2118 J. Am. Chem. Soc. 1983, 105, 2118-2127

Nuclear Magnetic Resonance Studies of Inversion and Diketonate R-Group Exchange in Dialkoxybis(β-diketonato)titanium(IV) Complexes. Evidence for a Twist Mechanism

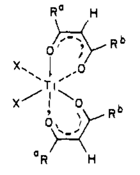
Robert C. Fay* and Alan F. Lindmark[1]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14853.

Received August 16, 1982

Abstract: Dialkoxybis(β-diketonato)titanium(IV) complexes, $Ti(dik)_2(OR)_2$, where dik = $CH_3COCHCOCH_3$ (acac) or $t\text{-}C_4H_9COCHCO\text{-}t\text{-}C_4H_9$ (dpm) and R = $CH_2C_6H_5$, $CH_2CH(CH_3)_2$, $CH(CH_3)_2$, or $C(CH_3)_2C_6H_5$, have been synthesized and characterized by chemical analysis, NMR and IR spectroscopy, and conductance measurements. Rates and activation parameters for inversion and diketonate R-group exchange in these complexes have been determined by ^1H NMR spectroscopy (total line-shape analysis). Inversion, probed by the diastereotopic groups in the alkoxide ligands, and exchange of diketonate methyl (or *tert*-butyl) groups occur at comparable rates by a common, intramolecular mechanism; $R_k = k_{inv}/k_{ex}$ decreases from $\sim$2.0 to $\sim$1.0 with increasing steric bulk of the alkoxide ligand. Activation parameters for the two processes are identical within experimental uncertainty. Permutational analysis indicates that the R_k values are consistent with a linear combination of NMR averaging sets A_5 and A_6. Certain intramolecular bond-rupture mechanisms can be ruled out as the sole rearrangement pathway on the basis of the R_k values. A dramatic decrease in rearrangement rate and increase in ΔH^* with increasing bulk of the OR group strongly suggest that these complexes rearrange by a twist mechanism. Supporting evidence includes (i) lack of solvent effects, (ii) negative values of ΔS^*, and (iii) lack of a correlation between rates and metal-diketonate bond strengths in $Ti(dik)_2(OR)_2$ and related complexes. The variation in R_k is attributed to a mixture of twists about the various octahedral C_3 axes, with the relative importance of the various twist transition states depending on steric effects.

The kinetics and mechanism of rearrangements of stereochemically nonrigid octahedral bis(chelate) complexes is a subject of considerable experimental[2] and theoretical[3] interest. Among the most thoroughly investigated compounds of this type are the bis(β-diketonato)titanium(IV) complexes, $Ti(dik)_2X_2$, where the monodentate X ligand is a halide,[4-15] pseudohalide,[9] or alkoxide.[8,13,14,16-23] All of these complexes exist in solution, exclusively, as the cis geometrical isomer **1**, except for $Ti(acac)_2I_2$,[7,24] which is found as an equilibrium mixture of both cis and trans isomers. NMR studies of *cis*-$Ti(dik)_2X_2$ complexes that contain diastereotopic groups[25] indicate that these complexes undergo (1) inversion of configuration and (2) exchange of diketonate R groups between the two inequivalent sites of the cis isomer (sites a and b in **1**). A simple and potentially fruitful approach[26] in mechanistic studies of *cis*-$Ti(dik)_2X_2$ complexes is to compare the rates of these two processes.



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We present herein a detailed account of our NMR studies of inversion and diketonate R-group exchange in the dialkoxybis(β-diketonato)titanium(IV) complexes, $Ti(dik)_2(OR)_2$, where dik = acac or dpm[24] and OR = $OCH_2C_6H_5$, $OCH_2CH(CH_3)_2$, $OCH(CH_3)_2$, or $OC(CH_3)_2C_6H_5$. The relative rates of inversion and R-group exchange and a dramatic decrease in these rates with increasing steric bulk of the alkoxide ligand strongly suggest that $Ti(dik)_2(OR)_2$ complexes rearrange by a twist mechanism. This result is in accord with an earlier study by Bradley and Holloway.[16] A preliminary report of our work has appeared,[19] and the results of a closely related study of diolatobis(acetylacetonato)titanium(IV) complexes have been published.[18]

Experimental Section

Reagents and General Techniques. Acetylacetone, bp 136-140 °C, and titanium tetrachloride (Matheson, Coleman and Bell), benzoylacetone (Eastman), and titanium(IV) benzyloxide (Alfa) were used as purchased

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(1) Present address: Department of Chemistry, Physics and Astronomy, Indiana University Northwest, Gary, IN 46408.

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(24) The following ligand abbreviations are used in this paper: acac, $CH_3COCHCOCH_3$; dpm, $t\text{-}C_4H_9COCHCO\text{-}t\text{-}C_4H_9$; bzac, $C_6H_5COCHCOCH_3$; bzbz, $C_6H_5COCHCOC_6H_5$; tfac, $CF_3COCHCOCH_3$; hfac, $CF_3COCHCOCF_3$; cat, dinegative anion of $o\text{-}C_6H_4(OH)_2$.

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without further purification. Dipivaloylmethane was prepared by the method of Man et al.[27] and purified by conversion to the copper chelate. Catechol (Matheson, Coleman and Bell) was purified by sublimation (100 °C (10^{-2} torr)). Isobutyl alcohol and α,α-dimethylbenzyl alcohol (Eastman) were dried and purified by distillation from calcium sulfate. Titanium(IV) isopropoxide (Alfa) was distilled (88–90 °C (10^{-2} torr)) shortly before use.

$[Ti(dik)_3][SbCl_6]$ (dik = acac, bzac, or bzbz[24]) were prepared by reaction of the appropriate $Ti(dik)_2Cl_2$ complex with $SbCl_5$ in glacial acetic acid.[28] $Ti(dik)_2Cl_2$ (dik = acac, bzac, bzbz, dpm, or hfac[24]) and $Ti(dik)_2(OCH_2CH_3)_2$ (dik = acac, tfac, or hfac) were synthesized by literature methods.[4,5,8,9]

Solvents were dried by refluxing for at least 24 h over calcium hydride or lithium aluminum hydride. Since the $Ti(dik)_2(OR)_2$ complexes are readily hydrolyzed, especially in solution, all syntheses and subsequent handling of compounds were carried out under anhydrous conditions in a dry nitrogen atmosphere.

Preparation of Titanium Alkoxides. The titanium(IV) alkoxides that were not commercially available, titanium(IV) isobutoxide and titanium(IV) α,α-dimethylbenzyloxide, were prepared by reaction of 4 mol of the appropriate alcohol with 1 mol of titanium(IV) isopropoxide. The reaction mixture was heated at 90 °C under a stream of dry nitrogen (for ~2 h) until no resonances due to titanium(IV) isopropoxide or isopropyl alcohol remained in the ^1H NMR spectrum. The resulting white solids were characerized by infrared and ^1H NMR spectra.

Bis(benzyloxy)bis(2,4-pentanedionato)titanium(IV). A mixture of acetylacetone (2.2 mL, 21.5 mmol) and titanium(IV) benzyloxide (5.1 g, 10.7 mmol) in 15 mL of dichloromethane was heated at 135 °C for 2 h under a stream of dry nitrogen and then in vacuo at 80 °C for ~48 h until the ^1H NMR spectrum of the product showed no trace of benzyl alcohol. A red oil (4.8 g, nearly quantitative yield) remained. All attempts to obtain a crystalline product failed. Vacuum distillation (~160 °C (10^{-2} torr)) decomposed the complex. Anal. Calcd for $Ti(C_5H_7O_2)_2(C_7H_7O)_2$: C, 62.61; H, 6.13; Ti, 10.40. Found: C, 61.05; H, 6.10; Ti, 11.15. An identical product was obtained from the reaction of 2 mol of benzyl alcohol with 1 mol of diisopropoxybis(2,4-pentanedionato)titanium(IV) in refluxing benzene.

Diisobutoxybis(2,4-pentanedionato)titanium(IV). A mixture of acetylacetone (3.2 mL, 31 mmol) and titanium(IV) isobutoxide (5.1 g, 15 mmol) in 20 mL of dichloromethane was heated at 110 °C for 1 h under a stream of dry nitrogen and then kept in vacuo overnight at room temperature to remove the isobutyl alcohol that had formed. The yield of red oil was quantitative (5.8 g). All attempts to obtain a crystalline product failed, and vacuum distillation (~160 °C (10^{-2} torr)) decomposed the complex. Anal. Calcd for $Ti(C_5H_7O_2)_2(C_4H_9O)_2$: C, 55.10; H, 8.22; Ti, 12.21. Found: C, 54.99; H, 8.11; Ti, 12.56.

Diisopropoxybis(2,4-pentanedionato)titanium(IV). A mixture of acetylacetone (8.9 mL, 88 mmol) and titanium(IV) isopropoxide (12.1 g, 43 mmol) in 50 mL of dichloromethane was heated at 100 °C for ~1 h under a stream of dry nitrogen and then kept in vacuo overnight at room temperature to remove all the isopropyl alcohol that had formed. The resulting dark red oil (15.0 g, nearly quantitative yield) was purified twice by dissolving the oil in a minimum amount of hexane and then cooling the solution in a liquid nitrogen bath until ~50% of the hexane had frozen. The mixture was then transferred to a freezer and allowed to stand overnight. Filtration of the cold solution afforded yellow crystals; mp 28–30 °C. Anal. Calcd for $Ti(C_5H_7O_2)_2(C_3H_7O)_2$: C, 52.75; H, 7.75; Ti, 13.15. Found: C, 52.28; H, 7.98; Ti, 13.01.

Bis((α,α-dimethylbenzyl)oxy)bis(2,4-pentanedionato)titanium(IV). A mixture of acetylacetone (2.8 mL, 27 mmol) and titanium(IV) α,α-dimethylbenzyloxide (7.8 g, 13 mmol) in 25 mL of dichloromethane was heated at 155 °C for 2 h under a stream of dry nitrogen and then in vacuo at 110 °C for several days until no trace of α,α-dimethylbenzyl alcohol was detected in the ^1H NMR spectrum of the product. A red oil remained (6.0 g, 88% yield). On standing for several weeks in vacuo, the oil solidified; mp 55–57 °C. Attempted recrystallization from several solvents resulted in oils. Vacuum distillation (~200 °C (~10^{-2} torr)) decomposed the product. Anal. Calcd for $Ti(C_5H_7O_2)_2(C_9H_{11}O)_2$: C, 65.11; H, 7.03. Found: C, 64.48; H, 6.77.

