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Facile Synthesis of Monoazidotitanium Isopropoxides

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The monoazidotitanium trisisopropoxide $\{(N_3)Ti(O\textit{i}Pr)_3\}_4$ (**2**) was obtained by the reaction of $(N_3)_2Ti(O\textit{i}Pr)_2$ (**1**) with $Ti(O\textit{i}Pr)_4$. Colorless **2** possesses an interesting tetrameric structure featuring bridging azide and isoproxide ligands and five- and six-coordinate titanium centers. It can be sublimed in vacuo at ca. 130 °C but decomposes rapidly above 180 °C. Controlled hydrolysis afforded the related yellow oxo cluster $(\textit{i}PrO)_8Ti_4(\mu\text{-}O\textit{i}Pr)_2(\mu_4\text{-}O)(\mu\text{-}N_3)_4$ (**3**).

Titania is a wide-band-gap semiconductor (rutile 3.03 eV, 409 nm; anatase 3.20 eV, 387 nm)[1] and an excellent photocatalyst for the decomposition of organic compounds and killing of microorganisms using UV light.[2] Nitrogen doping has been shown to extend its UV/vis absorption edge into the visible light range.[3] Because this enables photocatalysis utilizing sunlight, there has been a growing interest in the development of inexpensive synthetic procedures of nitrogen-doped titania. Most current approaches involve the treatment of preformed titania with various nitrogen sources often at rather high temperatures,[3−5] although recently a low-temperature process was reported involving the treatment of titania with amines.[6] Furthermore, the exact nature and activity of nitrogen-doped titania are strongly dependent on its synthesis. The dopant may be concentrated on the surface of the titania particles; it may substitute oxygen positions of the titania lattice or take up interstitial positions.[7−9]

We have been interested in developing nonhydrolytic sol−gel methods for the synthesis of interesting functionalized oxides such as aluminum oxyhydride HAlO.[10,11] The azide group has been investigated by several groups as a source for nitrogen in the synthesis of nitrides, but this method suffers from potential dangers during the azide decomposition and often requires high-pressure equipment.[12−16] We thought that this danger may be minimized by the synthesis of mixed materials such as oxynitrides or even nitrogen-doped oxides because the amount of azide in the precursors can be much lower. Here we report the facile synthesis of a monoazidotitanium trisalkoxide and a closely related oxo cluster as potential precursors for nitrogen-doped titania.

Initially, we focused on the only previously known mixed azidotitanium alkoxide $(N_3)_2Ti(O\textit{i}Pr)_2$ (**1**), which can be prepared by the reaction of $Ti(O\textit{i}Pr)_4$ with 2 equiv of Me_3SiN_3 in close to quantitative yield.[17] Compound **1** is obtained as a yellow microcrystalline solid from a pentane, hexane, dichloromethane, or toluene solution independent of the amount of Me_3SiN_3 applied. Its structure is unknown. It is soluble in donor solvents such as tetrahydrofuran but insoluble in all others, suggesting a polymeric structure with bridging azides. Attempts to obtain a sample suitable for single-crystal X-ray diffraction have been unsuccessful to date. Despite its high nitrogen content of 33.6%, it can be handled safely. It melts at 173−180 °C while turning into a

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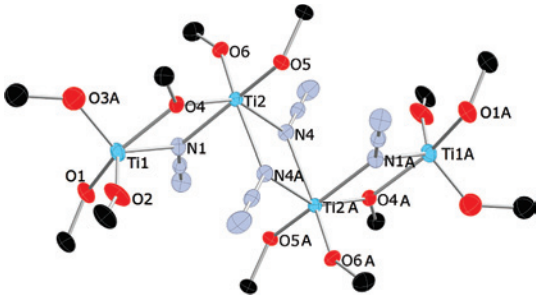

Figure 1. Thermal ellipsoid (50%) plot of **2**. Methyl groups and hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): N1−Ti1 2.095(2), N1−Ti2 2.225(2), N4−Ti2 2.135(2), N4−Ti2A 2.215(2), O1−Ti1 1.818(2), O2−Ti1 1.763(2), O4−Ti1 2.1308(19), O4−Ti2 1.9491(18), O5−Ti2 1.7893(18); Ti1−N1−Ti2 103.84(9), Ti2−N4−Ti2A 109.55(9), O1−Ti1−O4 160.20(8), N1−Ti1−O4 71.29(8), N1−Ti2−O4 71.96(8), N4−Ti2−N4A 70.45(9).

