

Chemistry of $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$ with Chloride and Oxygen-Containing Ligands: The Roles of Alkoxide and Solvents in the Six-Coordinate Titanium Complexes

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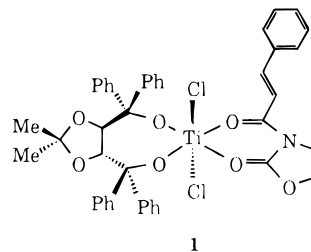
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Abstract: $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$ reacts easily with various ligands to form a series of six-coordinate complexes, $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_5]^{2-}(\text{HAm}^+)_2$ ($\text{Am} = \text{NEt}_3$ (**7a**) or NC_5H_5 (**7b**)), $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3\text{L}_2$ ($\text{L} = \text{THF}$ (**8**) or PhCHO (**9**)), $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3(\text{PhCHO})(\text{Et}_2\text{O})$ (**10**), and $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_2(\mu\text{-Cl})(\text{PhC}(\text{O})\text{OMe})_2]$ (**11**). Upon dissolution of **7a** in THF, **8** was obtained. When 1 mol equiv of HNEt_3Cl was added to **8**, $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_4(\text{THF})]^{-}(\text{HNEt}_3)^{+}$ (**12**) was obtained. With the addition of another 1 mol equiv of HNEt_3Cl , **12** was converted to **7a**. One THF in **8** can be removed in vacuo to give the chloride-bridged dimer $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_2(\mu\text{-Cl})(\text{THF})_2]$ (**13**) which can be converted back to **8** by dissolving in THF. **13** was found to react with 2 mol equiv of HNEt_3Cl or PhCHO to give **12** and $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3(\text{PhCHO})(\text{THF})$ (**14**), respectively. The molecular structures of **7b**, **8**, and **10–13** show short Ti–OⁱPr distances, and the relative bonding order of $\text{O}^i\text{Pr}^- > \text{Cl}^- > \text{THF} > \text{Et}_2\text{O} > \text{PhCHO} > \mu\text{-Cl}^- > \text{RC}(\text{O})\text{OMe}$ is discussed based on the solid state structures. This bonding sequence is very useful for the prediction of the geometry for six-coordinate complexes of early transition metals with the following principle: The strongest ligand prefers a trans position to the weakest ligand, and the second strongest ligand favors a trans position to the second weakest ligand in the complex. Kinetically, the trans position to the isopropoxide is rather labile for substitution, and the lability of the trans ligand ensures the effectiveness of titanium alkoxides for subsequent reactions or as catalysts in many asymmetric organic syntheses.

Introduction

The chemistry of group 4 metal alkoxides has been extensively studied for several decades by Bradley and others.¹ More recently, titanium(IV) alkoxides are found to be very useful reagents or catalysts in asymmetric synthesis such as the enantioselective aldol reactions,² asymmetric epoxidation of olefins,³ asymmetric Diels–Alder reactions,⁴ and asymmetric carbonyl–ene reactions.⁵ In general, the active titanium species are generated in situ from the reaction of $\text{Ti}(\text{OR})_{4-x}\text{Cl}_x$ with chiral ligands. However, the reactions concern mainly the chirality and the steric effect of ligands, and the intermediates or the transition states are proposed exclusively to account for the results. Recently, Jørgensen et al.⁶ reported the crystal

structure of titanium complex **1** which is conformationally



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different from the proposed intermediate⁷ in solution for the Diels–Alder reaction **1**.⁸ In reality, the solid state structures may not be available for every case, and therefore the prediction of structures for titanium complexes in solution seems extremely important for the understanding and development of asymmetric syntheses using titanium reagents.

Recently we found that ligands in titanium complexes play extremely important role in geometries and reactivities. In this report, various ligands commonly encountered in the titanium chemistry such as chloride, aldehyde, ester, THF, and diethyl ether were used to react with $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3$ (**6**) to form series of six-coordinate complexes. Through the analyses of the solid state structures of these complexes, the sequence of bonding order for ligands toward the titanium center are $\text{O}^i\text{Pr}^- > \text{Cl}^- > \text{THF} > \text{Et}_2\text{O} > \text{PhCHO} > \mu\text{-Cl}^- > \text{RC}(\text{O})\text{OMe}$. This

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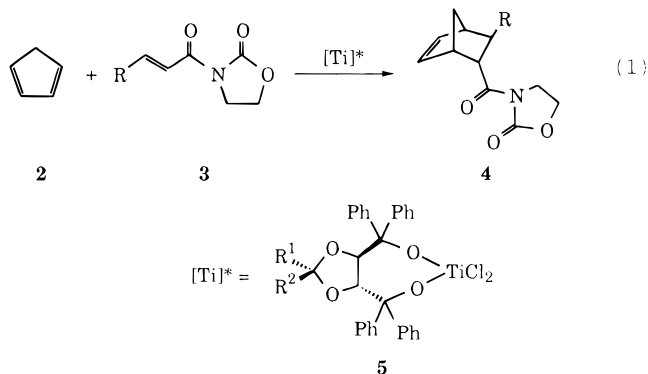
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bonding sequence provides useful information for the prediction of the geometries of six-coordinate titanium complexes with a simple rule of "the strong ligand trans to the weak ligand". This rule suggests that the strongest alkoxide ligands should be trans to the weakest ligands in a system, and indeed, the solid state structure of **1** shows that both alkoxides are trans to the weak carbonyl oxygens leaving two chlorides trans to each other.

