

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850**Stereochemistry and Lability of Dihalobis(β -diketonato)titanium(IV) Complexes. II. Benzoylacetates and Dibenzoylmethanates¹**BY NICK SERPONE² AND ROBERT C. FAY

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A series of complexes of the type $Ti(dik)_2X_2$ (dik = anion of 1-phenyl-1,3-butanedione, $bzac$, and of 1,3-diphenyl-1,3-propanedione, $bzbz$; X = F, Cl, or Br) has been prepared and characterized. Microscopy and X-ray powder patterns indicate that the solid chlorides and bromides are isomorphous. Molecular weight and conductance measurements show that the complexes behave as monomeric nonelectrolytes in nitrobenzene. Proton and fluorine nmr spectra of dichloromethane solutions demonstrate that these compounds exist in solution as geometrical isomers which have halogen atoms in *cis* positions. Spectra of $Ti(bzac)_2X_2$ are consistent with an equilibrium mixture of the three possible *cis*-dihalo isomers. Chemical shifts are reported, and proton shifts are interpreted in terms of the intramolecular electric field of the *cis* isomers and the magnetic anisotropy of the phenyl rings. Variable-temperature H^1 and F^{19} spectra exhibit line broadening, which is attributed to exchange of nuclei between the nonequivalent sites of the various isomers. For $Ti(bzac)_2X_2$, lability increases in the order $X = Cl < Br \sim F$. Possible twisting mechanisms for the exchange processes are described and discussed in relation to the nmr spectra. It is concluded that the configurational changes do not occur by twists which proceed through C_{2v} or pseudo- C_{2v} transition states or by twists about a single octahedral C_3 axis. The possibility of stepwise twists about different C_3 axes cannot be eliminated.

Introduction

In the previous paper of this series³ it was shown that the dihalobis(acetylacetonato)titanium(IV) complexes, $Ti(acac)_2X_2$ (X = F, Cl, or Br), are monomeric nonelectrolytes which exist in dichloromethane solution in the *cis* geometrical configuration. These compounds were found to undergo rapid rearrangement processes which exchange methyl groups between the two nonequivalent sites of the *cis* isomer.

For two reasons, we thought that it would be of interest to extend the previous work to include the benzoylacetate and dibenzoylmethanate derivatives, $Ti(bzac)_2X_2$ and $Ti(bzbz)_2X_2$, where $bzac$ and $bzbz$, respectively, represent the anions of 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione. In the first place, the phenyl-substituted derivatives were needed for current electronic spectral studies of β -diketone complexes of titanium(IV).⁴ Secondly, the benzoylacetates are of stereochemical interest because the $bzac$ ligand is unsymmetrical. Consequently, $Ti(bzac)_2X_2$ complexes may exist in a larger number of isomeric configurations; there are, in all, five possible geometrical isomers. Moreover, variable-temperature nmr studies of exchange of nuclei between nonequivalent sites of the various isomers were expected to throw some light on the mechanism of stereochemical rearrangements of dihalobis(β -diketonato)titanium complexes, especially on the question of whether these complexes rearrange by intramolecular twisting mechanisms.

In this paper we report syntheses, molecular weight and conductance data, microscopy, X-ray powder data, and variable-temperature proton and fluorine nmr

studies for $Ti(bzac)_2X_2$ and $Ti(bzbz)_2X_2$ (X = F, Cl, or Br). The dibromides and $Ti(bzbz)_2F_2$ are new compounds which have not been reported previously.

Experimental Section

Reagents and Techniques.—Eastman Organic Chemicals 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione were used as purchased without further purification. Sources of titanium tetrahalides and methods for drying solvents have been described previously.³ All syntheses, handling of compounds, and physical measurements were carried out under anhydrous conditions in a dry nitrogen atmosphere.

Difluorobis(1-phenyl-1,3-butanediono)titanium(IV).—Benzoylacetone (17.4 g, 0.108 mole) dissolved in 85 ml of dichloromethane was added slowly, with stirring to a suspension of titanium(IV) fluoride (5.40 g, 0.0436 mole) in *ca.* 350 ml of dichloromethane. A gentle stream of dry nitrogen was passed through the solution and stirring was continued for 21.5 hr until evolution of hydrogen fluoride was complete. The yellow-orange solution was filtered, then concentrated to half its volume, and the yellow product was allowed to crystallize in the cold (0°). The crystals (11.0 g, 62% theoretical) were collected and dried *in vacuo*; mp 196–198.5° dec; lit.,⁵ 195–199° dec.

Anal. Calcd for $Ti(C_{10}H_8O_2)_2F_2$: C, 58.84; H, 4.44. Found: C, 58.89; H, 4.38.

Difluorobis(1,3-diphenyl-1,3-propanediono)titanium(IV).—This compound was prepared in 51% yield by the same procedure as used for $Ti(bzac)_2F_2$; however, the reaction was complete in 9.5 hr. The yellow-orange product was crystallized from the dichloromethane solution by addition of an equal volume of hexane. The crystals were dried *in vacuo*; mp 204.5–206°.

Anal. Calcd for $Ti(C_{15}H_{11}O_2)_2F_2$: C, 67.68; H, 4.17; F, 7.14; Ti, 9.00. Found: C, 67.53; H, 3.99; F, 6.96; Ti, 9.21.

Dichlorobis(1-phenyl-1,3-butanediono)titanium(IV).^{6,7}—Titanium(IV) chloride (2.00 ml, 0.0182 mole) was added to benzoylacetone (8.0 g, 0.050 mole) dissolved in *ca.* 60 ml of benzene. The reaction mixture was allowed to reflux for 15 min with a slow stream of dry nitrogen passing through the solution to aid in dispelling evolved hydrogen chloride. The mixture was filtered hot in order to collect the brownish red product. The

(1) Presented in part at the 9th International Conference on Coordination Chemistry; see "Proceedings of the 9th International Conference on Coordination Chemistry," St. Moritz-Bad, Switzerland, 1966, p 486.

(2) National Research Council of Canada Predoctoral Fellow, 1966–1968.

(3) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).

(4) N. Serpone and R. C. Fay, to be published.

(5) E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

(6) Preparation of this compound in glacial acetic acid has been reported; no melting point was given.⁷

(7) M. Cox, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 6113 (1964).

TABLE
MICROSCOPY

Compd	Crystal form	Extinction	Pleochroism ^a
Ti(bzac) ₂ F ₂	Diamond-shaped plates	Symmetric	Yellow; light yellow
Ti(bzac) ₂ Cl ₂	Needles	Parallel; oblique ^b	Red; light yellow
Ti(bzac) ₂ Br ₂	Needles	Parallel; oblique ^b	Red; light orange-yellow
Ti(bzbx) ₂ F ₂	Prisms	Oblique	Yellow-orange; yellow
Ti(bzbx) ₂ Cl ₂	Needles	Parallel	Red-orange; red
Ti(bzbx) ₂ Br ₂	Needles	Parallel	Red-orange; red

^a First color listed is the color when the plane of polarization is parallel or more nearly parallel to the length of the crystal. ^b Some crystals give parallel extinction; others give oblique extinction. These observations probably represent different views of the same crystal, suggesting that the crystals are monoclinic.

crude product (7.56 g, 94% theoretical) was recrystallized twice from benzene-hexane and dried *in vacuo*; mp 209–210° dec.

Anal. Calcd for Ti(C₁₀H₉O₂)₂Cl₂: C, 54.45; H, 4.11; Cl, 16.07; Ti, 10.86. Found: C, 54.79, 54.61; H, 4.13, 4.23; Cl, 15.90; Ti, 11.01.

