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Synthesis and characterization of imidazole–triphenylsilane complexes

Tatiana Eliseeva, Matthew J. Panzner, Willey J. Youngs, Claire A. Tessier *

Department of Chemistry, University of Akron, 190 East Buchtel Commons, Akron, OH 44325-3601, United States

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ABSTRACT

Three imidazole-based triphenylsilane complexes were synthesized as preliminary model complexes to those that have been proposed as intermediates during the enzymatic biomineralization of silica by certain sponges. The active site of the enzyme includes histidine-serine moieties that appear to be vital to functionality. The model compounds include ligands that are bound to the silicon via a Si–O–C linkage and have a potentially chelating imidazole ring. Synthesis of these compounds was achieved by reaction of triphenylchlorosilane with two equivalents of ligand, one equivalent acting as a base for the HCl generated during the reaction. The compounds are highly reactive toward hydrolysis and were characterized by NMR, MS, elemental analysis, and X-ray crystallography.

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1. Introduction

The high level of interest in the mechanisms of silica biomineralization is associated with use of silicon compounds as reagents for new materials [1–3]. During biomineralization, amorphous silica forms from $Si(OH)_4$ under ambient condition and in the presence of biomolecules, especially proteins. In sponges the process is enzymatic and the enzymes are termed silicateins [4]. Studies by Cha and Morse using the non-biological reagent $Si(OEt)_4$ suggested that histidine and serine sites of silicateins play a crucial role in silica formation, and proposed that a five-coordinate silicon intermediate was involved (Fig. 1) [5]. Compounds with similar features to those of Fig. 1 could serve as models for this chemistry.

Described herein are compounds that model some of the features of Fig. 1. The synthesized compounds are of general form $SiPh_3OL$, where L contains imidazole and have been characterized by NMR, mass spectrometry, elemental analyses and X-ray crystallography.

2. Experimental

2.1. General comments

All solvents (THF, ether, acetonitrile, benzene, and methylene chloride) were purchased from Fisher, and were dried and purified by a Pure Solv system by Innovative Technology Inc. [6]. Triphenylchlorosilane ($SiPh_3Cl$) was purchased from Gelest and any trace amounts of HCl were removed under vacuum. 4-Hydroxymethyl-5-methyl imidazole was purchased from VWR and was dried on a high vacuum line by pumping overnight. Pyridine and triethylamine were dried by stirring over BaO overnight, distilled and stored under argon. Compound HOL^3 (6-imidazole-1-ylmethylpyridine-2-ylmethanol) was previously synthesized by the literature procedure and purified by sublimation under vacuum [7]. All deuterated solvents (THF, acetonitrile, methylene chloride, dimethyl sulfoxide) were purchased from Cambridge Isotope Inc. and were dried by literature procedures [8,9]. Unless otherwise specified, all reactions were assembled in a glove box under argon or assembled while the glassware was still hot and immediately pumped down using a Schlenk line [10]. The volatile components were removed from the final products on a high vacuum line, which had an ultimate capability of 2×10^{-4} torr, or using a Schlenk line ($\sim 1 \times 10^{-3}$ torr).

^1H, ^{13}C, and ^{29}Si NMR spectra were obtained on 400 MHz Inova instrument. ^1H spectra were referenced internally to the residual protons of the deuterated solvents. The ^{13}C NMR spectra were referenced internally to the solvent peaks. ^{29}Si NMR spectra referenced externally to $SiMe_4$. In all ^{29}Si NMR samples, chromium acetylacetonate ($Cr(acac)_3$) was added to decrease the relaxation time [11]. Mass spectrometry data were obtained on a Bruker Esquire-LC mass spectrometer. Elemental analyses were performed by Microanalysis Laboratory (University of Illinois, Urbana).

2.2. Synthesis

2.2.1. Synthesis of 1-hydroxydecyl-imidazole (HOL^1)

A solution of 1.4 g (21 mmol) imidazole in 50 mL of dry THF was added to a solution of 0.81 g (21 mmol) potassium hydride in 50 mL of dry THF by canula at 0 °C. The mixture was stirred for 2 h and a solution of 5.0 g (21 mmol) of bromodecanol in 20 mL of THF was added by canula. The mixture was refluxed at 60 °C

* Corresponding author. Tel.: +1 330 972 5304; fax: +1 330 972 6085.
E-mail address: tessier@uakron.edu (C.A. Tessier).

