Preparation and Structures of Methyltitanium Compounds

Sven Kleinhenz and Konrad Seppelt*[a]

Abstract: $[Ti(CH_3)_4]$ and its derivatives $[Ti(CH_3)_5]^-$, $[Ti_2(CH_3)_9]^-$, $[Ti(CH_3)_3Cl]$, $[Ti(CH_3)_2Cl_2]$, and $[Ti(CH_3)Cl_3]$ have been prepared and characterized structurally. $[Ti(CH_3)_4]$ can be crystallized only as a solvate $[Ti(CH_3)_4]\cdot Et_2O$ that has a trigonal-bipyramidal structure with an apically positioned oxygen. For unsolvated $[Ti(CH_3)_4]$ ab initio calculations predict a tetrahedral structure, but distortion to a trigonal pyramid does not require much energy. $[Ti(CH_3)_5]^-$ is predicted to have a tetragonal-pyramidal structure, but it appears in two separate forms in the crystal. One form is close to a tetragonal pyramid, the other to a trigonal bipyramid. $[Ti_2(CH_3)_9]^-$ can be viewed as a double trigonal bipyramid that is formed from $[Ti(CH_3)_4]$ and $[Ti(CH_3)_5]^-$ bridged by one methyl group. Solvent-free $[Ti(CH_3)_3Cl]$ is a tetramer with a cube-like structure, while $[Ti(CH_3)_3Cl]\cdot Et_2O$ is trigonal bipyramidal. $[Ti(CH_3)_2Cl_2]$ forms chains of *cis*-dichloro-bridged octahedra, and $[Ti(CH_3)Cl_3]\cdot Et_2O$ is a *cis*-dichloro-bridged dimer. In none of these structures is any indication found of an agostic interaction between a methyl group and an adjacent titanium atom. In $[Ti_2(CH_3)_9]^-$ the interaction between the $[Ti(CH_3)_4]$ and $[Ti(CH_3)_5]^-$ can be described as agostic with respect to the bridging methyl group and the second titanium atom.

Keywords: ab initio calculations · methyltitanium compounds · methyltitanium chlorides · structure elucidation · titanium

Introduction

Methyltitanium compounds play an important role as catalysts in Ziegler–Natta systems.[1] Therefore this class of compounds has long been known and intensively investigated. The aim of the present work was to obtain structural information on methyltitanium compounds with various degrees of methylation, not so much for gaining insight into catalytic activity, but rather for elucidating structural principles. Although much work had already been done in this particular field, many dark areas still remained.

The methyl ligand in organometallic chemistry is unique in that it is a pure σ-binding ligand of moderate electronegativity and is not subject to β-hydrogen elimination. This gives rise to some unique structures amongst hexamethylated transition metal compounds of which $[Zr(CH_3)_6]^{2-}$, $[Nb(CH_3)_6]^-$, $[Ta(CH_3)_6]^-$, $[W(CH_3)_6]$, and $[Re(CH_3)_6]$ are the most prominent examples. All of these complexes are have trigonal-prismatic structures, and $W(CH_3)_6$ and possibly $[Nb(CH_3)_6]^-$ are distorted even further into a C_{3v} geometry.[2–6] These results have also been the focus of much theoretical work.[5,7–12] Except for in $[Ti(CH_3)_6]^{2-}$, which is not presented here and to our knowledge has not yet been observed, the interconversion between octahedron and trigonal prism should not be observed in the type of molecules studied.

Results and Discussion

$[Ti(CH_3)_4]$: Of all the compounds discussed here, $[Ti(CH_3)_4]$ is most elusive. It was prepared long ago and has been described as an orange-yellow liquid, which occasionally forms orange crystals at low temperatures and is very sensitive towards oxygen, moisture, and temperatures above −40 °C.[13, 14] Methylation of $TiCl_4$ under various conditions does indeed give solutions that contain $[Ti(CH_3)_4]$. The compound is volatile in the presence of donor solvents, and a crystal structure of $[Ti(CH_3)_4]\cdot THF$ prepared in this way is already known. It has a trigonal-pyramidal structure with the THF oxygen atom occupying an axial position.[15] From solution in diethyl ether we were able to crystallize $[Ti(CH_3)_4]\cdot Et_2O$ with an essentially similar structure, except that the Ti–O distance is marginally longer because of the lower donor ability of Et_2O compared with THF (see Table 1, Figure 1). In solution in Et_2O it appears that $[Ti(CH_3)_4]$ is solvated by up to two diethyl ether molecules, according to its NMR spectra. We have never observed any unsolvated $[Ti(CH_3)_4]$ and so asked ourselves what its structure would be.

Ab initio calculations on the $[Ti(CH_3)_4]$ molecule have been performed before,[16] and we present here calculations with fairly large basis sets. All of these calculations agree that the

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Table 1. Results of the X-ray structural determinations and the calculated structures of $[\mathrm{Ti(CH_3)_4}]\cdot\mathrm{Et_2O}$ and $[\mathrm{Ti(CH_3)_3Cl}]\cdot\mathrm{Et_2O}$; bond lengths [pm] and angles [°].

$[\mathrm{Ti(CH_3)_4}]\cdot\mathrm{Et_2O}$						$[\mathrm{Ti(CH_3)_3Cl}]\cdot\mathrm{Et_2O}$			
Molecule 1		Molecule 2		Calculated[a]		X-ray		Calculated[a]	
Ti1–C	209.0(5)	Ti2–C5	209.9(5)	Ti–$\mathrm{C_{ap}}$	210.7	Ti–Cl	228.9(1)	Ti–Cl	225.8
Ti1–C1	209.3(5)	Ti2–C6	209.9(5)	Ti–$\mathrm{C_{equ}}$	209.0	Ti–C1	208.7(3)	Ti–C	208.9
Ti1–C3	210.0(5)	Ti2–C7	207.9(5)	Ti–$\mathrm{C_{equ}}$	209.9	Ti–C2	209.5(2)	Ti–C	210.2
Ti1–C4	207.4(4)	Ti2–C8	209.6(4)	Ti–$\mathrm{C_{equ}}$	209.5	Ti–C3	209.6(2)	Ti–C	209.6
Ti1–O1	225.1(2)	Ti2–O2	226.5(2)	Ti–O	240.1	Ti–O	215.9(2)	Ti–O	226.3
C2-Ti1-O1	177.8(2)	C5-Ti2-O2	177.6(2)	$\mathrm{C_{ap}}$-Ti-O	176.3	Cl-Ti-O	174.6(1)	Cl-Ti-O	176.8
C2-Ti1-C1	93.4(2)	C5-Ti2-C6	92.00(2)	$\mathrm{C_{ap}}$-Ti-$\mathrm{C_{equ}}$	97.8	Cl-Ti-C1	96.8(1)	Cl-Ti-$\mathrm{C_{equ}}$	93.4
C2-Ti1-C3	91.8(3)	C5-Ti2-C7	94.6(2)	$\mathrm{C_{ap}}$-Ti-$\mathrm{C_{equ}}$	94.3	Cl-Ti-C2	93.5(1)	Cl-Ti-$\mathrm{C_{equ}}$	95.0
C2-Ti1-C4	95.4(2)	C5-Ti2-C8	93.1(2)	$\mathrm{C_{ap}}$-Ti-$\mathrm{C_{equ}}$	94.8	Cl-Ti-C3	91.8(1)	Cl-Ti-$\mathrm{C_{equ}}$	98.0
C1-Ti1-C3	122.2(2)	C6-Ti2-C7	119.9(2)	$\mathrm{C_{equ}}$-Ti-$\mathrm{C_{equ}}$	115.1	C1-Ti-C2	115.1(1)	$\mathrm{C_{equ}}$-Ti-$\mathrm{C_{equ}}$	114.2
C1-Ti1-C4	116.7(2)	C6-Ti2-C8	122.2(2)	$\mathrm{C_{equ}}$-Ti-$\mathrm{C_{equ}}$	120.7	C1-Ti-C3	121.7(1)	$\mathrm{C_{equ}}$-Ti-$\mathrm{C_{equ}}$	120.6
C3-Ti1-C4	120.1(2)	C7-Ti2-C8	117.0(2)	$\mathrm{C_{equ}}$-Ti-$\mathrm{C_{equ}}$	121.4	C2-Ti-C3	121.8(1)	$\mathrm{C_{equ}}$-Ti-$\mathrm{C_{equ}}$	122.5