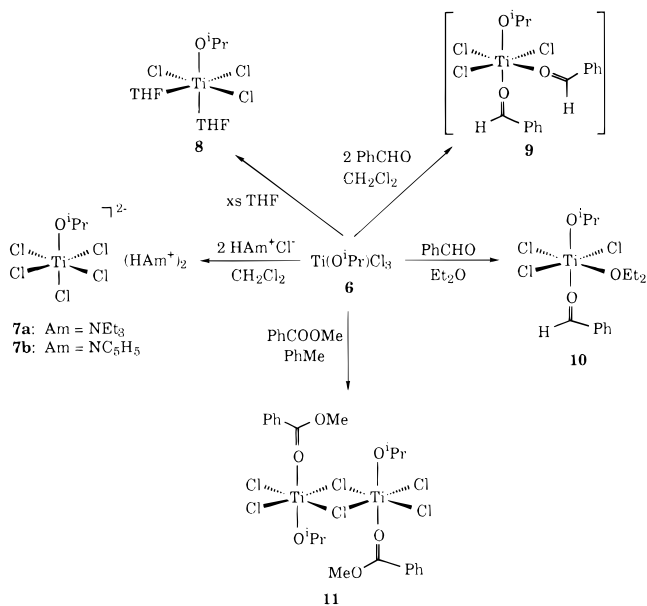
Besides the structural importance, this study clearly demonstrates the lability of ligand trans to the alkoxide. This lability of the trans ligand may be the key factor of efficiency of titanium alkoxides used as the reagents or catalysts for various organic syntheses.

Results and Discussion

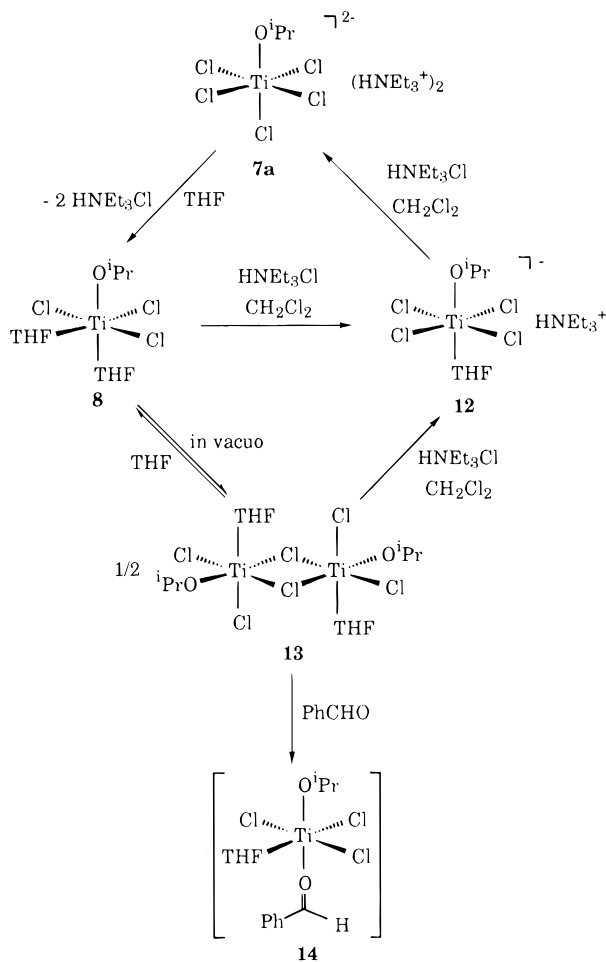
Synthesis of Complexes. The reactions of **6** with chloride, THF, benzaldehyde, or methyl benzoate are outlined in Scheme 1. Two mol equiv of chloride, THF, or benzaldehyde added easily to **6** afforded monomeric six-coordinate complexes [Ti(OⁱPr)Cl₅]²⁻(HAm⁺)₂ (Am = NEt₃ (**7a**) or NC₅H₅ (**7b**)), Ti(OⁱPr)Cl₃(THF)₂ (**8**), and Ti(OⁱPr)Cl₃(OCHC₆H₅)₂ (**9**) in high yield. When 1 mol equiv of benzaldehyde was added to **6** in diethyl ether, the complex Ti(OⁱPr)Cl₃(OEt₂)(OCHC₆H₅) (**10**) was obtained immediately as precipitate. In the reaction of **6** with methyl benzoate, the 1:1 stoichiometric dimeric [Ti(OⁱPr)Cl₂(μ-Cl)(OC(OMe)C₆H₅)₂] (**11**) was obtained even with the addition of 2 mol equiv of methyl benzoate.

The ligands, except isopropoxide, are rather labile and can be replaced in solution or removed in vacuo easily as shown in Scheme 2. When **7a** was dissolved in THF, two chlorides were replaced by the massively present THF to give **8**. Two THF's are inequivalent based on the molecular structure of **8**. However only one set of two sharp multiplets at δ 4.19 and 1.97 is observed in CD₂Cl₂ at room temperature for the indication of fast exchanges between two THF's. At -60 °C, the resonance at δ 1.97 broadens slightly, but the resonance at δ 4.19 splits into three broad peaks of relative intensities of 2:3:1 at δ 4.33, 4.20, and 3.79, respectively. Though, at low temperatures, the splitting of the resonances of the methylene protons adjacent to the oxygen donor is more complicated than the expected two peaks of equal intensities for two inequivalent THF's, the dynamic exchanges of two THF's are obvious from the VT NMR study. When 1 mol equiv of HNEt₃Cl was added to **8** in CH₂Cl₂, the chloride replaced one THF to form [Ti(OⁱPr)Cl₄(THF)]⁻(HNEt₃)⁺ (**12**). With the addition of another 1 mol equiv of HNEt₃Cl to **12**, **7a** was obtained. In vacuo, one of the THF's in **8** was removed to give the chloride-bridged dimeric complex [Ti(OⁱPr)Cl₂(μ-Cl)(THF)]₂ (**13**) which was converted back to **8** upon dissolution in THF. Complex **13** was found to react with 2 mol equiv of HNEt₃Cl or benzaldehyde to give **12** and Ti(OⁱPr)Cl₃(THF)(OCHC₆H₅) (**14**), respectively.

