A Comparative Dynamic Nuclear Magnetic Resonance Study of Degenerate Enantiomerization and Dionate Site Exchange in Octahedral Diolatobis(pentane-2,4-dionato)titanium(IV) Complexes

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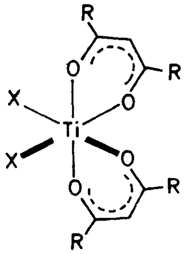
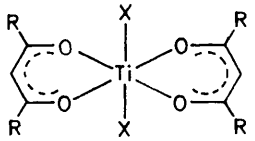
Dynamic ^{1}H n.m.r. spectroscopy is used to investigate the mechanism of metal-centred rearrangement in the title complexes containing 2,4-dimethylpentane-2,4-diolate, 2,3-dimethylbutane-2,3-diolate, and isopropoxide ligands. The rate of degenerate enantiomerization (k_1), determined from the coalescing diolate *gem*-dimethyl signals, is compared with the rate (k_2) of dionate methyl-site exchange. The value of k_1/k_2 is relatively insensitive to solvent but varies between 2.0 and 1.0 according to the nature of the diolate ligands. The free-energy barriers lie in the range 11.9—16.2 kcal mol^{-1}. The balance of evidence favours a common non-rupture trigonal twisting mechanism for both processes. A higher-energy process ($\Delta G^{\ddagger}$ 25 kcal mol^{-1}) bringing about coalescence of the pentanedionate and acetyl methyl signals in the spectrum of bis(3-acetylpentane-2,4-dionato)(2,4-dimethylpentane-2,4-diolato)titanium(IV) at 196 °C involves rupture of a Ti–O bond.

MANY octahedral metal chelate complexes are stereochemically labile or ' fluxional ' due to non-rigidity in the bonding framework about the metal atom. A plethora of mechanisms has been advanced to account for this phenomenon which may or may not involve transient rupture of a metal–ligand bond.[1] Following an early suggestion by Longuet-Higgins,[2] permutational analyses have recently been applied to the problem.[3,4] These enable all theoretically possible rearrangements to be considered. Experimental work is primarily concerned with those permutations which result in physically distinguishable changes in molecular properties such as *cis–trans* isomerization or racemization.

Following a pioneering ^{19}F n.m.r. study of non-rigid tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-complexes of Group 3B metals by Fay and Piper [5] in 1964, n.m.r. spectroscopy has proven to be a very powerful method for investigating ligand permutation in six-coordinate complexes.



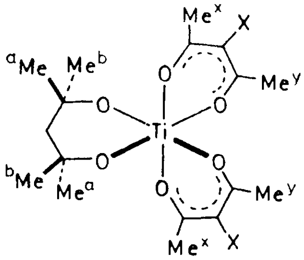
(1)



(2)

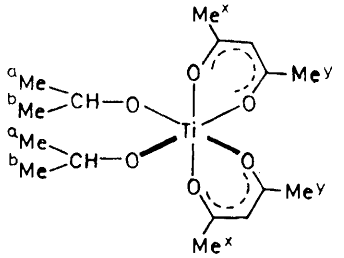
In the case of titanium(IV) complexes of type (1), two R-group resonances have been observed in accord with the non-equivalence of the bidentate ligand termini. At higher temperatures these signals broaden and coalesce due to fast interchange of the R-group environments on the n.m.r. time scale.[6-9] Bandshape studies on the exchanging signals have enabled the rate of this averaging process to be determined. Complexes (1) are chiral, but attempts to resolve them are likely to be thwarted by stereolability involving ligand permutation. However, enantiomerization of stereolabile compounds can be investigated by dynamic n.m.r. studies on racemic material provided that a prochiral substituent is incorporated into the structure to monitor change in chirality.[10,11]

An analysis of the various permutational modes available to complexes (1) indicates that site exchange of both sets of terminal R groups need not accompany enantiomerization and *vice versa*. Hence, by performing comparative dynamic n.m.r. studies on the signals from a prochiral substituent and the terminal R groups it should be feasible to identify the permutational modes that may be operative. Complexes (1) can exist in *cis* (as shown) and *trans* (2) diastereoisomeric forms, although dialkoxo-derivatives (X = OR') have been shown to exclusively adopt the *cis* configuration (1).[6] However, this observation does not rule out rearrangement pathways involving the transient formation of the *trans* form. In this respect tris(chelate) analogues of (1),



(3) X = H

(4) X = COMe



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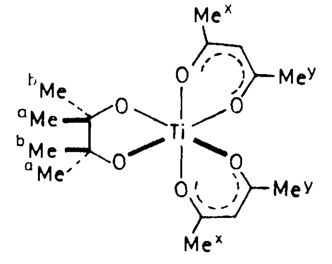


(5)

where X is a bridging diolate ligand, offer some advantages for study since the *trans* form is excluded due to the geometrical restraints. We now report the results of a comparative n.m.r. study of dionate methyl-group site exchange and degenerate enantiomerization in complexes (3)—(6).

Subsequent to the preliminary publication of this work,[12] Fay and Lindmark [13] have communicated the results of a closely related n.m.r. investigation of stereochemical non-rigidity in (6) and other dialkoxobis(β-diketonato)titanium(IV) complexes containing prochiral alkoxide groups (1; X = OR′). The process was shown to be intramolecular and enantiomerization was found to accompany β-diketonate terminal exchange. Finocchiaro [14] has since recognized the advantages of comparative n.m.r. studies on titanium(IV) chelate complexes.

