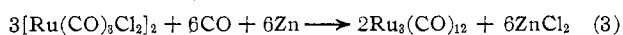
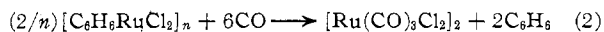
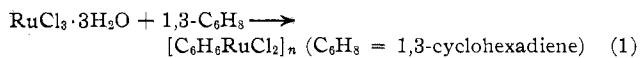


spheric pressures can best be done by the three-step sequence



Combination of steps 2 and 3 into a single step is less satisfactory since under conditions where the coor-

dated diolefin ligands in $[(\text{diene})\text{RuCl}_2]_n$ complexes can be replaced by carbon monoxide, the ultimate product $\text{Ru}_3(\text{CO})_{12}$ undergoes appreciable decomposition with the tetrametallic ruthenium carbonyl hydrides (e.g., $\text{H}_4\text{Ru}_4(\text{CO})_{12}$) among the decomposition products.

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CONTRIBUTION FROM THE CHRISTOPHER INGOLD LABORATORIES,
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The Chemistry of Methyltitanium Trichloride. II. Variable-Temperature Nuclear Magnetic Resonance and Infrared Spectra of Some Complexes of Methyltitanium Trichloride and of Titanium Tetrachloride with Unsymmetrical Bidentate Ligands

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The pseudooctahedral complexes of methyltitanium trichloride with the unsymmetrical bidentate ligands methyl β -dimethylaminoethyl ether, methyl β -methylthioethyl ether, and methyl β -dimethylaminoethyl sulfide are precipitated on mixing hexane solutions of methyltitanium trichloride and the appropriate ligand. They are intensely colored solids, extremely sensitive to atmospheric oxygen and moisture and thermally unstable, decomposing gradually on storage *in vacuo* at room temperature. The nmr spectra of the complexes show that, in solution, they prefer to adopt that meridional configuration in which the harder ligand atom lies trans to the titanium-methyl group. In their ir spectra, the complexes all show bands in the 450–490-cm⁻¹ region, which are assigned to $\nu(\text{Ti-C})$. These bands are absent from the ir spectra of the corresponding complexes of titanium tetrachloride, which we have also prepared and characterized (mainly to assist in the assignment of nmr data). By contrast to the foregoing, the product isolated from the reaction of methyltitanium trichloride with *N,N,N',N'*-tetramethyl-*o*-aminobenzylamine (B) is a titanium(III) derivative which can be formulated as $\text{TiCl}_3 \cdot \text{B}$.

Introduction

In the course of investigations directed toward the elucidation of detailed mechanisms for the action of Ziegler-type catalysts, we have reported,¹ on the basis of the results of a variable-temperature nmr study, that the pseudooctahedral complexes of methyltitanium trichloride with the symmetrical bidentate ligands $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, and $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$ prefer to adopt a mer configuration (I) at low temperatures. At room temperature, the ligand-methyl groups of each complex give rise to a single peak in the nmr spectrum due to the operation of what we have referred to as a primary exchange process, which could involve, e.g., opening and reclosure of the chelate ring, or a twist mechanism. No evidence could be found in the low-temperature spectra for the presence of fac isomer (II) (Figure 1). Indeed the observation that the chemical shift of the titanium-methyl group in each complex remained virtually constant (within 0.02 ppm) throughout the temperature range (+27 to -100°) in which the complexes were examined would suggest that the fac isomer does not participate in the exchange process occurring at the higher temperatures to any significant extent.

The present report is concerned principally with the preparation, properties, and variable-temperature nmr spectra of the complexes (III–V, respectively) of methyltitanium trichloride with the unsymmetrical bidentate ligands $\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, CH_3OCH_2 -

CH_2SCH_3 , and $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{SCH}_3$. An attempt to prepare the complex of methyltitanium trichloride with *o*- $\text{C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_3)_2]\text{N}(\text{CH}_3)_2$ led to the isolation of a 1:1 complex of this ligand with titanium trichloride (VI). We have also prepared the complexes (VII–X, respectively) of these four ligands and of $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (XI)² with titanium tetrachloride. It was hoped that, as a result of this study, we might be able to answer two questions. (i) If, as our earlier investigations suggest, the complexes of methyltitanium trichloride adopt a mer configuration, which of the two possible mer configurations (*vide infra*) would be preferred? (ii) What is the mechanism of the primary exchange process referred to above?

Experimental Section

Spectra.—Nmr spectra were run on methylene chloride solutions of the complexes in sealed tubes using a Varian Associates HA100 instrument. Samples were prepared and chemical shift (τ) values were determined as described previously.¹

Ir spectra were recorded on Nujol mulls using a Perkin-Elmer 225 spectrometer. The samples were prepared under dry nitrogen in an evacuable drybox and placed between thin polythene sheets supported between cesium iodide plates.

Analyses.—Carbon, halogen, and nitrogen analyses were performed by the departmental analyst. Titanium and chlorine were determined as outlined previously.¹

Starting Materials.—The treatment of solvents (hexane and dichloromethane) and titanium tetrachloride and the preparation of dimethylzinc were carried out as before.¹

$\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ was obtained by reaction of β -dimethyl-

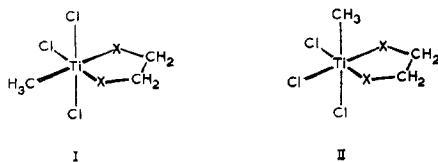
(1) R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. A*, 2026 (1970).

