Stannasiloxanes with Acyclic, Bicyclic, and Cubic Core Structures: X-ray Crystal Structure of the Bicyclic Compound [RSi(OSnPh$_2$O)$_3$SiR] (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$)†

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The reactions of the (arylamino)silanetriols with mono-, di-, and trifunctional alkyl/aryl tin(IV) chlorides have been investigated. Treatment of (arylamino)silanetriols RSi(OH)$_3$ (**1**, **2**) with Me$_3$SnCl leads to the isolation of the acyclic stannasiloxanes RSi(OSnMe$_3$)$_3$ (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$ (**3**), (2,6-*i*-Pr$_2$C$_6$H$_3$)NSiMe$_3$ (**4**)), which are potential precursors for the preparation of metallasiloxanes. The reactions between the silanetriols **1** and **2** and R′$_2$SnCl$_2$ in a 2:3 molar ratio yield the bicylic stannasiloxanes [RSi(OSnR′$_2$O)$_3$SiR] (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$, R′ = Me (**5**); R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$, R′ = Ph (**6**); R = (2,6-*i*-Pr$_2$C$_6$H$_3$)NSiMe$_3$, R′ = Me (**7**); R = (2,6-*i*-Pr$_2$C$_6$H$_3$)NSiMe$_3$, R′ = Ph (**8**)). The cubic stannasiloxanes [RSiO$_3$SnPh]$_4$ (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$ (**9**); (2,6-*i*-Pr$_2$C$_6$H$_3$)NSiMe$_3$ (**10**)) are easily prepared in good yields by starting from the respective silanetriols and PhSnCl$_3$. In all the reactions NEt$_3$ is used as the hydrogen chloride acceptor. The new stannasiloxanes **3**−**10** have been extensively characterized by means of their analytical data and mass, IR, and NMR (^{1}H, ^{29}Si and ^{119}Sn) spectral data. The solid-state structure of the bicyclic compound **6** has been determined by X-ray diffraction studies.

Introduction

In recent years there has been a considerable interest in the chemistry of organosilicon compounds containing the Si−O−M (M = a transition metal or a main-group element) moiety,[1−5] which originally dates back to the end of the last century.[6] This is in view of the increasing realization that such compounds would serve as useful model compounds to many naturally occurring minerals[7] in addition to their possible use in understanding the mechanisms of many catalytic processes employing silica-supported catalysts.[8] Our group[3] and others[4] have reported the synthesis of a number of metallasiloxanes derived from silanediols and disilanols. Feher and coworkers have utilized the incompletely condensed silsesquioxane [(c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_3$], with three terminal Si−OH groups, for the construction of a number of corner-capped metallasilsesquioxanes.[5]

In view of the fact that the alkyltin group from the stannasiloxanes can be easily removed as their halides in the reactions with transition-metal halides,[9] stannasiloxanes can be considered as important intermediates in metallasiloxane chemistry. Studies on stannasiloxanes also assume importance due to the known catalytic activity of various synthetic zeolites incorporating tin and microporous solids in organic transformations.[10]

The first stannasiloxanes containing a Si−O−Sn linkage were prepared in 1952 by Tatlock and Rochow.[11] Since then, several groups have studied the reactions of silanols with organotin halides and isolated different types of stannasiloxanes.[12,13] We have recently shown that discrete silanetriols (**A**−**D**; Chart 1) are better synthons for the preparation of a variety of hitherto unknown metallasiloxanes with a higher heteroelement to silicon ratio (1:1).[9,14] Thus, for example, the reaction

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† Dedicated to Professor C. N. R. Rao.