RESULTS

The ^{1}H n.m.r. spectra of complexes (3)—(5) at normal probe temperature (*ca.* 35 °C) showed singlet signals (each 12 protons) for the pentane-2,4-dionate (pd) and diolate methyl groups. In the case of the di-isopropoxo-complex (6) the isopropyl methyl signals showed as the usual doublet, ^3J(HCCH) 6.1 Hz. Clearly, at this temperature these complexes are rapidly fluxional on the n.m.r. time scale, although in some cases residual exchange broadening was evident for both methyl signals. On decreasing the temperature of the sample, both methyl signals collapsed and separated into two components; other signals remained unchanged. Bandshape analyses were confined to the region of maximum exchange broadening (near the coalescence temperature), since it is well established that the rate constant can be determined most accurately near coalescence. Nevertheless, even in this region, considerable errors can arise if the signal separations or natural linewidths are incorrectly estimated.[15] The problem is particularly acute where the signal separation is not very much greater than the natural linewidth. Accordingly, the solvents used for the various complexes under investigation were selected on the basis that: (*i*) they gave reasonably large signal separations ($\Delta\delta$) for *both* sets of methyl groups and (*ii*) they were reasonably mobile in the temperature range used (to minimize viscosity contributions to T_2 at low temperature).

The frequency separation of the components of the pentanedionate and diolate methyl signals in the slow-exchange region were found in most cases to be significantly temperature dependent. Estimates of these parameters near coalescence were therefore obtained by a linear extrapolation from a series of values determined in the slow-exchange region. Where necessary, small adjustments were made to these estimates in order to minimize the standard deviation between calculated and experimental bandshapes. A recent study of the errors inherent in the total lineshape analysis of uncoupled two-site exchange systems has highlighted the difficulty in obtaining accurate rate constants if insufficient linewidth data are available.[15] The problem is less acute near the coalescence point provided that the signal separation is not too small. In the present study, natural linewidths in the coalescence region were estimated by interpolation between measurements in the very slow and very fast exchange regions. In some cases these estimates were slightly adjusted to optimize the fit between calculated and experimental bandshapes. The linewidths in the very slow exchange region were in the range 1—3 Hz as compared with *ca.* 0.7 Hz in the fast-exchange region. The rate of tumbling of the bulky titanium complexes will decrease at low temperature thereby increasing the correlation time.

In most cases there was no appreciable overlap of the pentanedionate and diolate methyl signals at coalescence; hence the two exchange processes were analyzed independently. However, in the case of complex (3) in [$^2H_8$]toluene solution the bandshapes overlapped considerably; hence they were analyzed as a combined four-site system and k_1/k_2 was varied to afford the optimum fit between calculated and experimental bandshapes. In the spectra of complexes (3) and (4) the methylene signal was often superimposed on the coalescing pentanedionate methyl signals. Therefore this signal was included as an additional but non-exchanging site in the analysis (*i.e.* all elements in the exchange matrix R_{jk} involving this site were set equal to zero). Representative bandshapes for complex (3) at 17 °C in carbon disulphide solution are depicted in Figure 1.

Dynamic n.m.r. data for the exchanging diolate (process 1) and pentanedionate (process 2) methyl groups are given in Table 1. In some cases the comparative bandshape analyses were performed at more than one temperature in the region of maximum exchange broadening. It is very unlikely that k_1/k_2 will vary significantly over a few degrees; hence these repeated determinations provide some guide to the precision of the measurements.

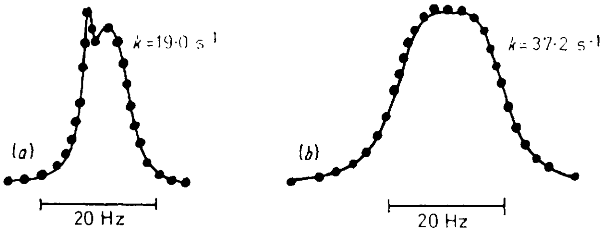


FIGURE 1 Experimental (●) and 'best-fit' calculated (——) n.m.r. bandshapes for the exchanging pentanedionate (*a*) and diolate (*b*) methyl groups of (3) at 17 °C in CS_2 solution. The relatively sharp signal superimposed on the methyl bandshape in (*a*) arises from the non-exchanging pentanediolate methylene protons. Only some of the data points used are depicted

DISCUSSION

Before considering the kinetic data in terms of various bond-rupture or twisting mechanisms for intramolecular rearrangement it is useful to engage in a permutational analysis to ensure that all possibilities are considered. Analyses of all rearrangements of complexes of the type $M(AB)_3$, $M(AB)_2(CC)$, and $M(AA)_2XY$ have been performed,[16,17] using the molecular-symmetry groups for non-rigid molecules introduced by Longuet-Higgins.[18] All possible permutations of nuclei are described mathematically without specifying the path by which the atoms move from initial to final positions. Physical observables, *i.e.* configurational changes and n.m.r. site interchanges, may then be deduced from the permutations. The complexes investigated in this study are of the type $M(AA)_2(BB)$.