[a] See Table 3.

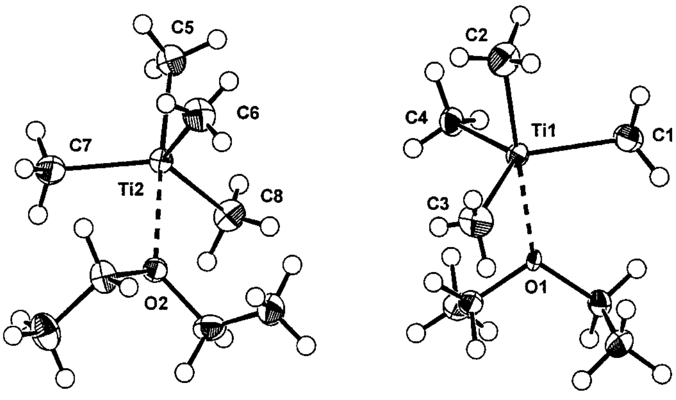

Figure 1. ORTEP plot of $[\mathrm{Ti(CH_3)_4}]\cdot\mathrm{Et_2O}$.

Abstract in German: *Präparationen und Strukturuntersuchungen von $[\mathrm{Ti(CH_3)_4}]$ und der Derivate $[\mathrm{Ti(CH_3)_5}]^-$, $[\mathrm{Ti_2(CH_3)_9}]^-$, $[\mathrm{Ti(CH_3)_3Cl}]$, $[\mathrm{Ti(CH_3)_2Cl_2}]$, und $[\mathrm{Ti(CH_3)Cl_3}]$ werden vorgestellt. $[\mathrm{Ti(CH_3)_4}]$ kann nur als Ethersolvat kristallisiert werden und hat dann eine trigonal bipyramidale Struktur mit dem Ethersauerstoffatom in apicaler Stellung. Nach ab initio Berechnungen soll unsolvatisiertes $[\mathrm{Ti(CH_3)_4}]$ tetraedrisch aufgebaut sein, die Verzerrung in eine trigonal pyramidale Struktur erfordert jedoch nur wenig Energie. Für $[\mathrm{Ti(CH_3)_5}]^-$ wird eine quadratisch pyramidale Struktur vorhergesagt. Im Kristall kommt es in zwei verschiedenen Formen vor. Eine ist einer tetragonalen Pyramide sehr ähnlich, die andere einer trigonalen Bipyramide. $[\mathrm{Ti_2(CH_3)_9}]^-$ kann als eine doppelt trigonale Bipyramide angesehen werden, die aus $[\mathrm{Ti(CH_3)_4}]$ and $[\mathrm{Ti(CH_3)_5}]^-$ zusammengesetzt ist, und mit einer Methylgruppe asymmetrisch verbrückt wird. Solvatfreies $[\mathrm{Ti(CH_3)_3Cl}]$ ist tetramer mit einer cubanartigen Struktur, $[\mathrm{Ti(CH_3)_3Cl}]\cdot\mathrm{Et_2O}$ dagegen trigonal bipyramidal aufgebaut. $[\mathrm{Ti(CH_3)_2Cl_2}]$ bildet Ketten cis-chlorverbrückter Oktaeder. $[\mathrm{Ti(CH_3)Cl_3}]\cdot\mathrm{Et_2O}$ ist ein cis-dichlorverbrücktes Dimer. In keiner dieser Strukturen gibt es Hinweise auf agostische Methylgruppen. Nur im $[\mathrm{Ti_2(CH_3)_9}]^-$ kann der Zusammenhalt zwischen den $[\mathrm{Ti(CH_3)_4}]$ und $[\mathrm{Ti(CH_3)_5}]^-$ Mokekülteilen als intermolekulare agostische Wechselwirkung zwischen Methylgruppe und dem zweiten Ti Atom angesehen werden.*

molecular frame of $[\mathrm{Ti(CH_3)_4}]$ will be tetrahedral, the lowest energy being obtained if the four methyl groups are rotated equally by about 152° against the mirror planes of the T_d structure to give T symmetry (Table 2). We have also calculated the energy of complex formation for the reaction of $[\mathrm{Ti(CH_3)_4}]$ with $\mathrm{Et_2O}$ or $\mathrm{Cl^-}$ which yields trigonal bipyramidal complexes. The reaction enthalpy turned out to be quite high, which indicates that unsolvated $[\mathrm{Ti(CH_3)_4}]$ should not exist in the presence of a donor solvent. The complexation energy can be split into two parts: first, the rearrangement of the tetrahedral $[\mathrm{Ti(CH_3)_4}]$ moiety to a trigonal-pyramidal geometry with the titanium atom in the basal plane, and second, the Lewis acid–Lewis base reaction of this distorted $[\mathrm{Ti(CH_3)_4}]$ with the donor molecule or ion. It is surprising to note that the calculated pyramidalization energy of $[\mathrm{Ti(CH_3)_4}]$ is remarkably low compared, for example, with that of $[\mathrm{Si(CH_3)_4}]$ or $[\mathrm{Ge(CH_3)_4}]$ (Table 2). According to these calculations, $[\mathrm{Ti(CH_3)_4}]$ appears to be a fluxional molecule, but this particular intramolecular movement does not give rise to an exchange of ligand positions. We also calculated the energy for the dimerization reaction [Eq. (1)] under the

$$2\,[\mathrm{Ti(CH_3)_4}] \longrightarrow (\mathrm{CH_3})_4\mathrm{Ti}\cdots\mathrm{CH_3Ti(CH_3)_3} \tag{1}$$

assumption that the bonding and geometry of this dimer are related to those found in $[\mathrm{Ti_2(CH_3)_9}]^-$ (see below). This energy comes out to be only 2.0 kJ mol^{-1} (Tables 3, 4). Therefore we conclude that in a donor-free environment, such as in solution in an alkane or without any solvent, $[\mathrm{Ti(CH_3)_4}]$ should exist as a discrete molecule and not as a dimer, oligomer, or polymer.