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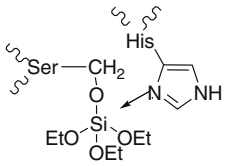


Fig. 1. The five-coordinated silicon intermediate proposed for the reaction of $Si(OEt)_4$ and a silicatein.

for 5 days. The color changed from white to light cream. The precipitate was removed via a frit. The volatile components were removed from the solution under vacuum. From this point, the reaction was conducted in air. Water (10 mL) and 40 mL of ether were added to the product. The ether portion was separated by the separatory funnel and dried with magnesium sulfate, filtered, and the volatile components were removed with a rotary evaporator. The solid product was washed with 20 mL of 4:1 hexane/ethyl acetate and the volatile components were removed on the vacuum line for 48 h. An air stable, colorless, crystalline, solid was obtained in 25% yield, 1.18 g. M.p. = 65 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 1.23 (b, 12H, CH_2), 1.39 (b, 2H, CH_2), 1.67 (m, 2H, CH_2), 3.34 (b, O*H*), 3.92 (t, *J* = 7 Hz, 2H, CH_2), 4.33 (t, *J* = 7 Hz, 2H, CH_2), 6.86, 7.14, 7.59 (s, 3H, imidazole ring). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 25.5 (CH_2), 25.9 (CH_2), 28.5 (CH_2), 28.9 (CH_2), 29.01 (CH_2), 30.6 (CH_2), 32.6 (CH_2), 46.6 (CH_2), 61.4 (CH_2), 119.6 (C*H*), 128.9 (C*H*), 134.8 (C*H*). ESI-MS, *m*/*z*: 225 [M+H$^+$].

2.2.2. Preparation of 1-oxy-10-imidazole-decyl-triphenylsilane ($SiPh_3(OL^1)$)

A solution of 0.26 g (0.9 mmol) $SiPh_3Cl$ in 15 mL acetonitrile was added to a mixture of 0.2 g (0.9 mmol) hydroxydecyl-imidazole (HOL^1) and 0.06 g of pyridine (0.9 mmol) in 30 mL of acetonitrile. The mixture was stirred overnight at RT and was heated 24 h at 50 °C. No precipitation was observed. The volatile components were removed slowly on a Schlenk line, which produced a white solid. Ether (30 mL) was added and the mixture was filtered to separate the product from the pyridine salt. Benzene (30 mL) was added and solution was filtered. A white solid was obtained in 45% yield, 0.20 g. M.p. = 105 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ 1.31 (b, 12H), 1.54 (b, 2H), 1.89 (b, 2H), 3.60 (t, *J* = 6 Hz, 2H, CH_2), 4.17 (b, 2H, CH_2), 7.29 (m), 7.36 (m), 7.49 (m, Ph and imidazole rings overlap), 8.71 (b). ^{13}C NMR (100 MHz, CD_2Cl_2, ppm): δ 26.2 (CH_2), 26.5 (CH_2), 29.1 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 30.6 (CH_2), 33.3 (CH_2), 50.3 (CH_2), 63.2 (CH_2), 100.6 (CH_2), 121.0 (C*H* aromatic), 128.3 (C*H* aromatic), 128.9 (C*H* aromatic), 130.4 (C*H* aromatic), 135.7 (C*H* aromatic), 136.0 (C*H* aromatic), 136.0 (C*H* aromatic). ^{29}Si (79 MHz, CD_2Cl_2, ppm): δ −19. ESI-MS, *m*/*z*: 484 [M+H]$^+$. Anal. Calc. for $C_{31}H_{38}OSiN_2$: C, 77.13; H, 7.93; N, 5.80. Found: C, 70.98; H, 6.10; N, 3.87%.

2.2.3. Preparation of 4-methoxy-5-methyl-imidazole-triphenylsilane ($SiPh_3(OL^2)$)

Route A. 4-Hydroxymethyl-5-methyl imidazole (HOL^2) (0.5 g, 4.5 mmol) was added to a solution of 0.66 g (2.3 mmol) $SiPh_3Cl$ in 40 mL acetonitrile and stirred under N_2 at RT. After 15 min, formation of a white precipitate was observed. The mixture was stirred for 24 h and filtered via a frit. The volatile components were removed under vacuum. Methylene chloride (30 mL) was added to dissolve the product. The suspension was filtered via a frit. The volatile components were removed under vacuum. A colorless, crystalline solid was obtained in 81% yield, 0.69 g. M.p. = 98 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ 1.99 (s, CH_3), 4.78 (s, CH_2), 7.39, 7.61 (m, phenyl and imidazole rings). ^{13}C NMR (100 MHz, CD_2Cl_2, ppm): δ 11.0 (CH_3), 58.1 (CH_2), 128.5, 129.3, 130.4, 130.7, 133.9, 134.6, 135.5, 135.7, 135.9, 136.3 (C*H* Ph and imidazole rings). ^{29}Si (79 MHz, CD_2Cl_2, ppm): δ −13. Anal. Calc. for $C_{23}H_{22}SiON_2$: C, 74.76; H, 5.73; N, 7.58. Found: C, 74.01; H, 5.77; N, 5.18%.

