The Chemistry of Methyltitanium Trichloride. Part III.[1,2] Oxidation of Six-co-ordinate Complexes of Methyltitanium Trichloride. Variable Temperature Nuclear Magnetic Resonance and Infrared Spectra of Complexes of Methoxytitanium Trichloride with Bidentate Ligands

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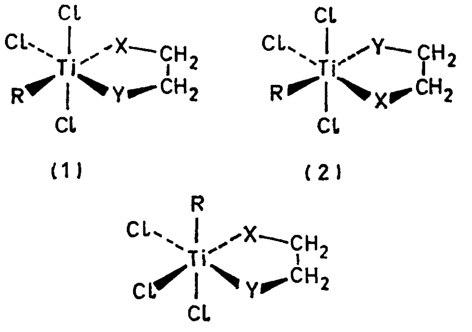
On oxidation, the pseudo-octahedral complexes of methyltitanium trichloride with symmetrical (X = Y) or unsymmetrical (X $\neq$ Y) substituted ethane ligands, $TiCl_3Me,XCH_2CH_2Y$ (X,Y = OMe, NMe_2, or SMe), give the corresponding complexes of methoxytitanium trichloride, $TiCl_3OMe,XCH_2CH_2Y$. Studies by variable-temperature n.m.r. spectroscopy indicate that most of the latter complexes are undergoing exchange between meridional and facial forms at room temperature. Electronic factors affecting the lability of the complexes of titanium(IV) in such exchange processes are discussed. In their i.r. spectra, the complexes of methoxytitanium trichloride all show strong bands *ca.* 1100 and 600 cm^{-1} which may be assigned to ν(C–O) and ν(Ti–O) respectively.

We have previously described the preparation and some properties of the pseudo-octahedral complexes of methyltitanium trichloride with symmetrical[3] and unsymmetrical[2] bidentate ligands of the substituted ethane type. On the basis of variable-temperature n.m.r. studies, it was concluded that they adopt a meridional (*mer*-) configuration [(1,2; R = Me) Figure 1] at low temperatures, the complexes with unsymmetrical ligands preferring to adopt that *mer*-configuration in which the harder ligand atom lies *trans* to the titanium-methyl group. At higher temperatures an exchange process, which apparently does not involve the facial (*fac*-) isomer (3; R = Me), interconverts the two possible *mer*-forms at a rate which is fast on the n.m.r. time scale. We have suggested that the exchange between the *mer*-forms involves an oscillating twist-process[2] and that the *fac*-form must have a significantly higher energy than the *mer*-forms. We also described the products of oxidation of the complexes of methyltitanium trichloride with symmetrical bidentate ligands,[3] concluding, on the basis of i.r. evidence, that they were the corresponding complexes of methoxytitanium trichloride. We have now carried out the oxidation of the complexes of methyltitanium trichloride with unsymmetrical bidentate ligands, and have undertaken a variable-temperature n.m.r. study of the series of complexes of methoxytitanium trichloride thus obtained. It was hoped that, as a result of this study, we might gain some insight into the relative importance of various electronic factors on the lability, in the exchange process mentioned above, of complexes of titanium(IV), particularly as in this system the complication of metal-to-ligand back-bonding is absent. Oxidation of methyltitanium trichloride itself in a hydrocarbon solvent gives a product formulated as $TiCl_3OMe,TiCl_2(OMe)_2$, which apparently results from the disproportionation of the methoxytitanium trichloride initially formed.[4] The preparation of methoxytitanium trichloride has been reported recently.[5]



(1) (2) (3)

(a) X = Y = OMe (b) X = Y = NMe_2 (c) X = Y = SMe
(d) X = OMe, Y = NMe_2 (e) X = OMe, Y = SMe (f) X = NMe_2, Y = SMe

FIGURE 1

RESULTS AND DISCUSSION

The complexes of methoxytitanium trichloride with 1,2-dimethoxyethane, *NNN'N'*-tetramethylethylenediamine, and 2,5-dithiahexane, (I)—(III) respectively, have already been described.[3] Physical and analytical data on the complexes of methoxytitanium trichloride with methyl-β-dimethylaminoethyl ether, methyl-β-methylthioethyl ether and methyl-β-dimethylaminoethyl sulphide, (IV)—(VI) respectively, are reported in Table 1. Data on the chemical shifts of ligand-methyl groups of complexes (I)—(VI), and, for the purposes of comparison, of the corresponding complexes of $TiCl_4$,[2] are given in Table 2.

