Synthesis and Reactivity of Ti(III) Tris(*tert*-butoxy)siloxy Complexes

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Dedicated to Professor Hubert Schmidbaur, in recognition of his many seminal contributions to inorganic chemistry

Reaction of $TiCl_3(THF)_3$ with 3 equivalents of $LiOSi(O^tBu)_3$ produces the Ti(III) siloxide $Ti[OSi(O^tBu)_3]_3(THF)_2$ (**1**), and a 1:4 ratio of the same reagents gives $\{LiTi[OSi(O^tBu)_3]_4\}_x$. Upon heating to 95 °C, compound **1** converts *via* THF ring-opening to $[(^tBuO)_3SiO]_3TiO(CH_2)_4Ti[OSi(O^tBu)_3]_3$. The pyridine adduct $Ti[OSi(O^tBu)_3]_3(pyr)_2$, and polymeric $\{Ti[OSi(O^tBu)_3]_3(4,4'\text{-bipyridine})\}_n$, are also described. Electronic spectra for the $Ti[OSi(O^tBu)_3]_3L_2$ complexes indicate D_{3h} symmetry, and similar results for the 4,4'-bipyridine adduct suggest a linear polymeric structure.

Key words: Titanium(III), Siloxide, Molecular Precursors, Coordination Polymer

Introduction

The use of sterically demanding alkoxide, siloxide, and aryloxide ligands has led to the isolation of numerous low valent, coordinatively unsaturated early transition metal complexes [1], which exhibit interesting reactivities toward organic molecules. For example, Wolczanski has shown that neutral ligands can coordinate to $Ta(silox)_3$ (silox = OSi^tBu_3) with unusual bonding geometries such as η^2-N,C-bound pyridine [1b]. He has also shown that $Ti(silox)_3$ can stabilize organic radicals which undergo reversible C-C bond forming reactions [1a, c]. A variety of early transition metal d^0 complexes containing the -$OSi(O^tBu)_3$ ligand have been isolated and characterized [2]. It is of interest to determine whether this ligand can also stabilize low valent transition metal complexes with coordinatively unsaturated metal centers.

Early syntheses of Ti(III) alkoxides, from Ti(III) halides or amides, gave products that were reported to be polymeric or oligomeric [3]. More recently attempts were made to prepare Ti(III) alkoxides by reduction of Ti(IV) alkoxides with trialkoxysilanes. However, these insoluble, diamagnetic materials were found to contain silicon as an impurity and were presumed to be polymeric [4]. Monomeric Ti(III) aryloxides and siloxides have been prepared by reduction of the corresponding trialkoxymonohalide or trisiloxymonohalide complexes [1].

A wide variety of coordination networks have been prepared by linking transition metal complexes with the linear connector 4,4'-bipyridine. The structures obtained in this way include one dimensional polymers [5], two dimensional layered materials [6], and three dimensional networks [7]. Such materials were studied for their potentially interesting magnetic [5b, d], conducting [5c], and clathrating properties [6a, 7d]. In contrast, coordination networks containing early transition metals, from groups 3 through 5, are rather rare [8].

Here, the synthesis and reactivity of tris(*tert*-butoxy)siloxy complexes of Ti(III) are described. The synthesis of a crystalline coordination polymer consisting of $Ti[OSi(O^tBu)_3]_3$ units connected with 4,4'-bipyridine is also described.

Results

Synthesis of Ti(III) siloxide complexes **1** – **5**. Slow addition of three equivalents of $LiOSi(O^tBu)_3$ in THF to a THF solution of $TiCl_3(THF)_3$ resulted in a color change of the initially blue solution to violet, black, and then dark green. From the reaction mixture the light blue Ti(III) tris(siloxide) complex,

$Ti[OSi(O^tBu)_3]_3(THF)_2$ (**1**), was isolated in 79% yield (eq. (1)).

$$TiCl_3(THF)_3 + 3\,LiOSi(O^tBu)_3 \xrightarrow{THF} \underset{\mathbf{1}}{Ti[OSi(O^tBu)_3]_3(THF)_2} + 3\,LiCl \quad (1)$$

The THF ligands could not be removed from **1** under prolonged vacuum. In diethyl ether the analogous reaction formed a brown solution from which only $HOSi(O^tBu)_3$ was isolated. When this reaction was carried out with four equivalents of $LiOSi(O^tBu)_3$ in THF the light blue *ate* complex $LiTi[OSi(O^tBu)_3]_4$ (**2**) was formed (eq. (2)).

$$TiCl_3(THF)_3 + 4\,LiOSi(O^tBu)_3 \xrightarrow{THF} \underset{\mathbf{2}}{\{LiTi[OSi(O^tBu)_3]_4\}_x} + 3\,LiCl \quad (2)$$

Light blue toluene solutions of **1** rapidly turn yellow when heated above 95 °C. The product of this reaction was found to be $\{Ti[OSi(O^tBu)_3]_3\}_2[O(CH_2)_4]$ (**3**), a dinuclear Ti(IV) complex containing an -$O(CH_2)_4$- bridge between the two metal centers. The stoichiometry of this reaction, with the generation of three equivalents of free THF from two equivalents of **1**, was confirmed by conducting the reaction in toluene-d_8 in a sealed NMR tube with ferrocene as internal standard (eq. (3)).

$$2\,\underset{\mathbf{1}}{Ti[OSi(O^tBu)_3]_3(THF)_2} \xrightarrow[-3\,THF]{\text{toluene}-d_8,\ \Delta} \underset{\mathbf{3}}{[(^tBuO)_3SiO]_3TiO(CH_2)_4Ti[OSi(O^tBu)_3]_3} \quad (3)$$

The ^{1}H NMR spectrum for **3** reveals two closely spaced singlets at 1.55 and 1.52 ppm corresponding to the two inequivalent titanium tris(siloxide) fragments. A DEPT ^{13}C NMR spectrum confirmed that the new ligand in **3** contains four methylene groups.

