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The First Structurally Characterized Nonorganometallic Titanium(III) Alkoxo-Bridged Dinuclear Complexes

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The reaction of [$Ti_4(OMe)_{14}Cl_2$] (**1**) with an excess of $AlMe_3$ gave the cocrystallite [$Ti_2(\mu\text{-}OMe)_2(\mu\text{-}Cl)Cl_3(thf)_3$]·[$Ti_2(\mu\text{-}OMe)_3Cl_3(thf)_3$] (**2·3**) species in a 1:1 ratio. Similar to **2**, [$Ti_2(\mu\text{-}OEt)_2(\mu\text{-}Cl)Cl_3(thf)_3$] (**4**) was obtained in the reaction of an equimolar mixture of $TiCl_4$ and $Ti(OEt)_4$ with Al/$AlMe_3$. The short distance [$2.543(1)_{av}$ Å in **2·3** and 2.599(1) Å in **4**] between "Ti(+3)" atoms, their diamagnetism, and ELF analysis indicate the presence of a Ti–Ti bond.

Our knowledge on the interaction among components of the inherently very complex $MX_{(3)4}/MgX_2/AlEt_3$ (M = Ti, Zr, or V; X = OR or Cl) Ziegler–Natta polymerization catalyst system is still very limited and presents a challenge.[1,2] Our research has been long projected on determining the role of each of the catalyst components that are still extensively used in the polyolefin industry.[3] We have shown that in the reaction of magnesium alkoxide [$Mg_4(thffo)_8$] (thffo = 2-tetrahydrofurfuroxide) with $AlMe_3$ the methylaluminoxane [$Al_3(\mu_3\text{-}O)(Me)_6$]$^+$ unit is formed, which was isolated and characterized as a molecular compound, [$Al_3Mg(\mu_3\text{-}O)(thffo)_3(Me)_6$].[4a] Very recently we reported the direct complexation of $AlMe_3$ by the oxygen atom of the $Zr_3(\mu_3\text{-}O)$ core that emerged in reaction of $ZrCl_4$ with MeOH to give the molecular solid [$Zr_3Al(\mu_4\text{-}O)(\mu\text{-}OMe)_6Cl_6(Me)(thf)_3$].[4b] The catalyst based on titanium species is much more complex than the zirconium system, and nothing is known about its intermediates.[3] Here we describe successful syntheses of dinuclear and diamagnetic "Ti(+3)" nonorganometallic species **2**–**4**, together with X-ray data which exhibit the new $Ti(\mu\text{-}OR)_2(\mu\text{-}X)Ti$ core (X = OR, Cl) which displays the shortest Ti···Ti distance between "Ti(+3)" atoms.

The precursor [$Ti_4(OMe)_{14}Cl_2$] (**1**) was obtained in the direct reaction of $TiCl_4$ with methanol at −70 °C in 40%.[5] Treatment of **1** with an excess of $AlMe_3$ (4 equiv, toluene/thf, −30 °C; Scheme 1) gave a dark-maroon solution from which after workup red cubes of cocrystallite [$Ti_2(\mu\text{-}OMe)_2(\mu\text{-}Cl)Cl_3(thf)_3$]·[$Ti_2(\mu\text{-}OMe)_3Cl_3(thf)_3$] (**2·3**) in a 1:1 ratio in 74% yield were obtained. Similar to **2**, red [$Ti_2(\mu\text{-}OEt)_2(\mu\text{-}Cl)Cl_3(thf)_3$] (**4**) was obtained in the reaction of an equimolar mixture of $TiCl_4$, $Ti(OEt)_4$, Al, and $AlMe_3$ (thf, −60 °C; Scheme 2). Workup that involved thf/toluene recrystallization afforded a neutral analytically pure sample of **4** in 20% yield. Addition of more than 1 equiv of $AlMe_3$ leads most probably to the formation of species containing a Ti–Me bond and reduces the yield of **4**. Reduction with only Al or $AlMe_3$ gave an oily product, purification of which was demanding and eventually gave a "problematic" result. Compounds **2**–**4** gave correct microanalyses. They are insoluble in aliphatic hydrocarbons but are easily soluble in toluene and halogenated solvents and could be stored under N_2 for weeks. Species **2**–**4** dissolved in thf undergo slowly decomposition to blue crystalline [$TiCl_3(thf)_3$] based on X-ray measurements of unit cell parameters.