$[\mathrm{Ti(CH_3)_5}]^-$: The first observations of $[\mathrm{Ti(CH_3)_5}]^-$ date back to 1972 when $\mathrm{Li[Ti(CH_3)_5]}$ was prepared as its dioxane complex.[17] Isolation of the pure compound was not possible then, since attempts to pump off the diethyl ether solvent resulted in inevitable loss of $[\mathrm{Ti(CH_3)_4}]$.[18] However, at −85 °C only the diethyl ether is volatile and the residual solid can be recrystallized from $\mathrm{CF_3CH_2CF_3}$. Light green crystals of $[\mathrm{Li(Et_2O)_2}]^+[\mathrm{Ti(CH_3)_5}]^-$ are obtained which are extremely sensitive to oxygen, water, and temperatures above −20 °C.

The crystallographic characterization revealed that there are two different $[\mathrm{Ti(CH_3)_5}]^-$ units in the lattice (Figure 2,

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Table 2. Density functional calculations of $[Ti(CH_3)_4]$, compared with $[Si(CH_3)_4]$ and $[Ge(CH_3)_4]$.

	Basis set	Symmetry	Energy [kJ mol^{-1}]	r_{Ti-C} [pm] ap/bas	methyl torsion [°]
$[Ti(CH_3)_4]$	HW3 - 6-31g(d)	T	0.0	207.4	151.9
$[Ti(CH_3)_4]$	HW3 - 6-31g(d)	T_d	2.4	206.0	180.0
$[Ti(CH_3)_4]$	HW3 - 6-31g(d)	C_{3v}[a]	46.7	212.2/208.2	180.0
$[Ti(CH_3)_4]$	HW3(VDZ) - 6-31g(d,p)	T	0.0	206.7	153.7
$[Ti(CH_3)_4]$	HW3(VDZ) - 6-31g(d,p)	T_d	1.1	206.7	180.0
$[Ti(CH_3)_4]$	HW3 - 6-311g(d,p)	T	0.0	206.0	162.2
$[Ti(CH_3)_4]$	HW3 - 6-311g(d,p)	T_d	0.6	206.0	180.0
$[Ti(CH_3)_4]$	Stutt - 6-311g(d,p)	C_1	0.0	207.2	154.6
$[Ti(CH_3)_4]$	Stutt - 6-311g(d,p)	T_d	no convergence	–	–
$[Si(CH_3)_4]$	HW3 - 6-31g(d)	T	0.0	189.6	180.0
$[Si(CH_3)_4]$	HW3 - 6-31g(d)	C_{3v}[a]	136.4	198.6/191.1	180.3
$[Ge(CH_3)_4]$	HW3 - 6-31g(d)	T	0.0	195.7	180.0
$[Ge(CH_3)_4]$	HW3 - 6-31g(d)	C_{3v}[a]	113.6	203.6/196.7	180.2

[a] Pyramidal structure with central atom in plane of three carbon atoms.

Table 3. Reaction enthalpies of $[Ti(CH_3)_4]$, $[TiCl(CH_3)_3]$, and $[Ti(CH_3)_5]^-$ reactions from density functional calculations.

Reaction	Basis set	Energy [kJ mol^{-1}]
$[Ti(CH_3)_4] + Et_2O \rightarrow [Ti(CH_3)_4]\cdots Et_2O$	HW3 – 6-31g(d)	– 11.7
$[Ti(CH_3)_4] + Et_2O \rightarrow [Ti(CH_3)_4]\cdots Et_2O$	HW3 – 6-311g(d,p)	– 5.2
$[Ti(CH_3)_4] + Et_2O \rightarrow [Ti(CH_3)_4]\cdots Et_2O$	Stutt – 6-311g(d,p)	– 9.1
$[TiCl(CH_3)_3] + Et_2O \rightarrow [Ti(CH_3)_3Cl]\cdots Et_2O$	HW3 – 6-31g(d)	– 25.0
$[Ti(CH_3)_4] + Cl^- \rightarrow [Ti(CH_3)_4Cl]^-$	HW3 – 6-31g(d)	– 146.8
$[Ti(CH_3)_4] + Cl^- \rightarrow [Ti(CH_3)_4Cl]^-$	Stutt – 6-311g(d,p)	– 118.9
$[Ti(CH_3)_4] + [Ti(CH_3)_4] \rightarrow [(CH_3)_3Ti\text{-}CH_3\text{-}Ti(CH_3)_4]$	HW3 – 6-311g(d,p)	– 2.0
$[Ti(CH_3)_4] + [Ti(CH_3)_5]^- \rightarrow [(CH_3)_4Ti\text{-}CH_3\text{-}Ti(CH_3)_4]$	HW3 – 6-31g(d)	– 58.4
$[Ti(CH_3)_5]^-$ $(C_{3h}) \rightarrow [Ti(CH_3)_5]^-$ (C_{4v})	HW3 – 6-31g(d)	– 10.5
$[Ti(CH_3)_5]^-$ $(C_{3h}) \rightarrow [Ti(CH_3)_5]^-$ (C_{4v})	HW3 – 6-311g(d,p)	– 9.5

Table 5). The methyl environment of Ti is irregular in both cases, which means neither metal atom has an almost regular trigonal-bipyramidal or square-pyramidal coordination geometry. If the angle criterion for the description of the transition from trigonal bipyramidal to square pyramidal is used as first defined by Muetterties and Guggenberger,[19] then $[Ti(CH_3)_5]^-$(**1**) is closer to square pyramidal with a characteristic angle difference of $\delta = 24.3°$ (ideally 0°). $[Ti(CH_3)_5]^-$(**2**) is closer to a trigonal-pyramidal unit with $\delta = 44.8°$ (ideally 60 °C).

