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Synthesis and Characterization of Neutral *cis*-Hexacoordinate Bis(*β*-diketonate) Silicon(IV) Complexes

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Three new neutral *cis*-hexacoordinate bis(*β*-diketonato) silicon(IV) complexes, $(thd)_2SiX_2$, where X = Me (**1**), ^tBuO (**2**), and ^tAmO (**3**), and thd = 2,2,6,6-tetramethyl-3,5-heptanedionato, were synthesized in high yield. Single crystal X-ray crystallographic analysis revealed that **1** was monomeric with *cis*-hexacoordinate octahedral geometry on the silicon and oxygen atoms. Crystal data: empirical formula $C_{24}H_{46}O_4Si$, crystal system monoclinic; space group $P2_1/n$; unit cell dimensions $a = 10.4195(5)$ Å, $b = 19.7297(10)$ Å, $c = 13.6496(7)$ Å; $\beta = 102.6590(10)°$; $Z = 4$. Variable temperature NMR confirmed $(thd)_2SiX_2$ maintained *cis*-geometry in solution by observing two distinct methyl proton resonances (of thd) at room temperature or low temperatures. These compounds show potential for use as low temperature silicon oxide CVD precursors for transition metal silicate high κ gate dielectrics.

1. Introduction

The synthesis, structure, and distinctive reactivity of silicon compounds with coordination numbers greater than five, six, and even higher continue to be an area of lively interest.[1−8] Ligands of β-diketonates are well-known in the synthesis of hypercoordinate silicon compounds. For example, the first ionic acetylacetonate (acac) silicon complex, e.g., $Si(acac)_3Cl\cdot HCl$, was reported in 1903.[9] However, only a few neutral hypercoordinate bis(β-diketonate) silicon(IV) complexes, where β-diketonate = acetylacetonate, have been reported to date.[10−13] The first complexes of $(acac)_2SiClMe$, $(acac)_2SiClPh$, and $(acac)_2SiMe_2$ were reported to be highly unstable, and the isolation yield of $(acac)_2SiMe_2$ was extremely low, only about 10%.[10] The preparation of $(acac)_2SiCl_2$ provided a very poor yield as well.[12] However, $(acac)_2Si(OAc)_2$ is more stable, most likely because of the greater electronegativity of the donor oxygen.[11] Structural characterization work of these bis(acetylacetonate) silicon(IV) compounds largely depended on indirect techniques, such as elemental analysis, UV, IR, and ^{29}Si NMR spectroscopic methods.[10,13−15] For example, the structures of $(acac)_2SiClMe$ and $(acac)_2SiClPh$ were proposed as hexa-

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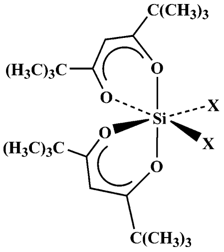
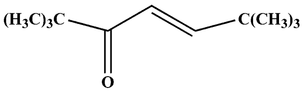
coordinate complexes and that of $(acac)_2SiMe_2$ as tetracoordinate by means of infrared spectroscopy.[10] Contrary to $(acac)_2SiMe_2$, the $(acac)_2SiPh_2$ was reported as a *trans*-hexacoordinate complex on the basis of NMR data.[13] It was concluded that the phenyl group is more favorable for hexacoordination than the methyl group despite the controversy.[1] No crystal structures have been reported previously for neutral hexacoordinate bis(β-diketonate) silicon(IV) complexes.

Our interest in synthesis and characterization of a number of new bis(β-diketonate) silicon(IV) compounds, in particular, $(thd)_2SiX_2$, is 2-fold: (i) to derive a better understanding of the structure of bis(β-diketonate) silicon(IV) complexes; and (ii) to synthesize stable silicon complexes in high yield with empirical formula $(\beta\text{-diketonate})_2SiX_2$ for emerging technological applications of silicate high κ gate thin films formed by chemical vapor deposition (CVD). There is a need to replace currently used SiO_2 or SiON gate dielectrics with high κ gate thin films.[16,17] Amorphous hafnium silicates and zirconium silicates, $M_xSi_{1-x}O_2$, where M = Hf or Zr are very promising candidates for replacing SiO_2 and SiON gate dielectrics.[18-20] To deposit $Hf_xSi_{1-x}O_2$ or $Zr_xSi_{1-x}O_2$ thin films, both Hf- (or Zr-) and Si-containing compounds are required for the use as CVD precursors. The compounds of $(thd)_2Zr(OR)_2$ and $(thd)_2Hf(OR)_2$ were demonstrated previously as low temperature CVD precursors for ZrO_2 and HfO_2 and related materials such as $PbZr_xTi_{1-x}O_3$ (PZT).[21-23] However, the stable analogous silicon compounds of $(thd)_2SiX_2$ compounds were not available. We believe these compounds of $(thd)_2SiX_2$ would achieve chemical compatibility with similar co-reactants, such as $(thd)_2M(OPr^i)_2$, where M = Zr and Hf. By utilizing similar ligand sets, it is likely that the two precursors would be chemically compatible upon mixing in solution for liquid delivery CVD or in the vapor phase, which significantly reduces the complication incurred by a set of incompatible precursors in a CVD process.[24]