Scheme 1



Scheme 2



Solid State Structures of 7b, 8, and 10–13. The molecular structures of **7b**,¹⁰ **8**,¹¹ **10**,¹² **11**,¹³ **12**,¹⁴ and **13**¹⁵ are shown in Figure 1, and the selected bond lengths and bond angles are

(10) **7b**: pale yellow plate of size 0.3 × 0.3 × 0.4 mm, orthorhombic *Pnma*, *a* = 16.995(3) Å, *b* = 15.083(3) Å, *c* = 7.498(2) Å, *V* = 1922.1(7) Å³, *Z* = 4, *R* = 0.042, and *R_w* = 0.041.

(11) **8**: colorless plate of size 0.4 × 0.7 × 0.7 mm, monoclinic *P2₁/c*, *a* = 8.056(2) Å, *b* = 12.889(2) Å, *c* = 16.242(5) Å, β = 92.06(2)°, *V* = 1685.4(7) Å³, *Z* = 4, *R* = 0.053, and *R_w* = 0.065.

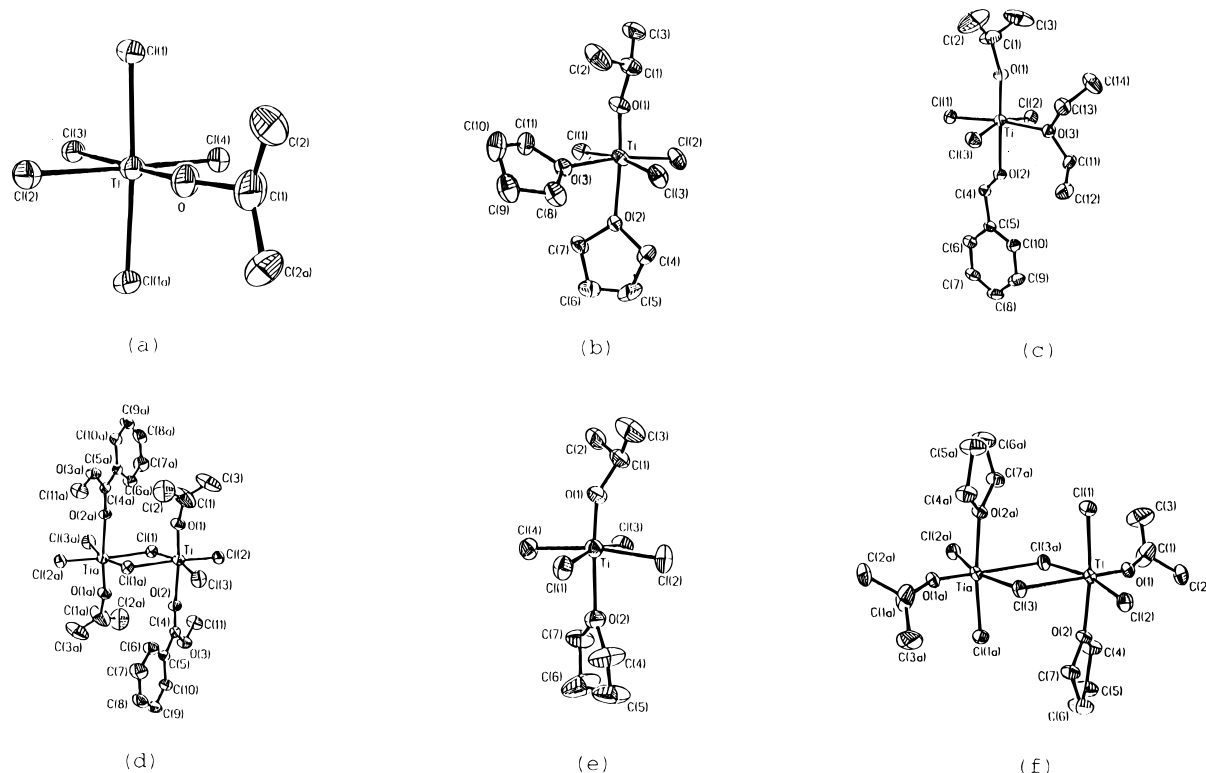


Figure 1. Molecular structures of (a) $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_5]^{2-}$ (**7b**), (b) $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3(\text{THF})_2$ (**8**), (c) $\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_3(\text{PhCHO})(\text{OEt}_2)$ (**10**), (d) $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_2(\mu\text{-Cl})(\text{PhC}(\text{O})\text{OMe})_2]$ (**11**), (e) $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_4(\text{THF})]^-$ (**12**), and (f) $[\text{Ti}(\text{O}^i\text{Pr})\text{Cl}_2(\mu\text{-Cl})(\text{THF})_2]$ (**13**). The hydrogen atoms are omitted for clarity.