The diamagnetism of **2**–**4** was indicated by solid state measurements.[6] The only EPR parameter recorded was the trivial isotropic *g* value of a single-line signal, which belonged to an $S = {}^1/_2$ impurity of 1% Ti(III) monomeric species.[7] The dinuclear structures of **2**–**4**, suggested by the diamagnetism in the solid state, were confirmed by an X-ray crystal structures. The structure of the cocrystallite **2·3** is

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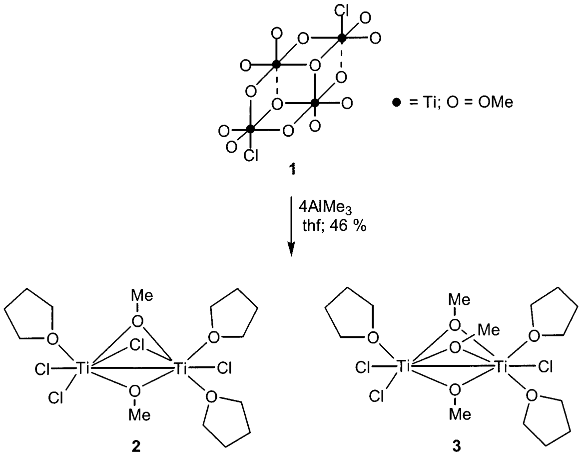
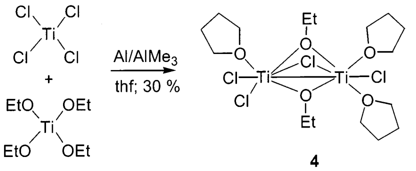
Scheme 1. Synthesis of $[Ti_2(\mu\text{-}OMe)_2(\mu\text{-}Cl)Cl_3(thf)_3]\cdot[Ti_2(\mu\text{-}OMe)_3Cl_3(thf)_3]$ (**2·3**)



Scheme 2. Synthesis of $[Ti_2(\mu\text{-}OEt)_2(\mu\text{-}Cl)Cl_3(thf)_3]$ (**4**)



composed of two chemically independent $[Ti_2(\mu\text{-}OMe)_2(\mu\text{-}Cl)Cl_3(thf)_3]$ and $[Ti_2(\mu\text{-}OMe)_3Cl_3(thf)_3]$ molecules which are statistically distributed in the crystal.[8] This gives rise to disorder of the $Ti_2(\mu\text{-}OMe)_2(\mu\text{-}X)$ (X = Cl, OMe) bridges observed in the X-ray experiment as shown in Figure 1. The dimeric structures of the units are composed of two $TiCl(thf)_2$ and $TiCl_2(thf)$ moieties bridged by one μ-Cl and two μ-OMe ligands in **2**, and three μ-OMe ligands in **3**. The dioctahedron is formed by two octahedral Ti(1) and Ti(2) atoms which share a face defined by O(1), O(2), Cl(4) atoms and O(1), O(2), O(3) atoms in **2** and in **3**. Compound **4** (Figure 2) possesses structure similar to that in **2**.[9] The only significant difference is that two μ-OMe moieties in **2** are substituted by two μ-OEt groups in **4**. The very short Ti···Ti distance [$2.543(1)_{av}$ Å in **2·3** and 2.599(1) Å in **4**] accompanied by diamagnetism of both species might indicate the presence of a Ti−Ti single bond. However, the metal−metal distance is not a good bond criterion,[10] especially in the systems where the bridging constraints are substantial.[11]

