38-1; $Cu^{II}(H_{-2}A_3)^-$, 42179-70-4; $Cu^{II}(H_{-2}leu_3)^-$, 29575-61-9; $Cu^{II}(H_{-3}G_3AOCH_3)^-$, 62882-66-0; $Cu^{II}(H_{-3}G_4a)^-$, 62801-43-8; $Cu^{II}(H_{-3}G_3a)^-$, 62801-35-8; $Cu^{II}(H_{-2}G_2A)^-$, 36515-85-2; $Cu^{II}(H_{-2}Aib_3)^-$, 89438-84-6; $Cu^{II}(H_{-3}Aib_3a)^-$, 85926-43-8; $Ni^{II}(H_{-2}Aib_3)^-$, 76757-48-7; $Ni^{II}(H_{-3}G_4a)^-$, 34722-99-1; $Ni^{II}(H_{-3}FG_2a)^-$, 89438-85-7; $Ni^{II}(H_{-3}A_4)^{2-}$, 62006-66-0; $Ni^{II}(H_{-3}G_4a)^-$, 34722-99-1; $Ni^{II}(H_{-3}G_3a)^-$, 34722-97-9; $Ni^{II}(H_{-3}Aib_3a)^-$, 89438-86-8; $Ni^{II}(H_{-2}G_2A)^-$, 19330-49-5; $Ni^{III}(H_{-2}Aib_3)$, 69990-32-5; $Ni^{III}(H_{-3}Aib_3a)$, 89438-87-9; $Ni^{III}(H_{-2}G_2A)$, 89438-88-0; $Ni^{III}(H_{-3}G_3a)$, 60165-87-9; $Ni^{III}(H_{-3}G_4a)$, 60108-87-4; $Ni^{III}(H_{-2}A_3)$, 62006-71-7.

Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

Complexes of $TiCl_4$ of Interest in Friedel–Crafts Reactions

LIANG K. TAN and SYDNEY BROWNSTEIN*[1]

Received July 20, 1983

Nuclear magnetic resonance studies of systems with $TiCl_4$ and HCl and dimethyl ether, acetyl chloride, acetophenone, or methyl mesityl ketone have provided positive identification of the various complexes that exist in these systems. The ternary complex of ketone, HCl, and $TiCl_4$ is shown to be the product first formed in the $TiCl_4$-mediated Friedel–Crafts reaction of acetyl chloride and mesitylene. The relatively slow Friedel–Crafts reaction in this system is due to charge-transfer complex formation between $TiCl_4$ and the aromatic.

Introduction

Complex formation between $TiCl_4$ and dimethyl ether to give a 1:1 complex has been briefly reported.[2] Both 1:1 and 1:2 complexes of $TiCl_4$ with acetophenone have been described.[3-5] Only a 1:1 complex has been reported with acetyl chloride.[6-9]

Since all these studies involved neat reactants it seemed worthwhile to investigate these systems in a dilute solution with an inert solvent. Sulfur dioxide shows a slight tendency to complex with $TiCl_4$ since a 1:1 complex separates at high $TiCl_4$ concentration.[10] It has been found that both $AlCl_3$ and $SnCl_4$ form ternary complexes with HCl and an oxygen donor such as dimethyl ether or acetophenone.[11] Therefore, it was decided to study all these systems under comparable conditions in sulfur dioxide as solvent.

Experimental Section

^1H and ^{13}C resonance spectra were obtained on a Varian Associates XL-100 spectrometer equipped with a Nicolet Fourier transform attachment. All spectra are reported with respect to tetramethylsilane, although neopentane was used as an internal reference since it is inert under these conditions. A correction of 0.92 ppm was applied for protons. Variable-temperature measurements were calibrated against a methanol sample. Peak areas were obtained either by integration using the software of the operating system or by measurement with a planimeter. Chemical shifts are accurate to at least 0.01 ppm.

Titanium tetrachloride was purified by fractional distillation and stored in a container on the vacuum system. All other reagents were purified as previously described.[11,12] Samples were prepared by condensing known quantities of vapors into the NMR tube and sealing under vacuum except for the nonvolatile liquids mesitylene and methyl mesityl ketone. A weighed quantity of these materials was transferred to an NMR tube, closed by a high-vacuum stopcock, in a good-quality drybox. The tube was then mounted on the vacuum system and sample preparation completed. All samples were prepared in sulfur dioxide as solvent, and all concentrations are reported as mole fractions.

