Chemistry of Metal Chelates.[1] VIII. Linkage Isomerization and Disproportionation of Unsymmetrically Substituted Metal Acetylacetonates[2]

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Unsymmetrically substituted tris(acetylacetonates) of cobalt(III) and chromium(III) disproportionate in solution at elevated temperatures. Linkage isomerization of (3-formyl-2,4-pentanediono)bis(2,4-pentanediono)cobalt(III) to (2-acetyl-1,3-butanediono)bis(2,4-pentanediono)cobalt(III) accompanies intermolecular ligand exchange in boiling toluene. Disproportionation and linkage isomerization of (2,4-pentanediono)bis(3-formyl-2,4-pentanediono)cobalt(III) occur in a similar manner. Dichlorinated tris(acetylacetonates) of cobalt(III) and chromium(III) also undergo thermal disproportionation. These processes take place at lower temperatures in polar solvents.

Introduction

Formyl groups can be introduced into acetylacetonate chelate rings by a modification of the Vilsmier reaction.[4] Earlier[4] we suggested that these aldehyde substituted chelates might undergo linkage isomerization[5] such that the aldehyde group becomes coordinated and an acetyl group becomes an uncoordinated ring substituent. We incorrectly supposed that this would be an intramolecular process.
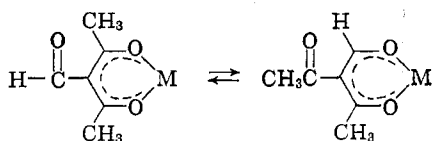
Herein is described the linkage isomerization of formyl-substituted cobalt acetylacetonates. This isomerization is accompanied by intermolecular ligand exchange. A similar disproportionation occurs with other unsymmetrically-substituted acetylacetonates.

Experimental

Disproportionation and Linkage Isomerization of (3-Formyl-2,4-pentanediono)bis(2,4-pentanediono)cobalt(III) (I).—A solution of 4.0 g. of pure monoformylcobalt acetylacetonate (I)[4] was heated under reflux in toluene (b.p. 111°) for 2 days. Samples of the solution were removed at intervals and analyzed by thin layer chromatography using alumina and a 2:1 chloroform–benzene eluent. After 6 hr. at least four compounds were detected. After 2 days the chromatograms revealed six components (Figure 1). Later chromatograms indicated a steady state had been reached. The solvent then was removed under reduced pressure and the crude solid was separated into two fractions by column chromatography on Florisil using chloroform as an eluent. The faster moving of the two bands was further separated into three bands by column chromatography on alumina using 1:1 chloroform–benzene as an eluent. Each of these three bands a, b, and c (listed in order of elution) was found to be homogeneous (thin layer analysis) and to correspond to components a, b, and c from the thin layer chromatographic analysis of the crude reaction mixture (Figure 1a).

(1) Part VII: R. H. Barker, J. P. Collman, and R. L. Marshall, *J. Org. Chem.*, **29**, 3216 (1964).

(2) This work was supported by National Science Foundation Grant No. NSF-G19756.

(3) Fellow of Alfred P. Sloan Foundation.

(4) J. P. Collman, R. L. Marshall, W. L. Young, III, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).

(5) F. Basolo, J. L. Burmeister, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 1700 (1963).

The first band, a, was identified as cobalt(III) acetylacetonate (II) by comparison of its R_f value, n.m.r. spectrum, and melting point with an authentic sample.

The second band, b, was found to be a new compound, III, identified as (2-acetyl-1,3-butanediono)bis(2,4-pentanediono)cobalt(III). After recrystallization from benzene–heptane, green prisms, m.p. 157°, were obtained; n.m.r. 7.80 (3), 7.79 (6), 7.77 (3), 7.65 (3), 7.32 (3), 4.40 (1), 4.37 (1), 2.08 (1) in CDCl₃. All chemical shift values are in τ units; integrated intensities are in parentheses and peaks are sharp singlets. The infrared spectrum of III showed peaks at 1660, 1600, 1575, 1520, 1380, 1280, and 1190 cm.⁻¹ (in CHCl₃ determined on a Perkin-Elmer 421 grating spectrophotometer).