A single crystal X-ray structure analysis of **3** yielded a disordered structural model. The most chemically reasonable model was obtained in the space group $P\bar{1}$. The asymmetric unit contains two independent half molecules. An inversion center located along the butoxy bridge generates the second half of each molecule. This results in considerable disorder in the asymmetric -$O(CH_2)_4$- bridge (Fig. 1) which was modeled as a symmetric -$O(CH_2)_3O$- bridge. In the structural model the oxygen atoms in the bridging ligand were both modeled with full occupancy although these sites are occupied by C and O atoms with equal probability. The displacement parameters for these atoms were reasonable and two different atom sites could not be resolved at each of these locations making a more complicated model unnecessary. The Ti-O bond lengths involving the siloxide ligands range from 1.806(5) to 1.787(5) Å. These bond lengths are very similar to Ti-OSi bond lengths found in other molecular titanosilicates [9]. The Ti-O(15) bond length is slightly longer (1.841(8) Å) as expected since O(15) represents a site which is occupied by carbon with 50% probability. Typical Ti-C bond lengths are about 2.1 Å [10]. The O-Ti-O bond angles are all close to those expected for a tetrahedral coordination environment about Ti (105.2(3) to 112.0(2)°).

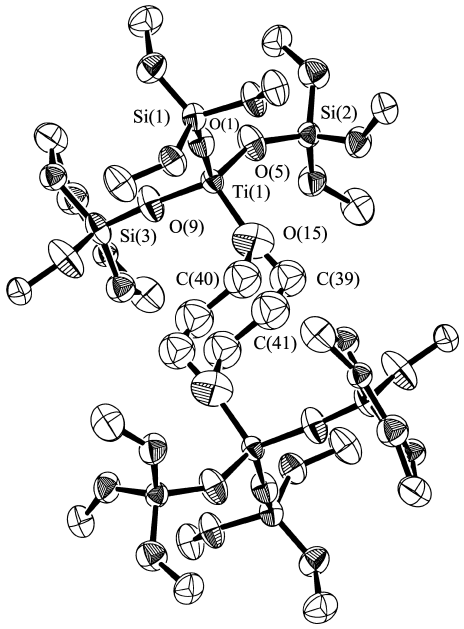

Fig. 1. ORTEP view of the molecular structure of $Ti_2[OSi(O^tBu)_3]_6[O(CH_2)_4]$ (**3**). Methyl groups removed for clarity. Displacement ellipsoids drawn to 50% probability. Pairs of disordered atoms, C(32)-C(33) and C(38)-C(37), were refined with 60% and 40% relative populations, respectively. Pairs of disordered atoms, O(29)-O(30), O(31)-O(32), C(58)-C(59), C(61)-C(60), C(80)-C(81), C(87)-C(86), C(93)-C(92), were refined with 70% and 30% relative populations, respectively.

The thermal conversion of **1** to **3** also occurs in the solid state. A sample of **1** was heated at 120 °C for 15 min and the volatile products were collected by vacuum transfer and quantified by ^{1}H NMR spectroscopy with ferrocene as standard. Within 5 min the solid changed color from blue to yellow and after 15 min

Compound	λ_{max}[nm] (ε [L mol^{-1} cm^{-1}])	Assignment
$Ti[OSi(O^tBu)_3]_3(THF)_2$ (**1**)[a]	218 (9000)	LMCT
	828 (23)	$E \rightarrow T_2$
$LiTi[OSi(O^tBu)_3]_4$ (**2**)[a]	220 (1400)	LMCT
	776 (71)	$E \rightarrow T_2$
$\{Ti[OSi(O^tBu)_3]_3\}_2[O(CH_2)_4]$ (**3**)[a]	218 (17800)	LMCT
$Ti[OSi(O^tBu)_3]_3(pyr)_2$ (**4**)[a]	224 (5900)	LMCT
	250 (5700)	$\pi - \pi^*$ (pyr)
	526 (290)	$^2E'' \rightarrow {}^2A_1'(D_{3h})$
	606 (190) (shoulder)	
	897	$^2E'' \rightarrow {}^2E'(D_{3h})$
$\{Ti[OSi(O^tBu)_3]_3(4,4'\text{-bipyridine})\}_n$ (**5**)[b]	255	$\pi - \pi^*$ (4, 4'- bipy)
	368	MLCT
	740	$^2E'' \rightarrow {}^2A_1'(D_{3h})$
	1014 (broad)	$^2E'' \rightarrow {}^2E'(D_{3h})$

Table 1. List of Uv-vis-near IR bands and their assignments for **1** to **5**.

[a] In isooctane, [b] Diffuse reflectance spectrum.

