Facile and Rational Route for High-Yield Synthesis of Titanasiloxanes from Aminosilanetriols

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Reactions of aminosilanetriols $RN(SiMe_3)(Si(OH)_3)$ (R = 2,6-$Me_2C_6H_3$ (**1a**), 2,6-*i*-$Pr_2C_6H_3$ (**1b**), 2,4,6-$Me_3C_6H_2$ (**1c**)) with titanium orthoesters $Ti(OR')_4$ (R′ = Et, *i*-Pr) in hexane at room temperature afford new cubic titanasiloxanes $[RN(SiMe_3)SiO_3Ti(OR')]_4$ (**2a**−**f**) in nearly quantitative yield. These compounds have been characterized by mass, IR, and multinuclear NMR spectroscopy. The X-ray crystal structure of $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3Ti(OEt)]_4$ (**2c**) is described. The molecular structure of **2c** reveals a $Si_4Ti_4O_{12}$ cubic core. The six Si−O−Ti puckered eight-membered rings in the cubic framework adopt a crown conformation with the two Si and two Ti atoms describing a plane and the four oxygen atoms in an almost parallel plane.

Introduction

There has been considerable interest, in recent times, in the chemistry of organosilicon compounds containing the Si−O−M (M = a transition metal or a main group element) moiety.[1] We[2] and others[3] have reported on the synthesis of a number of metallasiloxanes derived from silanediols $R_2Si(OH)_2$ with interesting structural features. Feher and co-workers[4] have utilized a trisilanol, $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$, with three terminal Si−OH groups for the construction of a number of corner capped metallasilsesquioxanes which contain a low metal to silicon ratio of 1:7. The possible application of these compounds as models for transition metal complexes supported on silica surfaces has been discussed.[4]

Moreover, recently, there have been reports on the utility of metal-incorporated silica surfaces as well as metal-doped zeolites for catalytic purposes.[5] Thus, for example, titanium-doped zeolites have been shown to catalyze the reactions of H_2O_2 with diverse substrates such as alkanes, arenes, alkenes, and amines.[6] In view of the impressive catalytic utility of these modified zeolite systems, it was of interest to synthesize metallasiloxanes containing a higher titanium content.

We have recently shown that discrete aminosilanetriols are better synthons for the synthesis of a variety of metallasiloxanes with a higher metal to silicon ratio (1:1).[7−9] Thus, for example, the reaction of *t*-$BuSi(OH)_3$ with Re_2O_7 affords an eight-membered siloxane ring with pendant $OReO_3$ units bonded to silicon (eq 1).[7]

$$4t\text{-BuSi(OH)}_3 + 4\text{Re}_2\text{O}_7 \rightarrow [t\text{-BuSiO(OReO}_3)]_4 + 2\text{Re}_2\text{O}_7\cdot 6\text{H}_2\text{O} \quad (1)$$

Interest in titanium-doped zeolite systems has prompted us to extend the use of this methodology to the synthesis of titanasiloxanes with cage structures. In a preliminary communication we have reported strategies for the synthesis of this class of compounds starting from discrete silanetriols.[9] We now report the details of this

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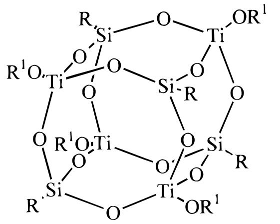
Scheme 1

$$4\,RSi(OH)_3 \quad + \quad 4\,Ti(OR^1)_4 \xrightarrow[-\,12\,R^1OH]{}$$



$R = (2,6\text{-}Me_2C_6H_3)N(SiMe_3)$; $R^1 = Et$ **2a**
$R^1 = i\text{-}Pr$ **2b**

$R = (2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)$; $R^1 = Et$ **2c**
$R^1 = i\text{-}Pr$ **2d**

$R = (2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)$; $R^1 = Et$ **2e**
R1 = *i*-Pr **2f**

facile procedure using a series of highly stable aminosilanetriols.[10] We also report on the X-ray crystal structure of one of the representative products.