In this work, we reacted 2 equiv of Na(thd) with 1 equiv of the corresponding silicon dichloride to synthesize the $(thd)_2SiX_2$ complexes. Three new compounds, $(thd)_2SiX_2$, have been synthesized in high yield and high purity, where X = $-$Me (**1**), $-OBu^t$ (**2**), and $-OAm^t$ (**3**) (^tAm = 1,1-dimethylpropyl). They are very stable. However, when we reacted 2 equiv of Na(thd) with 1 equiv of $H_2SiCl_2\cdot(tmeda)$ (tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$), instead of "$(thd)_2SiH_2$", 1,1,6,6-tetramethyl-hepta-3-one-4-ene (**4**) was isolated, a reduced and eliminated product of the "thd" ligand.



1, X = Me
2, X = OBu^t
3, X = OAm^t



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In this paper, we report the synthesis and characterization, in particular the structural characterization, of these new compounds. They have been characterized by elemental analysis, NMR, FT-IR, and single crystal X-ray diffraction. Thermal analysis has also been performed to qualitatively evaluate their volatility and thermal stability for potential use as CVD precursors. Recently, the compound of $(thd)_2Si(OBu^t)_2$ (**2**) has been used together with $(thd)_2Zr(OPr^i)_2$ in a hydrocarbon solution to deposit zirconium silicates ($Zr_xSi_{1-x}O_2$). High quality zirconium silicate high κ gate dielectric thin films have been successfully deposited on Si(100) at 550 °C under reactive gas of nitric oxide (NO).[25]

2. Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored in a drybox. H(thd) was purchased from Aldrich Chemical Co. and purified by distillation. $SiCl_4$, *tert*-butyl alcohol, and *tert*-amyl alcohol were purchased from Aldrich Chemical Co. and used without further purification. Me_2SiCl_2 and H_2SiCl_2 were purchased from Gelest, Inc., and used directly. $SiCl_2(OBu^t)_2$ and $SiCl_2(OAm^t)_2$ were synthesized in ATMI, Inc., using the procedure reported in the literature previously by reacting $SiCl_4$ with 2 equiv of the corresponding alcohol in the presence of 2 equiv of pyridine in a hexane solvent.[26] $H_2SiCl_2\cdot(tmeda)$ was synthesized in ATMI, Inc., using the procedure described in the literature.[27] Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini 300 NMR spectrometer by using the protio impurities of the deuterated solvents as a reference. ^{29}Si NMR spectra were recorded on a JEOL-400 NMR spectrometer (JEOL probe and console using an Oxford Magnet) by Acorn NMR, Inc., Livermore, CA. ^{29}Si nucleus was observed at 79.4 MHz. ^{29}Si chemical shifts were referenced by the spectrometer software on the basis of the lock such that if TMS were present it would theoretically be observed at 0 ppm. Thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) were performed on a NETZSCH 490 thermogravi-

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metric analyzer. FT-IR spectra were recorded on a Nicolet MAGANA-R 760 spectrometer.

