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Stepwise Reactions of $TiCl_4$ and $Ti(O^iPr)Cl_3$ with 2-Propanol. Variable-Temperature NMR Studies and Crystal Structures of $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}Cl)]_2$ and $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}O^iPr)]_2$

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The reactions of $TiCl_4$ and $Ti(O^iPr)Cl_3$ with 1−3 molar equiv of 2-propanol give the dimeric complexes $[TiCl_3(HO^iPr)(\mu\text{-}Cl)]_2$ (**1**), $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}Cl)]_2$ (**2**), and $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}O^iPr)]_2$ (**3**). The reactions are shown to proceed stepwise with the consecutive addition of 2-propanol. Complexes **2** and **3** are dynamic in solution. However, the proton VT NMR studies show that they are static and remain the dimeric features in solution at low temperatures. Two inequivalent methyl environments are observed for the 2-propanol ligand of complex **3**, probably due to the intramolecular hydrogen bonding from the isopropanolic hydrogen to the chloride on the second titanium metal center. **2** crystallizes in the orthorhombic space group *Pbca* with cell parameters of $a = 12.605(3)$ Å, $b = 12.841(4)$ Å, $c = 15.414(4)$ Å, $Z = 4$, $D_{\mathrm{calcd}} = 1.456$ g/cm^3, $R = 0.049$, $R_w = 0.062$, and $G_{\mathrm{OF}} = 1.38$. **3** crystallizes in the monoclinic space group $P2_1/c$ with cell parameters of $a = 9.457(2)$ Å, $b = 15.277(2)$ Å, $c = 11.354(4)$, $\beta = 112.76(2)°$, $Z = 2$, $D_{\mathrm{calcd}} = 1.305$ g/cm^3, $R = 0.032$, $R_w = 0.048$, and $G_{\mathrm{OF}} = 1.29$. Through the analysis of the bonding features of the solid-state structures **2** and **3**, the relative bonding sequence of $^-O^iPr > Cl^- > HO^iPr > \mu\text{-}^-O^iPr > \mu\text{-}Cl^-$ is established. This bonding order is useful for the prediction of the geometries of six-coordinate titanium complexes containing those ligands with the rule "*the strong ligand prefers a position trans to the weak ligand in the complexes*". Besides, the reaction features demonstrated in this study may apply to the reaction of $TiCl_4$ or $Ti(O^iPr)Cl_3$ with diols, especially for chiral diols used as ligands in titanium complexes for various asymmetric syntheses of organic compounds.

Introduction

Titanium alkoxides have been extensively studied for several decades by Bradley and others.[1] However, their chemistry is not well understood due to the limited structural data available. For example, the titanium complex with the formula $[Ti(OR)_2Cl_2(HOR)]$ was prepared 60 years ago by the reaction of $TiCl_4$ with excess alcohol.[2] Recently, Winter et al. reported the synthesis of the analogous complexes $[Ti(OCH_2CH_2X)_2Cl_2(HOCH_2CH_2X)]_2$ (X = Cl, Br, I)[3] by a similar procedure. The crystal structure for the complex with X = Cl shows a dimeric species bridged through two alkoxides. In our previous study of the structures of six-coordinate titanium complexes prepared from $Ti(O^iPr)Cl_3$,[4] it was found that the alkoxide plays an extremely important role in structures and in reactivities and that a relative bonding sequence for various ligands can be established. In continuation of this study, we here report the stepwise reactions of $TiCl_4$ and $Ti(O^iPr)Cl_3$ with 1−3 molar equiv of 2-propanol to give the dimeric complexes $[TiCl_3(HO^iPr)(\mu\text{-}Cl)]_2$ (**1**), $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}Cl)]_2$ (**2**), and $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}O^iPr)]_2$ (**3**), respectively. The solid-state structures show similar geometries for **2** and **3** with the only difference being in the bridging ligands. Both structures possess intramolecular hydrogen bonding from the hydroxy group to the chloride on the second metal center. These two complexes are dynamic in solution at room temperature. However, variable-temperature (VT) NMR studies show that they are static and are likely to retain the dimeric features in solution at low temperature. Through the analysis of the X-ray structures of **2** and **3**, the relative bonding abilities $^-O^iPr > Cl^- > HO^iPr > \mu\text{-}^-O^iPr > \mu\text{-}Cl^-$ are suggested.