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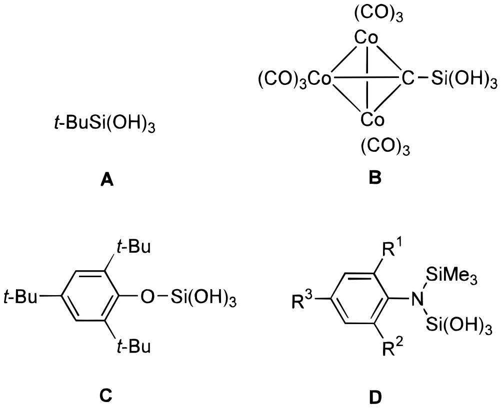
Chart 1

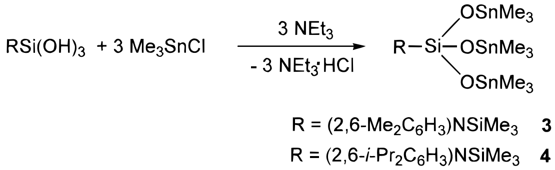


of t-BuSi(OH)$_3$ with Re_2O_7 affords an eight-membered siloxane ring with pendant OReO$_3$ units bonded to silicon.[14a]

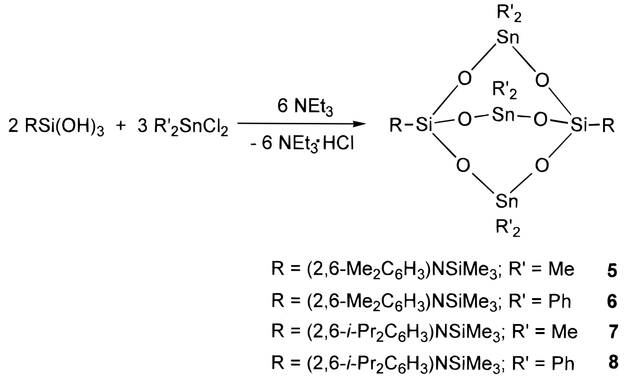
Interest in metal-doped zeolite systems[15] which catalyze many organic transformations has prompted us to synthesize a range of heterosiloxanes containing elements such as Ti, Al, Ga, and In. Extending this approach to other heterosiloxanes, we now report the details of our investigations on the preparation of acyclic and polyhedral stannasiloxanes using a series of highly stable aminosilanetriols. We also report on the X-ray crystal structure of one of the bicyclic stannasiloxanes.

In this context, it should be noted that the reactions of (arylamino)silanetriols (**D**) with various other main-group or transition-metal halides, in the presence of a tertiary base such as NEt$_3$, normally lead to the isolation of noncharacterizable products.[16] For example, the reactions of phosphorus halides with silanetriols do not yield any desired products and often cleavage of Si–N bonds of the silanetriols leading to arylamine hydrochloride salts is observed. Likewise, the reaction of silanetriols with transition-metal chlorides such as Cp*TiCl$_3$ yields products with skeletal rearrangments.[17] Similar side reactions have been observed by Feher and coworkers in the case of incompletely condensed silsesquioxanes.[5] Surprisingly, the reactions of alkyl/aryl tin chlorides with silanetriols is an exception to this kind of observation, which led to the isolation of the stannasiloxanes described in this paper.

Scheme 1



Scheme 2



Results and Discussion

Synthesis and Spectra. The reactions of the silanetriols RSi(OH)$_3$ (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$, **1**; R = (2,6-i-Pr$_2$C$_6$H$_3$)NSiMe$_3$, **2**) with Me$_3$SnCl in a 1:3 reactant ratio in the presence of triethylamine as HCl acceptor yield the tristannasiloxanes **3** and **4** (Scheme 1). The Me$_3$Sn– groups in this compound are labile and can be easily replaced as Me$_3$SnCl when reacted with transition-metal halides. This property of the trimethyltin group makes these compounds useful as latent sources of siloxide anions $RSiO_3^{3-}$ in the preparation of other metallasiloxanes. In this context, we have already demonstrated the use of t-BuSi(OSnMe$_3$)$_3$ as a starting material in the preparation of cyclopentadienyl-substituted cubic titanasiloxanes.[9]