Synthesis and Characterization of $(thd)_2SiMe_2$ (1). A 500 mL Schlenk flask was charged with 5 g (38.7 mmol) of $SiCl_2Me_2$, 50 mL of dry diethyl ether, and a stir bar. Then, 15.9 g (77.1 mmol) of Na(thd) in 200 mL of dry ether was added into the Schlenk flask slowly at 0 °C, under magnetic stirring. The mixture immediately became cloudy. Upon the completion of addition, the mixture was refluxed overnight. The solvent was then stripped off to dryness under vacuum. The solid residue was extracted by dry hexane. The mixture was filtered through a Celite filtration medium to obtain a slightly yellow solution. Removal of volatiles from the filtrate under vacuum gave 15 g of crystalline solid product (yield 91%). The product was characterized as $(thd)_2SiMe_2$ (**1**) by NMR, elemental analysis, FT-IR, and single crystal X-ray diffraction. NMR (C_6D_6) δ(ppm): ^1H, 5.69 (s, 2H, 2 × C*H* of thd), 1.10 (s, 36H, 12 × C*H₃* in thd), and 0.66 (s, 6H, 2 × Si−C*H₃*); $^{13}C\{^1H\}$, 199.2 (s, *C*═O), 89.9 (s, *C*H₂ of thd), 40.3 (s, −*C*(CH₃)₃ of thd), 27.9 (s, s, −C(*C*H₃)₃ of thd), 12.1 (s, Si−*C*H₃). ^{29}Si, 138.87. FT-IR (Nujol and KBr window), ν (cm^{-1}): 1680 (w), 1598(m), 1569(s), 1537(s), 1505(s), 1460(s), 1403(s), 1378(s), 1359(s), 1225(m). Anal. $C_{24}H_{44}O_4Si$, Calcd: C, 67.87; H, 10.44. Found: C, 67.57; H, 10.72.

$(thd)_2Si(OBu^t)_2$ (2). The synthesis was similar to that described above. Anhydrous toluene was used instead of dry ether as the solvent for the reaction. The reaction mixture was refluxed for 24 h. After filtration and evaporation of volatiles in a vacuum, a white solid product was obtained in a yield of 92%. The solid product was characterized in C_6D_6 as $(thd)_2Si(OBu^t)_2$ (**2**) by NMR, FT-IR, and elemental analysis. Mp: 222 °C. NMR (C_6D_6), δ (ppm): ^1H, 5.78 (s, 2H, 2 × C*H* of thd), 1.61 (s, 18H, 2 × −OC(C*H₃*)₃), 1.22 and 1.04 (broad, 36H, 12 × C*H₃* of thd); $^{13}C\{^1H\}$, 199.0 (b, *C*═O), 91.2(s, *C*H₂ of thd), 69.9 (s, −O*C*(CH₃)₃), 40.4 (s, −*C*(CH₃)₃ of thd), 28.2 (s, −C(*C*H₃)₃ of thd); ^{29}Si, 186.18. FT-IR (Nujol and KBr window) ν (cm^{-1}): 1599(m), 1570(m), 1537(s), 1507(s), 1460(s), 1410(m), 1376(s), 1226(m), 1037(s). Anal. $C_{30}H_{56}O_6Si$ Calcd: C, 66.62; H, 10.44. Found: C, 66.35; H, 10.57.

$(thd)_2Si(OAm^t)_2$ (3). This product is a white solid (yield 90%). The synthesis was the same as that described for **2**. The synthesized product was characterized by solution NMR in C_6D_6, FT-IR, and elemental analysis. Mp: 226 °C. NMR (C_6D_6), δ (ppm): ^1H, 5.76 (s, 2H, 2 × C*H* of thd), 1.77 (q, 4H, C*H₂* of Et), 1.56 (s, 12H, −OC(C*H₃*)₂Et), 1.15 (t, 6H, 2 × C*H₃* of Et), 1.22 and 1.02 (broad, 36H, 12 × C*H₃* of thd); $^{13}C\{^1H\}$, 198.2 and 199.0 (s, *C*═O of thd), 91.3 (s, *C*H of thd), 72.2 (s, −O*C*Me₂Et), 40.4 and 39.3 (s, −*C*(CH₃)₃ of thd), 29.1 and 29.3 (s, *C*H₂ of Et), 28.4 and 28.2 (s, OC(*C*H₃)₂), 10.3 (s, CH₂*C*H₃); ^{29}Si, 186.21. FT-IR (Nujol and KBr window) ν (cm^{-1}): 1599(m), 1571(m), 1537(s), 1508(s), 1460(s), 1410(m), 1377(s). Anal. $C_{32}H_{60}O_6Si$ Calcd: C, 67.56; H, 10.63. Found: C, 67.53; H, 10.27.