Table I. Chemical Shifts as a Function of Composition for the System $TiCl_4$–$(CH_3)_2O$ at −84 °C in SO_2

init concn[a]			chem shift, ppm				
				1:2			
$TiCl_4$	$(CH_3)_2O$	ratio	1:1	trans	cis	$(CH_3)_2O$	[trans]/[cis]
0.017 2	0.005 13	3.4:1	4.30				
0.007 23	0.004 94	1.5:1	4.20				
0.004 34	0.004 72	1:1.1		4.07	3.94		1.3
0.004 34	0.006 83	1:1.6		4.07	3.93		1.8
0.004 33	0.009 19	1:2.1		4.08	3.93		1.5
0.004 32	0.011 7	1:2.7		4.08	3.61		
0.004 31	0.014 1	1:3.3		4.06	3.44		
0	0.015					3.19	

[a] All concentrations in this and the following tables are reported as mole fractions.

Results and Discussion

Titanium tetrachloride reacts with dimethyl ether to give a 1:1 and two different 1:2 complexes. The 1:1 complex, whose methyl protons have a chemical shift of 4.30 ppm, is only observed when more than 1 equiv of $TiCl_4$ is nominally present in the sample. There is no information on its stereochemistry, and it may be a dimer or polymeric. The signal from the 1:2 complex at 4.07 ppm is assigned to the trans complex with octahedral geometry about titanium by analogy with similar chemical shift and exchange behavior of the analogous $SnCl_4$ complexes,[11] where the trans isomer has a signal at lower field and exchanges more slowly than the cis isomer. The signal from the 1:2 complex at 3.93 ppm is assigned to the cis complex. It exchanges rapidly on the NMR time scale at −84 °C with excess of uncomplexed ether. Results for samples of varying composition are presented in Table I. The signal at high field in the samples with a ratio of 1:2.7 and 1:3.3 is a weighted average from the cis isomer and free ether. Calculation of the expected shift for the averaged line of free ether and the complex agrees with that observed. At −74 °C, exchange between the cis and trans isomers, without excess ether, is sufficiently rapid that separate signals are no longer observed.

Positive identification of a ternary 1:1:1 complex of $TiCl_4$, dimethyl ether, and HCl in solution comes from the proton

---

(1) Issued as NRCC No. 23104.
(2) Loder, D. J.; Walker, K. E. U.S. Patent 2052889, 1936.
(3) Cullinane, N. M.; Chard, S. J.; Leyshon, D. M. *J. Chem. Soc.* **1952**, 4106–4108.
(4) Susz, B. P.; Lachavanne, A. *Helv. Chim. Acta* **1958**, *41*, 634–636.
(5) Hessett, B.; Perkins, P. G. *J. Chem. Soc. A* **1970**, 3229–3234.
(6) Sheldon, J. C.; Tyree, S. Y. *J. Am. Chem. Soc.* **1959**, *81*, 2290–2296.
(7) Susz, B. P.; Cassimatis, D. *Helv. Chim. Acta* **1961**, *44*, 943–955.
(8) Cassimatis, D; Gagnaux, P.; Susz, B. P. *Helv. Chim. Acta* **1960**, *43*, 424–433.
(9) Patai, S., Ed. "The Chemistry of the Acyl Halides"; Interscience: New York, 1972; Chapter 4.
(10) Bond, P. A.; Belton, W. E. *J. Am. Chem. Soc.* **1945**, *67*, 1691–1693.
(11) Tan, L. K.; Brownstein, S. *J. Org. Chem.* **1983**, 48, 3389–3393.
(12) Tan, L. K.; Brownstein, S. *J. Org. Chem.* **1983**, 48, 302–306.

