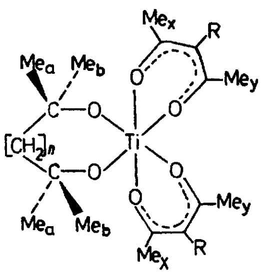
Nuclear Magnetic Resonance Investigation of the Dynamic Stereochemistry of Some Octahedral Titanium(IV) Chelate Complexes

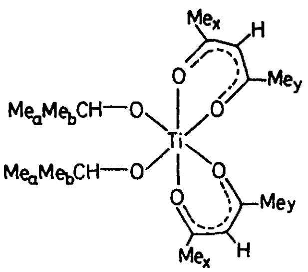
By Neil Baggett, David S. P. Poolton, and W. Brian Jennings*
(*Department of Chemistry, University of Birmingham, P.O. Box* 363, *Birmingham* B15 2TT)

Summary A variable temperature n.m.r. study of some titanium chelates shows that the relative rates of degenerate enantiomerisation and site exchange of the dionato methyl groups vary with structure.

Intramolecular metal-centred rearrangements of octahedral chelate complexes are of considerable interest and have recently been reviewed.[1,2] N.m.r. spectroscopy has been extensively used to investigate site exchange of terminal substituents in the chelate rings. In addition, degenerate enantiomerisation of labile chiral complexes can also be probed with the aid of prochiral substituents.[3] Although the mechanism of rearrangement determines the relative rates of these two processes, no quantitative



(1) $n = 1, R = H$
(2) $n = 0, R = H$
(4) $n = 1, R = COMe$



(3)

experimental investigations of this aspect appear to have been reported for titanium chelates.

We now report the determination of the relative rates of dione methyl site-exchange and degenerate enantiomerisation in some titanium(IV) complexes of the type $M(AA)(BB)_2$ in which the only stereoisomerism possible is enantiomerism [compounds (**1**), (**2**), and (**4**)]. Previous studies on complexes of other metals have generally been complicated by the presence of diastereoisomers or other chelate complexes.[4,5] Diastereoisomerism is possible in the di-isopropoxy compound (**3**), but the n.m.r. spectrum shows only the *cis*-isomer to be present as reported previously by Bradley and Holloway.[6]

At low temperature the ^1H n.m.r. spectra of compounds (**1**)—(**3**) show anisochronous geminal methyl groups (Me_a and Me_b) and acetylacetonato methyls (Me_x and Me_y) indicating that metal-centred rearrangement is slow on the n.m.r. time-scale. The rate of degenerate enantiomerisation (k_1) can be measured from the coalescence of the prochiral geminal methyl group signals and compared with the rate (k_2) of acetylacetonato methyl site exchange (Table).[7]

Table. Dynamic n.m.r. data (100 MHz) for degenerate enantiomerisation (process 1) and acac[a] methyl site exchange (process 2) in compounds (**1**)—(**4**).

Comp.	Solvent	T^b/°C	$\Delta\nu_1{}^c$/Hz	$k_1{}^d/s^{-1}$	$\Delta\nu_2{}^c$/Hz	$k_2{}^d/s^{-1}$	k_1/k_2	$\Delta G_1^{\ddagger e}$ /kJ mol^{-1}	$\Delta G_2^{\ddagger e}$ /kJ mol^{-1}
(**1**)	$CDCl_3$	12	14·6	20·4	5·5	9·6	2·13	62·6	64·3
(**1**)	CS_2	17	17·8	37·2	7·7	19·0	1·96	62·2	63·8
(**2**)	CS_2	−34	15·0	23·9	8·8	22·9	1·04	51·9	52·0
(**2**)	CH_2Cl_2	−45	21·9	18·6	9·3	18·6	1·00	49·7	49·7
(**3**)	CS_2	25	6·2	12·4	11·2	8·8	1·41	66·7	67·5
(**3**)	C_6D_6	28	6·4	13·7	9·3	10·2	1·34	67·1	67·9
(**4**)	$CDCl_3$	−8	16·6	34·5	8·7[f]	16·6	2·07	56·9	58·5

[a] acac = pentane-2,4-dionato. [b] Probe temperature as measured with a copper–constantan thermocouple. [c] Separation of the diastereotopic alcohol ($\Delta\nu_1$) and acac ($\Delta\nu_2$) methyl signals measured at low temperatures, extrapolated to T°, and optimised to afford the best fit between calculated and observed spectra. [d] Site-exchange rates were determined directly from the spectra using a multisite computer program (INMR); see W. B. Jennings, *Chem. Comm.*, 1971, 867. [e] $\Delta G^\ddagger$ values calculated assuming validity of the Eyring equation. [f] Frequency separation of the triac ring methyl signals.