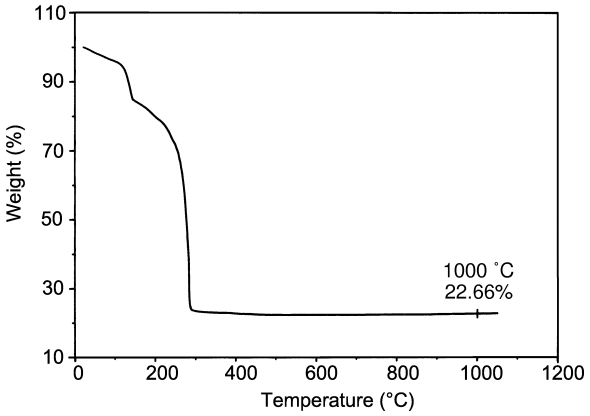

Fig. 2. TGA trace of **1** under N_2 with a heating rate of 10 °C min^{-1}.

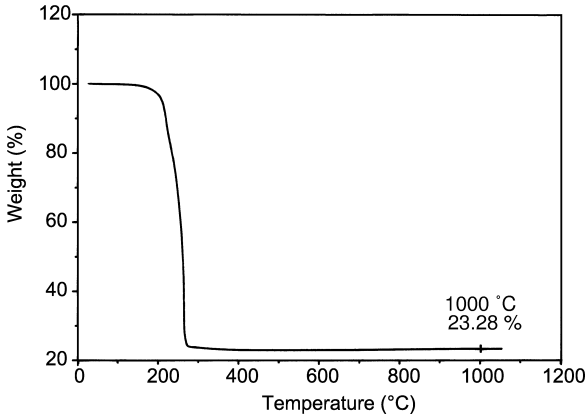

Fig. 3. TGA trace of **3** under N_2 with a heating rate of 10 °C min^{-1}.

0.38 equiv of THF and 0.03 equiv of isobutene were obtained. Thermal gravimetric analysis (TGA) of **1** shows that weight loss occurs in two steps (Fig. 2). The first weight loss has an onset temperature of 124 °C and a second weight loss begins above 200 °C. The ceramic yield at 1000 °C (22.7%) is lower than that expected for the formation of $TiSi_3O_8$ (26.5%). The TGA of **3** reveals a sudden weight loss with an onset temperature of 202 °C (Fig. 3). This is similar to the thermal behavior of $Ti[OSi(O^tBu)_3]_4$ which also has an onset to decomposition just above 200 °C [2a, c]. The ceramic yield of **3** at 1000 °C (23.3%) is also less than the theoretical ceramic yield of $TiSi_3O_8$ (29.8%).

The THF ligands of **1** can be readily replaced by more basic ligands. The addition of two equivalents of pyridine to a toluene solution of **1** resulted in a rapid color change of the solution from light blue to dark purple. Crystallization of the reaction product from pentane allowed isolation of the bis(pyridine) complex, $Ti[OSi(O^tBu)_3]_3(pyr)_2$ (**4**), in 73% yield. As with complex **1**, the datively coordinated ligands (pyridine) in complex **4** could not be removed under vacuum.

The availability of two coordination sites in **1** allowed formation of a coordination polymer by connecting the titanium tris(siloxide) units with a bifunctional connector. Layering a toluene solution of 4,4'-bipyridine on a THF solution of **1** resulted in formation of a purple color at the interface of the solutions. Over the course of several days blue blocky crystals of $\{Ti[OSi(O^tBu)_3]_3(4,4'\text{-bipyridine})\}_n$ (**5**) grew on the walls of the container. These air sensitive crystals are not soluble in excess THF or toluene. The polymer does dissolve in a toluene solution of excess 4,4'-bipyridine. Presumably the molecular bis(bipyridine) unit $Ti[OSi(O^tBu)_3]_3(4,4'\text{-bipy})_2$, similar in structure to **4**, is formed.

Electronic spectra of $\mathbf{1-5}$. The electronic spectra of $\mathbf{1-4}$ were measured from solution samples (isooctane) and the spectrum of **5** was obtained from a solid sample in reflectance mode. The bands observed for

each complex and their assignments are summarized in Table 1.