0020-1669/84/1323-1353$01.50/0 Published 1984 by the American Chemical Society

Table II. Methyl Group Chemical Shifts of Some Complexes with $TiCl_4$ in SO_2 at −84 °C

compd	$\delta(CH_3)$	compd	$\delta(CH_3)$	compd	$\delta(COCH_3)$
$(CH_3)_2O\cdot TiCl_4$	4.30	$PhCOCH_3\cdot TiCl_4$	3.51	$MMK\cdot TiCl_4$	3.41
$2(CH_3)_2O\cdot TiCl_4$ (trans)	4.08	$2PhCOCH_3\cdot TiCl_4$ (trans)	3.19	$2MMK\cdot TiCl_4$	3.04
$2(CH_3)_2O\cdot TiCl_4$ (cis)	3.93	$2PhCOCH_3\cdot TiCl_4$ (cis)	3.14	$MMK\cdot HCl$	2.74
$(CH_3)_2O\cdot TiCl_4\cdot HCl$	4.53	$PhCOCH_3\cdot HCl$	3.26		
$(CH_3)_2O\cdot HCl$	3.86				

Table III. Chemical Shifts of the Methyl Group as a Function of Composition for the System $TiCl_4$–$PhCOCH_3$ at −84 °C in SO_2

init concn			chem shift, ppm				
				1:2			
$TiCl_4$	$PhCOCH_3$	ratio	1:1	trans	cis	$PhCOCH_3$[a]	[trans]/[cis]
0.007 96	0.002 92	2.7:1	3.51				
0.003 63	0.005 98	1:1.6		3.19	3.15		5.3
0.004 34	0.007 52	1:1.7		3.19	3.12	3.07	5.4
0.004 31	0.015 1	1:3.5		3.18	3.14	2.84	4.8
0	0.015					2.66	

[a] Average position.

Table IV. Chemical Shifts of the Methoxyl Protons and Equilibrium Constants as a Function of Composition for the System $TiCl_4$–Methyl Mesityl Ketone in SO_2 at −84 °C

init concn		chem shift, ppm				
$TiCl_4$	MMK	1:1	1:2	av position	K_1	K_2
0.009 37	0.007 07	3.412				
0.004 35	0.005 50		3.044	2.779	185	447
0.004 67	0.012 5		3.036	2.666	216	445
0	0.012 5			2.501		

Table V. Peak Positions as a Function of Sample Composition for the System $TiCl_4$–MMK–HCl in SO_2 at −84 °C

init concn		peak position, ppm				
$TiCl_4$	MMK	HCl	$COCH_3$	2,6-CH_3	4-CH_3	CH
0.006 48	0.004 21	0.007 04	3.21	2.37	2.48	7.15
0.003 61	0.004 23	0.004 47	3.13	2.32		7.03
0.007 45	0.015 1	0.007 38	3.05	2.22	2.23	6.89
0.003 94	0.012 4	0.005 14	2.93, 3.04	2.30, 2.20		7.01, 6.88

resonance spectrum at −84 °C of a sample whose mole fraction is initially 0.0127 in $TiCl_4$, 0.00462 in dimethyl ether, and 0.0139 in HCl. A doublet at 4.530 ppm and the septet spin coupled to it by 3.37 Hz at 8.995 ppm arise from the dimethyl ether protons and a proton of the HCl coordinated to the ether oxygen, respectively. In addition, the signal from uncomplexed HCl is observed at 2.022 ppm. The fact that there are six methyl protons for each coordinated acidic proton, and hence that the stoichiometry is 1:1:1, is proven by two facts. The areas of the two absorptions were 6.5:1, and the ratio of peak intensities of the five central lines of the septet are 0.26:0.77:1.0:0.75:0.29. The theoretical intensity ratio for coupling to six equivalent spins is 0.30:0.75:1.0:0.75:0.30, while for coupling to 12 equivalent spins it is 0.54:0.86:1.0:0.86:0.54. It is probably safe to presume that this complex has one oxygen and five chlorine atoms octahedrally coordinated about titanium and two methyl groups, one hydrogen, and one titanium tetrahedrally coordinated about the oxygen.

As far as we are aware, this is the first time spin coupling has been observed between a proton coordinated to a quaternary oxygen and the protons of an adjacent methyl group. With increasing temperature or an increase in the relative proportion of dimethyl ether, the observed spin coupling is averaged to zero by rapid exchange. Also, with higher ether concentrations only a single averaged line is observed for the methyl ether protons among the species $2(CH_3)_2O\cdot TiCl_4$ (cis and trans), $(CH_3)_2O\cdot HCl$, the 1:1:1 complex, and free ether. The chemical shifts of the various $TiCl_4$–dimethyl ether complexes are listed in Table II, and that of the ether–HCl complex is listed for comparison.