Dichlorobis(1,3-diphenyl-1,3-propanediono)titanium(IV).^{6,7}—This compound was prepared in 94% yield by the same method used for synthesis of Ti(bzac)₂Cl₂. The bright red product was recrystallized twice from benzene-hexane; mp 262.5–263.5°.

Anal. Calcd for Ti(C₁₅H₁₁O₂)₂Cl₂: C, 63.74; H, 3.92; Cl, 12.54; Ti, 8.47. Found: C, 63.49; H, 4.00; Cl, 12.28; Ti, 8.30.

Dibromobis(1-phenyl-1,3-butanediono)titanium(IV).—Titanium(IV)bromide (7.0 g, 0.019 mole) dissolved in 40 ml of benzene was added to benzoylacetone (8.0 g, 0.050 mole) dissolved in 100 ml of benzene. The reaction mixture was allowed to reflux for 30 min with a slow stream of dry nitrogen passing through the solution. After distillation of *ca.* 40 ml of solvent, the brownish red product was collected, recrystallized twice from benzene-hexane, and dried *in vacuo* at 80°; mp 219–221° dec.

Anal. Calcd for Ti(C₁₀H₉O₂)₂Br₂: C, 45.32; H, 3.42; Br, 30.15; Ti, 9.04. Found: C, 45.53; H, 3.49; Br, 29.57; Ti, 8.86.

Dibromobis(1,3-diphenyl-1,3-propanediono)titanium(IV).—Reaction of dibenzoylmethane with titanium(IV) bromide under the conditions employed for preparation of Ti(bzac)₂Br₂ yielded a violet benzene solvate. *Anal.* Calcd for Ti(C₁₅H₁₁O₂)₂Br₂·C₆H₆: C, 59.04; H, 3.85. Found: C, 58.86; H, 3.67. The solvate turns red-violet at *ca.* 150° (presumably owing to loss of benzene) and melts at 272–274°. Benzene could not be removed from the solvate by heating at 80° *in vacuo* for 24 hr. The solvent-free complex was obtained as red-violet crystals by recrystallizing the solvate from dichloromethane-hexane. The complex was dried *in vacuo*; mp 273–274.5°.

Anal. Calcd for Ti(C₁₅H₁₁O₂)₂Br₂: C, 55.08; H, 3.39; Br, 24.43; Ti, 7.32. Found: C, 55.36; H, 3.50; Br, 24.84; Ti, 7.51.

Hydrolysis Experiments.—Ten-milliliter samples of 5.0 × 10⁻³ M solutions of the complexes in dry acetonitrile were treated with 20 μl of water. Turbidity or precipitation was noted after the following periods of time: Ti(bzac)₂Br₂, 1 day; Ti(bzbx)₂Br₂, immediately; Ti(bzac)₂Cl₂, 2.5 days; Ti(bzbx)₂Cl₂, 5 min. Solutions of Ti(bzac)₂F₂ and Ti(bzbx)₂F₂ gave no turbidity even after 1 week. The benzoylacetones (X = Cl, Br) gave a yellow precipitate, and the dibenzoylmethanates yielded an orange precipitate. Carbon-hydrogen analyses suggest that hydrolysis of Ti(bzac)₂X₂ gave mostly titanium(IV) oxide, whereas hydrolysis of Ti(bzbx)₂X₂ may have yielded mostly TiO(bzbx)₂.

Anal. Calcd for TiO(C₁₀H₉O₂)₂: C, 62.19; H, 4.60. Found for hydrolysis product from Ti(bzac)₂Br₂: C, 4.40; H, 2.44. Calcd for TiO(C₁₅H₁₁O₂)₂: C, 70.60; H, 4.35. Found for hydrolysis product from Ti(bzbx)₂Cl₂: C, 64.28; H, 4.47. Found for hydrolysis product from Ti(bzbx)₂Br₂: C, 60.79; H, 4.18.

Solid samples of the complexes were exposed to the atmosphere and then examined periodically under a polarizing microscope. Hydrolysis was evidenced by pitting of the crystal faces and loss of sharp extinction. For Ti(bzac)₂X₂ and Ti(bzbx)₂X₂ (X =

Cl, Br) hydrolysis was apparent after 1–1.5 weeks. The difluorides showed only very slight pitting of the crystal faces, even after 2 weeks.

Physical Measurements. Melting Points.—Melting points were measured using a calibrated thermometer; reported melting points are corrected.

Microscopy and X-Ray Powder Patterns.—Crystals of the compounds were studied with a polarizing microscope. Pertinent observations are summarized in Table I. In general, the dibenzoylmethanates gave better formed crystals than the benzoylacetones.

X-Ray powder patterns were obtained with nickel-filtered copper K_α radiation using 0.5-mm glass capillaries and a Debye-Scherrer camera of 360.0-mm circumference. Interplanar spacings and visually estimated relative intensities are listed in Table II.

Molecular Weights.—Molecular weights were determined cryoscopically in purified³ nitrobenzene. The freezing point depression constant of the solvent was determined using benzil (10⁻¹ M).

Conductance Measurements.—These were made in nitrobenzene solution at 25.00 ± 0.05° using previously described techniques.³

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra were obtained with a Varian A-60 spectrometer at 60,000 Mc. Fluorine spectra were recorded with a Varian HR-60 spectrometer at 56,444 Mc using audiofrequency side bands for calibration of the magnetic field sweep. Spectra were recorded in the temperature range +70 to -97°; techniques used to obtain variable-temperature spectra have been described in previous papers.^{3,8} The solvent was dichloromethane.

Results and Discussion

Reaction of titanium(IV) fluoride, chloride, or bromide with benzoylacetone or dibenzoylmethane in an inert solvent (dichloromethane or benzene) gives good yields of the dihalobis(β-diketonato)titanium(IV) complexes, Ti(bzac)₂X₂ and Ti(bzbx)₂X₂. The complexes are soluble in dichloromethane, chloroform, acetonitrile, and nitrobenzene, slightly soluble in benzene and acetone, but nearly insoluble in ether, carbon tetrachloride, and saturated hydrocarbons. Solubility in organic solvents decreases as the halogen varies in the order F > Cl > Br. In general, the dibenzoylmethanates are less soluble than the benzoylacetones; both Ti(bzac)₂X₂ and Ti(bzbx)₂X₂ are less soluble than the corresponding acetylacetones,³ solubility apparently decreasing with increasing number of phenyl substituents.

The benzoylacetones and dibenzoylmethanates are considerably more stable with respect to hydrolysis than the analogous acetylacetones,³ both in the solid