Bis(benzyloxy)bis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV). A mixtue of dipivaloylmethane (6.2 mL, 30 mmol) and titanium(IV) benzyloxide (7.0 g, 14.7 mmol) in 20 mL of dichloromethane was heated at 130 °C for 1 h under a stream of dry nitrogen and then kept in vacuo overnight at room temperature to remove the benzyl alcohol that had formed. The resulting crude, yellow solid (8.0 g, 86% yield) was purified twice by dissolving it in a minimum amount of hexane and partially evaporating the hexane under a stream of dry nitrogen until the first appearance of crystals. The mixture was then transferred to a freezer and allowed to stand overnight. Filtration of the cold solution afforded white crystals; mp 78–79 °C. Anal. Calcd for $Ti(C_{11}H_{19}O_2)_2(C_7H_7O)_2$: C, 68.78; H, 8.34; Ti, 7.62. Found: C, 68.58; H, 8.35; Ti, 7.66.

Diisobutoxybis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV). This compound was prepared in 92% yield by a procedure similar to that employed for $Ti(acac)_2(OCH_2CH(CH_3)_2)_2$. The resulting crude, yellow solid was purified twice by dissolving it in a minimum amount of hexane and then partially evaporating the hexane under a stream of dry nitrogen until crystals began to form. The mixture was then transferred to a freezer and allowed to stand overnight. Decantation of the cold solution afforded white crystals; mp 147–149 °C. Anal. Calcd for $Ti(C_{11}H_{19}O_2)_2(C_4H_9O)_2$: C, 64.27; H, 10.07, Ti, 8.54. Found: C, 63.93; H, 9.95; Ti, 8.30.

Diisopropoxybis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV). This compound was prepared in 85% yield and was purified by a procedure similar to that employed for $Ti(acac)_2(OCH(CH_3)_2)_2$, except that the hexane solution was completely frozen by immersion in the liquid nitrogen bath. The recrystallizations afforded white crystals, mp 187–190 °C dec. Anal. Calcd for $Ti(C_{11}H_{19}O_2)_2(C_3H_7O)_2$: C, 63.14; H, 9.84; Ti, 8.99. Found: C, 62.34; H, 9.97; Ti, 9.38.

Bis((α,α-dimethylbenzyl)oxy)bis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV). This compound was prepared in 80% yield by a procedure similar to that employed for $Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$. The product was a viscous yellow oil that solidified on standing for several weeks in vacuo; mp 90–92 °C. Problems in purification were idential with those encountered for $Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$. Anal. Calcd for $Ti(C_{11}H_{19}O_2)_2(C_9H_{11}O)_2$: C, 70.16; H, 8.83. Found: C, 67.61; H, 8.66.

Diisopropoxybis(1-phenyl-1,3-butanedionato)titanium(IV). This compound was prepared in quantitative yield by a procedure similar to that employed for $Ti(acac)_2(OCH(CH_3)_2)_2$. The resulting crude, yellow solid was recrystallized twice from dichloromethane–hexane, giving light yellow crystals; mp 105–106 °C (lit.[29] 89 °C). Anal. Calcd for $Ti(C_{10}H_9O_2)_2(C_3H_7O)_2$: C, 63.94; H, 6.60. Found: C, 63.49; H, 6.57.

(1,2-Benzenediolato)bis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV). A mixture of catechol (1.0 g, 9.1 mmol) and $Ti(dpm)_2(OCH(CH_3)_2)_2$ (4.85 g, 9.1 mmol) in 50 mL of dichloromethane (the solution turned dark red immediately upon mixing the reagents) was heated at 80 °C for 1 h under a stream of dry nitrogen. The resulting crude, red solid (4.5 g, 94% yield) was purified by a procedure similar to that employed for $Ti(acac)_2(OCH(CH_3)_2)_2$ except that the hexane solution was removed from the liquid nitrogen bath at the first sign of freezing. The compound was obtained as red crystals; mp 62–64 °C. Anal. Calcd for $Ti(C_{11}H_{19}O_2)_2(C_6H_4O_2)$: C, 64.36; H, 8.10. Found: C, 64.31; H, 8.06.

Preparation of Mixed-Ligand Complexes. Solutions containing mixed-ligand complexes of the type $Ti(dik)(dik')(OR)_2$, $Ti(dik)_2(OR)(OR')$, and $[Ti(dik)_2(dik')]^+$ were prepared by mixing the appropriate molar ratios of the parent complexes in dichloromethane and allowing the mixture to come to equilibrium at room temperature. The mixed-ligand complexes were not isolated.

Nuclear Magnetic Resonance Spectra. Proton chemical shifts and coupling constants were measured at ambient temperature (~39 °C) with a Varian A-60A spectrometer. Spectra were recorded in triplicate, and the values reported in Table I are average values. The magnetic field sweep was calibrated with a standard sample of chloroform and tetramethylsilane in carbon tetrachloride.

Variable-temperature spectra of degassed solutions were recorded in the temperature range −110 to 150 °C with a Varian A-60A or HA-100 spectrometer. Prior to a kinetic run, the sweep width was calibrated by the audio-frequency side-band technique. Solvents (dichloromethane, deuteriochloroform, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane) were dried by refluxing for at least 24 h over calcium hydride and then freshly distilling before use. Probe temperatures were determined from the chemical shift between the nonequivalent protons of methanol or 1,2-ethanediol.[30]

Rate constants k for exchange of acac methyl groups, dpm *tert*-butyl groups, isopropoxide methyl groups, and α,α-dimethylbenzyloxide methyl groups were determined by quantitative comparison of experimental spectra with theoretical spectra calculated by using the Gutowsky–Holm total line-shape equation.[31] Spectra were compared with respect to the following characteristic line-shape parameters that were used to deter-

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Table I. Proton Chemical Shift[a] and Coupling Constant[b] Data for Some $Ti(dik)_2(OR)_2$ Complexes

		diketonate		alkoxide			
compound	solvent	CH_3	–CH=	CH_3	$-CH_2-$	⟩CH–[c]	*J*
$Ti(acac)_2(OCH_2C_6H_5)_2$	$CDCl_3$	–1.92	–5.50		–5.50		
	CH_2Cl_2	–1.91	–5.56		–5.47		
$Ti(acac)_2(OCH_2CH(CH_3)_2)_2$	$CDCl_3$	–2.00	–5.58	–0.87[d]	–4.22[d]	–1.84	6.4, 6.6
	CH_2Cl_2	–1.95	–5.56	–0.86[d]	–4.14[d]	–1.77	6.4, 6.5
$Ti(acac)_2(OCH(CH_3)_2)_2$	$CDCl_3$	–1.98	–5.53	–1.19[d]		–4.81	6.4
	CH_2Cl_2	–1.95	–5.56	–1.15[d]		–4.76	6.3
$Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$	$CDCl_3$	–1.94[e]	–5.48	–1.62[e]			
	CH_2Cl_2	–1.93[e]	–5.53	–1.61[e]			
$Ti(dpm)_2(OCH_2C_6H_5)_2$	$CDCl_3$	–1.08	–5.83		–5.56		
	CH_2Cl_2	–1.10	–5.88		–5.52		
$Ti(dpm)_2(OCH_2CH(CH_3)_2)_2$	$CDCl_3$	–1.14	–5.81	–0.78[d]	–4.13[d]	–1.78	6.3, 6.6
	CH_2Cl_2	–1.14	–5.86	–0.83[d]	–4.12[d]	–1.76	6.3, 6.6
$Ti(dpm)_2(OCH(CH_3)_2)_2$	$CDCl_3$	–1.16[e]	–5.79	*f*		–4.68	6.3
	CH_2Cl_2	–1.13[e]	–5.83	*f*		–4.70	6.3
$Ti(dpm)_2(OC(CH_3)_2C_6H_5)_2$	$CDCl_3$	–1.11[e]	–5.79	–1.62[e]			
	CH_2Cl_2	–1.13[e]	–5.84	–1.63[e]			
$Ti(bzac)_2(OCH(CH_3)_2)_2$	$CDCl_3$	–2.15	–6.25	–1.25[d]		–4.93	6.3
	CH_2Cl_2	–2.09	–6.27	–1.21[d]		–4.93	6.3
$Ti(dpm)_2(cat)$	$CDCl_3$	–1.18	–6.05				
	CH_2Cl_2	–1.18	–6.12				

[a] In ppm (±0.01) relative to an internal reference of tetramethylsilane (1% by volume) at 39 °C. All resonances are singlets unless otherwise indicated. [b] In hertz (±0.1) at 39 °C. For the isobutoxy complexes, the first *J* value listed is *J* (CH_3-CH); the second is *J* (CH_2–CH). [c] Septet for OR = isopropoxide; most intense central peak of multiplet for OR = isobutoxide. [d] Doublet. [e] Two methyl resonances are observed since the probe temperature (39 °C) is below the coalescence temperature. The average chemical shift is given. [f] Resonances obscured by dpm *tert*-butyl resonances.

