pot by gas chromatographic fractionation. A trace quantity of a possible hexamethyl derivative, identified by GC/MS, also was observed.[19]

Nuclear Magnetic Resonance. Both ^{11}B (32.1 MHz) and ^{1}H (100.0 MHz) were recorded using a Varian HA-100 spectrometer operating at ambient conditions (Table I). Heteronuclear decoupled spectra were obtained with the auxiliary use of a Nuclear Magnetic Resonance Specialties Model HD-60 decoupler, modified for compatibility with the HA-100. The radiation frequency was controlled by a Hewlett-Packard 200CD wide-range oscillator. Another 200CD oscillator drives a pseudorandom binary noise generator the output of which phase-shifts the radiation frequency. Amplification of this signal by an Electronic Navigation Industries 3201 radiofrequency power amplifier is then applied to the HA-100 probe which has been double-tuned for decoupling.

Registry No. $C_2B_5H_7$, 20693-69-0; 5-$MeC_2B_5H_6$, 23810-32-4; 5,6-$Me_2C_2B_5H_5$, 58548-76-8; 1,5,6-$Me_3C_2B_5H_4$, 58548-77-9; 1,5,-6,7-$Me_4C_2B_5H_3$, 58540-73-1; 1,3,5,6,7-$Me_5C_2B_5H_2$, 18972-11-7.

References and Notes

(1) N. J. Blay, I. Dunstan, and R. L. Williams, *J. Chem. Soc.*, 430, 5006 (1960).
(2) G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. A. Weilmuenster, and A. B. Barrett, *Inorg. Chem.*, 2, 890 (1963).
(3) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, 9, 893 (1970).
(4) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, 88, 628 (1966).
(5) H. V. Seklemian and R. E. Williams, *Inorg. Nucl. Chem. Lett.*, 3, 289 (1967).
(6) J. F. Ditter, E. B. Klusmann, J. D. Oakes, and R. E. Williams, *Inorg. Chem.*, 9, 889 (1970); J. F. Ditter and R. E. Williams, *U.S.N.T.I.S, AD Rep.* AD-729692 (1971).
(7) R. N. Grimes, *J. Am. Chem. Soc.*, 88, 1895 (1966).
(8) (a) R. R. Olsen and R. M. Grimes, *J. Am. Chem. Soc.*, 92, 5072 (1970); (b) R. E. Kesting, K. F. Jackson, E. B. Klusmann, and F. J. Gerhart, *J. Appl. Polym. Sci.*, 14, 2525 (1970).
(9) R. A. Beaudet and R. L. Poynter, *J. Chem. Phys.*, 43, 2166 (1965).
(10) R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Chem. Phys.*, 64, 1583 (1960).
(11) T. Onak, *J. Am. Chem. Soc.*, 83, 2584 (1961).
(12) T. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, 88, 2061 (1966).
(13) T. Onak, D. Marynick, P. Mattschei, and G. Dunks, *Inorg. Chem.*, 7, 1754 (1968).
(14) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 9, 1430 (1970).
(15) A. R. Siedle, G. M. Bodner, A. R. Garber, D. C. Beer, and L. J. Todd, *Inorg. Chem.*, 13, 2321 (1974).
(16) J. B. Leach, G. Oates, S. Tang, and T. Onak, *J. Chem. Soc., Dalton Trans.*, 1018 (1975).
(17) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1797 (1969); T. Onak, D. Marynick, P. Mattschei, and G. B. Dunks, *Inorg. Chem.*, 7, 1754 (1968); T. Onak, D. Marynick, and P. Mattschei, *Chem. Commun.*, 557 (1968).
(18) T. Onak and E. Wan, *J. Chem. Soc., Dalton Trans.*, 665 (1974).
(19) That the MS cutoff for this hexamethyl derivative increased by the mass of a CH_2 group over that of the pentamethyl derivative does not necessarily prove that an additional methyl group is attached to one of the carbons since alternatively it could simply result from an ethyl group attached to one of the boron atoms of the cage rather than a methyl group. Such alkyl growth reactions have been noted before: R. E. Williams, unpublished information. When Me_2BCl and lithium react, peralkyldiboranes are produced: $(CH_3)_2BCl + Li \rightarrow (CH_3)_{4-x}(C_2H_5)_xB_2H_2$ + others. A possible mechanism could involve free radicals and methyl abstraction: $[(CH_3)_3B\cdot] \rightarrow CH_3BHCH_2\cdot$; $CH_3BHCH_2\cdot + (CH_3)_2BCl \rightarrow [CH_3B-HCH_2CH_3]_2 + CH_3ClB\cdot$. Similarly behaving species might be generated from mixtures involving CH_3Cl, $C_2B_5H_7$, and $AlCl_3$.

Contribution from the Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

Complexes of Titanium Tetrachloride with Terdentate Tripod Ligands. Competition among Oxygen, Sulfur, and Nitrogen for Coordination Sites on Titanium

ALAN J. McALEES,* ROBERT McCRINDLE, and ALBERT R. WOON-FAT

The precipitates obtained on mixing hexane solutions of equimolar quantities of titanium tetrachloride and the potentially terdentate tripod ligands $CH_3C(X)(Y)(Z)$ (X = Y = Z = CH_2OMe; X = Y = CH_2OMe, Z = CH_2SMe and CH_2NMe_2; X = CH_2OMe, Y = CH_2SMe, Z = CH_2NMe_2) consist of mixtures of products which may include the corresponding 1:1 complex, products in which oxygen–methyl cleavage has occurred to give a titanium alkoxide, and a 3:2 complex. When the same components are mixed in chloroform, solutions of the 1:1 complexes are obtained. Reactions leading to the other products take place very much more slowly in this case. A variable-temperature NMR study of the chloroform solutions shows that all four ligands act only as bidentates toward titanium and that exchange can take place between free and coordinated ligand atoms. Nitrogen is found to bond more strongly to titanium than oxygen or sulfur, oxygen coordination being preferred to sulfur coordination when nitrogen is already bound, whereas sulfur coordination is preferred to oxygen coordination when oxygen already occupies a site on titanium.

Introduction

Although the complex chemistry of titanium tetrachloride has been the subject of extensive studies,[1,2] there are few reports of investigations of the relative complexing abilities of ligands being of similar types but containing different donor atoms. In an early review[3] of the complexing abilities of metals, Ti(IV) was considered to have class a character; i.e., the order of relative coordinating ability of donor atoms toward the metal is F ≫ Cl > Br > I, O ≫ S > Se > Te, and N ≫ P > As > Sb > Bi. This conclusion was apparently supported by the subsequent observation[4] that whereas urea in the complex $TiCl_4 \cdot 2$(urea) is oxygen bonded, thiourea in $TiCl_4 \cdot 2$(thiourea) is nitrogen bonded. However, the prepa-

ration of stable complexes of $TiCl_4$ with phosphorus-, arsenic-, and sulfur-donor ligands made it appear likely that Ti(IV) has acceptor properties of borderline class a–class b character. Indeed, the ligand in $TiCl_4 \cdot 2$(thioxane) is bonded to titanium via the sulfur atom rather than the oxygen.[5,6] More recently,[7] thermochemical measurements have shown that tetrahydrothiophene bonds to $TiCl_4$ less strongly than tetrahydrofuran but somewhat more strongly than tetrahydropyran.

Reaction of $TiCl_4$ with the terdentate tripod ligands $CH_3C(X)(Y)(Z)$ [X = Y = Z = CH_2OMe (1); X = Y = CH_2OMe, Z = CH_2SMe (2); X = Y = CH_2OMe, Z = CH_2NMe_2 (3); X = CH_2OMe, Y = CH_2SMe, Z = CH_2NMe_2 (4)] in a 1:1 mole ratio was expected to give the

Table I. Analytical Data for Ligands and Organic Intermediates and Ir Data for Ligands

Formula	No.	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	Ir data for the region 1150–450 cm⁻¹
$CH_3C(CH_2OMe)_3$	1	59.23	58.95	11.18	11.18			1111 vs, 1040 w, 1007 m, 983 m, 972 ms, 942 wm, 825 m
$CH_3C(CH_2OMe)_2CH_2SMe$	2	53.91	53.73	10.18	10.19			1120 vs, 1020 w, 999 wm, 973 ms, 934 w, 911 w
$CH_3C(CH_2OMe)_2CH_2NMe_2$	3	61.68	61.85	12.08	11.95	7.99	8.21	1116 vs, 1048 ms, 999 w, 971 m, 914 w, 854 wm
$CH_3C(CH_2OMe)(CH_2SMe)CH_2NMe_2$	4	56.52	56.39	11.07	10.81	7.32	7.12	1114 vs, 1047 s, 987 wm, 967 wm, 937 w, 897 w, 858 wm, 847 wm
$MeOCH_2(CH_3)C(CH_2)_2O$	10	62.04	62.29	10.41	10.54			
$CH_3C(CH_2OMe)_2CH_2OH$	11	56.73	56.77	10.88	11.03			1112 vs, 1063 s, 1002 m, 974 ms, 938 w, 611, 587, 564, 532 all w, overlapping bands
$CH_3C(CH_2OMe)(CH_2NMe_2)CH_2OH$	12	59.59	59.58	11.88	11.92	8.69	8.76	
$CH_3CH_2CH_2C(CH_3)(CH_2OMe)_2$	13	67.45	67.55	12.58	12.35			1113 vs, 1020 wm, 971 ms, 925 wm
$(CH_3)_2C(CH_2OMe)_2$ [a]	14							1123 vs, 997 sh, 970 m, 949 wm, 745 w

[a] The high volatility of this compound made it difficult to obtain reliable analytical data. A mass spectrum was essentially identical with that already published.[10]

Table II. Analytical and Ir Data for the Solid Products Obtained from Reaction of Titanium Tetrachloride with the Ligands 1–4, 11, 13, and 14