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TABLE I

PHYSICAL DATA ON THE PRODUCTS OF REACTION OF METHYLTIANIUM TRICHLORIDE WITH UNSYMMETRICAL BIDENTATE LIGANDS

No.	Adduct	Color	—Ir spectrum, cm ⁻¹ —		Analytical data, %									
			$\nu(\text{Ti}-\text{C})$	$\nu(\text{Ti}-\text{Cl})$ and $\nu(\text{Ti}-\text{ligand})$	C		H		Cl		N		Ti	
III	$\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Pink rust	473 vs	398 s, 365 vs, 341 s, 290 m	26.5	24.4	5.9	5.75	39.05	38.45	5.15	4.55	17.6	18.25
IV	$\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{SCH}_3$	Maroon	470 m	370 vs, br, 295 w	21.8	21.5	4.75	4.55	38.6	38.7	17.4	18.1
V	$\text{CH}_3\text{TiCl}_3 \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{SCH}_3$	Dark pink	484 m, 459 w	390 s, vbr, 354 vs, 290 m	25.0	23.6	5.6	5.6	36.85	37.45	4.85	4.45	16.6	17.35
VI	$\text{TiCl}_3 \cdot o\text{-C}_6\text{H}_4(\text{CH}_2\text{N}(\text{CH}_3)_2)\text{N}(\text{CH}_3)_2$	Light green	...	382 s, 362 w, 330 w, sh, 315 m, 276 w, sh	39.75	38.75	5.45	5.5	32.0	31.6	8.4	8.35	14.4	14.25

Figure 1.—Mer (I) and fac (II) stereo formulas for the complex $\text{CH}_3\text{TiCl}_3 \cdot \text{XCH}_2\text{CH}_2\text{X}$ ($\text{X} = \text{OCH}_3, \text{N}(\text{CH}_3)_2, \text{or } \text{SCH}_3$).

aminoethyl chloride hydrochloride (Koch-Light) with 2 equiv of sodium methoxide in methanol³ (bp 105°).

$\text{CH}_3\text{OCH}_2\text{CH}_2\text{SCH}_3$ was prepared in two steps from β -methylthioethanol (Fluka). The latter was added dropwise with stirring over a period of 1–1.5 hr to thionyl chloride (1 mol) kept at about room temperature by being cooled in a cold water bath. The evolved gases were absorbed in caustic soda solution. The mixture was stirred overnight at room temperature and then heated for 1 hr on a water bath, during which time darkening of the solution occurred. The reaction mixture was cooled, ether (250 ml) was added, and the resulting solution was shaken with several 50-ml portions of 20% sodium hydroxide solution until all traces of hydrochloric acid and sulfur dioxide had been removed. The ether layer was then dried over magnesium sulfate, filtered, and fractionated to give methyl β -chloroethyl sulfide (yield 90–95%). This product was held under reflux for 16 hr with sodium methoxide (1 equiv) in methanol to give methyl β -methylthioethyl ether, which was isolated by fractional distillation of the solution remaining after filtration of precipitated sodium chloride (yield 70%; bp 131–132°).

$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{SCH}_3$ was obtained by a two-stage methylation of 2-aminoethanethiol (cysteamine). A solution of cysteamine hydrochloride (BDH) in methanol was added to 2 equiv of sodium methoxide in methanol. Methyl iodide (1 equiv) was added to the resulting mixture and the whole was stirred overnight at room temperature. The mixture was then held under reflux for 1 hr, cooled, filtered to remove precipitated salt, and distilled to give methyl β -aminoethyl sulfide (bp 148–150°). N-Methylation of this product was accomplished according to a literature method⁴ (yield, from cysteamine hydrochloride, 72%; bp 158–160°).

N,N,N',N'-Tetramethyl-*o*-aminobenzylamine was prepared according to a published method⁵ but isolated and purified as the dihydrochloride (mp 184–186°, uncorrected) by recrystallization from 95% ethanol. *Anal.* Calcd: C, 52.60; H, 8.03; N, 11.15. Found: C, 50.2; H, 8.15; N, 10.60.

All ligands were distilled under nitrogen from calcium hydride just prior to use.

Reactions with Methyltitanium Trichloride.—The apparatus and procedures employed in the preparation of methyltitanium trichloride and the adducts thereof have been described previously.¹ The reactions involving the substituted ethane ligands proceeded as expected. However, on treatment of methyltitanium trichloride with *N,N,N',N'*-tetramethyl-*o*-aminobenzylamine, a greenish precipitate tinged with orange and

brown was formed immediately. The color of the precipitate became a uniform green on being shaken for about 1 min, and some bubbling due to evolution of a gas was observed. The light green precipitate thus obtained (VI) proved to be a derivative of titanium(III) rather than of titanium(IV).

Preparation of the Adducts of Titanium Tetrachloride (VII–XI).—These adducts precipitated immediately on mixing hexane solutions of equimolar quantities of titanium tetrachloride and the appropriate ligand under dry nitrogen. In the case of the ligand *N,N,N',N'*-tetramethyl-*o*-aminobenzylamine, the adduct tended to come down initially as a dark red oil which rapidly solidified on standing. When precipitated directly as a solid, the adduct (X) is orange.