Table II. Characteristic Infrared Frequencies (cm^{-1}) for Some $Ti(dik)_2(OR)_2$ Complexes[a]

$OCH_2C_6H_5$	OCH_2-$CH(CH_3)_2$	OCH-$(CH_3)_2$	$OC(CH_3)_2$-C_6H_5	assignment[b]
		$Ti(acac)_2(OR)_2$		
1597 vs[c]	1604 vs	1607 vs	1590 vs	ν_s ($C\underset{..}{-}O$)
1580 vs	1584 vs	1588 vs	1575 sh	
1524 vs	1523 vs	1525 vs	1523 vs	ν_{as} ($C\underset{..}{-}C$)
615 w	*d*	613 m	623 m 619 m	ν ($Ti-\ddot{O}R$)
442 m	445 m	437 m	440 s	ν (Ti–O)
		$Ti(dpm)_2(OR)_2$		
1599 s	1600 vs	1599 vs	1600 vs	ν_s ($C\underset{..}{-}O$)
1580 vs	1583 vs	1582 vs	1581 s	
1567 vs	1569 vs	1570 vs	1570 vs	
1552 vs	1552 vs	1552 vs	1555 s	
1531 vs	1532 vs	1532 vs	1530 vs	
1502 vs	1504 vs	1503 vs	1502 vs	ν_{as} ($C\underset{..}{-}C$)
619 m	622 m	623 s	624 s 618 sh	ν ($Ti-\ddot{O}R$)
502 m	505 m	500 m	502 m	ν (Ti–O)

[a] As Nujol mulls between CsI plates. [b] ν_s, symmetric stretch; ν_{as}, asymmetric stretch. [c] s, strong; m, medium; w, weak; v, very; sh, shoulder. [d] ν (Ti–OR) band may be obscured by a strong band at 664 cm^{-1}.

mine an average value of k at each temperature: line widths at one-fourth ($\Delta_{1/4}$), one-half ($\Delta_{1/2}$), and three-fourths ($\Delta_{3/4}$) maximum amplitude; and, below coalescence, $\delta\nu_e$, the frequency separation between the two absorption maxima, and r, the ratio of the maximum amplitude to the central minimum. For exchange of diastereotopic benzyloxide (or isobutoxide) methylene protons, which are spin coupled to each other, theoretical spectra were calculated with the computer program DNMR 3,[32] and the two center lines of the AB pattern of experimental and theoretical spectra were compared with respect to the same line-shape parameters. The methylene proton resonances of the isobutoxide complexes were treated as two AB patterns rather than the AB part of an ABX pattern (since $J_{AX} = J_{BX}$).

Because the transverse relaxation times T_2 were temperature dependent, theoretical line shapes were computed for a range of T_2's, and the experimental line shape at each temperature was compared with a theoretical line shape computed with a value of T_2 appropriate to that temperature. T_2 values were obtained by extrapolating plots of log $\Delta_{1/2}$ vs. $1/T$ from the fast- and slow-exchange regions into the coalescence region. In cases where $\delta\nu$, the frequency separation in the slow-exchange limit, was temperature dependent, appropriate values of $\delta\nu$ in the coalescence region were determined by extrapolating plots of $\delta\nu$ vs. T or $\delta\nu$ vs. $1/T$ from the slow-exchange region into the coalescence region. The procedures used to eliminate or minimize the common sources of error in NMR line-broadening studies[33] are described in a previous paper.[34]

Infrared Spectra. Infrared spectra were recorded in the region 4000–300 cm^{-1} with a Perkin-Elmer 521 grating spectrophotometer. The complexes were studied as Nujol mulls supported between cseium iodide plates. The estimated uncertainty in reported frequencies (Table II) is ±4 cm^{-1}, except for the region 550–400 cm^{-1}, where spectra were run on a fivefold expanded frequency scale. The estimated uncertainty in frequencies in the 550–400-cm^{-1} region is ±2 cm^{-1}.

Results and Discussion

Synthesis and Characterization of Complexes. Titanium(IV) complexes of the type $Ti(dik)_2(OR)_2$, where OR = $OCH_2C_6H_5$, $OCH_2CH(CH_3)_2$, $OCH(CH_3)_2$, or $OC(CH_3)_2C_6H_5$ and dik = acac, dpm, or, in one case, bzac,[24] have been prepared in excellent yields by reaction of stoichiometric amounts of the β-diketone and the titanium(IV) alkoxide (eq 1). The reagents were mixed in

$$Ti(OR)_4 + 2Hdik \rightarrow Ti(dik)_2(OR)_2 + 2ROH \quad (1)$$

dichloromethane, and the alcohol was removed, as it formed, by heating the reaction mixture to 100–160 °C under a stream of dry nitrogen for 1–2 h. The catecholate derivative $Ti(dpm)_2(cat)$ was prepared by an alcohol interchange reaction (eq 2). All of

$$Ti(dpm)_2(OCH(CH_3)_2)_2 + H_2cat \rightarrow Ti(dpm)_2(cat) + 2HOCH(CH_3)_2 \quad (2)$$

the complexes are new except $Ti(acac)_2(OCH(CH_3)_2)_2$[35] and $Ti(bzac)_2(OCH(CH_3)_2)_2$.[29] They have been characterized by chemical analysis, NMR spectra (cf. Table I), infrared spectra (cf. Table II), and conductance measurements. All of the complexes are nonelectrolytes in nitrobenzene solution; molar conductances are less than 0.012 Ω^{-1} cm^2 mol^{-1} for 10^{-2}–10^{-3} M solutions at 25.0 °C. Purification of these compounds is somewhat problematic since they are oils, which decompose on vacuum distillation, or low-melting solids, which crystallize with difficulty. The complexes are sensitive to hydrolysis, especially in solution.

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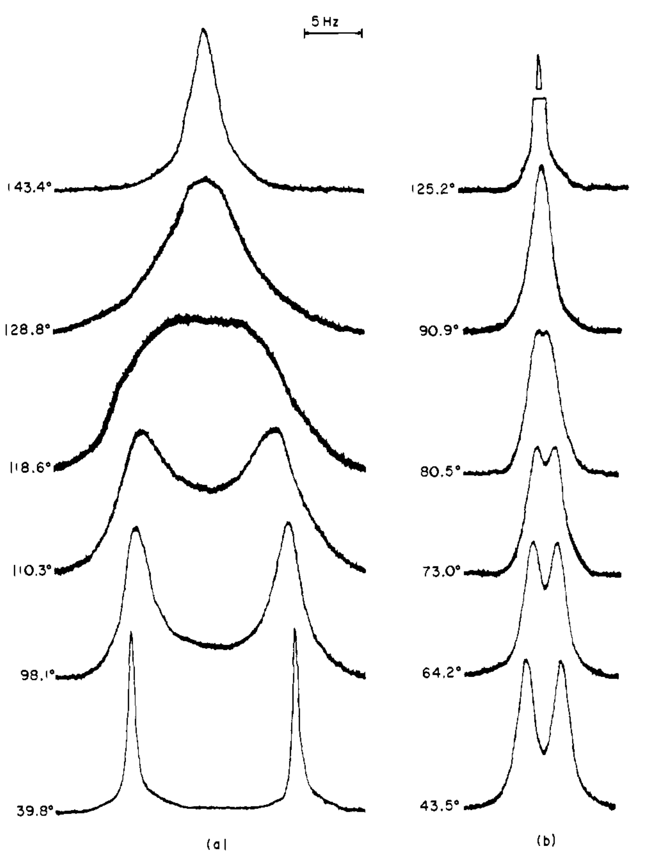

Figure 1. Variable-temperature ^{1}H NMR spectra of Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, 0.22 M in 1,1,2,2-tetrachloroethane: (a) dpm *tert*-butyl resonances at 60 MHz; (b) α,α-dimethylbenzyloxide methyl resonances at 100 MHz.

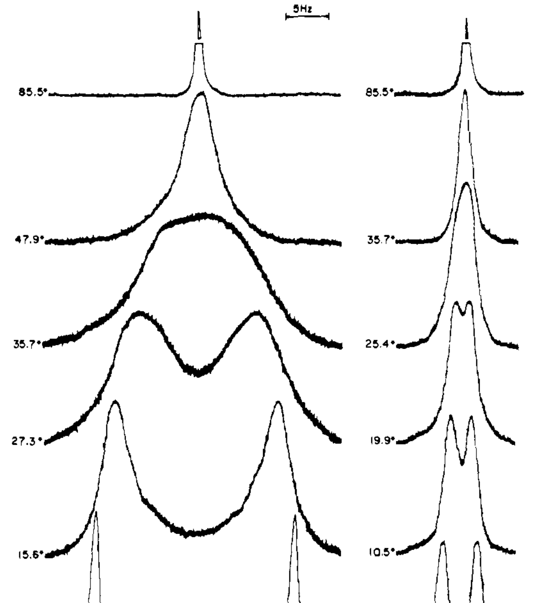

Figure 2. Variable-temperature ^{1}H NMR spectra of Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$, 0.24 M in CDCl$_3$, at 60 MHz: (a) dpm *tert*-butyl resonances; (b) benzyloxide methylene resonances. The lowest field resonance of the AB pattern in (b) at −15.4 °C (not shown) is obscured by the dpm ring-proton resonance.

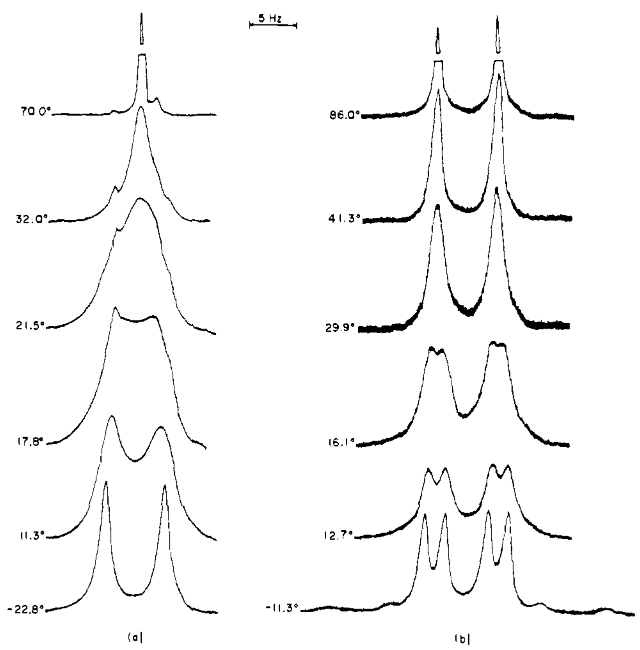

Figure 3. Variable-temperature ^{1}H NMR spectra of Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$, 0.52 M in CDCl$_3$: (a) acac methyl resonances at 60 MHz; (b) isobutoxide methylene resonances at 100 MHz. The weak, extra peaks in (a) are due to the isobutoxide methine resonances.