Attempted Synthesis of "$(thd)_2SiH_2$". Using the same procedure as described, 1 equiv of $SiH_2Cl_2\cdot$(tmeda) was reacted with 2 equiv of Na(thd) in dry diethyl ether in a Schlenk flask. The mixture was refluxed overnight. The solvent was then pumped off to dryness, and an off-white solid was obtained. Even at room temperature, colorless needle shaped crystals were grown on the top of the flask overnight. Sublimation gave the same crystalline solid material. The crystalline material was characterized by ^1H NMR in C_6D_6 as 1,1,6,6-tetramethyl-hepta-3-one-4-ene (**4**). NMR (C_6D_6), δ (ppm): ^1H, 7.38 (d, 1H, ═C*H*), 6.40 (d, 1H, ═C*H*), 1.07 (s, 9H, −C(C*H₃*)₃), 0.88 (t, 9H, 2 × −C(C*H₃*)₃).

X-ray Crystallographic Studies. Single crystals of **1** were grown from its hexane solution at −18 °C. Suitably sized single crystals were selected for crystallographic studies. A summary of the crystallographic data and experimental details for the X-ray diffraction studies is presented in Table 1.

Table 1. Crystallographic Data for **1**

empirical formula	C24 H46 O4 Si
fw	426.70
temp	173(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimensions	$a = 10.4195(5)$ Å
	$b = 19.7297(10)$ Å
	$c = 13.6496(7)$ Å
	$\beta = 102.6591(10)°$
V	2737.8(2) Å^3
Z	4
d (calcd)	1.035 Mg/m^3
abs coeff	0.109 mm^{-1}
reflns collected	10704
indep reflns	4336 [R(int) = 0.0207]
completeness to $\theta = 25.00°$	93.8%
max and min transm	0.9786 and 0.9578
data/restraints/params	4336/0/318
GOF on F^2	1.570
final R indices [$I > 2\sigma(I)$]	R1 = 0.0713, wR2 = 0.2495
largest diff peak and hole	0.551 and −0.366 e Å^{-3}

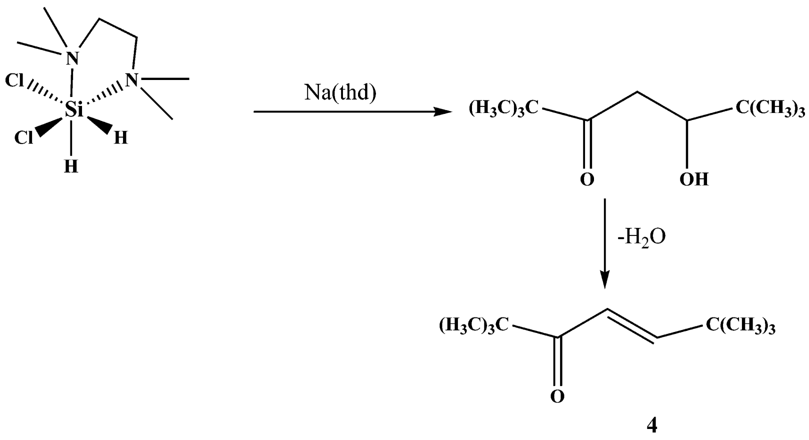
Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Si(1)−O(1)	1.8179(17)	Si(1)−O(3)	1.8251(17)
Si(1)−O(2)	1.8752(16)	Si(1)−C(7)	1.902(3)
Si(1)−C(8)	1.902(3)	Si(1)−O(4)	1.915(2)
O(1)−C(1)	1.284(3)	O(2)−C(3)	1.270(3)
O(3)−C(4)	1.283(3)	O(4)−C(6)	1.262(3)
C(1)−C(2)	1.378(3)	C(1)−C(11)	1.539(3)
C(2)−C(3)	1.405(3)	C(3)−C(31)	1.525(3)
C(4)−C(5)	1.374(3)	C(4)−C(41)	1.532(3)
C(5)−C(6)	1.411(4)	C(6)−C(61)	1.518(4)