Anal. Calcd. for $C_{16}H_{21}O_7Co$: C, 50.01; H, 5.47. Found: C, 50.20, 49.93; H, 5.40, 5.51.

The third band, c, was identified by its R_f value, n.m.r. spectrum, and melting point to be monoformylcobalt acetylacetonate (the starting material, I).

The second major portion separated from the crude reaction mixture contained three components as revealed by thin layer analysis. One of them had the same R_f value as an authentic sample of diformylcobalt acetylacetonate (IV). The n.m.r. spectrum of this mixture exhibited signals at τ 7.79 (6) apparent doublet, 7.64 (3), 7.33 (9) apparent doublet, 4.41 (1), 2.01 (1), −0.2 (1). The n.m.r. spectrum of an authentic sample of the diformyl chelate IV showed bands at τ 7.78 (6), 7.36 (6), 7.34 (6), 4.42 (1), and −0.20 (2).

Disproportionation and Linkage Isomerization of (2-Acetyl-1,3-butanediono)bis(2,4-pentanediono)cobalt(III) (III).—A solution of 20 mg. of the linkage isomer III in 12 ml. of toluene was heated under reflux for 4 days. Thin layer analysis revealed a pattern of six components identical with the pattern found from disproportionation of monoformylcobalt acetylacetonate (Figure 1). Visual comparison of the chromatograms from each reaction mixture indicated that the components were present in approximately the same ratios.

Disproportionation and Linkage Isomerism of (2,4-Pentanediono)bis(3-formyl-2,4-pentanediono)cobalt(III) (IV). (A) In Toluene.—A solution of 450 mg. of the diformylcobalt chelate IV[4] in 67.5 ml. of toluene was maintained at reflux for 3 days. Samples were taken at intervals and thin layer chromatographic analyses (alumina, 2:1 chloroform–benzene) were performed to observe the progress of the disproportionation. These analyses (Figure 1b) revealed the formation of all of the products obtained from the monoformyl chelate I in addition to some bands which combined into one band of the same R_f value as tris(3-formyl-2,4-pentanediono)cobalt(III) (V) on a silica gel (Type G) plate. However, this band separated into a string of at least three components on an alumina plate. The slowest moving of these three components had the same R_f value as an authentic sample of tris(3-formyl-2,4-pentanediono)cobalt(III) (V) (used as an internal standard on the same plate).
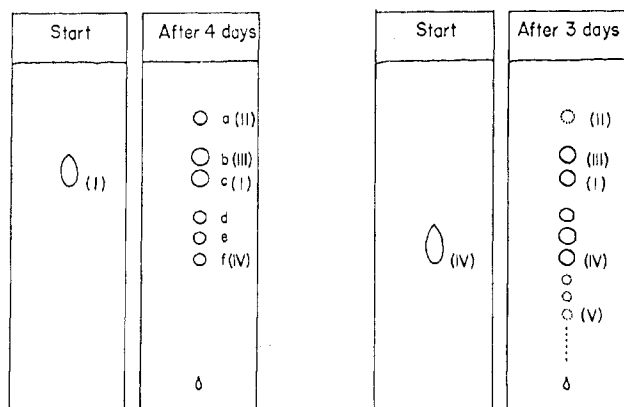
Figure 1.—Thin layer chromatography. Aluminum oxide G plate with 2:1 $CHCl_3$-C_6H_6 eluent.

The crude reaction mixture was fractionated by column chromatography (Florisil, chloroform). Two major bands were collected from the column. According to thin layer analyses these corresponded to the two major fractions (three components each) found earlier in the disproportionation of the monoformyl chelate I. Examination of the n.m.r. spectrum of each of these fractions revealed the same peaks found in the spectrum of the corresponding fraction from disproportionation of the monoformyl chelate. However, the relative peak areas were different, indicating that the components were formed in different ratios in one disproportionation than in the other. Material corresponding to the slowest moving three components on the thin layer chromatogram apparently remained on the column.