Compd no. or source	C Calcd	C Found	H Calcd	H Found	Cl Calcd	Cl Found	N Calcd	N Found	Ti Calcd	Ti Found	Ir data for the range 1150–450 cm⁻¹ [a]
TiCl₄ + 1 [b]	27.30	27.01	5.17	4.85	40.28	39.58			13.61	13.47	1108 s, 1060 ms, 1037 ms, 1033 ms, 1015 s, 980 m, 959 m, 948 m, 944 m, 922 m, 888 m, 862 m, 806 ms, 723 m, 642 m, 564 m, 556 sh, 536 w, 501 vw
TiCl₄ + 1 [c]											1063 s, 1033 m, 1022 ms, 1002 m, 945 wm, 902 wm, 794 wm, 764 m, 725 wm, 646 s, 561 ms, 520 w, 477 vw
TiCl₄ + 1 [d]	27.30	27.48	5.17	5.03	40.28	39.83			13.61	13.44	1110 s, 1065 s, 1040 m, 1016 sh, 1009 s, 983 wm, sp, 963 w, sp, 946 w, 934 w, 927 w, 915 vw, 904 vw, 889 m, sp, 864 m, sp 811 wm, br, 722 m, 644 ms, 564 s, 537 w, 514 w, 502 w
15	21.50	21.11	4.07	4.23	47.60	46.91			16.08	16.36	1065 w, 1024 s, sp, 998 s, sp, 946 w, 930 s, sp, 901 s, sp, 846 w, br, 758 ms, 747 ms, 721 m, 674 vw, 645 w, 562 s, 515 m
16	27.89	28.14	5.02	5.18	35.30	35.48			15.89	15.70	1063 s, 1033 ms, 1019 m, 942 m, sp, 926 m, sp, 911 m, sp, 836 w, sp, 722 w, 644 s, 557 ms, 506 vw, 475 w
TiCl₄ + 2	27.30	27.01	5.17	4.85	40.28	39.58			13.61	13.47	1101 s, 1064 s, 1020 s, br, 913 m, 762 m, br, 738 sh, 724 m, 640 ms, 600 vw, br, 558 vw, 537 m, 482 vw
TiCl₄ + 3	29.61	29.50	5.81	6.19	38.85	38.48	3.84	3.56	13.12	13.46	1100 m, 1063 s, 1034 m, 1020 wm, 981 wm, 917 m, 839 wm, 726 wm, 648 s, 560 m, 536 wm, 498 vw, 476 w
TiCl₄ + 4	28.36 22.72 [e]	23.94	5.55 4.46 [e]	5.35	37.20 44.69 [e]	40.56	3.68 2.94 [e]	3.16	12.57 15.10 [e]	15.40	1090 s, vbr, 876 m, br, 840 wm, vbr, 730 m, 651 m, 551 w, 492 vw

[a] All TiCl₄-containing products show a series of strong broad bands below 400 cm⁻¹, with principal maxima in the range 390–370 cm⁻¹, consistent with the presence of six-coordinate $Ti^{IV}Cl$.[13]   [b] Reaction in hexane.   [c] Initial precipitate from reaction in chloroform. Compound not analyzed.   [d] Reaction with excess ligand in the absence of solvent.   [e] Figures calculated for $3TiCl_4 \cdot 2CH_3C(CH_2OMe)(CH_2SMe)CH_2NMe_2$.

1:1 complexes (**5–8**, respectively) in which three ligand atoms would have to compete for two coordination sites if the titanium atom were to adopt its normal coordination number of 6.[8] However, the usual technique of precipitation of the complexes by mixing solutions of the components in an appropriate solvent gives mixtures of products in this case. Although we have therefore been unable to obtain pure samples of the 1:1 complexes in the solid state, solutions which could be studied by NMR were obtained on mixing TiCl₄ and the appropriate ligand in chloroform.

Experimental Section

Starting Materials. Hexane was dried by refluxing for several hours over calcium hydride followed by distillation under dry nitrogen. Chloroform and dichloromethane were dried over P₂O₅, decanted, and distilled under nitrogen. Ligands were distilled from calcium

hydride at atmospheric pressure and then from lithium aluminum hydride under reduced pressure. Solutions of titanium tetrachloride were prepared immediately before use from freshly distilled material.

Analyses. Carbon, hydrogen, and nitrogen analyses were carried out by Mr. H. S. McKinnon, Guelph, Canada, Galbraith Laboratories Inc., Knoxville, Tenn., and M-H-W Laboratories, Garden City, Mich. Titanium was determined as the dioxide after precipitation from an aqueous solution of the appropriate complex with excess aqueous ammonia. Chlorine was determined as AgCl or by the Volhard method using the filtrate from the titanium determination. Analytical data for organic ligands and intermediates are collected in Table I, while data for complexes are given in Table II.

Spectra. NMR spectra were run on a Varian Associates A-60A instrument using tetramethylsilane as internal standard. Temperatures are only approximate but should be within ±5 °C of the correct value. Ir spectra were recorded for Nujol mulls on a Beckman IR12 spectrophotometer. NMR data for complexes and ligands are collected

Table III. ^{1}H NMR Data for the Ligands 1–4, 13, and 14 and Their Complexes with Titanium Tetrachloride

Compound	No.	Chem shift, τ (CDCl₃ or CHCl₃)						
		C–Me	O–Me	OCH₂	SMe	SCH₂	NMe	NCH₂
CH₃C(CH₂OMe)₃	1	9.03	6.65	6.72				
TiCl₄·1^a	5	9.00	6.48^i	6.37^i				
			5.77	6.01, 5.18^j				
CH₃C(CH₂OMe)₂CH₂SMe^d	2	9.08	6.76	6.86	7.95	7.53		
TiCl₄·2^a	6a	8.86	6.53^i	~6.53^i	7.43	7.00		
			5.73	6.01, 5.15^j				
	6b	8.94	~5.73	5.81, 5.28^j	7.70^i	7.03^i		
CH₃C(CH₂OMe)₂CH₂NMe₂^d	3	9.19	6.78	6.93			7.81	7.87
TiCl₄·3^a	7	8.88	6.56^i	6.43, 6.63^{i,l}			7.05	7.15
			5.68	5.75, 5.27^k				
CH₃C(CH₂OMe)(CH₂SMe)CH₂NMe₂	4	9.04	6.68	6.76	7.88	7.43	7.72	7.72
TiCl₄·4^a	8a	8.75	5.57	5.43	7.72^i	~7^i	~7	7.13
	8b	8.60	6.55^i	~6.55^i	7.27	~7	~7	~7
CH₃CH₂CH₂C(CH₃)(CH₂OMe)₂	13	9.15^g	6.69	6.85				
TiCl₄·13^b	17	8.91	5.85	5.90				
		(8.84)	(5.72)	5.65^j				
(CH₃)₂C(CH₂OMe)₂	14	9.13	6.70	6.88				
TiCl₄·14^c	18	8.92	5.87	5.89				
5-Methyl-5-n-propyl-1,3-dioxane^e		9.08^g		6.51 6.45^h				
5,5-Dimethyl-1,3-dioxane^f		9.05		6.47^h				

^a Resonance positions at −50 °C. ^b Values of chemical shift at +37 °C. Parenthesized values are for −50 °C where some broadening and the onset of coalescence of the –OCH₂– multiplet are evident. ^c Chemical shifts at +37 °C. Little change at −50 °C apart from merging of –OCH₂– and –OCH₃ resonances. ^d Spectra run in CCl₄. Resonances appear ~0.05–0.15 ppm to lower field in CDCl₃. ^e The chemical shift of the C–CH₃ group and the shift difference between the C-4(6) protons found here for CDCl₃ solution are virtually identical with those which can be calculated from literature data[14] for this compound in deuterioacetone at −85 °C. ^f Literature values[15] for a solution in deuterioacetone. Δν at 60 MHz is 25.6 Hz for C-Me groups and 10 Hz for –OCH₂– protons below the coalescence temperature. ^g Chemical shift of quaternary C–CH₃. ^h Chemical shift values for C-4(6) protons only. ^i Uncomplexed. ^j $J \approx$ 12 Hz. ^k $J \approx$ 13 Hz. ^l $J \approx$ 9 Hz.

Scheme I
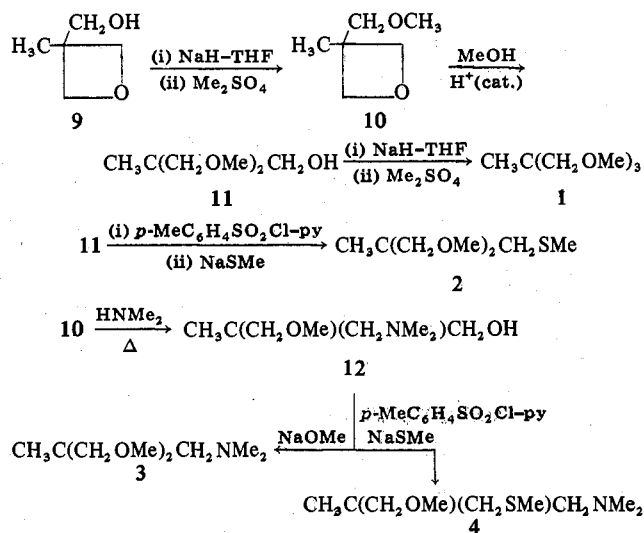
in Table III and ir data are given in Tables II and I, respectively.

The ligands (1–4) were prepared as outlined in Scheme I.

3-Methyl-3-oxetanemethanol (9) was prepared from 1,1,1-tris-(hydroxymethyl)ethane (Aldrich) according to the literature.[9]

3-Methoxymethyl-3-methyloxetane (10). Sodium hydride (39 g, 50% in mineral oil) was added to a solution of 9 (75.3 g) in tetrahydrofuran (1 l.) and the resulting mixture was stirred for 30 min. Dimethyl sulfate (99.0 g) was then added dropwise (exothermic reaction) and the mixture was stirred for 15 h at room temperature. A solution of sodium hydroxide (29.5 g in 50 ml of water) was added and most of the THF was distilled out. The residue was extracted with ether, and the ether extract was dried (Na₂SO₄) and distilled to give 10 (53.9 g, 63%), bp 139–141 °C.