Route B. By this route, formation of two products is observed. A solution of 1.32 g (4.5 mmol) $SiPh_3Cl$ in 20 mL acetonitrile was added to a suspension of 0.5 g (4.5 mmol) 4-hydroxymethyl-5-methyl imidazole (HOL^2) and 0.5 g (4.5 mmol) of triethylamine in acetonitrile. The mixture was refluxed at 80 °C for 24 h, cooled to RT and stirred for 24 h. No precipitate was observed. A quarter of the solvent was removed on Schlenk line and a white precipitate appeared. The mixture was filtered via a frit. The volatile components were removed under vacuum. Acetonitrile (30 mL) was added to the product and the mixture was filtered via a frit. The volatile components were removed from the solution slowly on the vacuum line. The acetonitrile extraction was repeated three times. Crystals formed over 12 h. M.p. = 97 °C. $SiPh_3OL^2$ was obtained in very low yield (under 10%). ^{1}H NMR (400 MHz, THF-d_8, ppm): δ 1.97 (s, CH_3), 3.62 (s, CH_2), 7.32, 7.60 (m, Ph and imidazole rings overlap). ^{13}C NMR (100 MHz, THF-d_8, ppm): δ 11.0 (CH_3), 58.8 (CH_2), 128.5, 128.7, 130.3, 130.8, 135.6, 136.0, 136.5, 138.2 (C*H* Ph and imidazole rings). ^{29}Si (79 MHz, THF-d_8, ppm): δ −14, −10. ESI-MS, *m*/*z*: 371 [M+H]$^+$.

Impurities: $(CH_3CH_2)_3N$ H^+Cl^-: ^{1}H NMR (400 MHz, THF-d_8, ppm): δ 1.77 (s), 3.60 (s). ^{13}C NMR (100 MHz, THF-d_8, ppm): δ 11.0, 58.8.

2.2.4. Preparation of 6-imidazole-1-ylmethyl-pyridine-2-yl-methoxy-triphenylsilane ($SiPh_3(OL^3)$)

A solution of 0.16 g (0.5 mmol) $SiPh_3Cl$ in 15 mL acetonitrile was added to a solution of 0.2 g (1.1 mmol) 6-imidazole-1-yl-methyl-pyridine-2-yl-methanol (HOL^3) in 15 mL of acetonitrile. The mixture was stirred overnight at RT and no precipitation was observed. The volatile components were removed slowly on a Schlenk line and a white precipitate formed. Methylene chloride (30 mL) was added to dissolve the product. The mixture was stirred and filtered via a frit. The volatile components from the solution were slowly removed on the vacuum line. Colorless crystals formed overnight. The yield was 89%, 0.20 g. M.p. = 89 °C. ^{1}H NMR (400 M Hz, CD_2Cl_2, ppm): δ 4.95 (s, CH_2), 5.13 (s, CH_2), 6.86 (b, C*H*), 6.96 (s, C*H*), 7.02 (s, C*H*), 7.27 (m, C*H*), 7.40 (m, C*H*), 7.47 (b, C*H*), 7.53 (b, C*H*, phenyl and imidazole rings overlap), 7.65, 7.67 (pyridine ring). ^{13}C NMR (100 MHz, CD_2Cl_2, ppm): δ 53.4 (CH_2), 67.7 (CH_2), 120.8 (C*H* aromatic), 128.9 (C*H* aromatic), 129.2 (C*H* aromatic), 130.6 (C*H* aromatic), 131.1 (C*H* aromatic), 131.5 (C*H* aromatic), 134.9 (C*H* aromatic), 136.3 (C*H* aromatic), 136.6 (C*H* aromatic), 138.8 (C*H* aromatic), 139.0 (C*H* aromatic). ^{29}Si (79 MHz, CD_2Cl_2, ppm): δ −11. ESI-MS, *m*/*z*: 448 [M+H$^+$]. Anal. Calc. for $C_{28}H_{25}SiON_3$: C, 75.15; H, 5.63; N, 9.39. Found: C, 68.76; H, 5.61; N, 11.33%.