O(1)−Si(1)−O(3)	170.72(8)	O(1)−Si(1)−O(2)	89.00(7)
O(3)−Si(1)−O(2)	84.26(7)	O(1)−Si(1)−C(7)	95.17(11)
O(3)−Si(1)−C(7)	91.23(11)	O(2)−Si(1)−C(7)	90.20(13)
O(1)−Si(1)−C(8)	90.03(10)	O(3)−Si(1)−C(8)	95.48(10)
O(2)−Si(1)−C(8)	169.84(12)	C(7)−Si(1)−C(8)	99.96(15)
O(1)−Si(1)−O(4)	83.94(8)	O(3)−Si(1)−O(4)	88.64(8)
C(8)−Si(1)−C(7)	99.96(15)	O(3)−Si(1)−O(4)	88.64(8)
O(2)−Si(1)−O(4)	80.31(10)	C(7)−Si(1)−O(4)	170.48(12)
C(8)−Si(1)−O(4)	89.53(11)	C(1)−O(1)−Si(1)	131.24(14)
C(3)−O(2)−Si(1)	130.03(14)	C(4)−O(3)−Si(1)	130.09(17)
C(6)−O(4)−Si(1)	128.65(18)	O(1)−C(1)−C(2)	123.8(2)
O(1)−C(1)−C(11)	113.06(19)	C(2)−C(1)−C(11)	123.1(2)
C(1)−C(2)−C(3)	120.6(2)	O(2)−C(3)−C(2)	123.29(19)
O(2)−C(3)−C(31)	114.31(19)	C(2)−C(3)−C(31)	122.4(2)
O(3)−C(4)−C(5)	123.2(2)	O(3)−C(4)−C(41)	114.6(2)
C(5)−C(4)−C(41)	122.1(2)	C(4)−C(5)−C(6)	122.0(2)
O(4)−C(6)−C(5)	122.4(3)	O(4)−C(6)−C(61)	116.5(2)
C(5)−C(6)−C(61)	121.1(2)		

The colorless crystals were found to belong to the monoclinic crystal system, and systematic absences in the diffraction data were uniquely consistent with the space group *P*2₁/*c*. Corrections for Lp effects and absorption were made. The structure was solved by direct methods and completed by a series of difference Fourier syntheses. Two *tert*-butyl groups of one chelate ring (those attached to C(4) and C(6)) were found to be rotationally disordered; refinement included a two-position model as an approximation of the diffuse electron density. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were treated as idealized contributions, except for those associated with the disordered groups. Selected bond lengths and angles are presented in Table 2. Further details are available as Supporting Information in CIF format.

Scheme 1

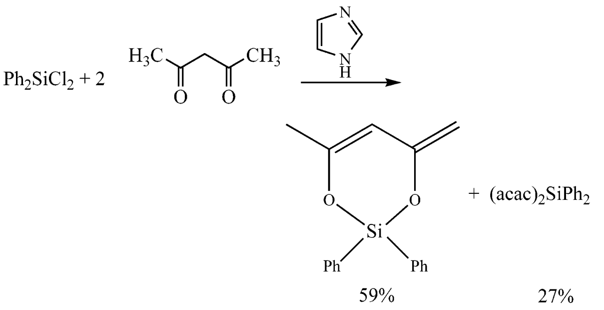


3. Results and Discussion

Synthesis. Three new complexes, **1**, **2**, and **3**, were synthesized in high yield by the reaction as expressed in eq 1.

$$2Na(thd) + SiCl_2X_2 \rightarrow (thd)_2SiX_2 + 2NaCl \quad (1)$$
$$X = -Me, -OBu^t, -OAm^t$$

Compound **1** was synthesized by reacting $SiCl_2Me_2$ with 2 equiv of Na(thd) in dry diethyl ether. The reaction mixture was refluxed overnight. After isolation and purification, a light yellow crystalline product was obtained in over 90% yield. For a comparison, the isolation yield of an analogous compound of $(acac)_2SiMe_2$ was only 11% when 2 equiv of (acac)H reacted with $SiCl_4$ in the presence of pyridine.[10] Lately, $(acac)_2SiPh_2$ was prepared in a yield of 27% when 2 equiv of (acac)H reacted with Ph_2SiCl_2 in the presence of imidazole with a side reaction leading to the formation of 1,1-diphenyl-2,6-dioxa-3-methyl-5-methylene cyclohexylsilyl-3-ene, an enolate product (in 59% yield).[13] The side reaction is attributed to the acidic protons of the methyl group in acetylacetone. The reaction is expressed in eq 2.



(2)

Unlike (acac)H, (thd)H does not have the acidic methyl protons, which prevents (thd)H from forming the tetracoordinate enolate product.

The $(acac)_2SiMe_2$ was reported to be very unstable, turning to red and then black in a few days when stored in a glass flask at room temperature under inert atmosphere.[10] However, **1** is very stable. No change was observed visually or by NMR when it was stored in a glass flask under nitrogen even after several months at room temperature.

Both **2** and **3** were synthesized in toluene by reacting 2 equiv of Na(thd) and 1 equiv of $SiCl_2(OBu^t)_2$ and $SiCl_2(OAm^t)_2$, respectively. The toluene mixtures were refluxed for 24 h. After isolation, both products are white solids and are very stable. Interestingly, both **2** and **3** exhibit relatively low solubility in nonpolar hydrocarbon solvents (approximately 0.1 M in octane at room temperature), compared to other neutral organosilicon compounds.