Results and Discussion

Synthesis. The reaction of silanetriols[10] with titanium orthoesters, $Ti(OR')_4$ ($R' = Et$, *i*-Pr), proceeds readily at room temperature within few hours yielding titanasiloxanes **2a**–**f** nearly quantitatively (Scheme 1). These compounds are extremely soluble in all organic solvents including hydrocarbons such as pentane and hexane.

The compound **2d** was also synthesized starting from the silanetriol **1b** and $TiCl(O\text{-}i\text{-}Pr)_3$ (eq 2).

$$\underset{\mathbf{1b}}{4(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)(Si(OH)_3)} + 4TiCl(O\text{-}i\text{-}Pr)_3 + 4Et_3N \rightarrow \underset{\mathbf{2d}}{[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3Ti(O\text{-}i\text{-}Pr)]_4} + 4Et_3N{\cdot}HCl + 8i\text{-}PrOH \quad (2)$$

However, this route requires the use of Et_3N as HCl acceptor. Another preparation of titanasiloxane used $OSnMe_3$ derivatives of the silanetriols such as $t\text{-}BuSi(OSnMe_3)_3$ as starting materials.[9]

The titanasiloxanes **2a**–**f** have been characterized by CHN analyses and mass, IR, and multinuclear NMR spectroscopy. Further, an X-ray structure investigation was carried out on **2c**. The characterization data for **3**, including a single-crystal X-ray structure determination, have been reported previously.[9]

Spectra. It is interesting to note that in spite of their high molecular weights, compounds **2a**–**f** give molecular ions (M^+) with high intensities (often 100%) under electron impact conditions. The subsequent fragmentations are due to the loss of methyl groups either from the aryl ring or from the $SiMe_3$ group. This observation indicates to the retention of the large cubic cores under the spectrometer ionization conditions. Moreover, all the compounds show a high thermal stability and do not melt below 300 °C.

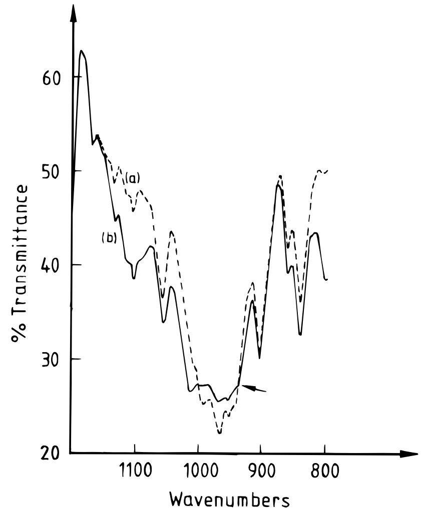


Figure 1. IR spectra of the (a) normal and (b) 10% ^{18}O-enriched samples of the titanasiloxane **2b** in the region 800–1200 cm^{-1}. The new shoulder appearing in (b) on ^{18}O enrichment is labeled with an arrow.

The ^1H NMR spectra of **2a**–**f** are consistent with their structures. It is interesting to note that in compounds **2c**,**d** the methyl groups of the isopropyl moiety on the aromatic ring show slight nonequivalances. However for all the compounds the alkoxy group attached to titanium shows only one set of resonances. The ^{29}Si NMR spectral data for **2a**–**f** are detailed in the Experimental Section. The resonances due to the $SiMe_3$ groups are observed around 5 ppm. The chemical shifts of the silicon atoms in the cubic framework occur around −95 ppm.

There has been considerable debate about an IR stretching frequency observed around 960–970 cm^{-1} in Ti-containing zeolites such as TS-1, TS-2, and TiZSM48. This absorption has been attributed to the Ti=O stretch by some authors[11] Others have assigned it to an $Si-O^-$ absorption[12] or to an $Si-O^{\delta-}-Ti^{\delta+}$ unit.[13] It has been suggested that the intensity of this absorption is related to the Ti content in the modified silicalites. In all our compounds **2a**–**f** we observe a very strong absorption in the range of 960–970 cm^{-1} (Figure 1). We assign this absorption to a Ti–O–Si stretching vibration as our compounds do not contain a Ti=O or a $Si-O^-$ unit.[9]