listed in Table 1. All structures show six-coordinate geometry around the titanium metal center, and the most prominent feature of the structures is the short Ti–O(isopropoxide) bond distances (1.702–1.742 Å) which indicates the strong O to Ti π bonding. For **7b**, the Ti–O distance is short at 1.742(6) Å, and the distance between the titanium metal and the chloride trans to the isopropoxide is extremely long at 2.581(3) Å (Ti–Cl(3)). This Ti–Cl distance is much longer than the average distance between the titanium metal and the cis chlorides at 2.375 Å. Moreover, this distance is comparable to or even longer than the distances between the titanium and the bridged chlorides¹⁶ and is believed to be the longest Ti–Cl(terminal) distance observed thus far. In connection to the strong Ti–O bonding, the Ti–O–C(1) angle is large at 161.8(7)° and the ligands cis to the isopropoxide bend away from the isopropoxide with the angles ranging from 91.1(2)° to 97.3(1)°. Due to the activation of the trans chloride by the isopropoxide, this chloride is quite labile in solution and the replacement of chlorides by THF's occurs easily to give complex **8** when **7a** dissolves in THF. Apparently the isopropoxide ligand in the six-coordinate titanium complexes exerts strong trans influence, and the weakest ligand finds a position trans to it. For complex **7b**

containing only chlorides and one isopropoxide, the phenomenon of the long trans chloride to Ti distance suggests the bonding order of $\text{OR}^- > \text{Cl}^-$. With the extension of this rule, then, the second strongest ligand would be trans to the second weakest ligand in a complex. For the neutral complex **8**, the Ti–O(isopropoxide) distance is even shorter at 1.726(4) Å and the THF ligand trans to the isopropoxide is the weakest one. The second THF is then trans to the second strongest chloride ligand with the Ti–Cl distance of 2.298 Å which is shorter by ~ 0.02 Å than the distances for chlorides trans to each other. The shortening of the Ti–Cl distance trans to the THF also supports the better bonding of Cl^- than THF, and the bonding order is $\text{O}^i\text{Pr}^- > \text{Cl}^- > \text{THF}$.

For **10**, the weakest ligand is the benzaldehyde ligand based on the trans position of it to the isopropoxide. Since the Ti–Cl distance for the chloride trans to the OEt_2 group at 2.296(1) Å is somewhat shorter than the values of 2.332(1) and 2.333(1) Å for the other two chlorides which are trans to each other, the bonding of Cl^- is ahead of OEt_2 with the bonding order of $\text{O}^i\text{Pr}^- > \text{Cl}^- > \text{OEt}_2 > \text{PhCHO}$.

Complex **11** is a dimeric species bridging through two chlorides, and the methyl benzoate bonds to the titanium metal through the carbonyl oxygen in trans position to the isopropoxide. Therefore the methyl benzoate ligand is an even weaker ligand than the bridging Cl^- and the Ti–O(isopropoxide) distance at 1.702(4) Å is believed to be the shortest Ti–OR distance observed thus far. For **11**, the relative bonding sequence of $\text{O}^i\text{Pr}^- > \text{Cl}^- > \mu\text{-Cl}^- > \text{PhC}(\text{O})\text{OMe}$ is obtained. The weak bonding of the methyl benzoate explains the formation of the 1:1 stoichiometric dimeric species **11** even with the addition of 2 mol equiv of methyl benzoate to **6**. The molecular structure of **11** has revealed a weaker bonding of the methyl benzoate ligand than the $\mu\text{-Cl}^-$, and therefore, the second molar equivalent of methyl benzoate is not capable of breaking the Ti–Cl(μ) bonds of the dimeric species **11** after the formation of **11** from the first molar equivalent of methyl benzoate.

(12) **10**: yellow plate of size 0.4 × 0.6 × 0.8 mm, triclinic $P\bar{1}$, $a = 9.003(2)$ Å, $b = 9.347(3)$ Å, $c = 12.078(3)$ Å, $\alpha = 93.17(2)^\circ$, $\beta = 93.03(2)^\circ$, $\gamma = 105.38(2)^\circ$, $V = 976.1(4)$ Å³, $Z = 2$, $R = 0.041$, and $R_w = 0.057$.

(13) **11**: pale yellow plate of size 0.2 × 0.4 × 0.6 mm, triclinic $P\bar{1}$, $a = 8.945(2)$ Å, $b = 9.549(3)$ Å, $c = 10.715(2)$ Å, $\alpha = 115.48(2)^\circ$, $\beta = 98.91(2)^\circ$, $\gamma = 102.38(2)^\circ$, $V = 774.6(3)$ Å³, $Z = 1$, $R = 0.038$, and $R_w = 0.046$.

(14) **12**: pale yellow plate of size 0.4 × 0.6 × 0.8 mm, orthorhombic $P2_12_1$, $a = 10.233(2)$ Å, $b = 11.428(3)$ Å, $c = 18.682(4)$ Å, $V = 2184.6(8)$ Å³, $Z = 4$, $R = 0.032$, and $R_w = 0.039$.