The reactions of the silanetriols RSi(OH)$_3$ (R = (2,6-Me$_2$C$_6$H$_3$)NSiMe$_3$, **1**; R = (2,6-i-Pr$_2$C$_6$H$_3$)NSiMe$_3$, **2**) using Me$_2$SnCl$_2$ or Ph$_2$SnCl$_2$ in a 2:3 reactant ratio under similar reaction conditions proceed neatly with all the OH groups of the silanetriol reacting and yielding the bicyclic products **5**–**8** (Scheme 2). While these compounds are formed in extremely good yields in reactions with a 2:3 molar ratio of the reactants, they are also formed in other stoichiometric reactions, albeit in varying yields. Compounds **5**–**8** show the presence of two fused eight-membered Si–O–Sn rings, where the two RSiO$_3$ groups are bridged by three R′$_2$Sn bridges. These compounds represent a rare class of bicyclic metallasiloxanes obtained from the reactions of silanetriols and metal halides.[18,19]

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Scheme 3

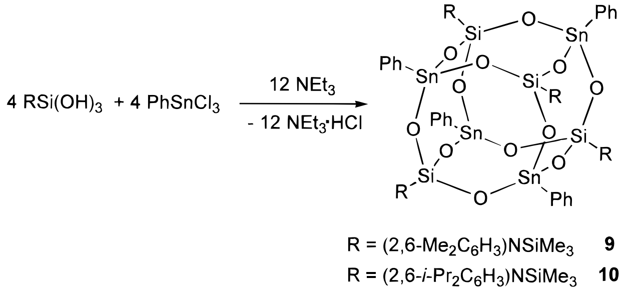

Table 1. Selected Spectroscopic Data for Stannasiloxanes[a]

compd	yield, %	^{29}Si NMR, ppm (δ(SiO$_3$), δ(SiMe3))	^{119}Sn NMR, ppm	$^2J_{\mathrm{Sn-Si}}$, Hz
3	75	−71.9, 1.4[b,c]	88.3[d]	
4	87	−71.8, 1.5[e]	99.3[f]	
5	78	−68.9, 3.6[c]	−2.0[d]	36
6	84	−68.9, 4.5[e]	−186.4[f]	32
7	86	−69.7, 3.4[c]	1.6[f]	31
8	91	−67.9, 4.9[b,c]	−180.0[d]	30
9	64	−70.2, 6.2[c]		
10	73	−74.1, 7.7[c]	−338.8[d]	34

[a] All spectra were recorded in CDCl$_3$, unless otherwise stated. [b] Spectrum recorded in C$_6$D$_6$. [c] Spectral frequency 79.5 MHz. [d] Spectral frequency 149.2 MHz. [e] Spectral frequency 49.7 MHz. [f] Spectral frequency 93.3 MHz.

The reactions of PhSnCl$_3$ with the silanetriols **1** and **2** in 1:1 molar ratio proved to be the best way to generate the cubic stannasiloxane clusters **9** and **10**, where Si and Sn occupy alternate corners of the cubic framework (Scheme 3). While the reactions of these silanetriols with *n*-BuSnCl$_3$ also yield the respective cubic stannasiloxanes, analytically pure samples of these compounds could not be obtained due to their very high solubility even in solvents such as pentane and hexane.[20]

The new stannasiloxanes **3**−**10** have been characterized by elemental analysis and IR, mass, and NMR (^{1}H, ^{29}Si, and ^{119}Sn) spectroscopy. All these compounds are thermally very stable and do not melt below 200 °C. On further heating, in a few cases, a small amount of decomposition was observed. The molecular ions for all the compounds have been observed in their electron impact mass spectra (EI MS) with varying intensities.