The ab initio calculations (Tables 3, 4) predict $[Ti(CH_3)_5]^-$ to be square pyramidal. The trigonal-bipyramidal species is about 10 kJ mol^{-1} higher in energy than the square-pyramidal one. Similar energies have been calculated for square-pyramidal $[Ta(CH_3)_5]$ (in contrast to trigonal-bipyramidal $[Sb(CH_3)_5]$). This prediction is indeed experimentally proven by electron diffraction in the gas phase and by X-ray crystallography in the solid phase.[20]

Cation–anion packing is certainly the reason for the distortions in $[Ti(CH_3)_5]^-$. Each lithium ion has contact

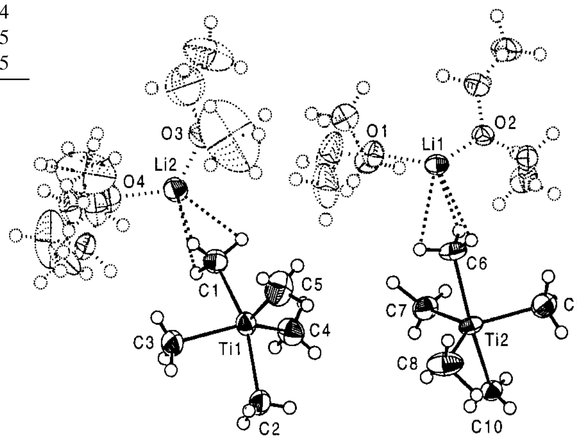

Figure 2. ORTEP plot of the two crystallographically different ion pairs **1** and **2** in $[Li(Et_2O)_2]^+[Ti(CH_3)_5]^-$.

Table 4. Ab initio calculation of $[Ti(CH_3)_4]$, $[Ti(CH_3)_5]^-$, $[Ti_2(CH_3)_8]^-$, $[Ti_2(CH_3)_9]$, $[Ti(CH_3)_4]\cdot Et_2O$, $[TiCl(CH_3)_3]\cdot Et_2O$, Et_2O, Cl^-. Energy [au] after geometry optimization with different basis sets; number of imaginary frequencies in brackets.

		HW3 - 6-31g(d)	HW3/6-311g(d,p)	Stutt – 6-311g(d,p)
$[Ti(CH_3)_4]$	(T)	– 217.663258427 (0)	– 217.741797865	no convergence
$[Ti(CH_3)_4]$	(T_d)	– 217.662339303 (– 4)	– 217.741578854 (– 1)	no convergence
$[Ti(CH_3)_4]$	(C_1)	–	–	– 218.008608325
$[Ti(CH_3)_4]$	(C_{3v})	– 217.644604253 (– 2)	–	–
$[Ti(CH_3)_3Cl]$		638.023061965(0)	–	–
$[Ti(CH_3)_5]^-$	(C_{3h})	– 257.580059912 (– 3)	– 257.683724133 (– 22)	–
	(C_{4v})	– 257.584058932	– 257.687352862	– 257.949115467 (0)
$[Ti_2(CH_3)_8]$		–	– 435.484369126	–
$[Ti_2(CH_3)_9]$		– 475.269571171 (0)	–	–
$[Ti(CH_3)_4]\cdot Et_2O$		– 451.327100983 (0)	– 451.475933129	– 451.744215361 (0)
$[Ti(CH_3)_3Cl]\cdot Et_2O$		– 871.691949419(0)	–	–
$[Ti(CH_3)_4Cl]^-$		– 677.971402797(0)	–	– 678.354576695 (– 1)
Et_2O		– 233.659385844 (0)	– 233.732161807 (0)	–
Cl^-		– 460.252232619	– 460.300690767	–

Table 5. $[Ti(CH_3)_5]^-$: Results of the X-ray structural determination and of density functional calculations. bond lengths [pm] and angles [°].

Anion 1		Anion 2		Calculated[a]		
					C_{3h}	C_{4v}
Ti1–C1	217.9(4)	Ti2–C6	219.6(3)	$Ti–C_{ap}$	220.7	214.2
Ti1–C2	219.4(4)	Ti2–C7	213.2(4)	$Ti–C_{equ}$	213.8	–
Ti1–C3	214.6(4)	Ti2–C8	209.3(4)	$Ti–C_{bas}$		217.3
Ti1–C4	213.1(4)	Ti2–C9	213.1(4)			
Ti1–C5	207.7(5)	Ti2–C10	219.5(3)			
C1-Ti1-C2	154.2(2)	C6-Ti2-C10	165.6(2)	C_{ap}-Ti-C_{equ}	90.0	–
C3-Ti1-C4	129.9(2)	C7-Ti2-C8	121.2(2)	C_{equ}-Ti-C_{equ}	120.0	–
C3-Ti1-C5	115.8(3)	C7-Ti2-C9	120.8(2)	C_{ap}-Ti-C_{bas}	–	109.7
C4-Ti1-C5	114.2(2)	C8-Ti2-C9	117.9(2)	C_{bas}-Ti-C_{bas}	–	83.5

[a] See also Table 3.

with two methyl groups as well as with Et_2O molecules, and this results in an elongation of the corresponding C–Ti distances and produces a chain structure. There are two different chains: one that contains only the more square-pyramidal $[Ti(CH_3)_5]^-$ (**1**) units, and the other with the more trigonal-bipyramidal $[Ti(CH_3)_5]^-$ (**2**) units. These different chains are at 90° to each other (Figure 3). Not surprisingly, the bridging methyl groups occupy basal positions in the square-pyramidal $[Ti(CH_3)_5]^-$ units and axial positions in the trigonal-bipyramidal analogues.

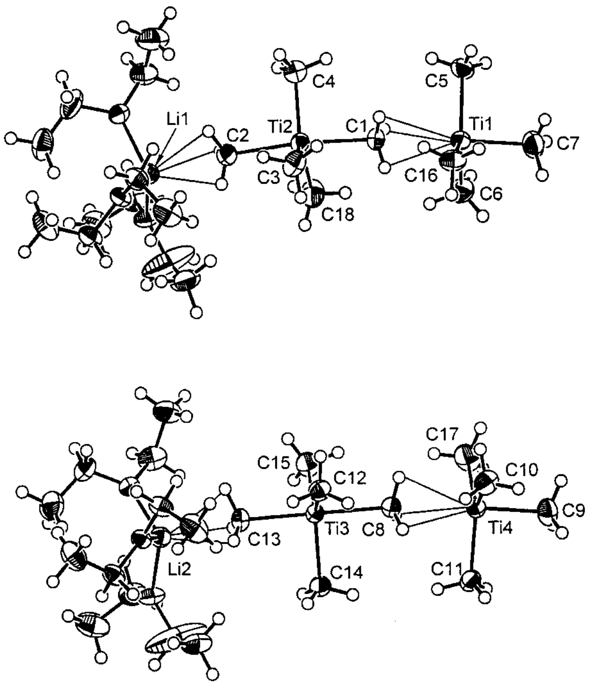

Figure 4. ORTEP plot of $[Li(Et_2O)_3]^+[Ti_2(CH_3)_9]^-$.