brown-colored liquid. Above 190 °C, a visible gas evolution commences, and at slightly higher temperatures, a rapid decomposition accompanied by a brief light flash occurs. The dark-gray product resembles the ash that is obtained from burning a newspaper. Because of this potentially hazardous decomposition behavior, we decided to focus on the monoazide $(N_3)Ti(OiPr)_3$, the decomposition of which is expected to be less intense because of the lower nitrogen content of 15.7%. Heating a mixture of neat $Ti(OiPr)_4$ and **1** at 135 °C for 1 h (eq 1) followed by crystallization of the resulting sticky yellow solid from hexanes at −20 °C afforded the desired monoazide in 79% yield as the colorless crystalline compound $\{(N_3)Ti(OiPr)_3\}_4$ (**2**).[18]

$$2\mathrm{Ti}(\mathrm{O}i\mathrm{Pr})_4 + \underset{\mathbf{1}}{2(\mathrm{N}_3)_2\mathrm{Ti}(\mathrm{O}i\mathrm{Pr})_2} \xrightarrow{135\ ^\circ\mathrm{C},\ 1\ \mathrm{h}} \underset{\mathbf{2}}{\{(\mathrm{N}_3)\mathrm{Ti}(\mathrm{O}i\mathrm{Pr})_3\}_4} \quad (1)$$

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** in a C_6D_6 solution at room temperature show several broadened peaks in the region expected for isopropoxide groups, indicating a dynamic behavior. The IR spectrum contains a strong absorption peak at 2090 cm^{-1}, which is assigned to azide stretching modes. The structure of **2**[19] was then determined by X-ray diffraction. Colorless **2** is indeed the expected monoazidotitanium trisisopropoxide, yet it forms a centrosymmetric tetramer (Figure 1). Two dimeric $\{(N_3)Ti(OiPr)_3\}_2$ units are linked by two bridging azides. The terminal titanium atoms are five-coordinate in a distorted trigonal-bipyramidal fashion. The dimeric units are joined by a bridging azide and a bridging isopropoxide. The central titanium atoms are six-coordinate in a distorted octahedral fashion with the three bridging azides in a facial arrangement. Both the azide and isopropoxide bridges are unsymmetric in a way that by cleavage of the longer Ti−N and Ti−O contacts in each fragment the monomeric $(N_3)Ti(OiPr)_3$ (**2a**) would be obtained. The shorter Ti−N distances range from 2.095(2) Å (Ti1−N1) to 2.135(2) Å (Ti2−N4) and the longer ones from 2.215(2) Å (Ti2−N4A) to 2.225(2) Å (Ti2−N1). The Ti−O distances for the bridging isopropoxide are 2.131(2) Å (Ti1−O4) and 1.949(2) Å (Ti2−O4), and the Ti−O distances for the terminal isopropoxides average 1.791 Å. The Ti−N distances are comparable to those observed in the dimeric $\{Cl_3Ti(\mu\text{-}N_3)\}_2$ [2.053(8) and 2.157(8) Å][20] and $\{(C_5H_4Me)TiCl_2(\mu\text{-}N_3)\}_2$ [2.116 (ave) and 2.138 (ave) Å].[21] Similarly, the Ti−O distances also compare well with those reported for the related compounds $\{(iPrO)_3Ti(\mu\text{-}OiPr)\}_2$,[22] $\{(iPrO)TiCl_2(HOiPr)(\mu\text{-}OiPr)\}_2$,[23] and $\{(iPrO)_3Ti(NH_2iPr)(\mu\text{-}OiPr)\}_2$[24] with $Ti{-}O_{terminal}$ distances of 1.789 (ave), 1.735(2), and 1.838 (ave) Å and $Ti{-}O_{bridging}$ distances of 1.937(11) and 2.062(8) Å, 1.938(2) and 2.129(2) Å, and 2.049(1) and 2.081(1) Å, respectively.