Results

The products (III–VI) obtained by reaction of methyltitanium trichloride with the unsymmetrical bidentate ligands are listed in Table I, together with infrared and analytical data. As is the case for the analogous adducts with symmetrical bidentate ligands,¹ complexes III–V are extremely sensitive to moisture and oxygen and are thermally unstable, decomposing on storage *in vacuo* at room temperature. Although a proper study of the relative stabilities of these complexes has not been carried out, the apparent stability order is III < IV < V, as judged from their apparent relative rates of decomposition on storage or on standing in methylene chloride solution. Nmr data on these complexes are listed in Tables III and IV, and representative nmr spectra are shown in Figures 2–4. For the purpose of comparison, Tables III and IV also contain nmr data on the previously prepared complexes of methyltitanium trichloride with symmetrical bidentate ligands, as well as nmr data on the adducts of the unsymmetrical bidentate ligands with titanium tetrachloride.

The adducts of titanium tetrachloride (VII–XI) prepared in the present work are listed in Table II along with infrared and analytical data. These are all moisture-sensitive compounds which have to be handled in a dry atmosphere. However, it was observed that hydrolysis of the adduct $\text{TiCl}_4 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ was very slow compared with the rate at which the other adducts were hydrolyzed.

Discussion

The complexes of methyltitanium trichloride with bidentate ligands are assumed to be six-coordinate monomers; no molecular weight determinations on these compounds have been carried out, but this assumption is consistent with the observed solubility and with the nmr properties of the adducts. Three configurations, based on a pseudooctahedron, may be envisaged for the complexes of methyltitanium tri-

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TABLE II
PHYSICAL DATA ON THE ADDUCTS OF TITANIUM TETRACHLORIDE WITH BIDENTATE LIGANDS

No.	Adduct	Color	-Ir spectrum, cm^{-1} $\nu(\text{Ti-Cl})$ and $\nu(\text{Ti-ligand})$	Analytical data, %									
				C		H		Cl		N		Ti	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
VII	$\text{TiCl}_4 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Bright yellow	412 m, sh, 392 s, 371 vs, 298 w	20.5	19.3	4.45	4.35	48.45	48.95	4.8	4.25	16.35	16.6
VIII	$\text{TiCl}_4 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{SCH}_3$	Bright orange-yellow	404 s, sh, 382 vs, 308 w	16.25	16.8	3.4	3.4	47.95	46.7	16.2	16.5
IX	$\text{TiCl}_4 \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{SCH}_3$	Dull yellow	419 w, 402 m, 385 vs, sh, 369 vs, 281 w	19.45	19.6	4.25	4.05	45.9	43.1	4.55	4.4	15.5	16.0
X	$\text{TiCl}_4 \cdot o\text{-C}_6\text{H}_4[\text{CH}_2\text{N}(\text{CH}_3)_2]\text{N}(\text{CH}_3)_2$	Light orange	409 s, 365 vs, br, 309 m	35.9	33.75	4.95	4.85	38.55	37.1	7.6	7.25	13.0	12.55
XI	$\text{TiCl}_4 \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Yellow	400 m, 376 s, sh, 367 vs	23.55	22.65	5.25	5.05	46.45	43.65	9.15	8.55	15.65	15.45

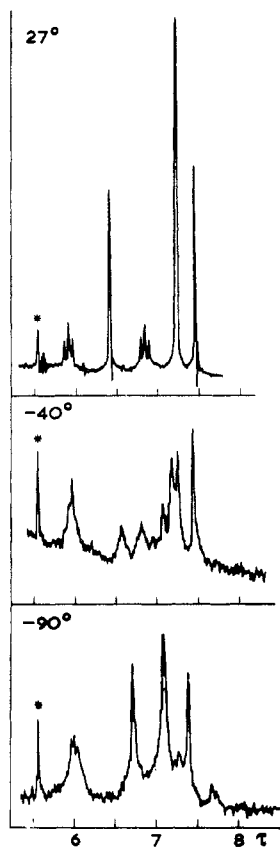


Figure 2.—Nmr spectra of the complex $\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ at 27, -40, and -90°; the asterisk denotes $^{13}\text{C-H}$ side band arising from the solvent (CH_2Cl_2).

chloride with unsymmetrical bidentate ligands. Two of these (XII and XIII) are mer, and one (XIV) is fac (Figure 5). For the fac isomer (XIV) we will refer to the configuration of a ligand-methyl group as syn or anti depending on whether this group lies on the same or the opposite side as the titanium-methyl group of the plane defined by the ligand donor atoms and the titanium atom.

Nmr Spectra.—In the following discussion of the nmr spectra of complexes III–V, inversion at oxygen is assumed to be fast at all temperatures involved.¹ Chemical shift data for ligand- and titanium-methyl groups are collected in Tables III and IV, respectively.