Experimental Section

Reagents and General Techniques. $Ti(O^iPr)Cl_3$ was prepared according to the literature procedures.[5] $TiCl_4$ was distilled at reduced pressure and stored in a septum-sealed flask. 2-Propanol was refluxed over CaH_2, distilled, and then stored over 4 Å molecular sieves. Solvents were dried by refluxing at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (toluene) and were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

Synthesis of Bis(μ-chloro)bis[trichloro(2-propanol)titanium(IV)] (1). 2-Propanol (0.62 mL, 8.00 mmol) was added to a solution of $TiCl_4$ (0.88 mL, 8.00 mmol) in 25 mL of CH_2Cl_2 at room temperature, and the mixture was stirred for 2 h. The solvent was removed in vacuo to give a pale yellow solid (1.72 g, 86.0%); mp 81.0−83.0 °C. MW: 460 ± 50. ^{1}H NMR ($CDCl_3$): δ 5.15 (sept, 2H), 1.59 (d, 12H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 96.1 (CH), 24.7 (CH_3) ppm. IR (Nujol): 3385 (w, br), 1261 (m), 1127 (m), 1095 (s), 1017 (s), 861 (w), 799 (s), 719 (w), 547 (w), 473 (m) cm^{-1}. Anal. Found: C, 15.65; H, 3.07. Calcd for $C_6H_{16}O_2Cl_8Ti_2$: C, 14.43; H, 3.23.

Synthesis of Bis(μ-chloro)bis[dichloro(2-propanol)isopropoxotitanium(IV)] (2). Method a. 2-Propanol (0.42 mL, 5.40 mmol) was added to a solution of **1** (1.35 g, 2.70 mmol) in 25 mL of CH_2Cl_2 at room temperature, and the mixture was stirred for 5 h. The resulting solution was repeatedly concentrated, cooled to −15 °C, and filtered to afford a total of 1.05 g (70.9%) of colorless crystals; mp 91.1−95.0 °C. ^{1}H NMR ($CDCl_3$): δ 5.00 (br, 4H), 1.50 (d, 24H) ppm. $^{13}C\{^1H\}$

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

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NMR ($CDCl_3$): δ 94.8 (CH), 23.8 (CH_3) ppm. IR (Nujol): 3325 (m, br), 1311 (m), 1279 (m), 1163 (m), 1129 (m), 1095 (vs), 1085 (vs), 1005 (vs), 929 (m), 905 (m), 865 (m), 797 (vs), 617 (m), 479 (m), 469 (m) cm^{-1}. Anal. Found: C, 26.35; H, 5.55. Calcd for $C_{12}H_{30}O_4Cl_6Ti_2$: C, 26.36; H, 5.53.

Method b. 2-Propanol (0.46 mL, 6.00 mmol) was added to a solution of $Ti(O^iPr)Cl_3$ (1.28 g, 6.00 mmol) in 20 mL of CH_2Cl_2 at room temperature. The solution was stirred for 30 min and then was concentrated to ~10 mL. The resutling solution was cooled to −25 °C to afford colorless crystals (0.73 g, 44.5% yield). The second crop (0.36 g, 22.0%) was obtained by concentrating the filtrate further and cooling to −25 °C.