The electronic spectrum of **1** consists of a LMCT band at 218 nm and a d-d band at 828 nm. The higher energy transition is assigned to a LMCT transition by comparison with the UV-vis spectrum of $Ti[OSi(O^tBu)_3]_4$ [2] which possesses a single band at 216 nm (11000 L mol^{-1} cm^{-1}). The low energy transition at 828 nm may be due to a $E \rightarrow T_2$ (d-d) transition in a tetrahedral ligand field. The complex $[Ti(O\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)_4 \bullet Na(THF)_2]$, containing a tetrahedrally coordinated Ti atom, also has a single low energy band in the UV-vis spectrum at 970 nm which was assigned to a $E \rightarrow T_2$ (d-d) transition [1d]. Complex **2** also shows two bands in the UV-vis spectrum, a LMCT band at 220 nm and a d-d band at 776 nm. The d-d band of **2** may also be due to a $E \rightarrow T_2$ transition since the Ti atom in this complex is presumably also tetrahedrally coordinated. As expected, the Ti(IV) complex, **3**, only shows a LMCT band at 218 nm in the UV-vis spectrum. The UV-vis spectrum of the bis(pyridine) complex, **4**, consists of a LMCT transition at 224 nm and a $\pi - \pi^*$ transition associated with the pyridine ligands at 250 nm. The assignment of the $\pi - \pi^*$ transition was made by comparison to a UV-vis spectrum of pure pyridine which exhibits only one transition at 252 nm. At lower energies there are three d-d transitions, at 526 nm with a small shoulder at 606 nm and at 897 nm. The electronic spectra for five coordinate, d^1, MX_3L_2 complexes with D_{3h} symmetry, are predicted to have two d-d transitions assigned as $^2E'' \rightarrow {}^2A_1'(d_{xz,yz} \rightarrow d_{z^2})$ and $^2E'' \rightarrow {}^2E'(d_{xz,yz} \rightarrow d_{xy,x^2-y^2})$ [11]. The two major low energy bands of **4** may be assigned to these transitions. The origin of the small shoulder on the higher energy band is not clear. The related complex $[Ti(O\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)_3(pyr)_2]$ has two d-d bands at similar energies (580 and 920 nm) as observed for **4** [1d]. For the polymer **5**, no well resolved band could be assigned to a LMCT transition. The band at 255 nm was assigned to the $\pi - \pi^*$ transition associated with the bipyridine ligands, by comparison to a UV-vis spectrum of pure 4,4'-bipyridine. A lower intensity band was observed at 368 nm, and two d-d transitions were observed at 740 nm ($^2E'' \rightarrow {}^2A_1'$) and 1014 nm ($^2E'' \rightarrow {}^2E'$), again consistent with a D_{3h} coordination geometry about the metal center. Electronic spectra of $Ti(III)Cl_3$-pyridine complexes were found to possess bands around 400 nm which were assigned to MLCT transitions [12]. The band in the UV-vis spectrum of **5** at 368 nm may be assigned to such an MLCT transition.

The infrared spectra of **4** and **5** contained the ring stretching bands of pyridine and 4,4'-bipyridine, respectively. In the related complex $(silox)_3Ti(pyr)$ the pyridine ring stretching bands were absent from the IR spectrum which was attributed to the partial reduction of the pyridine ligand by the metal center [1b]. The disappearance of the ring stretching bands in the IR spectrum seems to be very sensitive to partial reduction of this ligand since NMR and EPR experiments indicate that most of the spin density remains localized on the metal center in this complex. Thus, the IR spectra of **4** and **5** give no evidence for partial reduction of the pyridyl ligands in these complexes.

Discussion

The Ti(III) siloxide, **1**, is formed in high yield by the direct reaction between $LiOSi(O^tBu)_3$ and $TiCl_3(THF)_3$. This complex presumably adopts a trigonal bipyramidal structure with axial THF ligands. However, this was not confirmed by the UV-vis spectrum which revealed only one d-d transition, inconsistent with D_{3h} symmetry. However, there are reports describing Ti(III) complexes known to posses D_{3h} symmetry which did not display two d-d transitions in their UV-vis spectrum [1a, e]. However, the energy of the d-d transition of **1** is similar to that found for other complexes containing a 4-coordinate Ti(III) center, such as **2** [1d]. It is possible that one of the THF ligands in **1** is labile resulting in a solution species that is 4-coordinate.

The "ate" complex **2** is similar to the structurally characterized aryloxide complex, $[(THF)_2NaTi(O\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)_4]$ [1d]. This complex consists of a Ti atom coordinated by four aryloxide ligands and a Na atom coordinated by two aryloxide ligands and two THF ligands. Since complex **2** contains no coordinated THF it may form an oligomeric complex in order to increase the coordination number of the Li atom.

Interestingly, the chemistry of **1** is very different from that displayed by the related complex $Ti(silox)_3$ (silox = OSi^tBu_3) reported by Wolczanski [1a]. The titanium tris(silox) complex reversibly coordinates Lewis bases such as DME, PMe_3, nitriles, and isonitriles. These ligands are readily removed by heating or under vacuum. The addition of THF to $Ti(silox)_3$ was reported to form a transiently stable complex that decomposed via cleavage of the THF. The prod-

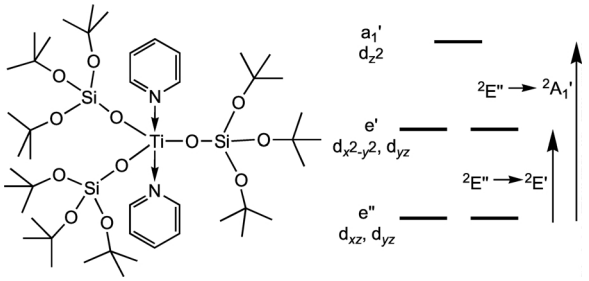

Fig. 4. Probable geometry for $Ti[OSi(O^tBu)_3]_3(pyr)_2$ (**4**) and a d orbital splitting diagram for five coordinate complexes with D_{3h} symmetry.

ucts of this reaction were, however, not characterized. In contrast, the THF ligands in complex **1** are stable at room temperature and cannot be removed under vacuum. The stability of the Lewis base adducts of **1** are presumably due to the lower steric demand of the $-OSi(O^tBu)_3$ ligands compared with the silox ligands. The greater apparent reactivity of $Ti(silox)_3$ with THF may be partially attributed to a more electron rich metal center which results from a greater inductive effect of the silox ligands. When **1** is heated in toluene it cleanly forms a dinuclear Ti(IV) complex (**3**) with a $-O(CH_2)_4-$ bridge between the metal centers. This occurs formally by two one-electron reductions of the THF to form a dianionic ligand. Interestingly, $Ti(silox)_3$ reacts with 0.5 equiv of ethylene to form an insoluble yellow complex proposed to be $(silox)_3Ti\text{-}CH_2CH_2\text{-}Ti(silox)_3$ on the basis of analytical and IR data [1b]. This reaction also occurs by two one electron oxidations of an initially neutral molecule to form a dianionic bridging ligand.