A symmetry group of a non-rigid molecule is defined [18]

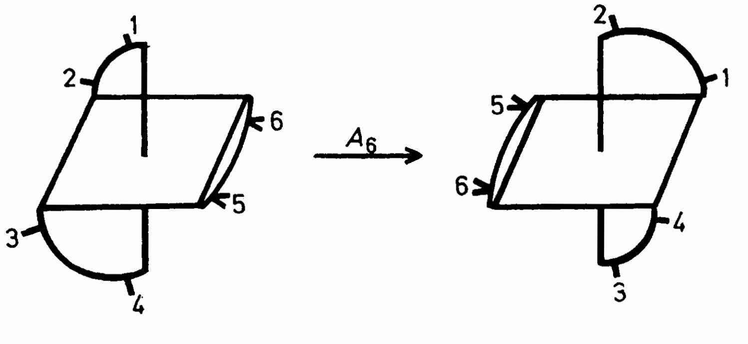
TABLE 1

Dynamic ^1H n.m.r. data for degenerate enantiomerization (process 1) and pentanedionate terminal methyl-site exchange (process 2)

Complex	Solvent	θ_c/°C	$\Delta\delta_1$ [a]	$\Delta\delta_2$ [a]	k_1 [b]	k_2 [b]	k_1/k_2	$\Delta G_1^\ddagger$ [c]	$\Delta G_2^\ddagger$ [c]
			p.p.m.		s^{-1}			kcal mol^{-1}	
(3)	CS_2	17.0	0.178	0.077	37.2	19.0	1.96 ± 0.3	14.9	15.3
	$CDCl_3$	12.0	0.146	0.055	20.4	9.6	2.13 ± 0.3	15.0	15.4
	[$^2H_8$]Toluene	15.0 [d]	0.200	0.170	25.2	15.4	1.64 ± 0.35 [d]	15.0	15.3
	[$^2H_5$]Pyridine	18.0 [d]	0.177	0.182	27.2	16.6	1.64 ± 0.35 [d]	15.1	15.4
	[$^2H_5$]Pyridine	20.0 [d]	0.175	0.180	31.3	18.6	1.69 ± 0.35 [d]	15.1	15.4
	Chlorobenzene	12.0 [d]	0.182	0.167	20.0	12.2	1.63 ± 0.35 [d]	15.0	15.2
	Chlorobenzene	20.0	0.176	0.171	38.9	20.9	1.87 ± 0.3	15.0	15.4
	Chlorobenzene	24.0	0.175	0.170	76.0	39.5	1.93 ± 0.3	14.8	15.2
(4)	$CDCl_3$	−8.0	0.166	0.087	34.5	16.6	2.07 ± 0.3	13.6	14.0
(5)	CS_2	−38.8	0.156	0.095	16.3	17.9	0.91 ± 0.15	12.3	12.3
	CS_2	−37.6	0.149	0.091	14.5	16.9	0.86 ± 0.15	12.4	12.4
	CS_2	−33.6	0.150	0.088	23.9	22.9	1.04 ± 0.15	12.4	12.4
	CH_2Cl_2	−45.4	0.219	0.093	18.6	18.6	1.00 ± 0.15	11.9	11.9
	CH_2Cl_2	−36.8	0.205	0.087	47.1	43.4	1.09 ± 0.15	11.9	12.0
(6)	CS_2	24.7	0.062	0.112	12.4	8.8	1.41 ± 0.2	15.9	16.1
	CCl_4	26.0	0.061	0.117	14.5	9.5	1.53 ± 0.2	15.9	16.2
	C_6D_6	27.9	0.064	0.093	13.7	10.2	1.34 ± 0.2	16.1	16.2

[a] Separation of the diolate ($\Delta\delta_1$) and pentanedionate ($\Delta\delta_2$) methyl signals interpolated to θ °C and optimized to minimize the standard deviation between calculated and observed bandshapes. [b] It is estimated that k can be measured to ±7% from 100 MHz spectra (±10% at 60 MHz); hence k_1/k_2 is ±15% (±20% at 60 MHz). [c] Calculated from the Eyring equation; ±0.15 kcal mol^{-1}. [d] Data obtained at 60 MHz; all other data obtained at 100 MHz.

as the set of all feasible permutations (P) of the positions and spins of identical nuclei (including the identity operation E), and of all permutation inversions ($P^* = E^*P = PE^*$) which simultaneously permute and invert the co-ordinates of all atoms about the centre of mass of the molecule (E^* is the inversion of all atomic positions and is not always a feasible operation). For an octahedral complex with six different ligands there are $6! = 720$ permutations, but this reduces to 384 for a tris(chelate) of the type $M(AA)_2(BB)$ since the bidentate ligands cannot span *trans* positions. The set can be factorized into a group of order 24 consisting of the 24 rigid-body rotations about the proper symmetry axes of the octahedron and a group of order 16 representing the complete set of all the possible rearrangements in stereochemically non-rigid complexes. There is thus a unique set of 16 permutamers in 8 (ΔΛ) enantiomeric pairs, and each permutamer can undergo $8P$ and $8P^*$ operations. The effect of each of the 16 operations on the [153—642] permutamer † is analyzed in Table 2,[19] and a representative permutational operation on [153—642] is depicted in Figure 2. An equivalent analysis has recently been reported by Bickley and Serpone.[20] The 16 operations may be divided into six n.m.r. averaging sets (A_i in Table 2) according to the site interchanges which result. Operations A_3 and A_6 simultaneously exchange the terminal sites (labelled x and y) on both β-diketonate ligands whereas A_2 and A_5 exchange the termini of only one of these ligands at a time. Operations A_1 and A_4 do not affect the chemical environments of the β-diketonate ligands. The permutational inversions A_4—A_6 exchange the sites of the diastereotopic *geminal* methyl groups (a and b) on the diol moiety.‡