The absorptions around 3600 cm^{-1} in the IR spectra of the parent silanetriols are completely absent in the case of stannasiloxanes **3**−**10**, indicating that all the Si−OH groups of these starting compounds have reacted. Moreover, a new absorption between 950 and 1000 cm^{-1} appears in the case of compounds **3**−**10** which could be attributed to Sn−O−Si stretching on the basis of our previous assignments for this peak for a variety of metallasiloxanes derived from aminosilanetriols.[21]

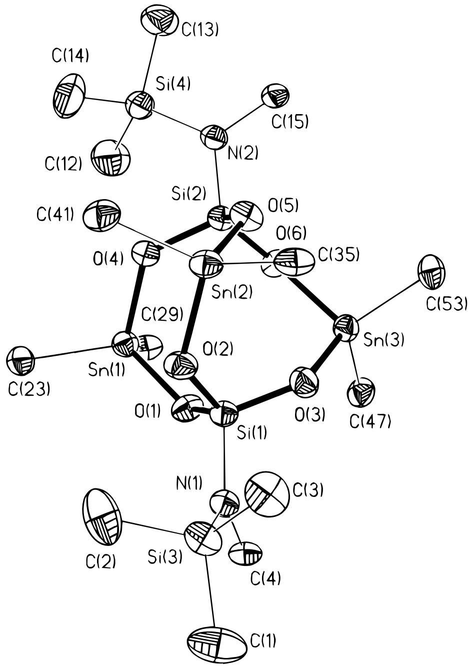

Figure 1. Thermal ellipsoid plot (at the 50% probability level) of the molecular structure of the bicyclic stannasiloxane **6**. For the sake of clarity, only the *ipso* carbons of the aryl groups are shown.

The ^{1}H NMR spectral data and the integration of the intensities match well with the proposed structures for the new stannasiloxanes. The protons from the −SnMe$_3$ groups of compounds **3** and **4** resonate as singlets at 0.26 and 0.20 ppm, respectively. Selected spectroscopic data are listed in Table 1. The ^{29}Si NMR chemical shifts for the SiO$_3$ silicon centers in the acyclic compounds **3** and **4** are shifted upfield compared to the values in the parent silanetriols[14d] and appear at around −72 ppm. A similar coordination shift of around 7 ppm is observed for the cubic stannasiloxanes **9** and **10**. In the case of bicyclic compounds **5**−**8**, this resonance is almost invariant with respect to the starting materials **1** and **2**. The ^{119}Sn NMR spectra of compounds **3**−**10** show a large variation of chemical shifts (+99.3 to −338.8 ppm). The replacement of the Me substituent by Ph on the Sn centers in the bicyclic structures causes a shift of more than 180 ppm. While positive chemical shifts are observed for the acyclic stannasiloxanes, the most negative chemical shift of −338.8 ppm is observed for the cubic stannasiloxane **10**.

Molecular Structure of 6. Although we were successful in obtaining single crystals of the bicyclic compounds **5**−**8** and the cubic stannasiloxanes **9** and **10**, we could refine the final structure successfully only in the case of **6**. The other bicyclic compounds suffered from severe disorder problems in the peripheral organic moieties. The crystals of the cubic stannasiloxanes were found to be only poorly diffracting.

Compound **6** crystallizes in the monoclinic space group *P*2$_1$/*n*. The molecular structure of the compound along with the atom-labeling scheme is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The molecule shows the presence of three fused eight-membered rings, resulting in a bicyclic structure. A view of the molecule along the Si−Si vector showing the presence of 3-fold symmetry in the molecule is depicted in Figure 2. As is evident from this figure, each of the eight-membered rings exists in a symmetrical boat conformation. The three tin atoms in the molecule are flanked between the two silanetrioxy groups and retain the two phenyl groups. The substituent on the silicon atom of the silanetriol does not show any interactions with the rest of the molecule.

The average Sn−O and Si−O distances in the molecule are 1.96 and 1.62 Å, respectively. The Si−O bond

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(20) Quantities of 3 mmol are freely soluble in less than 2 mL of pentane, even below −20 °C.