TABLE II
X-RAY POWDER DIFFRACTION DATA

Ti(bzac) ₂ F ₂ ^a	Ti(bzac) ₂ Cl ₂ ^b	Ti(bzac) ₂ Br ₂ ^b	Ti(bzbx) ₂ F ₂ ^a	Ti(bzbx) ₂ Cl ₂ ^b	Ti(bzbx) ₂ Br ₂ ^c
...	10.13 (3)	...	14.55 (4)
9.36 ^d (7) ^e	9.38 (3)	9.52 (5)	...	10.95 (3)	...
7.45 (5)	7.69 (2)	7.71 (10)	...	9.55 (10)	9.56 (8)
...	7.33 (10)	7.32 (10)	8.87 (10)	8.64 (3)	8.80 (3)
6.78 (5)	7.77 (5)	...	8.13 (3)
6.36 (10)	6.57 (9)	6.55 (8)	...	7.58 (1)	...
...	6.05 (3)	...	6.80 (3)	6.88 (9)	6.93 (5)
5.51 (0.5)	6.35 (4)	6.46 (4)
5.17 (2)	5.21 (2)	5.33 (3)	...	5.89 (1)	6.05 (4)
4.76 (7)	4.86 (4)	4.84 (5)	5.59 (3)	...	5.64 (1)
4.59 (9)	4.70 (3)	4.70 (5)	5.28 (10)
4.36 (4)	4.44 (3)	4.47 (5)	5.00 (4)	5.04 (9)	5.09 (10)
4.03 (1)	4.07 (5)	4.11 (3)	...	4.80 (4)	4.83 (3)
3.87 (2)	3.93 (3)	3.96 (3)	4.63 (4)	4.56 (4)	4.63 (2)
...	3.84 (3)	...	4.42 (6)	...	4.43 (1)
3.61 (3)	...	3.74 (4)	4.16 (5)	4.21 (8)	4.26 (10)
...	3.50 (4)	3.55 (4)	...	4.04 (3)	4.09 (5)
3.39 (6)	3.39 (8)	3.41 (7)	3.90 (3)	3.86 (1)	3.89 (3)
...	...	3.28 (0.5)	...	3.73 (1)	3.74 (3)
3.17 (2)	3.13 (4)	3.17 (3)	3.55 (4)	3.52 (3)	3.58 (1)
3.06 (3)	...	3.07 (1)	3.38 (6)	3.38 (3)	3.39 (4)
2.96 (2)	2.99 (5)	3.00 (3)	3.28 (0.5)	...	3.31 (4)
...	2.82 (2)	2.87 (2)	...	3.13 (3)	3.17 (3)
2.75 (0.5)	...	2.79 (1)	3.05 (2)	3.04 (3)	3.07 (7)
2.60 (2)	2.65 (1)	2.69 (1)	2.93 (2)	...	2.96 (3)
...	2.56 (4)	2.58 (5)	2.80 (2)	2.81 (1)	2.84 (2)
...	...	2.54 (1)	...	2.75 (1)	2.75 (3)
2.47 (0.5)	...	2.50 (1)	2.63 (2)	...	2.67 (1)
2.40 (2)	...	2.44 (2)	2.53 (2)	...	2.57 (3)
2.36 (2)	2.45 (1)	2.49 (2)	2.47 (1)
2.29 (1)	2.32 (5)	2.34 (5)	2.34 (1)	2.37 (1)	2.41 (3)
...	...	2.28 (1)	2.27 (1)	2.32 (1)	2.33 (3)
2.20 (2)	2.21 (1)	2.21 (1)	2.21 (2)	2.25 (1)	2.25 (1)
...	2.13 (2)	2.13 (1)	...	2.19 (2)	2.20 (3)
2.07 (0.5)	2.07 (1)	2.09 (2)	2.11 (1)	2.14 (2)	2.14 (1)
...	...	2.06 (1)	2.06 (1)	2.06 (1)	2.07 (2)
2.01 (3)	2.01 (1)	1.996 (2)	...	2.04 (1)	...
1.939 (1)	1.969 (2)	...	1.985 (1)	...	2.01 (1)
1.912 (1)	1.903 (2)	1.917 (2)	1.941 (1)	...	1.959 (1)
1.844 (0.5)	...	1.866 (1)
1.806 (1)
...	...	1.710 (1)

^a Samples recrystallized from dichloromethane-hexane and benzene-hexane gave the same powder pattern. ^b Recrystallized from benzene-hexane. ^c Recrystallized from dichloromethane-hexane. ^d d_{hkl} , Å. ^e Visually estimated relative intensities.

state and in solution. In solution Ti(bzbx)₂X₂ appears to hydrolyze more rapidly than Ti(bzac)₂X₂. It is interesting that hydrolytic stability is not simply related to the number of phenyl groups, but rather increases in the order Ti(acac)₂X₂ < Ti(bzbx)₂X₂ < Ti(bzac)₂X₂. For complexes having the same diketonate ligand, resistance to hydrolysis increases in the order X = Br < Cl < F.

Microscopy (Table I) and X-ray powder patterns (Table II) indicate that Ti(bzac)₂Cl₂ and Ti(bzac)₂Br₂ are definitely isomorphous. The dibenzoylmethanates, Ti(bzbx)₂Cl₂ and Ti(bzbx)₂Br₂, are also isomorphous. The fluorides do not appear to be isomorphous with the corresponding chlorides and bromides, although it is somewhat difficult to draw a definite conclusion for Ti(bzac)₂F₂, the powder pattern of which is quite similar to those of Ti(bzac)₂Cl₂ and Ti(bzac)₂Br₂.

Molecular weight and conductance data in the ionizing solvent nitrobenzene are presented in Table III. These data show that all of the complexes behave as

TABLE III
MOLECULAR WEIGHT AND CONDUCTANCE DATA

Compd	Mol wt ^a		Molar conductance ^b		
	Calcd	Found	Concn, M × 10 ²	Concn, M × 10 ³	Δ_M , ohm ⁻¹ cm ² mole ⁻¹
Ti(bzac) ₂ F ₂	408	393 ^c	3.68	1.7	0.11
Ti(bzac) ₂ Cl ₂	441	440 ^d	1.56	1.1	0.30 ^e
Ti(bzac) ₂ Br ₂	530	559	0.839	2.1	0.44
Ti(bzbx) ₂ F ₂	532	534	4.00	1.6	0.08
Ti(bzbx) ₂ Cl ₂	564	537 ^f	1.01	1.4	0.14 ^g
Ti(bzbx) ₂ Br ₂	654	627	1.03	2.6	0.41

^a Determined cryoscopically in nitrobenzene. ^b In nitrobenzene. ^c Lit.,⁵ 216 in ethanol. ^d Lit.,⁷ 395. ^e Lit.,⁷ 2.20 in nitromethane. ^f Lit.,⁷ 580. ^g Lit.,⁷ 1.4 in nitromethane.

monomeric nonelectrolytes in nitrobenzene, although Ti(bzac)₂F₂ is apparently highly dissociated in ethanol.⁵ The conductance data indicate that the apparent degree of dissociation is small (0.3–1.5%, assuming $\Lambda_0 \approx 30$ ohm⁻¹ cm² mole⁻¹ for a 1:1 electrolyte in nitro-

benzene⁷). The degree of dissociation increases as the halogen is varied in the order $\text{Br} > \text{Cl} > \text{F}$.⁹ This trend suggests that the source of conductance is halide dissociation rather than dissociation of a diketonate ligand since the variation in Λ_M is in accord with qualitative estimates for relative Ti-X bond energies.¹⁰ Halide dissociation is also supported by the fact that the dialkoxides $\text{Ti}(\text{bzac})_2(\text{OC}_2\text{H}_5)_2$ and $\text{Ti}(\text{bzbz})_2(\text{OC}_2\text{H}_5)_2$ give very low conductances; Λ_M is $< 0.003 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for $10^{-2} M$ nitrobenzene solutions.

Infrared spectra of the $\text{Ti}(\text{dik})_2\text{X}_2$ complexes show no bands in the carbonyl region above 1600 cm^{-1} . Therefore, all carbonyl groups must be coordinated, and titanium must exhibit coordination number six.

Stereochemistry. Benzoylacetates.—Figure 1 shows the possible octahedral configurations for an $\text{M}(\text{bzac})_2\text{X}_2$ complex. Because the diketonate ligand is unsymmetrical, there are five possible isomers. Three of these have halogen atoms in *cis* positions; two have halogens in *trans* positions. We shall refer to the isomers by three *cis* or *trans* prefixes which specify first the relative position of the halogens, then the relative orientation of the benzoyl groups, and finally the relative orientation of the acetyl ends of the benzoylacetate ligands. Thus, the first isomer in the figure is designated the *cis,cis,cis* isomer.