$[Ti_2(CH_3)_9]^-$: $[Li(Et_2O)_3]^+[Ti_2(CH_3)_9]^-$ can also be crystallized from $CF_3CH_2CF_3$ as a yellow-green product. The crystal contains two crystallographic units for $[Li(Et_2O)_3]^+[Ti_2(CH_3)_9]^-$ that differ largely only in the orientation of the ethyl groups of the diethyl ether molecules, whereas the bond lengths and overall C_{3v} symmetry of the $[Ti_2(CH_3)_9]^-$ ions are virtually identical (Figure 4, Table 6). The anion can be viewed as a pyramidal $[Ti(CH_3)_4]$ molecule that is complexed by $[Ti(CH_3)_5]^-$, which gives an unsymmetrical but essentially linear Ti–C ··· Ti bridge. In both units the hydrogen positions on the bridging methyl groups could be located by difference Fourier analyses and refined independently (as well as all of the other hydrogen atoms of the Ti-bonded methyl groups). The Ti-C-H angles in the bridging methyl groups are smaller than the tetrahedral angle of 109.45°, so there is a tendency for planarization of these particular methyl groups. A completely planar methyl group could be expected only in a linear symmetric bridge. The interaction between the methyl group and the more distant Ti atom is certainly largely electrostatic in nature, but the flattening of the methyl group mentioned above is indicative of an agostic bond between the C–H bonds and the Ti atom. Such an interaction has a precedent in $Cp^*_2Yb \cdots CH_3BeCp^*$ ($Cp^* = C_5(CH_3)_5$).[21] Of course the interaction between the Li ions and the methyl groups, both in $[Ti_2(CH_3)_9]^-$ and $[Ti(CH_3)_5]^-$, is of the same nature (Figures 2, 4), but the lower electronegativity of Li should give an even higher degree of ionicity to these particular interactions. The formation of $[Ti_2(CH_3)_9]^-$ from $[Ti(CH_3)_4]$ and $[Ti(CH_3)_5]^-$ was also investigated by calculation, and was found to be

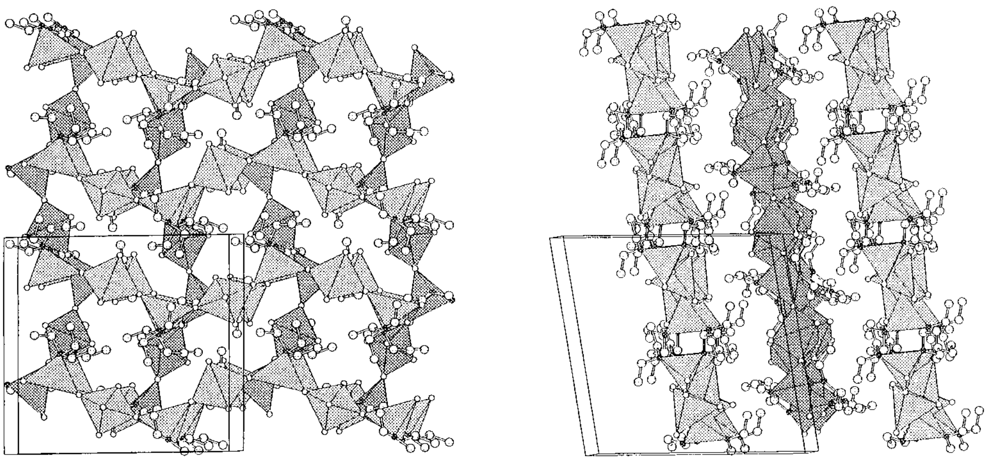

Figure 3. Cation–anion packing in $[Li(Et_2O)_2]^+[Ti(CH_3)_5]^-$ that results in a chain structure. The different crystallographic units **1** and **2** are expressed by different degrees of shading.

Table 6. Results of the X-ray structural determination and of density functional calculation of $[Li(Et_2O)_3]^+[Ti_2(CH_3)_9]^-$; bond lengths [pm] and angles [°].

Anion 1		Anion 2		Calculated
Ti1–C7	211.3(4)	Ti4–C9	211.2(4)	215.9
Ti1–C6	210.1(3)	Ti4–C10	210.0(3)	212.2
Ti1–C5	210.1(3)	Ti4–C11	211.1(3)	212.2
Ti1–C16	211.7(4)	Ti4–C17	211.2(3)	212.1
Ti1–C1	246.5(4)	Ti4–C8	248.2(3)	239.2
Ti2–C1	223.7(4)	Ti3–C8	223.3(3)	229.7
Ti2–C4	209.9(3)	Ti3–C15	212.4(3)	212.4
Ti2–C3	211.4(4)	Ti3–C14	211.7(3)	212.5
Ti2–C18	212.2(3)	Ti3–C12	210.9(3)	212.6
Ti2–C2	218.0(4)	Ti3–C13	217.7(4)	216.9
C2–Li1	241.3(4)	C13–Li2	241.5(4)	–
C7-Ti1-C1	175.16(16)	C9-Ti4-C8	176.68(14)	179.5
C1-Ti2-C2	173.69(15)	C8-Ti3-C13	175.75(15)	179.0
C7-Ti1-C6	92.70(15)	C9-Ti4-C10	92.58(15)	88.9
C7-Ti1-C5	92.23(15)	C9-Ti4-C11	89.73(14)	89.3
C7-Ti1-C16	89.61(17)	C9-Ti4-C17	91.54(15)	88.7
C1-Ti2-C4	92.49(14)	C8-Ti3-C15	88.51(14)	88.3
C1-Ti2-C3	87.56(14)	C8-Ti3-C14	89.59(13)	88.5
C1-Ti2-C18	87.54(15)	C8-Ti3-C12	89.86(14)	89.0

exothermic by 58.4 kJ mol^{-1}, which is higher than for the formation of $[Ti(CH_3)_4]\cdot Et_2O$ from $[Ti(CH_3)_4]$ and Et_2O.

$[Ti(CH_3)_3Cl]$ and $[Ti(CH_3)_3Cl]\cdot Et_2O$: The methylation of $TiCl_4$ proceeds in steps, and $[Ti(CH_3)_3Cl]\cdot Et_2O$ can be crystallized by reaction of $TiCl_4$ and CH_3Li in Et_2O in a molar ratio of 1:3. The orange-colored material is, like all of the previously mentioned methyltitanium derivatives, very sensitive towards oxygen in particular. The crystal structure is shown in Figure 5, from which the relation to the structure of $[Ti(CH_3)_4]\cdot Et_2O$ is obvious (Figure 1). The Ti···O contact of 215.9 pm is 10 pm shorter than that in $[Ti(CH_3)_4]\cdot Et_2O$ (Table 1). Interestingly, it is possible to obtain solvent-free $[Ti(CH_3)_3Cl]$ by treating solutions of $[Ti(CH_3)Cl_3]$ with solid CH_3Li that should contain only traces of diethyl ether.[22] The $[Ti(CH_3)_3Cl]$ now crystallizes as dark red, cube-shaped crystals. The result of this single-crystal structure determination is shown in Figure 6. Interestingly, removal of the solvent molecule leads to an increase in the coordination number from 5 to 6. The result is a cubane structure with alternating Ti and triple bridging Cl atoms. There is a parallel with $[Pt(CH_3)_3Cl]$ which, according to data from an early powder determination, crystallizes essentially identically, but in the latter case only the Pt and Cl positions were determined.[23]

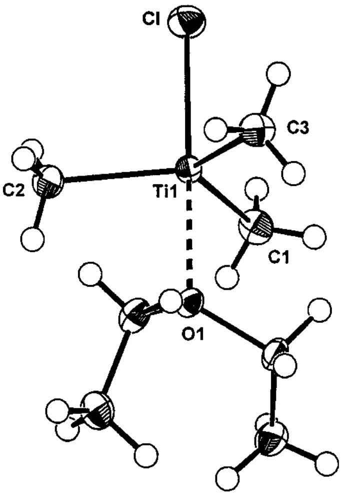

Figure 5. X-ray crystal structure of $[TiCl(CH_3)_3]\cdot Et_2O$.