$\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ (III).—If complex III were to adopt a mer configuration (XIIa or XIIIa), the oxygen-methyl and nitrogen-methyl protons should

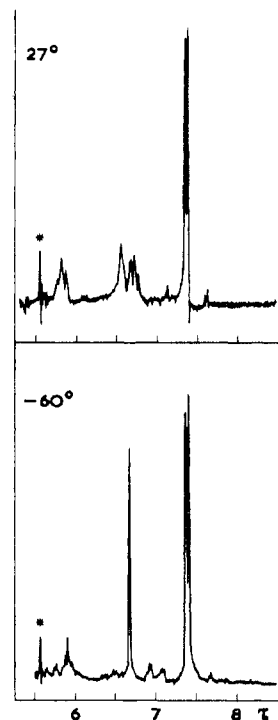


Figure 3.—Nmr spectra of the complex $\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{SCH}_3$ at 27 and -60°.

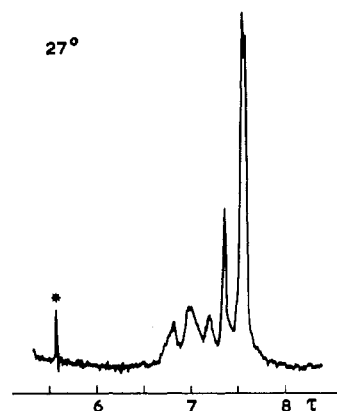


Figure 4.—Nmr spectrum of the complex $\text{CH}_3\text{TiCl}_3 \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{SCH}_3$ at 27°. The apparent broad triplet centered at τ 7.0 is due to the CH_2 protons of the ligand.

give rise to two peaks in the nmr spectrum, in the ratio 1:2, respectively, whereas should it adopt the fac configuration (XIVa), three peaks (ratio 1:1:1, correspond-

TABLE III
CHEMICAL SHIFTS (τ) FOR LIGAND METHYL GROUPS IN THE COMPLEXES OF METHYLTITANIUM TRICHLORIDE AND OF
TITANIUM TETRACHLORIDE, WITH BIDENTATE LIGANDS (METHYLENE CHLORIDE SOLUTION)

Group	Ligand	Chem shifts			
		Free ligand	TiCl ₄ complex ^a	CH ₃ TiCl ₃ complex	
				(a) At 27°	(b) Below coalescence point ^b
-OCH ₃	CH ₃ OCH ₂ CH ₂ OCH ₃	...	Insol	6.32	5.94 and 6.71
	CH ₃ OCH ₂ CH ₂ N(CH ₃) ₂	6.70	5.90	6.43	6.71
	CH ₃ OCH ₂ CH ₂ SCH ₃	6.73	5.91	6.57	6.66
-N(CH ₃) ₂	(CH ₃) ₂ NCH ₂ CH ₂ N(CH ₃) ₂	7.87	7.01	7.31	7.01 and 7.59
	(CH ₃) ₂ NCH ₂ CH ₂ OCH ₃	7.80	7.05	7.17	7.09
	(CH ₃) ₂ NCH ₂ CH ₂ SCH ₃	7.84	7.05	7.54	7.55
-SCH ₃	CH ₃ SCH ₂ CH ₂ SCH ₃	7.54	7.44 and 7.86
	CH ₃ SCH ₂ CH ₂ OCH ₃	7.95	7.41	7.38	7.38
	CH ₃ SCH ₂ CH ₂ N(CH ₃) ₂	7.94	7.37	7.35	7.35
-N(CH ₃) ₂	<i>o</i> -C ₆ H ₄ [CH ₂ N(CH ₃) ₂] ₂	7.63	7.20 (aliphatic)		
		7.20	6.97 (aromatic)		

^a Chemical shifts at 27°. These remained constant to within ± 0.02 ppm when the temperature was lowered to -60° . ^b Chemical shifts measured at such temperatures that further lowering of the temperature produced no observable change in the spectrum. In case of the dithiahexane complex, chemical shifts are those observed at -70° , since on lowering below this point, further splitting of the sulfur-methyl resonances occurs.¹

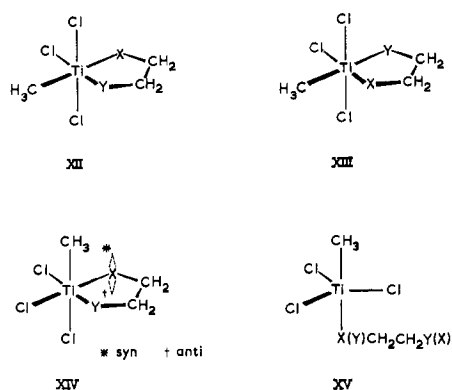


Figure 5.—Stereo formulas of complexes described in the text: (a) X = OCH₃, Y = N(CH₃)₂; (b) X = OCH₃, Y = SCH₃; (c) X = N(CH₃)₂, Y = SCH₃.

ing to O-CH₃, syn N-CH₃, and anti N-CH₃) should be observed. Figure 2 shows representative spectra of III at various temperatures. As the temperature is lowered from 27°, broadening of all peaks in the spectrum including that due to the Ti-CH₃ group is observed. (By contrast the peaks due to TiCH₃ in the complexes of methyltitanium trichloride with symmetrical bidentate ligands remained sharp and at constant resonance position as the temperature was lowered.¹) At around -60° , the peaks assigned to methyl groups (Tables III and IV) have sharpened once more,