Synthesis of Bis(μ-isopropoxo)bis[dichloro(2-propanol)isopropoxotitanium(IV)] (3). 2-Propanol (1.54 mL, 20.0 mmol) was added to a solution of $Ti(O^iPr)Cl_3$ (2.13 g, 10.0 mmol) in 30 mL of toluene at room temperature. The solution was stirred for 30 min and then was concentrated to about 10 mL. The resulting solution was cooled to −25 °C to give colorless crystals (2.12 g, 71.4% yield); mp 86.7−87.8 °C. ^1H NMR ($CDCl_3$): δ 5.00 (br, 6H), 1.45 (d, 36H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 87.1 (CH), 24.4 (CH_3) ppm. IR (Nujol): 3185 (m, br), 1261 (w), 1165 (w), 1097 (s), 1011 (m), 995 (m), 925 (w), 903 (w), 799 (s), 551 (w), 463 (w) cm^{-1}. Anal. Found: C, 36.30; H, 7.20. Calcd for $C_{18}H_{44}O_6Cl_4Ti_2$: C, 36.39; H, 7.46.

Physical Measurements. ^1H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer, and the ^1H VT and ^{13}C NMR spectra were recorded with the Varian VXR-300 spectrometer. The temperatures for the VT NMR studies are calibrated with the methanol peaks. The ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane as the internal reference. Infrared spectra were recorded on a Hitachi 270-30 spectrometer in the region of 4000−400 cm^{-1}; the peak positions were calibrated with the 1601.4 cm^{-1} peak of polystyrene. Melting points were measured with a Büchi 535 instrument, and the temperatures were not calibrated. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument. The molecular weight was determined by the method of freezing point depression in benzene.

Crystal Structure Determinations. Colorless crystals of **2** of size 0.40 × 0.50 × 0.60 mm and **3** of size 0.40 × 0.50 × 0.70 mm in sealed capillaries were used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An absorption correction was performed on complex **2** only. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVax 3100-80 computer. The positions of heavy atoms for the structure were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms, except for the hydroxy hydrogens, which were also located from the successive Fourier difference map calculations, were considered as the riding atom on the carbon atom with a C−H bond length of 0.96 Å; hydrogen atom temperature factors were fixed at 0.08 Å. The hydrogen atoms were included for refinements in the final cycles. The crystallographic data for complexes **2** and **3** are summarized in Table 1.