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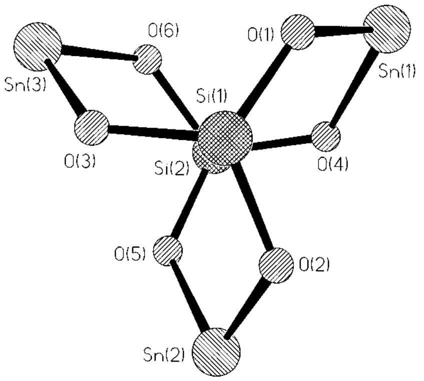

Figure 2. The Si/O/Sn bicyclic core viewed down the Si–Si axis, showing the boat conformation of the eight-membered rings.

Table 2. Bond Lengths (Å) and Angles (deg) for 6

Sn(1)–O(1)	1.959(2)	Sn(1)–O(4)	1.968(2)
Sn(2)–O(5)	1.959(2)	Sn(2)–O(2)	1.966(2)
Sn(3)–O(3)	1.962(2)	Sn(3)–O(6)	1.970(2)
Sn(1)–C(29)	2.119(3)	Sn(1)–C(23)	2.119(3)
Sn(2)–C(35)	2.114(3)	Sn(2)–C(41)	2.116(3)
Sn(3)–C(53)	2.120(3)	Sn(3)–C(47)	2.122(3)
Si(1)–O(2)	1.621(2)	Si(1)–O(1)	1.622(2)
Si(1)–O(3)	1.623(2)	Si(1)–N(1)	1.719(2)
Si(2)–O(5)	1.621(2)	Si(2)–O(4)	1.625(2)
Si(2)–O(6)	1.626(2)	Si(2)–N(2)	1.715(2)
Si(3)–N(1)	1.748(2)	Si(4)–N(2)	1.748(2)

O(1)–Sn(1)–O(4)	103.88(8)	O(1)–Sn(1)–C(29)	108.7(1)
O(4)–Sn(1)–C(29)	113.4(1)	O(1)–Sn(1)–C(23)	113.3(1)
O(4)–Sn(1)–C(23)	103.9(1)	C(29)–Sn(1)–C(23)	113.4(1)
O(2)–Si(1)–O(1)	111.8(1)	O(2)–Si(1)–O(3)	108.9(1)
O(1)–Si(1)–O(3)	107.7(1)	O(2)–Si(1)–N(1)	107.5(1)
O(1)–Si(1)–N(1)	109.9(1)	O(3)–Si(1)–N(1)	111.1(1)
Si(1)–O(1)–Sn(1)	134.6(1)	Si(1)–O(2)–Sn(2)	127.5(1)
Si(1)–O(3)–Sn(3)	132.2(1)	Si(2)–O(4)–Sn(1)	127.2(1)
Si(2)–O(5)–Sn(2)	131.2(1)	Si(2)–O(6)–Sn(3)	127.9(1)
C(4)–N(1)–Si(1)	115.2(2)	C(4)–N(1)–Si(3)	119.7(2)
Si(1)–N(1)–Si(3)	125.1(1)		

lengths are somewhat shorter compared to the distances observed for the silanetriols. The Sn–O distances are comparable to the values reported for the other stannasiloxanes. The geometry around the tin atoms is distorted tetrahedral. The average O–Sn–O angle is 105.5°. Unlike the tin atom, the two silicons show ideal tetrahedral geometry around them; for example, the average O–Si–O angle is 109.3°.

Conclusion

Unlike the case of reactions between many main-group halides and silanetriols, the reactions using organotin mono-, di-, and trichlorides and (arylamino)-silanetriols lead to the isolation of acyclic, bicyclic, and cubic stannasiloxanes, respectively. The acyclic stannasiloxanes, in particular, have the potential of acting as an alternative source of $RSiO_3^{3-}$ anions. Hence, many reactions involving metal halides that have not been possible directly from silanetriols can now be carried out using compounds such as **3** and **4** (eq 1).

$$nRSi(OSnMe_3)_3 + nR'MX_3 \rightarrow [RSiO_3MR']_n + 3nMe_3SnX \quad (1)$$

Moreover, it would be interesting to exploit the hydrolyzable Si–N bonds in the cubic stannasiloxanes **9** and **10** to generate supramolecular networks based on siloxane frameworks. We are currently exploring these possibilities.