TABLE IV
CHEMICAL SHIFTS (τ) FOR TITANIUM-METHYL GROUPS IN
COMPLEXES OF METHYLTITANIUM TRICHLORIDE WITH
BIDENTATE LIGANDS (CH₂Cl₂ SOLUTION)

Adduct	Chem shift (CH ₃ -Ti)
CH ₃ TiCl ₃ ·CH ₃ OCH ₂ CH ₂ OCH ₃	7.41
CH ₃ TiCl ₃ ·CH ₃ OCH ₂ CH ₂ N(CH ₃) ₂	7.38 ^a
CH ₃ TiCl ₃ ·CH ₃ OCH ₂ CH ₂ SCH ₃	7.39 ^a
CH ₃ TiCl ₃ ·(CH ₃) ₂ NCH ₂ CH ₂ N(CH ₃) ₂	7.62
CH ₃ TiCl ₃ ·(CH ₃) ₂ NCH ₂ CH ₂ SCH ₃	7.55 ^a
CH ₃ TiCl ₃ ·CH ₃ SCH ₂ CH ₂ SCH ₃	7.49

^a The chemical shifts were measured below the coalescence points, where they are independent of temperature.

that due to O-CH₃ having moved to higher field and those due to N-CH₃ and Ti-CH₃ having moved to lower field compared with their resonance positions in the spectrum at $+27^\circ$. Little change occurs on low-

ering the temperature further to -90° . These observations indicate that an exchange process, which is fast on the nmr time scale at 27°, is occurring in III. The presence of a single peak due to the N-CH₃ protons in the spectrum at -90° [Figure 2] suggests that III prefers to adopt one of the two possible mer configurations (XIIa or XIIIa) at this temperature. Peaks due to a small quantity of the second mer isomer may lie under the methylene multiplet at $\tau \sim 6$ (O-CH₃) and at $\tau \sim 7.7$ (N-CH₃ and Ti-CH₃). These would be expected to be found at τ 5.9 and 7.6, respectively (*vide infra*).

CH₃TiCl₃·CH₃OCH₂CH₂SCH₃ (IV).—If inversion at sulfur is slow on the nmr time scale,¹ a mer isomer (XIIb or XIIIb) should give rise to three singlets (ratio 1:1:1) due to O-, S-, and Ti-CH₃ groups. The fac isomer should, however, give rise to six peaks, three each from the two forms in which the S-CH₃ group is syn or anti. The nmr spectrum of IV at 27° (Figure 3) shows three peaks due to methyl groups. On lowering the temperature to -60° sharpening of the O-CH₃ peak occurs, and it moves to somewhat higher field, while little or no change occurs in the width and resonance positions of the S-CH₃ and Ti-CH₃ peaks. No significant change occurs in this spectrum on lowering the temperature further to -90° (contrast the behavior of the complex CH₃TiCl₃·CH₃SCH₂CH₂SCH₃¹). As in the case of adduct III, the low-temperature (-60°) spectrum of IV indicates the presence of a single mer isomer (XIIb or XIIIb). No evidence could be found for the presence of some of the second mer isomer at low temperature.

CH₃TiCl₃·(CH₃)₂NCH₂CH₂SCH₃ (V).—A mer isomer (XIIc or XIIIc) of this complex should give an nmr spectrum showing three singlets due to methyl groups if inversion at sulfur is fast and four if it is slow (N-CH₃ may be cis or trans to S-CH₃) while the fac isomer similarly should give rise to four or to eight (four from the isomer having syn S-CH₃ and four more from that with anti S-CH₃). The spectrum of V at 27° shows three peaks due to methyl groups (Figure 4). On lowering the temperature to -90° , the only change observed in the spectrum is the coalescence of the peaks assigned to N-CH₃ and Ti-CH₃ groups. Like the other two adducts (III and IV), complex V apparently favors one of the two possible mer configurations. We cannot say whether the failure to observe four peaks

due to methyl groups at the lowest temperature (-90°) at which V was examined is due to the fact that inversion at sulfur is fast even at -90° or that the chemical shift difference between N-CH₃ cis to S-CH₃ and N-CH₃ trans to S-CH₃ is too small to be observed.

In deciding which of the two possible mer configurations is preferred by the above complexes, attention is drawn to the data in Table III. From this table, it can be seen that on complex formation between titanium tetrachloride and the symmetrical or unsymmetrical bidentate ligands the resonances due to ligand-methyl groups are shifted downfield and that the resonance position of any particular ligand-methyl group (in the substituted ethane derivatives) is fairly constant in all of the complexes of titanium tetrachloride in which it occurs, *viz.*, O-CH₃ at $\tau \sim 5.9$, N-CH₃ at $\tau \sim 7.0$, and S-CH₃ at $\tau 7.4$. On comparing these results with those obtained earlier¹ for the complexes of methyltitanium trichloride with symmetrical bidentate ligands at low temperature (where they were effectively fixed as the mer isomers I), it can be seen (Table III, last column) that the resonance position of the lower field ligand-methyl peaks of the methyltitanium trichloride adducts lies very close to the resonance position of the same ligand-methyl groups in the titanium tetrachloride adducts; *e.g.*, in the low-temperature spectrum of the complex CH₃TiCl₃·CH₃OCH₂CH₂OCH₃, the lower field O-CH₃ peak appears at $\tau 5.94$, while in the titanium tetrachloride complexes VII and VIII it appears at $\tau 5.90$ and 5.91 , respectively. This would suggest that the lower field ligand-methyl groups in the methyltitanium trichloride adducts are in a similar environment to ligand-methyl groups in titanium tetrachloride adducts. Since numerous properties of a ligand in octahedral and square-planar complexes have been found to depend more markedly on the nature of the ligand trans to it than on those ligands in cis positions,⁶ it seems reasonable to suggest that the ligand-methyl groups giving rise to the lower field signal in the complexes of methyltitanium trichloride with symmetrical bidentate ligands are attached to the ligand atom which is trans to the chlorine in the mer complex (I). The higher field shift of some of the ligand-methyl group resonances in the complexes of methyltitanium trichloride compared with their values in the corresponding complexes of titanium tetrachloride is then a result of the trans influence of the Ti-CH group.