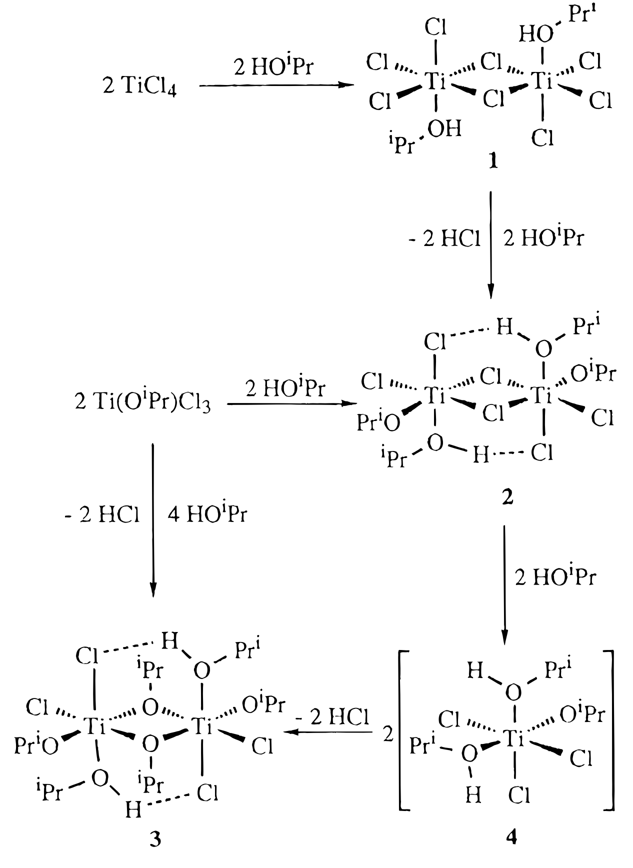
Results and Discussions

Table 1. Crystallographic Data for **2** and **3**

	2	3
formula	$Ti_2Cl_6O_4C_{12}H_{30}$	$Ti_2Cl_4O_6C_{18}H_{44}$
fw	546.9	594.1
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a (Å)	12.605(3)	9.457(2)
b (Å)	12.841(4)	15.277(2)
c (Å)	15.414(4)	11.354(4)
β (deg)		112.76(2)
V (Å^3)	2494.9(12)	1512.5(5)
Z	4	2
D_{calcd} (g cm^{-3})	1.456	1.305
λ(Mo Kα) (Å)	0.710 73	0.710 73
abs coeff (mm^{-1})	1.295	0.907
range (deg)	4.0−50.0	4.0−45.0
scan type	$\theta/2\theta$	$\theta/2\theta$
no. of rflns collected	2443	4259
no. of indep rflns	1626 (R_{int} = 3.70%)	1992 (R_{int} = 1.30%)
no. of obsd rflns	1125 ($I > 2.0\sigma(I)$)	1751 ($I > 2.0\sigma(I)$)
no. of refined params	109	136
R^a for sign rflns	0.049	0.032
$R_w{}^b$ for signif rflns	0.062	0.048
goodness of fit^c	1.38	1.29

[a] $R = [\Sigma(F_o - F_c)/\Sigma F_o]$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2]^{1/2}$. [c] The goodness of fit equals $[\Sigma w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$.

Scheme 1



Synthesis of Complexes. The reactions of $TiCl_4$ and $Ti(O^iPr)Cl_3$ with 2-propanol are outlined in Scheme 1. One molar equivalent of HO^iPr added easily to $TiCl_4$ to give the chloride-bridged dimeric complex $[TiCl_3(HO^iPr)(\mu\text{-}Cl)]_2$ (**1**). The dimeric structure of **1** is suggested from the molecular weight deterrmination of 460 ± 50. With the addition of 2 molar equiv of HO^iPr to the dimeric complex **1**, another chloride-bridged dimeric complex, $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}Cl)]_2$ (**2**), is obtained with the evolution of 2 molar equiv of HCl gas. The reaction of $Ti(O^iPr)Cl_3$ with 1 molar equivalent of HO^iPr in dichloromethane also leads to the formation of **2**. With the addition of 2 molar equiv of 2-propanol to **2**, the isopropoxide-bridged dimeric complex $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}O^iPr)]_2$ (**3**) is obtained. **3** is a complex that was reported 60 years ago with the formula $[Ti(OR)_2Cl_2(HOR)]$ from the reaction of $TiCl_4$ with excess alcohol.[2] **3** can also be obtained from the reaction of $Ti(O^iPr)Cl_3$ with 2 molar equiv of HO^iPr. Since 2-propanol is a better ligand than the bridging chloride on the basis of the structual data, the formation of **3** is likely to proceed via the monomeric intermediate **4** followed by the reaction of 2 molecules of **4** with the evolution of two molecules of HCl. These complexes