[153-642] [153-264]

FIGURE 2

The qualitative experimental observation that

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† The notation is obtained by viewing the complex down one of the C_3 axes with atom 1 in the upper vertex of the octahedron. The labels of the ligating atoms positioned towards the viewer are then read in a clockwise manner. Next the label on the ligand *trans* to the third label is read, followed by the remaining two labels on the lower triangular face in a clockwise sequence. In the case of the diolatobis(β-diketonato)titanium(IV) complexes, labels 1,2 and 3,4 denote the pentanedionate ligands and 5,6 denotes the diolate moiety.

‡ Actually a is exchanged with a site enantiotopic to b and *vice versa*, although the signals are isochronous in achiral solvents. Similarly, operations A_5 and A_6 exchange x with a site enantiotopic to y.

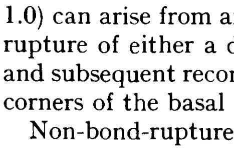
TABLE 2

Permutational analysis of $M(AA)_2(BB)$ rearrangements

Operation	Resulting permutamer	Averaging set	Net configurational change	Net site interchanges
E	[153—642]	A_1	None	None
(56)	[163—542]	A_1	None	None
(12)	[146—352]	A_2	None	(xy)
(34)	[154—632]	A_2	None	(xy)
(12) (56)	[145—362]	A_2	None	(xy)
(34) (56)	[164—532]	A_2	None	(xy)
(12) (34) (56)	[135—462]	A_3	None	2(xy)
(12) (34)	[136—452]	A_3	None	2(xy)
E*	[135—246]	A_4	$\Delta = \Lambda$	2(ab)
(56) *	[136—245]	A_4	$\Delta = \Lambda$	2(ab)
(12) *	[164—253]	A_5	$\Delta = \Lambda$	2(ab), (xy)
(34) *	[145—236]	A_5	$\Delta = \Lambda$	2(ab), (xy)
(12) (56) *	[154—263]	A_5	$\Delta = \Lambda$	2(ab), (xy)
(34) (56) *	[146—235]	A_5	$\Delta = \Lambda$	2(ab), (xy)
(12) (34) (56) *	[153—264]	A_6	$\Delta = \Lambda$	2(ab), 2(xy)
(12)(34) *	[163—254]	A_6	$\Delta = \Lambda$	2(ab), 2(xy)

enantiomerization accompanies β-diketonate terminal exchange in complexes (3)—(6) enables averaging sets A_1—A_4 to be eliminated from further consideration. Furthermore, the quantitative observation that k_1/k_2 varies between 2.0 and 1.0 (within experimental error) is consistent with sets A_5 and A_6. Clearly neither of these averaging sets is dominant in the series. Set A_5 is primarily operative in (3) and (4) ($k_1/k_2 \approx 2.0$), set A_6 dominates in (5) ($k_1/k_2 \approx 1.0$). Both sets contribute in the case of the di-isopropoxo-complex (6) ($k_1/k_2 \approx 1.4$), assuming that *trans* structures are not involved for this bis(chelate).

Several pathways can give rise to the permutations in sets A_5 and A_6. These can be partitioned into those which involve transient rupture of a Ti–O bond and others which involve twisting about C_3 axes of the intact octahedron. Bond-rupture mechanisms may be formally subdivided into those involving five-co-ordinate trigonal-bipyramidal (t.b.p.) and square-pyramidal (s.p.) intermediates as depicted in (7) and (8) respectively. Permutations (12)* and (34)* in set A_5 may be brought about by rupture of a diolato Ti–O bond to give an axial t.b.p. intermediate (7), followed by reconnection of the pendant diolate ligand at the alternative sites to form the enantiomeric structure. Permutations in set A_4 ($k_1/k_2 =$ 1.0) can arise from axial s.p. intermediates (8) formed by rupture of either a diolate or a β-diketonate Ti–O bond and subsequent reconnection of the pendant ligand at the corners of the basal plane.



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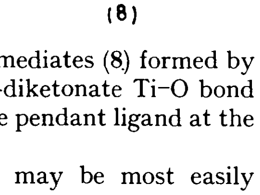


(8)

Non-bond-rupture mechanisms may be most easily visualized in terms of twisting motions of the three chelate rings about pseudo (p) and imaginary (i) C_3 axes which bisect opposite triangular faces of the co-ordination octahedron. However, this is an idealized model and the actual pathway for ligand reorganization is experimentally indeterminate and may be more complex. The consequences of these motions about the p-C_3 and the three i-C_3 axes are depicted in Figure 3.

