Interaction Modes of Titanium Tetrachloride with the Carbonyl Functionality

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Mesityl aldehyde binds $TiCl_4$ leading to the first structurally characterized $TiCl_4$-aldehyde adduct, *cis*-[$(MesCHO)_2TiCl_4$] (Mes = 2,4,6-$Me_3C_6H_2$) (**1**), which contains a pseudooctahedral titanium and two aldehyde carbonyl groups in a *cis* arrangement. However, in the case of a 1:1 $TiCl_4$−acetone adduct [$\{(Me_2CO)TiCl_3\}_2(\mu\text{-}Cl)_2$] (**3**) the solid-state structure of this acid-base complex is that of a chloro-bridged dimer. Both kinds of structures were suggested for the products [$\{(PhCOMe)TiCl_3\}_2(\mu\text{-}Cl)_2$] (**4**) and [*cis*-$(PhCOMe)_2TiCl_4$] (**5**) formed by the reaction of $TiCl_4$ with acetophenone in 1:1 and 1:2 molar ratio. Thioesters behave like acetone in that they give adducts **8** and **9** with $TiCl_4$, where **9**, [$\{(PhSC(Me)O)TiCl_3\}_2(\mu\text{-}Cl)_2$], exhibits a solid-state dimeric structure like **3**. The bidentate bonding mode of the chiral propionyloxazolidone **12** with $TiCl_4$ was revealed by an X-ray analysis of **13**.

Lewis acid complexation plays a fundamental role in organic synthesis[1]. Interactions of carbonyl compounds with Lewis acids change the stereoelectronic demands of the reaction center, making enhanced reactivities possible[2]. Moreover, the possibility of controlling the steric bulk and chirality of the Lewis acid offers one of the best methodologies known to date for enantioselective catalytic reactions. With a thorough knowledge of the structural and conformational demands of Lewis acid-carbonyl complexes, it should be possible to influence the stereoselectivities for Lewis acid-mediated reactions.

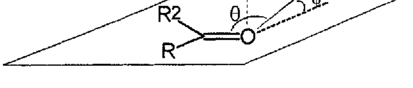
In the last ten years, a number of transition metal Lewis acid adducts of ketones and aldehydes were structurally characterized[3]. In the case of $TiCl_4$, numerous reports were published describing the use of this Lewis acid in Diels-Alder[4], ene[5], Hosomi-Sakurai[6], hetero Diels-Alder[7], and Mukaiyama reactions[8]. Although a number of crystal structures for $TiCl_4$ carbonyl adducts have been reported[9], the structural characterization of the geometrical relationship between $TiCl_4$ and ketones was only addressed in a few cases. In particular, the structural characterization of a complex between $TiCl_4$ and an aldehyde has not yet been reported[10].

Our interest in the mechanism of $TiCl_4$-mediated reactions such as those of Passerini[11] and Mukaiyama[12] motivated us to isolate and characterize some novel $TiCl_4$−carbonyl complexes. For example, we present the structural characterization of two new $TiCl_4$−carbonyl adducts, a $TiCl_4$−thiol ester and a $TiCl_4$−acyloxazolidinone adduct. These two classes of carbonyl compounds were shown to interact with $TiCl_4$, and the resulting complexes can be used for the in situ formation of the corresponding titanium enolates.

Results and Discussion

Certain factors were established as critical to the understanding of interactions between carbonyl compounds and Lewis acids[1,13]. The Lewis acid may be characterized by a high oxidation state, early transition metal, or lanthanide ion. The position of the carbonyl compound relative to the Lewis acid is defined by three parameters: *r*, θ, and ϕ (Scheme 1). The parameter *r* represents the Lewis acid carbonyl oxygen distance, θ defines the in-plane C−O−M angle, and ϕ the out-of-plane distortion of the interaction between the carbonyl group and the Lewis acid.

Scheme 1



Although the adducts of aldehydes with $TiCl_4$ have been employed in organic synthesis to accomplish acyclic stereoselection, it is quite unusual that structural data of these complexes have never been reported. What has been described is the coordination of other Lewis acids with aldehydes. In all the crystallographically defined σ complexes between aldehydes and other Lewis acids the metal is coordinated *syn* to the hydrogen and *trans* to the aldehyde residue. Reetz determined the X-ray crystal structure of BF_3 ·

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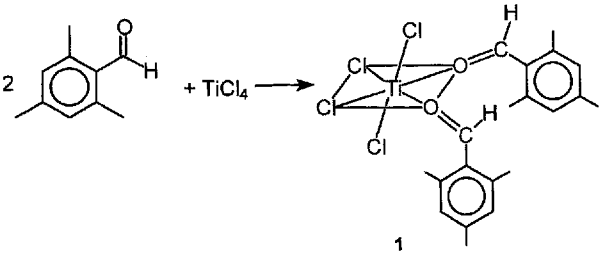
benzaldehyde[14] which clearly shows the BF_3 unit to be located *syn* to the hydrogen atom of benzaldehyde. Denmark performed an X-ray crystallographic analysis of $SnCl_4 \cdot$ (4-*t*Bu-benzaldehyde)$_2$[15] and showed that it is possible to correlate solid-state relationships with spectroscopic data for a 1:2 complex in solution. Three other crystallographically characterized Lewis acid-benzaldehyde complexes were reported[16].

We successfully isolated **1**, the first crystallographically characterized $TiCl_4$−aldehyde adduct, prepared by the reaction of $TiCl_4$ with 2 equiv. of mesityl aldehyde (Scheme 2).

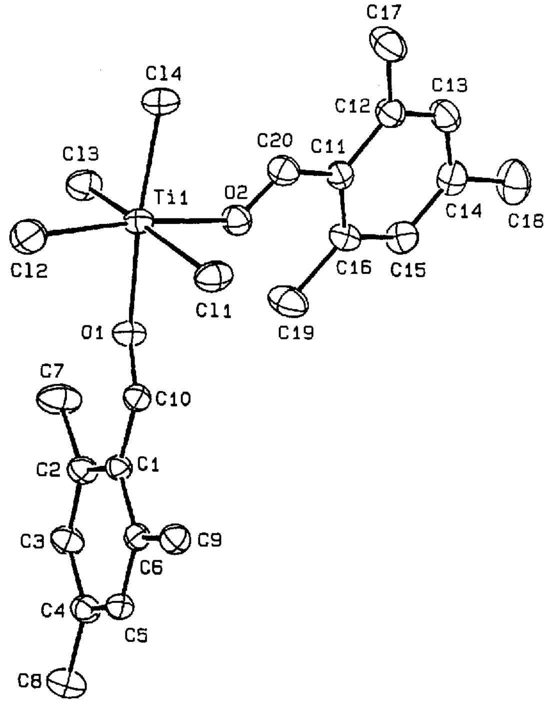
Scheme 2



1

The coordination sphere can be described as a distorted octahedron with the best equatorial plane running through titanium being defined by the Cl2 and Cl4 chlorine atoms and the O1 and O2 oxygen atoms from the aldehydes (Figure 1).