(15) **13**: colorless plate of size 0.25 × 0.60 × 0.80 mm, monoclinic $C2/c$, $a = 18.588(4)$ Å, $b = 7.192(2)$ Å, $c = 19.487(4)$ Å, $\beta = 109.03(3)^\circ$, $V = 2462.7(9)$ Å³, $Z = 4$, $R = 0.043$, and $R_w = 0.061$.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **7b**, **8**, and **10–13**

		7b		8		10	
type of bond length							
Ti–O ⁱ Pr	Ti–O	1.742(6)	Ti–O(1)	1.726(4)	Ti–O(1)	1.721(2)	
Ti–Cl(terminal, cis)	Ti–Cl(1)	2.361(2)	Ti–Cl(1)	2.324(2)	Ti–Cl(1)	2.296(1)	
	Ti–Cl(2)	2.359(3)	Ti–Cl(2)	2.298(2)	Ti–Cl(2)	2.333(1)	
	Ti–Cl(4)	2.406(3)	Ti–Cl(3)	2.318(2)	Ti–Cl(3)	2.332(1)	
Ti–Cl(terminal, trans)	Ti–Cl(3)	2.581(3)					
Ti–Cl(bridging, cis)							
Ti–Cl(bridging, trans)							
Ti–O(THF, cis)			Ti–O(3)	2.165(4)			
Ti–O(THF, trans)			Ti–O(2)	2.164(4)			
Ti–O(Et ₂ O, cis)					Ti–O(3)	2.141(2)	
Ti–O(PhCHO, trans)					Ti–O(2)	2.171(2)	
Ti–O(ester, trans)							
type of bond angle							
Ti–O–C	Ti–O–C(1)	161.8(7)	Ti–O(1)–C(1)	153.7(4)	Ti–O(1)–C(1)	154.4(3)	
ⁱ PrO–Ti–L(cis)	O–Ti–Cl(1)	93.3(1)	O(1)–Ti–Cl(1)	96.7(1)	O(1)–Ti–Cl(1)	93.7(1)	
	O–Ti–Cl(2)	97.3(2)	O(1)–Ti–Cl(2)	99.4(1)	O(1)–Ti–Cl(2)	96.4(1)	
	O–Ti–Cl(4)	91.1(2)	O(1)–Ti–Cl(3)	92.1(1)	O(1)–Ti–Cl(3)	97.6(1)	
			O(1)–Ti–O(3)	90.1(2)	O(1)–Ti–O(3)	93.1(1)	
		11	12			13	
type of bond length							
Ti–O ⁱ Pr	Ti–O(1)	1.702(4)	Ti–O(1)	1.740(3)	Ti–O(1)	1.715(3)	
Ti–Cl(terminal, cis)	Ti–Cl(2)	2.271(2)	Ti–Cl(1)	2.372(1)	Ti–Cl(1)	2.283(2)	
	Ti–Cl(3)	2.272(2)	Ti–Cl(2)	2.391(2)	Ti–Cl(2)	2.276(2)	
			Ti–Cl(3)	2.337(2)			
			Ti–Cl(4)	2.334(1)			
Ti–Cl(terminal, trans)							
Ti–Cl(bridging, cis)	Ti–Cl(1)	2.495(2)			Ti–Cl(3A)	2.463(1)	
	Ti–Cl(1A)	2.507(2)					
Ti–Cl(bridging, trans)					Ti–Cl(3)	2.557(1)	
Ti–O(THF, cis)					Ti–O(2)	2.109(3)	
Ti–O(THF, trans)			Ti–O(2)	2.227(3)			
Ti–O(Et ₂ O, cis)							
Ti–O(PhCHO, trans)							
Ti–O(ester, trans)	Ti–O(2)	2.142(4)					
type of bond angle							
Ti–O–C	Ti–O(1)–C(1)	157.5(6)	Ti–O(1)–C(1)	144.3(3)	Ti–O(1)–C(1)	157.3(4)	
ⁱ PrO–Ti–L(cis)	O(1)–Ti–Cl(1)	95.5(2)	O(1)–Ti–Cl(1)	98.3(1)	O(1)–Ti–Cl(1)	95.7(1)	
	O(1)–Ti–Cl(2)	97.1(2)	O(1)–Ti–Cl(2)	91.4(1)	O(1)–Ti–Cl(2)	103.3(1)	
	O(1)–Ti–Cl(3)	94.5(2)	O(1)–Ti–Cl(3)	92.5(1)	O(1)–Ti–Cl(3A)	89.2(1)	
	O(1)–Ti–Cl(1A)	91.0(2)	O(1)–Ti–Cl(4)	96.6(1)	O(1)–Ti–O(2)	90.8(1)	

The structure of complex **12** provides no further information about the bonding order. The molecular structure of **13** is a dimeric species with two chloride bridges, similar to the structure of **11**. However the strongest isopropoxide ligand is trans to the $\mu\text{-Cl}^-$ rather than the coordinating THF, indicating stronger bonding of THF than the $\mu\text{-Cl}^-$ with the order of $\text{O}^i\text{Pr} > \text{Cl}^- > \text{THF} > \mu\text{-Cl}^-$. Unfortunately, the solid state structures provide no information about the relative orders between THF and Et₂O and between PhCHO and $\mu\text{-Cl}^-$. Since THF is in general considered to be the better ligand than Et₂O, we put it ahead of Et₂O.¹⁷ Besides, the isolation of the di-THF complex **8** from the reaction of **6** with 2 mol equiv of PhCHO in THF is an indirect evidence for the stronger bonding of THF than Et₂O. In Et₂O, the addition of 2 mol equiv of PhCHO to **6** gives the complex **10** which contains one PhCHO and one Et₂O. In order to differentiate the relative order of PhCHO and $\mu\text{-Cl}^-$, two mol equiv of PhCHO were reacted with the chloride-bridged dimeric complex **13** to afford the monomeric complex **14**. The capability of PhCHO to break up the dimeric species **13** suggests stronger bonding of PhCHO than $\mu\text{-Cl}^-$. Therefore the overall bonding order in this study is $\text{O}^i\text{Pr} > \text{Cl}^- > \text{THF} > \text{Et}_2\text{O} > \text{PhCHO} > \mu\text{-Cl}^- > \text{PhC}(\text{O})\text{OCH}_3$.