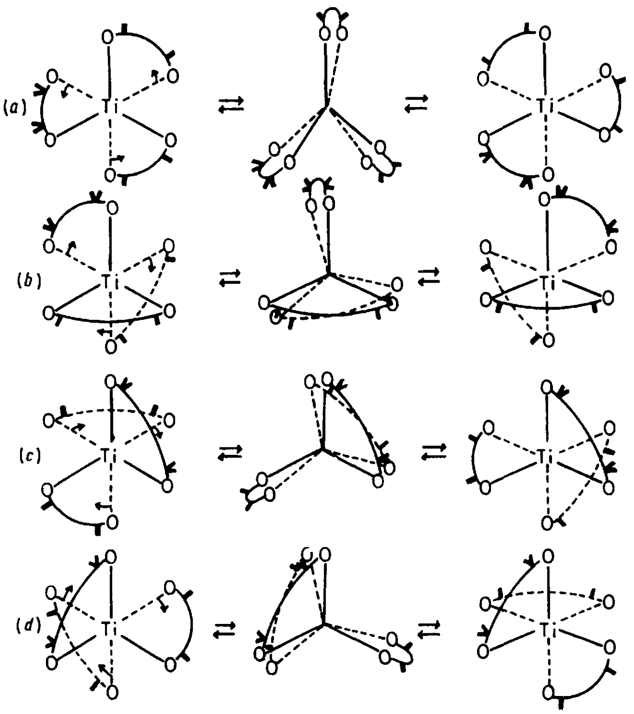


FIGURE 3

The p-C_3 axis (a) involves all three chelate rings bridging between the front and rear triangular faces and twisting may be considered to occur *via* a trigonal-prismatic structure. Only the diolate ligand bridges the triangular faces in (b) and the transition state formally has rhombic symmetry. The remaining axes (c) and (d) are degenerate and involve a single pentane-2,4-dionate ligand in bridging and a rhombic transition state. The permutations and predicted k_1/k_2 values for twisting around these axes are given in Table 3.

TABLE 3

Twist axis [a]	Permutation	Averaging set	Predicted k_1/k_2
(a) p-C_3, all three rings bridging	(12) (34) (56) *	A_6	1.0
(b) i-C_3, diol bridging	(12) (34) *	A_6	1.0
(c) i-C_3, β-diketone bridging	(12) (56) *	A_5	2.0
(d) i-C_3, β-diketone bridging	(34) (56) *	A_5	2.0

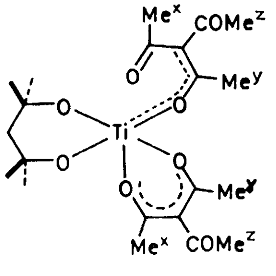
[a] See Figure 3.

Previous investigations [6,13] into ligand rearrangement in dialkoxobis(β-diketonato)titanium(IV) complexes have provided strong support for intramolecular twisting rather than bond-rupture mechanisms. The data for the present series of complexes (Table 1) support this conclusion. Thus the free energies of activation ($\Delta G^\ddagger$) for enantiomerization and β-diketonate terminal exchange are insensitive to solvent. The barriers to bond rupture might be expected to depend on the nature of the solvent and be lower in donor solvents such as pyridine. Furthermore the values of k_1/k_2 vary between 1.0 and 2.0 (within experimental error) which is precisely the predicted range for twist mechanisms (Table 3).

Complexes (3) and (4) which contain a six-membered diolate chelate ring favour twisting about axes (c) and (d) where a pentane-2,4-dionate bridges front and rear triangular faces. On the other hand in complex (5), which contains a five-membered diolate ring, twisting about axis (a) (three chelate rings bridging) or (b) (diolate ring bridging) is energetically favoured. On a purely intuitive basis, twisting about axis (a) might be expected to be less favourable since the process involves significant contraction of the O–Ti–O bond angles in all three bridging chelate rings (from 90 to *ca.* 70° using an ideal rigid model). The free-energy barriers for twisting in (5) are *ca.* 3 kcal mol^{-1} lower than in the six-membered diolato-analogue (3); * hence it would seem that the barrier to twisting about axis (b) is considerably reduced on decreasing the size of the bridging diolate ring from six to five atoms. Possibly a five-membered diolate ring can more readily accommodate a contraction of the O–Ti–O bond angle along the twisting pathway. However, steric interactions within the diolate ring and between the substituents on the diolate and pentanedionate rings could also contribute to the observed changes in $\Delta G^\ddagger$ and in the k_1/k_2 (*cf.* the data of ref. 13).

The k_1/k_2 value for the di-isopropoxo-complex (6) is inconsistent with a single rearrangement pathway and indicates that two (or more) twist modes have almost identical free energies of activation. Pathways involving transient formation of the *trans* isomer are also possible for this bis(chelate). Fay and Lindmark[13] have independently reported a k_1/k_2 value of 1.78 ± 0.3 for (6) in deuteriochloroform solution. This value is higher than those determined for (6) in other solvents (Table 1); however, the deviation is just within the quoted error limits and there is no evidence for a significant solvent effect on this quotient. The anisochronism of the *geminal* isopropyl methyl signals in (6) is rather small in deuteriochloroform solution ($\Delta\delta_1$ 0.049) and the errors in determining k_1 may be larger in this solvent than in the solvents used in the present study. The free-energy barriers in (6) are somewhat higher than in the tris(chelates) (3)—(5).