2.3. Single-crystal X-ray diffraction studies

Crystal structures of HOL^1, $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$ were obtained. In the glovebox, the crystals were put into paratone oil on a glass slide and were placed in a desiccator. In air and as quickly as possible, the oil-covered crystals were examined under a microscope and mounted in the cold stream of the diffractometer.

Crystal data were collected on Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cells were determined as a result of reflection of three different orientations. Integrations of the data were done by SAINT and for an empirical absorption corrections (as well as and other corrections) multi-scan SADABS were applied [12]. Structure solution, refinement and modeling were completed using the Bruker SHELXTL package [13]. The structure was determined by full-matrix least-squares refinement of F^2 and the selection of the appropriate atoms

Table 1
Crystallographic and data collection parameters.

	$C_{13}H_{24}N_2O$ (HOL^1)	$C_{23}H_{22}N_2OSi$ ($SiPh_3OL^2$)	$C_{28}H_{25}N_3OSi$ ($SiPh_3OL^3$)
Formula weight	224.34	370.52	447.60
T (K)	100(2)	100(2)	100(2)
Crystal dimension (mm)	0.34 × 0.32 × 0.08	0.70 × 0.13 × 0.07	0.46 × 0.18 × 0.09
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$
a (Å)	7.3483(14)	9.7024(15)	9.9518(11)
b (Å)	5.0942(10)	14.885(2)	23.709(3)
c (Å)	17.320(3)	16.040(3)	10.7519(12)
α (°)	90	111.814(3)	90
β (°)	94.455(3)	106.339(3)	113.432(2)
γ (°)	90	95.631(3)	90
V (Å^3)	646.42(2)	2009.6(5)	2327.7(4)
Z	2	4	4
ρ_{calc} (mg m^{-3})	1.153	1.225	1.277
μ (mm^{-1})	0.073	0.131	0.127
2θ limit (°)	52.6	56.6	52.6
	$-9 \leqslant h \leqslant 9$	$-12 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 12$
	$-6 \leqslant k \leqslant 6$	$-19 \leqslant k \leqslant 19$	$-29 \leqslant k \leqslant 29$
	$-21 \leqslant l \leqslant 21$	$-21 \leqslant l \leqslant 21$	$-13 \leqslant l \leqslant 13$
Total data collected	5156	17 597	18 458
Number of independent reflections	2585	9093	4730
R_{int}	0.0302	0.0448	0.0424
Absorption correction	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SADABS)
Transmission: t_{min}/t_{max}	0.9773/0.9942	0.9137/0.9909	0.9439/0.9887
Number of data/restraints/parameters	2585/1/146	9093/0/489	4730/0/298
R_1 [$F_o^2 \geqslant 2(F_o^2)$]	0.0514	0.0619	0.0455
wR_2 [$F_o^2 \geqslant -3(F_o^2)$]	0.1229	0.1225	0.0996
Goodness-of-fit	1.182	1.069	1.077

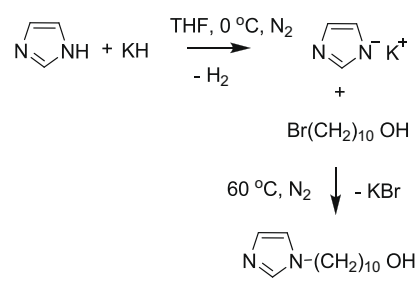
from the generated difference map. Hydrogen atom positions were calculated with the exception of the imidazole N-hydrogen atoms in the structure of $SiPh_3(OL^2)$. Crystallographic and data collection parameters are listed in Table 1.

3. Results and discussion

Three compounds of general formula $SiPh_3OL$ where L contains an imidazole were prepared. The three HOL precursor ligands are defined in Eq. (1). HOL^2 was available commercially and HOL^3 by following a literature synthesis [7]. The synthesis of HOL^1 is reported below.