A brown residue in the reaction flask was found to be water-soluble. The n.m.r. spectrum of this substance in D_2O did not exhibit an HOD peak, suggesting the presence of a paramagnetic species. The infrared spectrum of the residue did not resemble an acetylacetonate chelate.

(B) In Benzene.—A solution containing 200 mg. of diformyl chelate in 30 ml. of benzene was heated at reflux (80°) and the solution was examined periodically by thin layer chromatography. After 2 days, no ligand exchange products were detected. After 4 days, only a trace of disproportionation was indicated.

(C) In Acetonitrile.—A solution of 100 mg. of diformyl chelate in 30 ml. of acetonitrile was heated at reflux (83°). The monoformyl chelate I and its rearrangement product III were detected by thin layer analysis after 6 hr. After 4 days the reaction appeared to achieve a steady-state equilibrium and thin layer analysis revealed all of the components from the corresponding experiment in boiling toluene.

Disproportionation and Linkage Isomerization of a Mixture of Tris(3-formyl-2,4-pentanediono)cobalt(III) (V) and Tris(2,4-pentanediono)cobalt(III) (II).—A solution containing 20 mg. of cobalt acetylacetonate (II) and 20 mg. of triformylcobalt acetylacetonate (V) in 12 ml. of toluene was heated under reflux for 2 days. Thin layer chromatographic analysis revealed the same pattern of peaks found from disproportionation of the diformyl chelate (Figures 2 and 3).

Disproportionation of (2,4-Pentanediono)bis(3-chloro-2,4-pentanediono)cobalt(III) (VI). (A) In Toluene.—A solution of 450 mg. of dichlorocobalt acetylacetonate in 67.5 ml. of toluene was heated at reflux. Substantial quantities of a precipitate formed as the temperature reached the boiling point. After 1 hr., tris(3-chloro-2,4-pentanediono)cobalt(III) (VII) and (3-chloro-2,4-pentanediono)bis(2,4-pentanediono)cobalt(III) (VIII) were detected by thin layer analysis on silica G using chloroform as the eluent. Within 6 hr. all of the soluble chelates had decomposed.

(B) In Benzene.—A solution of 450 mg. of dichlorocobalt acetylacetonate (VI) in 67.5 ml. of benzene was heated at reflux for 6 hr. Thin layer chromatographic analysis indicated the presence of trichloro, dichloro, monochloro, and unsubstituted cobalt acetylacetonate. After removing the solvent, the reac-

tion mixture was separated by column chromatography on Florisil using benzene and then 1:1 chloroform–benzene eluents. The first band was identified as trichlorocobalt acetylacetonate (VII) by comparison of its n.m.r. spectrum with that of an authentic sample. In the same way the second band was shown to be dichlorocobalt acetylacetonate (VI) and the third band to be monochlorocobalt acetylacetonate (VIII). Unsubstituted cobalt acetylacetonate (II) was identified by thin layer chromatography using an authentic sample as an internal standard.

Disproportionation of (2,4-Pentanediono)bis(3-chloro-2,4-pentanediono)chromium(III) (IX).—A solution of 350 mg. of dichlorochromium acetylacetonate (IX) in 52.5 ml. of toluene was heated at reflux for 2 days. After removal of the solvent the crude mixture was separated by column chromatography on Florisil (benzene eluent) into three bands. The first band was identified by comparison of its R_f value and infrared spectrum with those of an authentic sample to be trichlorochromium acetylacetonate (X). The second band was similarly shown to be the starting material, IX. The third band was subjected to further purification by preparative thin layer chromatography on silica gel G, using chloroform as an eluent. Monochlorochromium acetylacetonate (XI) was isolated and identified by its infrared spectrum. Unsubstituted chromium acetylacetonate (XII) was shown to be a minor component by comparison of its R_f value with that of an authentic sample.