Comparison of the data for complex (4; X = COMe) with those for (3; X = H) shows that although the k_1/k_2 values are identical, $\Delta G^\ddagger$ is lowered by 1.4 kcal mol^{-1} on introduction of the acetyl groups into the dionate moiety. Both these complexes probably rearrange by twisting around axis (c) where the pentanedionate bridges the triangular faces. Therefore it is quite consistent with this analysis that the introduction of an acetyl substituent into the bridging ligand should affect the energy of the twisting process, since the geometry and bonding of this ligand will alter along the twisting path.



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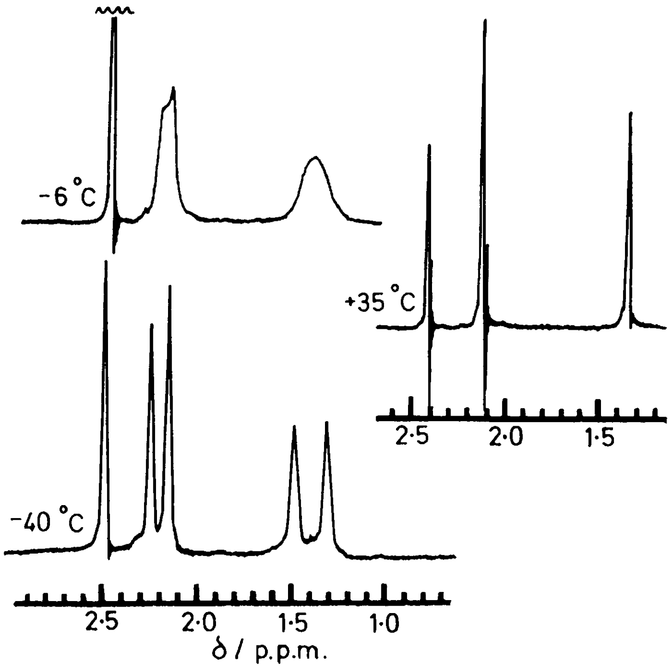

FIGURE 4 Hydrogen-1 n.m.r. spectra of (4) in deuteriochloroform solution at various temperatures (for assignments see Experimental section); the diolate CH_2 resonance is superimposed on the pentanedionate methyl signal

In principle complex (4) could provide information on the rate of Ti–O bond rupture. The 3-acetylpentane-2,4-dionate ligand has been used previously to investigate bond rupture in complexes of other metals.[21] Provided that rotation around the central $C\overset{\cdots}{-}C$ bond in the partly dissociated intermediate (9) is fast, bond rupture would lead to an exchange of the terminal and acetyl methyl groups (x, y, and z) on both dionate ligands in (9). Variable-temperature n.m.r. spectra of this complex showed that the terminal pentanedionate methyl signals (x and y) coalesced at *ca.* −8 °C whereas the 3-acetyl signal (z) remained a sharp singlet in this temperature range (Figure 4). Indeed, high-temperature

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* Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

studies in 1,2,4-trichlorobenzene solution established that the 3-acetyl signal did not exchange with the terminal x,y signal until *ca.* 196 °C. Analysis of the exchange modified bandshape at 196 °C gave $k = 22.4$ s^{-1} (site z exchanging to site x,y), corresponding to $\Delta G^{\ddagger} =$ 25.0 kcal mol^{-1}. Both Ti–O bond rupture *and* rotation about the 2,3 C$\overset{\cdots}{-}$C bond of the pendant 3-acetylpentanedionate ligand in the five-co-ordinate intermediate (9) is necessary to bring about exchange of the 3-acetyl and terminal methyl environments. Therefore, the measured barrier of 25.0 kcal mol^{-1} only refers to Ti–O bond rupture if C$\overset{\cdots}{-}$C bond rotation in the intermediate (9) is more rapid than Ti–O bond reconnection. It is difficult to assess the magnitude of the C$\overset{\cdots}{-}$C rotational barrier in (9), but literature data are available for sodium pentane-2,4-dionate ($\Delta G^{\ddagger}$ 12.9 kcal mol^{-1} at −21 °C)[22] and Ph(Me)NCH=C(COMe)$_2$ ($\Delta G^{\ddagger}$ 13.9 kcal mol^{-1} at −6.5 °C).[23] Neither of these compounds are ideal models for C=C rotation in intermediate (9), and since this intermediate will have higher energy than the octahedral complex from which it is derived the rate of Ti–O bond reconnection will be considerably greater than that of bond cleavage. Nevertheless the balance of evidence probably lies in favour of assigning the 25 kcal mol^{-1} high-temperature barrier in (4) to Ti–O bond rupture. Furthermore, this conclusion is consistent with the assignment of the lower-energy process ($\Delta G^{\ddagger}$ 14.0 kcal mol^{-1}), which exchanges only the terminal pentanedionate methyl groups x and y, to a non-rupture trigonal twisting process.