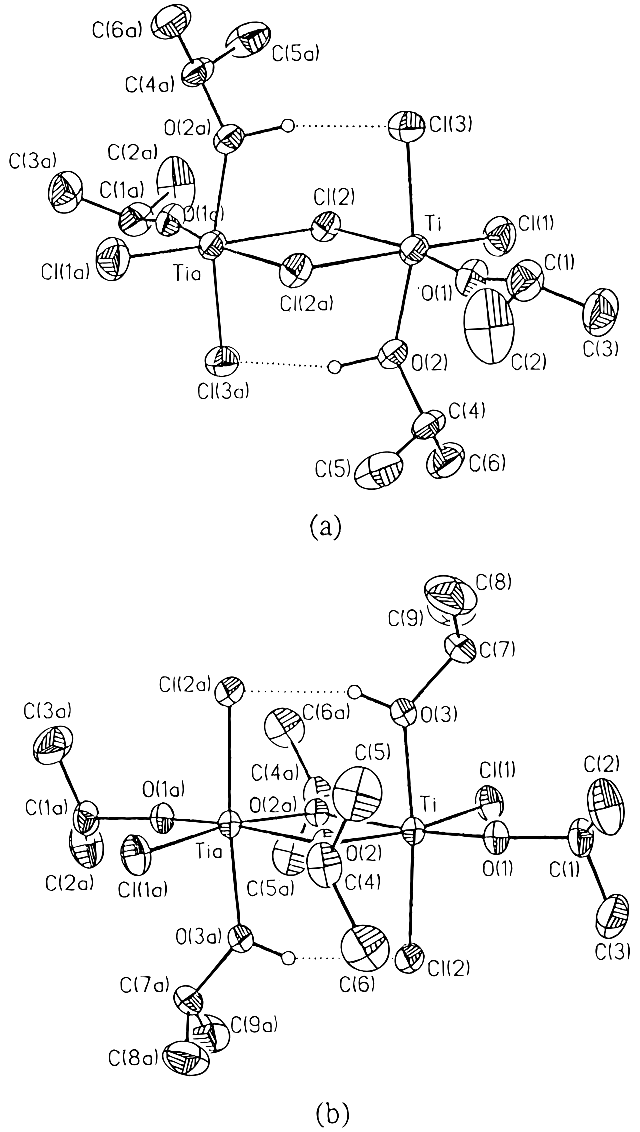


Figure 1. Molecular structures of (a) $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}Cl)]_2$ (**2**) and (b) $[TiCl_2(O^iPr)(HO^iPr)(\mu\text{-}O^iPr)]_2$ (**3**).

are all quite soluble in toluene or in CH_2Cl_2, and complexes **2** and **3** crystallize easily in these solvents.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of **2** and **3**

Compound **2**			
Ti−O(1)	1.700(5)	Ti−O(2)	2.087(4)
Ti−Cl(1)	2.253(2)	Ti−Cl(2)	2.551(2)
Ti−Cl(3)	2.300(2)	Ti−Cl(2a)	2.478(2)
Ti···Tia	3.848	H2···Cl(3a)	2.268
O(1)−Ti−O(2)	94.1(2)	O1−Ti−Cl(1)	98.6(2)
O(1)−Ti−Cl(2a)	93.3(1)	O1−Ti−Cl(3)	96.5(2)
Ti−O(1)−C(1)	164.2(4)	Ti−O(2)−C(4)	128.0(3)
Cl(2)−Ti−Cl(2a)	80.2(1)	Ti−Cl(2)−Tia	99.8(1)
O(2)−H(2)−Cl(3a)	156.3		
Compound **3**			
Ti−O(1)	1.735(2)	Ti−O(3)	2.093(2)
Ti−O(2)	1.938(2)	Ti−O(2a)	2.129(2)
Ti−Cl(1)	2.340(1)	Ti−Cl(2)	2.368(1)
Ti···Tia	3.245	H3···Cl(2a)	2.174
O(1)−Ti−O(2)	102.4(1)	O(1)−Ti−O(3)	91.3(1)
O(1)−Ti−Cl(1)	90.9(1)	O(1)−Ti−Cl(2)	96.6(1)
Ti−O(1)−C(1)	153.4(2)	Ti−O(3)−C(7)	133.8(2)
Ti−O(2)−C(4)	127.9(1)		
O(2)−Ti−O(2a)	74.2(1)	Ti−O(2)−Tia	105.8(1)
O(3)−H−Cl(2a)	158.5		