The above conclusions can now be used to determine which mer configuration (XII or XIII) is preferred by the complexes III-V; *e.g.*, in complex III, below the coalescence point, the O-CH₃ resonance appears at $\tau 6.71$ (Table III), exactly the same position as the higher field O-CH₃ resonance in the complex CH₃TiCl₃·CH₃OCH₂CH₂OCH₃. This suggests that the O-CH₃ group in III lies trans to the Ti-CH₃ group at low temperature; *i.e.*, III has configuration XIIa. This conclusion is confirmed by the observation that the resonance position of the N-CH₃ group in III at low temperature ($\tau 7.09$) is close to the lower field N-CH₃ resonance position in the complex CH₃TiCl₃·(CH₃)₂NCH₂CH₂N(CH₃)₂ ($\tau 7.01$), as well as to those in the titanium tetrachloride complexes ($\tau 7.01-7.05$), suggesting that the N-CH₃ group is trans to a chlorine

atom. Similarly it can be deduced that the preferred configurations of complexes IV and V are XIIb and XIIc, respectively; *i.e.*, the relative preference of different ligand atoms for the site trans to the Ti-CH₃ group is O > N > S. This conclusion is supported by the observed trans influence of the various bidentate ligands on the resonance position of the Ti-CH₃ group (Table IV).

The changes in the nmr spectra of complexes III-V with temperature may now be readily explained. If, as has been suggested for the complexes of methyltitanium trichloride with symmetrical bidentate ligands (see Introduction), the fac isomer (XIV) does not participate in the exchange process occurring in these complexes, the spectra of III and IV (and possibly V to a small extent) at $+27^\circ$ are averaged, due to the equilibrium XII \rightleftharpoons XIII, which is fast on the nmr time scale. Since the two possible mer forms (XII and XIII) have different energies, the equilibrium lies to the left as indicated above. As the temperature is lowered, not only does the rate of exchange decrease but also the contribution of the less favored isomer (XIII) falls, so that at temperatures where the rate of exchange is slow on the nmr time scale, the proportion of XIII present is small (III) or not detectable (IV and V).

Infrared Spectra.—The complexes of methyltitanium trichloride with unsymmetrical bidentate ligands show a complicated series of overlapping bands in the region *ca.* 400–300 cm⁻¹ (Table I) which can be assigned to Ti-Cl and Ti-ligand stretching vibrations. This pattern is very similar to that already observed for the complexes of methyltitanium trichloride with symmetrical bidentate ligands¹ and is consistent with the presence of titanium in the quadrivalent state. This complex series of bands lies at somewhat lower energies than the corresponding bands for the complexes of titanium tetrachloride (Table II), the shift being consistent with the replacement of a Ti-Cl bond with a Ti-C bond.⁷ As has been observed previously,¹ bands assignable to $\nu(\text{Ti-C})$ are found in the region 450–490 cm⁻¹. Complexes III and IV show a band (at 473 and 470 cm⁻¹, respectively), close to that found for the complex CH₃TiCl₃·CH₃OCH₂CH₂OCH₃ (at 472 cm⁻¹),¹ while complex V shows two bands in this region, one of which (at 484 cm⁻¹) lies close to that in the complex CH₃TiCl₃·CH₃SCH₂CH₂SCH₃ (at 483 cm⁻¹), while the other (at 459 cm⁻¹) lies close to that found for the complex CH₃TiCl₃·(CH₃)₂NCH₂CH₂N(CH₃)₂ (at 462 cm⁻¹).¹ If, as has been found in other instances,⁶ the position of the absorption band arising from a particular metal-ligand bond is influenced principally by the nature of the ligand trans to it, these observations would confirm that in complexes III and IV, in the solid state, the Ti-CH₃ group lies trans to the O-CH₃ group. The infrared spectrum of V, however, suggests that it consists of a mixture of isomers with Ti-CH₃ trans to S-CH₃ in one and to N-CH₃ in the other.

The adoption of the configurations suggested above for the complexes in the solid state may be explained as follows. Attack of a bidentate ligand, XCH₂CH₂Y, on methyltitanium trichloride might occur by preliminary formation of a five-coordinate, trigonal-bi-

(6) See, *e.g.*, L. Venanzi, *Chem. Brit.*, **4**, 162 (1968).