In the above bonding sequence, the chloride ligand is second to the isopropoxide, and this result is consistent with the relative

order of the mean bond dissociation energy of $\bar{D}(\text{Ti}-\text{O}^i\text{Pr})$ (115 kcal/mol) $> \bar{D}(\text{Ti}-\text{Cl})$ (102.7 kcal/mol).¹⁸ However the difference between these two ligands is small, and the chloride ligand also forms rather strong bond with titanium metal. The chloride ligand is expected to show considerable trans influence to the trans ligands weaker than it. For example, the Ti–Cl distance for the chloride trans to the Et₂O group in complex **10** is shorter than the distances for the chlorides trans to each other, and the Ti–Cl distance for the chloride trans to THF in complex **8** is also shorter. In principle, a longer Ti–O(THF) distance is expected for the THF trans to the strongest isopropoxide ligand in the di-THF complex **8** than the distance for the THF trans to the chloride. However nearly identical Ti–O(THF) distances (2.164(4) and 2.165(4) Å) are observed, and this may arise from the fact of the also strong Ti–Cl bond (probably partially) and/or the effect of crystal packing.

The above structural study reveals the following general features. The Ti–OⁱPr distances are relatively short for complexes containing only one terminal alkoxide. Also the Ti–OⁱPr distances are strongly subjected to the variations of the trans ligand with the observation of shorter Ti–O distances for the trans ligand lower in the bonding sequence. The overall electronic state of the complexes is a function of the donation

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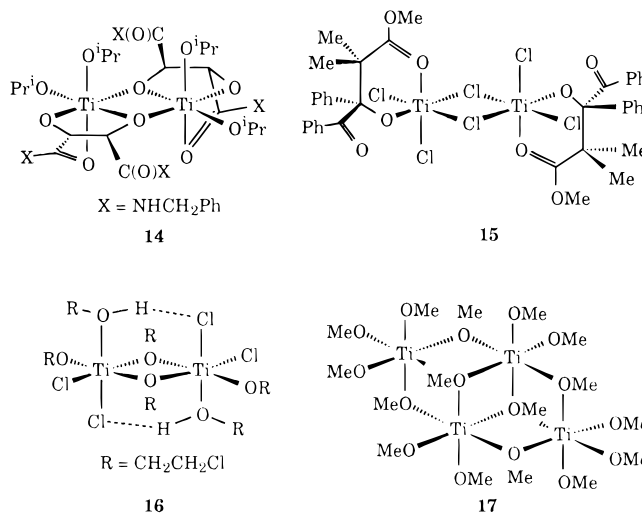
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abilities of ligands. For example, the corresponding bond distances for dianionic complex **7b** containing more Cl⁻ ligands are longer than that for the monoanionic complex **12** and, in turn, longer than that for the neutral complexes. The bond distance for the trans ligand to the strong isopropoxide is usually long in comparison with the values for the ligand trans to others.¹⁹ Due to the strong effect of the isopropoxide, all cis ligands bend away from isopropoxide with the observation of the ⁱPrO-Ti-L(cis) angles >90°.

Conclusions

Six-coordination is the predominant geometry for titanium metal with ligands of small to moderate size.²⁰ Though several geometric isomers are possible for complexes containing several different ligands, the structures of complexes are governed by the bonding order of ligands with the following principle for the six-coordinate titanium complexes: The strongest ligand prefers a trans position to the weakest ligand, and the second strongest ligand favors a trans position to the second weakest ligand in the complex. Without the steric constrain or the geometrical requirement of bi- or multidentate ligands, the validity of this rule is demonstrated extremely well for complexes of known structures such as **1**,⁶ **14**,²¹ **15**,²² **16**,²³ **17**,²⁴ and others.²⁰ Interestingly, in the cases of complexes containing two or more alkoxides, some of the alkoxides are in the bridging position to minimize the number of the strong terminal alkoxides on a metal center or to prevent two strong alkoxides trans to each other as in the structures of complexes **14**, **16**, **17**, and others.²⁵ Oxygen-containing solvents such as THF or Et₂O can participate in the coordination to achieve a six-coordinate structure when there is not enough free ligand in solution. However, due to the strong trans effect of alkoxide, the volatile trans ligand or the

coordinated solvent like alcohol, Et₂O, or THF may be removed in vacuo to form dimers or oligomers through the bridging of chlorides or alkoxides. If the reaction system contains volatile ligands or if a volatile solvent capable of coordination is used, the species in solution may not be the same as the solid material which is obtained from evaporating the solvent completely.



Kinetically the trans ligand to the alkoxide is rather labile for substitutions, and the reaction site of a given complex containing alkoxide is predictable in solution. Most importantly, the lability of the trans ligand to the alkoxide would secure the efficiency of the titanium alkoxides as catalysts in practical usages. Therefore, by using the bonding sequence and with the incorporation of the dominating effect of the alkoxide and also of the steric effect of the bi- or multidentate chiral ligands or other ligands in complexes, it seems highly promising to design effective catalysts possessing only a specific reaction site. Obviously, a more complete and comprehensive bonding sequence is necessary, and we are continuously working on this and also on the syntheses of chiral metal complexes for the asymmetric catalytic reactions.