All of these new compounds were characterized by solution NMR, FT-IR, thermal analysis, and elemental analysis. Satisfactory elemental analysis was obtained for all of the three new compounds. Compound **1** was characterized by single crystal X-ray diffraction.

In an attempt to make "$(thd)_2SiH_2$", we first synthesized solid H_2SiCl_2•(tmeda) by bubbling H_2SiCl_2 into a tmeda hexane solution. H_2SiCl_2•(tmeda) was then isolated as a white solid. Then, 2 equiv of Na(thd) dissolved in diethyl ether were added into a suspension of H_2SiCl_2•(tmeda) in diethyl ether, and instead of "$(thd)_2SiH_2$", 2,2,6,6-tetramethyl-hepta-3-one-4-ene (**4**) was isolated. The ligand of thd was reduced and followed by elimination of water, leading to the formation of **4** (see Scheme 1).

X-ray Diffraction Studies. Single crystals of **1** were grown from a hexane solution at −18 °C and studied by single crystal X-ray diffraction. An ORTEP plot of the molecular structure of **1** is shown in Figure 1. The molecular geometry around silicon is approximately octahedral, consisting of two bidentate chelating β-diketonate (thd) ligands and two methyl groups in *cis*-orientation. For a comparison, $(acac)_2SiPh_2$ was reported as an isomer-free *trans*-hexacoordinate complex on the basis of NMR data, and $(acac)_2SiMe_2$ was reported as a tetracoordinate complex from IR data.[10,13] The planes of the two thd-chelate rings in **1** reveal some distortion from the ideal octahedral symmetry; their dihedral angle is 79.8° rather than 90° as expected in ideal octahedral symmetry. The dihedral angle is close to that observed in the *cis*-hexacoordinate $(tropolonato)_2SiPh_2$ (an α-diketonate compound) in which the angle of the two tropolonate chelating planes is 81.1°.[28] It is noteworthy that the two Si−O bond distances for each thd group differ

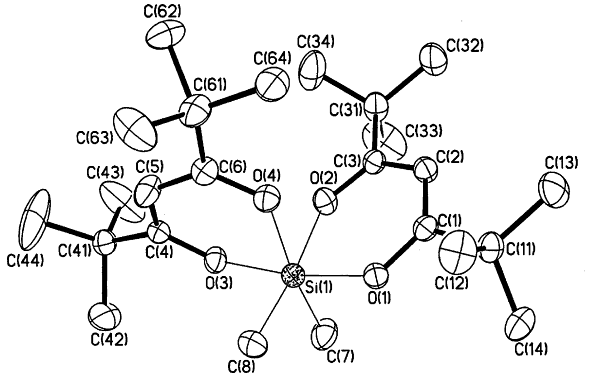


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability level with the following bond distances [Å]: Si(1)−O(1) 1.8179(17), Si(1)−O(3) 1.8251(17), Si(1)−O(2) 1.8752(16), Si(1)−O(4) 1.915(2), Si(1)−C(7) 1.902(3), Si(1)−C(8) 1.902(3). The bond angles are as follows [deg]: O(1)−Si(1)−O(3) 170.72(8), O(1)−Si(1)−O(2) 89.00(7), O(3)−Si(1)−O(2) 84.26(7), O(1)−Si(1)−C(7) 95.17(11), O(3)−Si(1)−C(7) 91.23(11), O(2)−Si(1)−C(7) 90.20(13), O(1)−Si(1)−C(8) 90.03(10), O(3)−Si(1)−C(8) 95.48(10), O(2)−Si(1)−C(8) 169.84(12), C(7)−Si(1)−C(8) 99.96(15), O(1)−Si(1)−O(4) 83.94(8), O(3)−Si(1)−O(4) 88.64(8).