The rate ratio k_1/k_2 has been predicted for rearrangements of $M(AA)(BB)_2$ complexes proceeding *via* various mechanisms and it falls in a narrow range.[1] Activation parameters derived by the dynamic n.m.r. method are known to be associated with large systematic errors, particularly where approximate methods are used to derive exchange rates;[8] hence it is advantageous to compare rates directly in the same sample and at the same temperature, as in this study. Exchange rates were obtained directly from the spectra by complete line-shape analysis and solvents were selected to afford a reasonable separation of the signals in the slow-exchange region (Table). The ratio k_1/k_2 is very sensitive to the structure of the diolato unit and is *ca.* 2·0 for 2,4-dimethylpentane-2,4-diolatobis(pentane-2,4-dionato)titanium(IV) (**1**), *ca.* 1·0 for the 5-membered ring analogue (**2**), and 1·3—1·4 for the di-isopropoxy complex (**3**). Structural differences are also reflected in the variation of $\Delta G^\ddagger$. Dynamic n.m.r. spectra of (**3**) have been investigated previously.[9]

Musher[10] has listed all possible modes of isomerisation of tris chelate complexes. Neither mode M_2 (requiring absence of site exchange in the pentane-2,4-dionato ligands) nor mode M_4 (requiring retention of configuration) can solely account for the observed data for complexes (**1**)—(**3**), whereas modes M_1 or M_3, which may have contributions from bond-rupture and intramolecular twisting processes, are consistent with the results.

Information on the problem of bond-rupture *vs.* twisting was obtained from a study of the 3-acetylpentane-2,4-dionato (triac) complex (**4**). The triac acetyl methyl signal at τ 7·59 remained sharp even at +35 °C indicating that rearrangement is not occurring by a bond-rupture process involving the triac rings (provided that internal rotation in the partly dissociated triac ligand is rapid at this temperature).

We thank Ranks Hovis McDougall (Research) Ltd. for a maintenance grant to D.S.P.P.

(*Received*, 15*th January* 1975; *Com.* 047.)

---

[1] J. J. Fortman and R. E. Sievers, *Co-ordination Chem. Rev.*, 1971, **6**, 331.

[2] N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, 1972, **17**, 391.

[3] W. B. Jennings, *Chem. Rev.*, in the press.

[4] 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 references therein.

[5] B. Jurado and C. S. Springer, *Chem. Comm.*, 1971, 85.

[6] D. C. Bradley and C. E. Holloway, *J. Chem. Soc.* (*A*), 1969, 282. However, this observation does not necessarily preclude isomerisation involving transient formation of the *trans*-isomer.

[7] It is assumed that the 6-membered diol ring in compounds (**1**) and (**4**) is inverting rapidly throughout the temperature range considered. If ring inversion were slow, the methylene protons would be diastereotopic; this signal remained a singlet in the temperature range considered. The barrier to ring inversion in 4,4,6,6-tetramethyl-1,3-dioxan has been reported to be < 30 kJ mol^{-1}, *i.e.* much lower than the barriers reported here: H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magnetic Resonance*, 1969, **1**, 67.

[8] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 1966, **88**, 3185; G. Binsch, *Topics Stereochem.*, 1968, **3**, 97; R. R. Shoup, E. D. Becker, and M. L. McNeel, *J. Phys. Chem.*, 1972, **76**, 71.

[9] Bradley and Holloway[6] observed nonequivalence of the isopropyl methyl groups in (**3**) below 17 °C but rationalised this in terms of restricted rotation. However, the geminal methyl groups are diastereotopic for symmetry reasons even when rotation is free: K. Mislow and M. Raban, *Topics Stereochem.*, 1967, **1**, 1.

[10] J. I. Musher, *Inorg. Chem.*, 1972, **11**, 2335.