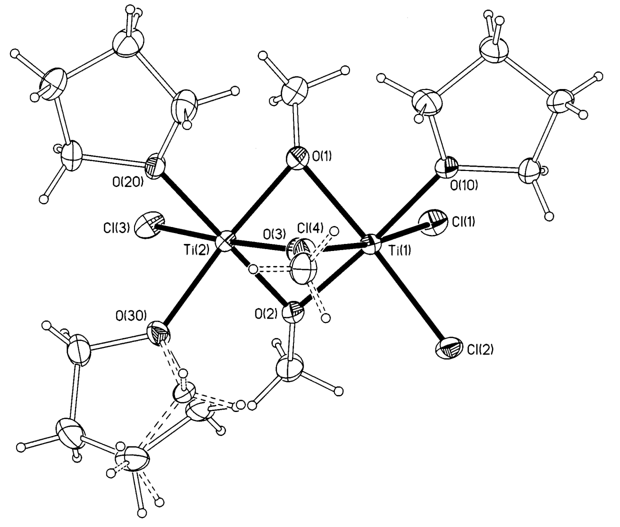


Figure 1. The molecular structure of the cocrystallite **2·3**. The displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Ti(1)···Ti(2) 2.543(1), Ti(1)−Cl(1) 2.386(2), Ti(1)−Cl(2) 2.387(1), Ti(1)−Cl(4) 2.530(3), Ti(2)−Cl(3) 2.373(2), Ti(2)−Cl(4) 2.554(3), Ti(1)−O(1) 2.016(2), Ti(1)−O(2) 1.964(2), Ti(1)−O(3) 1.946(5), Ti(1)−O(10) 2.118(2), Ti(2)−O(3) 1.857(5), Ti(2)−O(1) 1.978(2), Ti(2)−O(2) 1.939(2), Ti(2)−O(20) 2.124(2), Ti(2)−O(30) 2.122(2).

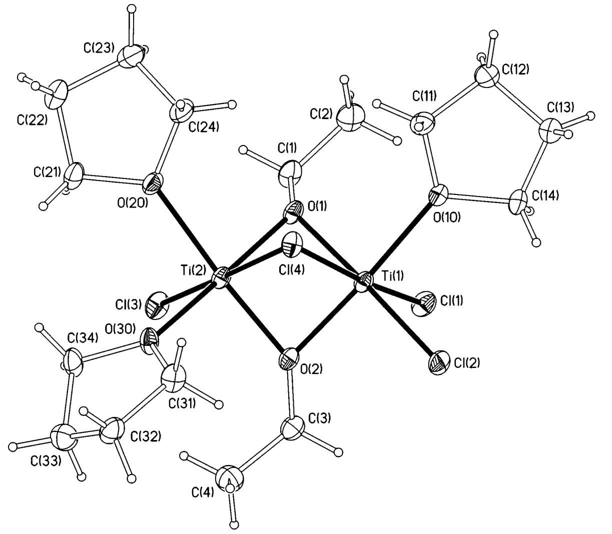


Figure 2. The molecular structure of **4**. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Ti(1)···Ti(2) 2.599(1), Ti(1)−Cl(1) 2.379(2), Ti(1)−Cl(2) 2.383(1), Ti(1)−Cl(4) 2.483(2), Ti(2)−Cl(3) 2.376(1), Ti(2)−Cl(4) 2.464(1), Ti(1)−O(1) 2.010(2), Ti(1)−O(2) 1.971(2), Ti(1)−O(10) 2.118(2), Ti(2)−O(1) 1.972(2), Ti(2)−O(2) 1.946(2), Ti(2)−O(20) 2.145(2), Ti(2)−O(30) 2.133(2).

For comparison the simple Ti(IV) oxide bridged dimer $[Ti_2(\mu\text{-}O)_2(acac)_4]$ displays also a short Ti···Ti distance, 2.796(1) Å.[12] It is, therefore, well possible that both the short intermetallic separation in **2−4** and the diamagnetism result from the particular nature of the μ-OR bridging ligands.