Stereochemistry and Kinetics of Rearrangements. Variable-temperature ^{1}H NMR spectra of the Ti(dik)$_2$(OR)$_2$ complexes (dik = acac or dpm; OR = OCH$_2$C$_6$H$_5$, OCH$_2$CH(CH$_3$)$_2$, OCH(CH$_3$)$_2$, or OC(CH$_3$)$_2$C$_6$H$_5$) have been studied in deuteriochloroform, 1,2-dichloroethane, or 1,1,2,2-tetrachlorethane. Typical spectra for Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$, and Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$ are presented in Figures 1–3; spectra of Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$ are shown in Figure 1 of ref 19. The low-temperature spectra show two alkoxide methyl resonances for Ti(acac)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$ and Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$ (Figure 1), two isopropoxide methyl doublets for Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$ (Figure 1 of ref 19), an AB pattern for the methylene protons of Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$ (Figure 2), and the AB part of an ABX pattern for the methylene protons of Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$ (Figure 3) and Ti(dpm)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$. These signals coalesce at higher temperatures to give a single, time-averaged resonance for Ti(acac)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, and Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$ and a single time-averaged doublet for Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$, Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$, and Ti(dpm)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$. All of the complexes display two equally intense acac methyl or dpm *tert*-butyl resonances at low temperatures (cf. Figures 1–3). These coalesce to a single time-averaged resonance in approximately the same temperature range in which the alkoxide resonances coalesce.

The low-temperature spectra indicate that the Ti(dik)$_2$(OR)$_2$ complexes exist as the cis geometrical isomer. The two acac methyl or dpm *tert*-butyl resonances arise from inequivalent diketonate R groups (a and b in **1**), and the alkoxide resonances result from geminal methyl groups or geminal methylene protons, which are diastereotopic because the cis isomer is dissymmetric (point group C_2). In early studies of Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$, the presence of two isopropoxide methyl doublets was attributed to restricted rotation.[16,17] However, it is now generally recognized[18-20] that the geminal methyl groups are diastereotopic for symmetry reasons even when rotation is free. Accordingly, we find that the sterically unhindered mixed-ligand complex Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)Cl exhibits an AB pattern for the methylene protons.[36]

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(36) Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)Cl was prepared in dichloromethane solution by mixing equimolar amounts of Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$ and Ti(dpm)$_2$Cl$_2$. Conversion of the parent complexes to the mixed-ligand complex is essentially complete. The ^{1}H NMR spectrum at −35 °C exhibits an AB pattern for the methylene protons, three dpm *tert*-butyl resonances (relative intensities 2:1:1) and two dpm ring-proton resonances. This spectrum is indicative of the cis configuration (point group C_1). A time-averaged spectrum is observed at 30 °C.

Table III. Rate Constants for Inversion and Diketonate R-Group Exchange in Ti(dik)$_2$(OR)$_2$ Complexes

Ti(acac)$_2$(OCH$_2$C$_6$H$_5$)$_2$[a]			
T, °C	k_{ex}, s^{-1}	T, °C	k_{ex}, s^{-1}
35.4	105	11.1	18
29.8	65	10.0	16
25.5	45	8.1	14
21.4	35	6.4	12
19.4	30	0.6	7.4
17.3	26	−4.1	5.2
14.5	22		

T, °C	k_{inv}, s^{-1}	T, °C	k_{ex}, s^{-1}
Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$[b]			
41.3	114	34.7	39
37.1	93	32.0	33
29.9	62	29.8	27
27.5	50	25.5	21
24.8	39	21.5	15
21.4	32	19.7	13
19.3	28	17.8	11
16.1	24	16.9	11
14.2	19	15.5	9.3
12.7	17	11.3	7.9
8.4	12	7.0	5.2
7.8	11	4.4	4.6
4.2	7.9		
Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$[c]			
28.4	23	56.5	93
25.5	17	44.9	42
24.0	15	39.8	30
21.2	11	37.2	24
18.1	8.9	32.0	16
16.9	7.2	30.9	15
14.4	6.0	28.4	12
10.0	4.2	25.5	9.2
6.6	3.1	21.2	6.9
2.7	2.2	18.1	4.8
−1.9	1.5	16.9	4.0
		14.4	3.4
		10.0	2.4
		6.6	1.8
Ti(acac)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$[d]			
77.3	56	92.5	107
70.3	35	86.7	73
64.6	23	81.0	49
55.4	13	75.0	33
54.2	11	71.8	26
49.4	8.3	68.9	22
46.1	6.0	66.1	18
43.3	4.7	64.9	17
41.4	3.9	63.2	15
38.1	3.2	61.5	14
37.0	2.9	59.6	12
36.2	2.6	55.4	9.1
34.4	2.2	46.7	4.4

T, °C	k_{inv}, s^{-1}	T, °C	k_{ex}, s^{-1}
Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$[e]			
43.3	106	52.2	128
41.4	92	47.9	91
38.3	83	43.3	69
35.7	70	41.4	62
31.9	56	39.8	53
29.0	42	38.3	49
27.3	38	35.7	40
25.4	31	34.7	36
22.9	28	31.9	32
19.9	23	29.0	26
17.4	19	27.3	23
15.6	17	25.4	19
10.5	11	22.9	17
		19.9	14
		17.4	11
		15.6	10
		10.5	7.1
		7.0	5.1
Ti(dpm)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$[f]			
39.8	55	63.2	206
34.8	38	57.8	134
30.0	28	50.6	81
27.4	20	44.5	57
26.1	19	39.8	37
25.7	19	34.4	26
24.7	16	32.2	22
21.9	13	31.1	21
18.7	10	30.5	20
14.5	7.6	27.7	16
		25.2	13
		21.4	10
		16.8	6.6
Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$[g]			
96.4	7.8	143.4	119
90.9	4.9	138.6	87
86.7	3.6	135.0	68
83.8	3.2	131.8	56
80.5	2.5	128.8	48
79.6	2.2	126.2	39
77.1	2.0	123.4	34
73.0	1.5	118.6	28
70.9	1.3	115.2	22
68.4	0.96	110.3	17
64.2	0.74	104.9	12
		98.1	7.9
		92.2	5.3
		86.1	3.4

[a] 0.42 M in 1,2-dichloroethane. For the acac methyl resonances, the frequency separation in the slow-exchange limit, $\delta\nu$, is 9.87 Hz at 60 MHz. The coalescence temperature, T_c, is 15 °C. [b] 0.52 M in CDCl$_3$. Isobutoxide CH$_2$ $\delta\nu$ = 7.02 Hz at 100 MHz, J = 10.4 Hz, T_c = 20 °C; acac CH$_3$ $\delta\nu$ = 6.45 Hz at 60 MHz, T_c = 19 °C. [c] 0.42 M in CDCl$_3$. Isopropoxide CH$_3$ $\delta\nu$ = 2.95 Hz at 60 MHz, T_c = 15 °C; acac CH$_3$ 6.50 Mz at 60 Mz; T_c = 29 °C. [d] 0.32 M in 1,1,2,2-tetrachloroethane. Alkoxide CH$_3$ $\delta\nu$ at 100 Mz varies from 3.5 Hz (77 °C) to 3.9 Hz (35 °C), T_c = 45 °C; acac CH$_3$ $\delta\nu$ = 9.80 Hz at 60 MHz, T_c = 67 °C. [e] 0.24 M in CDCl$_3$. Benzyloxide CH$_3$ $\delta\nu$ at 60 MHz varies from 6.23 Hz (43 °C) to 9.01 Hz (10 °C), J = 14.3 Hz, T_c = 20 °C; dpm C$_4$H$_9$ $\delta\nu$ at 60 MHz varies from 14.8 Hz (52 °C) to 20.0 Hz (7 °C), T_c = 34 °C. [f] 0.36 M in CDCl$_3$. Isobutoxide CH$_2$ $\delta\nu$ at 60 MHz varies from 4.72 Hz (40 °C) to 6.27 Hz (14 °C), J = 10.7 Hz, T_c = 28 °C; dpm C$_4$H$_9$ $\delta\nu$ = 11.04 Hz at 60 MHz, T_c = 33 °C. [g] 0.22 M in 1,1,2,2-tetrachloroethane. Alkoxide CH$_3$ $\delta\nu$ at 100 MHz varies from 1.7 Hz (96 °C) to 2.3 Hz (65 °C), T_c = 82 °C; dpm C$_4$H$_9$ $\delta\nu$ at 60 MHz varies from 13.4 Hz (143 °C) to 13.9 Hz (86 °C), T_c = 119 °C.

The observed coalescence of diketonate and alkoxide resonances (cf. Figures 1–3) is due to simultaneous exchange of diketonate R groups and inversion of configuration; first-order rate constants for inversion, k_{inv}, and exchange, k_{ex}, are presented in Table III. The rate constants are independent of concentration (cf. Table IV), as expected for first-order kinetics. Accurate rate constants for Ti(dpm)$_2$(OCH(CH$_3$)$_2$)$_2$ could not be determined because of overlap of the dpm *tert*-butyl and isopropoxide methyl resonances; an approximate value of k_{ex} = 6 s^{-1} was estimated at 25 °C for a CDCl$_3$ solution. Only k_{ex} could be determined for Ti(acac)$_2$(OCH$_2$C$_6$H$_5$)$_2$; the chemical shift between the methylene protons is evidently very small since the methylene resonance remained unresolved at low temperatures.