Figure 1. ORTEP drawing for complex **1** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti1−Cl4 2.244(1), Ti1−O2 2.091(2), Ti1−Cl2 2.231(1), O1−C10 1.234(5), Ti1−Cl3 2.293(1), O2−C20 1.229(5), Ti1−Cl1 2.308(1), Ti1−O1 2.100(3); O2−Ti1−O1 83.1(1), Cl2−Ti1−O1 89.9(1), Cl4−Ti1−O2 90.5(1), Ti1−O2−C20 133.7(2), Cl4−Ti1−O1 173.6(1), Ti1−O1−C10 134.4(2), Cl4−Ti1−Cl2 96.5(0), O1−C10−C1 125.2(3), Cl3−Ti1−Cl1 165.3(1), O11−C20−C11 126.0(3), Cl2−Ti1−O2 172.7(1)



The Ti−Cl bond lengths involving the *trans* chlorine atoms [Ti−Cl1 2.308(1) and Ti−Cl3 2.293(1) Å] are significantly longer than those in the plane which are opposite to the oxygen atoms [Ti−Cl2 2.231(1) and Ti−Cl4 2.244(1) Å]. The two Ti−O distances [Ti−O1 2.100(3), Ti−O2 2.091(2) Å] are not significantly different from each other and fall in the usual range[11,17]. The two organic ligands are arranged in a *cis* fashion around the metal [O2−Ti1−O1 83.1(1)°]. They are oriented in such a way as to give rise to short intramolecular contacts involving the aldehyde hydrogen atom and a chlorine atom. In particular, the O1−C10−C1···C6 fragment is nearly parallel to the O1,Cl1,Cl3,Cl4 coordination plane [dihedral angle 6.7(1)°] giving a H10···Cl1 distance of 2.56 Å (H10 is the hydrogen atom bound to C10), while the O2−C20−C11···C16 fragment is nearly parallel to the O1,O2,Cl2,C4 coordination plane [dihedral angle 12.4(1)°] giving a H20···Cl4 distance of 2.66 Å (H20 is the hydrogen atom bound to C20). Strictly speaking, the organic ligands are not planar, the methyl carbon atoms protruding significantly out of the aromatic ring. Also the aldehyde carbonyl groups are slightly rotated with respect to the aromatic ring, the O1−C10−C1−C2 and O2−C20−C11−C16 torsion angles being −5.9(5) and 5.0(6)°, respectively. The C1−C10 [1.430(5) Å] and C11−C20 [1.433(5) Å] bonds have some double bond character. Titanium does not lie in the planes of the aldehyde carbonyl groups, being out of the C1,C10,O1 and C11,C20,O11 planes by 0.219(1) and 0.327(1) Å, respectively.

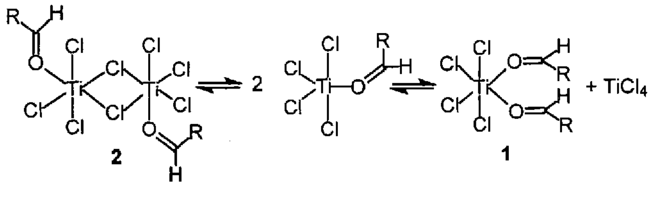
Theoretical studies showed that a bent coordination mode is preferred for Lewis acid interactions with carbonyl compounds[18]. Recent ab initio calculations performed on a $TiCl_4$−formaldehyde complex[19] also showed this preferential mode of coordination, which is clearly evident from our data of complex **1**. The formation of the *cis* isomer was theoretically predicted to be more exothermic and, in fact, this is the isomer which we observed in the case of complex **1**. Moreover, this theoretical paper also predicted average values of Ti−Cl bond lengths in the range between 2.28 and 2.30 Å, which are also in accord with our experimental values.

We examined the addition reaction of one equivalent of mesityl aldehyde with $TiCl_4$ which gave the analytically characterized complex **2**, the proposed 1:1 complex. However, the ^1H- and ^{13}C-NMR spectra (in CD_2Cl_2) of this complex are only slightly different from those obtained for our previously mentioned 1:2 complex **1**. Despite the fact that a 1:1 stoichiometry is more commonly employed for reactions promoted by $TiCl_4$, a 1:2 complex between $TiCl_4$ and carbonyl compounds was reported to be the more stable species[19]. The stoichiometry for aldehyde complexation can have significant implications on the outcome of the stereoselectivity of the nucleophilic attack[20].

The identity of $TiCl_4$ complexes of aldehydes was addressed by Denmark (in solution) and Branchadell and Oliva (in theoretical studies). In the first case, Denmark was able to characterize two distinct complexes of *p*-*t*Bu-benzaldehyde with $TiCl_4$ by means of titration studies and observed distinct chemical shifts for the two species. In the second case, Branchadell and Oliva showed in theoretical studies that H_2CO and $TiCl_4$ can form three kinds of complexes, the 1:1 complex, two isomers of the 2:1 $(H_2CO)_2$–$TiCl_4$ complex, and a chloride-bridged $(H_2CO-TiCl_4)_2$ complex. However, it is important to note that among the known X-ray diffraction studies of complexes of $TiCl_4$ with carbonyl compounds there is no reported evidence for a monodentate 1:1 structure. The theoretical results previously discussed show that the coordination of a second H_2CO molecule in the $H_2CO-TiCl_4$ complex involves a higher stabilization of the system.

Often, this question of complex stoichiometry is raised by cryoscopic studies. However, we were hampered by technical difficulties inherent in the study of our complexes by cryosopy. Our attempts to study the nature of the 1:1 complex in solution by using variable-temperature NMR spectroscopy were impeded by the precipitation of the complex (Scheme 3).