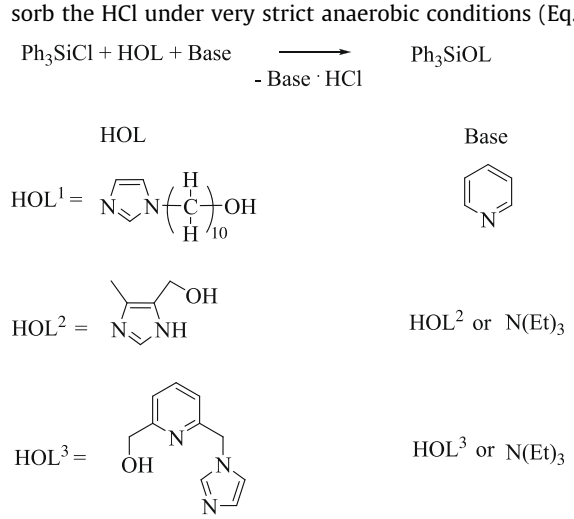
HOL^1 was synthesized by a two-step reaction sequence (Scheme 1). Imidazole was deprotonated with KH in THF at 0 °C to the potassium imidazole salt. The potassium imidazole was reacted with bromodecanol in refluxing THF to give HOL^1 and a precipitate, presumably KBr. The low yield of the compound HOL^1 was due to its partial solubility in water during the ether extraction in the work-up. The ^1H NMR spectrum of HOL^1 showed a broad signal at δ 1.23, 1.39 and multiplet at δ 1.67 ppm, consistent with the long organic chain. A broad signal at δ 3.34 ppm was assigned to the hydroxyl group and triplets at δ 3.92 and 4.33 ppm indicated methylene groups next to a hydroxyl group and an imidazole ring. The three singlets at 6.87, 7.14 and 7.59 ppm were assigned to imidazole ring. ^{13}C NMR data supported structure of HOL^1. ES mass spectroscopy showed m/z 225 for $H(HOL^1)^+$. HOL^1 was soluble in DMSO, acetonitrile, methylene chloride, and THF.

The thermal ellipsoid plot of HOL^1 is depicted in Fig. 2. The asymmetric unit contains one HOL^1 molecule. The solid state structure consists of an imidazole ring substituted at the N_1 nitrogen atom by a linear decanol chain. All bond lengths and angles are at the expected values. Extended linear chains of HOL^1 molecules are generated in the solid by means of O–H···N hydrogen-bonds (N(2)···O(1) = 2.834 Å) at both ends of the molecules.



Scheme 1. Synthesis of HOL^1.

The three $SiPh_3(OL)$ compounds were obtained from the reactions of $SiPh_3Cl$ with the three HOL in the presence of a base to absorb the HCl under very strict anaerobic conditions (Eq. (1))



(1)

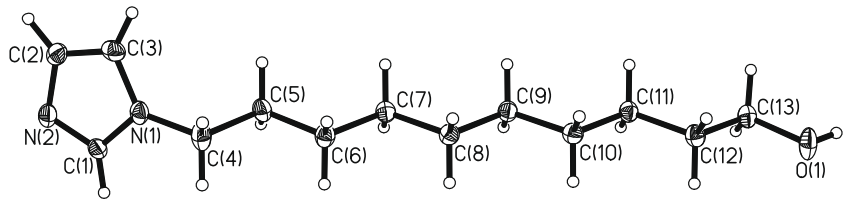


Fig. 2. Molecular structure of HOL[1] with thermal ellipsoids depicted at 50% probability.

The best syntheses of $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$, which were obtained in over 80% yields, involved the reactions of 1 M equivalent of $SiPh_3Cl$ with 2 M equivalents of the respective HOL at room temperature. Under these conditions, the imidazole of one equivalent of HOL removes HCl from reaction by formation of HOL(HCl) and second equivalent of the ligand reacts with $SiPh_3Cl$ to form $SiPh_3OL$. The use of cheaper base pyridine was acceptable in the synthesis of $SiPh_3OL^1$, which was obtained in 45% yield. The use of the cheaper and less basic (than the imidazole of HOL) NEt_3 was not the best choice for the synthesis of $SiPh_3OL^2$ and $SiPh_3OL^3$ because low yields were obtained. The $SiPh_3OL^2$ and $SiPh_3OL^3$ products from such reactions were difficult to separate from $HNEt_3Cl$ and formation of both $SiPh_3OL$ and $Ph_3SiOSiPh_3$ was observed. The formation of the by-product $SiPh_3OSiPh_3$ is probably due to the reaction of HOL with HCl to first give Cl–L and H_2O. The H_2O then reacts with $SiPh_3Cl$ to give $Ph_3SiOSiPh_3$ and more HCl, which can reinitiate the process that leads to the $Ph_3SiOSiPh_3$ [14]. Apparently, with the weaker bases, HCl is less tightly bound and more able initiate the two-step synthesis of $SiPh_3OSiPh_3$. The crystal structure and other characterizational data for $SiPh_3OSiPh_3$ were as those in the literature [15,16].