Effect of Chromium(II) on Disproportionation of Dichlorocobalt Acetylacetonate (VI).—To a solution of 140 mg. of dichlorocobalt acetylacetonate (VI) in 30 ml. of tetrahydrofuran was added 10 drops of a solution of chromous chloride. The latter was prepared by treating a suspension of anhydrous chromium trichloride in tetrahydrofuran under a nitrogen atmosphere with zinc dust. The reducing power of the chromium(II) solution was verified by testing with a neutral solution of $KMnO_4$.

A control solution of the dichloro chelate VI was prepared without the reducing agent. Neither the reducing solution nor the control exhibited disproportionation at room temperature under nitrogen for 4 days.

The two tetrahydrofuran solutions were heated at reflux for 2 days. Thin layer chromatographic analyses were performed periodically to determine the progress of the reaction. Chromatograms from the reducing solution and the control appeared to be identical. Trichloro, dichloro, monochloro, and unsubstituted cobalt acetylacetonates were observed.

Results and Discussion

Treatment of monoformylcobalt acetylacetonate (I) in boiling toluene affords a mixture of at least six components as revealed by a thin layer chromatogram of the mixture (Figure 1). In order of their elution the components of this mixture were found to be: cobalt acetylacetonate (II), the linkage isomer III, the starting material I, the diformyl chelate IV, and two unknown substances—presumably linkage isomers of IV. Components II, III, and I were isolated and thoroughly characterized. The diformyl chelate IV was identified by comparison of its thin layer chromatographic behavior with that of an authentic sample. The proton magnetic resonance spectrum of the mixture of three slower moving components (d, e, f in Figure 1) exhibited all of the signals found in the spectrum of an authentic sample of pure diformyl chelate IV as well as additional signals which would be compatible with linkage isomers. Perhaps the most noteworthy signal in the spectrum of this mixture occurs at τ 2.01 and is assigned to a coordinated aldehyde proton.