Arrhenius and Eyring activation parameters were obtained in the usual way from the least-squares straight lines of log k vs. $1/T$ and log (k/T) vs. $1/T$ plots, respectively. Typical Arrhenius plots are shown in Figure 4. The activation parameters are presented in Table V along with extrapolated values of k at 25 °C, values of k and ΔG^{*} at the coalescence temperature, and values of $R_k = k_{inv}/k_{ex}$, the relative rate of inversion and diketonate

Table IV. Concentration Dependence of Rate Constants for Exchange of Diketonate Methyl or *tert*-Butyl Groups in $CDCl_3$ Solution

compound	concention, M	k_{ex}, s^{-1} 14.4 °C	30.9 °C	39.8 °C
$Ti(acac)_2(OCH(CH_3)_2)_2$	0.10	3.6	15	
	0.22	3.6	15	
	0.42	3.4	15	
$Ti(dpm)_2(OCH_2C_6H_5)_2$	0.07			54
	0.10			55
	0.24			53
	0.32			53

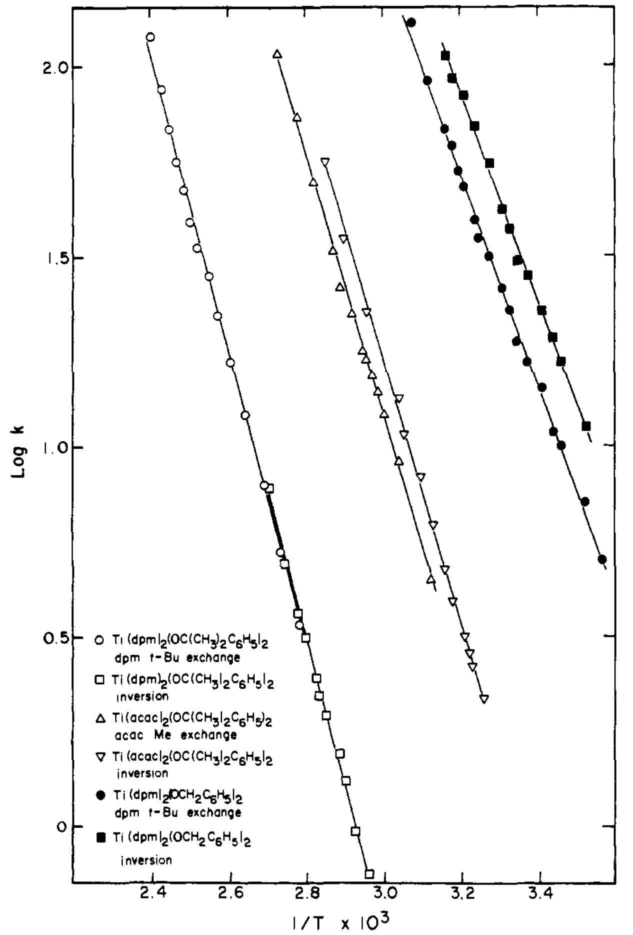

Figure 4. Arrhenius plots for inversion and diketonate R-group exchange in $Ti(dpm)_2(OC(CH_3)_2C_6H_5)_2$, $Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$, and $Ti(dpm)_2(OCH_2C_6H_5)_2$.

R-group exchange. The rate constants decrease and the values of ΔH^* increase with increasing steric bulk of the alkoxide ligand. This effect is particularly dramatic for the $Ti(dpm)_2(OR)_2$ complexes where $k_{25°C}$ decreases by a factor of $\sim 10^3$ and ΔH^* increases by 5 kcal/mol on going from a primary alkoxide (OR = $OCH_2C_6H_5$) to a tertiary alkoxide (OR = $OC(CH_3)_2C_6H_5$). For the $Ti(acac)_2(OR)_2$ complexes, the corresponding variation is a factor of ~ 65 in $k_{25°C}$ and 3.6 kcal/mol in ΔH^*. The values of R_k lie between 1.0 and 2.0, and R_k decreases with increasing steric bulk of the alkoxide ligand. Activation parameters for inversion and R-group exchange are essentially identical.

Rates of inversion and R-group exchange are nearly independent of solvent, and these rearrangements are not catalyzed by pyridine. $Ti(acac)_2(OCH(CH_3)_2)_2$, $Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$, and $Ti(dpm)_2(OCH_2C_6H_5)_2$ were studied in a variety of solvents including benzene, toluene, chlorobenzene, nitrobenzene, dichloromethane, deuteriochloroform, 1,1,2,2-tetrachloroethane, and acetonitrile. NMR line shapes in the coalescence region exhibit little dependence on solvent. A quantitative study of $Ti(acac)_2$-

Table V. Kinetic Data for Inversion and Diketonate R-Group Exchange in $Ti(dik)_2(OR)_2$ Complexes[a]

compound	process	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$k_{25\,°C}$, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol (T_c,[b] °C)	k, s^{-1} ($\sim T_c$, °C)	$R_k = k_{inv}/k_{ex}$ at $\sim T_c$
$Ti(acac)_2(OCH_2C_6H_5)_2$[c]	exchange	12.2 ± 0.5	10.63 ± 0.36	11.6 ± 0.5	−11.8 ± 1.6	47.1	15.05 ± 0.06 (15)	23.2 ± 2.6 (15)	
$Ti(acac)_2(OCH_2CH(CH_3)_2)_2$	inversion	12.4 ± 0.5	10.72 ± 0.40	11.8 ± 0.5	−11.4 ± 1.8	41.3	15.19 ± 0.07 (20)	26.9 ± 3.2 (19)	2.09 ± 0.4
	exchange	12.4 ± 0.7	10.18 ± 0.55	11.6 ± 0.7	−13.9 ± 2.4	19.6	15.61 ± 0.07 (19)	12.9 ± 1.7 (19)	
$Ti(acac)_2(OCH(CH_3)_2)_2$	inversion	14.6 ± 0.7	11.86 ± 0.50	14.0 ± 0.7	−6.2 ± 2.3	15.8	15.76 ± 0.07 (15)	12.3 ± 1.5 (22)	1.78 ± 0.3
	exchange	14.7 ± 0.8	11.76 ± 0.24	14.1 ± 0.3	−6.8 ± 1.1	8.9	16.19 ± 0.05 (29)	6.9 ± 0.6 (22)	
$Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$[d]	inversion	16.0 ± 0.4	11.70 ± 0.29	15.3 ± 0.4	−7.2 ± 1.3	1.01	17.59 ± 0.06 (45)	12.7 ± 1.2 (56)	1.41 ± 0.2
	exchange	15.9 ± 0.4	11.48 ± 0.28	15.2 ± 0.4	−8.3 ± 1.2	0.73	17.99 ± 0.05 (67)	9.0 ± 0.7 (56)	
$Ti(dpm)_2(OCH_2C_6H_5)_2$	inversion	12.3 ± 0.4	10.55 ± 0.31	11.7 ± 0.4	−12.2 ± 1.5	32.5	15.33 ± 0.05 (20)	45.9 ± 3.8 (30)	1.64 ± 0.2
	exchange	12.7 ± 0.3	10.57 ± 0.24	12.1 ± 0.3	−12.2 ± 1.1	19.7	15.80 ± 0.06 (34)	28.0 ± 2.6 (30)	
$Ti(dpm)_2(OCH_2CH(CH_3)_2)_2$	inversion	14.5 ± 0.8	11.83 ± 0.58	13.9 ± 0.8	−6.4 ± 2.6	17.4	15.78 ± 0.05 (28)	26.0 ± 2.7 (30)	1.37 ± 0.2
	exchange	14.1 ± 0.3	11.45 ± 0.23	13.5 ± 0.3	−8.2 ± 1.0	12.8	16.01 ± 0.05 (33)	19.0 ± 1.6 (30)	
$Ti(dpm)_2(OC(CH_3)_2C_6H_5)_2$[d]	inversion	17.6 ± 0.9	11.27 ± 0.55	16.9 ± 0.9	−9.3 ± 2.5	0.023	20.20 ± 0.07 (82)	9.2 ± 1.0 (100)	1.06 ± 0.2
	exchange	17.9 ± 0.5	11.42 ± 0.29	17.1 ± 0.5	−8.8 ± 1.3	0.020	20.57 ± 0.08 (119)	8.7 ± 0.9 (100)	

[a] In $CDCl_3$ unless indicated otherwise. All errors are random errors estimated at the 95% confidence level. [b] Coalescence temperature. [c] In 1,2-dichloroethane. [d] In 1,1,2,2-tetrachloroethane solution.

$(OCH(CH_3)_2)_2$ in five solvents afforded the following values of k_{ex} (s^{-1}) at 25 °C: 11 ($C_6H_5CH_3$), 7 (C_6H_5Cl), 9 (CH_2Cl_2), 9 ($CDCl_3$), and 13 (1,1,2,2-$C_2H_2Cl_4$). Thus, the solvent-induced variation in rates is only a factor of 2. The line widths of the *tert*-butyl and methylene proton resonances of $Ti(dpm)_2(OCH_2C_6H_5)_2$ in acetonitrile at ~40 °C, a temperature in the coalescence region, are unchanged upon addition of pyridine; pyridine concentrations up to 40% (v/v) were investigated. Attempts to catalyze the rearrangement of $Ti(dpm)_2(OCH_2C_6H_5)_2$ with monochloroacetic acid in 1,1,2,2-tetrachloroethane resulted in decomposition of the complex.

NMR studies indicate that intermolecular ligand exchange between the $Ti(dik)_2(OR)_2$ complexes and free alcohol or free diketone is slow on the NMR time scale at temperatures where inversion and R-group exchange are fast. $Ti(acac)_2(OCH(CH_3)_2)_2$ and $Ti(acac)_2(OCH_2C_6H_5)_2$ were studied at temperatures up to 40 °C, and $Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$ and $Ti(dpm)_2(OC(CH_3)_2C_6H_5)_2$ were studied up to 130 °C. In all cases, the NMR spectra exhibited separate, sharp resonances for the alcohol or diketone, and separate, time-averaged resonances for the complex, with line widths that were unaltered by the presence of alcohol or diketone.

The methyl region of the ^1H NMR spectrum of $Ti(bzac)_2(OCH(CH_3)_2)_2$ in dichloromethane solution exhibits four resonance lines at −25 °C. These coalesce to a single time-averaged resonance at higher temperatures. The spectra indicate that (1) $Ti(bzac)_2(OCH(CH_3)_2)_2$ exists in solution as an equilibrium mixture of the three geometrical isomers that have alkoxide ligands in cis positions and (2) the rearrangement process exchanges methyl groups among all four inequivalent sites of the three cis isomers. Similar results have been obtained independently by Serpone and Bickley.[22]

The catecholate complex $Ti(dpm)_2(cat)$ appears to rearrange more rapidly than the $Ti(dik)_2(OR)_2$ complexes. The *tert*-butyl region of the ^1H NMR spectrum of $Ti(dpm)_2(cat)$ in dichloromethane shows a single, sharp resonance (line width, 2.0 Hz) at −70 °C. This signal broadens to a line width of 10 Hz at −103 °C, but no splitting is observed.