The stereochemistry of the complexes will be inferred from nmr spectra. The *cis,cis,cis* isomer (point group C_1) has no symmetry and, therefore, may give rise to two methyl, two phenyl, and two ring proton resonances. Fluorine nmr spectra of *cis,cis,cis*- $\text{Ti}(\text{bzac})_2\text{F}_2$ should show two nonequivalent fluorine atoms. The other four isomers, *cis,cis,trans* (point group C_2), *cis,trans,cis* (C_2), *trans,cis,cis* (C_{2v}), and *trans,trans,trans* (C_{2h}), all possess at least a twofold axis; these isomers, as Figure 1 indicates, should give a single resonance for each type of group.

Variable-temperature fluorine nmr spectra of $\text{Ti}(\text{bzac})_2\text{F}_2$ are reproduced in Figure 2. Above -11° , a single line is observed (line width: 5 cps at 70°) which broadens with decreasing temperature. Below -46° , six lines are observed; these sharpen as temperature decreases. The positions at -85° of the five lines at higher field relative to the lowest field line are 0.73, 0.97, 2.69, 3.37, and 4.10 ppm. Lines 1, 2, 5, and 6 comprise an AB pattern due to the two nonequivalent fluorine atoms of the *cis,cis,cis* isomer. Lines 1 and 2 and lines 5 and 6 are equally spaced, and these lines exhibit the expected¹² relative intensities. The chemical

(9) Observed values of the molar conductance Λ_M for the chlorides and bromides increased by 10–20% during the first three hours after preparation of solutions. The time dependence is probably due to a bit of hydrolysis; however, the resulting uncertainty in the Λ_M values is generally small compared with differences among the Λ_M values.

(10) Ti-X bond energies for $\text{Ti}(\text{dik})_2\text{X}_2$ complexes (dik = diketonate ligand) are unknown; however, the Ti-X bond in the titanium tetrahalides becomes progressively weaker as the halogen varies from fluorine to bromine. Mean thermochemical bond energies (kcal/mole) for the tetrahalides were computed from enthalpy data¹¹ to be 139.7 (Ti-F), 102.6 (Ti-Cl), and 87.8 (Ti-Br).

(11) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1960.

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 119–122.

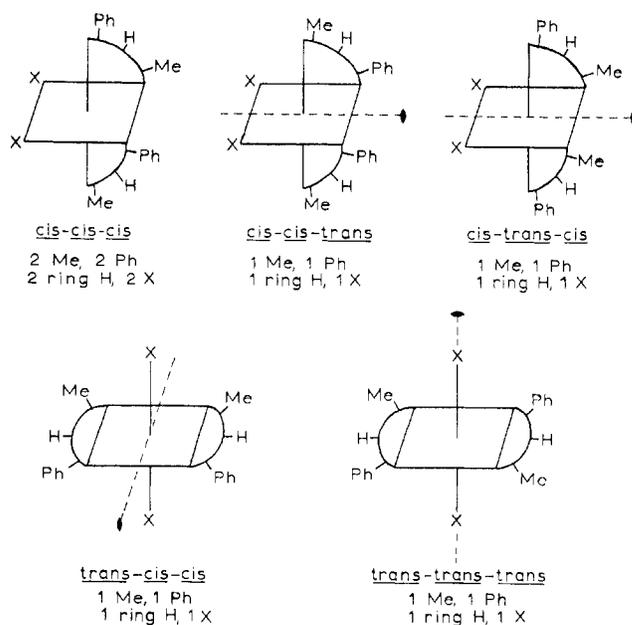


Figure 1.—Possible isomers for $\text{M}(\text{bzac})_2\text{X}_2$ complexes.

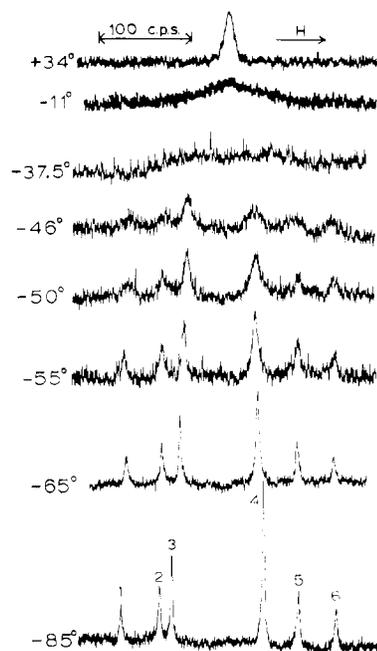


Figure 2.—Fluorine nmr spectra of $\text{Ti}(\text{bzac})_2\text{F}_2$ in dichloromethane solution, 10 g/100 ml.

shift between the two nonequivalent fluorine atoms at -85° was calculated¹² to be 3.30 ppm. The spin-spin coupling constant is 40.8 ± 0.5 cps, a value similar to those reported by Ragsdale and co-workers¹³ for *cis* octahedral adducts of titanium(IV) fluoride with organic bases. Lines 3 and 4 must arise from two of the other isomers. Since the *cis,cis,cis* isomer is definitely present and since the corresponding $\text{Ti}(\text{acac})_2\text{X}_2$ complexes exist exclusively in the *cis* configuration in dichloromethane solution,³ it is most reasonable to assign lines 3 and 4 to the other two isomers which have halogen atoms in *cis* positions, *i.e.*, *cis,cis,trans* and *cis,trans,cis*. The line broadening is attributed to an ex-

(13) R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963); D. S. Dyer and R. O. Ragsdale, *ibid.*, **6**, 8 (1967).

change process which rapidly exchanges fluorine atoms between the four nonequivalent sites of the three *cis*-difluoro isomers.

The fluorine spectra indicate that the relative equilibrium concentrations are close to the statistical values of 0.50 (*cis,cis,cis*) and 0.25 (*cis,cis,trans* and *cis,trans,-cis*). Assuming that the entropy change for conversion of the *cis,cis,trans* and *cis,trans,cis* isomers to the *cis,cis,cis* isomer is $R \ln 2$, the isomer responsible for line 4 is calculated to be more stable than the other two isomers by *ca.* 0.2 kcal/mole.

The *cis*-difluoro structures for $\text{Ti}(\text{bzac})_2\text{F}_2$ are confirmed by variable-temperature proton spectra. At room temperature (37°) the proton spectrum consists of single, sharp methyl and ring proton resonances (line widths 0.5–0.6 cps) and, in the region -7.3 to -8.1 ppm, relative to an internal reference of tetramethylsilane, complex multiplets of sharp lines due to the phenyl protons. Below room temperature, line broadening is observed. The methyl resonance (Figure 3) begins to split into two lines at *ca.* -40° , and at *ca.* -64° each of these lines splits again to give a total of four lines. The four lines are assigned to the four nonequivalent methyl groups of the three isomers which have fluorine atoms in *cis* positions. The line broadening is due to a rapid isomerization process which exchanges methyl groups between the four nonequivalent environments.

The ring proton resonance also broadens with decreasing temperature; however, only one line is observed even in low-temperature spectra. Line widths at half maximum amplitude are 0.50 cps (37°), 0.85 cps (-43.5°), and 1.7 cps (-64.5°). Although symmetry demands four nonequivalent ring protons, the ring proton environments in the three *cis*-difluoro isomers are very similar. Apparently the chemical shifts are not large enough to allow resolution of the CH resonances at accessible temperatures.