Since the linkage isomer III is a new compound, its characterization requires comment. Elemental an-
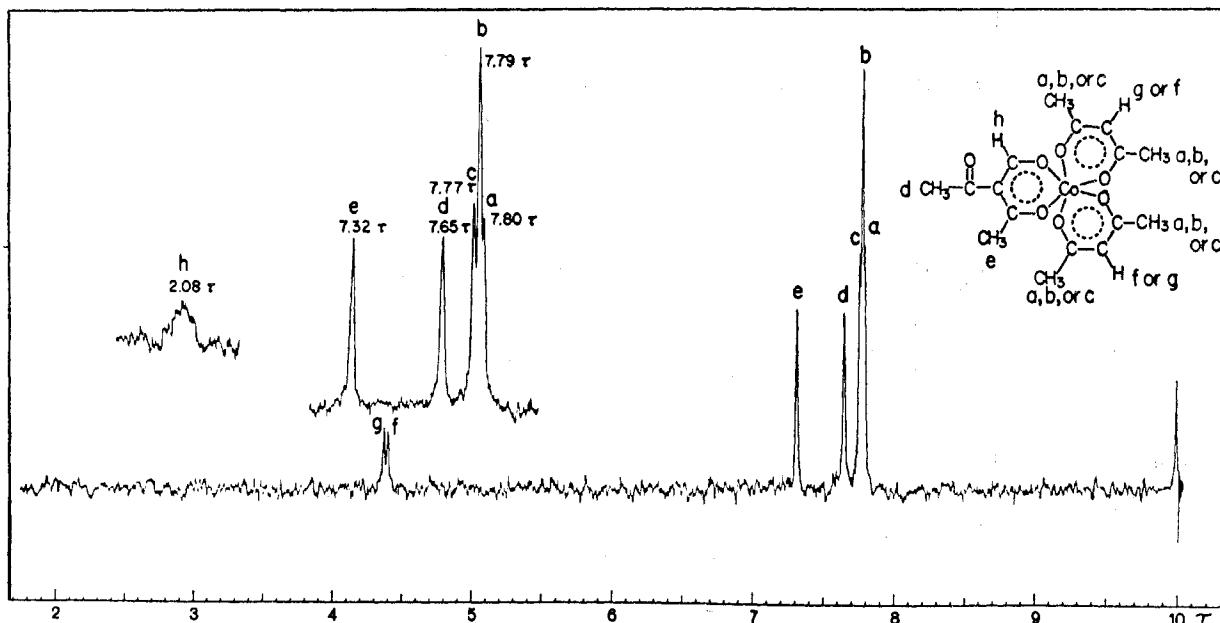
Figure 2.—Proton magnetic resonance spectrum of (3-formyl-2,4-pentanediono)bis(2,4-pentanediono)cobalt(III) (I).
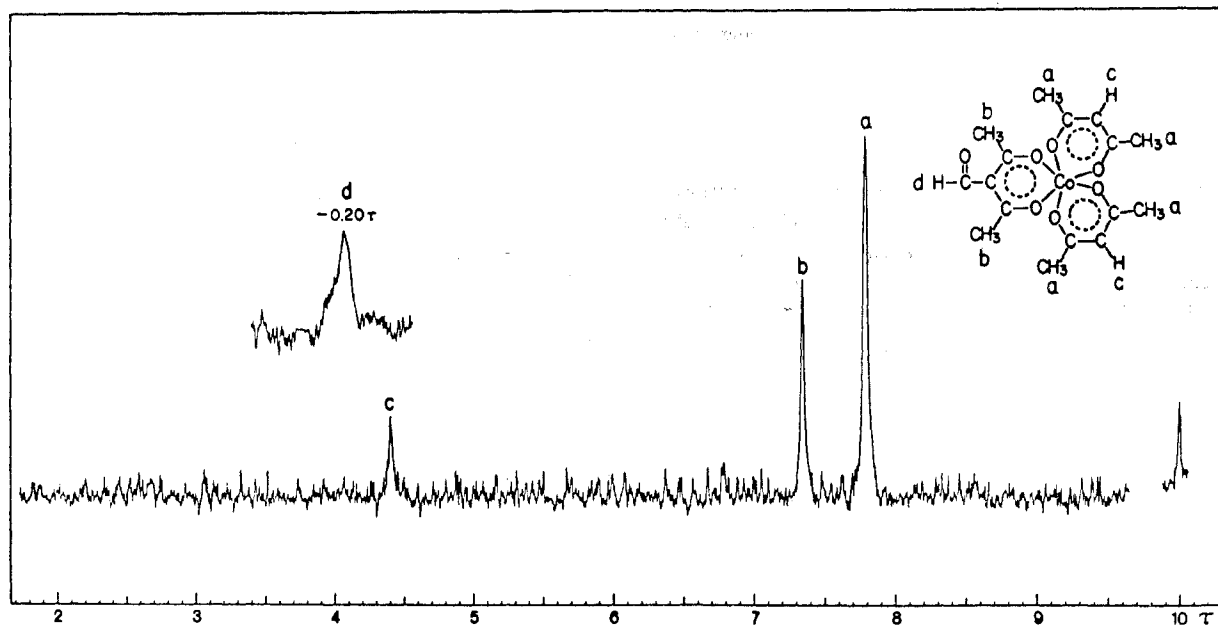

Figure 3.—Proton magnetic resonance spectrum of (2-acetyl-1,3-butanediono)bis(2,4-pentanediono)cobalt(III) (III).

alysis show III to be isomeric with the monoformyl chelate I. The infrared spectra of III and I are quite similar, both exhibiting uncoordinated carbonyl group absorption bands at 1660 cm.$^{-1}$. The proton magnetic resonance spectrum of III supports the structure assigned to it. Examination of a molecular model of III shows a complete lack of symmetry so that nine different types of protons should result. The n.m.r. spectrum of III exhibits eight types of protons at τ 7.80, 7.79, 7.77, 7.65, 7.32, 4.40, 4.37, and 2.08 in area ratios of 3:6:3:3:3:1:1:1 (Figure 3). Evidently the signal at τ 7.79 represents two (presumably different) methyl groups which have not been resolved. Using n.m.r. spectra of the monoformyl and the diformyl