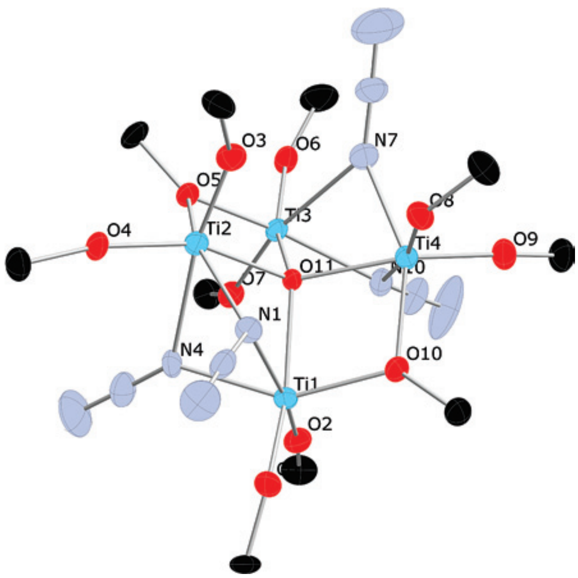

Figure 2. Thermal ellipsoid (50%) plot of **3**. Methyl groups and hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): N1−Ti1 2.280(4), N1−Ti2 2.109(3), N4−Ti1 2.096(3), N4−Ti2 2.343(4), N7−Ti4 2.108(4), N7−Ti3 2.374(4), N10−Ti3 2.112(4), N10−Ti4 2.370(4), O1−Ti1 1.792(3), O2−Ti1 1.753(3), O10−Ti1 2.010(3), O10−Ti4 1.991(3), O11−Ti1 2.097(3), O11−Ti2 2.043(3), O11−Ti3 2.044(3), O11−Ti4 2.045(3); O2−Ti1−O1 100.27(16), O1−Ti1−O10 104.45(13), N4−Ti1−N1 74.85(14), O1−Ti1−N1 84.12(14), O1−Ti1−N4 99.61(14), Ti1−O11−Ti2 98.28(13), Ti1−O11−Ti3 127.52(13), Ti1−O11−Ti4 101.63(13), Ti2−O11−Ti3 102.56(13), Ti2−O11−Ti4 129.45(13), Ti3−O11−Ti4 101.03(13).

During the initial small-scale synthesis of **2**, a small amount of a yellow crystalline material, **3**, was obtained from

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(18) A mixture of **1** (6.8 g, 27 mmol) and $Ti(OiPr)_4$ (8.3 mL, 28 mmol) was heated at 140 °C for 1.5 h. The resulting yellow liquid solidified upon cooling to room temperature and was extracted twice with hexanes (70 mL each). Cooling at −20 °C for 2 days afforded colorless crystals of **2**. Yield: 11.4 g, 79%. Mp: 74−76 °C. ^1H NMR (400.13 MHz, C_6D_6): δ 5.09 (s, broad, $w_{1/2} \approx 73$ Hz, $OCH(CH_3)_2$, 1H), 4.69 (s, broad, $w_{1/2} \approx 32$ Hz, $OCH(CH_3)_2$, 3H), 1.38 (d, broad, $w_{1/2} \approx 30$ Hz, $W = 6.0$ Hz, $OCH(CH_3)_2$, 6H), 1.30 (d, broad, $w_{1/2} \approx 13$ Hz, $J = 4.2$ Hz, $OCH(CH_3)_2$, 18H). $^{13}C\{^1H\}$ NMR (100.61, MHz, C_6D_6): δ 75.96 (broad, $w_{1/2} \approx 93$ Hz, $OCH(CH_3)_2$), 20.18 (broad, $w_{1/2} \approx 9$ Hz, $OCH(CH_3)_2$). ATR-IR: 2090 cm^{-1} vs ($\nu(N_3)$). Anal. Calcd for $C_9H_{21}N_3O_3Ti$: C, 40.46; H, 7.92. Found: C, 40.04; H, 7.24.

(19) Crystal data for **2**: triclinic, space group $P\bar{1}$, $a = 10.4433(9)$ Å, $b = 11.9712(10)$ Å, $c = 13.2598(11)$ Å, $\alpha = 66.767(1)°$, $\beta = 72.717(2)°$, $\gamma = 69.662(1)°$, $V = 1403.5(2)$ Å^3, $Z = 1$, $\mu(\text{Mo K}\alpha) = 0.608$ mm^{-1}, $D_c = 1.264$ Mg/m^3, $F(000) = 568$, GOF on $F^2 = 1.046$, R1 = 0.0586, wR2 = 0.1194, (F^2, all data), data/restraints/parameters 5078/7/293.