2,2-Bis(methoxymethyl)-1-propanol (11).[10] Concentrated sulfuric acid (3 drops) was added to a solution of 10 (24.1 g) in methanol (100 ml). The solution was heated at the reflux for 4 h; then excess aqueous sodium hydroxide was added and the methanol was distilled. The residue was extracted with ether, and the ether extract was dried

(Na₂SO₄) and distilled to give 11 (24.3 g, 90%), bp 80–82 °C at the water pump. (Water pump pressure in this and subsequent distillations was ~15–20 mmHg).

1,1,1-Tris(methoxymethyl)ethane (1).[10] Methylation of 11 (22.2 g) with NaH–Me₂SO₄ in THF as described for the preparation of 10 gave 1 (16.5 g, 68%), bp 153–155 °C.

1,1-Bis(methoxymethyl)-1-methylthiomethylethane (2). Pyridine (27.0 g) was added to a solution of 11 (24.0 g) and toluene-p-sulfonyl chloride (31.0 g) in benzene (200 ml) and the solution was left for 3 days at room temperature. The resulting mixture was shaken with ice-cold hydrochloric acid (100 ml, 1:1 concentrated HCl–water) and the benzene layer was separated, dried (Na₂SO₄), and evaporated in vacuo to leave a heavy oil (crude tosylate). This was dissolved in methanol (100 ml) a solution of sodium methyl mercaptide (prepared by addition of 7.5 g of MeSH to a solution of 3.6 g of Na in 100 ml of MeOH) was added, and the resulting solution was heated at reflux under nitrogen for 24 h. The methanol was then distilled off and the residue was partitioned between ether and water. Separation of the ether layer and evaporation of the solvent gave an oil whose NMR spectrum showed the presence of unreacted tosylate. The oil was therefore heated at reflux for 3 days with aqueous methanolic (1:1) sodium hydroxide (10 g). The usual ether workup gave a mixture of 2 and 11 (27.3 g). Treatment of the mixture with excess benzoyl chloride in pyridine converted 11 to its benzoate. Workup as described above for the crude tosylate, followed by distillation, gave a fraction (16.2 g), bp 80–84 °C (water pump), containing 2 plus some benzoyl chloride. Hydrolysis of this fraction (aqueous NaOH), ether workup, and distillation finally gave 2 (7.1 g, 24.6%), bp 81–84 °C (water pump).

2-Dimethylaminomethyl-2-methoxymethyl-1-propanol (12). A mixture of 10 (40.0 g) and aqueous dimethylamine (100 ml, 40%) was heated at 220 °C in a 500-ml bomb for 24 h (cf. ref 11). Distillation of the resulting mixture gave impure 12 (20.2 g). Pure 12 (8.5 g, 14.6%), bp 86–88 °C (water pump), was obtained by conversion of the crude material to its benzoate, distillation of the benzoate (bp 165–175 °C at the water pump; checked by NMR), hydrolysis (aqueous NaOH), and ether workup followed by distillation.

1-Dimethylaminomethyl-1,1-bis(methoxymethyl)ethane (3). Triethylamine (12.7 g) was added to a solution of 12 (20.2 g) and toluene-p-sulfonyl chloride (23.9 g) in benzene. Immediate reaction occurred, and the resulting mixture was left for 18 h at room temperature. A solution prepared by dissolving sodium (5.8 g) in methanol (200 ml) was added to the mixture and heated at reflux
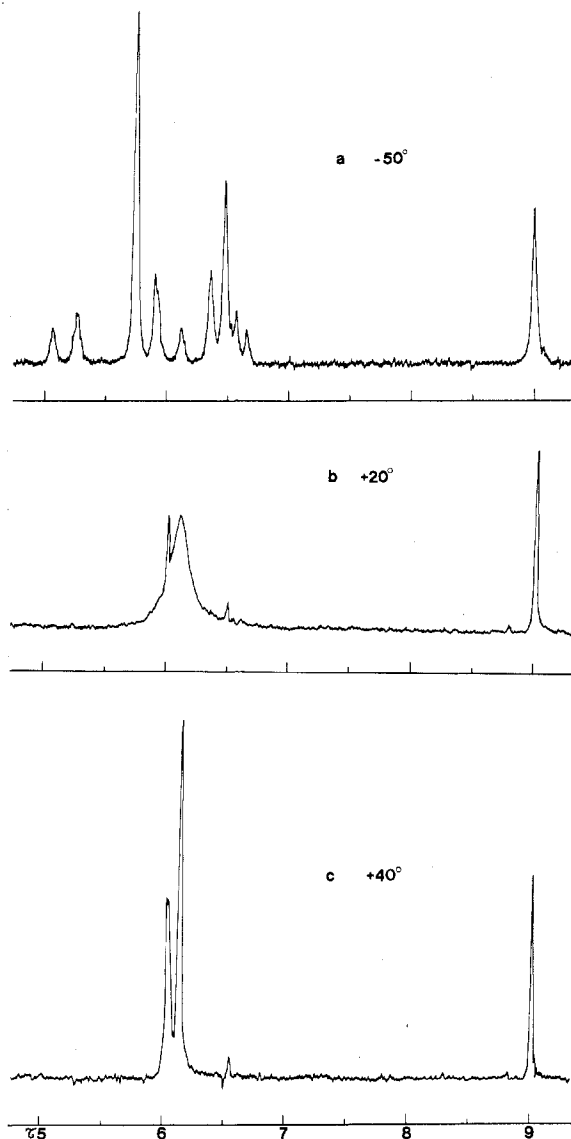
Figure 1. The 60-MHz ^{1}H NMR spectra of the solution obtained on mixing TiCl$_4$ and CH$_3$C(CH$_2$OMe)$_3$ in chloroform (1:1 mole ratio). The additional sharp peak of somewhat variable chemical shift at τ ~6 is due to HCl.[25]

Figure 2. Conformations of the complexes of TiCl$_4$ with terdentate tripod or bidentate ligands and of the corresponding 2-isopropyl-5-methoxymethyl-5-methyl-1,3-dioxanes. ^{1}H NMR data for the latter (CDCl$_3$ solution) are taken from ref 26.

for 24 h. Methanol and benzene were then distilled off and the residue was partitioned between water and ether. The usual workup and distillation gave **3** (14.5 g, 66%), bp 70–72 °C (water pump).

1-Dimethylaminomethyl-1-methoxymethyl-1-methylthiomethylethane (4). Triethylamine (7.0 g) was added to a solution of **12** (11.0 g) and toluene-*p*-sulfonyl chloride (13.3 g) in benzene (50 ml) and the resulting mixture was left for 18 h at room temperature. A solution prepared from sodium (4.0 g) and methanethiol (5.0 g) in methanol (200 ml) was added to the mixture and heated at reflux for 24 h under nitrogen. Workup as for **3** above gave **4** (7.6 g, 58%), bp 88–92 °C (water pump).

2,2-Bis(methoxymethyl)pentane (13), bp 53–54 °C (water pump), was prepared by methylation of 2-methyl-2-*n*-propyl-1,3-propanediol (Aldrich) using sodium hydride and dimethyl sulfate in THF.

2,2-Bis(methoxymethyl)propane (14),[10,12] bp 118–122 °C, was obtained similarly from 2,2-dimethyl-1,3-propanediol (Aldrich).

Reaction of Titanium Tetrachloride with Ligands 1–4. A solution of the appropriate ligand in dry hexane or chloroform was filtered, under dry nitrogen, into an equimolar quantity of titanium tetrachloride in the same solvent cooled to 0–5 °C.

With hexane as solvent, immediate precipitation of yellow solids was obtained. Very fine precipitates formed with ligands **1, 2,** and **3** and prevented filtration of the products which were isolated by pumping off the solvent. The solid obtained from **4** was separated by filtration, washed with fresh hexane, and dried in vacuo. Analytical
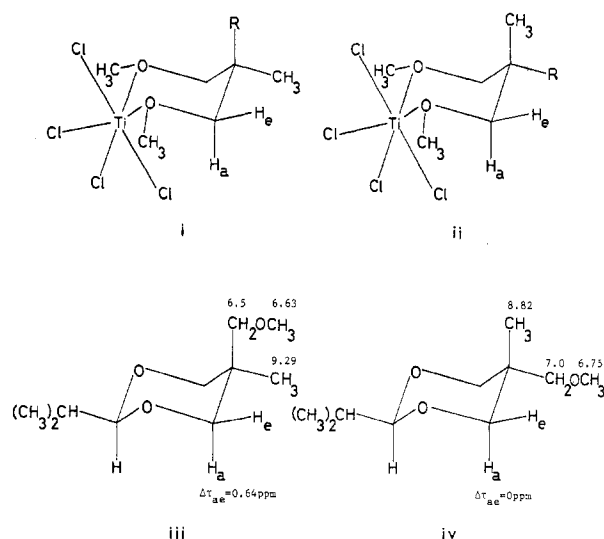
and ir data for these products are collected in Table II. Samples of the solid products were stirred with chloroform, the resulting mixtures were filtered, and the filtrates were examined by NMR spectroscopy with the following results.

TiCl$_4$ + 1. The NMR spectrum of the chloroform extract showed the presence of 1:1 complex and free ligand. See Discussion and Table III.

TiCl$_4$ + 2. The NMR spectrum showed peaks at τ 5.63 and 6.13 (both br s) and 6.18, 6.69, 7.01, 7.12, 7.49, 7.61, 8.94, and 8.97 (all s). Integration was not satisfactory. Some broadening of most peaks was observed on cooling to –50 °C. An extract of a sample of this complex which had been stored in vacuo for over 1 year showed peaks at τ 5.55, 6.12, 6.61, 6.84, 6.98, 7.45, and 8.94.