chelates I and IV as models the signals in the spectrum of the linkage isomer III can be assigned as illustrated (Figure 2). The assignments of the peaks at τ 7.80, 7.79, and 7.77 are ambiguous. However, the peak signals at τ 7.65 and 7.32 can be assigned by comparing these with known chemical shift values for methyl groups in the monoformyl chelate I and the monoacetyl chelate. The signal at τ 7.65 in III corresponds to the uncoordinated acetyl methyl signal at τ 7.60 in the monoacetyl chelate. The methyl group on the acetyl-substituted ring in III gives rise to the peak at τ 7.34 which compares favorably with the signal (τ 7.32) of the methyl groups on the aldehyde-substituted ring in the monoformyl chelate I. The lower value, τ 7.32, for the

I

II

III

I

IV

+ isomers of IV
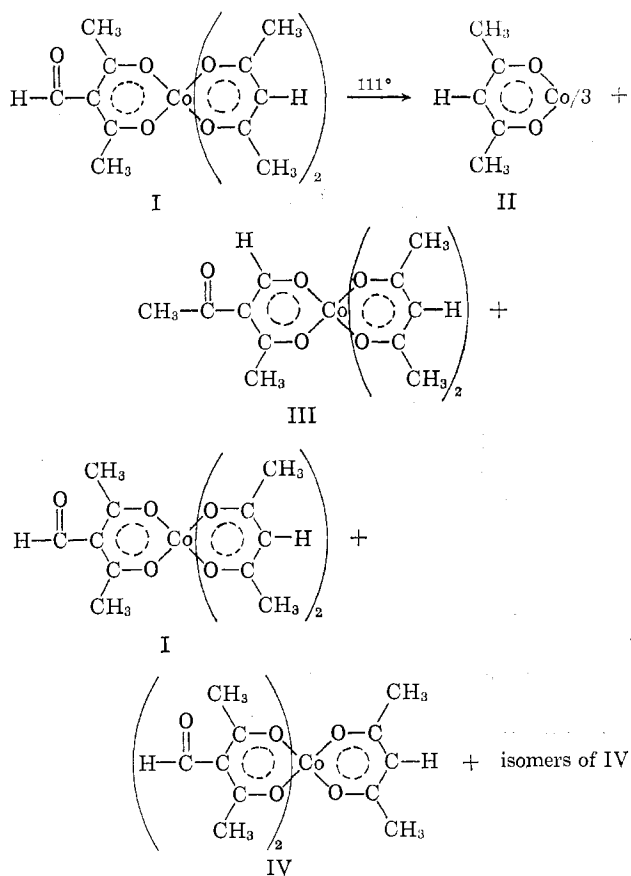
methyls on the aldehyde-substituted ring compared with τ 7.65 for methyl groups on the acetyl-substituted ring is probably caused by coplanarity and resonance interaction of the uncoordinated carbonyl groups in I and III. Molecular models indicate steric inhibition of resonance in the monoacetyl chelate.

τ7.34

I

τ7.60

τ7.75

I
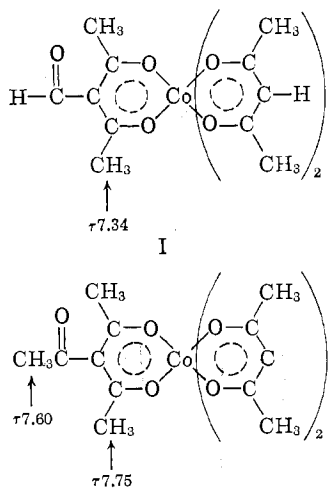
The signal at τ 2.08 is unlike any proton signal we have found in our earlier studies of the n.m.r. spectra of acetylacetonate chelates. From the position of this signal, it is reasonable to assign this absorption to the proton on the coordinated aldehyde group.

The linkage isomer III represents a type of cobalt complex we have previously been unable to synthesize. Although chromium(III) chelates of malondialdehyde

and formylacetone are well-known,[6] all attempts to prepare a cobalt(III) complex of an aldehyde have failed. In each instance cobalt(III) oxidizes the aldehyde group. The stability of III is significant in that coordination of an aldehyde to cobalt(III) inhibits electron transfer.