Scheme 3



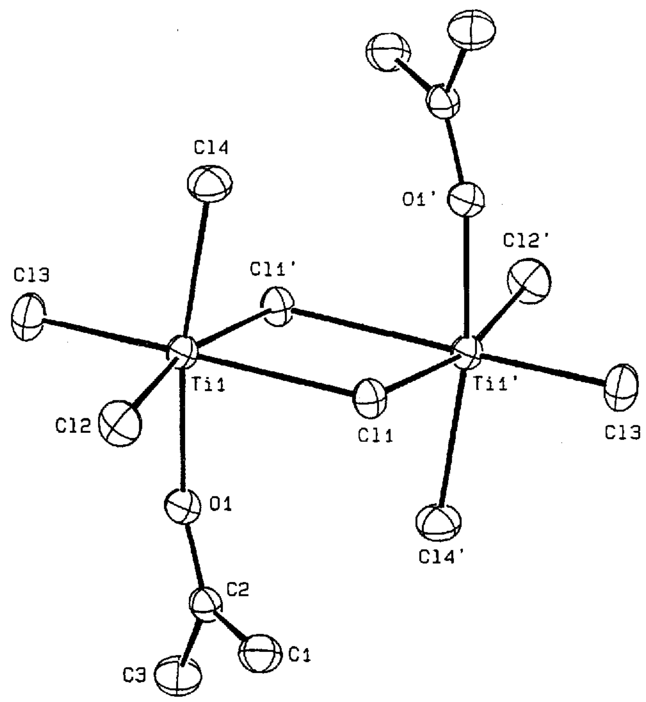
In the solid state, our crystallographic data of complex **1** confirmed Denmark's titration studies proposing the existence of an octahedral 1:2 $TiCl_4$–aldehyde adduct. Denmark also suggested that with a 1:1 stoichiometry for $TiCl_4$–aldehyde adducts, a dimeric species results by the formation of chloride bridges. This was crystallographically demonstrated for the $TiCl_4$ adducts of ethyl acetate[21], ethyl anisate[22], and dimethyl terephthalate[23]. A similar chloride-bridged structure also seems likely for our complex **2**. In fact, in a related example we isolated a complex **3** whose crystal structure shows a dimeric, chloride-bridged, 1:1 Lewis acid ketone species, a complex of $TiCl_4$ with acetone[24].

$$[\{(Me_2CO)TiCl_3\}_2(\mu\text{-}Cl)_2]$$

3

The structure of **3** consists of centrosymmetric dimers. Each titanium atom is surrounded by four chlorine atoms and an acetone ligand, and the octahedron is completed by dimerization through symmetric chlorine bridges (Figure 2), with the Ti−Cl1 [2.489(1) Å] and Ti−Cl1′ [2.498(1) Å] distances being very similar.

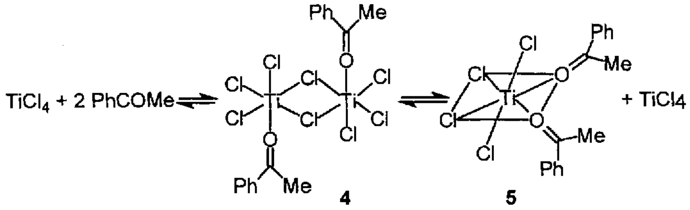
Figure 2. ORTEP drawing for complex **3** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti1−Cl1 2.489(1), Ti1−O1 2.061(1), Ti1−Cl1′ 2.498(1), O1−C2 1.233(2), Ti1−Cl2 2.208(1), Ti1−Cl3 2.222(1), Ti1−Cl4 2.230(1); Cl4−Ti1−O1 169.9(1), Cl1′−Ti1−Cl3 89.0(1), Cl3−Ti1−Cl2 99.4(1), Cl1′−Ti1−Cl1 78.6(1), Cl1−Ti1−Cl2 92.0(1), Ti1−Cl1−Ti1′ 101.4(1), Cl1−Ti1−Cl3 166.6(1), Ti1−O1−C2 149.8(1), Cl1′−Ti1−Cl2 167.7(1). Prime indicates a transformation of $-x, -y, -z$



The best equatorial plane, from wich titanium protrudes by 0.147(3) Å towards the O1 oxygen atom, is defined by the chlorine atoms Cl1, Cl1′, Cl2, and Cl3 [maximum displacement 0.029(5) Å for Cl2]. The Ti−Cl terminal and bridging bond distances are in agreement with those in the literature. The Ti−O1 bond length [2.061(1) Å] and the Ti−O1−C2 [149.8(1)°] bond angle are significantly shorter and larger, respectively, than the corresponding values in the case of **1**. These differences can be ascribed to the presence of a keto instead of an aldehyde group. Titanium lies nearly in the plane of acetone, the out-of-plane distance being 0.043(4) Å.

We also synthesized the 1:1 (**4**) and 1:2 (**5**) complexes of acetophenone with $TiCl_4$ (Scheme 4). We were able to distinguish the two complexes only on the basis of elemental analysis.

Scheme 4

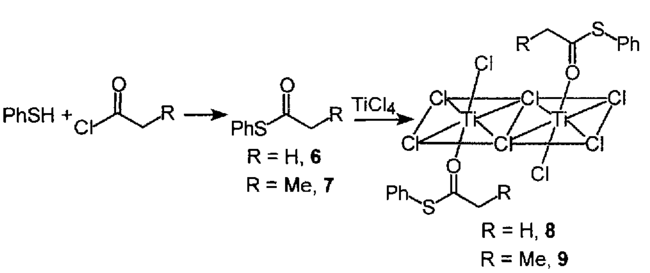


The NMR spectra of complexes **4** and **5** were identical. Our explanation of this observation is based on the different solubilities of these two complexes. We propose that in the case of complex **4** an equilibrium exists between the poorly soluble 1:1 complex and the more soluble 1:2 complex[24b]. According to this assumption, the NMR data are probably due in both cases to the more soluble species (the 1:2 complex).