N.m.r. Spectra and Configurations adopted by the Complexes.—The spectra obtained for each complex are described in turn, and conclusions are drawn as to the configurations adopted. Some implications of the results with regard to electronic factors involved in the lability of the complexes in intramolecular exchange are then discussed. The configurations available to the pseudo-octahedral complexes of methoxytitanium trichloride [(1,2,3; R = OMe) Figure 1] are analogous to those

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[1] Presented in part at the Fifth International Conference on Organometallic Chemistry, Moscow, August, 1971.

[2] Part II, R. J. H. Clark and A. J. McAlees, *Inorg. Chem.*, 1972, in the press.

[3] R. J. H. Clark and A. J. McAlees, *J. Chem. Soc.* (*A*), 1970, 2026.

[4] C. Beerman and H. Bestian, *Angew. Chem.*, 1959, **71**, 618.

[5] V. V. Yastrebov and A. J. Chernyshev, *Zhur obshchei Khim.*, 1970, **40**, 604.

TABLE 1

Physical properties of the complexes of methoxytitanium trichloride with unsymmetrical bidentate ligands

Formula (M = $TiCl_3OMe$)	Colour	I.r. spectrum (cm^{-1})			Analytical data									
					Found (%)					Calc. (%)				
		ν(C–O)	ν(Ti–O)	ν(Ti–Cl)	C	H	Cl	N	Ti	C	H	Cl	N	Ti
(IV) M,$MeO\cdot CH_2\cdot CH_2\cdot NMe_2$	Yellow	1100vs,br	612s	404s *ca.* 350vs,vbr	24·8	5·3	35·85	4·9	16·6	25·0	5·6	36·85	4·85	16·6
(V) M,$MeO\cdot CH_2\cdot CH_2\cdot SMe$	Pale yellow	1104vs	612s	400ms 369vs 298w	19·8	4·35	34·95		16·6	20·6	4·5	36·5		16·45
(VI) M,$Me_2N\cdot CH_2\cdot CH_2\cdot SMe$	Fawn	1106vs 1078vs	605s,asym. 615s,sh	388s,br 345vs,vbr 270vw,sh	22·85	5·5		4·3	15·9	23·65	5·3	34·95	4·6	15·75

TABLE 2

Chemical shifts (τ) of ligand-methyl groups in the complexes of methoxytitanium trichloride, and of titanium tetrachloride, with bidentate ligands

Group	Ligand	Chemical shift in		
		Free ligand	$TiCl_4$ complex	$TiCl_3OMe$ complex (below coalescence point)
–OMe	$MeO\cdot CH_2\cdot CH_2\cdot OMe$		Insol.	6·02 and 6·20 (*mer*)[a]
	$MeO\cdot CH_2\cdot CH_2\cdot NMe_2$	6·70	5·90	5·97 (*mer*);[a] 6·21 (*mer*)[a]
	$MeO\cdot CH_2\cdot CH_2\cdot SMe$	6·73	5·91	5·90 (*mer*); 6·20 (*mer*)
–NMe_2	$Me_2N\cdot CH_2\cdot CH_2\cdot NMe_2$	7·87	7·01	7·16 and 7·25 (*mer*) 7·08 and 7·21 (*fac*)
	$Me_2N\cdot CH_2\cdot CH_2\cdot OMe$	7·80	7·05	7·16 (*mer*);[a] 7·26 (*mer*)[a]
	$Me_2N\cdot CH_2\cdot CH_2\cdot SMe$	7·84	7·05	Not assigned. See text
–SMe	$MeS\cdot CH_2\cdot CH_2\cdot SMe$			7·48 and 7·63 (*mer*) 7·32 and 7·89 (*fac*)
	$MeS\cdot CH_2\cdot CH_2\cdot OMe$	7·95	7·42	7·50 (*mer*); 7·62 (*mer*)
	$MeS\cdot CH_2\cdot CH_2\cdot NMe_2$	7·94	7·37	7·48 (*mer*); 7·64 (*mer*) 7·88 (*fac*)

[a] These figures are for dichloromethane solution. The remainder are for chloroform solution.

already considered[2,3] for the corresponding complexes of methyltitanium trichloride, and the pattern of ligand-methyl peaks to be expected for any particular configuration of a $TiCl_3OMe$ complex should be similar to that already discussed for the same configuration of the analogous $TiCl_3Me$ complex.[2,3]