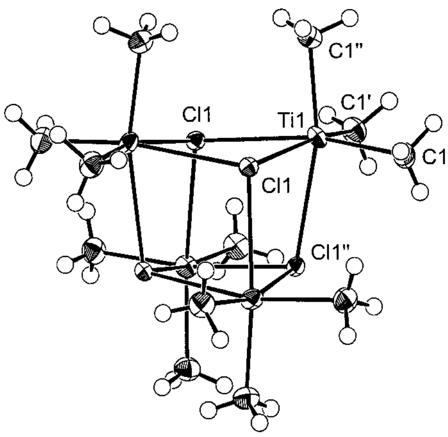

Figure 6. ORTEP plot of tetrameric $[TiCl(CH_3)_3]$.

$[Ti(CH_3)_2Cl_2]$: A reliable synthesis of $[Ti(CH_3)_2Cl_2]$ makes use of $Zn(CH_3)_2$ as methylating agent for $TiCl_4$. Furthermore, this reaction can be carried out in pentane, which avoids complexation by any donor solvents. Interestingly, $[Ti(CH_3)_2Cl_2]$ dissolves in pentane to give a yellow solution, while its crystals are dark violet or almost black. It is very sensitive towards oxygen and stable to about 0 °C. The crystallographic structure determination revealed a polymeric chain structure (Figure 7, Table 7). The Ti atoms are surrounded in an almost octahedral manner and carry two terminal CH_3 groups that have an angle of 95.8(3)° to each other. All of the chlorine atoms are engaged in asymmetric and bent bridging.

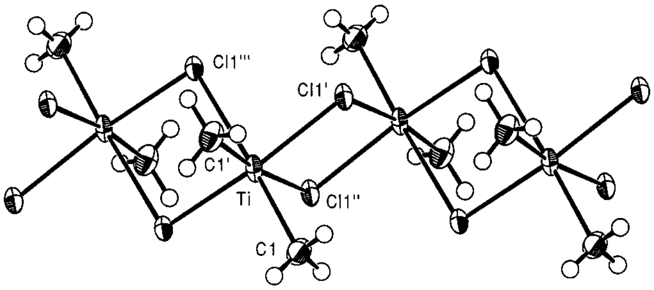

Figure 7. X-ray crystal structure of $[TiCl_2(CH_3)_2]$.

$[Ti(CH_3)Cl_3]$: The compound $[Ti(CH_3)Cl_3]$ has been synthesized before,[24] and a fair amount of information already exists about its structure under various conditions. The structural investigation in the gas phase by means of electron diffraction was at first interpreted in terms of an agostic interaction of the hydrogen atoms with the Ti atom.[25] However, repetition of this measurement did not show such a result, and the discrepancy has been explained by the presence of some impurities, possibly $TiCl_4$, that were not taken into account in the previous electron-diffraction

Table 7. Results of the X-ray structural determination of $[Ti(CH_3)Cl_3] \cdot Et_2O$, $[Ti(CH_3)_2Cl_2]$, and $[Ti(CH_3)_3Cl]$; bond lengths [pm] and angles [°].

$[Ti(CH_3)Cl_3] \cdot Et_2O$				$[Ti(CH_3)_2Cl_2]$		$[Ti(CH_3)_3Cl]$	
Molecule 1		Molecule 2					
Ti1−C1	206.4(3)	Ti2−C2	207.2(3)	Ti−C1	205.5(5)	Ti−C	206.1(2)
Ti1−Cl11	240.2(2)	Ti2−Cl22	237.7(2)	Ti−Cl1	233.1(1)	Ti−Cl	265.8(1)
Ti1Cl11′	266.8(2)	Ti2Cl22′	275.5(2)	Ti−Cl1‘	271.3(2)		
Ti1−Cl12	225.2(2)	Ti2−Cl21	223.9(2)				
Ti1−Cl13	224.0(2)	Ti2−Cl23	224.1(2)				
Ti1−O1	212.7(2)	Ti2−O2	212.9(2)				
C1-Ti1-Cl11′	171.4(1)	C2-Ti2-Cl22′	173.5(1)	C1-Ti-C1′	95.8(3)	C-Ti-C′	98.2(1)
C1-Ti1-Cl11	94.3(1)	C2-Ti2-Cl22	101.0(1)	C1-Ti-Cl1′	94.2(2)	C-Ti-Cl′	91.4(1)
C1-Ti1-Cl12	96.6(1)	C2-Ti2-Cl21	91.5(1)	C1-Ti-Cl1	96.6(2)	Cl-Ti-Cl′	77.1(1)
C1-Ti1-Cl13	92.8(1)	C2-Ti2-Cl23	94.9(1)	C1-Ti-Cl1″	91.0(2)	C-Ti-Cl	165.3(1)
C1-Ti1-O1	88.6(2)	C2-Ti2-O2	87.7(2)	C1-Ti-Cl1‴	172.3(2)	Ti-Cl-Ti	101.5(1)
Cl11-Ti-Cl12	166.5(1)	Cl22-Ti-Cl23	162.8(1)	Cl1-Ti-Cl1′	163.8(6)		
Cl13-Ti-O1	175.1(1)	Cl21-Ti2-O2	171.9(1)	C1′-Ti-Cl1″	172.3(2)		

study.[26] $[Ti(CH_3)Cl_3]$ has also been the subject of ab initio calculations,[27] and the calculated structure agrees very well with that obtained by the second electron-diffraction study.

Single crystals of diethyl ether free $[Ti(CH_3)Cl_3]$ have already been obtained by sublimation and then submitted for X-ray analysis.[28] This compound forms dimers with two bridging chlorine atoms, two terminal chlorine atoms per titanium atom, and one methyl group, bringing the ligand count up to five. One hydrogen atom of the methyl is tilted towards the Ti atom to give a Ti−H distance of 203 pm. A similar intramolecular agostic Ti−H interaction is proposed for solvated $[Ti(CH_3)Cl_3]$ as in $[\{(CH_3)_2PCH_2\}_2Ti(CH_3)Cl_3]$.[29] Here, the positions of the the $TiCH_3$ protons were also established by a single-crystal neutron structure determination.[29] The neutron data show a much smaller tilt of the methyl group (only about 16°) towards the Ti atom. We have been successful in crystallizing a $[Ti(CH_3)Cl_3] \cdot Et_2O$ solvate in which the methyl groups appear normal, that is, the Ti-C-H angles vary between 104.5(2) and 110(2)° according to the X-ray structure determination (Figure 8). The molecule appears to be a double chlorine-bridged dimer, very much like the unsolvated $[Ti(CH_3)_3Cl_3]$.