EXPERIMENTAL

Melting points are not corrected. Benzene (AnalaR grade), toluene, and hexane were distilled and dried over sodium wire. Commercial pentane-2,4-dione was purified by fractional distillation and the fraction of b.p. 139—140 °C was used. 2,4-Dimethylpentane-2,4-diol, b.p. 60—61 °C at 2 mmHg (lit.,[24] 113 °C at 35 mmHg), was obtained in 80% yield by reaction of 4-hydroxy-4-methylpentan-2-one with a two-fold excess of methylmagnesium iodide in diethyl ether. Unchanged ketone was removed as its hydrogensulphite addition compound. Hydrated 2,3-dimethylbutane-2,3-diol was dried by refluxing with dry toluene for 5 d in a Soxhlet apparatus containing a thimble of type 3A molecular sieve. Tetrapropoxotitanium(IV), tetraisopropoxotitanium(IV), and 3-acetylpentane-2,4-dione were obtained commercially and used without further purification. Bis(pentane-2,4-dionato)dipropoxotitanium(IV) was prepared from Ti(OPr)$_4$ and pentane-2,4-dione according to the literature method.[25]

2,4-Dimethylpentane-2,4-diolatobis(pentane-2,4-dionato)-titanium(IV) (3).—Bis(pentane-2,4-dionato)dipropoxotitanium(IV) (2.88 g) was injected *via* a serum cap into a dry-nitrogen-flushed flask containing 2,4-dimethylpentane-2,4-diol (1.04 g). The resulting crystals were filtered from the oily mother liquor, washed with hexane, and recrystallized twice from hexane to yield the title complex (1.64 g, 55%) as non-hygroscopic colourless needles, m.p. 141—142 °C (Found: C, 54.4; H, 7.6. $C_{17}H_{28}O_6Ti$ requires C, 54.3; H, 7.5%); δ(CDCl$_3$ at 35 °C) 1.35 (12 H, s, diolate CH$_3$), 2.04 (12 H, s, dionate CH$_3$), 2.11 (2 H, s, CH$_2$), and 5.68 p.p.m. (2 H, s, CH); ($\nu_{max.}$ at 665, 785, 935, 1 185, 1 280, and 1 580 cm^{-1}; $\lambda_{max.}$ in hexane 233 (14 600), 263 (12 900), and 326 nm (ε 11 000 dm^3 mol^{-1} cm^{-1}). The mother liquor afforded another crop (1.1 g) of the title complex on standing for 10 d.

Bis(3-acetylpentane-2,4-dionato)dipropoxotitanium(IV).—3-Acetylpentane-2,4-dione (0.40 g) was added dropwise at ambient temperature to tetrapropoxotitanium(IV) (0.40 g) under nitrogen. When heat evolution had ceased, the mixture was heated to 70 °C *in vacuo* (3 mmHg) for 1 h to remove propan-1-ol and then cooled to afford the title complex as a yellow oil (0.60 g, 89%). The complex was stored and handled in an inert atmosphere (Found: C, 53.9; H, 7.5. $C_{20}H_{32}O_8Ti$ requires C, 53.6; H, 7.2%); δ(CDCl$_3$ at 35 °C) 0.91 (6 H, t, propyl CH$_3$), 1.60 (4 H, m, propyl CH$_2$), 2.14 (12 H, s, dionate CH$_3$), 2.43 (6 H, s, acetyl CH$_3$), and 4.38 p.p.m. (4 H, t, OCH$_2$); $\nu_{max.}$ at 692, 765, 925, 1 245, 1 575, and 1 690 cm^{-1}; $\lambda_{max.}$ in CH$_2$Cl$_2$ 278 nm (ε 21 500 dm^3 mol^{-1} cm^{-1}).

Bis(3-acetylpentane-2,4-dionato)(2,4-dimethylpentane-2,4-diolato)titanium(IV) (4).—The reaction was carried out as for (3). 2,4-Dimethylpentane-2,4-diol (previously dried over molecular sieves) (0.16 g) and bis(3-acetylpentane-2,4-dionato)dipropoxotitanium(IV) (0.54 g) afforded colourless crystals after precipitation with hexane (1 cm^3). Recrystallization from hexane–benzene afforded the title complex as hygroscopic colourless plates (0.44 g, 79%), m.p. 146—147 °C (sealed capillary) (Found: C, 54.9; H, 7.3. $C_{21}H_{32}O_8Ti$ requires C, 54.8; H, 7.0%); δ(CDCl$_3$ at 35 °C) 1.34 (12 H, s, diolate CH$_3$), 2.12 (12 H, s, dionate CH$_3$), 2.12 (2 H, s, CH$_2$), and 2.41 p.p.m. (6 H, s, acetyl CH$_3$); $\nu_{max.}$ at 790, 820, 930, 995, 1 062, 1 185, 1 245, 1 575—1 580, and 1 690 cm^{-1}; $\lambda_{max.}$ in hexane 238 (15 600), 270 (15 200), and 326 nm (ε 8 800 dm^3 mol^{-1} cm^{-1}).

2,3-Dimethylbutane-2,3-diolatobis(pentane-2,4-dionato)-titanium(IV) (5).—Bis(pentane-2,4-dionato)dipropoxytitanium(IV) (19.20 g) was added dropwise during 20 min to a stirred refluxing mixture of anhydrous 2,3-dimethylbutane-2,3-diol (6.23 g) in dry toluene (50 cm^3). The mixture was heated under reflux for another 30 min, the solvent removed, and the residual yellow syrup was heated at 70 °C *in vacuo* (20 mmHg) for 30 min. The oil crystallized after triturating with hexane (20 cm^3), and recrystallization from hexane–benzene afforded the title complex as hygroscopic colourless prisms, m.p. 123—124 °C (sealed capillary) (Found: C, 53.1; H, 7.2. $C_{16}H_{26}O_6Ti$ requires C, 53.0; H, 7.2%); δ(CDCl$_3$ at 35 °C) 1.3 (12 H, s, diolate CH$_3$), 2.05 (12 H, s, dionate CH$_3$), and 5.68 p.p.m. (2 H, s, CH); $\nu_{max.}$ at 670, 783, 890, 938, 1 153, 1 195, 1 287, and 1 580 cm^{-1}; $\lambda_{max.}$ in hexane 238 (11 000), 271 (15 200), and 324 nm (ε 6 900 dm^3 mol^{-1} cm^{-1}).

