (1953).

(25) It is noteworthy that a recent semiempirical INDO molecular orbital calculation comparing acac to tfa (both in their enol form) has shown that replacing CH$_3$ by CF$_3$ affects the various bond energies in the molecules by only ±2-4 kcal/mol.[26]

(26) M. S. Gordon and R. D. Koob, *J. Amer. Chem. Soc.*, 95, 5863 (1973).

(27) Although we noted earlier that $\Delta S^{\ddagger}$ values obtained in solution are not always a reliable indicator of mechanism, the same uncertainty is less likely in the gas phase. Here solvation effects in the transition state are absent, and thus $\Delta S^{\ddagger}$ should more faithfully reflect the inherent probability of the molecular motions involved.

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