Recently, the Evans group reported[25] that titanium enolates can be obtained by complexation of $TiCl_4$ with carbonyl compounds using simple organic bases (Et_3N, Hünig base). This convenient, new enolization protocol was also extended to thiol ester substrates[26]. This procedure is conceptually similar to the well-known and utilized preparation of tin[27] and boron[28] enolates. In all of these cases, the coordination of carbonyl substrates by a Lewis acid allows the simple generation of the enolate and probably also controls the geometry of the generated enolate[29]. The use of titanium is similar to that of boron in that titanium enolates prepared from thiol ester and oxazolidinones give diastereoselectivities comparable to those reported for analogous boron-mediated aldol processes. To better understand the thiol ester and oxazolidinone coordination modes and with the increasing importance of direct generation of titanium enolates in organic synthesis[30], we decided to isolate the corresponding $TiCl_4$ adducts.

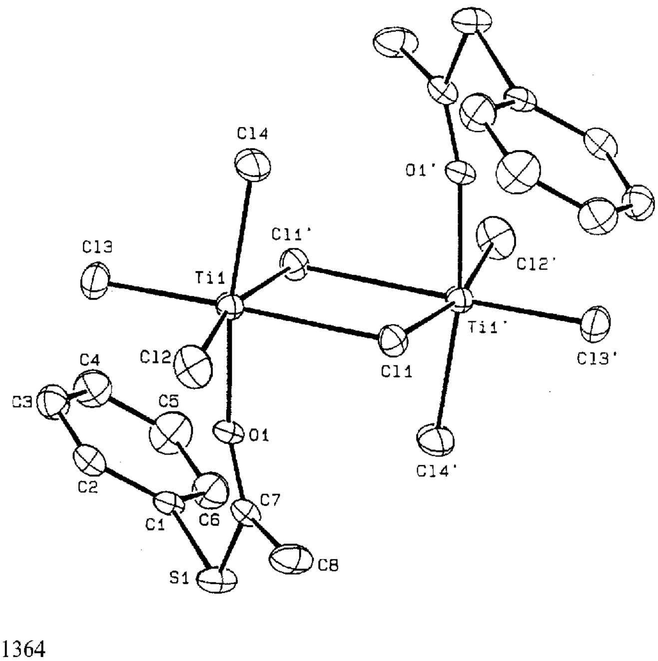
We prepared the thiol esters **6** and **7**[31] and their respective titanium adducts **8** and **9**, as shown in Scheme 5.

Scheme 5



The structure of **8** consists of two independent centrosymmetric dimers of formula $[\{TiCl_3(PhSC(Me)O)(\mu\text{-}Cl\}_2]$, both having the same geometry (Figure 3).

Figure 3. ORTEP drawing of molecule A in complex **8** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti1−Cl1 2.496(2), Ti1−Cl1′ 2.481(1), Ti1−Cl2 2.212(1), Ti1−Cl3 2.198(2), Ti1−Cl4 2.230(2), Ti1−O1 2.040(3), S1−C1 1.763(4), S1−C7 1.729(4), O1−C7 1.233(6); Cl4−Ti1−O1 170.4(1), Cl2−Ti1−Cl3 98.9(1), Cl1′−Ti1−Cl3 90.0(1), Cl1′−Ti1−Cl2 167.8(1), Cl1−Ti1−Cl3 168.4(1), Cl1−Ti1−Cl2 90.7(1), Cl1−Ti1−Cl1′ 79.6(0), C1−S1−C7 102.8(2), Ti1−O1−C7 152.4(3). Prime indicates a transformation of $1 - x, - y, -z$



Values hereafter reported in square brackets refer to molecule B. The dimer is very similar to that of complex **4** as far as the coordination geometry and the corresponding bond lengths and angles are concerned. As observed in **4**, the best equatorial plane could be defined by the chlorine atoms Cl1, Cl1′, Cl2, Cl3 {maximum deviation from planarity 0.025(2) [0.009(1)] Å for Cl3}. Titanium lies in the plane of the thioacetic moiety {displacement 0.005(1) [0.032(1)] Å}.

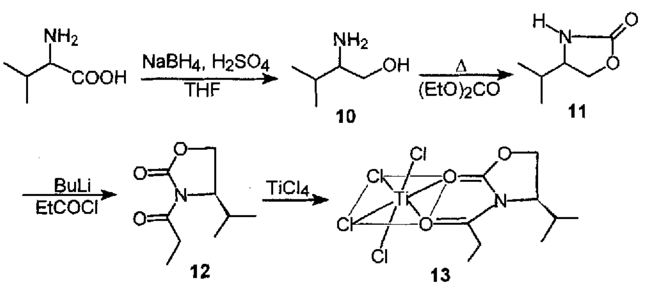
An interesting characteristic of the structure of **8** is the distortion of the aromatic ring towards the titanium atom. This kind of interaction is important in chiral recognition[32] and may have some influence on the determination of the stereoselection in reactions mediated by Lewis acid complexes[33].

A low-temperature NMR study of complex **8** and **9** was not possible for the same reason as stated before. However, we were able to obtain evidence for the presence of a new species in solution at room temperature resulting from the addition of 1 equiv. of thiol ester to complex **9**. Although we presume that this new species is the 1:2 complex, it was not possible to confirm the result due to spectral complexities arising from the presence of free thiol ester.

The *N*-acyloxazolidinone introduced by Evans[34] is an efficient template for stereoselective organic synthesis. In 1990, Castellino reported ^1H-, ^{13}C-, and ^{119}Sn-NMR data of $SnCl_4$ adducts of *s-trans*-3-(4,4-dimethyl-2-pentenoyl)-4-(1-methylethyl)oxazolidin-2-one[35]. The ^{119}Sn-chemical shift of this adduct allowed the assignment of a hexacoordinated tin species, indicating bidentate association of the oxazolidinone. The structure of the preferred mode for the coordination of an acyloxazolidinone by a bidentate Lewis acid has a strong influence on the product stereochemistry. The observed facial selectivity should be correlated with the orientation of the acyl moiety with respect to the oxazolidinone ring. A chelated structure for the mode of coordination of the oxazolidinone with $SnCl_4$ was proposed by Castellino, based on a consideration of the facial selectivities of these complexes which are strictly dependent on the C−N conformation and the mutual steric interaction between the other ligands in the complex. The same bidentate structure was suggested by Castellino in studies of cationic aluminium complexes of acyloxazolidinones[36]. A recent paper of Seebach[37] presented a model for the bidentate acyloxazolidinone ligand based on the assumption of hexacoordinated complexation by a neutral chiral titanium complex. Di Mare[38] showed that the same kind of coordination is present when an achiral α,β-unsaturated oxazolidinone is combined with $TiCl_2(O\textit{i}Pr)_2$ as indicated by the chemical shift change for several protons of the unsaturated acyloxazolidinone. The ^{13}C-NMR chemical shifts of the $TiCl_2(O\textit{i}Pr)_2$ complex with α,β-unsaturated oxazolidinone point to a pattern similar to that observed by Castellino, indicating that also in the case of $TiCl_2(O\textit{i}Pr)_2$ the oxazolidinone is coordinated in a bidentate manner and that the titanium is hexacoordinated and presumably octahedral. Finally, the isolation and characterization of a chiral alkoxytitanium-acyloxazolidinone complex were recently reported by Jørgensen[39]. Experimental data concerning the structure and stability of complexes between $TiCl_4$ and bidentate Lewis bases are available[40]. Moreover, chelate complexes of $TiCl_4$ with carbonyl compounds are frequently used in organic synthesis for achieving highly stereoselectiveorganic transformations[33]. However, in the case of the chiral acyloxazolidinone and $TiCl_4$, the bidentate octahedral coordination mode is only presumed because there have been no previous crystallographic reports available so far to clarify the situation. Thus, we decided to study the structure of the $TiCl_4$-acyloxazolidinone adduct.