Rapid isomerization also results in exchange of nonequivalent phenyl groups. Broadening of the phenyl multiplets with decreasing temperature obscures the fine structure caused by spin coupling of *ortho*, *meta*, and *para* protons. At -47° all fine structure is lost; two broad lines remain, separated by 0.36 ppm. The lower field line (line width 21 cps, relative intensity 2) is assigned to the *ortho* protons; the higher field line (line width 10 cps, relative intensity 3) is assigned to the *meta* and *para* protons. Below -55° , where the exchange process is slower, fine structure begins to appear again.

Variable-temperature proton spectra of $\text{Ti}(\text{bzac})_2\text{Cl}_2$ and $\text{Ti}(\text{bzac})_2\text{Br}_2$ exhibit most of the same features found for $\text{Ti}(\text{bzac})_2\text{F}_2$. The most significant difference is that low-temperature spectra of the methyl region (*cf.* Figure 4) show resolution of only three resonance lines. For the dichloride, the methyl resonance splits below -24° into two lines of approximately equal intensity. Below -38.5° the lower field line splits further into two equally intense lines. The corresponding coalescence temperatures for the dibromide are -31.5 and -53° .

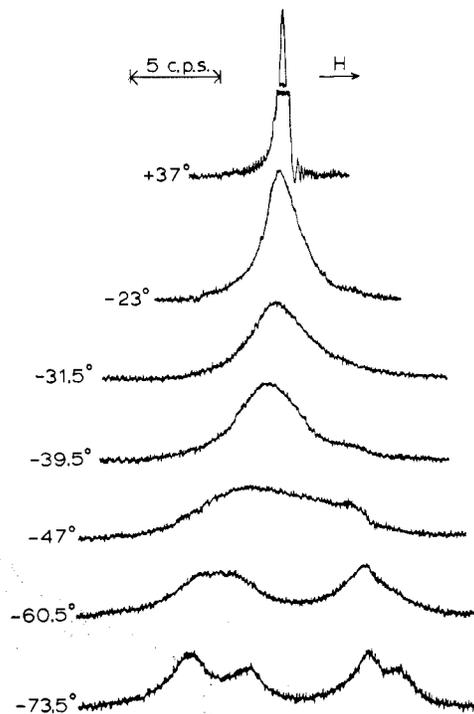


Figure 3.—Methyl region of proton nmr spectra of $\text{Ti}(\text{bzac})_2\text{F}_2$ in dichloromethane solution, 10 g/100 ml.

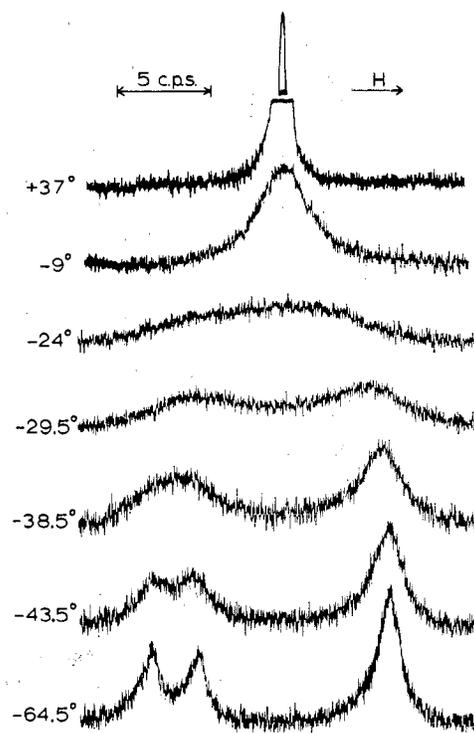


Figure 4.—Methyl region of proton nmr spectra of $\text{Ti}(\text{bzac})_2\text{Cl}_2$ in dichloromethane solution, 5 g/100 ml.

If the highest field resonance is due to a superposition of two lines having nearly the same chemical shift, then the spectra consist of four methyl resonances of approximately equal intensity. Such spectra are consistent with a random statistical equilibrium mixture of the three isomers which have halogen atoms in *cis* positions.

Recently, in a related paper¹⁴ the nmr spectrum of

(14) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc., Sect. A*, 1749 (1966).

Ge(bzac)₂Cl₂ was reported and interpreted in terms of a mixture of the three *cis*-dichloro isomers contaminated with a small amount of free ligand. The nmr spectra of Ge(bzac)₂Cl₂, Ge(acac)₂Cl₂, and Sn(acac)₂X₂ show nonequivalent methyl groups at room temperature.¹⁴ Apparently, chelate rings in the germanium and tin compounds undergo configurational changes more slowly than in the corresponding titanium compounds.

Dibenzoylmethanates.—Room-temperature nmr spectra of Ti(bzbz)₂X₂ complexes show a single, sharp, ring proton resonance and a series of sharp lines due to the phenyl protons. With decreasing temperature the phenyl resonance broadens until only two broad lines remain at *ca.* -20 to -40°. Below these temperatures the phenyl region sharpens again, showing the effects of spin-spin splitting. The low-temperature spectra extend over a somewhat larger frequency region than the room-temperature spectra, and they appear to consist of a superposition of the two phenyl resonances expected for the *cis* geometrical isomer. The line broadening (not expected for the *trans* isomer) is accounted for by exchange of phenyl groups between the two nonequivalent environments of the *cis* isomer.

Chemical Shifts.—Protons and fluorine chemical shifts at room temperature are presented in Table IV.

TABLE IV

CHEMICAL SHIFT DATA^a

Compd	Concn ^b	CH	CH ₃	F
H(bzac)				
(enol form)	10	-6.19 ^c	-2.16 ^c	...
Ti(bzac) ₂ F ₂	10	-6.58	-2.24	-232.8 ^d
Ti(bzac) ₂ Cl ₂	4	-6.69	-2.29	...
Ti(bzac) ₂ Br ₂	1	-6.76	-2.30	...
H(bzbz)				
(enol form)	10	-6.87
Ti(bzbz) ₂ F ₂	8	-7.25	...	-231.8
Ti(bzbz) ₂ Cl ₂	4	-7.35
Ti(bzbz) ₂ Br ₂	1	-7.41

^a In dichloromethane. Temperature is 37° (H¹) and 34° (F¹⁹). ^b Grams/100 ml solvent. ^c Ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume). ^d Ppm (±0.4) relative to an internal reference of CCl₄ (5% by volume).

Values for the enol form of the free diketones are included for comparison. The CH resonances of Ti(bzac)₂X₂ are shifted to lower field by 0.4–0.6 ppm relative to the CH resonances of metal tris benzoylacetates¹⁵ and the enol form of benzoylacetone; in contrast, the methyl resonances are shifted only slightly to lower field. The CH resonances of Ti(bzbz)₂X₂ exhibit analogous downfield shifts of 0.4–0.5 ppm relative to the CH resonances of Al(bzbz)₃¹⁴ and the enol form of H(bzbz). These downfield shifts are presumably a consequence of the intramolecular electric field of the highly dipolar *cis* isomers;¹⁴ they provide additional, confirmatory evidence for the *cis* configuration. It is interesting to note that downfield shifts of the CH resonance increase as X varies in the order F < Cl < Br. A possibly related observation is that chemical shifts

(15) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).

between nonequivalent methyl groups in low-temperature M(bzac)₂X₂ spectra increase as X varies in the same order (see Table V). It would be desirable to have some dipole moment data before trying to interpret these trends.