TiCl$_4$ + 3. The NMR spectrum showed peaks at τ 5.61 (s, 2 H), 6.03 (s, 5 H), 7.21 and 7.23 (br s and s, 8 H), and 9.08 (s, 3 H). Integration was rather unreliable since the solution was very dilute. No change, apart from a slight increase in the resolution of the peaks at τ 7.21 and 7.23, was observed on cooling to –50 °C.

TiCl$_4$ + 4. The chloroform extract of this product gave a very weak solution which showed very broad, ill-defined peaks at τ 6.44, 6.61, 6.83, 7.08, 7.64, and 8.77.

NMR data on the solutions obtained by mixing titanium tetrachloride with each of **1–4** in chloroform are collected in Table III and Figures 1, 3, 4, and 5. The reaction between TiCl$_4$ and **1** gave some precipitate, ir data for which are given in Table II. A small amount of red-orange precipitate was obtained with **4,** but it was not examined further. The solution obtained from TiCl$_4$ and **3** deposited some yellow solid accompanied by a brown gum on storage for some weeks at –10 °C. If the temperature of this solution was allowed to rise to room temperature, rapid deposition of a black tar took place. On standing for a few weeks at –10 °C, the solution obtained from TiCl$_4$ and **2** deposited a small amount of a yellow solid which is slightly soluble in chloroform. The NMR spectrum of this chloroform solution shows peaks at τ 5.53, 6.13, 6.41, 6.60, 6.83, 7.45, 8.84, and 8.93. On lowering the temperature to –50 °C some broadening of all peaks, except that at τ 6.60, takes place, and the peak at τ 6.41 is lost.

Reaction of TiCl$_4$ with Excess CH$_3$C(CH$_2$OCH$_3$)$_3$. Titanium tetrachloride (~1.5 ml) was distilled into a stirred, ice-cooled sample (10 ml) of the ligand (**1**). A yellow solid precipitated immediately and the supernatant liquid remained essentially colorless. The product was filtered, washed with dry hexane, and dried in vacuo. Most of a sample of this material dissolved readily in chloroform.

Preparation of 3TiCl$_4$·2CH$_3$C(CH$_2$OCH$_3$)$_3$ (15). A solution of the ligand (**1**) in dry chloroform was filtered into an ice-cooled, stirred solution of 1.5 molar equiv of TiCl$_4$ in the same solvent. A yellow solid precipitated immediately. This was stirred for 30 min and then filtered, washed, and dried in vacuo. The filtrate was somewhat yellow and deposited solid material which consisted of a mixture of **15** and **16** (see below) on standing. The product **15** is insoluble in chloroform.
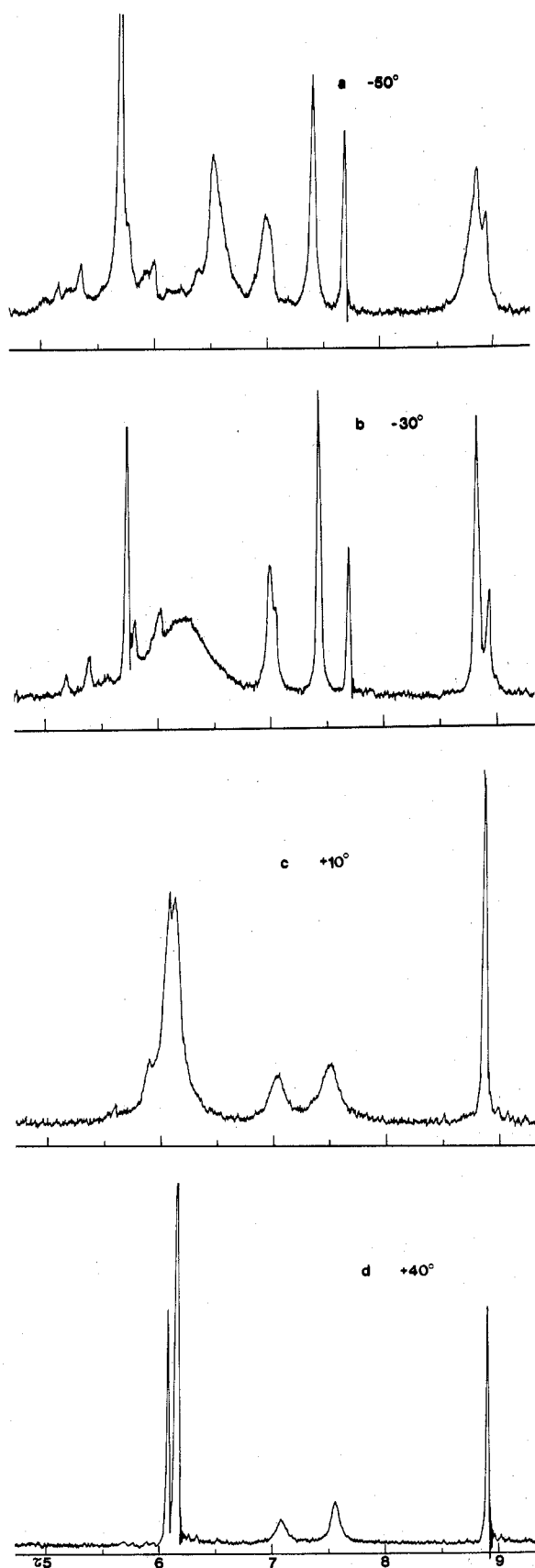
Figure 3. The 60-MHz ^{1}H NMR spectra of the solution obtained on mixing TiCl$_4$ and CH$_3$C(CH$_2$OMe)$_2$CH$_2$SMe in chloroform (1:1 mole ratio).

Preparation of TiCl$_3$OCH$_2$C(CH$_3$)(CH$_2$OCH$_3$)$_2$ (16). Small amounts of water were removed from the ligand (11) by azeotropic distillation with benzene. The alcohol was then heated at reflux for

3 h with magnesium activated with iodine and distilled under dry nitrogen. On mixing equimolar quantities of TiCl$_4$ and 11 in dry dichloromethane, a rapid reaction ensued with evolution of HCl and deposition of a yellow solid. The mixture was stirred and held at a gentle reflux for 1 h. The resulting crystalline product was filtered, washed with dichloromethane, and dried in vacuo. It is slightly soluble in chloroform and somewhat more soluble in dichloromethane. The NMR spectrum (CDCl$_3$) showed peaks at τ 5.64 (br s, 2 H), 6.14 (br s, 10 H), and 9.08 (s, 3 H). On cooling to -50 °C, partial resolution of the peak at τ 6.14 into two peaks is observed.

Preparation of TiCl$_4$·CH$_3$CH$_2$CH$_2$C(CH$_3$)(CH$_2$OCH$_3$)$_2$ (17). The complex was obtained as a yellow precipitate on mixing hexane solutions containing equimolar amounts of TiCl$_4$ and the ligand (13). The solid was filtered, washed with hexane, and dried in vacuo. It is readily soluble in chloroform.

Preparation of TiCl$_4$·(CH$_3$)$_2$C(CH$_2$OCH$_3$)$_2$ (18). The preparation from TiCl$_4$ and 14 was analogous to that described for 17 above.

Results and Discussion

Except where indicated, equimolar amounts of reagents were used in the reactions discussed below.

Reaction of TiCl$_4$ and CH$_3$C(CH$_2$OMe)$_3$. Although the analytical data obtained for the product of reaction of TiCl$_4$ and 1 in hexane (Table II) are in reasonable agreement with those calculated for the 1:1 adduct, the ir spectrum, which shows a large number of bands with similar intensities in the region 1150–800 cm^{-1}, and the fact that most of a sample of the solid would not dissolve in chloroform indicate that it is not the pure adduct (5). However, the NMR spectrum of the chloroform extract showed the presence of 5 and of free ligand (vide infra). On mixing chloroform solutions of TiCl$_4$ and 1, a yellow solution and some yellow precipitate were obtained. The ir spectrum of this precipitate (Table II) is less complex than that of the solid obtained from hexane, and the bands in the former are sharper. In particular, a band at 1108 cm^{-1} (ν(C–O) of uncomplexed ether) in the spectrum of the latter sample is absent from the spectrum of the former. This suggested the possibility of the presence of material of stoichiometry 3TiCl$_4$·2L (L = 1 with all oxygens complexed). Further, a fairly sharp band at $\sim$640 cm^{-1} (ν(Ti–O) in metal alkoxide[16,17]) in the spectra of both products suggested that cleavage of ether linkages by TiCl$_4$ is occurring.[18-24] When the chloroform solution containing TiCl$_4$ and 1 was stored under nitrogen, more solid material was deposited over a period of several days and weeks, and the NMR spectrum of the supernatant liquid showed a buildup of free ligand. Comparison of the ir spectrum of the solid material with that of the initial precipitate showed that while the same bands are present, the relative intensities of certain bands had increased, notably that at $\sim$640 cm^{-1} and a band at $\sim$1060 cm^{-1} (ν-(C–O) of a titanium alkoxide moiety[16,17]). Comparison of these band positions with those assigned[16,17] to ν(Ti–O) ($\sim$600 cm^{-1}) and ν(C–O) ($\sim$1100 cm^{-1}) for a series of six-coordinate complexes of MeOTiCl$_3$ with bidentate ligands might be taken to suggest that cleavage of the ether linkage has taken place to give a Ti–O–CH$_2$–moiety rather than Ti–OMe. Confirmation of this was obtained on examining the NMR spectrum of a sample of the chloroform solution which had been kept for over 1 year. This was still pale yellow in color, but the spectrum showed little other than free ligand plus two sharp singlets at τ 6.02 and 6.98 which can be ascribed to HCl[25] and methyl chloride, respectively. As a result of these observations, authentic samples of the complexes 3TiCl$_4$·2CH$_3$C(CH$_2$OMe)$_3$ (15) and Cl$_3$TiOCH$_2$C(CH$_3$)-(CH$_2$OMe)$_2$ (16) were prepared by reaction of TiCl$_4$ with 1 in chloroform and with the diether alcohol 11 in dichloromethane, respectively. The ir spectra of these products (Table II) show several strong, fairly sharp bands which permitted their ready distinction and their identification in the solid material obtained by reaction of TiCl$_4$ with 1 in hexane or chloroform. Thus, the 3:2 complex (15)