Titanium tetrachloride reacts with acetophenone in the same manner as with dimethyl ether to give a 1:1 and trans and cis 1:2 complexes. The assignment to trans and cis isomers is based solely upon the analogy of the chemical shifts and relative abundances with those of the ether adducts and $AlCl_3$–acetophenone complexes.[11] The exchange behavior of these complexes with free acetophenone is rather different from that of the dimethyl ether system. In the acetophenone system the 1:1 adduct exchanges with free acetophenone much more readily than either of the 1:2 adducts; however, the temperature interval of intermediate-exchange rates is too narrow for quantitative studies. Experimental data for five samples are shown in Table III. The chemical shifts are included in Table II.

There is no spectral evidence for formation of a ternary complex of acetophenone, $TiCl_4$, and HCl.

Methyl mesityl ketone (MMK) was chosen as the third base for complexing studies since it is the primary product of the acetylation of mesitylene by acetyl chloride. Experimental data for samples with four different compositions are listed in Table IV. For these systems only a single 1:2 complex was observed. There is rapid exchange between the 1:1 complex and free ketone. The equilibria involved may be represented by eq 1 and 2

$$MMK + TiCl_4 \rightleftharpoons TiCl_4\cdot MMK \tag{1}$$

$$MMK + TiCl_4\cdot MMK \rightleftharpoons TiCl_4\cdot 2MMK \tag{2}$$

where

$$K_1 = \frac{[TiCl_4\cdot MMK]}{[MMK][TiCl_4]} \qquad K_2 = \frac{[TiCl_4\cdot 2MMK]}{[MMK][TiCl_4\cdot MMK]}$$

From the known composition of the samples, the relative areas of the different peaks, and the chemical shift of the averaged signal, it is possible to calculate the concentrations of the various species and hence K_1 and K_2. These are also listed in Table IV. Two additional signals, presumably from polymeric species, are observed at 3.27 and 3.20 ppm in the sample with an excess of $TiCl_4$. One can confirm which signal is that of the 1:1 complex since it is the only one that gives reasonable and constant values for K_1 and K_2.

Data for the ternary system $TiCl_4$–MMK–HCl are given in Table V. From these results we may conclude that the 1:1 $TiCl_4$–MMK complex reacts with HCl to give a ternary complex. The extent of ternary complex formation and its chemical shift cannot be determined since only averaged line positions are observed. There is no evidence for ternary complex formation between the 1:2 $TiCl_4$–MMK complex and HCl.

Titanium tetrachloride and acetyl chloride from a 1:1 complex as was observed with $AlCl_3$[13] but not with $SnCl_4$.[11] There is exchange between free acetyl chloride and that complexed with $TiCl_4$, but at low relative concentrations of acetyl chloride and at −84 °C separate signals are observed for the free and complexed acetyl chloride. The data are listed

---

[13] Glavincevski, B.; Brownstein, S. *J. Org. Chem.* **1982**, *47*, 1005–1007.

Table VI. Proton Resonance Signal Parameters as a Function of Sample Composition for the System $TiCl_4$-CH_3COCl in SO_2 at −84 °C

init concn		position, ppm		width, Hz		concn	
$TiCl_4$	CH_3COCl	free	complex	free	complex	free	complex
0.009 01	0.004 92		4.18		7.4		
0.004 71	0.004 72	2.77	4.21	20.8	23.7	0.002 85	0.001 87
0.004 34	0.005 42	2.77	4.18	17.6	30.2	0.003 56	0.001 86
0.005 06	0.007 07	2.76	4.18	14.9			
0.003 63	0.005 44	2.77	4.13	13.1			

Table VII. Dependence of Complexed Acetyl Chloride Concentration upon Sample Composition in SO_2 at −84 °C

init concn		aromatic concn	$[TiCl_4 \cdot CH_3COCl]$	width due to CH_3COCl, Hz
$TiCl_4$	CH_3COCl			
0.005 04	0.005 17	0.005 93[a]	not obs	4
0.004 34	0.002 83	0.003 65[a]	just obs	3
0.008 26	0.004 67	0.004 70[a]	just obs	4
0.004 33	0.004 47	0.004 30[b]	0.002 23	15
0.003 98	0.004 24	0.004 15[c]	0.001 35	14
0.005 04	0.004 93	0.005 97[d]	0.001 39	14