TABLE V

LOW-TEMPERATURE CHEMICAL SHIFTS FOR M(bzac)₂X₂ METHYL RESONANCES^a

Compd	Temp, °C	Line 2	Line 3	Line 4
Ti(bzac) ₂ F ₂	-97	0.064	0.167	0.195
Ti(bzac) ₂ Cl ₂	-64.5	0.041	0.212	0.212
Ti(bzac) ₂ Br ₂	-70	0.034	0.245	0.245

^a Chemical shifts of the resonances which occur at higher field (lines 2, 3, and 4) are reported in ppm relative to the methyl resonance which occurs at lowest field. Solute concentrations are the same as in Table IV. Solvent is dichloromethane. Shifts for Ti(bzac)₂F₂ at -97° were obtained with a Varian HR-60 spectrometer.

The substitution of phenyl groups for methyl groups also results in down-field shifts. Thus, the CH resonances of Ti(bzac)₂X₂ (Table IV) are shifted to lower field by 0.70 ± 0.02 ppm relative to the CH resonances of the corresponding Ti(acac)₂X₂ complexes.³ The CH signals of Ti(bzbz)₂X₂ are shifted by an additional 0.66 ± 0.01 ppm. The downfield shift in the methyl resonances on going from Ti(acac)₂X₂³ to Ti(bzac)₂X₂ is only 0.16 ± 0.01 ppm. These shifts may be due in part to inductive effects; however, comparison of chemical shifts of metal benzoylacetates¹⁵ and metal trifluoroacetylacetates¹⁶ suggests the importance of the magnetic anisotropy of the phenyl group. Recent X-ray studies of *cis*-VO(bzac)₂¹⁷ and *trans*-Cu(bzac)₂¹⁸ indicate that the phenyl and metal diketone rings are nearly coplanar. Assuming exact coplanarity in solution, we have computed the expected downfield shifts for the CH and methyl protons of a benzoylacetate ligand due to ring currents in the phenyl ring to be 0.53 and 0.10 ppm, respectively.^{19–21} Comparison with the observed shifts of 0.70 and 0.16 ppm for the Ti(bzac)₂X₂ complexes indicates that the observed downfield shifts are caused primarily by a ring-current effect. Smith and Wilkins¹⁴ have noted similar downfield shifts for aluminum and boron complexes. For example, they report a shift in the CH resonance of 0.57 ppm per phenyl ring for the series of compounds B(acac)F₂, B(bzac)F₂, B(bzbz)F₂.

(16) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).(17) P. K. Hon, R. L. Belford, and C. E. Pfluger, *J. Chem. Phys.*, **43**, 1823 (1965).(18) P. K. Hon, C. E. Pfluger, and R. L. Belford, *Inorg. Chem.*, **5**, 516 (1966).(19) We assume that the distance from the center of the phenyl ring to the CH proton is 3.70 Å and that the corresponding distance to the methyl protons is 6.8 Å. These values are based on the experimental bond angles and C–C distances in *trans*-Cu(bzac)₂.¹⁸ The shift of the CH proton was obtained from Johnson-Bovey tables;²⁰ the shift of the methyl protons was calculated using the dipolar approximation of McConnell.²¹ If the phenyl rings are twisted with respect to the metal diketone rings by 14°, as in crystalline *trans*-Cu(bzac)₂, the expected downfield shifts for the CH and methyl protons are reduced slightly to 0.45 and 0.08 ppm, respectively.(20) "Johnson-Bovey Tables," reproduced in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Inc., New York, N. Y., 1965, Appendix B; cf. C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).(21) H. M. McConnell, *ibid.*, **27**, 226 (1957).

Kinetics and Mechanism of Exchange Processes.—

It has been suggested throughout this paper that observed line broadening is due to processes which exchange nuclei between the nonequivalent sites of the various isomers. These processes may or may not involve racemization of optical isomers. In the case of the benzoylacetate complexes, the exchange processes must involve geometrical isomerization.

For the acetylacetonates, $\text{Ti}(\text{acac})_2\text{X}_2$, where there are only two nonequivalent methyl groups and one first-order rate constant for exchange, spectra have been analyzed in detail to obtain rate constants and activation energies and entropies.³ In the case of the $\text{Ti}(\text{bzac})_2\text{X}_2$ complexes, Figures 2–4 show that resonance lines due to nonequivalent nuclei simultaneously broaden and then merge into a single line. These spectra imply simultaneous exchange of identical nuclei between all four environments of the three *cis*-dihalo isomers. Three, independent, first-order rate constants are needed to describe the four-site exchange process. Thus, analysis of the $\text{Ti}(\text{bzac})_2\text{X}_2$ spectra is much more complicated than $\text{Ti}(\text{acac})_2\text{X}_2$ spectra. To make matters worse, the relaxation times appear to be temperature dependent, as in the case of the acetylacetonates. Because of these complications, we have not attempted to extract accurate, quantitative rate constants from the $\text{Ti}(\text{bzac})_2\text{X}_2$ spectra.

It is possible, however, to make estimates of approximate rate constants at the temperatures of coalescence of the methyl resonances. Such estimates are useful indications of the relative lability of $\text{Ti}(\text{bzac})_2\text{X}_2$ and $\text{Ti}(\text{acac})_2\text{X}_2$ and also of the dependence of lability on the nature of the halogen. Figures 3 and 4 and Table V suggest that the four nonequivalent methyl groups may be classified into a set of two which give rather closely spaced resonances at lower field and a set of two which give closely spaced resonances at higher field. In fact, for the dichloride and dibromide, the higher field resonances are not resolved. For purposes of estimating rate constants, we approximate the four-site exchange process by a two-site process, the chemical shift $\delta\nu$ between the two sites being the chemical shift between the centers of gravity of the higher and lower field doublets in the low-temperature spectra. Since the two sites are approximately equally populated, the first-order rate constant k at the coalescence temperature T_c for exchange of methyl groups between the two sites is given by $\pi\delta\nu/\sqrt{2}$.²² The coalescence temperature is taken as the temperature at which the entire spectrum just collapses into a single broad line.

Approximate rate constants obtained by this procedure are listed in Table VI along with values for $\delta\nu$ and T_c . Listed in the fifth column of the table are values of k for exchange of methyl groups in the $\text{Ti}(\text{acac})_2\text{X}_2$ complexes.³ The latter values are quoted at T_c for the corresponding benzoylacetates. Comparison of the fourth and fifth columns indicates that lability of the acetylacetonates and benzoylacetates

TABLE VI
APPROXIMATE RATE CONSTANTS FOR EXCHANGE OF
METHYL GROUPS FOR $\text{Ti}(\text{bzac})_2\text{X}_2$ COMPLEXES

X	$\delta\nu$, cps ^a	T_c , °C	k , sec ⁻¹	k , sec ⁻¹	k , sec ⁻¹
			(at T_c) Ti- (bzac) ₂ X ₂	(at T_c) Ti- (acac) ₂ X ₂	(at -31.5°) Ti- (bzac) ₂ X ₂
F	9.0	-37 ± 3	20	91	35
Cl	11.5	-24 ± 2	25	16	12
Br	13.7	-31.5 ± 3	30	22	30

^a Frequency separation between centers of gravity of higher and lower field doublets in absence of exchange. Calculated from data in Table V.

is quite comparable. In the last column of Table VI, we have listed values of k for $\text{Ti}(\text{bzac})_2\text{X}_2$ extrapolated to a common temperature, -31.5°, T_c for $\text{Ti}(\text{bzac})_2\text{Br}_2$. These values were calculated assuming that the activation energies for $\text{Ti}(\text{bzac})_2\text{X}_2$ are the same as those for the corresponding acetylacetonates [11.6 kcal/mole ($X = \text{F}$); 11.2 kcal/mole ($X = \text{Cl}$)].³ The rate of methyl group exchange for $\text{Ti}(\text{bzac})_2\text{X}_2$ increases as X varies in the order $\text{Cl} < \text{Br} \sim \text{F}$. For the acetylacetonates, the exchange rates increase in the order $\text{X} = \text{Cl} < \text{Br} < \text{F}$.