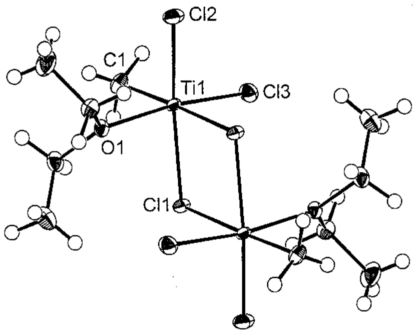

Figure 8. ORTEP plot of the $[TiCl_3(CH_3)]$ dimer.

Conclusion

All of the structures determined here show the methyltitanium and methyltitanium chloride compounds as having coordination numbers of 5 or 6 at the titanium atom. However, only $[Ti(CH_3)_4]$ would be tetrahedral if it could be obtained free of solvent. Our work has presented no evidence for intramolecular interactions between the methyl groups and the titanium atom. Only in $[Ti_2(CH_3)_9]^-$ can the bridging of a methyl group between two titanium atoms be interpreted in terms of intermolecular agostic Ti···H interactions, although an electrostatic description is equally possible.

Experimental Section

All experiments were carried out under pure, dry argon that had been freed from traces of O_2 by passage through green MnO deposited on silica gel. This procedure turned out to be essential in order to prevent oxidation of $Ti{-}CH_3$ to $Ti{-}O{-}CH_3$ groups. Solvents were dried over sodium/benzophenone and kept under argon. Hydrolytically sensitive starting materials were handled in a glove box (Braun GmbH, Germany) fitted with automatic gas purification; H_2O and O_2 content was typically below 1 ppm. All glassware was heated twice in vacuo before use. Liquids were transferred through teflon tubes (inner diameter = 1 mm) by applying a pressure of argon. $TiCl_4$ was purchased from Merck Co., Germany, purified by distillation, and stored over Cu. Pure $Zn(CH_3)_2$ was obtained from $ZnCl_2$ and CH_3MgI by complexation with 4,4′-trimethylenedipyridine and subsequent pyrolysis.[30] Solid CH_3Li was prepared from CH_3Cl and Li in diethyl ether in the usual manner.[22] The diethyl ether was pumped off at 100 °C under high vacuum, but traces of ether remained in the colorless solid, as detected by ^1H and ^{13}C NMR spectroscopy.

$[Ti(CH_3)_4] \cdot Et_2O$: $TiCl_4$ (1 g, 5.3 mmol) in Et_2O (100 mL) was treated with MeLi (21.2 mmol, 1.6 M solution in Et_2O) at −78 °C and kept at this temperature overnight. The dark green suspension was stirred at −30 °C for 20 min. All of the volatile components were distilled under high vacuum from −30 °C into a trap at −196 °C. The entire tubing had to be kept at −30 °C in order to avoid thermal decomposition of the product in the gas phase. The product/solvent mixture was reduced to a highly viscous liquid by pumping at a pressure $p < 10^{-4}$ mbar at −85 °C. This liquid was redissolved in CH_2F_2 at −50 °C and was transferred to and sealed in an ampule (10 mL). Two phases were formed, and upon cooling from −45 to −85 °C orange crystals grew at the phase interface. These crystals melted above −75 °C to give an orange oil. Oxygen caused immediate decomposition with formation of a black residue. ^1H NMR (400 MHz, CH_2F_2, −50 °C): $\delta = 1.44$ (12 H, $TiCH_3$), 1.03 (12 H, $(CH_3CH_2)_2O$), 3.60 (8 H, $(CH_3CH_2)_2O$); $[^1H]^{13}C$ NMR (100.4 MHz, CH_2F_2, −50 °C): $\delta = 69.5$ ($TiCH_3$), 18.1 ($(CH_3CH_2)_2O$), 58.5 ($(CH_3CH_2)_2O$).

$[Li(Et_2O)_2]^+[Ti(CH_3)_5]^-$: MeLi in Et_2O was added to a solution of $[Ti(CH_3)_4]$ also in Et_2O (prepared as described above) until the yellow color had changed completely to light green. The solvent was removed at −85 °C, and the resulting residue was dissolved in $CF_3CH_2CF_3$ at −40 °C. This solution was cooled slowly to −78 °C until faint yellow crystals were formed. The product was thermally stable to −20 °C, but was very sensitive towards oxygen. ^1H NMR (400 MHz, CH_2F_2, −50 °C): $\delta = 2.58$ ($TiCH_3$); $[^1H]^{13}C$ NMR (100.4 MHz, CH_2F_2, −50 °C): $\delta = 128.5$ ($TiCH_3$); Raman (solid, 80 mW, $\lambda = 1040$ nm): $\tilde{\nu} = 3030(3)$, 2988(10), 1427(5), 1308(3),

Table 8. Experimental crystallographic data.

	$[Ti(CH_3)_4]\cdot Et_2O$	$Li[Ti(CH_3)_5]\cdot 2\,Et_2O$	$Li[Ti_2(CH_3)_9]\cdot 3\,Et_2O$	$[Ti(CH_3)_3Cl]$	$[Ti(CH_3)_3Cl]\cdot Et_2O$	$[Ti(CH_3)_2Cl_2]$	$[Ti(CH_3)Cl_3]\cdot Et_2O$
M_r [g mol^{-1}]	182.16	278.25	460.41	128.45	202.57	148.87	243.41
T [K]	123	133	1.30	130	130	130	133
space group	$P2_1/c$	$P2_1/c$	$P2_1/a$	$I\bar{4}3m$	$Pbca$	$Pcnb$	$P\bar{1}$
a [pm]	671.2(4)	1535.2(4)	1511.5(1)	1052.8(1)	1076.0(3)	604.6(2)	717.1(3)
b [pm]	2620.1(4)	1584.1(2)	2097.3(1)	1052.8(1)	1130.0(3)	603.4(1)	1006.5(4)
c [pm]	1315.8(4)	1572.0(4)	1989.6(1)	1052.8(1)	1799.2(3)	1521.2(5)	1510.6(4)
α [°]	90.0	90.0	90.0	90.0	90.0	90.0	82.35(4)
β [°]	96.72(2)	98.70(2)	103.25(1)	90.0	90.0	90.0	82.93(3)
γ [°]	90.0	90.0	90.0	90.0	90.0	90.0	71.41(3)
V [10^6 pm^3]	2298(2)	3779(2)	6139.3(6)	1166.7(2)	2187.6(9)	555.0(3)	1020.4(6)
Z	8	8	8	8	8	4	2
absorption coeff [mm^{-1}]	0.056	0.444	0.534	1.768	0.974	2.337	1.565
θ_{max} [°]	24.98	24.96	21.98	29.89	24.99	25.00	24.97
reflections collected	2872	5775	7076	2905	1925	485	3583
independent reflections	2872	5775	7076	350	1925	485	3583
R	0.0378	0.0554	0.0467	0.0173	0.0282	0.0317	0.0308
wR^2	0.0811	0.1795	0.1384	0.0410	0.0677	0.0740	0.0780

1208(3), 1099(3), 1054(5), 912(5), 874(2), 841(100), 720(22), 650(8), 532(10), 522(12), 498(8), 332(40), 312(15), 156(4) cm^{-1}.