shows strong bands at 1024, 998, 930, and 901 cm^{-1}. Weak bands at 1063 and 645 cm^{-1} probably indicate the presence of some of the cleavage product (16), which itself shows strong bands at 1063 and 644 cm^{-1} and a very characteristic group of three sharp bands of medium intensity at 942, 926, and 911 cm^{-1}. The complete insolubility of 15 precluded NMR investigation of its structure, but the alkoxide complex (16) was sufficiently, though sparingly, soluble in chloroform (or better, dichloromethane) to give a spectrum (Experimental Section) consistent with its being a monomer with both ether oxygens coordinated. In conclusion, the reaction of TiCl$_4$ with 1 in hexane results in the precipitation of a mixture of 1:1 complex (5), 3:2 complex (15), and a cleaved product (16). The precipitate may also contain occluded ligand. The same reaction in chloroform gives mainly 5 initially, the remaining products accumulating slowly at the expense of 5 on standing.

In an attempt to prepare authentic 1:1 complex in the solid state, titanium tetrachloride was distilled directly into excess 1 at 0 °C. The resulting yellow precipitate gave analytical results in good agreement with 1:1 stoichiometry, and most of a sample dissolved readily in chloroform to give a yellow solution, the NMR spectrum of which (vide infra) showed it to be the required complex (5). However, the ir spectrum showed prominent bands at 644 and 1065 cm^{-1} in addition to the bands corresponding to free (1100 cm^{-1}) and complexed (1009 cm^{-1}) ether functions of 5, indicating that this material contained some of the cleaved product (16). In the ir spectrum of a sample of this material which had been stored for about 1 year in vacuo, the peaks at 644 and 1065 cm^{-1} have greatly increased relative intensities, showing that the cleavage reaction can proceed in the solid state.

NMR spectra, at various temperatures, of the solution obtained on mixing TiCl$_4$ and 1 in chloroform are shown in Figure 1. The spectrum at −50 °C (Figure 1a) shows both free and coordinated −CH$_2$OMe groups, from which it can be concluded that 1 acts as a bidentate ligand toward TiCl$_4$. The coordinated −OCH$_2$− protons appear as a widely spaced AB quartet (Table III). The extra peaks at τ 6.57 and 6.65 are due to the presence of some free ligand, this being confirmed by the observed increase in the relative intensities of these peaks (at −50 °C) and of that due to C−CH$_3$ on addition of 1 to the solution. The additional intensity of the peak at τ 5.90 in the AB multiplet is probably due to the presence of HCl.[25] The relative intensity of this peak increased for solutions which were kept for several days or weeks. When the solution is allowed to warm up, noticeable broadening of all peaks, except that due to C−CH$_3$, is observed at ∼−10 °C, and on further warming, all resonances due to methoxy and methylene protons (including those from uncomplexed 1) coalesce to give a broad peak (Figure 1b). Finally, resolution of this peak occurs to give two sharp singlets (Figure 1c). At this stage, exchange of free and coordinated −CH$_2$OMe groups is rapid on the NMR time scale. The AB multiplet in Figure 1a is very reminiscent of those observed for a series of 5,-5-disubstituted 1,3-dioxanes[26] in which the six-membered ring adopts a chair conformation and precludes the possibility that the ring is fixed in a skewed conformation at this temperature. The large chemical shift difference between the components of the AB multiplet is inconsistent with rapidly equilibrating skewed conformations. These observations and analogy with recent studies on six-membered chelate ring complexes[27,28] suggest that only chair conformers need be considered for TiCl$_4$·CH$_3$C(CH$_2$OMe)$_3$ (5). Comparison of the spectrum in Figure 1a with the literature data[26] for the 2-isopropyl-5-methoxymethyl-5-methyl-1,3-dioxanes (Figure 2), which are conformationally rigid at room temperature, suggests that the complex prefers that chair conformation in which the −CH$_2$OMe group is axial (Figure 2i; R = CH$_2$OMe); viz., the

chemical shift difference between the ring methylene protons is large, the −CH$_2$− protons of the uncoordinated −CH$_2$OMe group resonate at lower field than the −Me protons, and the C−CH$_3$ protons resonate at relatively high field (if allowance is made for an additional downfield shift in going from the 1,3-dioxane to the TiCl$_4$ complex; vide infra). Although there may be a rapid equilibrium involving the conformer in which the C−CH$_3$ group is axial[29] (Figure 2ii; R = CH$_2$OMe), the wider separation of the components of the AB multiplet for the complex compared with that for the dioxane model shows that the contribution from this conformer must be less in the former case than in the latter. The literature value[26] of ΔG for the conformational energy difference between the dioxanes indicates that the equilibrium mixture should contain ∼80% of the compound with axial −CH$_2$OMe at −50 °C. The greater preference for the axial orientation of the −CH$_2$OMe group in the complex could reflect the different geometries of the six-membered rings in 5 and the dioxanes and possibly a reduction in the steric requirements of the axial oxygen lone pairs in the former relative to the latter. Another possibility we have considered is that there is some weak bonding interaction between the oxygen of the free −CH$_2$OMe group of 5 and the titanium atom. Examination of a model of the complex suggests that some flattening of the six-membered ring about the −O−Ti−O− region relieves interactions between Cl atoms and coordinated −OMe groups and possibly between a Cl atom and the axial hydrogens of the ring. This distortion might also reduce a "rabbit ear" interaction[30] between the ring oxygen lone pairs. As a result, the free ether oxygen can be brought to a distance of ∼2.7–2.8 Å from the Ti atom if the axial ether function is rotated to bring it over the ring.

In order to obtain some idea as to whether or not the greater axial preference of −CH$_2$OMe in 5 compared to the corresponding dioxane is due to differences in ring geometry, we have prepared the complex TiCl$_4$·CH$_3$CH$_2$CH$_2$C(CH$_3$)-(CH$_2$OMe)$_2$ (17). The n-propyl group should have similar steric requirements to −CH$_2$OMe but is unable to interact with the titanium. The NMR spectrum of 17 (Table III) shows a clearly resolved AB quartet for the ring −CH$_2$− protons at room temperature. On cooling to −50 °C, some broadening of this multiplet was observed. Spectra were run at temperatures down to −95 °C (CH$_2$Cl$_2$ solution) in an attempt to resolve the resonances for the individual conformers (Figure 2i and ii; R = CH$_2$CH$_2$CH$_3$) of 17, but, although the AB multiplet appeared to have coalesced at ∼−60°, spectra at lower temperatures were still broadened.[31] However, the separation of the components of the AB multiplet at room temperature (0.27 ppm) is significantly greater than that observed (0.06 ppm; Table III) for 5-methyl-5-n-propyl-1,3-dioxane. Since it has been estimated[14] that the two chair conformers of the dioxane contribute equally to the equilibrium, this observation indicates that one possible conformer of 17 (Figure 2i or ii) is preferred to some degree. Using the literature data[14] for 5-methyl-5-n-propyl-1,3-dioxane and the observed AB multiplet separation (0.27 ppm) for complex 17 it can be calculated that the equilibrium for 17 involves either ∼70% or ∼20% of that conformation in which the n-propyl group is axial. A tentative decision in favor of the latter was made on the basis of the chemical shift of the quaternary C−CH$_3$ group in the spectrum of 17 (τ 8.84 at −50 °C). Thus, comparison of the chemical shifts in the complex TiCl$_4$·(C-H$_3$)$_2$C(CH$_2$OCH$_3$)$_2$, 18, and in 5,5-dimethyl-1,3-dioxane[15] (Table III) indicates that C-5 C−CH$_3$ groups have similar shift values in both when axial but resonate 0.3 ppm to lower field in 18 vs. the dioxane when equatorial. On this basis the anticipated shift value for the quaternary C−CH$_3$ group in 17 can be calculated as τ 8.97 (70% n-Pr axial) or 8.87 (20% n-Pr axial). An increased axial preference of the −CH$_2$OMe group

in **5** compared with the corresponding dioxane is the opposite of what would be expected if similar steric factors are operative for the $-CH_2OMe$ and $-CH_2CH_2CH_3$ groups. Thus some attractive interaction between the free oxygen and titanium in complex **5** may have to be considered to account for the axial preference of the $-CH_2OCH_3$ group.

Reaction of TiCl₄ and CH₃C(CH₂OMe)₂CH₂SMe. Analysis of the material which precipitated on mixing hexane solutions of TiCl₄ and **2** gave figures (Table II) in good agreement with the stoichiometry 1:1. However, the ir spectrum of the solid and the NMR spectrum of a chloroform extract showed it to be a mixture. Thus, the ir spectrum (Table II) shows bands at 1101 and 1020 cm⁻¹ indicative of both free and complexed ether functions, which suggest the presence of a six-coordinate complex in which the sulfur atom and one ether oxygen are bonded to titanium.[32] However, the spectrum also shows strong bands at 1064 and 640 cm⁻¹, strongly reminiscent of the bands found for the ether cleavage product **16**, so that it can be concluded that C–O cleavage is a significant side reaction in this case also. When fresh, a fair amount of a sample of the precipitate obtained from hexane dissolved in chloroform to give an orange-yellow solution. The NMR spectrum of this solution (Experimental Section) shows the presence of at least two products, the principal one of which is probably the 1:1 complex (**6**). Particularly noticeable in the spectrum is a broadened singlet at τ 5.53, which did not change on lowering the temperature to –50 °C and which can be ascribed to Ti–O–C*H₂*–, confirming the conclusion reached on the basis of the ir data. Material precipitated from hexane and stored for about 1 year in vacuo was markedly less soluble in chloroform, and the resulting very weak solution showed peaks (Experimental Section) which could be ascribed to the complex TiCl₃·OCH₂C(CH₃)(CH₂OMe)CH₂SMe, in which both ether and sulfide are coordinated, but no complex **6**, showing that as with **5**, cleavage of C–O in **6** can take place in the solid. This solution also showed peaks at τ 6.61, which we are unable to explain, and 6.98, which is probably due to CH₃Cl.