Experimental Section

Reagents and General Techniques. Ti(OⁱPr)Cl₃ was prepared according to the literature procedures. NEt₃ and pyridine were distilled and stored over molecular sieves. HPyCl and HNEt₃Cl salts were obtained by bubbling HCl gas into a solution of pyridine or NEt₃ in benzene, respectively. Benzaldehyde and methyl benzoate were dried and stored over molecular sieves. Solvents were dried by refluxing for at least 24 h over P₂O₅ (dichloromethane) or sodium/benzophenone (benzene, toluene, hexane, diethyl ether, tetrahydrofuran) and 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 Triethylammonium Pentachloroisopropoxotitanate(IV) (7a). HNEt₃Cl (1.10 g, 8.00 mmol) was added to a solution of Ti(OⁱPr)Cl₃ (0.853 g, 4.00 mmol) in 40 mL of CH₂Cl₂ at room temperature. The color of the solution changed to yellowish-green, and the solution was stirred for another 2 h. The solvent was removed to give a pale green solid (1.78 g, 91.4%). ¹H NMR (CDCl₃): δ 9.47 (br, 2H), 5.27 (m, 1H), 3.25 (m, 12H), 1.51 (d, 6H), 1.43 (t, 18H). ¹³C{¹H} NMR (CDCl₃): δ 91.3 (CH), 46.6 (NCH₂CH₃), 23.4 (OCH-(CH₃)₂), 8.7 (NCH₂CH₃). Anal. Calcd for C₁₅H₃₉N₂OCl₅Ti: C, 36.87; N, 5.73; H, 8.04. Found: C, 36.93; N, 5.72; H, 8.01.

Synthesis of Pyridinium Pentachloroisopropoxotitanate(IV) (7b). HPyCl (0.924 g, 8.00 mmol) was added to a solution of Ti(OⁱPr)Cl₃ (0.853 g, 4.00 mmol) in 40 mL of CH₂Cl₂ at room temperature. A pale green solid precipitated gradually, and the resulting mixture was stirred for 12 h. The solid was filtered to give a pale green product (1.62 g, 91.1%). ¹H NMR (NC₅D₅): δ 8.71 (m, 4H), 7.56 (m, 2H),

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7.19 (m, 4H), 4.16 (m, 1H), 1.28 (d, 6H), -0.38 (br, 2H). Anal. Calcd for C₁₃H₁₉N₂OCl₅Ti: C, 35.13; N, 6.30; H, 4.31. Found: C, 34.48; N, 6.31; H, 4.23.

Synthesis of Trichloroisopropoxobis(tetrahydrofuran)titanium(IV) (8). THF (30 mL) was added to Ti(OⁱPr)Cl₃ (0.853 g, 4.00 mmol) in a reaction flask, and the reaction was exothermic. The mixture was stirred for 20 min, and then 40 mL of hexane was slowly added to make two layers. The solution was cooled to -15 °C to give colorless crystals (1.34 g, 93.6%). ¹H NMR (CDCl₃): δ 5.45 (m, 1H), 4.33 (m, 8H), 2.02 (m, 8H), 1.55 (d, 6H). ¹³C{¹H} NMR (CDCl₃): δ 94.3 (CH), 73.9 (THF), 25.4 (THF), 23.5 (CH₃). Anal. Calcd for C₁₁H₂₃O₃Cl₃Ti: C, 36.95; H, 6.48. Found: C, 36.14; H, 6.14.

Synthesis of Bis(benzaldehyde)trichloroisopropoxotitanium(IV) (9). Benzaldehyde (0.61 mL, 6.00 mmol) was added to a solution of Ti(OⁱPr)Cl₃ (0.640 g, 3.00 mmol) in 30 mL of toluene at room temperature. The reaction mixture was stirred for 12 h and then was allowed to stand at -15 °C for 48 h to afford yellow crystals (1.16 g, 90.9%). ¹H NMR (CDCl₃): δ 10.17 (s, 2H), 8.05 (m, 4H), 7.79 (m, 2H), 7.60 (m, 4H), 5.40 (m, 1H), 1.61 (d, 6H). ¹³C{¹H} NMR (CDCl₃): δ 200.6 (CHO), 137.6, 133.9, 132.4, 129.5, 93.8 (CH), 23.6 (CH₃). IR (Nujol mull): 1683 (w), 1644 (s) cm⁻¹. Anal. Calcd for C₁₇H₁₉O₃Cl₃Ti: C, 47.98; H, 4.50. Found: C, 47.39; H, 4.59.

Synthesis of (Benzaldehyde)trichloro(diethyl ether)isopropoxotitanium(IV) (10). Benzaldehyde (0.31 mL, 3.00 mmol) was added to a solution of Ti(OⁱPr)Cl₃ (0.640 g, 3.00 mmol) in 10 mL of diethyl ether at room temperature. A large quantity of white solid precipitated immediately, and then 30 mL of toluene was added to dissolve the precipitate completely. The resulting clear solution was allowed to stand at -15 °C for 24 h to afford yellow crystals (0.820 g, 69.5%). ¹H NMR (CDCl₃): δ 10.17 (s, 1H), 8.08 (m, 2H), 7.81 (m, 1H), 7.61 (m, 2H), 5.31 (m, 1H), 3.55 (q, 4H), 1.60 (d, 6H), 1.22 (t, 6H). ¹³C{¹H} NMR (CDCl₃): δ 201.3 (CHO), 138.1, 133.7, 132.8, 129.6, 94.7 (CH), 66.3 (OCH₂), 23.8 (CH₃), 14.8 (OCH₂CH₃). IR (Nujol mull): 1686 (w), 1635 (s) cm⁻¹. Anal. Calcd for C₁₄H₂₃O₃Cl₃Ti: C, 42.72; H, 5.89. Found: C, 42.39; H, 5.59.