[a] Mesitylene. [b] *p*-Xylene. [c] Toluene. [d] Benzene.

in Table VI. From the two samples where the area of each of the signals can be adequately measured, an equilibrium constant of 220 ± 10 is calculated for formation of the 1:1 complex. There is sufficient uncertainty in the line widths in the absence of exchange for this system that reliable exchange rates could not be calculated.

There is no spectral evidence for formation of a ternary complex of acetyl chloride, $TiCl_4$, and HCl. It is assumed that all of the adducts are covalent simple Lewis acid–Lewis base coordination complexes, but this has not been proven.

There is no Friedel–Crafts reaction, even at room temperature, between the acetyl chloride–$TiCl_4$ complex and benzene, toluene, or *p*-xylene at the concentrations used in the studies of the various Lewis base–$TiCl_4$ complex species. At much higher concentrations, *p*-xylene reacts slowly at room temperature. With mesitylene as the aromatic species, there is some reaction immediately upon thawing the sample after its preparation, even for low-concentration samples. Subsequent reaction is extremely slow at −84 °C but largely complete after 2 h at room temperature. The proton resonance spectrum of such samples, at low temperature, are the same as those prepared from $TiCl_4$, HCl, and methyl mesityl ketone.

The most striking observation is that there is a single narrow signal from CH_3COCl in the samples containing both mesitylene and $TiCl_4$ while broad signals from exchanging free and complexed acetyl chloride are observed in the absence of mesitylene, or if the aromatic compound is benzene, toluene, or *p*-xylene. The data are listed in Table VII. It is well-known that $TiCl_4$ forms charge-transfer complexes with aromatic hydrocarbons and that the strength of these complexes increases with an increasing number of methyl groups on the aromatic ring.[14,15] It appears that mesitylene competes successfully with acetyl chloride to complex $TiCl_4$. There is no evidence from either proton or ^{13}C resonance spectroscopy of an intermediate composed of $TiCl_4$. acetyl chloride, and mesitylene.

The salient facts in the relative reactivities for acetylation of simple aromatic hydrocarbons by acetyl chloride and $AlCl_3$, $SnCl_4$, or $TiCl_4$ can perhaps be described in terms of formation of a ternary intermediate. With $AlCl_3$, one can obtain the equilibrium constants for such intermediates and acetylation is rapid.[12] There is no complex formation between $SnCl_4$ and acetyl chloride, no evidence for a ternary intermediate exists, and acetylation is slow. Similarly with $TiCl_4$ there is no evidence for a ternary intermediate because the weak $TiCl_4$–acetyl chloride complex is decomposed by the aromatic hydrocarbon. It is possible that the rate of acetylation is roughly proportional to the strength of the metal chloride–acetyl chloride complex. Other systems will be investigated to test this hypothesis. A complex is formed between ferric chloride and acetyl chloride, but the sensitivity of the chemical shifts to the concentration of paramagnetic ferric chloride did not permit a quantitative study of this system.

Registry No. MMK, 1667-01-2; MMK·$TiCl_4$, 89178-70-1; 2MMK·$TiCl_4$, 89178-71-2; $(CH_3)_2O$·$TiCl_4$, 89178-69-8; 2-$(CH_3)_2O$·$TiCl_4$ (trans), 89253-92-9; 2$(CH_3)_2O$·$TiCl_4$ (cis), 89253-93-0; $PhCOCH_3$·$TiCl_4$, 31011-60-6; 2$PhCOCH_3$·$TiCl_4$ (trans), 89253-94-1; 2$PhCOCH_3$·$TiCl_4$ (cis), 89254-76-2; CH_3COCl·$TiCl_4$, 89178-72-3; HCl, 7647-01-0; $PhCOCH_3$, 98-86-2.

---

(14) Krauss, H. L.; Huettmann, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1963**, *18B*, 976–978.

(15) Hammond, P. R.; Lake, R. R. *J. Chem. Soc., Chem. Commun.* **1968**, 987–988.