Using a modification of the procedure described in the literature[41], we prepared the chiral oxazolidinone **12** the reaction of which with $TiCl_4$ gave complex **13** (Scheme 6).

Scheme 6

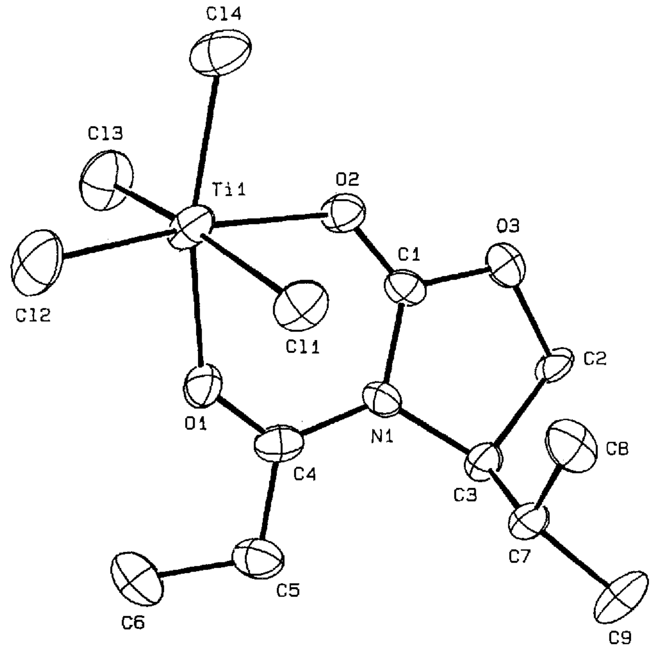


The structure of **13** consists of discrete molecules of the complex and THF molecules of crystallization in a 2:1 molar ratio (Figure 4).

Two crystallographically independent complex molecules are present in the asymmetric unit (values in square brackets refer to molecule B). The pseudooctahedral coordination geometry is very similar to that observed in the case of complex **1**. The best equatorial plane running through titanium is defined by the Cl2, Cl4, O1, and O2 atoms {maximum displacement 0.045(7) [0.033(7)] Å for O2}. The chelating ligand gives rise to a six-membered ring showing a boat conformation, the folding along the O1···O2 and C1···C4 lines being 18.4 [17.4(4)] and 11.6 [12.8(9)]°, respectively (the folding is defined by the dihedral angles formed by the Ti1,O1,O2 and N1,C1,C4 atoms with the mean plane through O1,O2,C1,C4). The stereogenic C3 assumes an *S* configuration (see atomic coordinates in deposited material).

The different basicities of the carbonyl oxygen and *N*-acyloxazolidinones were observed by Castellino[35,36] and invoked for explaining the facial stereoselectivity in Diels-Alder reactions[37,38] mediated by chiral ligands. The more Lewis basic external carbonyl group coordinates to the metal in the position opposite to the weakest π donor ligand. The different basicity of the two carbonyl oxygen atoms is reflected in the different bond lengths between the carbonyl oxygen atom and $TiCl_4$. The O1–Ti1 distance is shorter than O2–Ti1, while the Ti1–Cl4 distance is longer than that of Ti1–Cl2.

Figure 4. ORTEP drawing of molecule A in complex **13** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Ti1–Cl1 2.300(3), Ti1–Cl2 2.196(5), Ti1–Cl3 2.269(3), Ti1–Cl4 2.231(4), Ti1–O1 2.098(8), Ti1–O2 2.145(7), O1–C4 1.230(14), O2–C1 1.210(14); O2–Ti1–O1 77.9(3), Cl4–Ti1–O1 164.8(2), Cl4–Ti1–O2 86.9(2), Cl2–Ti1–O1 96.0(2), Cl2–Ti1–O2 173.5(2), Cl2–Ti1–Cl4 99.2(1), Cl1–Ti1–Cl3 165.4(1). Prime indicates a transformation of $-x$, $-y$, z



What is interesting is the comparison between **13** and the previously mentioned chiral alkoxytitanium–acyloxazolidinone complex characterized by Jørgensen. Concerning the two coordinated carbonyl groups in Jørgensen's complex, the Ti–O bond lengths are similar to ours, with a small difference in length (2.168 and 2.137 Å) observable between the two Ti–O distances. Taking into consideration the *trans* disposition of the two chlorine ligands in the Jørgensen's complex, the Ti–Cl distances are similar to those of our complex, with the chlorine atoms tilted towards the oxazolidinone in both complexes. However, in our complex, the Ti–Cl1 distance is longer than the Ti–Cl3 distance. In Jørgensen's complex, the plane of the coordinated α,β-unsaturated oxazolidinone is tilted 33° out of the plane containing the titanium atom complex. In our complex, we found a similar out-of-plane orientation of the bidentate ligand. These findings are of great interest for the design of chiral Lewis acids. The commonly held assumption of an in-plane geometry for titanium-based Lewis acid complexation may be erroneous[42]. In the case of the chelate complex of $TiCl_4$ studied by Frenking[43], an out-of-plane arrangement was theoretically predicted. Another noteworthy point is that of the position of the ethyl chain *syn* to the coordinated carbonyl group easily observable in structure **13**. A recent model of Lewis acid radical-mediated reactions performed on a chiral oxazolidinone[44] presents a disposition similar to that which we observe for **13** as possible explanation for the high diastereoselections observed.