We sought to further clarify the nature of the Ti···Ti interaction in **2** and **3** computationally using the single-point, B3LYP/6-31G(d,p) calculations[13] with experimentally de-

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(8) Crystal data for **2·3**: $C_{14.50}H_{31.50}Cl_{3.50}O_{5.50}Ti_2$, $M = 513.77$, monoclinic, $a = 8.306(1)$ Å, $b = 17.325(2)$ Å, $c = 15.949(1)$ Å, $\alpha = 90°$, $\beta = 100.45(1)°$, $\gamma = 90$, $V = 2257.0(4)$ Å^3, $T = 100$ K, space group $P2_1/n$, $Z = 4$, (Mo K) = 0.71073 Å, 12400 reflections measured, 4565 unique reflections ($R_{int} = 0.019$). The final R value was 0.0493 and $R_w(F^2)$ 0.1144 for $I > 2\sigma(I)$. Corresponding values for all data: $R = 0.0563$ and $R_w(F^2) = 0.1183$.

(9) Crystal data for **4**: $C_{16}H_{34}Cl_4O_5Ti_2$, $M = 544.03$, monoclinic, $a = 8.116(2)$ Å, $b = 17.305(3)$ Å, $c = 15.951(3)$ Å, $\alpha = 90°$, $\beta = 98.72(4)°$, $\gamma = 90$, $V = 2353.2(8)$ Å^3, $T = 100$ K, space group $P2_1/n$, $Z = 4$, (Mo K) = 0.71073 Å, 11302 reflections measured, 4283 unique reflections ($R_{int} = 0.0375$). The final R value was 0.0435 and $R_w(F^2)$ 0.0791 for $I > 2\sigma(I)$. Corresponding values for all data: $R = 0.0561$ and $R_w(F^2) = 0.0838$.

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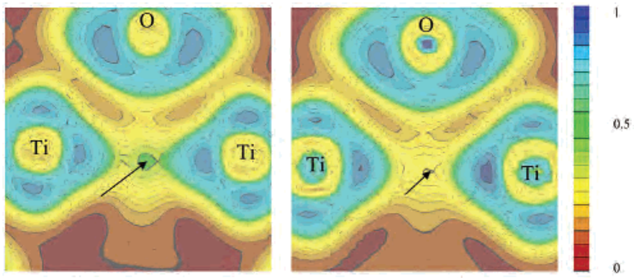

2 3

Figure 3. ELF contour plots for the selected planes containing two Ti atoms and oxygen atom of one μ-OMe ligand of **2** and **3**. The arrow shows the position of attractor located between two Ti atoms.

termined geometries. In both species we replaced thf with dimethyl ether molecules. As expected, the singlet state is more stable than the triplet one by 6.8 kcal/mol in **2** and 12.4 kcal/mol in **3**. Since the electron localization function (ELF)[14] is an acknowledged tool for the description of the bonding in molecules and solids,[15] we performed the topological analysis of ELF[16] to clarify the Ti···Ti interaction. Figure 3 displays the graphical representation of the ELF values in selected planes. For **2** and **3** complexes the local ELF maximum is found between Ti atoms, and this attractor can be identified with a Ti−Ti bond. The obtained results at least on the level of calculations used suggest the presence of a bonding interaction between metal atoms which could be responsible for the diamagnetism of **2**·**3**.

In conclusion, we have discovered a surprising new class of alkoxo-bridged "Ti(+3)" stable species that can be accessed by direct syntheses (Schemes 1 and 2). It seems most likely that the course of the reactions discussed here depends on the solution equilibrium. The precipitated solid from the Al/AlMe$_3$ reduction of TiX$_4$ (X = Cl, OMe, OEt) or **1** probably is the least soluble species and causes the shift of the reaction course to **2**−**4** formation. However, it could be supposed that chloride ligands in **2**−**4** undergo in solution substitution by an excess of AlMe$_3$ to give [Ti$_2$(μ-OMe)$_2$(μ-Cl)(thf)$_3$(Me)$_3$] which is relevant to [Ti$_2$(μ-OMe)$_2$(O^{t}Bu)$_2$(Me)$_4$][17] but up to now was not isolated in pure form. It can be expected that these compounds will find application in several branches of chemistry such as olefin polymerization, organic catalysis,[2,3] sol−gel chemistry,[18] and many others.[19] Further studies are needed to determine possible incorporation of **2**−**4** into catalytic cycles.

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Supporting Information Available: Experimental procedures, the ELF analysis, and two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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