Experimental Section

General Data. All experimental manipulations were carried out under a dry nitrogen atmosphere, rigorously excluding air and moisture. The samples for spectral measurements were prepared in a drybox. Solvents were purified employing conventional procedures and were freshly distilled prior to use. Me_2SnCl_2, Ph_2SnCl_2, and $PhSnCl_3$ (Aldrich) were purchased from commercial sources and were used as received. Silanetriols **1** and **2** were prepared using published procedures.[14d] NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument, and the chemical shifts are reported in ppm with reference to $SiMe_4$ for ^1H and ^{29}Si nuclei and $SnMe_4$ for ^{119}Sn nuclei. The upfield shifts are negative. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer (only the strong absorption bands are given; *vide infra*). Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH5 mass spectrometer. 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.

Preparation of Acyclic Stannasiloxanes 3 and 4. To a solution of $RSi(OH)_3$ (2 mmol; 0.54 g for **1** and 0.65 g for **2**) and NEt_3 (6 mmol, 0.61 g) in hexane (30 mL) and THF (10 mL) was slowly added Me_3SnCl (6 mmol, 1.20 g) in THF (10 mL) dropwise using a dropping funnel at room temperature. After the addition was complete, the reaction mixture was heated under reflux for 6 h and cooled. The solvent was completely removed *in vacuo*, and the residue was extracted with hot hexane (20 mL, approximately 5 times) and filtered to remove $NEt_3{\cdot}HCl$. From the filtrate, on cooling, the stannasiloxanes **3** and **4** are obtained as microcrystalline powders in an analytically pure state.

Preparation of Bicyclic Stannasiloxanes 5–8. To a solution of $RSi(OH)_3$ (2 mmol; 0.54 g for **1** and 0.65 g for **2**) and NEt_3 (6 mmol, 0.61 g) in hexane (30 mL) and THF (10 mL) was added R_2SnCl_2 (R = Me or Ph) (3 mmol, 0.66 g for Me_2SnCl_2, 1.03 g for Ph_2SnCl_2) in THF (10 mL) dropwise at room temperature. The reaction mixture was heated under reflux for 10 h. The solvent from the reaction flask was completely removed *in vacuo*, and the resulting white residue was repeatedly extracted with hot hexane (20 mL, approximately 10 times) and filtered to remove $NEt_3{\cdot}HCl$. When the concentrated filtrate (15 mL) was cooled, the stannasiloxanes **5–8** were obtained as microcrystalline powders. The products can be further purified by recrystallizing from CH_2Cl_2/hexane (1:5 v/v) at 0 °C.

Preparation of Cubic Stannasiloxanes 9 and 10. To a vigorously stirred solution of $RSi(OH)_3$ (2 mmol; 0.54 g for **1** and 0.65 g for **2**) and NEt_3 (6 mmol, 0.61 g) in ether (60 mL), placed in a 100 mL Schlenk flask, was slowly added $PhSnCl_3$ (2 mmol, 0.60 g) dropwise through a 1 mL syringe at room temperature. After the addition, the reaction mixture was stirred for 18 h and subsequently heated under gentle reflux for 3 h. The reaction mixture was cooled to room temperature and filtered to remove $NEt_3{\cdot}HCl$ formed in the reaction. Removal of the solvent from the filtrate *in vacuo* at room temperature yielded the crude stannasiloxanes **9** and **10**. The compounds were purified by crystallizing from CH_2Cl_2/hexane (1:5 v/v) at −20 °C.