Conclusions

We have described novel crystal structures for $TiCl_4$–aldehyde and -ketone complexes. For aldehydes, **1** represents the first crystallographically characterized (1:2) $TiCl_4$ complex. This structural information complements that of other Lewis acid–aldehyde complexes and serves to broaden the scope of understanding for the origin of stereoselectivities of Lewis acid-mediated reactions with aldehydes. We have also shown that with ketones the 1:1 coordination mode is possible, although it is the less favored one in the solid state. Complex **13** represents the first X-ray determination of Lewis acid–chiral oxazolidinone complexes. The bidentate coordination mode presumed for Lewis-acidic chiral oxazolidinones were confirmed by our result.

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Experimental

All reactions were carried out under purified nitrogen. Solvents were dried and distilled before use by standard methods. – IR: Perkin-Elmer 883. – ^{1}H NMR: 200-AC Bruker.

Synthesis of **1**: $TiCl_4$ (1.31 g, 6.9 mmol) was added to a toluene (70 ml) solution of MesCHO (2.04 g, 13.8 mmol). Orange microcrystals formed instantaneously, which dissolved by heating to afford a red solution. An orange crystalline solid formed on standing, which was filtered, washed and dried (93%). – ^{1}H NMR (CD_2Cl_2): δ = 10.53 (s, 1H, CHO), 7.05 (s, 2H, aromatic), 2.68 (s, 6H, CH_3), 2.39 (s, 3H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 201.84 (CO), 132.84 (aromatic), 22.81 (CH_3), 22.06 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1578, 1544 cm^{-1} (CO); free aldehyde 1688 (CO). – $C_{20}H_{24}Cl_4O_2Ti$ (486.1): calcd. C 49.42, H 4.98; found C 49.24, H 4.96.

Synthesis of **2**: $TiCl_4$ (1.89 g, 10.0 mmol) was added to a toluene (50 ml) solution of MesCHO (1.6 g, 10.0 mmol). After 1 h, an orange solid formed, and the suspension was stirred at room temp. for 2 h. The solid was collected, washed with hexane (80 ml), and dried (53%). – ^{1}H NMR (CD_2Cl_2): δ = 10.41 (s, 1H, CHO), 7.08 (s, 2H, aromatic), 2.73 (s, 6H, CH_3), 2.41 (s, 3H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 201 (CO), 148.15 (aromatic), 132.38 (aromatic), 127.40 (aromatic), 22.80 (CH_3), 22.06 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1604, 1583, 1550 cm^{-1} (CO). – $C_{10}H_{12}Cl_4OTi$ (337.9): calcd. C 35.55, H 3.58; found C 35.65, H 4.17.

Synthesis of **3**: Acetone (2.12 g, 36.5 mmol) was added at room temp. to a stirred toluene (70 ml) solution of $TiCl_4$ (3.64 g, 18.2 mmol). After a few hours, a crystalline yellow solid precipitated. The mixture was cooled to –20°C and filtered cold. The solid was when washed with *n*-hexane and dried (80%). An X-ray analysis of the unsolvated species was carried out. – ^{1}H NMR (CD_2Cl_2): δ = 2.62 (s, 6H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 32.64 (CH_3), 28.45 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1650 cm^{-1} (CO). – $C_3H_6Cl_4OTi \cdot (C_7H_8)_{0.5}$ (293.8): calcd. C 26.56, H 3.43; found C 25.80, H 4.03.

Synthesis of **4**: $TiCl_4$ (4.7 g, 25.0 mmol) was added at room temp. to a benzene (100 ml) solution of acetophenone (3.0 g, 25.0 mmol). The resulting pale yellow suspension was stirred for 2 h at room temp., and then the solid was filtered, washed with dry *n*-hexane (50 ml), and dried (74%). – ^{1}H NMR (CD_2Cl_2): δ = 8.16 (dd, *J* = 1.1, 8.05 Hz, 2H, aromatic), 7.73 (t, *J* = 1.3, 6.33 Hz, 1H, aromatic), 7.52 (t, *J* = 8.05 Hz, 2H, aromatic), 3.11 (s, 3H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 212.00 (C=O), 138.67 (aromatic), 132.30 (aromatic), 130.33 (aromatic), 26.35 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1610, 1588, 1554 cm^{-1} (CO). – $C_8H_8Cl_4Ti$ (293.8): calcd. C 32.70, H 2.74; found C 32.18, H 3.06.

Synthesis of **5**: $TiCl_4$ (4.7 g, 25.0 mmol) was added at room temp. to a benzene (120 ml) solution of acetophenone (5.0 g, 50.0 mmol). The resulting pale yellow suspension was stirred for 1 h at room temp., and then the solid was filtered, washed with dry *n*-hexane (60 ml), and dried (75%). – ^{1}H NMR (CD_2Cl_2): the same signals as for the complex **4**. – ^{13}C NMR (CD_2Cl_2): δ = 211.66 (C=O), 137.74 (aromatic), 136 (aromatic), 131.77 (aromatic), 130.06 (aromatic), 125.31 (aromatic), 26.42 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1628, 1592, 1567 cm^{-1} (CO). – $C_{16}H_{16}Cl_4O_2Ti$ (430.0): calcd. C 44.69, H 3.75; found C 44.51, H 4.06.

Synthesis of **6** *and* **7**: These products were prepared according to ref.[29].

Synthesis of **8**: To a benzene (30 ml) solution of thiophenol acetate (1.5 g, 10 mmol) $TiCl_4$ (1.89 g, 10.0 mmol) was added. The orange solution was stirred at room temp. overnight. It was then concentrated to about 30 ml, and the orange solid which precipitated was filtered off, washed with *n*-hexane (30 ml), and dried (35%). – ^{1}H NMR (CD_2Cl_2): δ = 7.49 (m, 5H, aromatic), 2.70 (s, 3H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 135.19 (aromatic), 131.67 (aromatic), 30.67 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1562.5 cm^{-1} (CO). – $C_8H_8Cl_4OSTi$ (341.9): calcd. C 28.10, H 2.36; found C 27.49, H 3.04.