significantly. The bond distance of Si(1)−O(2) is 1.875(2) Å, while Si(1)−O(1) is 1.818(2) Å. In the second thd group, the bond distance of Si(1)−O(4) is 1.915(2) Å, while Si(1)−O(1) is 1.825(2) Å. The elongation of Si−O bonds at O(2) and O(4) was most likely caused by steric repulsion due to the closeness of the two bulky *tert*-butyl groups. The bond distances of C(1)−C(2) of 1.378(3) Å and C(4)−C(5) of 1.374(4) Å are shorter than those of C(2)−C(3) of 1.405(3) Å and C(4)−C(5) of 1.411(4) Å. The bond distances of C(1)−O(1) of 1.284(3) Å and C(4)−O(3) of 1.283(3) Å are longer than those of C(3)−O(2) of 1.270(3) Å and C(6)−O(4) of 1.262(3) Å. This pattern of C−O and C−C bond distance variations in the two chelate thd rings suggests some localization of valency; that is, the longer Si−O distances reflect greater localized ketonic character in the C−O linkage. This localization or elongation leads to a more polar molecule, which might be the explanation for our observation of low solubility of both **2** and **3** in nonpolar solvents. The thd ligand bite angles are nearly identical and average 88.82(2)°. The structures of neutral hexacoordinate β-diketonate silicon complexes have rarely been reported to date.

Single crystals of **2** and **3** were also grown from their hexane or toluene solutions at −18 °C. Suitably sized crystals were selected and studied by X-ray diffraction. However, though the hexacoordinate core structure of silicon was observed for each of them, severe disorder in both **2** and **3** prevented further refinement of their final structures. Interestingly, we cannot solve the molecular structures of (β-diketonate)$_2$M(OR)$_2$ by single crystal X-ray diffraction, where M = Hf, Ti, and Zr, because of the disorder problems.

NMR Studies. ^{1}H, ^{13}C{^{1}H}, and ^{29}Si NMR studies for **1**, **2**, and **3** in C_6D_6 were carried out. At room temperature, the ^{1}H NMR spectrum of Si(thd)$_2$Me$_2$ in C_6D_6 showed one singlet at 1.10 ppm for the methyl protons of thd and one singlet at 0.66 ppm for methyl protons of Si−CH$_3$. The ^{1}H NMR spectrum of **2** at room temperature showed two distinct *tert*-butyl proton resonances of thd ligand, appearing at 1.22 and 1.04 ppm, and the ^{1}H NMR of **3** also showed two resonances at 1.22 and 1.02 ppm. The NMR results were consistent with the *cis*-hexacoordinate structure of **2** and **3**. Hexacoordinate (thd)$_2$SiX$_2$ exists in two possible isomers, e.g., *cis*- and *trans*-isomers as shown in Figure 2. In a *trans*-isomer, the two groups of R^a and R^b are equivalent, and thus, in theory the proton should appear as only one singlet resonance in the NMR spectrum regardless of temperature (prior to decomposition). However, in a *cis*-isomer the two groups of R^a and R^b are nonequivalent. A *cis*-isomer undergoes inversion of configuration and β-diketonate ligand exchange between the two nonequivalent sites.[29−32] When the temperature is high, the exchange rates are rapid, and thus, the difference cannot be distinguished. As a result, only one resonance is observed. However, at low temperatures, two resonances can be observed. The exchange was confirmed by variable temperature (VT) NMR studies of **2** in toluene-d_8. Shown in Figure 3 are the proton NMR spectra recorded at temperatures from 25 to 65 °C. At low temperatures (below 45 °C), two distinct resonances of the *tert*-butyl protons of thd ligand are observed at 1.22 and 1.04 ppm, while at high temperatures (above 45 °C), only one resonance appears at 1.12 ppm. These data confirm that **2** possesses a *cis*-hexacoordinate geometry in solution. The coalescence temperature was about 318 K with $\Delta\nu$ = 56

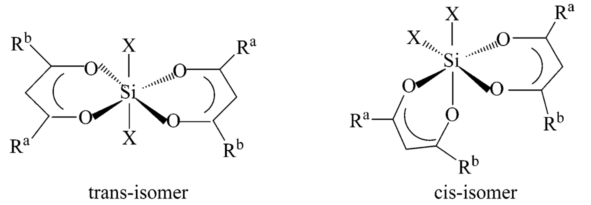


Figure 2. Two possible isomers for hexacoordinate (thd)$_2$SiX$_2$.

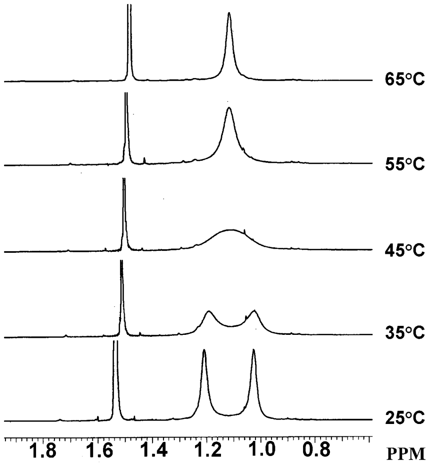


Figure 3. Variable temperature (VT) NMR studies of **2** in toluene-d_8.