Molecular Structures of 2 and 3. Complexes **2** and **3** were subjected to X-ray structural analysis. The molecular structures are shown in Figure 1, and the selected bond lengths and bond angles are listed in Table 2. **2** is a chloride-bridged dimeric species with the center of the molecule on the crystallographic inversion center. **2** shows intramolecular hydrogen bonding from the hydroxy group to the chloride on the second titanium metal center. The intramolecular hydrogen bonding seems to be a general feature for complexes containing both alcohol and alkoxides or chlorides.[3,6] The isopropoxide is trans to the bridged chloride and the Ti−O(isopropoxide) bond length (Ti−O(1)) is extremely short at 1.700(5) Å, which is one of the shortest Ti−OR distances observed.[4,7] Due to the strong Ti-O(isopropoxide) bonding, the isopropoxide group shows a strong trans influence with the observation of the long distance from the titanium metal to the trans-bridged chloride at 2.551(2) Å. This distance is comparable or even longer than the Ti−Cl(bridged) distances in the anionic complexes $[Ti_2Cl_9]^-$ at 2.48−2.55 Å and $[Ti_2Cl_{10}]^{2-}$ at 2.48−2.51 Å.[8] The Ti−Cl(bridged) distances are inequivalent with the distance from the titanium metal to the cis μ-Cl shorter by ~0.07 Å at 2.478(2) Å. The phenomenon of a long Ti−Cl distance for the μ-Cl atom trans to the isopropoxide relative to the distance for the μ-Cl atom trans to the terminal chloride is consistent with the relative bond dissociation energies of Ti−O^{i}Pr > Ti−Cl.[9] The Ti−O(1)−C(1) angle opens up to 164.2(4)°, which is a common characteristic associated with the strong π bonding of alkoxide ligands to a metal.[10] The Ti−O(2)−C(4) angle for the coordinated 2-propanol is relatively small at 128.0(3)°, indicating very little π bonding. 2-Propanol is trans to one chloride with a Ti−O(2) distance of 2.087(4) Å. The phenomenon that all cis ligands bend away from the isopropoxide with O(1)−Ti−X(cis) angles ranging from 93.3(1) to 98.6(2)° is also an effect of the strong trans influence of the isopropoxide group. The Ti-Cl distances for two terminal chlorides are also inequivalent with a distance of 2.253(2) Å for the chloride trans to μ-Cl and a distance of 2.300(2) Å for the chloride trans to 2-propanol. The inequivalent Ti−Cl(terminal) distances reflect the relative bonding abilities of the trans ligands with the stronger ligand being trans to the chloride of longer Ti-Cl distance. In this case, the 2-propanol ligand bonds more strongly to the titanium metal than does the bridging chloride. All the above features clearly suggest a relative bonding sequence of $^-O^iPr > Cl^- > HO^iPr > \mu\text{-}Cl^-$.

Complex **3** is an isopropoxide-bridged dimeric species which is different from **2** only in the bridging ligands, and the center

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of the molecule also is located on the crystallographic inversion center. The bonding parameters around the titanium metal core are similar to those in $[Ti(OCH_2CH_2Cl)_2Cl_2(HOCH_2CH_2Cl)]_2$.[3] Due to the strong trans influence of the trans isopropoxide, the Ti−O(2a) distance of a bridging alkoxide at 2.129(2) Å is substantially longer than another Ti−O distance (Ti−O(2) at 1.938 Å) by almost 0.2 Å. Excluding the bridging ligands, all the corresponding Ti−X distances in **3** are longer than the distances in **2**. For example, the $Ti-O^iPr$ distance is 1.735(2) Å in comparison with 1.700(5) Å in **2** and the $Ti-O(HO^iPr)$ distance at 2.093(2) Å is slightly longer than the distance in **2** at 2.087(4) Å. The Ti−Cl distances also reveal similar longer distances in **3** than in **2**. Clearly, the lengthening of all bonds around the titanium metal core in **3** arises from the better bonding of the bridging alkoxide in comparison to the bridging chloride. Therefore, the overall bonding sequence based on the structural features of **2** and **3** is concluded to be $^-O^iPr > Cl^- > HO^iPr > \mu\text{-}^-O^iPr > \mu\text{-}Cl^-$.