An attractive mechanism for exchange of nonequivalent nuclei involves twisting the octahedral coordination geometry so as to generate a trigonal prismatic transition state. This mechanism requires no rupture of metal-ligand bonds.

Figure 5 shows a *cis*- $\text{M}(\text{dik})_2\text{X}_2$ complex viewed along one of the fourfold axes of the octahedron. The threefold axes of the octahedron, perpendicular to the equilateral triangular faces, are numbered 1–4 for later reference. The mechanisms we shall examine involve twisting three of the donor atoms (one octahedral face) through an angle of 120° with respect to the other three donor atoms (the opposite octahedral face). The twist may be carried out about any one of the four C_3 axes of Figure 5.

Figure 6 shows how twisting about C_3 axes 1 and 2 (of Figure 5) leads to exchange of nonequivalent ring sub-

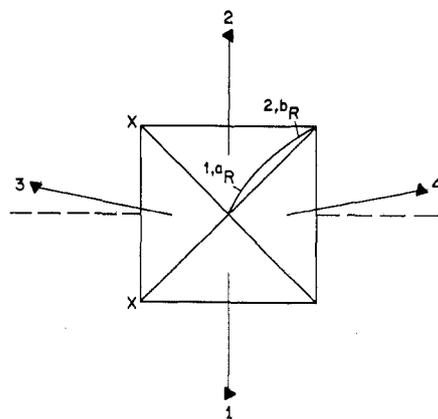


Figure 5.—View of a *cis*- $\text{M}(\text{dik})_2\text{X}_2$ complex along a fourfold axis of the octahedron. The symbol R represents substituents on the diketone ligand, e.g., CH_3 or C_6H_5 . The numerical superscripts label the R groups; the letter superscripts label nonequivalent environments.

(22) Reference 12, p 223; H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

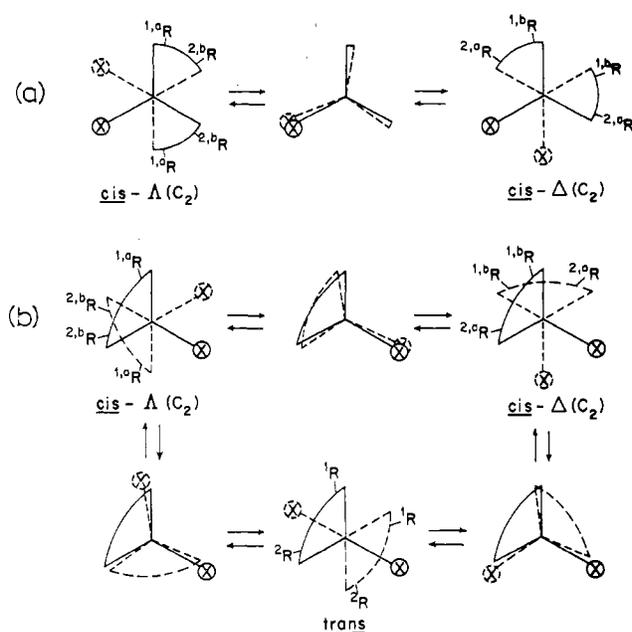


Figure 6.—Twist mechanisms for a *cis*- $M(\text{dik})_2X_2$ complex having symmetrical diketonate ligands. In (a) the twist is carried out about C_3 axis 1 of Figure 5; in (b), about C_3 axis 2 of Figure 5. Numbers label R groups; letters label environments.

stituents in *cis*- $M(\text{dik})_2X_2$ complexes having symmetrical diketonate ligands, e.g., $\text{Ti}(\text{acac})_2X_2$ and $\text{Ti}(\text{bzbz})_2X_2$. The complexes are viewed along the C_3 axis about which the twist is performed. Solid lines represent metal–ligand bonds which point above the plane of the paper; dotted lines, metal–ligand bonds which extend below the plane of the paper. The lower face of the octahedron (dotted bonds) is twisted through 120° with respect to the upper face (solid bonds) which is thought of as remaining stationary. The trigonal prismatic transition state is reached after a twist of 60° . The twist about C_3 axis 1 [Figure 6(a)] resembles the racemization mechanism for tris-chelate complexes proposed by Bailar²³ and the corresponding rigid-ring analog recently described by Springer and Sievers.^{24–28} Twisting about C_3 axis 2 [Figure 6(b)] generates a motion similar to the racemization mechanism of Ray and Dutt.²⁹ The two twists give transition states which differ in the orientation of the chelate rings about the trigonal prism; however, both transition states have C_{2v} symmetry. Both twists interconvert the $\Lambda(C_2)$ and $\Delta(C_2)$ enantiomers,³⁰ and both exchange ring substitu-

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

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

(25) In the present paper, we make no distinction between twists which maintain fixed bond angles within the chelate ring and those which allow changes in the intraring donor–metal–donor bond angles. In general, these angles may undergo modest adjustments so as to minimize the free energy of activation. However, the kind of experimental data presently available, i.e., coalescence of nmr lines^{26,27} and studies of the fate of a particular isomer in isomerization reactions,^{26,28} provide no information about changes in intraring bond angles. The experimental data can be compared with predictions based on the general type of twisting motion and the symmetry of the transition state. Therefore, we restrict our attention to the latter aspects of the twisting process.

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

(27) R. A. Palmer, R. C. Fay, and T. S. Piper, *ibid.*, **3**, 875 (1964).

(28) R. G. Denning and T. S. Piper, *ibid.*, **5**, 1056 (1966).

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

(30) Absolute configurations of the optical isomers are specified using the notation of J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

ents, 1R and 2R , between the two nonequivalent environments, a and b.

It is interesting to note that twisting about C_3 axis 2 can be carried through a full cycle since the bidentate ligands do not span the upper and lower octahedral faces. Figure 6(b) shows how twisting about C_3 axis 2 provides a path for conversion of *cis* enantiomers to the *trans* isomer; this is the same path proposed by Bailar for *cis*–*trans* isomerization of complexes of the type $[\text{Co}(\text{en})_2XY]^{n+}$.²³

Although the mechanisms of Figure 6 are able to account for exchange of nonequivalent ring substituents in symmetrical diketonate complexes, it is unlikely that either of these twists is the correct mechanism since neither is able to account for the variable-temperature nmr spectra of the unsymmetrical diketonates, $\text{Ti}(\text{bzac})_2X_2$. Figure 7 shows the effect of a twist about C_3 axis 1 (of Figure 5) on the three isomers of $M(\text{bzac})_2X_2$ which have halogen atoms in *cis* positions. Figure 8 shows the effect of a twist about C_3 axis 2 (of Figure 5). Both twists give pseudo- C_{2v} transition states, and both reverse the chirality of the chelate rings. Both interconvert the *cis,cis,trans* and *cis,trans,cis* enantiomers of opposite chirality, and both interconvert the two *cis,cis,cis* enantiomers. Interconversion of the *cis,cis,cis* enantiomers is accompanied by exchange of methyl groups between the two nonequivalent environments of the *cis,cis,cis* isomer. Isomerization from *cis,cis,trans* to *cis,trans,cis* exchanges methyl groups between the two environments characteristic of these two isomers. Therefore, the twist mechanisms of Figures 7 and 8 predict collapse of two of the methyl resonances into one line and collapse of the other two methyl signals into another line. Coalescence of all four resonances is not expected since these mechanisms provide no path for exchange of methyl groups between all four nonequivalent environments. The nmr spectra (Figures 3 and 4), which show simultaneous broadening and coalescence of all four methyl resonances, cannot be accounted for in terms of twists proceeding through pseudo- C_{2v} transition states.