The three $SiPh_3OL$ compounds had limited solubility in organic solvents. The compounds were reactive towards water, especially in solution. Satisfactory elemental analyses were difficult to attain. Though there was no evidence of a persistent bond between the imidazole nitrogen atom and the silicon center of the three $SiPh_3OL$ (see below), the presence of an imidazole-containing L substituent appears to increase their water reactivity relative to $SiPh_3OR$ that contain hydrocarbon R groups [17].

The three $SiPh_3OL$ were characterized by ^{29}Si NMR spectroscopy. The ^{29}Si chemical shifts for $SiPh_3(OL^1)$, $SiPh_3(OL^2)$, and $SiPh_3(OL^3)$ were observed at −19, −13, and −11 ppm, respectively, which is consistent with four-coordinated silicon compounds of the general form $SiPh_3OR$ [18]. For example, the chemical shift for $SiPh_3OEt$ is −14 ppm (DMSO-d_6).

The $SiPh_3OL$ compounds were characterized by other spectral means. The ^1H NMR spectrum of $SiPh_3(OL^1)$ showed broad signals at δ 1.31, 1.54, and 1.89 ppm that are assigned to the long organic chain, and broad signals at δ 3.60 ppm and δ 4.17 ppm indicated methylene groups next to the oxygen and an imidazole ring of the complex. Some broadening of the signals and discrepancies in the elemental analysis may be attributed to partial protonation of the imidazole ring by HCl generated in the reaction. A multiplet at δ7.29–7.49 ppm is attributed to the overlap the resonances from the imidazole and phenyl rings of $SiPh_3(OL^1)$. The ^1H NMR spectrum of the compound $SiPh_3(OL^2)$ showed a singlet at δ 1.97 ppm corresponding to the methyl group, a singlet at δ 4.77 ppm for methylene group, and two multiplets at δ 7.32 and 7.60 ppm for the imidazole and phenyl rings protons. The ^1H NMR spectrum of $SiPh_3(OL^3)$ showed broad signals at δ 4.95 and 5.13 ppm for the methylene groups near to oxygen and imidazole and pyridine. The signals at δ 6.86, 7.02, 7.27, 7.40, 7.47, and 7.53 ppm assigned to the phenyl and imidazole rings. The signals at δ 6.96, 7.65, and 7.67 ppm are attributed to the pyridine ring of $SiPh_3(OL^3)$. ^{13}C NMR data of the three $SiPh_3(OL)$ supported the structures shown on Scheme 1 and ES mass spectroscopy showed m/z for a protonated $SiPh_3(OL\text{-}H)^+$ ion.

Crystals of $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$ suitable for single crystal X-ray diffraction studies were grown from concentrated acetonitrile and methylene chloride solutions, respectively, but suitable crystals of $SiPh_3(OL^1)$ could not be obtained. Selected distances and angles of $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$are listed in Table 2 and thermal ellipsoid plots are shown in Figs. 3 and 4, respectively. The asymmetric unit of $SiPh_3(OL^2)$ consists of two slightly different molecules whereas that of $SiPh_3(OL^3)$ consists of one molecule. In both $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$, the distorted, tetrahedral silicon atom is coordinated to three phenyl groups and one OL ligand.

Table 2
Selected distances and angles in the crystal structures of $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$.

Bond length (Å)	$SiPh_3(OL^2)$		$SiPh_3(OL^3)$
	Molecule 1	Molecule 2	
Si–O	1.6443(16)	1.6430(16)	1.6394(13)
Si–C	1.867(2)	1.864(2)	1.8628(17)
	1.868(2)	1.875(2)	1.8697(18)
	1.871(2)	1.880(2)	1.8711(17)
Bond angle (°)			
O–Si–C	103.15(9)	104.11(9)	104.07(7)
	110.66(9)	109.55(10)	109.76(7)
	111.83(9)	112.61(9)	112.15(7)
C–Si–C	109.49(10)	107.52(10)	109.10(8)
	110.41(10)	109.66(10)	109.38(8)
	111.08(10)	113.33(10)	112.35(8)
Si–O–C	124.87(15)	126.16(14)	125.58(11)