Synthesis of **9**: To a benzene (50 ml) solution of thiophenol propionate (3.3 g, 20 mmol) $TiCl_4$ (3.8 g, 20.0 mmol) was added. The solution turned red, and a microcrystalline orange product formed after 30 min. The reaction mixture was filtered and the solid washed with *n*-hexane (30 ml) and dried (40%). – ^{1}H NMR (CD_2Cl_2): δ = 7.51 (s, 5H, aromatic), 3.03 (q, *J* = 7.31 Hz, 2H, CH_2), 1.38 (t, *J* = 7.31 Hz, 3H, CH_3). – ^{13}C NMR (CD_2Cl_2): δ = 135.53 (aromatic), 131.85 (aromatic), 130.71 (aromatic), 38.030 (aromatic), 10.87 (CH_3). – IR (nujol): $\tilde{\nu}$ = 1550 cm^{-1} (CO). – $C_9H_{10}Cl_4OSTi$ (355.9): calcd. C 30.37, H 2.83; found C 30.50, H 2.98.

Synthesis of **10**: To a stirred THF (600 ml) suspension of $NaBH_4$ (60.0 g, 1493 mmol) (*S*)-valine (70 g, 600 ml) was added. The flask was immersed in an ice/water bath, and a solution of concentrated H_2SO_4 (40 ml, 750 mmol) in Et_2O (120 ml) was added dropwise at such a rate as to maintain the reaction mixture temp. below 20°C. Stirring of the mixture was continued at room temp. overnight, and MeOH (60 ml) was added carefully to destroy excess BH_3. The mixture was concentrated to 500 ml and NaOH (500 ml, 5 M) was added. After removal of the solvent that distilled below 100°C, the mixture was cooled and filtered through Celite, which was then washed with H_2O (200 ml). The filtrate and the washing were combined and extracted 4 times with CH_2Cl_2 (300 ml). The solvent was evaporated from the combined extracts at low pressure, and the resulting oil was distilled to give a colorless oil (b.p. 112°C at 3 Torr, 86%); $[\alpha]_D^{25}$ = +14.7 (*c* = 0.1, neat). – ^{1}H NMR (CD_2Cl_2): δ = 3.63 (dd, *J* = 3.8, 10.5, 1H, $\mathrm{C}H_2\mathrm{OH}$), 3.31 (dd, *J* = 7.2, 10.6 Hz, 1H, $\mathrm{C}H\mathrm{OH}$), 2.56 (dd, *J* = 3.8, 6.4, 8.6 Hz, $\mathrm{C}H\mathrm{NH_2}$), 2.5–2.1 (m, 3H, NH_2, OH), 1.59 [dqq, *J* = 6.7, 6.7, 6.7 Hz, 1H, $\mathrm{C}H(\mathrm{CH_3})_2$], 0.93 (d, *J* = 6.8, 6H, $\mathrm{C}H_3\mathrm{CHC}H_3$). – IR ($CCl_4$): $\tilde{\nu}$ = 1570, 1450, 1370 cm^{-1}.

Synthesis of **11**: To a suspension of K_2CO_3 (7.46 g, 54 mmol) in diethyl carbonate (131 ml, 1087 mmol) (*S*)-valine (56 g, 543 mmol) was added. A 25-cm Vigreux column was used, the flask was immersed into an oil bath preheated to 140°C, and ethanol was distilled from the reaction mixture. After 4 h, 500 ml of CH_2Cl_2 and

500 ml of water were added to the mixture at room temp., and the solution was transferred to a separatory funnel. The organic phase was dried with Na_2SO_4, filtered and concentrated at low pressure to give a crystalline solid that was filtered and washed with *n*-hexane (76%). $[\alpha]_D^{25} = +16$ ($c = 0.018$, $CHCl_3$). m.p. 70 °C. – ^1H NMR ($CDCl_3$): $\delta = 4.45$ (dd, $J = 8.7$, 8.7 Hz, 1 H, OCH), 4.11 (dd, $J = 8.7$, 6.3 Hz, 1 H, OCH), 3.61 (dd, $J = 8.7$, 6.5 Hz, 1 H, $CHCH_2O$), 1.74 [m, $J = 6.7$ Hz, 1 H, $CH(Me)_2$], 0.96 (d, $J = 6.7$ Hz, 6 H, CH_3CHCH_3). – ^{13}C NMR: $\delta = 160.00$ (C=O), 65.5 (CH_2O), 58.4 (CHN), 32.6 (CH), 17.9 (CH_3), 17.6 (CH_3). – IR (CCl_4): $\tilde{\nu} = 1760\ cm^{-1}$ (CO).

Synthesis of **12**: To a THF (300 ml) solution of oxazolidone **13** (6.27 g, 79.0 mmol) an *n*-hexane solution of BuLi 1.6 M (50 ml) was added dropwise and with stirring at −78 °C. Propionyl chloride (8.14 g, 88 mmol) was then added in one portion by means of a syringe. After 20 min at −78 °C, the solution was allowed to warm to room temp., and then the reaction was quenched with a saturated solution of ammonium chloride (100 ml). The bulk of THF and hexane were removed at low pressure, and the resulting slurry was extracted with CH_2Cl_2 (2 × 80 ml). The combined organic extracts were washed with a solution of 1 N NaOH (50 ml) and brine (50 ml), then dried with sodium sulfate, and the solvent was evaporated at low pressure to give a clear, colorless oil utilized for the preparation of the titanium complex (92%). $[\alpha]_D^{25} = +94$ ($c = 0.08$, CH_2Cl_2). – ^1H NMR ($CDCl_3$): $\delta = 4.5-4.2$ (m, 3 H, OCH_2CHN), 3.0–2.85 (m, 2 H, $COCH_2CH_3$), 2.38 [dqq, $J = 3.88$, 7.0, 7.0 Hz, 1 H, $CH(CH_3)_2$], 1.80 (dd, $J = 7.35$, 7.35 Hz, 3 H, CH_2CH_3), 0.92 [d, $J = 7.0$ Hz, 3 H, $CH(CH_3)_2$], 0.88 [d, $J = 7.0$ Hz, 3 H, $CH(CH_3)_2$]. – ^{13}C NMR ($CDCl_3$): $\delta = 172.7$ (CH_2C=O), 153.0 (NC=O), 62.8 (CH_2O), 57.9 (CHN), 28.6 (CH), 28.3 (CH_2), 17.7 (CH_3), 8.8 (CH_3). – IR (CCl_4): $\tilde{\nu} = 1785$, $1720\ cm^{-1}$ (CO).