Finally, the methyl region of the ^1H NMR spectra of the tris(β-diketonato)titanium(IV) cations, $[Ti(acac)_2(bzbz)]^+$, $[Ti(bzac)_2(bzbz)]^+$, and $[Ti(bzac)_3]^+$, was examined at temperatures down to −105 °C in dichloromethane solution. If these complexes were stereochemically rigid and all of the expected geometrical isomers were present, they should exhibit 2, 4, and 4 methyl resonances, respectively. In all three cases, only a single time-averaged methyl resonance was observed (line width ≤5 Hz at −105 °C).

Permutational Mechanisms. A permutational analysis for complexes of the type *cis*-$M(AA)_2X_2$, where AA is a symmetrical bidentate ligand and X is a monodentate ligand, has been reported by Bickley and Serpone.[3a] The allowed permutations and permutation–inversions are listed in Table VI, grouped into NMR averaging sets (A_i). The operations that effect the same net site interchanges belong in the same averaging set. For $Ti(dik)_2(OR)_2$ complexes that contain diastereotopic nuclei in the alkoxide ligands, the allowed site interchanges involve (1) exchange of diketonate R groups between the inequivalent a and b sites in one diketonate ligand (interchange (ab)) or both diketonate ligands (interchange 2(ab)) and (2) exchange of the diastereotopic nuclei between the inequivalent sites (labeled r and s) in the alkoxide ligands. The latter exchange results from inversion of configuration ($\Delta \rightleftarrows \Lambda$) and occurs simultaneously in both alkoxide ligands (interchange 2(rs)). Also included in Table VI are predicted values of R_k for each of the averaging sets.

Since rearrangements of the $Ti(dik)_2(OR)_2$ complexes involve simultaneous inversion and R-group exchange, with experimental values of R_k in the range 2.0–1.0, the permutational mechanism is described by averaging sets A_5, A_6, or a linear combination of A_5 and A_6. Averaging set A_5 involves inversion and R-group exchange in one diketonate ligand at a time; A_6 involves inversion and simultaneous R-group exchange in both diketonate ligands. It is evident from Tables V and VI that averaging set A_6 becomes increasingly important with increasing steric bulk of the alkoxide ligand.

Table VI. Permutational Analysis for Rearrangements of a *cis*-$M(AA)_2X_2$ Complex

operation	configurational change	net site interchanges	averaging set	$R_k = k_{inv}/k_{ex}$
E (56)	none	none	A_1	
(12) (12)(56) (34) (34)(56)	none	(ab)	A_2	0
(12)(34) (12)(34)(56)	none	2(ab)	A_3	0
E* (56)*	$\Delta \rightleftarrows \Lambda$	2(rs)	A_4	∞
(12)* (12)(56)* (34)* (34)(56)*	$\Delta \rightleftarrows \Lambda$	2(rs), (ab)	A_5	2.0
(12)(34)* (12)(34)(56)*	$\Delta \rightleftarrows \Lambda$	2(rs), 2(ab)	A_6	1.0

Our qualitative NMR studies of $Ti(bzac)_2(OCH(CH_3)_2)_2$ and the mixed-ligand complexes, $Ti(dpm)_2(OCH_2CH(CH_3)_2)(OCH_2C_6H_5)$ and $Ti(acac)(bzac)(OCH(CH_3)_2)_2$, provide additional evidence for the importance of averaging set A_5. Coalescence of four methyl resonances for $Ti(bzac)_2(OCH(CH_3)_2)_2$ implies interconversion of all three cis geometrical isomers and hence a permutational mechanism that involves R-group exchange in one diketonate ligand at a time. The same conclusion can be drawn from the coalescence patterns for the mixed-ligand complexes. For $Ti(dpm)_2(OCH_2CH(CH_3)_2)(OCH_2C_6H_5)$, four dpm *tert*-butyl resonances coalesce to a single time-averaged signal at higher temperatures. For $Ti(acac)(bzac)(OCH(CH_3)_2)_2$, which exists in dichloromethane solution as a mixture of the two geometrical isomers that have alkoxide ligands in cis positions, four acac methyl resonances and two bzac methyl resonances coalesce to give one acac methyl resonance and one bzac methyl resonance at higher temperatures. These results also imply R-group exchange in one diketonate ligand at a time. If it is assumed that R-group exchange is accompanied by inversion, as is the case for the other $Ti(dik)_2(OR)_2$ complexes, the permutational mechanisms for $Ti(bzac)_2(OCH(CH_3)_2)_2$, $Ti(dpm)_2(OCH_2CH(CH_3)_2)(OCH_2C_6H_5)$, and $Ti(acac)(bzac)(OCH(CH_3)_2)_2$ involve averaging sets that correlate with averaging set A_5 for a *cis*-$M(AA)_2X_2$ complex.[37-39]

Physical Mechanisms. The comparable values of rate constants and essentilly identical values of activation parameters for inversion and R-group exchange strongly suggest that these two processes occur by a common physical mechanism. This mechanism must be intramolecular since (1) the rearrangements are independent of concentration (Table IV) and (2) intermolecular ligand exchange between the complexes and free alcohol or free diketone is slow compared with the rates of inversion and R-group exchange. The latter observation rules out mechanisms involving dissociation of alkoxide or β-diketonate ligands.

On the basis of highly negative activation entropies derived from approximate line-shape analyses, Harrod and Taylor[17] proposed a mechanism involving dissociation of an alkoxide ligand to give a tight ion pair, followed by migration of the alkoxide ion across the surface of the cationic complex and subsequent collapse of the ion pair to give the rearranged six-coordinate complex. This

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(37) The coalescence patterns do not preclude a linear combination of averaging sets A_5 and A_6. They do indicate that A_5 is important.

(38) Bickley and Serpone[3a,39] have reported permutational analyses for the *cis*-$M(AB)_2X_2$ and *cis*-$M(AA)_2XY$ systems. The averaging sets A_9'' for *cis*-$M(AB)_2X_2$ and A_{13}' for *cis*-$M(AA)_2XY$ correlate with averaging set A_5 for *cis*-$M(AA)_2X_2$ and are consistent with the coalescence behavior that is observed for $Ti(bzac)_2(OCH(CH_3)_2)_2$ and $Ti(dpm)_2(OCH_2CH(CH_3)_2)(OCH_2C_6H_5)$.

(39) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1974**, *13*, 2908.

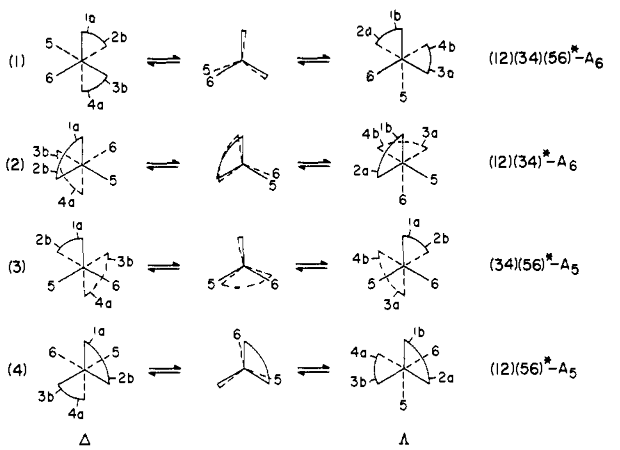


Figure 5. Rearrangements of a $Ti(dik)_2(OR)_2$ complex via twisting about the four C_3 axes shown in **2**. Numbers label the diketonate R groups (1, 2, 3, and 4) and the alkoxide ligands (5 and 6), and letters designate the inequivalent R-group environments (a and b). The permutation-inversion and averaging set for each mechanism are given on the right.

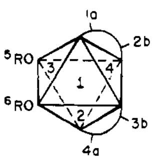
Table VII. Summary of Averaging Sets and R_k Values for Physical Rearrangement Mechanisms for a $Ti(dik)_2(OR)_2$ Complex

mechanism	averaging set	$R_k = k_{inv}/k_{ex}$
twist (C_3 axes 1 and/or 2)	A_6	1.0
twist (C_3 axes 3 and 4)	A_5	2.0
twist (mixture of C_3 axes)	$A_5 + A_6$	1.0-2.0
TBP-axial (a cleavage)	A_5	2.0
TBP-axial (b cleavage)	A_4	∞
TBP-axial (mixture of a and b cleavage)	$A_4 + A_5$	>2.0
TBP-equatorial	A_2	0
SP-axial (exclusive a or b cleavage)	$A_1 + A_5$	2.0
SP-axial (random a and b cleavage)	$A_1 + A_2 + A_5 + A_6$[a]	1.0
SP-axial (mixture of a and b clevage)	$A_1 + A_2 + A_5 + A_6$[b]	1.0-2.0

[a] Equally weighted linear combination. [b] Nonequally weighted linear combination.

mechanism may be discounted because complexes that contain bidentate alkoxides, e.g., $Ti(dpm)_2(cat)$, $Ti(OC(CH_3)_2C(CH_3)_2O)(acac)_2$,[18] and $Ti(OCH_2C(CH_3)_2CH_2O)(acac)_2$,[16] rearrange much more rapidly than complexes that contain two monodentate alkoxides. Dissociation of a bidentate alkoxide ligand to give the proposed ion pair is less likely than dissociation of a monodentate alkoxide. It should also be noted that the highly negative activation entropies reported by Harrod and Taylor[17] are almost certainly in error.[21,40,41]

More likely mechanisms for rearrangement of $Ti(dik)_2(OR)_2$ complexes involve (1) rupture of one metal–diketonate bond to give a five-coordinate intermediate or (2) twisting of an octahedral face to give a trigonal-prismatic transition state. The twisting process can be carried out about any one of the four C_3 axes of the octahedron;[5] these axes are labeled 1, 2, 3, and 4 in structure **2**, and this same notation is employed in Figure 5. Figure 5 shows that twists about C_3 axes 1 and 2 effect inversion and R-group exchange in both diketonate ligands (averaging set A_6, $R_k = 1.0$) while twists about symmetry-equivalent C_3 axes 3 and 4 effect inversion and R-group exchange in one diketonate ligand at a time (averaging set A_5, $R_k = 2.0$). Averaging sets and values of R_k for the twist mechanisms are summarized in Table VII. It is evident that the observed values of R_k (Table V), which vary from 1.0 to 2.0, are consistent with a linear combination of twists about C_3 axes 1 and/or 2 and twists about symmetry-equivalent C_3 axes 3 and 4.