The orange-yellow solution obtained on mixing chloroform solutions of TiCl₄ and **2** deposited a small amount of a yellow solid on standing for a few weeks. The ir spectrum of this material is similar to that described for the solid obtained from TiCl₄ and **2** in hexane, but the relative strength of the bands due to the cleaved product has increased. However, in contrast to what was found for the precipitate obtained from TiCl₄ and **1** in chloroform, this material still showed some absorption at ~1100 cm⁻¹, possibly indicating the presence of uncoordinated ether. The solid was slightly soluble in chloroform, and the NMR spectrum shows all of the peaks found (with the exception of that at τ 6.98) for the solid precipitated from hexane after prolonged storage (vide supra).

NMR spectra of a freshly prepared solution of TiCl₄·CH₃C(CH₂OMe)₂CH₂SMe (**6**) are shown in Figure 3. The spectrum at –50 °C (Figure 3a and Table III) shows the presence of two isomers. In the major isomer, **6a**, one oxygen and the sulfur are coordinated, while in the minor isomer, **6b**, both oxygens are coordinated and sulfur is free; i.e. **2** acts only as a bidentate ligand toward TiCl₄. The AB multiplets for the ring $-CH_2O-$ protons in both cases again indicate that chair forms of the six-membered rings are involved. The separation (0.86 ppm) of the components of the ring AB multiplet corresponding to **6a** suggests that the uncoordinated $-CH_2OMe$ group prefers the axial orientation (Figure 2i; R = CH₂OMe; replace one ring O with S). The spectrum of this isomer should show two additional AB multiplets. One, due to the $-CH_2$ protons of the uncoordinated $-CH_2OMe$ group, is obscured by the broadened peak at τ 6.53, and the other, due to the ring $-CH_2S-$ protons, appears as a broadened
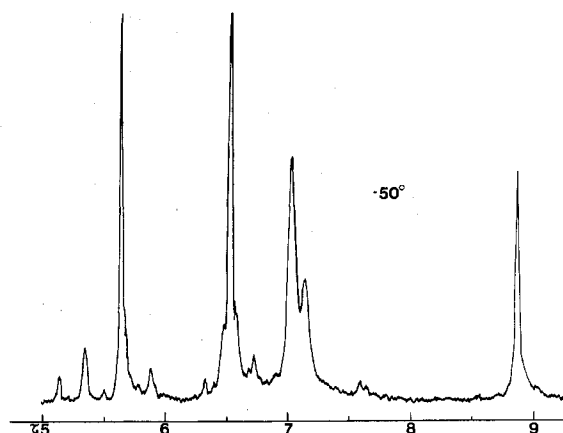

Figure 4. The 60-MHz ¹H NMR spectrum of the solution obtained on mixing TiCl₄ and CH₃C(CH₂OMe)₂CH₂NMe₂ in chloroform (1:1 mole ratio).

peak at τ 7.00. The resonance position of the C–CH₃ protons in **6a** (τ 8.86) cannot be used to indicate whether the methyl group prefers the axial or equatorial orientation, since, if the literature[15] values for axial (τ 9.12) and equatorial (τ 8.84) methyls in 5,5-dimethyl-1,3-oxathiane are employed, the approximate resonance positions expected for axial and equatorial methyls in **6a** are τ 8.82 (9.12–0.3) and 8.84, respectively.

When the temperature of the chloroform solution of **6** is allowed to rise to –30 °C (Figure 3b), the peaks due to coordinated and free $-CH_2OMe$ groups of **6a** broaden and coalesce. The only other observable change in the spectrum is some sharpening of the resonances due to coordinated $-SCH_2-$ and $-C-CH_3$ in **6a**. The observations show that exchange of free and coordinated $-CH_2OMe$ groups in **6a** is becoming rapid on the NMR time scale, while any exchange involving sulfur is slow. The sharpening of the peak due to coordinated $-SCH_2-$ is consistent with their becoming equivalent when $-CH_2OMe$ groups are exchanging. Free sulfur is unable to undergo rapid exchange with coordinated oxygen under these conditions, as shown by the fact that no observable change has occurred to those peaks corresponding to **6b**. Exchange involving sulfur only becomes evident when the temperature is raised somewhat further (Figure 3c), and even at +40° (Figure 3d), the peaks due to $-SCH_2-$ and $-SMe$ protons are still broad.

Reaction of TiCl₄ with CH₃C(CH₂OMe)₂CH₂NMe₂. Once again, the analytical figures obtained for the product of reaction of the components in hexane are in reasonable agreement with the stoichiometry 1:1, and indeed, the ir spectrum of this material shows bands which can be ascribed to both free (1100 cm⁻¹) and coordinated (1034, 1020 cm⁻¹) ether functions, suggesting the presence of 1:1 complex (**7**) in which the nitrogen and one ether oxygen are bound to titanium. However, the most prominent bands in the ir spectrum (above 450 cm⁻¹) appear at 1063 and 648 cm⁻¹, indicating the presence of the product TiCl₃·OCH₂C-(CH₃)(CH₂OMe)CH₂NMe₂, in which O–CH₃ cleavage has occurred. The precipitate obtained from hexane was almost insoluble in chloroform, but the NMR spectrum of an extract (Experimental Section) was consistent with that expected for this cleavage product.

The NMR spectrum, at –50 °C, of a solution prepared from TiCl₄ and **3** in chloroform (Figure 4), shows clearly that **3** acts as a bidentate ligand toward TiCl₄, the nitrogen atom and one oxygen being coordinated while one oxygen remains free. Weak absorption at τ 7.65 and 7.60 (Figure 4) could be due to the presence of some of that isomer in which both oxygens are coordinated while nitrogen is free or possibly to some excess

free ligand. The smaller separation of the components of the AB multiplet due to the ring $-OCH_2-$ protons of this complex (7) compared with those of **5** and **6a** and the lower field position of the peak due to the $C-CH_3$ protons of **7** (Table III) suggest that the chair conformation in which the uncoordinated $-CH_2OMe$ group is axial is relatively less favorable for **7** than for **5** or **6a**. This is not unexpected, since one of the *N*-methyl groups in **7** would have to adopt an axial orientation, thereby giving rise to a 1,3-diaxial interaction with either the free $-CH_2OMe$ or the $C-CH_3$ group (Figure 2i and ii; R = CH_2OMe; replace one ring OMe with NMe_2). Such an interaction would probably reduce the axial affinity of the $-CH_2OMe$ group to a greater extent than that of the $-CH_3$ group[26] and would certainly block any interaction of the former, when axial, with titanium. The *N*-methyl groups and $N-CH_2-$ protons of **7**, which should be nonequivalent, appear as rather broad singlets at -50 °C (Figure 4). On warming up the solution to -10 °C, the peak due to the former sharpens somewhat while that due to the latter broadens and splits, possibly reflecting some temperature dependence of chemical shifts, since the remainder of the spectrum is unchanged. As the temperature is allowed to approach 20 °C, rapid decomposition[33] of the sample occurs with formation of a black insoluble tar, but there is little or no indication of the onset of exchange of free and coordinated $-CH_2OMe$ groups.

Reaction of $TiCl_4$ with $CH_3C(CH_2OMe)(CH_2SMe)-CH_2NMe_2$. In contrast to what was found with ligands 1–3, reaction of $TiCl_4$ with **4** gave a solid for which analysis indicates considerable deviation from 1:1 stoichiometry, and an approach to 3:2 stoichiometry (Table II). The ir spectrum of this material shows few bands, and these are mostly rather broad. Although difficulties in mulling this material meant that spectra obtained were of rather poor quality, a band at 651 cm^{-1} probably shows the presence of some product of $O-CH_3$ cleavage, the expected accompanying band at ~ 1060 cm^{-1} being obscured by a broad band centered at 1090 cm^{-1}. Chloroform extracts of this product gave very weak solutions which showed broad peaks in the regions expected for $-OMe$ and SMe groups in the free ligand, while absorption which presumably corresponded to NMe groups was shifted to lower field (Experimental Section). It seems likely that the chloroform solution contained protonated ligand,[34] although we have not investigated this further. Confirmation of the occurrence of $O-CH_3$ cleavage was obtained when the solid was hydrolyzed and the liberated ligand extracted with ether and distilled. The NMR spectrum of the distillate (bp 180–200 °C) showed peaks corresponding to both the starting ligand (**4**) and the compound $CH_3C(CH_2SMe)(CH_2NMe_2)CH_2OH$.