$TiCl_3OMe,(MeOCH_2\cdot)_2$, (I).—At 27°, complex (I) shows three somewhat broadened peaks (Figure 2a) at τ 6·05, 5·88, and 5·22, which can be assigned to ligand oxygen-methyl, methylene, and titanium oxygen-methyl protons respectively. On lowering the temperature, further broadening of the first two peaks occurs, and finally, the peak due to ligand oxygen-methyl groups is resolved into two peaks in a 1 : 1 ratio (Figure 2b,c); this shows the presence of the *mer*-isomer [(1a ≡ 2a; R = OMe) Figure 1]. At low temperatures, the titanium oxygen-methyl group gives rise to two peaks, one much larger than the other. The larger peak may be ascribed to *mer*-(I), and the smaller one is probably due to the *fac*-isomer [(3a; R = OMe) Figure 1], the single ligand oxygen-methyl peak expected[3] for this isomer being obscured by the methylene absorption.

$TiCl_3OMe,(Me_2NCH_2\cdot)_2$, (II).—The n.m.r. spectrum of complex (II) is invariant with temperature in the range +27 to −60°. The nitrogen-methyl groups give rise to two pairs of peaks, at τ 7·25 and 7·16 and at τ 7·21 and 7·08, showing the presence of both *mer*- (1b ≡ 2b; R = OMe) and *fac*- (3b; R = OMe) forms of this complex (see Figure 1). This is confirmed by the presence of two peaks, at τ 5·40 and 5·33, due to the oxygen-methyl group. Since the nitrogen-methyl resonances are all somewhat close together, it is not possible to decide, on the basis of chemical shifts, which peaks arise from the

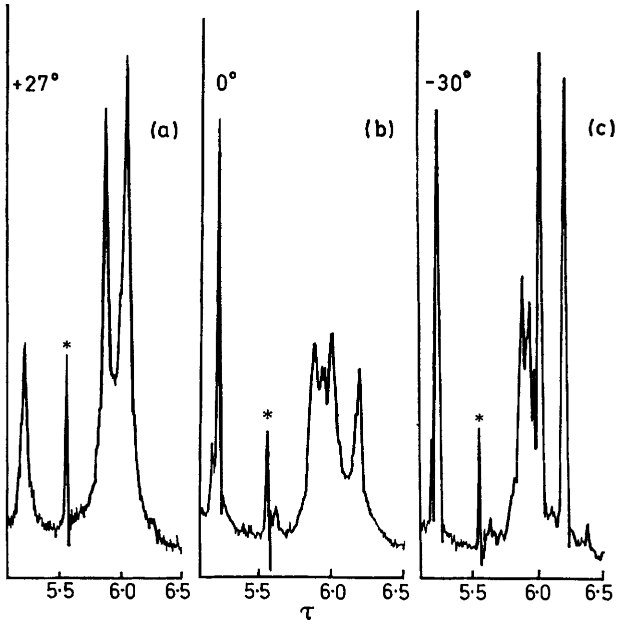

FIGURE 2 N.m.r. spectra (CH_2Cl_2 solution) of the complex $TiCl_3OMe,(MeOCH_2\cdot)_2$ at (a) 27°, (b) 0°, (c) −30°. * ^{13}C side-band due to dichloromethane

mer-isomer and which from the *fac*-isomer. However, since the *mer*-form appears to be preferred in the other complexes of methoxytitanium trichloride, we suggest on intensity (*i.e.* abundance) grounds that the peaks at τ 7·25 and 7·16 are due to *mer*-(II).

$TiCl_3OMe,(MeSCH_2\cdot)_2$, (III).—The changes which occur in the n.m.r. spectrum of complex (III) as the temperature is lowered are quite complex, but can be divided into three stages (i—iii below). At 27°, an averaged spectrum, consisting of three peaks at τ 7·57 (sulphur-methyl groups), 6·84 (methylene groups) and 5·37 (oxygen-methyl group), is observed (Figure 3a).

(i) As the temperature is lowered, broadening of the first two peaks occurs, the peak assigned to sulphur-methyl groups resolving into two peaks (at τ 7·63 and 7·48) at *ca.* −10 to −20° (Figure 3b). (ii) As the temperature is lowered further, additional small peaks build up in the region of sulphur-methyl group resonances at τ 7·89 and 7·32 (Figure 3c). (iii) Finally, lowering the temperature through −60° results in further splitting of the two main peaks in the sulphur-methyl group region (Figure 3d).