The disproportionation and linkage isomerization of the monoformyl chelate I was found to resemble a steady-state equilibrium in that boiling a solution of the pure linkage isomer III in toluene resulted in a mixture of the same six components.

Disproportionation of the diformyl chelate IV was also studied. In boiling toluene, IV is transformed into a mixture of at least nine components as determined by thin layer chromatographic analysis (Figure 1b). The six fastest moving components were found to be the same as those from disproportionation of the monoformyl chelate I (Figure 1a). The last three components were not isolated, but one of these exhibited the same R_f value as an authentic sample of the triformyl chelate V. The remaining two components are presumed to be a mixture of linkage isomers of V.[7]

The structures assigned to the nine chelates resulting from disproportionation of the diformyl chelate IV were substantiated by reproducing the same pattern of nine bands from thermal treatment of a solution of unsubstituted chelate II and the triformyl chelate V.

Heating the diformylcobalt chelate IV in boiling benzene (80°) failed to effect disproportionation or isomerization. However, rearrangement and disproportionation did take place in boiling acetonitrile (83°). The

IV

I + II + III + IV + isomers of IV
+

V

II

V
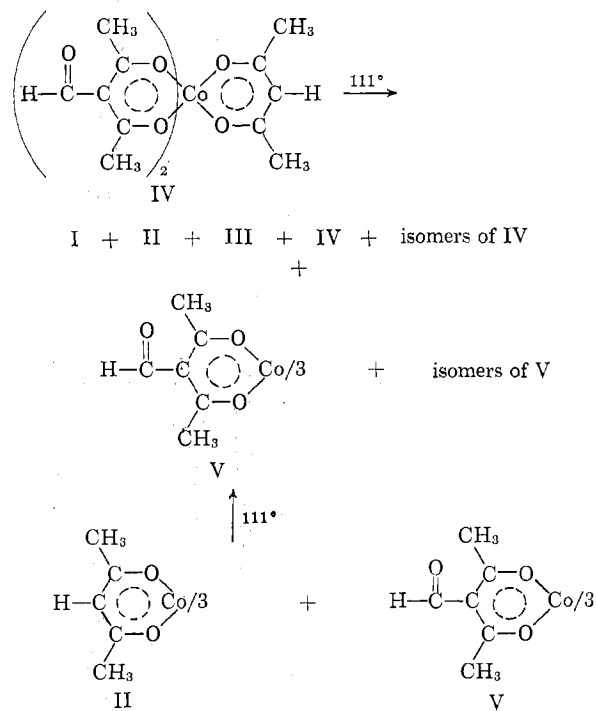
(6) J. P. Collman and E. T. Kittleman, *J. Am. Chem. Soc.*, **83**, 531 (1961).

(7) There are six enantiomorphic pairs of linkage isomers which can be derived from the diformyl chelate and seven in the case of the triformyl chelate.

pattern of products was the same as that described earlier (Figure 1b). Evidently polar solvents lower the activation energy for this reaction. This is reasonable since the transition state must involve charge separation.

Disproportionation was also studied with chelates which could not undergo linkage isomerization. Dichlorocobalt acetylacetonate (VI) was found to disproportionate rapidly in boiling toluene but the chelates were simultaneously degraded at this temperature. However, disproportionation of the dichloro chelate (VI) into a mixture of the monochloro, dichloro, trichloro, and unsubstituted chelates (VIII, VI, VII, and II) took place smoothly in boiling benzene without decomposition. The analogous dichlorochromium chelate (IX) was found to disproportionate in a similar manner except that the temperature of boiling toluene was required for the reaction to take place.

These results suggest that disproportionation of cobalt chelates requires a lower activation energy than disproportionation of chromium chelates. Formyl-substituted chelates seem to require higher activation energies than chloro-substituted chelates.

No evidence was found for the intermediacy of cobalt(II) species in the disproportionation of the dichlorocobalt(III) chelate VI. Introduction of chromium(II) species into the reaction mixture failed to enhance the rate of disproportionation in boiling tetrahydrofuran.