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Hz, in the absence of exchange, giving an approximate activation barrier for exchange of $\Delta G^{\ddagger} \sim 14.4$ kcal/mol (60.3 kJ/mol).[33] VT NMR studies of **1** were also performed in toluene-d_8. Similarly, the data revealed that, below −30 °C, the methyl protons of the thd ligand appear as two distinct resonances, a characteristic of *cis*-hexacoordination.

Not surprisingly, the rates of inversion and exchange of nonequivealent protons of $(thd)_2SiX_2$ depend on the size of the X ligands, the rates decreasing with the increase of the ligand size. We observed, with small ligands of X like methyl in **1**, two distinct resonances below −30 °C, while **2** and **3** with bulky X groups show two distinct resonances even at room temperature. Interestingly, the trend of the size effect of X in $(thd)_2SiX_2$ was reflected in $^{13}C\{^1H\}$ NMR spectra as well. For example, at room temperature, **1** exhibits only a singlet for the carbonyl carbon, while **2** shows a broad carbonyl signal, and **3** clearly exhibits two distinct carbonyl resonances located at 198.2 and 199.0 ppm. In general, solution NMR and VT NMR studies (both ^1H and $^{13}C\{^1H\}$ NMR) clearly confirmed a *cis*-isomeric, hexacoordinate silicon geometry of **1**, **2**, and **3**.

The ^{29}Si NMR resonances for **1**, **2**, and **3** in C_6D_6 appeared at 138.87, 186.18, and 186.21 ppm, respectively. The chemical shifts are in the expected region for hexacoordinate silicon complexes in solution, which further confirmed the hexacoordinate geometry of compounds **1**, **2**, and **3** in solution.[7a,13,14,28]

Thermal Analysis. We performed thermal studies to understand the stability of these new compounds. One of the important characteristics of CVD precursors is volatility and thermal stability. To determine thermal transport behavior, thermal analyses of $(thd)_2SiX_2$ were carried out under Ar ambient. Shown in Figure 4 is the data of simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) of **2** at an Ar flow rate of 10 mL/min. The results show a melting endothermic peak at 222 °C, and a complete transport by 278 °C. Similarly, **1** transports completely below 250 °C in Ar; however, a melting endothermic peak is not observed. Therefore, we conclude that the $(thd)_2SiX_2$ complexes are volatile and thermally stable for CVD delivery and are thus suitable for use as CVD precursors. In fact, $(thd)_2Si(OBu^t)_2$ (**2**) has been successfully delivered in a CVD process, and high quality zirconium silicate high κ gate thin films have been deposited.[25]

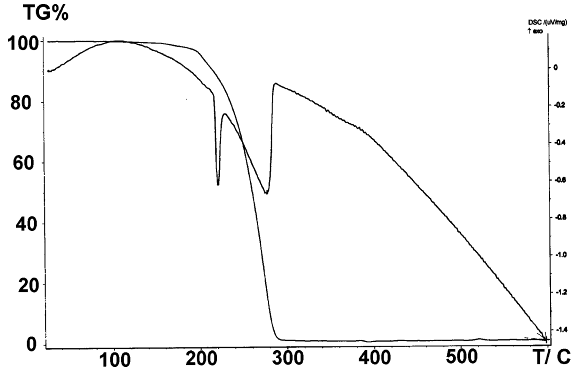

Figure 4. Simultaneous thermogravimetric and differential scanning calorimetric analysis of **2** in Ar.

4. Summary and Conclusions

In summary, three new neutral bis(β-diketonate) silicon(IV) complexes of **1**, **2**, and **3** have been synthesized in high yield and high purity. Characterization indicated these complexes were hexacoordinate with only the *cis*-isomer. The *cis*-hexacoordinate geometry was determined by single crystal X-ray diffraction analysis in the solid state and confirmed by ^1H, $^{13}C\{^1H\}$ NMR studies in solution, e.g., the observation of two methyl (thd) proton resonances and two carbonyl resonances (thd). ^{29}Si NMR studies also confirmed the hexacoordinate silicon in solution. They are monomeric solids. Thermal analysis revealed they are volatile and thermally stable and, thus, represent promising CVD precursors for depositing high quality transition metal silicate gate dielectric thin films.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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