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the third fraction of the crystallization. Similar to **2**, NMR spectra of C_6D_6 solutions of **3** displayed broad signals, and the IR spectrum showed a strong azide absorption at 2076 cm^{-1}. The crystal structure[25] revealed that compound **3** also contains four titanium centers and four azide ligands, but in this case, the center of the complex is a μ_4-oxide (Figure 2). Two $\{(i\mathrm{PrO})_2\mathrm{Ti}(\mu\text{-}\mathrm{N}_3)_2\}_2$ units are connected via two bridging isopropoxide groups and the central μ_4-oxide, resulting in a flattened tetrahedral arrangement of the four titanium centers. Although the titanium centers are six-coordinate, the long Ti−μ_4-O distances with values ranging from 2.043 to 2.096 Å lead to a significant distortion of the expected octahedral geometry. The arrangement of the azide and isopropoxide ligands is close to square pyramidal, where the μ_4-oxide is positioned trans to the terminal isopropoxide ligand, which marks the top of the square pyramid. The terminal Ti−O(*i*Pr) distances average 1.776 Å, and the almost symmetrical bridging Ti−O(*i*Pr) distances average 1.999 Å. The Ti−N distances are unsymmetrical, similar to those observed for **2**, with the shorter distances averaging 2.106 Å and the longer ones averaging 2.342 Å.

Titanium clusters with a central μ_4-oxide core are limited to only a few examples including $\mathrm{Ti}_4(\mu_4\text{-O})(\mu\text{-O})(\mathrm{O_2CH})_2(\mu\text{-O}i\mathrm{Pr})_4(\mathrm{O}i\mathrm{Pr})_6$,[26] $\mathrm{Ti}(\mu_4\text{-O})(\mu_2\text{-O})(\mathrm{O_2COO}i\mathrm{Pr})_2(\mathrm{O}i\mathrm{Pr})_{10}$,[27] $\{(\mathrm{Me_3Si})\text{-}\mathrm{FlSi}\}_2\mathrm{O}_5(\mathrm{TiOEt})_4(\mu_2\text{-OEt})_6(\mu_4\text{-O})$ (Fl = 9-fluorenyl),[28] and $(\mathrm{MeC_5H_4})_4\mathrm{Ti}_4(\mu_2\text{-S}_2)_4(\mu_2\text{-O})(\mu_4\text{-O})$.[29]

We suspected that the formation of **3** was most likely due to adventitious water: First, compound **3** was isolated during the workup of a small-scale reaction (4 mmol; eq 1). When the reaction was scaled up to 30 mmol, the yield of **2** increased to 79%, and **3** was not isolated. Second, NMR samples of **2** in NMR tubes capped with plastic caps show the presence of **3** after 1 day at room temperature. Indeed, the reaction of a hexane solution of **2** with water at 0 °C according to eq 2 resulted in the isolation of large (>3 mm) yellow crystals of **3** in 54% yield.[30] Their identity was confirmed by X-ray diffraction, although their elemental analysis returned too low on both batches from which crystal structures have been determined. However, it is possible that a small fraction of the azide and/or isopropoxide ligands may have been replaced by bridging hydroxides without affecting the overall structure. These small amounts may not have been discernible because of twinning and disorder problems in both samples.

$$\underset{\mathbf{2}}{\{(\mathrm{N_3})\mathrm{Ti}(\mathrm{O}i\mathrm{Pr})_3\}_4} + \mathrm{H_2O} \rightarrow \underset{\mathbf{3}}{(i\mathrm{PrO})_8\mathrm{Ti}_4(\mu\text{-O}i\mathrm{Pr})_2(\mu_4\text{-O})(\mu\text{-N}_3)_4} + 2i\mathrm{PrOH} \quad (2)$$

A preliminary investigation of the thermal properties of **2** and **3** has been performed. Both compounds darken when heated past their melting points and decompose rapidly at 185 and 190 °C, respectively. The volatile materials were collected in a trap cooled with liquid nitrogen and were identified as mainly isopropyl alcohol and a few percent of propene by NMR spectroscopy. The gray fluffy solids that remained in the reaction flask in both cases were analyzed by IR spectroscopy and showed a very strong absorption below 900 cm^{-1}, which is typical for Ti−O and Ti−N bands. Some residual peaks due to hydrocarbons and azide indicate that the decomposition is not complete and/or clean. Current investigations focus on the thermal decomposition in high boiling liquids such as octadecene.