Ring openings of the THF ligands in $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$[13] and $[(C_5H_4Me)_2Zr(H)(THF)][BPh_4]$ [14] also produce alkoxide ligands. In these cases the reaction is thought to occur by nucleophilic attack by an anion at the carbon atom adjacent to the oxygen atom in THF. The Lewis-acid initiated ring opening polymerizations of THF are also believed to proceed by nucleophilic attack of an oxonium intermediate by a free THF molecule [15]. The mechanism for ring opening of the THF ligand in **1** is distinct from these cases since no nucleophilic species are present. It is possible that the THF first undergoes a one electron reduction to form an n-butoxy radical intermediate $[(^tBuO)_3SiO]_3TiOCH_2CH_2CH_2CH_2\bullet$, which then undergoes another one electron reduction upon coupling with a second Ti(III) center.

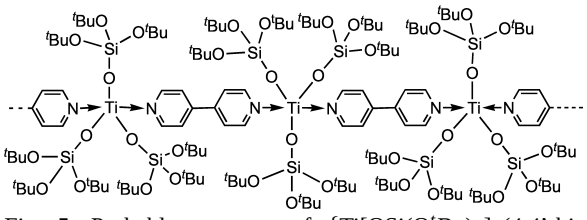

Fig. 5. Probable structure of $\{Ti[OSi(O^tBu)_3]_3(4,4'\text{-bipyridine})\}_n$ (**5**).

The THF ligands of complex **1** are readily displaced by pyridine to form the bis(pyridine) complex $Ti[OSi(O^tBu)_3]_3(pyr)_2$ (**4**). In comparison, the addition of excess pyridine to $Ti(silox)_3$ yields only the four coordinate $Ti(silox)_3(pyr)$ complex [1b]. This can be attributed to that of the greater steric demand of the silox ligand compared to the $-OSi(O^tBu)_3$ ligand. Complex **4** is structurally related to the $Ti(III)X_3L_2$ (X = halide, L = neutral donor ligand) complexes studied by Fowles [12, 16]. The metal centers in these complexes possess trigonal bipyramidal coordination with the halides occupying equatorial positions and the neutral ligands occupying the axial positions. The electronic spectra of these complexes reveal two d-d transitions. This is in accord with theory which predicts $^2E'' \rightarrow {}^2A_1'(d_{xz,yz} \rightarrow d_{z^2})$ and $^2E'' \rightarrow {}^2E'(d_{xz,yz} \rightarrow d_{xy,x^2-y^2})$ transitions for d^1 complexes with D_{3h} symmetry (Fig. 4) [11]. Similarly, the electronic spectrum of **4** contains two bands that can be assigned to d-d transitions indicating that this complex also possesses D_{3h} symmetry (Fig. 4). A very similar complex, $Ti(O\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)_3(pyr)_2$, reported by Rothwell, was also presumed to have a trigonal bipyramidal structure based on the electronic spectrum [1d].

The crystalline, insoluble material analyzed to be $\{Ti[OSi(O^tBu)_3]_3(4,4'\text{-bipyridine})\}_n$ (**5**) is presumably polymeric. The linear nature of the 4,4'-bipyridine linker and the D_{3h} geometry about the metal center, inferred from the electronic spectrum, suggest that this material has a linear polymeric structure as depicted in Fig. 5.

The formation of well-ordered coordination networks requires conditions in which assembly of the network is reversible [6c, 17]. Under such conditions defects in the growing network can be corrected before becoming embedded in the structure. The solubility of **5** in solutions containing excess 4,4'-bipyridine indicates that the reversibility required for the formation of well ordered crystals of **5** may come in part from the equilibrium between the coordination polymer

and a soluble species such as Ti[OSi(O^tBu)$_3$]$_3$(4,4'-bipyridine)$_2$.

Conclusion

A variety of stable Ti(III) complexes can be prepared containing the -OSi(O^tBu)$_3$ ligand. This ligand is, however, not sterically demanding enough to stabilize a three coordinate Ti(III) complex. The metal center in these complexes is less reducing than in Ti(silox)$_3$. Crystalline coordination polymers can also be prepared with early transition metals and 4,4'-bipyridine provided that the assembly of the network is reversible.

Experimental Section

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or a Vacuum Atmospheres dry box. Diethyl ether, tetrahydrofuran, and pentane were distilled from sodium benzophenone under nitrogen. Toluene and benzene were distilled from sodium under nitrogen and then degassed. NMR spectra were recorded on a Bruker AMX-300 spectrometer at 300 (^{1}H) or 75.5 (^{13}C) MHz, or on a Bruker AMX-400 spectrometer at 400 (^{1}H) or 100 (^{13}C) MHz. Benzene-d_6, vacuum transferred from a Na/K alloy, was used as the solvent for all NMR studies. Infrared spectra were collected as Nujol mulls on a Mattson Galaxy 3000 spectrometer, using CsI cells. Electronic spectra were collected on a Hewlett-Packard 8452A or a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic moments of solution samples were measured by the Evans method[18] and solid samples were measured on a Johnson Matthey magnetic susceptibility balance. Thermal analyses were performed on a DuPont model 2000 thermal analysis system. LiOSi(O^tBu)$_3$ was prepared according to literature procedures [2a].