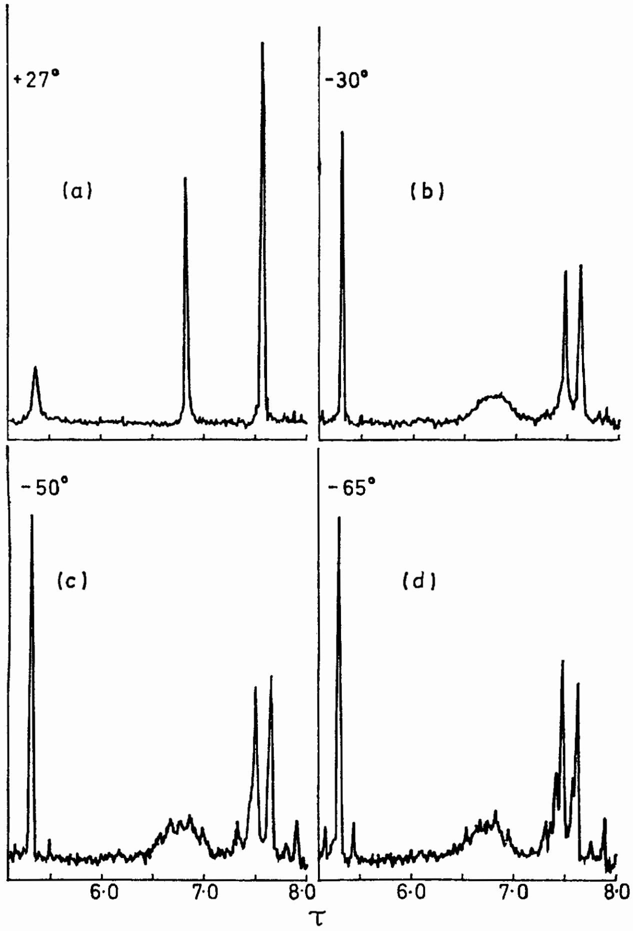

FIGURE 3 N.m.r. spectra of the complex $TiCl_3OMe,(MeSCH_2\cdot)_2$ ($CHCl_3$ solution) at (a) 27°, (b) −30°, (c) −50°, (d) −65°

No splitting of the peak due to oxygen-methyl protons could be detected in this case, implying that the chemical shift difference for this group for different isomers must be small. The two main peaks assigned to sulphur-methyl groups in Figure 3 can be ascribed (*cf.* Figure 1) to *mer*-(III) (1c ≡ 2c; R = OMe), while the minor peaks must arise from the *fac*-isomer (3c; R = OMe). The further splitting of the former pair of peaks must be a result of the slowing of inversion at sulphur on the n.m.r. time scale.[3] No further change in the spectrum of complex (III) was observed at temperatures down to −90°.

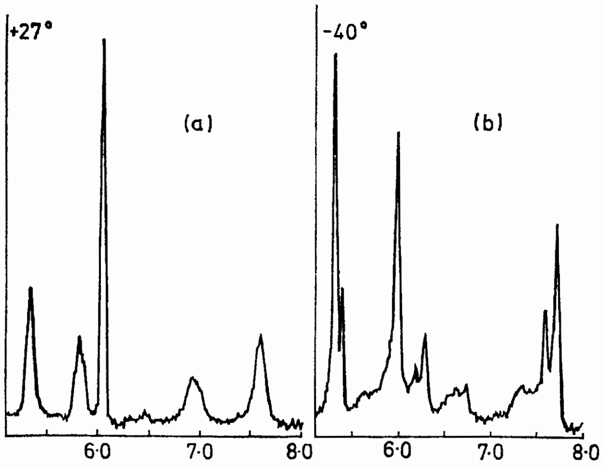

FIGURE 4 N.m.r. spectra ($CHCl_3$ solution) of the complex $TiCl_3OMe,MeOCH_2CH_2SMe$ at (a) 27°, (b) −40°

$TiCl_3OMe,MeOCH_2CH_2NMe_2$, (IV).—The n.m.r. spectrum of complex (IV) varies little with temperature in the range +27 to −60°, but some sharpening of the peaks occurs as the temperature is lowered from +27°. The three principal peaks, at τ 7·26 (nitrogen-methyl), 5·97 (oxygen-methyl), and 5·24 (titanium oxygen-methyl) show the presence of a *mer*-isomer (1d or 2d; R = OMe). The presence of a smaller quantity of the alternative *mer*-isomer is shown by the peaks at τ 7·16 (nitrogen-methyl), 6·21 (oxygen-methyl) and 5·36 (titanium oxygen-methyl). The *fac*-isomer (3d; R = OMe) may be present in small quantity, but cannot be detected in the n.m.r. spectra of complex (IV).