Although the thermal decompositions of **2** and **3** were unsatisfactory with respect to the formation of nitrogen-doped titania, it was found that **2** can be sublimed at 130 °C in a dynamic vacuum with a pressure of ca. 0.1 Torr without decomposition and only minor amounts of nonvolatile residue. Attempts to sublime the oxo cluster **3** led to its rearrangement to **2** and other yet unknown compounds, and **2** could be sublimed out of the reaction mixture.

In summary, a novel monoazidotitanium alkoxide and its primary hydrolysis product were prepared in a simple procedure. Preliminary results in our laboratory involving $\mathrm{Al(O}i\mathrm{Pr)_3}$ and $\mathrm{Me_3SiN_3}$ suggest that this process is transferable to other metals. Furthermore, the volatile nature of **2** makes it a candidate for chemical vapor deposition and related processes.

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Supporting Information Available: Complete X-ray data in CIF format and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Crystal data for **3**: monoclinic, space group *P*2(1), $a = 12.4138(15)$ Å, $b = 14.9548(18)$ Å, $c = 13.2278(16)$ Å, $\beta = 91.892(3)°$, $V = 2454.3(5)$, Å^3, $Z = 2$, μ(Mo Kα) = 0.686 mm^{-1}, $D_c = 1.308$ Mg/m^3, $F(000) = 1020$, GOF on $F^2 = 1.082$, R1 = 0.0400, wR2 = 0.1045, (F^2, all data), data/restraints/parameters 9157/1/537.

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(30) Water (38 mg, 2.1 mmol, 38 μL) was added in two portions via syringe to a solution of **2** (2.30 g, 2.1 mmol) in hexanes (60 mL) with cooling in an ice bath. The water droplets appeared to solidify upon contact with the cooled solution. A small amount of a fine colorless precipitate formed after ca. 15 min. The reaction mixture was slowly warmed to room temperature and stirred overnight. Filtration, concentration of the pale-yellow filtrate to ca. 5 mL, and redissolution of the precipitate by brief gentle heating afforded large (>3 mm) yellow crystals of **3** after 1 h (0.49 g) at room temperature. A second crop was obtained after cooling of the concentrated mother liquor at −20 °C for 2 days. Yield: 0.94 g, 54%. Mp: 105−107 °C. ^{1}H NMR (400.13 MHz, C_6D_6): δ 5.19 (sept, $J = 6.0$ Hz, OC*H*(CH$_3$)$_2$, 5H), 5.10 (s, broad, $w_{1/2} \approx 67$ Hz, OC*H*(CH$_3$)$_2$, 2H), 4.86 (s, broad, $w_{1/2} \approx 43$ Hz, OC*H*(CH$_3$)$_2$, 2H), 4.56 (s, broad, $w_{1/2} \approx 19$ Hz, OC*H*(CH$_3$)$_2$, 1H), 1.46 (d, broad, $w_{1/2} \approx 14$ Hz, $J = 5.0$ Hz, OCH(C*H*$_3$)$_2$, 24H), 1.41 (s, broad, $w_{1/2} \approx 27$ Hz, OCH(C*H*$_3$)$_2$, 30H), 1.26 (d, broad, $w_{1/2} \approx 11$ Hz, $J = 5.9$ Hz, OCH(C*H*$_3$)$_2$, 6H). ^{13}C{^{1}H} NMR (100.61, MHz, C_6D_6): δ 82.49 (broad, $w_{1/2} \approx 144$ Hz, OCH(CH$_3$)$_2$), 78.19 (OC*H*(CH$_3$)$_2$), 76.90 (broad, $w_{1/2} \approx 48$ Hz, OCH(CH$_3$)$_2$), 26.62 (OCH(*C*H$_3$)$_2$), 26.03 (OCH(*C*H$_3$)$_2$), 25.87 (OCH(*C*H$_3$)$_2$), 24.23 (broad, $w_{1/2} \approx 24$ Hz, OCH(*C*H$_3$)$_2$). ATR-IR: 2076 cm^{-1} vs (ν(N$_3$)). Anal. Calcd for $C_{30}H_{70}N_{12}O_{11}Ti_4$: C, 37.28; H, 7.30; N, 17.39. Found: C, 34.44; H, 6.74; N, 15.50.