The leaning of the isopropanolic oxygen toward the chloride on the second titanium metal is the effect of the strong trans influence of the isopropoxide and is not due to hydrogen bonding. Since, in view of the $^iPrO-Ti-X$(cis) angles in **2**, the O(1)−Ti−O(2) angle at 94.1(2)° and the O(1)−Ti−Cl(3) angle at 96.5(2)° are not larger than the other two cis angles at 93.3(1) and 98.6(2)°. Similar observations are found in **3** with the O(1)−Ti−O(3) angle at 91.3(1)° and the O(1)−Ti−Cl(2) angle at 96.1(1)°, which are not larger than the other two cis angles of 90.9(1) and 102.4(1)°.

VT NMR Studies of 2 and 3. Complexes **2** and **3** are dynamic in solution with the observation of one set of ^1H NMR signals for the isopropyl groups at ambient temperature. In order to probe the solution structures of **2** and **3**, both complexes were subjected to VT NMR studies in CD_2Cl_2 and selected spectra are shown in Figure 2. For **2** at ambient temperature, the broad peak at δ 4.88 ppm and the peak at δ 1.47 ppm are signals for the methine and methyl protons, respectively. At 0 °C, two sets of ^1H NMR signals in the methine region are observed. The downfield peak at δ 5.28 ppm is the methine proton of the isopropoxide ligand, and the signal at 4.68 ppm is due to the 2-propanol ligand. Still, the methyl signals are not well-resolved at this temperature. When the temperature was lowered to −20 °C, two sets of doublets at 1.52 and 1.41 ppm were seen for methyl protons of the isopropoxide and the 2-propanol, respectively. Interestingly, the upfield methyl signals of 2-propanol split further into two doublets at 1.38 and 1.34 ppm at −80 °C. The further splitting of the methyl signals is likely due to hydrogen bonding, which fixes the molecular geometry of **2** at low temperature to make two methyls magnetically inequivalent. The ^1H signal of the hydroxy hydrogens appears at δ 5.46 ppm as a broad peak at −20 °C and shifts downfield at lower temperatures. At temperatures below −60 °C, the proton chemical shift of the hydroxy hydrogens appears as a doublet and remains static at δ 5.89 ppm. For complex **3**, one set of ^1H chemical shifts at δ 4.92 and 1.41 ppm is observed at ambient temperature. At 0 °C, though the methyl signals are not well resolved, two methine signals are clearly seen. At −30 °C, three methine signals are observed and the methyl signals split into two sets in a ratio of 2:1. The upfield chemical shift with a ratio of 1 at δ 1.33 ppm is the methyl signal for the 2-propanol ligand, and the methyl signals of two isopropoxide groups overlap to form the resonances in the ratio 2. The proton resonance of the hydroxy group remains intact at 7.12 ppm at temperatures below −30 °C. The above VT NMR studies suggest that both complexes remain dimeric species in solution, at least at low temperatures, as well as in the solid state.