Ti[OSi(O^tBu)$_3$]$_3$(THF)$_2$ (**1**). A THF solution (30 ml) of LiOSi(O^tBu)$_3$ (2.850 g, 10.50 mmol) was added dropwise to a THF solution (35 ml) of $TiCl_3(THF)_3$ (1.302 g, 3.51 mmol). The reaction mixture was stirred for 12 h. The solvent was then removed under vacuo, and the resulting solid was extracted into pentane (30 ml). The resulting blue-green solution was filtered, concentrated to 5 ml, and cooled (−40 °C) affording 2.71 g of **1** as blue crystals in 79% yield. UV/vis (isooctane): $\lambda(\varepsilon$, L mol^{-1} cm^{-1}) = 218 (9000), 828 (23) nm. – IR (CsI, Nujol): $\tilde{\nu}$ 1386, 1362, 1237, 1218, 1194, 1050, 1024, 972, 886, 825, 699, 649, 500, 463, 434 cm^{-1}. – $C_{40}H_{89}O_{13}Si_3Ti$: calcd. C 53.79, H 9.95; found: C 53.85, H 9.90. – μ_{eff} (B.M., 22 °C): 1.2(1) (solid), 1.5(1) (solution).

LiTi[OSi(O^tBu)$_3$]$_4$ (**2**). A toluene solution (30 ml) of LiOSi(O^tBu)$_3$ (2.02 g, 7.47 mmol) was added dropwise to a toluene solution (30 ml) of $TiCl_3(THF)_3$ (0.692 g, 1.87 mmol). The reaction mixture was stirred for 12 h. The solvent was then removed under vacuo, and the resulting solid was extracted into pentane (30 ml). The resulting deep blue solution was filtered, concentrated to 5 ml, and cooled (−40 °C) affording 1.56 g of **2** as blue crystals in 75% yield. The flame test of **2** is positive for Li. UV/vis (isooctane): $\lambda(\varepsilon$, L mol^{-1} cm^{-1}): 220 (1400), 776 (71) nm. – IR (CsI, Nujol): $\tilde{\nu}$ 1387, 1363, 1241, 1186, 1054, 1026, 997, 954, 826, 802, 699, 639, 519, 479, 438 cm^{-1}. – $C_{48}H_{108}LiO_{16}Si_4Ti$: calcd. C 52.01, H 9.82; found C 51.69, H 9.87.

{Ti[OSi(O^tBu)$_3$]$_3$}$_2$[O(CH_2)$_4$] (**3**). A sample of **1** (0.733 g, 0.746 mmol) was dissolved in 15 ml toluene. The solution was heated to 90 °C for 30 min during which time the color of the solution turned from blue to yellow. The solvent was then removed under vacuo, and the resulting solid was extracted into pentane (20 ml). The solution was filtered, concentrated to 3 ml, and cooled (−40 °C) affording 0.515 g of **3** as yellow crystals in 79% yield. UV/vis (isooctane): $\lambda(\varepsilon$, L mol^{-1} cm^{-1}): 218 (17800) nm. – IR (CsI, Nujol): $\tilde{\nu}$ 1386, 1364, 1241, 1192, 1065, 1026, 975, 928, 831, 806, 703, 675, 626, 501, 476, 430 cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 4.60 (t, 2 H, TiOCH_2CH$_2$-), 2.31 (m, 2 H, TiOCH$_2$CH_2-), 2.04 (m, 4 H, TiOCH$_2$CH$_2$CH_2CH_2Ti), 1.55 (s, 81 H, -OTi(OSiR$_3$)$_3$), 1.52 (s, 81 H, -CH$_2$Ti(OR$_3$)$_3$). – ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 81.05 (TiO*C*H$_2$-), 78.87 (TiOCH$_2$*C*H$_2$-), 72.81 (-OTi(OSi*C*Me$_3$)$_3$), 72.62 (-CH$_2$Ti(O*C*Me$_3$)$_3$), 37.45 (-*C*H$_2$CH$_2$Ti), 32.03 (-OTi(OSiC*Me*$_3$)$_3$), 31.99 (-CH$_2$Ti(OC*Me*$_3$)$_3$), 26.40 (-*C*H$_2$Ti). – $C_{76}H_{170}O_{25}Si_6Ti_2$: calcd. C 52.20, H 9.80; found C 52.13, H 9.76.