Synthesis of Bis(μ-chloro)dichloro(methyl benzoate)isopropoxotitanium(IV) (11). Methyl benzoate (1.08 mL, 6.00 mmol) was added to a solution of Ti(OⁱPr)Cl₃ (1.28 g, 6.00 mmol) in 30 mL of toluene at room temperature. The solution changed color to light yellow and was stirred for 3 h. The solution was concentrated to about 10 mL and cooled to -25 °C to afford a yellow plate of crystals (1.47 g, 70.1%). ¹H NMR (CDCl₃): δ 8.20 (m, 4H), 7.63 (m, 2H), 7.47 (m, 4H), 5.32 (m, 2H), 4.16 (s, 6H), 1.57 (d, 12 H). ¹³C{¹H} NMR (CDCl₃): δ 170.8 (CO), 134.5, 130.9, 128.6, 128.5, 95.6 (CH), 55.1 (OCH₃), 24.0 (CH₃). Anal. Calcd for C₂₂H₃₀O₆Cl₆Ti₂: C, 37.80; H, 4.33. Found: C, 36.77; H, 4.44.

Synthesis of Triethylammonium Tetrachloroisopropoxo(tetrahydrofuran)titanate(IV) (12). HNEt₃Cl (0.275 g, 2.00 mmol) was added to a solution of Ti(OⁱPr)Cl₃(THF)₂ (8) (0.715 g, 2.00 mmol) in 30 mL of CH₂Cl₂ at room temperature. The HNEt₃Cl dissolved completely in 20 min to give a clear green solution, and the solvent was removed to give a pale green solid in nearly quantitative yield (0.820 g, 96.9%). ¹H NMR (CDCl₃): δ 8.42 (br, 1H), 5.39 (m, 1H), 4.25 (m, 4H), 3.27 (br, 6H), 1.95 (m, 4H), 1.52 (d, 6H), 1.43 (br, 9H). ¹³C{¹H} NMR (CDCl₃): δ 92.0 (CH), 72.8 (THF), 47.0 (NCH₂), 25.3 (THF), 23.3 (CH₃), 8.8 (NCH₂CH₃). Anal. Calcd for C₁₃H₃₁O₂NCl₄Ti: C, 36.90; N, 3.31; H, 7.39. Found: C, 35.78; N, 3.40; H, 7.22.

Synthesis of Bis(μ-chloro)dichloroisopropoxo(tetrahydrofuran)titanium(IV) (13). Crystals of 8 (1.43 g, 4.00 mmol) in a flask were under vacuum for 12 h to give a white powder (1.10 g, 96.4%).

Colorless crystals of 13 can be obtained by slowly diffusing hexane into a solution of 13 in toluene. ¹H NMR (CDCl₃): δ 5.36 (m, 2H), 4.43 (m, 8H), 2.07 (m, 8H), 1.56 (d, 12H). ¹³C{¹H} NMR (CDCl₃): δ 94.1 (CH), 74.0 (THF), 25.3 (THF), 23.3 (CH₃). Anal. Calcd for C₁₄H₃₀O₄Cl₆Ti₂: C, 29.45; H, 5.30. Found: C, 28.96; H, 5.09.

Synthesis of (Benzaldehyde)trichloroisopropoxo(tetrahydrofuran)titanium(IV) (14). Benzaldehyde (0.31 mL, 3.00 mmol) was added to a solution of complex 13 (0.856 g, 1.50 mmol) in 15 mL of CH₂Cl₂ at room temperature. The solution changed color from light yellow to orange and was stirred for another 1 h. After the removal of solvent, a yellowish-orange powder (1.01 g, 85.7%) was obtained. ¹H NMR (CDCl₃): δ 10.2 (s, 1H), 8.05 (m, 2H), 7.77 (m, 1H), 7.60 (m, 2H), 5.47 (m, 1H), 4.34 (m, 4H), 2.05 (m, 4H), 1.69 (d, 6H). ¹³C{¹H} NMR (CDCl₃): δ 199.3 (CHO), 137.0, 134.5, 131.9, 129.5, 93.8 (CH), 74.4 (THF), 25.4 (THF), 23.5 (CH₃). Anal. Calcd for C₁₄H₂₁O₃Cl₃Ti: C, 42.94; H, 5.41. Found: C, 43.09; H, 5.49.

Physical Measurements. ¹H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer, and ¹³C NMR spectra were recorded with the Varian VXR-300 (75.43 MHz) spectrometer. The ¹H and ¹³C NMR 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 poly(styrene). Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument.

Crystal Structure Determinations. Crystals of 7b, 8, and 10–13 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). The absorption correction was not performed on the samples. 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 were considered as the riding atom on the carbon atom with a C–H bond length of 0.96 Å, and the hydrogen atom temperature factors were fixed at 0.08. The hydrogen atoms were included for refinements in the final cycles. The structure of 12 was found to possess two disordered THF's of equal populations.

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Supporting Information Available: Tables of crystallographic data including final coordinates, bond lengths, bond angles, and anisotropic displacement coefficients for complexes 7b, 8, and 10–13 (61 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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