$TiCl_3OMe,MeOCH_2CH_2SMe$, (V).—At 27°, complex (V) gives an averaged n.m.r. spectrum (Figure 4a) with peaks at τ 7·60 (sulphur-methyl), 6·94 (sulphur-methylene), 6·05 (oxygen-methyl), 5·82 (oxygen-methylene), and 5·35 (titanium oxygen-methyl). As the temperature is lowered, these peaks first broaden and finally split, each of the peaks due to methyl groups finally resolving into two peaks of different intensities (Figure 4b). The principal set of peaks in the low-temperature spectrum (Figure 4b), at τ 7·62 (sulphur-methyl), 5·90 (oxygen-methyl), and 5·22 (titanium oxygen-methyl), can be ascribed to one *mer*-isomer (1e or 2e; R = OMe), while the less intense set of three peaks at 7·50 (sulphur-methyl), 6·20 (oxygen-methyl), and 5·29 (titanium oxygen-methyl) can be ascribed to the other *mer*-isomer. These peaks are assigned to the *mer*-isomers (1e, 2e; R = OMe, Figure 1) rather than the *fac*-isomer on the basis of the close agreement between the chemical shifts found for the ligand-methyl groups with the chemical shifts of the same methyl groups in the *mer*-isomers of complexes (I) and (III) (see Table 2).

$TiCl_3OMe,Me_2NCH_2CH_2SMe$, (VI). This complex shows an averaged spectrum at 27° (Figure 5a), the peaks at τ 7·64, 7·18, and 5·31 being attributable to sulphur-methyl, nitrogen-methyl, and oxygen-methyl protons respectively. On lowering the temperature below *ca.* +20°, the peak at τ 7·64 is split into three peaks (Figure 5b), at τ 7·48, 7·64, and 7·88. The first two peaks can be ascribed to sulphur-methyl groups in the *mer*-forms of complex (VI) (1f, 2f; R = OMe), and the third to *fac*-(VI) (3f; R = OMe) (*cf.* Figure 1). The pattern of peaks due to sulphur-methyl groups does not change as the temperature is lowered further, although some broadening of the peak at τ 7·88 is observed at temperatures at and below —60° (Figure 5c, d). However, the pattern of peaks in the nitrogen-methyl group region varies with temperature (Figure 5b, c, d) and, in the intermediate temperature range (*ca.* +10 to —40°), with solvent ($CHCl_3$ or CH_2Cl_2). This is probably due at least in part to the fact that chemical shift differences between nitrogen-methyl groups in different environments is small, so that small changes in chemical shift with temperature give rise to readily observable changes in the overall peak pattern. In addition, the peaks due to nitrogen-methyl groups are superimposed on the methylene proton absorption, so that it is not possible to identify peaks due to individual isomers of complex (VI) with certainty. At the lower temperatures (Figure 5b,c,d) the oxygen-methyl group gives rise to two peaks in dichloromethane, at τ 5·29 and 5·32, the former of which appears somewhat distorted and may in fact consist of two overlapping peaks. In dichloromethane, three peaks can be discerned in this region.