NMR spectra of the solution obtained on mixing $TiCl_4$ and **4** in chloroform are shown in Figure 5. The spectrum at -50 °C (Figure 5a, Table III) shows that **4** acts as a bidentate ligand toward $TiCl_4$ and that the major component in solution is the complex (**8a**) in which nitrogen and oxygen are bonded while sulfur is free. Some of the complex (**8b**) in which nitrogen and sulfur are bonded while oxygen is free is also present, but none of the third possible isomer, with free nitrogen, can be detected. In contrast to the earlier examples, (**5, 6a, 6b, 7**), the ring $-OCH_2-$ protons of **8a** appear as a somewhat broadened singlet, which may suggest that this complex prefers that chair conformation in which the $-CH_2SMe$ substituent is equatorial (Figure 2ii; R = CH_2SMe; replace one OMe with NMe_2). Both the $-NCH_2-$ and $-SCH_2-$ protons in **8a** should give rise to AB multiplets, but the resonances due to these protons are superimposed on each other, on the broadened singlet due to the nonequivalent *N*-methyl groups, and on resonances due to **8b**. As the temperature is raised, some sharpening of these resonances occurs (Figure 5b), and the peak due to uncoordinated
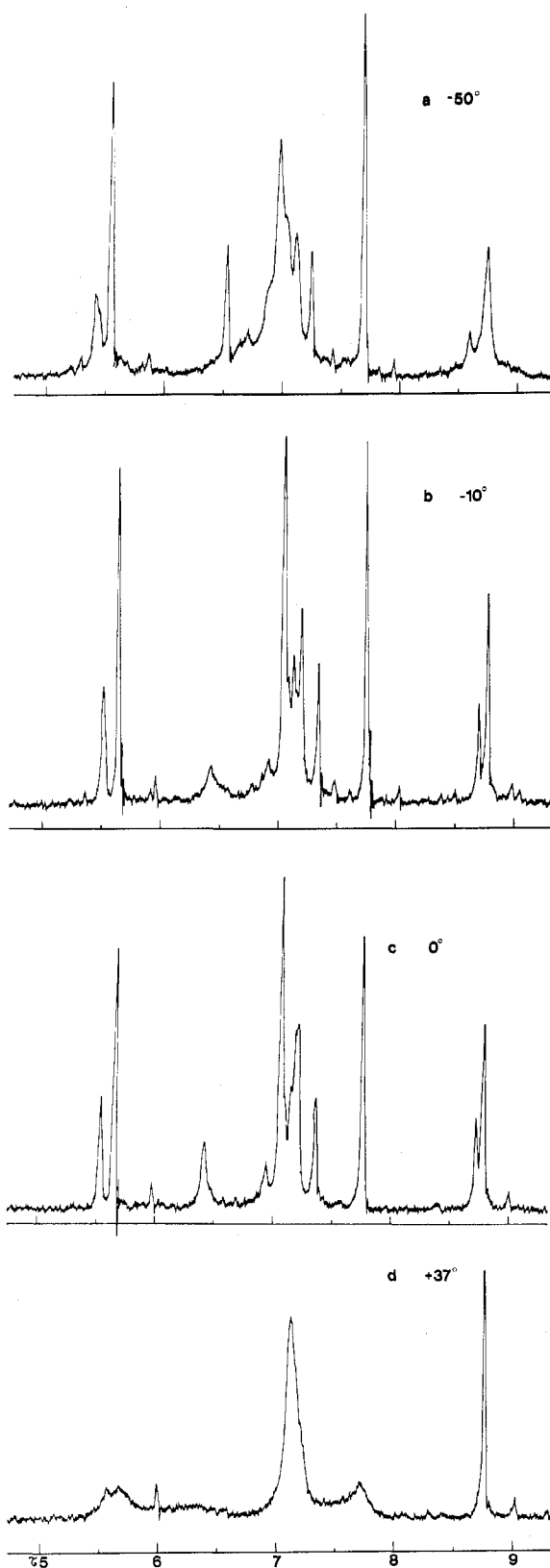

Figure 5. The 60-MHz ^{1}H NMR spectra of the solution obtained on mixing $TiCl_4$ and $CH_3C(CH_2OMe)(CH_2SMe)CH_2NMe_2$ in chloroform (1:1 mole ratio).

$-CH_2OMe$ (the AB multiplet expected for the $-OCH_2-$ protons is not resolved) of **8b** broadens and moves somewhat downfield. Since the resonance due to coordinated–SMe remains sharp during this process, it cannot involve exchange of free oxygen with coordinated sulfur. The only explanation

we are able to suggest is that the solution contained a slight excess of TiCl₄ which is exchanging among the uncoordinated oxygens of **8b**. Similar exchange involving sulfur in **8a** might not be noticeable since there is much more free sulfur available than free oxygen, and coordination to oxygen results in larger downfield shifts for neighboring C–H protons than coordination to sulfur. On further increasing the temperature, the resonance due to free –CH₂OMe sharpens once more (Figure 5c) and finally all resonances begin to broaden (Figure 5d). At this stage, exchange between oxygen and sulfur is becoming fast on the NMR time scale, while, by analogy with the results for **7**, any exchange involving nitrogen is probably still slow.

Conclusions

The attempted isolation of 1:1 complexes of TiCl₄ with the ligands **1–4**, by precipitation from hexane, gives mixtures, which in all cases contain product in which cleavage of an *O*-methyl group has occurred. The mixtures may also contain complex of stoichiometry 3TiCl₄·2L (L = **1, 2, 3,** or **4**), although this has been established conclusively only for the case where L = **1**. Some authentic 1:1 complex is present in the mixtures obtained from **1** and **2**, and ir evidence suggests that it is also present in the product from **3**, although it could not be extracted with chloroform. The product obtained from **4** would appear to have contained little or no 1:1 complex. It is possible that some reduction of titanium to Ti(III) occurred in the reactions with **3** and **4**.

Solutions of the 1:1 complexes can be obtained by mixing the components in chloroform, in which medium the side reactions of ether cleavage and formation of insoluble 3:2 complex occur relatively slowly, thereby permitting NMR studies of the 1:1 complexes. The information thus obtained shows that Ti(IV), in TiCl₄, bonds to nitrogen more strongly than to oxygen or sulfur. The relative binding affinities for the last two depend on the nature of the other ligand atom attached to TiCl₄. Thus, if one available coordination site is occupied by nitrogen, oxygen is bound in preference to sulfur at the remaining site. If the first site is occupied by oxygen, then sulfur is bound in preference to oxygen at the second site. These observations can be rationalized by considering that the most favorable combination of ligand atoms allows optimization of the relative contributions of polar and covalent components to the titanium–ligand atom bonds.

Finally, the conclusion that the potentially terdentate ligands **1–4** act as bidentates toward TiCl₄ led us to reexamine the published data[35] on the analogous arsine complex TiCl₄·CH₃C(CH₂AsMe₂)₃. It was concluded[35] that all three arsenic atoms are coordinated since all of the arsenic–methyl groups resonate downfield from their resonance position in the free ligand. Comparison of shift differences is complicated by the fact that the spectrum of the complex was run in nitrobenzene, while that of the ligand was run in deuteriochloroform. However, the downfield shift found for one pair of arsenic–methyl groups is only 0.3 ppm[36] compared with 0.8 ppm for the other two pairs. Examination of the data in Table III shows that the resonance positions of the uncoordinated –OMe and –SMe groups in the TiCl₄ complexes are about 0.15 ppm downfield of the resonance positions in the free ligands (CHCl₃ solution). If allowance is made for a similar downfield shift for arsenic–methyl resonances, it seems clear that one arsenic in TiCl₄·CH₃C(CH₂AsMe₂)₃ is uncoordinated. A similar conclusion can be reached on the basis of the shifts observed for the As–CH₂– protons (τ 7.70, AB multiplet, bonded; 8.03, free in complex; 8.27, free ligand).