Ti[OSi(O^tBu)$_3$]$_3$(pyr)$_2$ (**4**). A toluene solution (15 ml) of pyridine (0.092 ml, 1.14 mmol) was added to a toluene solution (15 ml) of **1** (0.532 g, 0.542 mmol). The reaction mixture was stirred for 12 h. The solvent was then removed under vacuo, and the resulting solid was extracted into pentane (30 ml). The resulting violet solution was filtered, concentrated to 5 ml, and cooled (−80 °C) affording 0.393 g of **2** as violet crystals in 73% yield. UV/vis (isooctane): $\lambda(\varepsilon$, L mol^{-1} cm^{-1}): 224 (5900), 250 (5700), 526 (290), 606 (190) sh, 897 nm. – IR (CsI, Nujol): $\tilde{\nu}$ 3076, 3056, 1605, 1547, 1491, 1447, 1385, 1361, 1238, 1221, 1197, 1057, 1024, 962, 941, 825, 754, 698, 653, 632, 500, 463, 432 cm^{-1}. – $C_{46}H_{91}N_2O_{12}Si_3Ti$: calcd. C 55.45, H 9.21, N 2.81; found C 55.05, H 9.21, N 2.61. – μ_{eff} (B.M., 22 °C): 1.7(1).

{Ti[OSi(O^tBu)$_3$]$_3$(4,4'-bipyridine)}$_n$ (**5**). A toluene solution (15 ml) of 4, 4'-bipyridine (0.0485 g, 0.311 mmol) was carefully layered on top of a THF (10 ml) solution of **1** (0.049 g, 0.311 mmol). The Schlenk tube containing this reaction mixture was allowed to stand for 5 d during which time dark blue crystals of **5** deposited on the walls of the flask. The liquid was removed *via* canula and the crystals were dried under vacuum affording 0.108 g of **5** in 35% iso-

lated yield. UV/vis (isooctane): λ : 255, 368, 740, 1014 nm. – IR (CsI, Nujol): $\tilde{\nu}$ 1609, 1532, 1491, 1419, 1385, 1362, 1238, 1218 , 1194, 1048, 1024, 958, 854, 824, 734, 697, 650, 635, 515, 492, 470, 433 cm^{-1}. – $C_{46}H_{89}N_2O_{12}Si_3Ti$: calcd. C 55.56, H 9.02, N 2.81; found C 55.56, H 8.89, N 2.74. – μ_{eff} (B.M., 22 °C): 1.2(1) (solid).

Crystallographic structure determination of **3**. Crystals of $Ti_2[OSi(O^tBu)_3]_6[O(CH_2)_4]$ were grown from a concentrated pentane solution at −40 °C. A colorless blocky crystal of dimensions $0.40 \times 0.31 \times 0.15$ mm was mounted on a glass fiber using Paratone N hydrocarbon oil. Data was collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using ω scans of 0.3° and a collection time of 20-s per frame. Frame data was integrated (XY spot spread = 1.60°; Z spot spread = 0.60°) using SAINT. The data were corrected for Lorentz and polarization effects. An absorption correction was performed using XPREP ($\mu R = 0.10$, $T_{max} = 0.85$, $T_{min} = 0.77$). The 21893 integrated reflections were merged to give 14671 unique reflections ($R_{int} = 0.035$). Of these 10321 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. The structure was solved using direct methods (SIR92) in the space group $P\bar{1}$. The atoms that were modeled as disordered over two sites were refined isotropically. The pairs of disordered atoms, O(11)-O(12), O(13)-O(14), O(21)-O(22), O(23)-O(24), O(25)-O(26), C(39)-C(39)*, C(40)-C(40)*, C(41)-C(41)*, C(47)-C(48), C(49)-C(50), C(51)-C(52), C(62)-C(63), C(66)-C(67), C(68)-C(69), C(71)-C(72), C(73)-C(74), C(75)-C(76), C(78)-C(79), C(82)-C(83), C(94)-C(94)*, C(95)-C(95)*, C(96)-C(96)* were refined with equal populations at each site. The pairs of disordered atoms, C(32)-C(33), C(38)-C(37) were refined with 60% and 40% relative populations, respectively. The pairs of disordered atoms, O(29)-O(30), O(31)-O(32), C(58)-C(59), C(61)-C(60), C(80)-C(81), C(87)-C(86), C(93)-C(92), were refined with 70% and 30% relative populations, respectively. The remaining atoms were refined anisotropically. No hydrogen atoms were included in the model. The number of variable parameters was 954 giving a data/parameter ratio of 10.82. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.74 and −0.48 e^- $Å^{-3}$: $R = 0.091$, $R_w = 0.120$, GOF = 4.05.

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[1] a) K. J. Covert, P. T. Wolczanski, S. A. Hill, P. J. Krusic, Inorg. Chem. **31**, 66 (1992); b) K. J. Covert, D. R. Neithamer, M. C. Zonnevylle, R. E. LaPointe, C. P. Schaller, P. T. Wolczanski, Inorg. Chem. **30**, 2494 (1991); c) K. J. Covert, P. T. Wolczanski, Inorg. Chem. **28**, 4565 (1989); d) L. D. Durfee, S. L. Latesky, I. P. Rothwell, J. C. Huffman, K. Folting, Inorg. Chem. **24**, 4569 (1985); e) S. L. Latesky, J. Keddington, A. K. McMullen, I. P. Rothwell, J. C. Huffman, Inorg. Chem. **24**, 995 (1985); f) D. R. Neithamer, R. E. LaPointe, R. A. Wheeler, D. S. Richeson, G. D. Van Duyne, P. T. Wolczanski, J. Am. Chem. Soc. **111**, 9056 (1989); g) P. T. Wolczanski, Polyhedron **14**, 3335 (1995).