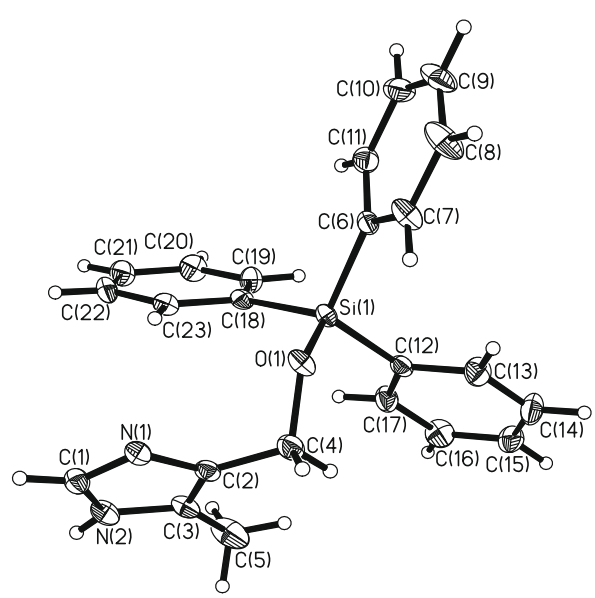


Fig. 3. Molecular structure of one of the two molecules of $SiPh_3(OL^2)$ with thermal ellipsoids depicted at 50% probability.

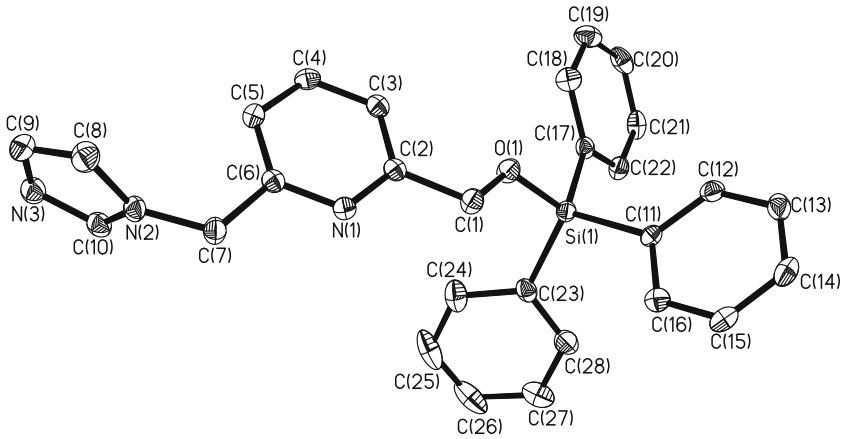


Fig. 4. Molecular structure of complex $SiPh_3(OL^3)$ with thermal ellipsoids depicted at 50% probability. Hydrogen atoms were removed for clarity.