Our data suggest (but do not prove) that linkage isomerism is an intermolecular process. Careful examination of reaction mixtures during the earliest stages of every isomerization involving formyl chelates revealed mixtures of linkage isomers and ligand exchange products. To the limits of our thin layer chromatographic analyses, isomerization always accompanies ligand exchange—regardless of the temperature or the solvent
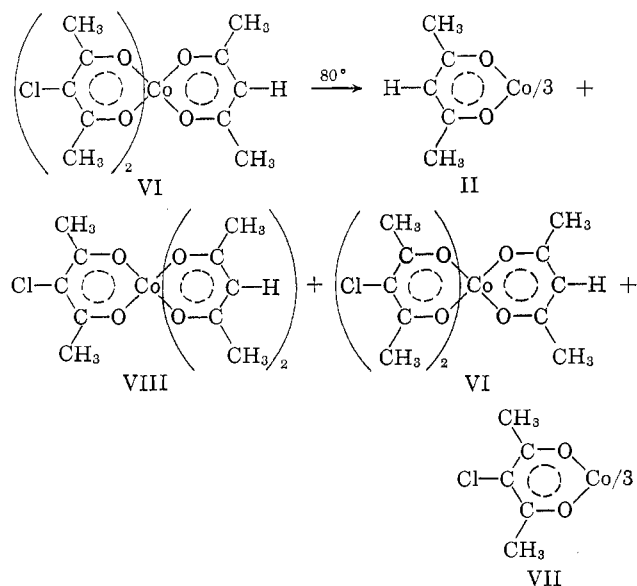
employed. We were unable to find experimental conditions where isomerization could be distinguished from ligand exchange.

In one experiment isomerization must be intermolecular. When the diformyl chelate IV is heated to 111° in toluene, disproportionation takes place. Thin layer analysis reveals formation of the monoformyl chelate 1 and its linkage isomer III in the *same* ratio from the beginning of the reaction. The *relative* intensities of spots from I and III remained unchanged with time, although the concentrations of 1 and III slowly increased. Our previous experiments converting pure I or pure III into a mixture of these isomers under the same conditions required a much longer time to reach an equilibrium state (about 2 days). Therefore, it can be argued that both I and III are formed from IV by an exchange (intermolecular) process. However, one cannot rule out an additional intramolecular exchange between I and III.

Intramolecular isomerization is not ruled out by our experiments, but we were unable to find any evidence to verify this pathway. Examination of the conformation of the ruptured ring in the probable intermediate is revealing. Rotation must occur about the partial carbon–carbon bond before intramolecular isomerization can occur. Thus, each bond rupture does not easily lead to intramolecular isomerization.
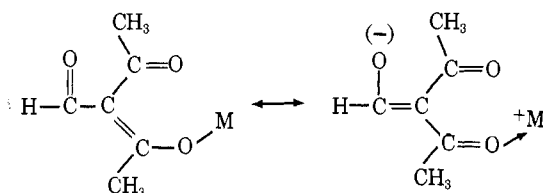
Fay and Piper's results indicate that *cis–trans* interconversions of geometric isomers of unsymmetrical tris-1,3-diketone chelates of aluminum, gallium, indium, and tin take place in an intramolecular manner.[8] Their evidence indicates a mechanism involving rupture of one bond and formation of a symmetrical five-coordinate intermediate with charge separation. *cis–trans* isomerization of cobalt(III) trifluoroacetylacetonate was measurable at 66° in chloroform. Racemization and *cis–trans* isomerism of the *cis*-chromium(III) benzoylacetone chelate takes place at 95°.[8] These results as well as our own suggest that electronegative substituents on the chelate ring facilitate cleavage of the coordinate bond.

Linck and Sievers[9] have studied disproportionation of mixtures of aluminum acetylacetonate and aluminum hexafluoroacetylacetonate. Intermolecular ligand exchange takes place in carbon tetrachloride.

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

(9) R. G. Linck and R. E. Sievers, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 25-O.