[2] a) M. P. Coles, C. G. Lugmair, K. W. Terry, T. D. Tilley, Chem. Mater. **12**, 122 (2000); b) K. L. Fujdala, T. D. Tilley, J. Catal. **216**, 265 (2003); c) K. W. Terry, T. D. Tilley, Chem. Mater. **3**, 1001 (1991); d) Y. Abe, K. Hayama, I. Kijima, Bull. Chem. Soc. Jpn. **45**, 1258 (1972); e) Y. Abe, I. Kijima, Bull. Chem. Soc. Jpn. **43**, 466 (1970); f) J. W. Kriesel, T. D. Tilley, Chem. Mater. **12**, 1171 (2000); g) J. W. Kriesel, M. S. Sander, T. D. Tilley, Adv. Mater. **13**, 331 (2001); h) R. L. Brutchey, T. D. Tilley, Chem. Mater. **15**, 1040 (2003).

[3] a) R. W. Adams, E. Bishop, R. L. Martin, G. Winter, Aust. J. Chem. **19**, 207 (1966); b) M. F. Lappert, A. R. Sanger, J. Chem. Soc. **(A)** 1314 (1971).

[4] E. Albizzati, L. Abis, E. Pettenati, E. Giannetti, Inorg. Chim. Acta. **120**, 197 (1986).

[5] a) M. Andruh, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, Z. Naturforsch. **49b**, 31 (1994); b) S. Wang, H. L. Tsai, K. Folting, J. D. Martin, D. N. Hendrickson, G. Christou, J. Chem. Soc., Chem. Commun. 671 (1994); c) N. Masciocchi, P. Cairati, L. Carlucci, G. Mezza, G. Ciani, A. Sironi, J. Chem. Soc., Dalton Trans. 2739 (1996); d) R. Xiong, Z. Yu, C. Liu, X. You, Polyhedron. **16**, 2667 (1997); e) M. Li, Z. Xu, X. You, Z. Dong, G. Guo, Polyhedron. **12**, 921 (1993); f) M. Li, G. Xie, Y. Gu, J. Chen, P. Zheng, Polyhedron. **14**, 1235 (1995); g) M. Handa, M. Mikuriya, T. Kotera, K. Yamada, T. Nakao, H. Matsumoto, K. Kasuga, Bull. Chem. Soc. Jpn. **68**, 2572 (1995).

[6] a) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. **116**, 1151 (1994); b) C. M. Bell, M. F. Arendt, L. Gomez, R. H. Schmehl, T. E. Mallouk, J. Am. Chem. Soc. **116**, 8374 (1994); c) C. M. Bell, S. W. Keller, V. M. Lynch, T. E. Mallouk, Mater. Chem. Phys. **35**, 225 (1993); d) A. J. Blake, S. J. Hill, P. Hubberstey, W. S. Li, J. Chem. Soc., Dalton Trans. 913 (1997).

[7] a) O. M. Yaghi, H. Li, J. Am. Chem. Soc. **117**. 10401 (1995); b) O. M. Yaghi, H. Li, Angew. Chem. Int. Ed. Engl. **34**, 207 (1995); c) T. Soma, H. Yuge, T. Iwamoto, Angew. Chem. Int. Ed. Engl. **33**. 1665 (1994); d) O. M.

Yaghi, in C. U. Pittman, C. E. Carraher, M. Zeldin, J. E. Sheats, B. M. Culbertson (eds): Metal-Containing Polymeric Materials, pp. 219 – 228, Plenum Press, New York (1996).

[8] a) F. Q. Liu, T. D. Tilley, J. Chem. Soc., Chem. Commun. **103** (1998); b) T. P. Vaid, E. B. Lobkovsky, P. T. Wolczanski, J. Am. Chem. Soc. **119**, 8742 (1997).

[9] A. Voigt, R. Murugavel, M. L. Montero, H. Wessel, F-Q. Liu, H. W. Roesky, I. Usón, T. Albers, E. Parisini, Angew. Chem. Int. Ed. Engl. **36**, 1001 (1997).

[10] P. C. Wailes, R. S. P. Coutts, H. Weigold, Organometallic Chemistry of Titanium, Zirconium, and Hafnium, pp. 18 – 26, Academic Press, New York (1974).

[11] a) J. S. Wood, Inorg Chem. **7**, 852 (1968); b) N. D. Fenton, M. Gerloch, J. Chem. Soc., Dalton Trans. 2201 (1988).

[12] G. W. A. Fowles, R. A. Hoodless, J. Chem. Soc. 33 (1963).

[13] W. J. Evans, T. A. Ulibarri, L. R. Chamberlain, J. W. Ziller, D. Alvarez (Jr.), Organometallics 9, 2124 (1990).

[14] Z. Guo, P. K. Bradley, R. F. Jordan, Organometallics. **11**, 2690 (1992).

[15] M. E. Woodhouse, F. D. Lewis, T. J. Marks, J. Am. Chem. Soc. **104**, 5586 (1982).

[16] a) M. W. Duckworth, G. W. A. Fowles, P. T. Greene, J. Chem. Soc. (A) 1592 (1967); b) P. C. Crouch, G. W. A. Fowles, R. A. Walton, J. Chem. Soc. (A) 2172 (1968).

[17] B. F. Hoskins, R. Robson, J. Am. Chem. Soc. **112**, 1546 (1990).

[18] D. F. Evans, T. A. James, J. Chem. Soc., Dalton Trans. 723 (1979).