In order to further confirm this assignment we have carried out ^{18}O-labeling studies for one of the titanasiloxanes. From a 10% ^{18}O-enriched sample of the silanetriol **1a** we prepared the titanasiloxane **2b** and confirmed the enrichment of ^{18}O by mass spectral studies. We observed that this stretching frequency around 960 cm^{-1} undergoes considerable broadening on ^{18}O enrichment with a new shoulder appearing at a lower frequency (Figure 1). In views of the unambiguous nature of the structural assignment of **2a**–**f** by X-ray diffraction studies (*vide infra*) and ^{18}O-labeling studies, we are confident that this absorption is due to a Si–O–Ti

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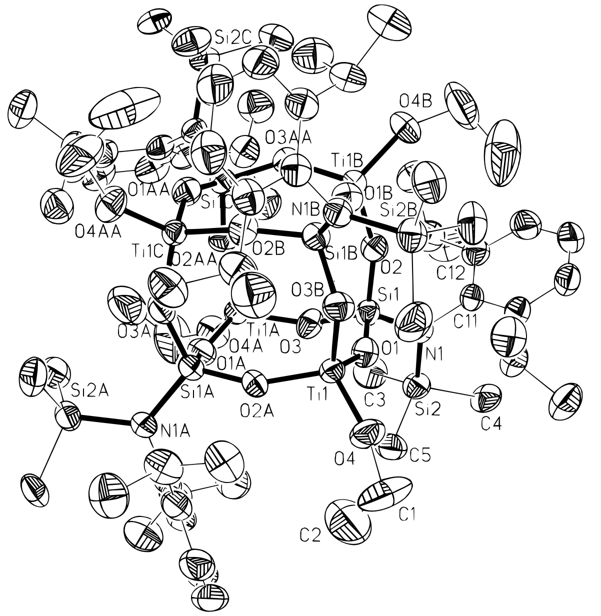

Figure 2. Structure of $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3Ti(OEt)]_4$ (**2c**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)–O(1) 1.803(3), Ti(1)–O(2A) 1.807(3), Ti(1)–O(3B) 1.803(3), Ti(1)–O(4) 1.768(3), Si(1)–O(1) 1.632(3), Si(1)–O(2) 1.622(3), Si(1)–O(3) 1.641(3), Si(1)–N(1) 1.712(4); O(4)–Ti(1)–O(1) 110.9(2), O(4)–Ti(1)–O(3B) 109.5(2), O(1)–Ti(1)–O(3A) 109.0(2), O(4)–Ti(1)–O(2A) 111.7(2), O(1)–Ti(1)–O(2A) 107.4(2), O(3B)–Ti(1)–O(2A) 108.2(2), O(2)–Si(1)–O(1) 107.3(2), O(2)–Si(1)–O(3) 112.3(2), O(1)–Si(1)–O(3) 106.3(2), O(2)–Si(1)–N(1) 109.6(2), O(1)–Si(1)–N(1) 113.3(2), O(3)–Si(1)–N(1) 108.0(2), Si(1)–O(1)–Ti(1) 150.2(2), Si(1)–O(2)–Ti(1B) 155.3(2), Si(1)–O(3)–Ti(1A) 155.3(2).

stretching frequency. The high intensities of the 960–970 cm^{-1} peak in **2a**–**f** are certainly due to the high Ti to Si ratio of 1:1, whereas in the modified zeolites this peak is observed with varying intensities, depending on the extent of Ti incorporation in the silicalite structure.[13]

X-ray Crystal Structure of 2c. In order to further confirm the molecular structure of these titanasiloxanes, we performed a single-crystal X-ray study of **2c**, whose molecular structure with atom-numbering scheme is shown in Figure 2 along with the selected structural parameters. The $Ti_4Si_4O_{12}$ polyhedron is completely enclosed in a hydrophobic sheath of alkyl-substituted aryl and $SiMe_3$ groups which explains the high solubility of compounds **2a**–**f** in hydrocarbon solvents such as pentane.