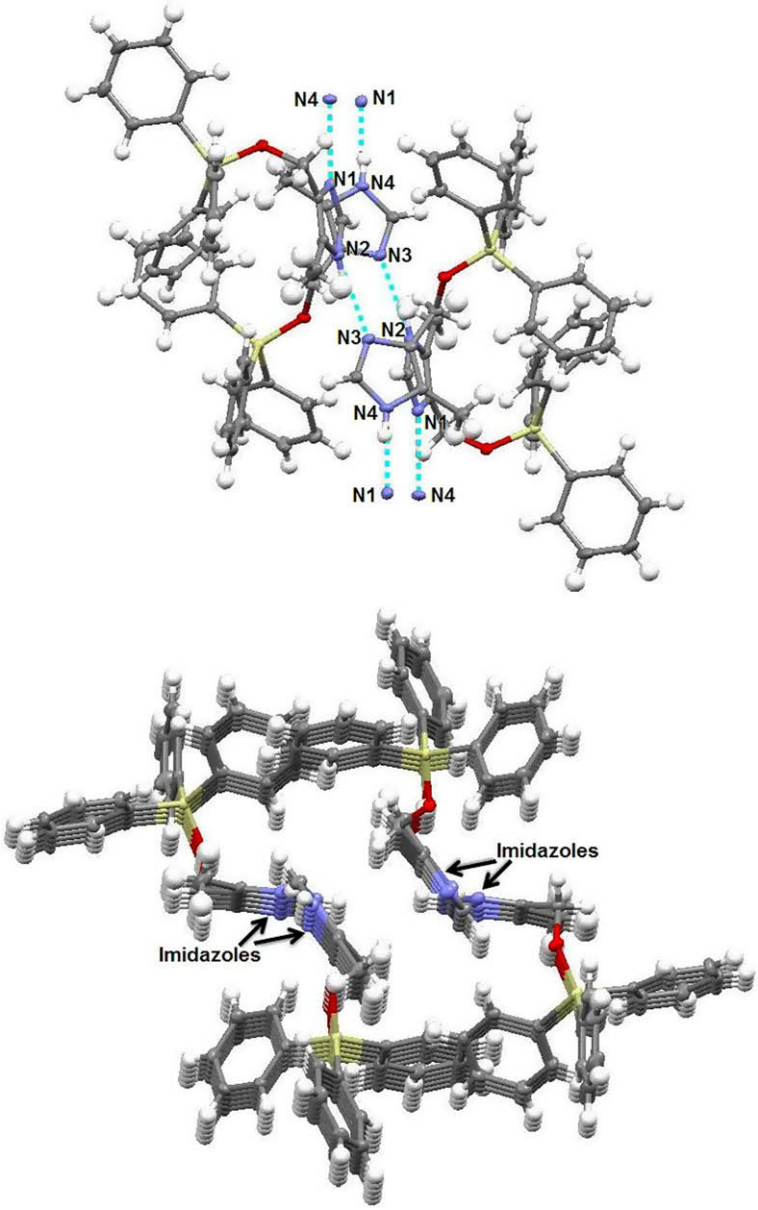


Fig. 5. (Top) One of the two chains of N–H···N hydrogen bonds in a column of $SiPh_3OL^2$ molecules viewed roughly along the *a* axis with thermal ellipsoids depicted at 50% probability. Four molecules of $SiPh_3OL^2$ are shown completely. The nitrogen atoms of four next nearest molecules (additional N1 and N4 atoms) are also shown to indicate the direction of the next N–H···N hydrogen bonds. (Bottom) A column of stacked $SiPh_3OL^2$ molecules viewed roughly perpendicular to the *a* axis and shown with thermal ellipsoids depicted at 50% probability. There are two chains of N–H···N hydrogen-bonded imidazoles per column of $SiPh_3OL^2$ molecules.

The Si–O distances of the two molecules of $SiPh_3OL^2$ are slightly longer than those in $SiPh_3OL^3$ and both are shorter than those in $O(SiPh_3)_2$ (1.616(1) Å). As expected [16], the Si–O–C angles in both structures are about 15–16° higher than that expected of a tetrahedral structure.

Several intermolecular distances shorter than the sum of van der Waal's radii were observed in both the structures $SiPh_3(OL^2)$ and $SiPh_3(OL^3)$ and these may account for the low solubility of the compounds. Most importantly, N–H···N hydrogen bonding interactions were observed between molecules of $SiPh_3(OL^2)$ with a donor-acceptor distance of 2 .83 Å between N(2) and N(3) and 2.80 Å between N(1) and N(4). As in unsubstituted imidazole [19], the N–H···N hydrogen bonds connect the imidazole rings of $SiPh_3(OL^2)$ into a chain. The long range structure of $SiPh_3(OL^2)$ consists of columns along the *a* axis, with two such imidazole chains running along the center of the column and the triphenylsilyl groups at the periphery of the column (Fig. 5). Other short contacts in the crystal structure of $SiPh_3(OL^2)$ were observed, specifically O···H-C, C–H···π(Ph) and C–H···π(imidazole) contacts. N(imidazole)···H–C, C–H···π(Ph) and C–H···π(imidazole) short contacts were observed in the crystal structure of $SiPh_3(OL^3)$. Neither the pyridine nitrogen atom nor the oxygen atom of $SiPh_3(OL^3)$ were involved in the short contacts.

The lack of persistent Si-imidazole contacts in the $SiPh_3(OL)$ compounds described above appears to be due to the steric congestion at silicon provided by the three phenyl groups. We have investigated the synthesis of several other $Si(OL)_nR_{4-n}$ (n = 1–4, OL = OL^1, OL^2, OL^3) compounds that have lower steric hindrance at the silicon atom. In some cases, ^{29}Si NMR spectra indicated that five- or six-coordinated silicon centers had formed ($\delta < -150$ ppm) [18] but the compounds were impure and even more hydrolytically unstable than $SiPh_3(OL)$ compounds reported herein.

4. Conclusion

New triphenylsilicon complexes with different imidazole-containing ligands were synthesized and characterized by NMR, mass spectroscopy and crystallographic methods. The syntheses were complicated by formation of the by-product $(O(SiPh_3)_2$ during the reactions which involved the use of the bases pyridine and triethylamine. In reactions where HOL was used as a base and as a ligand, $O(SiPh_3)_2$ was not formed. No interaction between the silicon atoms and the basic imidazole nitrogen was observed in solution or the solid state, probably because of the steric congestion provided by the three phenyl rings on the silicon atom. We will continue our efforts to isolate such five-coordinated compounds.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.005.

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