(7) R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965).

pyramidal intermediate (XV) in which the attacking ligand group (X or Y) lies trans to the Ti-CH₃ group and which would give a mer complex (XII or XIII) on ring closure. The nature of the intermediate complex (XV) and that immediately derivable from it by ring closure (XIII or XII) will depend on the relative rates of attack of X and Y on the titanium atom. (Subsequent isomerization may, however, occur in solution.) If, as in our preparations, the methyltitanium trichloride complex is precipitated immediately on mixing the components, the solid obtained may be, at least in part, a consequence of kinetic rather than of thermodynamic factors. The relative rates of attack of X and Y would be expected to depend on at least two factors, *viz.*, the nature of the nucleophilic atom (a hard⁸ atom being expected to attack the hard titanium center more rapidly than a soft nucleophile) and the steric requirements of the reactant (a more highly substituted nucleophile being expected to react more slowly than a less highly substituted one). In the formation of complex III, both factors (and in formation of IV the former factor only) favor initial attack by the oxygen atom with subsequent ring closure giving XIIa (and XIIb). With the ligand (CH₃)₂NCH₂CH₂SCH₃, the former factor favors attack by the nitrogen atom while the latter favors attack by the sulfur atom. The steric factor is apparently sufficiently large that significant preliminary attack by sulfur is obtained to give, after ring closure, complex V with structure XIIc as well as XIIc from initial attack by nitrogen or isomerization of XIIc. On dissolution, XIIc apparently isomerizes virtually completely to XIIc.

The low-energy portion of the infrared spectrum of the product which is formulated as TiCl₃·*o*-C₆H₄·[CH₂N(CH₃)₂N(CH₃)₂] (VI) has an appearance different from that of the same region in the spectra of the adducts of methyltitanium trichloride. No band assignable to $\nu(\text{Ti}-\text{C})$ could be found in the 500–400-cm⁻¹ region, and the bands in the region 400–300 cm⁻¹ are narrow and well defined.

Mechanism of the Exchange Process in the Adducts of CH₃TiCl₃ in Solution.—At least three mechanisms, (i)–(iii) below, may be envisaged for interconversion of the two possible mer forms of the pseudooctahedral adducts of methyltitanium trichloride with bidentate ligands. They are as follows: (i) The chelate ring may open to give a five-coordinate intermediate and then reclose in a different sense to give the isomeric species. (ii) Ionization may take place to give a chloride ion plus a five-coordinate titanium cation, followed by return of the chloride ion to a different site. (iii) Exchange could result as suggested, for example, by Bailar,⁹ from a process involving twisting of one face of the pseudooctahedral complex with respect to the opposite face *via* a trigonal-prismatic intermediate (Figure 6). Twisting may be envisaged as occurring about imaginary axes passing through the centers of opposite faces of the pseudooctahedron. Of the four possible axes, two permit interconversion of both mer forms and a fac form (there are two fac forms, interconvertible formally by interchange of the ligand-CH₃ groups between syn and anti positions) while each of

the other two permits only the interconversion of one mer and one fac form. Since only the first two axes would permit the exchange observed in the present work, twisting about one axis of this type only is illustrated in Figure 6.

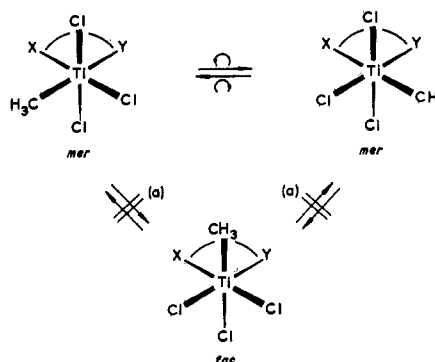


Figure 6.—The interconversion of the isomers of adducts of methyltitanium trichloride with bidentate ligands by a twist mechanism. The reference axis with respect to which the twisting is taking place is normal to the plane of the paper. The arrows indicate the directions of twist of the front face with respect to the back face, which is kept fixed.

Titanium tetrahalides are essentially hard⁸ or class A¹⁰ acceptors and are found to bond somewhat more strongly to hard bases on adduct formation.¹¹ Thus of the three symmetrical bidentate ligands of the substituted ethane type we have used,¹ dimethoxyethane and *N,N,N',N'*-tetramethylethylenediamine should form stronger bonds to methyltitanium trichloride than 2,5-dithiahexane. One might therefore expect that opening of the chelate ring in these complexes to give a five-coordinate intermediate should occur most readily with the sulfur-containing ligand. However, our earlier nmr studies¹ indicate that the complex with dimethoxyethane is the most labile of the three in the exchange reaction. Further, it might be expected that steric factors would favor ring opening of the *N,N,N',N'*-tetramethylethylenediamine complex, but this is considerably less labile than the dimethoxyethane complex. These observations appear to suggest that the exchange process does not involve opening of the chelate ring. The observed relative labilities of the complexes with unsymmetrical bidentate ligands (III > IV > V) are also consistent with this conclusion. Further, the complexes with the harder ligands might be expected to ionize more readily, with ionization being particularly favored by the steric requirements of *N,N,N',N'*-tetramethylethylenediamine ligand. Again, the observed relative labilities of the complexes of methyltitanium trichloride with symmetrical bidentate ligands are inconsistent with this expectation.