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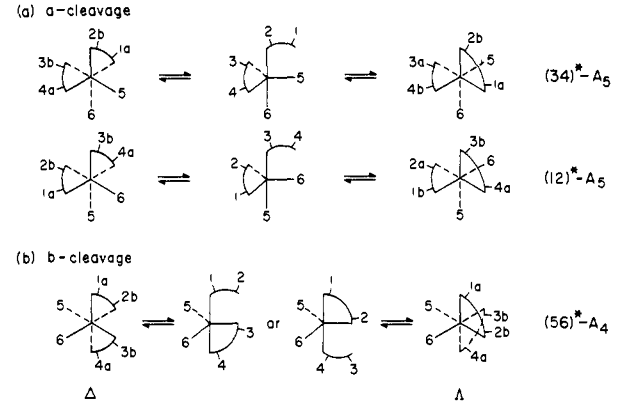

Figure 6. Rearrangements of a $Ti(dik)_2(OR)_2$ complex via bond rupture to give a TBP-axial intermediate. The numbers and letters have the same significance as in Figure 5.

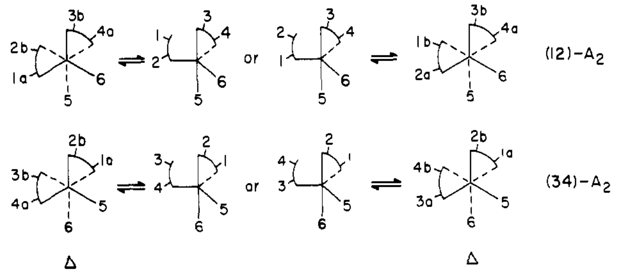

Figure 7. Rearrangement of a $Ti(dik)_2(OR)_2$ complex via bond rupture (a or b cleavage) to give a TBP-equatorial intermediate. The numbers and letters have the same significance as in Figure 5.

Rearrangements involving rupture of one metal–diketonate bond to give a five-coordinate intermediate are illustrated in Figures 6–8, and averaging sets and R_k values for these mechanisms are listed in Table VII. The metal–oxygen bond that breaks may be trans to another diketonate oxygen atom (a cleavage) or trans to an alkoxide ligand (b cleavage). The intermediate may have trigonal-bipyramidal geometry with the dangling ligand in an axial position (TBP-axial; cf. Figure 6), trigonal-bipyramidal geometry with the dangling ligand in an equatorial position (TBP-equatorial; cf. Figure 7), or square-pyramidal geometry with the dangling ligand in an axial position (SP-axial; cf. Figure 8); SP intermediates with the dangling ligand in a basal position are not considered here because SP-basal and TBP-axial intermediates may be shown to be kinetically equivalent.[42]

Bond rupture to give a TBP-axial intermediate (Figure 6) may be ruled out as the sole rearrangement path because this mechanism gives inversion with exchange of R groups in one diketonate ligand (averaging set A_5, $R_k = 2.0$) or inversion without R-group exchange (averaging set A_4, $R_k = \infty$), depending on whether bond rupture involves a or b cleavage. Thus, for any mixture of a- and b-cleavage processes involving a TBP-axial intermediate, $R_k > 2.0$, which does not agree with the experimental results.

Similarly, rearrangement via a TBP-equatorial intermediate (Figure 7) may be excluded as the sole reaction pathway since such a mechanism effects R-group exchange without inversion

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(40) Bickley, D. G.; Serpone, N. *Can. J. Spectrosc.* **1974**, *19*, 40.

(41) For inversion of $Ti(acac)_2(OCH(CH_3)_2)_2$, Harrod and Taylor[17] have reported $\Delta S^\ddagger = -33.0$ eu. Bradley and Holloway[16] obtained $\Delta S^\ddagger = -20 \pm 5$ eu, a value that they recognized may be too highly negative because of systematic errors in their approximate line-shape analysis. Our value of $\Delta S^\ddagger$ (Table V), determined from a total line-shape analysis, is -6.2 ± 2.3 eu.

(42) Gordon, J. G., II; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5319.

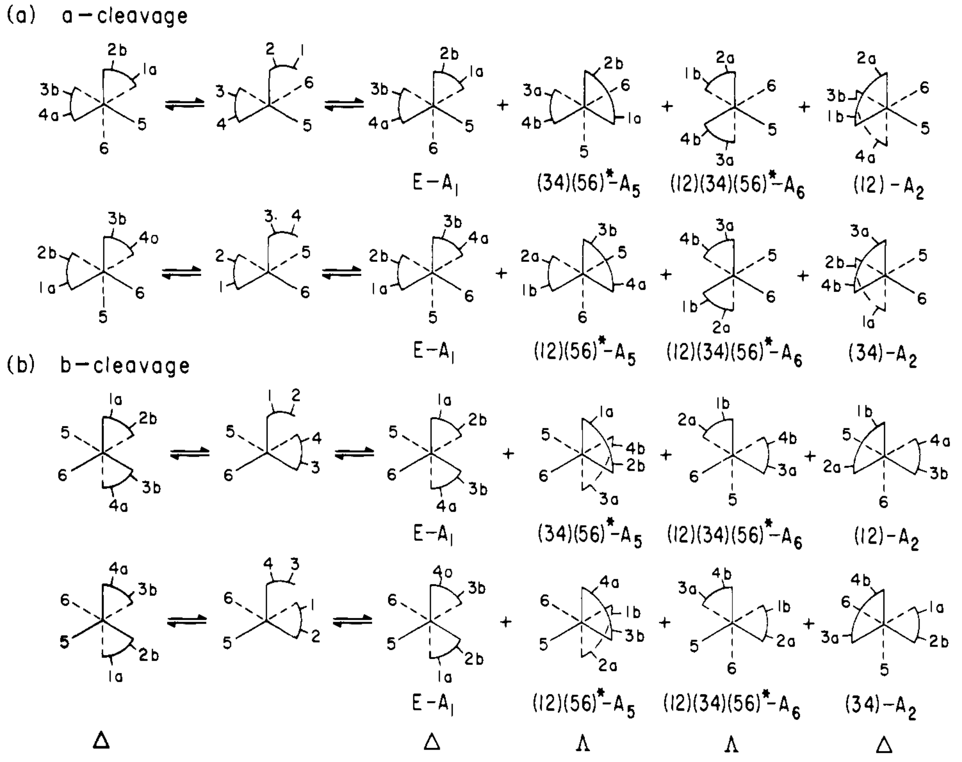

Figure 8. Rearrangements of a $Ti(dik)_2(OR)_2$ complex via bond rupture to give a SP–axial intermediate. The numbers and letters have the same significance as in Figure 5.

(averaging set A_2, $R_k = 0$). Although one could account for the observed values of R_k with bond rupture to give a mixture of TBP-axial and TBP-equatorial intermediates, these two kinds of intermediates are likely to have rather different energies. Thus the two TBP pathways are not expected to be competitive.

Rearrangements via a SP-axial intermediate are illustrated in Figure 8; only primary processes[42] are considered since they involve less motion than secondary processes. Formation of a SP-axial intermediate via a cleavage entails migration of an alkoxide ligand to the vacant coordination site, while formation of the intermediate via b cleavage involves migration of a diketonate oxygen atom to the vacant site. If formation of the intermediate occurs exclusively by alkoxide migration (a cleavage), then microscopic reversibility requires that the intermediate decays to products exclusively by alkoxide migration. This means that the intermediate decays to products exclusively by attack of the dangling ligand at one of the two symmetry-equivalent basal sites that are occupied by an alkoxide ligand. On the other hand, if the formation of the intermediate occurs exclusively by migration of a diketonate oxygen atom (b cleavage), then microscopic reversibility requires that products form by exclusive migration of a diketonate oxygen atom, i.e., exclusive attack of the dangling ligand at one of the two symmetry-equivalent basal sites occupied by a diketonate oxygen atom. Figure 8 shows that exclusive a cleavage or exclusive b cleavage afford an equally weighted linear combination of averaging sets A_1 and A_5, which results in $R_k = 2.0$.

If both a and b cleavage occur with equal probability, then one gets random migration of alkoxide ligands and diketonate oxygen atoms and random attack of the dangling ligand at the four basal sites of the SP-axial intermediate. This results in an equally weighted linear combination of averaging sets A_1, A_5, A_6, and A_2 (cf. Figure 8) and gives a value of $R_k = 1.0$ (Table VII). For any nonrandom mixture of a and b cleavage, R_k is predicted to have a value between 1.0 and 2.0. Although one could account for the observed values of R_k (Table V) in terms of a SP-axial mechanism, the bond cleavage (a or b), ligand migration (alkoxide or diketonate oxygen atom), and dangling ligand attack at the basal site of the intermediate would have to become *more* random with *increasing* steric bulk of the alkoxide ligand. This seems unlikely. Increased steric crowding should make the process *less* random.