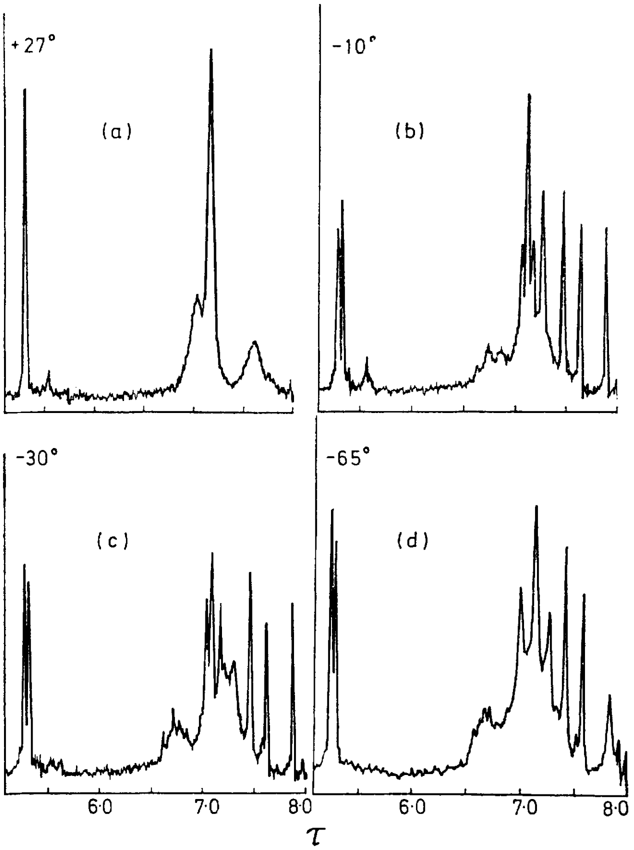

FIGURE 5 N.m.r. spectra ($CHCl_3$ solution) of the complex $TiCl_3OMe,Me_2NCH_2CH_2SMe$ at (a) 27°, (b) —10°, (c) —30°, (d) —65°

General Discussion of the Structures.—In the previous paper of this series,[2] we concluded that the chemical shift of ligand-methyl groups in the pseudo-octahedral complexes of methyltitanium trichloride depends on the nature of the species (Cl or Me) *trans* to the ligand donor atom. Ligand-methyl groups *trans* to chlorine in the complexes of methyltitanium trichloride are found to have chemical shifts very close to the chemical shifts of the same methyl groups in the corresponding complexes of titanium tetrachloride, whereas if they are *trans* to the titanium-methyl group, they resonate at significantly higher fields. If we could apply the same argument to the chemical shifts of ligand-methyl groups in the complexes of methoxytitanium trichloride, then the lower field peaks assigned to *mer*-isomers of complexes (I)—(III) (see Table 2) would result from ligand-methyl groups *trans* to chlorine. However, this assignment cannot be made with any certainty for two reasons. First, the chemical shift differences between ligand-methyl groups *trans* to chlorine and *trans* to methoxy in complexes of methoxytitanium trichloride are much smaller than the chemical shift differences between ligand-methyl groups *trans* to chlorine and *trans* to methyl in the corresponding complexes of methyltitanium trichloride.[2,3] This probably reflects mainly the closer similarity of the σ-electronic effects of chloro- and methoxy-groups compared with chloro- and methyl-groups. Secondly, the titanium-methoxy-group may exert a significant *cis*-influence on the chemical shifts of ligand-methyl groups due to a contribution from $p_\pi \longrightarrow d_\pi$ oxygen $\longrightarrow$ titanium bonding. This is illustrated by the high values of the chemical shifts of sulphur-methyl groups in the *fac*-isomers of complexes (III) and (VI) (Table 2). Evidence for a contribution from oxygen $\longrightarrow$ titanium $p_\pi \longrightarrow d_\pi$ bonding is discussed below. Such bonding has been suggested previously, notably in the case of the complex $[(\pi\text{-}C_5H_5)TiCl_2]_2O$, where an *X*-ray study indicates that the Ti–O–Ti bond system is linear.[6,7]

Now that the n.m.r. spectra of the pseudo-octahedral complexes of methoxytitanium trichloride have been

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[6] P. Corradini and G. Allegra, *J. Amer. Chem. Soc.*, 1959, **81**, 5510.

[7] R. J. H. Clark, 'The Chemistry of Titanium and Vanadium,' Elsevier, Amsterdam, 1968.