In the structure of **2c**, a cubic polyhedron can be defined with four silicon and four titanium atoms occupying its alternate corners. Each of the Si···Ti edges of the cube is bridged by an oxygen atom in a μ^2 fashion which is between 0.38 and 0.52 Å out of the Si–Ti line. There are six puckered $Si_2Ti_2O_4$ eight-membered rings which define the cube, and each of these rings adopts a pseudo-C_4 crown conformation. The four oxygen atoms on any of these eight-membered rings are in a plane (mean deviation 0.008 Å) while the two Al and two Si atoms form an almost parallel plane (mean deviation 0.01 Å)[14] with a dihedral angle of 2.6° between them.

The average Ti–O bond length in the framework is 1.80 Å which is slightly longer than the exocyclic Ti–O distance of 1.768(3) Å. These values are comparable to the Ti–O distances found in $[t\text{-}BuSiO_3Ti(MeC_5H_4)]_4$ (**3**). The average Si–O distance found in **2c** (1.63 Å) is slightly longer than the corresponding distances found in **3**. The Si(1)–N(1) distance of 1.712(4) Å is considerably shorter than the Si(2)–N(1) distance of 1.761(4) Å. This observation is consistent with the presence of three electron-withdrawing oxygen atoms attached to Si(1). The average length of the Si···Ti edge of the cube is 3.32 Å. The body diagonal of the Si_4Ti_4 cube is 5.75 Å. The framework Si–O–Ti angles in **2c** are 150.2(2), 155.3(2), and 145.2(2)°, which compare with the values found in **3**. The Ti and Si atoms adopt nearly ideal tetrahedral geometries with the average angles around each of them being 109.5°. The sum of angles around the nitrogen atom in **2c** is 359.9° corresponding to a trigonal planar geometry.

It is of interest to compare the structural parameters of **2c** with that of a titana(III)silsesquioxane dimer $[(c\text{-}C_6H_{11})_7(Si_7O_{12})Ti^{III}]_2$ (**4**) prepared by Feher et al.[4b] There is a steric congestion in **4** owing to the presence of a Ti_2O_2 four-membered ring which bridges the two trisilanol moieties. Perhaps as a consequence of this, along with the fact that Ti is in a lower oxidation state, the average Ti–O bond length is much longer in **4** (1.904 Å). Moreover the Si–O–Ti angles in the framework in **4** vary from extremely small angles of 131.6° to normal values of 156.6°.

Conclusion

We have shown that discrete aminosilanetriols are excellent synthons for generating a new class of oligomeric cage structures containing Ti, O, and Si in the framework. The X-ray structure of **2c** reveals that the Si and Ti are bridged by oxygen atoms in a three-dimensional cubic cage structure. The strong absorption observed for these compounds around 960–970 cm^{-1} is assigned to the Si–O–Ti stretch. In view of this assignment, it is possible that the stretching frequency in the same region observed in titanium-modified zeolites is also due to a similar absorption.

The synthetic methodology adopted here is likely to be quite general and can possibly be extended for the realization of other metal-containing oligomeric siloxanes. Further, the presence of easily hydrolyzable Si–N and Ti–O pendant groups offer possible access to supramolecular cage structures. We are actively pursuing these aspects.

Experimental Section

General Data. All reactions were carried out in an inert atmosphere using Schlenk methods. Moisture-sensitive materials were handled in a dry-box. Solvents were purified and dried using conventional procedures. Titanium ethoxide (Merck) and titanium isopropoxide (Riedel) were used as received. The syntheses of silanetriols **1a**–**c** have been described previously.[10] NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument. Chemical shifts are reported in ppm with reference to $SiMe_4$ with upfield shifts being negative. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer (only strong absorption bands are given; *vide infra*). Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH5 mass spectrometer.

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(14) SHELXTL-PLUS, Siemens Analytical X-ray Instruments, Madison, WI, 1990.

Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany.

Synthesis of Titanasiloxanes 2a–f. The titanasiloxanes were synthesized by following a general procedure. To a suspension of $RN(SiMe_3)(Si(OH)_3)$ (3 mmol) in hexane (20 mL) was added the titanium orthoester $Ti(OR')_4$ (3 mmol) using a syringe. Immediately the solution became clear. The reaction mixture was further stirred for a period of 4 h at room temperature. The solvent was stripped off *in vacuo*, and the resulting residue was dried thoroughly for 12 h in high vacuum. The solid material obtained was recrystallized from a minimum amount of pentane or hexane and was identified as tetrameric titanasiloxane $[RN(SiMe_3)SiO_3Ti(OR')]_4$.