The strongest positive argument in favor of a twist mechanism for rearrangements of $Ti(dik)_2(OR)_2$ complexes is the dramatic decrease in rate and increase in $\Delta H^{\ddagger}$ with increasing steric bulk of the alkoxide ligand. For the $Ti(dpm)_2(OR)_2$ complexes, $k_{25^\circ C}$ decreases by a factor of $\sim 10^3$ and $\Delta H^{\ddagger}$ increases by 5 kcal/mol as OR varies in the order $OCH_2C_6H_5$, $OCH_2CH(CH_3)_2$, $OC(CH_3)_2C_6H_5$ (cf. Table V). For the $Ti(acac)_2(OR)_2$ compounds, $k_{25^\circ C}$ decreases by a factor of ~ 65 and $\Delta H^{\ddagger}$ increases by 3.6 kcal/mol as OR varies in the order $OCH_2C_6H_5$, $OCH_2CH(CH_3)_2$, $OCH(CH_3)_2$, $OC(CH_3)_2C_6H_5$. Earlier, Bradley and Holloway[16] found a 12-fold decrease in rate for $Ti(acac)_2(OR)_2$ complexes as OR varies in the series OCH_3, OC_2H_5, $OCH(CH_3)_2$, $OC(CH_3)_3$. These steric effects are consistent with a twist mechanism since the trigonal-prismatic transition states are more congested than the octahedral ground state. On the other hand, a bond-rupture process should be accelerated as the OR group becomes more bulky since steric strain is relieved on going to an intermediate of reduced coordination number. Also consistent with a twist mechanism are the faster rearrangement rates of related but less sterically hindered tris(chelate) complexes. The diolato complexes studied by Baggett et al.,[18] $Ti(OC(CH_3)_2C(CH_3)_2O)(acac)_2$ and $Ti(OC(CH_3)_2CH_2C(CH_3)_2O)(acac)_2$, and the $Ti(dpm)_2(cat)$ and $[Ti(dik)_3]^+$ complexes studied in this work all rearrange more rapidly than the $Ti(dik)_2(OR)_2$ complexes.

The following additional evidence may be cited in support of a twist mechanism and in opposition to the bond-rupture possibilities: (i) the absence of significant solvent effects on the rates of rearrangement of the $Ti(dik)_2(OR)_2$ complexes;[43,44] (ii) the lack of catalysis by pyridine;[44,45] (iii) the negative values of the activation entropy[46] ($\Delta S^{\ddagger} = -6$ to -14 eu; cf. Table V); and (iv) the lack of a correlation between rearrangement rates and qualitative estimates of metal–diketonate bond strengths.

This last point is illustrated by the relative rearrangement rates

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

(44) Nagasawa, A.; Saito, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 131.

(45) (a) Inoue, T.; Saito, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2417. (b) Inoue, T.; Fujita, J.; Saito, K. *Ibid.* **1975**, *48*, 1228.

(46) (a) Lawrance, G. A.; Suvachittanont, S. *Inorg. Chim. Acta* **1979**, *32*, L13. (b) Ray, P.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81. (c) Schmulbach, C. D.; Brady, J.; Dachille, F. *Inorg. Chem.* **1968**, *7*, 287.

Table VIII. Rate Constants for Diketonate R-Group Exchange in Some Ti(dik)$_2$(OC$_2$H$_5$)$_2$ and Ti(dik)$_2$Cl$_2$ Complexes in CH$_2$Cl$_2$ Solution

compound	k, s^{-1} (T_c, °C)[a]	$k_{35°C}$, s^{-1}	compound	$k_{-10°C}$, s^{-1}
Ti(acac)$_2$(OC$_2$H$_5$)$_2$	16 (10)	~90[b]	Ti(dpm)$_2$Cl$_2$	275[d]
Ti(tfac)$_2$(OC$_2$H$_5$)$_2$	~18 (5)[c]	~150[b]	Ti(acac)$_2$Cl$_2$	55[e]
Ti(hfac)$_2$(OC$_2$H$_5$)$_2$	255 (35)	255	Ti(hfac)$_2$Cl$_2$	290[a]

[a] Rate constant at the coalescence temperature calculated from $k(T_c) = \pi\delta\nu/2^{1/2}$. [b] Estimated from $k(T_c)$ assuming an activation energy of 12 kcal/mol. [c] For exchange of tfac methyl groups. [d] Calculated from the data in ref 9. [e] Calculated from the data in ref 4.

Table IX. Fraction of the Rearrangements Proceeding by the Various Twist Transition States

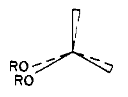
compound	transition state	
	3 and/or 4[a]	5[b]
Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$	0.00 ± 0.17[c]	1.00 ± 0.17[c]
Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$	0.12 ± 0.17	0.88 ± 0.17
Ti(acac)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$	0.42 ± 0.17	0.58 ± 0.17
Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$	0.22 ± 0.15	0.78 ± 0.15
Ti(dpm)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$	0.46 ± 0.20	0.54 ± 0.20
Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$	0.89 ± 0.28	0.11 ± 0.28

[a] These transition states arise from twists about C_3 axes 1 and/or 2 (Figure 5); averaging set A$_6$. [b] This transition state arises from twists about C_3 axes 3 and 4 (Figure 5); averaging set A$_5$. [c] Errors are estimated at the 95% confidence level.

of Ti(dik)$_2$(OR)$_2$ complexes (Table V), Ti(dik)$_2$X$_2$ complexes (dik = acac or dpm, X = halide or pseudohalide), and cationic [Ti(dik)$_3$]$^+$ complexes such as [Ti(bzac)$_3$]$^+$, [Ti(acac)$_2$(bzbz)]$^+$, and [Ti(bzac)$_2$(bzbz)]$^+$. Coalescence temperatures are 15–119 °C for Ti(dik)$_2$(OR)$_2$ (Table V), –63 to –26 °C for Ti(dik)$_2$X$_2$,[4,9] and less than –105 °C for [Ti(dik)$_3$]$^+$; the rearrangement rate increases substantially in the order Ti(dik)$_2$(OR)$_2$ < Ti(dik)$_2$X$_2$ < [Ti(dik)$_3$]$^+$. On the basis of electronegativity considerations[16b] and the charge on the cationic complexes, the strength of the Ti–O bonds to the diketonate ligands might be expected to increase in the same order. Indeed, this order of bond strengths is supported by the following typical values of Ti–O infrared stretching frequencies: Ti(acac)$_2$(OR)$_2$ (~440 cm^{-1}; cf. Table II) < Ti(acac)$_2$Cl$_2$ (474 cm^{-1})[9] < [Ti(acac)$_3$]$^+$ (496 cm^{-1}); and Ti(dpm)$_2$(OR)$_2$ (~500 cm^{-1}; cf. Table II) < Ti(dpm)$_2$Cl$_2$ (515 cm^{-1}).[9] The fact that the rearrangement rate increases as the Ti–O bond strength increases argues against a mechanism involving rupture of a Ti–O bond.

The relative rearrangement rates of Ti(dik)$_2$X$_2$ (X = OC$_2$H$_5$ or Cl) complexes that contain different diketonate ligands also fail to support a Ti–O bond-rupture mechanism. Fluorinated substituents on the diketonate ligands are expected to weaken the metal–oxygen bonds and appreciably increase the rate of a bond-rupture process. Thus M(acac)$_2$(hfac) and M(acac)$_2$(bzbz) (M = Al or Ga), which are believed to rearrange by an M–O bond-rupture mechanism, have values of $k_{25°C}$ that differ by a factor of ~10^4; the hfac complexes rearrange more rapidly.[47] In contrast, Table VIII shows that rate constants for Ti(dik)$_2$(OC$_2$H$_5$)$_2$ (dik = acac, tfac, or hfac) differ by only a factor of 3, and rate constants for Ti(dpm)$_2$Cl$_2$ and Ti(hfac)$_2$Cl$_2$ are almost identical. These results also favor a twist mechanism over a bond-rupture process.

The observed variation in R_k (Table V) indicates that twisting about C_3 axes 1 and/or 2 (Figure 5) becomes relatively more important and twisting about C_3 axes 3 and 4 relatively less important as the steric bulk of the alkoxide ligand increases. Thus steric congestion favors C_{2v} transition states **3** and/or **4** over C_s transition state **5**.



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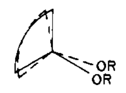

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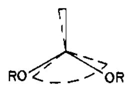

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Table IX lists, for each of the Ti(dik)$_2$(OR)$_2$ complexes, the fraction of the rearrangements that proceed by each of the two types of twist transition state. The least sterically hindered complex, Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$, rearranges essentially entirely via transition state **5**, while the most hindered complex, Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, rearranges almost entirely via transition states **3** and/or **4**. Examination of molecular models suggests that the presence of bulky OR groups results in unfavorable steric interactions between the two OR groups in **3** and **4** and unfavorable steric interactions between the OR groups and the diketonate ligand that is located on the same quadrilateral face in **5**. The latter interaction appears to be more important in the dpm complexes, where the diketonate ligands carry bulky *tert*-butyl groups, than in the acac complexes. Another factor that may favor transition states **3** and/or **4** over **5** in the case of the most crowded complexes is the relative ability of the two types of transition state to distort so as to minimize unfavorable steric interactions. It may be that the higher symmetry transition states **3** and **4** can better do this by opening the RO–Ti–OR angle. We do not pretend to understand the variation in the R_k values in detail. However, it is not unreasonable to expect R_k to be sensitive to steric effects, and it is pleasing to see a monotonic relationship between the R_k values and steric crowding. The effect on R_k of chelate ring size in (diolato)bis(acetylacetonato)titanium(IV) complexes has been discussed by Baggett et al.[18]

Acknowledgment. The support of this research by National Science Foundation Grants GP-30691X and MPS7424297 is gratefully acknowledged.

Registry No. Ti(acac)$_2$(OCH$_2$C$_6$H$_5$)$_2$, 84824-24-8; Ti(acac)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$, 84848-10-2; Ti(acac)$_2$(OCH(CH$_3$)$_2$)$_2$, 23072-32-4; Ti(acac)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, 84848-11-3; Ti(dpm)$_2$(OCH$_2$C$_6$H$_5$)$_2$, 84848-12-4; Ti(dpm)$_2$(OCH$_2$CH(CH$_3$)$_2$)$_2$, 84848-13-5; Ti(dpm)$_2$(OCH(CH$_3$)$_2$)$_2$, 84848-14-6; Ti(dpm)$_2$(OC(CH$_3$)$_2$C$_6$H$_5$)$_2$, 84848-15-7; Ti(bzac)$_2$(OCH(CH$_3$)$_2$)$_2$, 72439-63-5; Ti(dpm)$_2$(cat), 84824-25-9; Ti(acac)$_2$(OC$_2$H$_5$)$_2$, 23072-30-2; Ti(tfac)$_2$(OC$_2$H$_5$)$_2$, 51022-49-2; Ti(hfac)$_2$(OC$_2$H$_5$)$_2$, 51022-50-5.

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