Further evidence for rejecting the mechanisms of Figures 7 and 8 is found in the fluorine spectra of $\text{Ti}(\text{bzac})_2F_2$. Figure 2 reveals simultaneous broadening of all six resonance lines and collapse of all six lines into a single resonance. These spectra imply exchange of fluorine atoms between all four nonequivalent sites of the three *cis*-difluoro isomers. The twist mechanism about C_3 axis 1 (Figure 7) predicts collapse of the two resonances due to the *cis,cis,trans* and *cis,trans,cis* isomers, but no collapse of the AB pattern due to the *cis,cis,cis* isomer. The twist about C_3 axis 2 (Figure 8) predicts coalescence of the *cis,cis,trans* and *cis,trans,cis* signals and collapse of the *cis,cis,cis* AB pattern to give a total of two lines in the high-temperature spectra.

Similarly, twists about C_3 axis 3 or 4 (of Figure 5), which proceed through pseudo- C_s transition states, provide a path for exchange of methyl groups and halogen atoms between some, but not all, of the four nonequivalent environments. Hence, exchange of nuclei

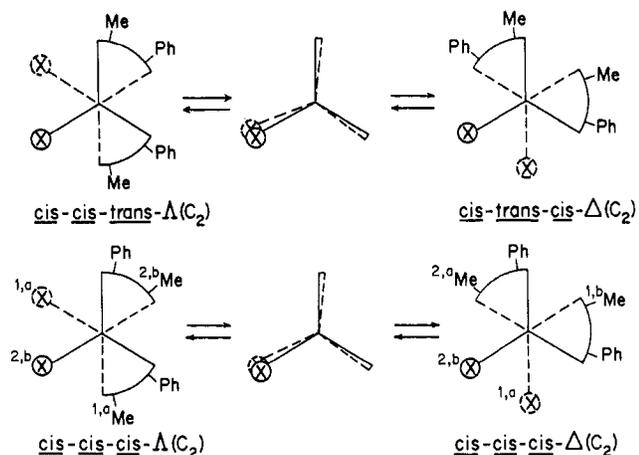


Figure 7.—Configurational changes for *cis*-dihalo $M(\text{bzac})_2X_2$ isomers produced by twisting about C_3 axis 1 of Figure 5. Numbers label nonequivalent methyl groups and halogen atoms; letters label nonequivalent environments.

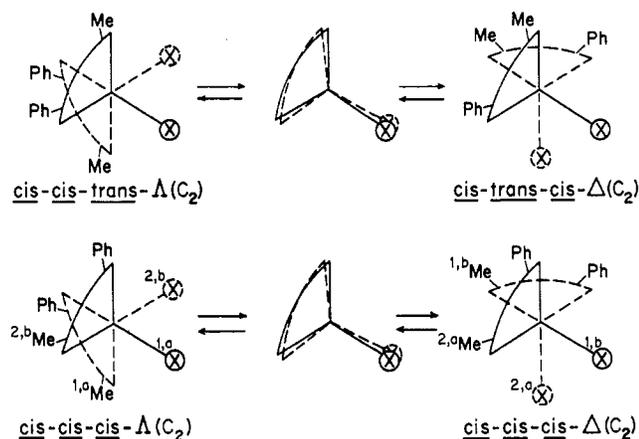


Figure 8.—Configurational changes for *cis*-dihalo $M(\text{bzac})_2X_2$ isomers produced by twisting about C_3 axis 2 of Figure 5. Numbers label nonequivalent methyl groups and halogen atoms; letters label nonequivalent environments.

between all four nonequivalent environments of *cis*- ML_2X_2 complexes (where L is an unsymmetrical bidentate ligand) cannot be achieved by twisting about *any one* of the four C_3 axes of the octahedron.

We must also consider, however, the possibility of stepwise twisting about different C_3 axes. Activation energies for twisting about C_3 axes 3 and 4 should be nearly identical since these axes are equivalent in the *cis,cis,trans* and *cis,trans,cis* isomers and nearly equivalent in the *cis,cis,cis* isomer owing to the C_2 or pseudo- C_2 axis which bisects the X-M-X angle (*cf.* Figure 5). Therefore, if a twist occurs about C_3 axis 3, it most likely also occurs about C_3 axis 4. Figure 9 shows how successive twists about C_3 axes 3 and 4 lead to exchange of methyl groups and halogen atoms between all four nonequivalent environments. In this figure the transition states have been omitted; however, the twists are carried out in the same manner as in previous figures; *viz.*, the

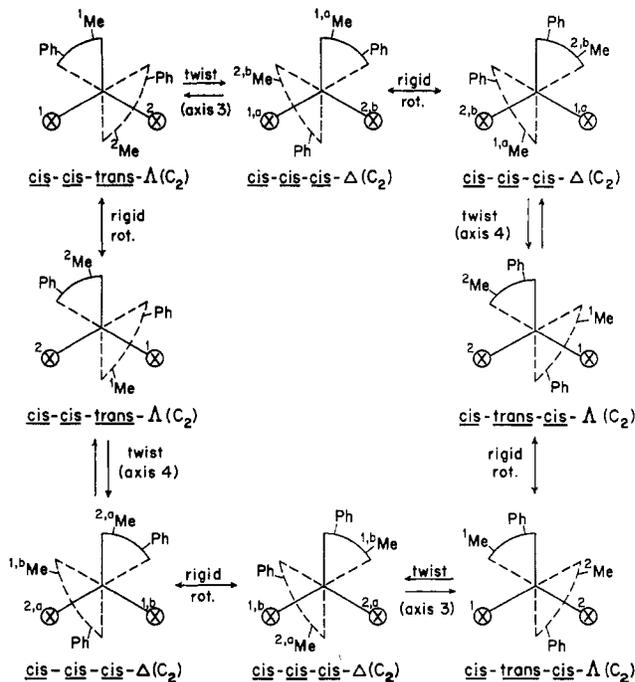


Figure 9.—Exchange of nuclei between all nonequivalent environments *via* successive twists about C_3 axes 3 and 4 of Figure 5. Numbers label methyl groups and halogen atoms; letters label nonequivalent environments.

bottom octahedral face is twisted, with respect to the top face, about the C_3 axis perpendicular to the plane of the paper. In order alternately to orient C_3 axes 3 and 4 perpendicular to the plane of the paper, each twist is followed by a 180° rigid rotation of the entire molecule about the C_2 or pseudo- C_2 axis.

The nmr results and mechanistic arguments presented herein allow the conclusion that rearrangements of $Ti(\text{dik})_2X_2$ complexes do not occur by twisting mechanisms about a single C_3 axis. However, because of the possibility of successive twists about different C_3 axes, a definite choice between twisting mechanisms and bond-rupture processes cannot be made on the basis of presently available data. Faller and Davison have suggested that well-resolved nmr spectra of complexes of the type $MYZ(\text{acac})_2$ would allow a choice between twist mechanisms and five-coordinate intermediates.³¹ Although spectra of $MYZ(\text{acac})_2$ would permit elimination of one-step twisting mechanisms about a single C_3 axis, in this case also, it is unfortunately true that multistep twists about different C_3 axes can give the same nmr coalescence behavior as bond-rupture processes.

Acknowledgments.—The support of this research by National Science Foundation Grant GP-5515 is gratefully acknowledged. N. S. wishes to thank the Woodrow Wilson Foundation (1964–1965), Cornell University (1965–1966), and the National Research Council of Canada (1966–1968) for fellowships.

(31) J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 182 (1967).