$[Li(Et_2O)_3]^+[Ti_2(CH_3)_9]^-$: $TiCl_4$ (0.7g, 3.7 mmol) in pentane (100 mL) was allowed to react with MeLi (9.0 mL, 14.4 mmol, 1.6 M solution in Et_2O) at −78 °C; the mixture was kept at this temperature overnight. The dark green suspension formed was then stirred at −20 °C for 20 min. The solvents were pumped off at −78 °C under high vacuum. The solid residue was extracted with $CF_3CH_2CF_3$ at −60 °C. Two phases were formed: a dark green one of high viscosity and lower density, and a heavier, yellow-green phase that contained mainly $CF_3CH_2CF_3$. This latter phase was transferred to and sealed in an ampule (10 mL). Slow cooling from −60 to −90 °C afforded large, cube-shaped, yellow-green crystals that have a stability similar to that of $[Ti(CH_3)_5]^-$.

$[Ti(CH_3)_3Cl]\cdot Et_2O$: $TiCl_4$ (1 g, 5.3 mmol) in Et_2O (100 mL) was treated with MeLi (16.8 mmol, 1.6 M solution in Et_2O) at −78° and kept at this temperature overnight. The dark-red suspension was stirred at −30 °C for 20 min. All of the volatile components were distilled under high vacuum from −30 °C into a trap at −196 °C. The entire tubing had to be kept at −30 °C in order to avoid thermal decomposition of the compound in the gas phase. The product/solvent mixture was reduced to a highly viscous liquid by pumping at a pressure of $p < 10^{-4}$ mbar at −85 °C. This liquid was redissolved in $CF_3CH_2CF_3$ at −50 °C and then transferred to and sealed in an ampule (10 mL). Two phases were formed, and upon cooling from −45 to −85 °C orange crystals grew at the phase surface.

$[Ti(CH_3)_3Cl]$: $[Ti(CH_3)Cl_3]$ solution in pentane (20 mL) was combined with solid MeLi (0.75 g) at −78 °C. The color changed from yellow-green to orange to dark red. Sedimentation after 30 min afforded a red solid and a lemon-yellow solution, which was transferred to and sealed in an ampule. Storage at −90 °C yielded cube-shaped, dark red crystals. ^{1}H NMR (400 MHz, pentane, −50 °C): $\delta = 2.0$; ^{49}Ti NMR (22.552 MHz, pentane, −50 °C): $\delta = 1258$.

$[Ti(CH_3)_2Cl_2]$: $TiCl_4$ (100 mg, 0.5 mmol) in pentane (3 mL) was treated with $Zn(CH_3)_2$ (190 mg, 2.0 mmol) in a sealed ampule at −20 °C for 30 min. Slow cooling to −75 °C afforded black, needle-shaped crystals.

$[Ti(CH_3)Cl_3]\cdot Et_2O$: Solid CH_3Li (1 g, 11.4 mmol) in pentane (50 mL) was made to react with $TiCl_4$ (1 g, 5.3 mmol) in a Schlenk tube. The red-brown solution was stirred for 30 min at −30 °C. After cooling to −77 °C, the yellow solution was separated from the dark brown solid, transferred into an ampule, and reduced to about one quarter of its volume by pumping at −78 °C in vacuo. After 1 day at −78 °C black, needle-shaped crystals were formed. ^{1}H NMR (400 MHz, $CDCl_3$, −30 °C): $\delta = 2.93$; [^{1}H]^{13}C NMR (100.4 MHz, $CDCl_3$, −30 °C): $\delta = 114.0$; ^{35}Cl NMR (39.193 MHz, −30 °C, pentane): $\delta = 719.6$; ^{49}Ti NMR (22.552 MHz, −30 °C, pentane): $\delta = 608.5$; Raman (solid, 80 mW, $\lambda = 1040$ nm): $\tilde{\nu}$ 3011 (10), 2247(10), 772(10), 753(12), 731(14), 668(50), 650(45), 367(100), 270(80), 259(70) cm^{-1}.

Calculations: All ab initio calculations were processed with the GAUSSIAN-94 package[31] on an SGI Origin 2000 with 16 processors. Within the applied B3LYP DFT method, different basis sets for titanium and for all other elements were used. For C, H, O, Cl, Si, and Ge the implemented 6-311g(d) and 6-31g(d,p) basis sets were employed. For Ti, a nonrelativistic effective core potential (ECP) basis set with a 10 electron core [$1s^22s^22p^6$] and a $3s^23p^63d^24s^2$ valence shell (called an HW3 basis set) from Hay and Wadt were used.[32] Each valence orbital was described by five primitive GTOs (55/5/5). To verify these calculations two higher ECP basis sets were used for Ti. The first had the same core as in HW3, but with a split valence shell (341/311/41) with diffuse functions, called HW3(VDZ), also from Hay and Wadt. The second was an ECP (STUTT) from Preuss et al. at the Universität Stuttgart[33] which has a 10-electron core, a diffuse and pseudopotential shell, combined with a 6-311g(d,p) basis set for the lighter atoms. Use of the "larger" basis sets for Ti predicted no significant changes in energy, so all of the calculations were performed in the HW3/6-31g(d) basis sets so as to minimize computation time.

Crystal structure determinations: (See Table 8) Glass tubes containing single crystals were opened into the mouth of a special piece of apparatus designed for handling moisture-, oxygen-, and temperature-sensitive compounds.[34] Suitable crystals were selected under a microscope and cut, if necessary. The crystals were mounted on a glass tip with perfluoropolyether ($[Ti(CH_3)_4]\cdot Et_2O$) or with nujol/methylcyclohexane, and were subsequently transferred to the Enraf–Nonius CAD 4 diffractometer. Cell dimensions were obtained by fine orientation of 25 reflections with $20° < \Theta < 25°$. Data were obtained in the ω-scan mode with a maximum of 60 s for each reflection, depending on intensity, and leaving 25 % of the time for background measurements. After Lorentz polarization and psi scan absorption corrections[35] the data were reduced to intensities (F^2).[36] The structures were solved and refined against F^2 with the SHELX procedures.[37] Hydrogen atoms of the metal methyl groups were in general refined isotropically; solvent hydrogen atoms were normally generated by the program and refined with riding models. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-116598–CCDC-116604. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

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