described, it is evident that, like the corresponding complexes of methyltitanium trichloride,[2,3] most of them are labile at about room temperature and some exchange process resulting in the interconversion of the possible *mer*- (1,2; R = OMe) and *fac*- (3; R = OMe) forms takes place at a rate which is fast on the n.m.r. time scale. We have already suggested that the exchange process occurring in the complexes of methyltitanium trichloride, which involves only the *mer*-forms (1,2; R = Me), proceeds [2] by an oscillating twist mechanism. For reasons similar to those discussed earlier,[2] we also favour a twist mechanism for the exchange process occurring in the complexes of methoxytitanium trichloride, with the addition of the participation of the *fac*-isomer. For these complexes, in contrast to the methyltitanium trichloride analogues, twisting may also occur about a second type of axis which permits only the interconversion of one *mer*-form and the *fac*-form (Figure 6; R = OMe). If we now compare the results of the n.m.r. study of the complexes of methoxytitanium trichloride with the results already obtained for the corresponding complexes of methyltitanium trichloride,[2,3] it is evident (in the case of the complexes with the symmetrical bidentate ligands) that the former complexes are significantly less labile than the latter. This can be explained if significant oxygen ⟶ titanium $p_\pi \longrightarrow d_\pi$ bonding in the titanium-methoxy group reduces the availability, for the twisting process, of the titanium *d* orbitals not involved in σ bonding. A further indication of the effect of oxygen ⟶ titanium $p_\pi \longrightarrow d_\pi$ bonding is the fact that, for the complexes of methyltitanium trichloride with symmetrical bidentate ligands, the order of labilities for the twisting process is $TiCl_3Me,(MeOCH_2\cdot)_2 > TiCl_3Me,(MeSCH_2\cdot)_2 > TiCl_3Me,(Me_2NCH_2\cdot)_2$, whereas for the corresponding complexes of methoxytitanium trichloride [(I), (III), and (II) respectively] the order is (III) > (I) > (II), *i.e.* the relative labilities of the complexes with the O and S ligands are different. We have already suggested that the lability order $TiCl_3Me,(MeOCH_2\cdot)_2 > TiCl_3Me,(MeSCH_2\cdot)_2$ results from sulphur ⟶ titanium $p_\pi \longrightarrow d_\pi$ bonding in the latter complex.[2] The reversal of this order of labilities in the complexes of methoxytitanium trichloride may mean that the contribution of sulphur ⟶ titanium $p_\pi \longrightarrow d_\pi$ bonding is reduced in complex (III) compared with that in the complex $TiCl_3Me,(MeSCH_2\cdot)_2$ due to the more effective oxygen ⟶ titanium $p_\pi \longrightarrow d_\pi$ bonding. Further support for this suggestion comes from the observation that sulphur-methyl group inversion is observably slow on the n.m.r. time scale at −60° for complex (III), while cooling below −70° is necessary before a similar slowing is evident for the complex $TiCl_3Me,(MeSCH_2\cdot)_2$,[3] *i.e.* the titanium *d* orbitals not involved in σ bonding are rather less available for interaction with the second ligand-sulphur atom lone pair in the former complex (III). On comparison of the labilities of the complexes with unsymmetrical bidentate ligands ($TiCl_3Me,MeOCH_2CH_2NMe_2 > TiCl_3Me,MeOCH_2CH_2SMe > TiCl_3Me,Me_2NCH_2CH_2SMe$; $TiCl_3OMe,MeOCH_2CH_2SMe > TiCl_3OMe,Me_2NCH_2CH_2SMe > TiCl_3OMe,MeOCH_2CH_2NMe_2$), an increase in the relative labilities of the S-containing ligands is again evident on going from the $TiCl_3Me$ complexes to the $TiCl_3OMe$ analogues. Indeed, complex (VI) is more labile than its analogue, $TiCl_3Me,Me_2NCH_2CH_2SMe$, in spite of the presence of oxygen ⟶ titanium $p_\pi \longrightarrow d_\pi$ bonding in the former, this presumably reflecting the smaller energy difference between the different isomers of complex (VI) as compared with the $TiCl_3Me$ analogue. We feel that these observations are entirely consistent with a twist mechanism, but not with a mechanism involving dissociation followed by reassociation,[2] for the exchange process.

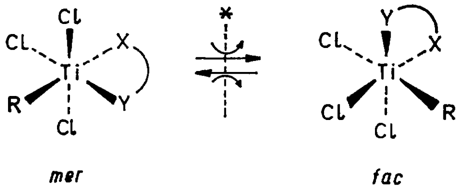

FIGURE 6 The interconversion of the isomers of the complexes of methyltitanium trichloride and methoxytitanium trichloride with bidentate ligands (XCH_2CH_2Y) by a twist mechanism. The reference axis with respect to which twisting is taking place is normal to the plane of the paper. The curved arrows indicate the direction of twist of the front face with respect to the back face, which is kept fixed. * Not observed when R = Me