$[(2,6\text{-}Me_2C_6H_3)N(SiMe_3)SiO_3Ti(OEt)]_4$ (2a). Yield: 0.98 g (90%). IR (Nujol): 1305, 1258, 1201, 1154, 1101, 1056, 1016, 970, 928, 903, 843, 765, 728, 687, 640, 588, 555, 509, 455 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 0.08 (s, 36H, $SiMe_3$), 1.15 (t, 12H, $J = 7$ Hz, Me), 2.30 (s, 24H, Me), 3.90 (q, 8H, $J = 7$ Hz, CH_2), 6.92 (m, 12H, aromatic). ^{29}Si NMR (49.7 MHz, $CDCl_3$): −98.4 (SiO_3), 5.7 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1446 (M^+). Anal. Calcd for $C_{52}H_{92}N_4O_{16}Si_8Ti_4$: C, 43.2; H, 6.4; N, 3.9. Found: C, 43.0; H, 6.2; N, 3.4.

$[(2,6\text{-}Me_2C_6H_3)N(SiMe_3)SiO_3Ti(O\text{-}i\text{-}Pr)]_4$ (2b). Yield: 1.07 g (95%). IR (Nujol): 1333, 1257, 1249, 1200, 1165, 1132, 1117, 1102, 1056, 1010, 953, 905, 860, 841, 765, 743, 728, 686, 643, 588, 542, 503, 465 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 0.08 (s, 36H, $SiMe_3$), 1.06 (d, $J = 6.5$ Hz, 24H, Me_2), 2.28 (s, 24H, Me), 4.37 (m, 4H, CH), 6.88 (m, 12H, aromatic). ^{29}Si NMR (49.7 MHz, $CDCl_3$): −97.4 (SiO_3), 6.6 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1502 (M^+). Anal. Calcd for $C_{56}H_{100}N_4O_{16}Si_8Ti_4$: C, 44.8; H, 6.7; N, 3.7. Found: C, 44.5; H, 6.5; N, 3.9.

$[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3Ti(OEt)]_4$ (2c). Yield: 1.15 g (92%). IR (Nujol): 1362, 1249, 1183, 1143, 1106, 1042, 1021, 998, 968, 958, 905, 841, 802, 756, 646, 603, 511, 468 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 0.04 (s, 36H, $SiMe_3$), 0.96 (m, 48H, Me), 1.19 (m, 24H, Me), 3.47 (m, 8H, CH), 3.95 (m, 8H, CH_2), 6.98 (m, 12H, aromatic). ^{29}Si NMR (79.5 MHz, $CDCl_3$): −96.6 (SiO_3), 6.4 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1669 (M^+). Anal. Calcd for $C_{68}H_{124}N_4O_{16}Si_8Ti_4$: C, 48.9; H, 7.5; N, 3.4. Found: C, 48.9; H, 7.2; N, 3.2.

$[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)SiO_3Ti(O\text{-}i\text{-}Pr)]_4$ (2d). Yield: 1.25 g (98%). IR (Nujol): 1323, 1250, 1183, 1131, 1107, 1056, 993, 968, 905, 861, 842, 722, 644, 604 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): 0.02 (s, 36H, $SiMe_3$), 0.95 (d, 24H, $J = 6.1$ Hz, Me), 1.15 (d, 24H, $J = 6.8$ Hz, Me), 1.24 (d, 24H, $J = 6.8$ Hz, Me), 3.50 (sept, 8H, $J = 6.8$ CH), 4.25 (sept, 4H, $J = 6.1$ Hz, CH), 6.98 (m, 12H, aromatic). ^{29}Si NMR (49 MHz, $CDCl_3$): −96.5 (SiO_3), 6.3 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1725 (M^+). Anal. Calcd for $C_{72}H_{132}N_4O_{16}Si_8Ti_4$: C, 50.1; H, 7.7; N, 3.3. Found: C, 50.2; H, 8.4; N, 3.3.