We therefore conclude that the most likely mechanism for the exchange process in the complexes of methyltitanium trichloride with bidentate ligands is the oscillating twist process illustrated in Figure 6. The failure to observe the fac isomer in the equilibrium must mean that this isomer has a significantly higher energy than the mer forms. The relative labilities of the complexes

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of methyltitanium trichloride with symmetrical bidentate ligands in the exchange reaction ($N < S < O$)¹ may be explained as follows. Steric hindrance to twisting should be greatest in the complex with the bulkiest ligand, *viz.*, the complex $\text{CH}_3\text{TiCl}_3 \cdot (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, so that this complex exhibits the highest coalescence temperature in the nmr study. If we now consider the complexes $\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ and $\text{CH}_3\text{TiCl}_3 \cdot \text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$, it might be expected that, if steric factors alone were important, the latter complex should undergo exchange more readily since titanium-sulfur bonds would be longer than titanium-oxygen bonds. However, as already noted (*vide supra*), the dimethoxyethane complex is the more labile. This can be rationalized if there is significant

interaction between the second lone pair of electrons on each sulfur atom and empty titanium d orbitals, interaction which would block the empty d orbitals to some extent and hinder the twisting process. The existence of such $p_\pi(\text{S}) \rightarrow d_\pi(\text{Ti})$ bonding has been invoked previously for d^0 complexes to account for the fact that, according to thermochemical measurements, the Zr-S bonds in the complex $\text{ZrCl}_4 \cdot 2(\text{tetrahydrothiophene})$ are stronger than the Zr-O bonds in the complex $\text{ZrCl}_4 \cdot 2(\text{tetrahydrofuran})$.¹²

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Electron Paramagnetic Resonance Studies of the Electronic Structure of Dicyclooctatetraenylvanadium(IV) and Cyclooctatetraenyl(cyclopentadienyl)titanium(III)

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The epr spectra of $\text{V}(\text{C}_8\text{H}_8)_2$ and $\text{Ti}(\text{C}_8\text{H}_8)(\text{C}_5\text{H}_5)$ show both to be sandwich compounds with the unpaired electron in an a_{1g} orbital which is essentially metal d_{z^2} . The Ti compound shows a proton hyperfine structure which must be ascribed to σ bonding.

Introduction

Experimental studies of the electronic structure of organometallic compounds have been relatively common in the last few years. Most of the recent studies have involved the use of nmr or of epr, partly because the optical spectra of organometallic compounds are complicated and hard to interpret.

Much of the recent work has involved dicyclopentadienyl compounds of the iron series elements. Electron paramagnetic resonance studies of $\text{V}(\text{C}_5\text{H}_5)_2$,¹ $\text{Fe}(\text{C}_5\text{H}_5)_2^+$,² and the related $\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2^{2-3}$ have appeared, as have magnetic susceptibility studies of $\text{Ni}(\text{C}_5\text{H}_5)_2^4$ and $\text{Fe}(\text{C}_5\text{H}_5)_2^+.$ ⁵ Photoelectron spectra of $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Ni}(\text{C}_5\text{H}_5)_2$, and $\text{Co}(\text{C}_5\text{H}_5)_2$ have been reported.⁶ There has been, also, an extensive comparison of the nmr contact shifts of iron series dicyclopentadienyl compounds with the predictions of Wolfsberg-Helmholz theory, including both σ and π electrons.⁷

Simple theoretical arguments⁸ suggest that the elec-

tronic structure of the iron series dicyclopentadienyl compounds involves extensive interaction between the $d_{\pm 1}$ orbitals of the metal and the e_1 orbitals of the cyclopentadienyl rings, yielding a low-lying pair of orbitals responsible for the greater part of the ring-metal binding and a high-lying pair of orbitals. Let us call these e_{1g} and e_{1g}^* , respectively. Between the e_{1g} and e_{1g}^* pairs are found, relatively undisturbed, the d_0 and $d_{\pm 2}$ orbitals of the metal. They become a_{1g} and e_{2g} molecular orbitals.

This picture is in accord with the data on iron series dicyclopentadienyl compounds now available. The data on $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ suggest that, in this compound at least, e_{2g} lies above a_{1g} and the similarity between the magnetic properties of $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ and $\text{Fe}(\text{B}_9\text{C}_2\text{H}_{11})_2^{2-}$ suggests that e_{2g} is not much involved with the ligands. The photoelectron spectroscopic data show that a_{1g} is about 0.5 eV below e_{2g} in $\text{Fe}(\text{C}_5\text{H}_5)_2$.

The application of simple theoretical ideas to the cyclooctatetraenide compounds of the iron series suggests that the most important interaction for covalency would be that between the $d_{\pm 2}$ orbitals of the metal and the e_2 orbitals of the cyclooctatetraene dianion but that this should be slightly less than the corresponding interaction in the cyclopentadiene compounds because of geometrical factors. The d_0 and $d_{\pm 1}$ orbitals should be relatively undisturbed. According to Fischer's estimates of ring-metal overlaps and of orbital energies in the $\text{Ti}-\text{C}_8\text{H}_8$ system,⁹ the d_0 overlap with the ring is

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