Analytical and Spectroscopic Data for 3–10. 3. Yield: 1.14 g (75%). Mp: >200 °C. Anal. Calcd for $C_{20}H_{45}NO_3Si_2Sn_3$: C, 31.6; H, 6.0; N, 1.8. Found: C, 31.5; H, 6.2; N, 2.0. MS (EI, 70 eV): 744 (M^+ − Me, 9%), 165 ($SnMe_3$, base peak). IR (Nujol): 1569, 1303, 1257, 1248, 1153, 1080, 1000, 973, 884, 766, 682 cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): 0.19 (s, $SiMe_3$, 9H), 0.26 (s, $SnMe_3$, 27H), 2.52 (s, Me (aryl), 6H), 6.8–7.0 (m, aromatic CH, 3H).

4. Yield: 1.41 g (87%). Mp: >300 °C. Anal. Calcd for $C_{24}H_{53}NO_3Si_2Sn_3$: C, 35.4; H, 6.5; N, 1.7. Found: C, 35.5; H, 6.6; N, 1.7. MS (EI, 70 eV): 815 (M^+, 14%), 165 ($SnMe_3$, base peak). IR (Nujol): 1245, 1185, 1106, 1045, 965, 938, 837, 770, 539 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 0.0 (s, $SiMe_3$, 9H), 0.2 (s, $SnMe_3$, 27H), 1.1 (dd, $^3J_{HH} = 6.8$ Hz, $CHMe_2$, 12H), 3.7 (sept, CH, 2H), 7.0 (m, aromatic CH, 3H).

5. Yield: 0.75 g (78%). Mp: >220 °C. Anal. Calcd for $C_{28}H_{54}N_2O_6Si_4Sn_3$: C, 34.2; H, 5.5; N, 2.9. Found: C, 34.4; H, 5.5; N, 3.0. MS (EI, 70 eV): 982 (M^+, 5%), 967 ($M^+ - Me$, 10%), 165 ($SnMe_3$, base peak). IR (Nujol): 1257, 1204, 1089, 964, 947, 838, 781, 763, 603, 567, 479 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 0.28 (s, $SiMe_3$, 18H), 0.31 (s, $SnMe_2$, 18H), 2.51 (s, Me (aryl), 12H), 6.8−7.2 (m, aromatic CH, 6H).

6. Yield: 1.15 g (84%). Mp: >280 °C. Anal. Calcd for $C_{58}H_{66}N_2O_6Si_4Sn_3$: C, 51.4; H, 4.9; N, 2.1. Found: C, 50.8; H, 5.0; N, 2.1. MS (EI, 70 eV): 1356 (M^+, 5%), 1162 ($M^+ -$ $RNSiMe_3$, 20%), 154 (Ph_2, base peak). IR (Nujol): 1431, 1257, 1245, 1203, 1080, 1001, 977, 954, 898, 835, 728, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 0.12 (s, $SiMe_3$, 18H), 2.18 (s, Me (aryl), 12H), 6.7−8.6 (m, aromatic, 36H).

7. Yield: 0.94 g (86%). Mp: >250 °C. Anal. Calcd for $C_{36}H_{70}N_2O_6Si_4Sn_3$: C, 39.5; H, 6.4; N, 2.6. Found: C, 39.1; H, 6.2; N, 2.4. MS (EI, 70 eV): 1094 (M^+, 50%), 846 (M − $RNSiMe_3$, base peak). IR (Nujol): 1320, 1243, 1181, 1156, 1106, 1043, 966, 933, 900, 836, 801, 781, 752, 612, 587, 546, 484 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 0.02 (s, $SiMe_3$, 18H), 0.45 (s, $SnMe_2$, 18H), 1.09, 1.12 (d, $CHMe_2$, $^3J_{HH} = 6.8$ Hz, 24H), 3.65 (sept, CH, 4H), 6.97 (m, aromatic, 6H).