One further point, concerning the n.m.r. spectra of complexes (III) and (VI), has to be considered. The sulphur-methyl group peak patterns assigned to the *mer*-isomers of these complexes (*vide supra*) and their variation with temperature are analogous to the peak patterns observed for the complexes $TiCl_3Me,(MeSCH_2\cdot)_2$ (1c ≡ 2c; R = Me) and $TiCl_3Me,Me_2NCH_2CH_2SMe$ (1f only; R = Me) respectively, and can be explained similarly.[2,3] However, in the case of complex (III), at least two minor peaks, which apparently can only be due to the *fac*-isomer (3c; R = OMe), are evident already at temperatures just below −20° (Figure 3c). If sulphur-methyl group inversion were still fast in *fac*-(III) (3c; R = OMe) at such temperatures, only a single peak should show in the n.m.r. spectrum, so it would appear that slowing of sulphur-methyl inversion occurs at much higher temperatures in *fac*- (III) than in *mer*- (III). In contrast, visible broadening of the peak assigned to the sulphur-methyl group of *fac*- (VI) (3f; R = OMe) occurs only at and below −60°, a temperature range similar to that in which sulphur-methyl group inversion in *mer*-(III) becomes slow on the n.m.r. time scale. (No further broadening of the peaks assigned to *fac*- (III) was found at temperatures down to −90°.) We are unable to account for these observations.

Infrared Spectra of the Complexes of Methoxytitanium Trichloride.—The complexes of methoxytitanium trichloride were prepared in dichloromethane solution, and isolated by evaporation of the solvent at room temperature. On the basis of the n.m.r. results just discussed, the solids thus obtained probably consist of a mixture of isomers. I.r. data on complexes (IV)—(VI) are given in

Table 1, while similar data for complexes (I)—(III) have been published.[3] Like the last three complexes,[3] adducts (IV)—(VI) show strong bands *ca.* 600 and 1100 cm^{-1} which can be assigned to ν(Ti–O) and ν(C–O) of the titanium-methoxy group respectively. The band *ca.* 600 cm^{-1} appears symmetrical in the spectra of all the complexes except (VI), which gives rise to at least two closely spaced bands in this region (Table 1). Unfortunately, it appears that ν(Ti–O) in the complexes of methoxytitanium trichloride, unlike ν(Ti–C) in the corresponding complexes of methyltitanium trichloride,[2] does not give an indication of the configuration(s) adopted by the complexes in the solid state. Complex (VI), in contrast to the other complexes of methoxytitanium trichloride (I)—(V), shows two bands attributable to ν(C–O) *ca.* 1100 cm^{-1}.

In the region appropriate to ν(TiCl), the adducts of methoxytitanium trichloride show a complex series of broad overlapping bands (Table 1) in the region typical of titanium(IV) complexes.[7,8]

EXPERIMENTAL

Carbon, hydrogen, and nitrogen analyses were performed by the Departmental analyst. Titanium and chlorine were determined as previously.[3]

Spectra.—N.m.r. spectra were run on methylene chloride and chloroform solutions of the complexes (*ca.* 50 g l^{-1}) in sealed tubes using a Varian Associates HA 100 instrument. The τ values reported were calculated assuming that dichloromethane and chloroform resonate at τ 4·67 and 2·76 respectively.[9] The chemical shifts thus determined differed only slightly from one solvent to the other, the largest difference found being 0·06 p.p.m. Temperatures at which the spectra were run are correct to within ±5°.

The i.r. spectra were recorded on Nujol mulls supported between CsI plates on a Perkin-Elmer 225 spectrometer. Mulls were prepared under dry nitrogen in an efficient dry box.

Preparation of the Complexes of Methoxytitanium Trichloride.—Oxidation of the complexes of methyltitanium trichloride [2,3] was accomplished by stirring the complex (2 g) in methylene chloride solution (40—50 ml) under dry oxygen at room temperature.[3] The $TiCl_3OMe$ derivatives thus formed were isolated by pumping off the solvent and drying the resulting solid products for several hours *in vacuo* at room temperature. In certain cases, some precipitation of the $TiCl_3OMe$ complex took place during the reaction. Oxidation of the complex $TiCl_3Me,MeOCH_2CH_2NMe_2$ gave a somewhat brownish yellow solution which tended to give oily material on evaporation of the solvent. A more tractable product was obtained if hexane (15 ml) was first added to the methylene chloride solution to precipitate a small quantity of light brown oil, and leave a clear yellow solution on standing overnight. The yellow solution was then filtered from the oily material and evaporated to give the $TiCl_3OMe$ complex, which tended to come down initially as a yellow oil, but soon solidified after the last traces of solvent had been removed.

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