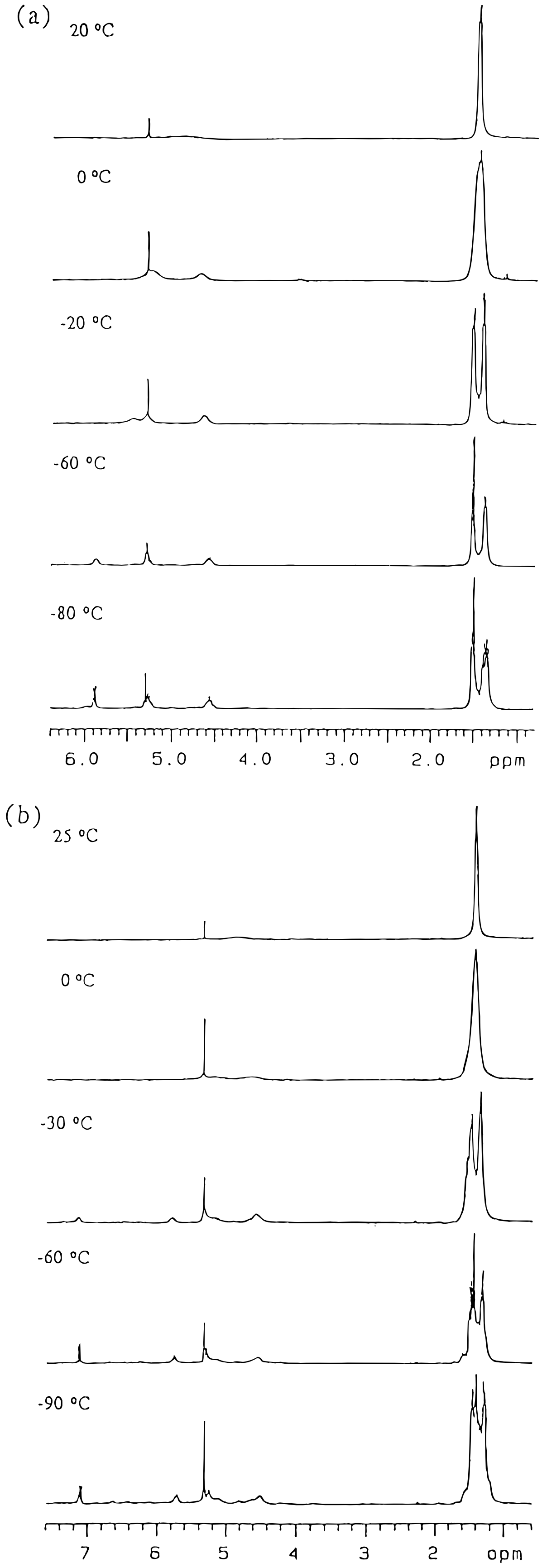

Figure 2. Selected ^1H VT NMR spectra of (a) complex **2** and (b) complex **3** in CD_2Cl_2.

Conclusions

In summary, complexes **2** and **3** are dimeric in the solid state and possess intramolecular hydrogen bonding. Though **2** and

3 are dynamic in solution, it seems that both complexes are dimers at low temperatures. At −80 °C, complex **2** is rigid enough due to the hydrogen bonding to show inequivalent methyl environments for the 2-propanol ligands. In general, for titanium complexes containing not enough ligands for the formation of six-coordinate monomeric complexes, dimerization or oligomerization occurs usually through the bridging of alkoxides or chlorides if alkoxides or chlorides are present in the complexes.[11] However, if chlorides and two or more alkoxides are present, bridging through the alkoxides is preferable to that through the chloride for two reasons. First, the bridging alkoxide is preferred to prevent the existence of two or more strong terminal alkoxides. Second, the bridging alkoxide bonds better to the titanium metal than does the bridging chloride. Through the analysis of the structural features of **2** and **3**, the bonding sequence $^{-}O^{i}Pr > Cl^{-} > HO^{i}Pr > \mu\text{-}^{-}O^{i}Pr > \mu\text{-}Cl^{-}$ is established. The importance of this bonding sequence is that it includes the relative bonding abilities of the bridging ligands such as the bridging alkoxide and the bridging chloride. Besides, the stepwise reaction features may apply to reactions of $TiCl_4$ and $Ti(O^{i}Pr)Cl_3$ with diols, especially for the chiral diols used in titanium complexes for various asymmetic syntheses of organic compounds. Usually, solid-state structures are not easily obtainable for Ti−chiral diol complexes.

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Supporting Information Available: Tables of crystallographic data, including final coordinates, bond lengths, bond angles, and anisotropic displacement coefficients for complexes **2** and **3** (16 pages). Ordering information is given on any current masthead page.

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