8. Yield: 1.33 g (91%). Mp: >300 °C. Anal. Calcd for $C_{66}H_{82}N_2O_6Si_4Sn_3$: C, 54.0; H, 5.6; N, 1.9. Found: C, 54.4; H, 5.9; N, 1.9. MS (EI, 70 eV): 1468 (38, M^+), 289 (Ph_2SnO, base peak). IR (Nujol): 1246, 972, 960, 901, 728, 611, 546, 482 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): −0.4 (s, $SiMe_3$, 18H), 1.00, 1.03 (d, $^3J_{HH} = 6.8$ Hz, $CHMe_2$, 24H), 3.7 (sept, CH, 4H), 7.0−7.4 (m, aromatic CH, 36H).

9. Yield: 0.59 g (64%). Mp: 210−215 °C dec. Anal. Calcd for $C_{68}H_{92}N_4O_{12}Si_8Sn_4$: C, 44.0; H, 5.0; N, 3.0. Found: C, 44.2; H, 4.9; N, 3.2. MS (EI, 70 eV): 1856 (M^+, 3%), 309 (base peak). IR (Nujol): 1260, 1202, 1092, 1080, 1018, 972, 839, 800, 728 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 0.12 (s, $SiMe_3$, 36H), 2.31 (s, CH_3(aryl), 24H), 6.8−7.5 (m, aromatic CH, 32H).

10. Yield: 0.76 g (73%). Mp: >230 °C. Anal. Calcd for $C_{84}H_{124}N_4O_{12}Si_8Sn_4$: C, 48.5; H, 6.0; N, 2.7. Found: C, 48.7; H, 6.1; N, 2.7. MS (EI, 70 eV): 2080 (M^+, 5%), 162 (2,6-*i*-$Pr_2C_6H_3NH_2$, base peak). IR (Nujol): 1261, 1181, 1146, 1092, 1081, 1023, 972, 843, 802, 728 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 0.04 (s, $SiMe_3$, 36H), 0.99, 1.03 (d, $^3J_{HH} = 6.9$ Hz, $CHMe_2$, 48H), 3.60 (sept, CH, 8H), 6.8−7.5 (m, aromatic CH, 32H).

X-ray Structure Determination of 6. Colorless single crystals suitable for X-ray diffraction studies were grown from hexane/CH_2Cl_2 (5:1 v/v) at −10 °C. A suitable crystal of dimensions 0.7 mm × 0.6 mm × 0.6 mm was mounted on a glass fiber and coated with paraffin oil. Diffraction data were collected at 210 K on a Siemens-Stoe AED2 four-circle instrument equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structure was solved by direct methods using SHELXS-90[22a] and refined against F^2 on all data by full-matrix least squares with SHELXL-93.[22b] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. Other details pertaining to the data collection, structure solution, and refinement are listed in Table 3.

Table 3. Crystal Data and Structure Refinement Details for 6

empirical formula	$C_{58}H_{66}N_2O_6Si_4Sn_3$
fw	1355.56
temp, K	210(2)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	14.488(3)
b, Å	23.211(5)
c, Å	18.080(4)
α, deg	90
β, deg	90.71(3)
γ, deg	90
V, Å^3	6080(2)
Z	4
D_{calcd}, g cm^{-3}	1.481
μ, mm^{-1}	1.350
$F(000)$	2728
cryst size, mm	0.7 × 0.6 × 0.6
θ range, deg	3.5−22.6
index range	$-15 \le h \le 15, -3 \le k \le 25, -19 \le l \le 19$
total no. of rflns	9448
no. of indep rflns	7968 ($R_{int} = 0.013$)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	7967/0/668
R1, R2 ($I > 2\sigma(I)$)	0.0205, 0.0493
R1, R2 (all data)	0.0221, 0.0505
S	1.129
largest diff peak and hole, e Å^{-3}	0.487, −0.285

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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, bond distances, and bond angles for **6** (11 pages). Ordering information is given on any current masthead page.

OM960522G

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[22] (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.