Synthesis of **13**: To an *n*-hexane (20 ml) solution of oxazolidone (1.0 g, 5.38 mmol) $TiCl_4$ (1.02 g, 5.37 mmol) was added dropwise with stirring at room temp. A voluminous yellow solid immediately precipitated which was collected, washed with hexane, and dried in vacuo (72%). The solid was recrystallized by extraction with CH_2Cl_2 in the presence of 5% of THF. – ^1H NMR (CD_2Cl_2): $\delta = 5.0-4.6$ (m, 3 H, OCH_2CHN), 3.0–2.7 (m, 2 H, $COCH_2CH_3$), 2.27 [dqq, $J = 6.95$, 6.95, 3.29 Hz, 1 H, $CH(CH_3)_2$], 1.33 (dd, $J = 6.95$, 6.95 Hz, 3 H, CH_2CH_3), 1.05 [d, $J = 6.95$ Hz, 3 H, $CH(CH_3)_2$], 1.04 [d, $J = 6.95$ Hz, 3 H, $CH(CH_3)_2$]. – ^{13}C NMR (CD_2Cl_2): $\delta = 181.12$ (CH_2C=O), 158.02 (NC=O), 68.34 (CH_2O), 62.10 (CHN), 31.33 (CH), 30.88 (CH_2), 18.14 (CH_3), 14.75 (CH_3), 8.44 (CH_2CH_3). – IR (nujol): $\tilde{\nu} = 1739$, 1596 (CH_2C=O) cm^{-1}. – $C_9H_{15}Cl_4NO_3Ti$ (374.9): calcd. C 28.74, H 4.03, N 3.74; found C 28.80, H 4.89, N 3.68.

X-ray Crystallography: Suitable crystals of compounds **1**, **3**, **8**, and **13** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with the use of TRACER[45]. Crystal data and details associated with data collection are given in Table 1. Data were collected at room temperature (295 K) with a Philips PW1100 single-crystal diffractometer. For intensities and background, individual reflection profiles[46] were analyzed. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[47], and the absolute scale was established by the Wilson method[48]. The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. Data were then corrected for absorption using a semiempirical method for **1**, **3**, **8**[49] and ABSORB for **13**[50]. Anomalous scattering corrections were included in all structure factor calculations[51]. Scattering factors for neutral atoms were taken from ref.[51a] for non-hydrogen atoms and from ref.[52] for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. The function minimized during the least-squares refinement was $\Sigma w(\Delta F^2)^2$. Weights were applied according to the scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ ($P = (F_o^2 + 2F_c^2)/3$) with $a = 0.0413$, 0.0223, 0.0122, 0.0839 for complexes **1**, **3**, **8**, and **13**, respectively. – Solution and refinement of the structures were based on the unique observed reflections [$I > 2\sigma(I)$]. The structures of **3** and **13** were solved by the heavy-atom method starting from three-dimensional Patterson maps, while the structures of **1** and **8** were solved with SHELX86[53]. Refinement of **1**, **3**, and **8** was straightforward. In complex **13**, the THF molecule of crystallization was found to be distributed around and along a C_2 axis. Attempts to describe the disorder in terms of "partial" atoms and to locate the oxygen atom were unsuccessful. The atom lying on the C_2 axis was labeled as an oxygen atom only for symmetry requirements. Refinement was therefore carried out isotropically by fixing all the bond lengths to be 1.54(1) Å. All hydrogen atoms but those related to the disordered THF molecule in **13**, which were ignored, were located from difference Fourier maps and introduced in the subsequent refinements as fixed atom contributions with isotropic *U* values fixed at 0.08 for **1**, **13** and 0.10 $Å^2$ for **3**, **8**. The crystal chirality of complex **13**, which crystallizes in a polar space group, was tested by inverting all of the coordinates ($x, y, z \leftrightarrow -x, -y, -z$) and refining them to convergence once again. The resulting *R* values quoted in Table 1 indicated that the original choice should be considered the correct one. All calculations were performed by using SHELX76[54] for the early stages of solution and SHELXL92[55] for the refinements. The final difference maps showed no unusual features, with no significant peak above the general background. – Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405703 (**1**), -405704 (**3**), -405705 (**8**), -405706 (**13**), the names of the authors, and the journal citation.

Table 1. Experimental data for the X-ray diffraction studies on crystalline compounds **1**, **3**, **8**, and **13**. $R = \Sigma |\Delta F| / \Sigma |F_o|$. – $wR2 = [\Sigma(w\Delta F^2)^2/\Sigma(wF_o)^2)^2]^{1/2}$ (calculated for the unique observed data for all complexes)

compound	**1**	**3**	**8**	**13**
formula	$C_{20}H_{24}Cl_4O_2Ti$	$C_6H_{12}Cl_8O_2Ti_2$	$C_{16}H_{16}Cl_8O_2S_2Ti_2$	$C_9H_{15}Cl_4NO_3Ti \cdot C_4H_8O$ (2/1)
a [Å]	9.449(1)	8.961(1)	10.322(1)	22.036(2)
b [Å]	9.607(1)	11.726(1)	14.871(1)	16.223(2)
c [Å]	13.842(1)	8.644(1)	9.400(1)	9.580(1)
α [°]	109.04(1)	90	100.08(1)	90
β [°]	91.25(1)	95.83(1)	98.76(1)	90
γ [°]	104.16(1)	90	103.99(1)	90
V [$Å^3$]	1144.6(2)	903.6(2)	1349.6(2)	3424.8(6)
Z	2	2	2	8
M [g·mol^{-1}]	486.1	495.6	683.9	411.0
space group	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P2_12_12$ (18)
t [°C]	22	22	22	22
λ [Å]	0.71069	0.71069	0.71069	0.71069
ρcalc, [g cm^{-3}]	1.411	1.822	1.683	1.594
μ [cm^{-1}]	8.53	20.61	15.48	11.32
transmn coeff	0.958-1.000	0.696-1.000	0.843-1.000	0.956-1.000
R	0.032	0.022	0.029	0.053 [0.054] [a]
wR2	0.075	0.048	0.047	0.129 [0.133]

[a] Values in square brackets refer to the "inverted structure".

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