Di-isopropoxobis(pentane-2,4-dionato)titanium(IV) (6).—This complex was prepared from tetraisopropoxotitanium(IV) and pentane-2,4-dione according to the literature method,[26] b.p. 119 °C at 0.2 mmHg; δ(CDCl$_3$ at 35 °C) 1.18 (12 H, d, isopropyl CH$_3$), 1.95 (12 H, br s, dionate CH$_3$), 4.71 (2 H, septet, isopropyl CH), and 5.45 p.p.m. (2 H, s, dionate CH).

Dynamic N.M.R. Studies.—Hydrogen-1 n.m.r. measurements were generally made at 100 MHz using a Varian XL-100 spectrometer operating in the continuous-wave mode, although in a few cases (see Table 1) spectra were recorded at 60 MHz using a Perkin-Elmer R-12B instrument. Probe temperatures were determined using a Doric Thermocouple Indicator (readout ±0.1 °C) coupled to a fine copper–constantan thermocouple inserted into the sample at the level of the receiver coil. Temperature measurements were made before and after recording the two sets of bandshapes and the spectra were only accepted if the temperature had remained constant. Rate constants were determined directly from the digitized bandshapes using the multi-site exchange program INMR [27] and the University ICL 1906A computer equipped with a Calcomp plotter. Spectral parameters in the coalescence region were estimated by extrapolation and then adjusted slightly, if necessary, to minimize the standard deviation between calculated and experimental bandshapes.

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REFERENCES

[1] Some recent reviews are J. J. Fortman and R. E. Sievers, *Co-ordination Chem. Rev.*, 1971, **6**, 331; N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, 1972, **17**, 391; R. H. Holm in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 317.

[2] H. C. Longuet-Higgins, *Mol. Phys.*, 1963, **6**, 445.

[3] S. S. Eaton and G. R. Eaton, *J. Amer. Chem. Soc.*, 1973, **95**, 1825.

[4] For related analyses see J. I. Musher, *Inorg. Chem.*, 1972, **11**, 2335; D. G. Bickley and N. Serpone, *ibid.*, 1974, **13**, 2908; D. J. Klein and A. H. Cowley, *J. Amer. Chem. Soc.*, 1975, **97**, 1633.

[5] R. C. Fay and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 348.

[6] D. C. Bradley and C. E. Holloway, *J. Chem. Soc. (A)*, 1969, 282.

[7] R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1967, **6**, 1512; N. Serpone and R. C. Fay, *ibid.*, p. 1835; R. C. Fay and R. N. Lowry, *ibid.*, 1974, **13**, 1309.

[8] J. F. Harrod and K. R. Taylor, *Chem. Comm.*, 1971, 696.

[9] H. Weingarten, M. G. Miles, and N. K. Edelmann, *Inorg. Chem.*, 1968, **7**, 879.

[10] B. Jurado and C. S. Springer, *Chem. Comm.*, 1971, 85; S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1973, **95**, 1116; L. Que and L. H. Pignolet, *Inorg. Chem.*, 1974, **13**, 351 and refs. therein.

[11] W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.

[12] N. Baggett, D. S. P. Poolton, and W. B. Jennings, *J.C.S. Chem. Comm.*, 1975, 239.

[13] R. C. Fay and A. F. Lindmark, *J. Amer. Chem. Soc.*, 1975, **97**, 5928.

[14] P. Finocchiaro, *J. Amer. Chem. Soc.*, 1975, **97**, 4443.

[15] R. R. Shoup, E. D. Becker, and M. L. McNeel, *J. Phys. Chem.*, 1972, **76**, 71.

[16] S. S. Eaton and G. R. Eaton, *J. Amer. Chem. Soc.*, 1973, **95**, 1825.

[17] D. G. Bickley and N. Serpone, *Inorg. Chem.*, 1974, **13**, 2908.

[18] H. C. Longuet-Higgins, *Mol. Phys.*, 1963, **6**, 445.

[19] D. S. P. Poolton, Ph.D. Thesis, University of Birmingham, 1976.

[20] D. G. Bickley and N. Serpone, *Inorg. Chem.*, 1976, **15**, 948.

[21] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 5319; A. Y. Girgis and R. C. Fay, *ibid.*, p. 7061; J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, 1971, **10**, 1004.

[22] E. A. Noe and M. Raban, *J. Amer. Chem. Soc.*, 1974, **96**, 6184.

[23] Y. Shvo, E. C. Taylor, and J. Bartulin, *Tetrahedron Letters*, 1967, 3259.

[24] J. Lemaire, *Chem. Zentr.*, 1909, **80**(1), 1982.

[25] A. Yamamoto and S. Kambara, *J. Amer. Chem. Soc.*, 1957, **79**, 4344.

[26] D. M. Puri, K. C. Pande, and R. C. Mehrotra, *J. Less Common Metals*, 1962, **4**, 393.

[27] J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J.C.S. Perkin II*, 1976, 1052.