$[(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)SiO_3Ti(OEt)]$ (2e). Yield: 1.05 g (94%). IR (Nujol): 1259, 1250, 1214, 1153, 1094, 1056, 1000, 969, 959, 889, 841, 755, 734, 687, 647, 594, 562, 506, 452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 0.09 (s, 36H, $SiMe_3$), 1.18 (t, 12H, $J = 7.1$ Hz, Me), 2.18 (s, 12H, Me), 2.30 (s, 24H, Me), 3.90 (q, 8H, $J = 7.1$ Hz, CH_2), 6.92 (m, 12H, aromatic). ^{29}Si NMR (49.7 MHz, $CDCl_3$): −97.9 (SiO_3), 5.2 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1500 (M^+). Anal. Calcd for $C_{56}H_{100}N_4O_{16}Si_8Ti_4$: C, 44.8; H, 6.7; N, 3.7. Found: C, 44.9; H, 6.7; N, 3.9.

$[(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)SiO_3Ti(O\text{-}i\text{-}Pr)]_4$ (2f). Yield: 1.15 g (99%). IR (Nujol): 1333, 1304, 1259, 1250, 1214, 1154, 1132, 1059, 994, 968, 891, 862, 840, 755, 733, 686, 647, 594, 561, 504, 454 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 0.08 (s, 36H, $SiMe_3$), 1.08 (d, 24H, $J = 6.2$ Hz, Me), 2.20 (s, 12H, Me), 2.28 (s, 24H, Me), 4.39 (m, 4H, CH), 6.76 (m, 8H, aromatic). ^{29}Si NMR (49.7 MHz, $CDCl_3$): −96.9 (SiO_3), 6.3 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1557 (M^+). Anal. Calcd for $C_{60}H_{108}N_4O_{16}Si_8Ti_4$: C, 46.3; H, 7.0; N, 3.6. Found: C, 46.0; H, 7.0; N, 3.7.

X-ray Crystal Structure Determination of 2c. Colorless crystals of **2c** suitable for single-crystal X-ray diffraction studies were obtained from a saturated pentane solution at room temperature. A 0.75 × 0.75 × 0.40 mm^3 sized crystal was mounted on a glass fiber in a rapidly cooled perfluoropolyether.[15] Diffraction data were collected on a Siemens-Stoe AED2 four-circle instrument at 150(2) K, with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $\omega{-}2\theta$ scans in the range $7 \leq 2\theta \leq 50°$, on line profile fitting,[16] and constant scan speed. Crystal data for $C_{68}H_{124}N_4O_{16}Si_8Ti_4{\cdot}{}^4/_3C_2H_6O$: Cubic, $I\bar{4}3d$, unit cell dimensions $a = b = c = 31.180(4)$ Å, unit cell volume 30313(7) Å^3, $\rho_{calcd} = 1.138$ g·cm^{-3}, $\mu = 0.454$ mm^{-1}; total number of reflections measured 15 157, unique 2901 ($R_{int} = 0.051$). The structure was solved by direct methods using SHELXS-90[17] and refined against F^2 on all data by full-matrix least squares with SHELXL-93.[18]

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The unit cell also contains 16 molecules of ethanol, disordered around 3-fold axes. The three atoms in the asymmetric unit were refined with the help of similar and rigid bond restraints on the thermal parameters. Data/restraints/parameters: 2898/15/253. Final R indices with $I > 2\sigma(I)$: $R1 = 0.045$, $wR2 = 0.121$. R indices on all data: $R1 = 0.053$, $wR2 = 0.135$. Goodness-of-fit S on F^2 1.073. Largest difference peak and hole: 0.053 and −0.254 e·Å^{-3}. $R = ||F_o| - |F_c||/\sum|F_o|$; $wR2 = [[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]]^{1/2}$; $S = [[\sum w(F_o^2 - F_c^2)^2]/[\sum(n - p)]]^{1/2}$. The final fractional atomic coordinates are given in the Supporting Information.

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Supporting Information Available: Listings of crystal data, atomic coordinates and equivalent isotropic displacement parameters for all non-hydrogen atoms, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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