References and Notes

(1) R. J. H. Clark, "The Chemistry of Titanium and Vanadium", Elsevier, Amsterdam, 1968, pp 68–84.
(2) R. Feld and P. L. Cowe, "The Organic Chemistry of Titanium", Butterworths, London, 1965, pp 114–128.
(3) S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev., Chem. Soc.,* **12**, 265 (1958).
(4) R. Rivest, *Can. J. Chem.,* **40**, 2243 (1962).
(5) G. W. A. Fowles and R. A. Walton, *J. Chem. Soc.,* 4330 (1964).
(6) E. C. Alyea and E. G. Torrible, *Can. J. Chem.,* **43**, 3468 (1965).
(7) B. Hesset and P. G. Perkins, *J. Chem. Soc. A,* 3229 (1970).
(8) Although seven- and eight-coordinate complexes of TiCl₄ are known, these are apparently formed only by phosphorus or arsenic donors with low steric requirements: W. P. Crisp, R. L. Deutscher, and D. L. Kepert, *J. Chem. Soc. A,* 2199 (1970).
(9) D. B. Pattison, *J. Am. Chem. Soc.,* **79**, 3455 (1957).
(10) The mass spectrum of this compound has been described, but it was not characterized further: H. F. Grutzmacher and J. Winkler, *Org. Mass Spectrom.,* **1**, 295 (1968).
(11) H. Reiff, D. Dieterich, R. Braden, and H. Ziemann, *Justus Liebigs Ann. Chem.,* 365 (1973).
(12) A minor product of the reaction (CH₃)₂C=CH₂ + H₂C(OMe)₂ [BF₃] → etc. was thought to have this structure. However the reported boiling point is 149–152 °C (745 mm): O. C. Dermer and J. J. Hawkins, *J. Am. Chem. Soc.,* **74**, 4595 (1952).
(13) R. J. H. Clark, *Spectrochim. Acta,* **21**, 955 (1965).
(14) V. I. P. Jones and J. A. Ladd, *J. Chem. Soc. B,* 567 (1971).
(15) H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magn. Reson.,* **1**, 67 (1969).
(16) R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. A,* 2026 (1970).
(17) R. J. H. Clark and A. J. McAlees, *J. Chem. Soc., Dalton Trans.,* 640 (1972).
(18) Cleavage of diisopropyl ether[19] and of cyclic ethers bearing an α-methyl substituent[20–22] occurs readily on reaction with TiCl₄ at room temperature or low temperature. The same reaction of *n*-alkyl ethers requires significantly more drastic conditions (>100 °C),[23,24] cleavage of the longer alkyl chain being preferred in unsymmetrical ethers. The relative difficulty of cleavage of methyl ethers is shown by the finding that anisole is unaffected on heating with TiCl₄, whereas alkyl group cleavage occurs with homologous aralkyl ethers under the same conditions.[24]
(19) P. M. Hamilton, R. McBeth, W. Bekebrede, and H. H. Sisler, *J. Am. Chem. Soc.,* **75**, 2881 (1953).
(20) N. I. Shuikin and I. F. Belskii, *Dokl. Akad. Nauk SSSR,* **111**, 1048 (1956).
(21) N. I. Shuikin, I. E. Grushko, and I. F. Belskii, *Dokl. Akad. Nauk SSSR,* **141**, 649 (1961).
(22) N. I. Shuikin, I. F. Belskii, and I. E. Grushko, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1486 (1962).
(23) P. Mastagli, C. Gnanadickam, and G. Garat, *C. R. Hebd. Seances Acad. Sci.,* **250**, 4381 (1960).
(24) C. Gnanadickam, *Ann. Chim. (Paris),* **7**, 807 (1962).
(25) A solution prepared by bubbling HCl into CDCl₃ showed a sharp singlet at τ 9.18. Addition of **1** to this solution (~4 mol/mol of HCl) caused this singlet to shift to τ 6.03.
(26) E. L. Eliel and R. M. Enanoza, *J. Am. Chem. Soc.,* **94** 8072 (1972).
(27) W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, *Can. J. Chem.,* **53**, 366 (1975), and references therein.
(28) T. G. Appleton and J. R. Hall, *Inorg. Chem.,* **10**, 1717 (1971).
(29) Inversion at oxygen is expected to be fast at all temperatures employed for NMR, so that the coordinated –OMe groups remain equatorial. Coordinated –SMe probably behaves similarly, cf. ref 16.
(30) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *J. Am. Chem. Soc.,* **90**, 7174 (1968).
(31) The coalescence point for 5-methyl-5-*n*-propyl-1,3-dioxane has been estimated to be –57 °C.[14] The coalescence temperature for **17** might be expected to be lower than this if some analogy can be drawn between the complex and 2,2-disubstituted 1,3-dioxanes.[15]
(32) Unfortunately, no band which might be ascribed to ν(C–S) could be detected in the ir spectrum of the ligand so that confirmation of Ti–S bonding is not possible.
(33) Decomposition may be due to reduction of the titanium by the ligand. Reduction of Ti(IV) has been reported to occur when TiCl₄ is allowed to react with *N*-methylmorpholine[5] and other nitrogen-containing ligands.
(34) This would most likely arise from some hydrolysis of complex during extraction, although it is not impossible that it could have been formed as a result of reduction of Ti(IV) by the ligand.
(35) R. J. H. Clark, M. L. Greenfield, and R. S. Nyholm. *J. Chem. Soc. A,* 1254 (1966).
(36) This relatively small downfield shift was regarded as being significant, since the free arsenic-methyl resonance for the complex W-(CO)₄CH₃C(CH₂AsMe₂)₃,[37] where the ligand is bidentate, appears at τ 9.02 (nitrobenzene; cf. free ligand (CDCl₃), τ 9.05). However comparison of the chemical shifts for the corresponding protons in

TiCl$_4$·CH$_3$C(CH$_2$AsMe$_2$)$_3$ and the tungsten complex shows that all of the peaks in the former, including that due to C–CH$_3$, lie at 0.13–0.4 ppm to lower field than those in the latter. It should be noted that the C–CH$_3$ and uncomplexed –AsCH$_2$– resonances for the tungsten complex

(and for Re(CO)$_3$CH$_3$C(CH$_2$AsMe$_2$)$_3$Cl, in which the ligand is bidentate) have been misassigned in the original publication.[37]

(37) R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 6564 (1965).

Linear Free Energy Relationship for Some Inner-Sphere Electron-Transfer Reactions

KEITH M. DAVIES and JOSEPH E. EARLEY*

Second-order rate constants k_2 have been measured for the reactions by which various chromous complexes, Cr^{II}L, are oxidized to corresponding chromic complexes, Cr^{III}L, by Cr(NH$_3$)$_5$Cl^{2+} acting as oxidant. Reversible reduction potentials, $\mathscr{E}°$, of the Cr^{III}L complexes have also been studied. At 25 °C, in 1 M NaClO$_4$, values of k_2, M^{-1} s^{-1} ($-\mathscr{E}°$, V vs. SCE), for various ligands L are as follows: EDDaDp, 7.1 × 10^4 (1.42); EDTA, 1.2 × 10^3 (1.23); HEDA, 3.4 × 10^3 (1.22); MIDA, 3.15 (0.82). These data and previously measured values for L = H$_2$O follow the linear free energy relationship $\Delta \log k_2 = 0.48\Delta\mathscr{E}°$. There is firm evidence that the reactions of the aquo ion and the MIDA complex follow the inner-sphere electron-transfer mechanism and the same mechanism is probable for the other reactions. The enthalpies of activation (kJ mol^{-1}) for the EDTA and EDDaDp reactions are 54 and 32. Entropies of activation (J deg^{-1} mol^{-1}) for the same reactions are −6 and −44. These results are interpreted in terms of rate-determining electron transfer in a binuclear intermediate.

Introduction

Reversible electrode potentials ($\mathscr{E}°$) for Fe(III)–Fe(II) couples vary over a wide range, depending on the nature of the ligands coordinated to iron. In particular, the series of tris(orthophenanthroline) complexes[1] (with various substituents on the ligand rings) has been used a number of years ago to demonstrate that simple outer-sphere electron-transfer reactions[2] and also more complex reactions, probably initiated by outer-sphere electron transfer,[3] follow linear free energy relationships. For such reactions, changes in free energy of activation directly parallel changes in overall free energy of reaction, measured by changes in the reduction potential of the Fe(III) complexes involved. This result is consistent with Marcus' theory[4] as well as with less elaborate rationalizations[5].

The effectiveness of changes in ligands on Co(III) complexes in causing changes in rate of reaction depends on the reducing agent, being large for Fe(II)–Co(III) reactions[6] but small for Cr(II)–Co(III)[7] reactions. Guenther and Linck[8] demonstrated that linear free energy relationships existed between log rates of reduction of a series of common oxidants, by Fe^{2+} on the one hand and either Ru(NH$_3$)$_6$$^{2+}$ or V^{2+} on the other hand. The order of sensitivity to changes in the nonbridging ligands on Co(III) was Fe^{2+} > Ru(NH$_3$)$_6$$^{2+}$ > V^{2+}. The authors interpreted this order on the basis that lower reducing power (Fe^{2+}) corresponds to a transition state which more closely resembles the reactants but that more powerful reductants (as V^{2+}) give rise to a transition state more like the products. This version of the maxim "the more reactive, the less selective" has also been expressed in a more formal way.[9]

Shortly after the elucidation of the inner-sphere electron-transfer mechanism, Taube[10] suggested that reactions following this mechanism should follow linear free energy relationships. Characteristics which favor the bridged electron-transfer mechanism are not conducive to measurement of free energy data. Bustin and Earley[11] studied polarographic reductions of various chromium(III)–amino acid complexes and demonstrated that these Cr(III)–Cr(II) systems covered a wide range of potentials. Using these data, Earley[12] summarized evidence[13] that Cr(II)–Cr(III) electron-transfer reactions (involving OH$^-$ as bridging ligand) followed a linear

free energy relationship over many orders of magnitude. We now present more detailed results of a related study of Cr(II)–Cr(III) electron transfers, in this case involving chloride ion as bridging group.

Experimental Section

Materials. The compound [Cr(NH$_3$)$_5$Cl]Cl$_2$ was prepared according to the method of Schlessinger.[14] The perchlorate salt was precipitated from solutions of the chloride by slow addition of a solution of perchloric acid and cooling. The precipitate was washed with ice-cold water, ethanol, and ether and was air-dried. The complex was stored in the dark to prevent photochemical decomposition. The visible and ultraviolet absorption spectra of the complex showed maxima at λ 513 (ε 35.6) and 376 nm (ε 36.8 M^{-1} cm^{-1}) in good agreement with published data.[15]

Deionized water that had been doubly distilled through a quartz apparatus was used throughout. Sodium perchlorate was prepared by neutralization of analytical grade HClO$_4$ with Na$_2$CO$_3$ and was recrystallized twice from distilled water. Stock solutions of chromium(II) perchlorate were obtained by allowing excess Cr metal (99.999%) to react with HClO$_4$ for about 1 week. The resultant solution, after filtration from the excess Cr metal, showed a pH of ~3. It was standardized by oxidation with potassium dichromate, the excess chromium(VI) being determined iodometrically. "Analyzed reagent" disodium ethylenediaminetetraacetate dihydrate (J. T. Baker), recrystallized from ethanol–water mixtures, was used as the source of the ligand EDTA. Standard solutions were made up by weight. *N*-(2-Hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and *N*-methyliminodiacetic acid (MIDA) obtained from the Aldrich Chemical Co. (99%) were twice recrystallized from water and standardized by pH titration. The ligand ethylenediamine-*N,N'*-diacetic-*N,N'*-di-3-propionic acid (EDDaDp) (LaMont Laboratories) was further purified prior to use by treating weighed aliquots of the acid with 2 equiv of NaOH to effect solution, followed by the addition of HClO$_4$ to precipitate the free acid. The solid obtained, after drying in air, analyzed as the trihydrate C$_{12}$H$_{20}$O$_8$N$_2$·3H$_2$O. Anal. Calcd: C, 38.5; H, 6.95; N, 7.49. Found: C, 38.0; H, 7.06; N, 7.23. It underwent a 14.6% loss in weight (≡3 H$_2$O) on heating at 110 °C for 1 h. A further check on the ligand EDDaDp was obtained from its pH titration in 0.1 M KCl solution. Titration data in good agreement with those reported earlier by Chaberek and Martell[16] were obtained.

Kinetic Measurements. Many of the rate constant determinations were made using a Durrum stopped-flow instrument with a 2-cm