

N-Alkoxy Carboxylamide-Stabilized Tin(II) and Germanium(II) Complexes for Thin Film Applications

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Dedication ((optional))

Abstract: A new series of germanium (1-5) and tin (6-10) complexes were successfully synthesized by employing N-alkoxy functionalized carboxylamide as the stabilizing ligands and these complexes could potentially serve as precursors for thin film applications. All complexes were characterized by Fourier transform (FT) infrared, and nuclear magnetic resonance spectroscopies as well as elemental and thermogravimetric (TG) analyses. The single crystal X-ray study of complexes 5 and 10 revealed that they crystalized in the monoclinic space group (P2(1)/c) as monomers. The metal centers in these complexes are coordinated to four oxygen atoms and display a distorted trigonal-bipyramidal geometry. Thermogravimetric analysis and volatility study of complexes demonstrated good volatility and stability for the compounds 2-4 and **6-9**. Among these complexes, $Ge(mdpa)_2$ (**3**) and $Sn(edpa)_2$ (**9**) exhibited excellent physcio-chemical properties with clean single step curves and low residual mass in their TG analyses.

Introduction

Group 14 elements such as tin and germanium have great importance owing to their unique applications in the field of electronics. Tin oxide exhibits a wide band gap of ~3.62 eV which gives it a greater importance in the field of semiconductor¹⁻³ compared to other oxide species. The high transparency and infrared reflectivity of tin oxide have led to various applications such as energy conserving windows for buildings,⁴ gas sensors,⁵ and transparent conductive electrodes in thin film solar cells.⁶⁻⁸ At the same time germanium films have gained much attention owing to their applications in phase-change random access memory (PRAM) devices. Their higher programming speed, non-volatility, high endurance, and lower programming current have attracted great deal of interest. Ge₂Sb₂Te₅ (GST) is the most popular phase change material for PRAM.⁹⁻¹³

In the last few decades, there has been a tremendous progress in the deposition of Ge metallic films and SnO_x films via atomic layer deposition (ALD)/chemical vapor deposition (CVD) techniques.¹⁴ Many applications of Ge and SnO_x films require, the conformal deposition of films on challenging surfaces that

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include deep trenches and pores.¹⁵⁻¹⁷ This makes the precursors for these applications more important and their properties such as volatility, stability, and reactivity must be fine turned to attain the required growth and conformal coverage of the deposited thin films. The demands in meeting the required properties of the precursors have spurred the development of new metal complexes, which are hoped to provide better results.

In our attempt to prepare new Ge and Sn precursors, we decided to explore the use of N-alkoxy carboxylamidate ligands. To our knowledge the N-alkoxy carboxylamidate ligand system has never been explored in the field of precursor chemistry. The tunability of the carboxylamidate ligands on both side of the amide group $\{-C(=O)N(H)-\}$ and their small size make them attractive ligands for precursor preparation. In this work, we have prepared a series of *N*-alkoxy amides: Nmethoxypropanamide (mpaH), N-ethoxy-2-methyl propanamide (empaH), N-methoxy-2,2-dimethyl propanamide (mdpaH), Nethoxy-2,2-dimethyl propanamide (edpaH), and N-methoxy benzamide (mbaH), along with their Ge and Sn complexes. The germanium complexes $Ge(mpa)_2(1)$, $Ge(empa)_2(2)$, $Ge(mdpa)_2$ (3), $Ge(edpa)_2$ (4), and $Ge(mba)_2$ (5), as well as the tin complexes $Sn(mpa)_2$ (6), $Sn(empa)_2$ (7), $Sn(mdpa)_2$ (8) Sn(edpa)₂ (9), and Sn(mba)₂ (10) were synthesized, purified, and characterized by Fourier transform infrared (FT-IR), and FTnuclear magnetic resonance (FT-NMR) spectroscopies, as well as elemental analysis, Mass spectra (EI-MS) and thermogravimetric (TG) analyses. These complexes demonstrated high thermal stability and volatility; with 3 and 9 in particular, displaying both excellent volatility and stability.

Results and Discussion

The new germanium and tin complexes were carefully prepared as shown in Scheme 1. In a single step reaction, the diethyl ether or hexane solution of germanium bis(trimethylsilyl)amide [Ge(btsa)₂] or tin bis(trimethylsilyl)amide [Sn(btsa)₂] was reacted with the corresponding ligand, and the reaction mixture was stirred overnight at room temperature to afford the desired complexes. The final products were purified via distillation (complexes 1, 2, 4, 6, 7, and 9), sublimation (complexes 3 and 8) or recrystallization from hexane solution (complexes 5 and 10) with moderate yields. These novel complexes appeared to be highly stable under inert conditions but are sensitive to air and moisture. They displayed good solubility in organic solvents like toluene, benzene, hexane, and diethyl ether.

High quality crystals of **5** and **10** for the single crystal X-ray diffraction study were grown from saturated hexane solutions of

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Scheme 1. Synthetic procedure for complexes 1-10.

	Complex 5	Complex 10
Empirical formula	C ₁₆ H ₁₆ GeN ₂ O ₄	$C_{16}H_{16}N_2O_4Sn$
Formula weight	372.90	419.00
Temperature (K)	100(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a (Å)	a = 9.4541(5)	9.5216(4)
b (Å)	b = 19.0070(10)	18.8309(7)
c (Å)	c = 9.0753(5)	9.2379(3)
α (°)	90	90
β (°)	96.372(4)	96.227(2)
γ(°)_	90	90
$V(A^3)$	1620.70(15)	1646.59(11)
Z	4	4
ρ_{calcd} (Mg/m ³)	1.528	1.690
µ (mm⁻¹)	1.911	1.573
F(000)	760	832
Crystal size (mm ³)	0.20 x 0.16 x 0.05	0.16 x 0.08 x 0.02
Theta range for data collection(°)	2.14 to 28.37	2.15 to 28.27
	0<= <i>h</i> <=12,	0<= <i>h</i> <=12,
Index ranges	-25<= <i>k</i> <=0,	-25<= <i>k</i> <=0,
	-12<= <i>l</i> <=12	-12<=/<=12
Total Reflections	3969	4050
Independent reflns [R _{int}]	0.00	0.00
parameters	208	208
GOF on F ²	1.035	1.122
$R_1 [> 2\sigma()]$	0.0379	0.0330
$wR2 [l>2\sigma(l)]$	0.0828	0.0590

the corresponding complexes at 0 °C. The study revealed that both the complexes were crystalized as monomers in the monoclinic space group of P2(1)/c (Table 1). In 5 (Figure 1), the central Ge atom displayed a tetra-coordinate state, where the oxygen atoms from the amide and alkoxy groups of the coordinated mba ligands complete the coordination sphere. The crystal structure of [Sn(mba)₂] (10) is displayed in Figure 2, and is isostructural to that of 5. The central metal atoms in both 5 and 10 showed a distorted pseudo trigonal bipyramidal geometry,¹⁸ where the methoxy oxygen atoms occupy the top of the pyramid and the amide oxygen atoms and a lone pair of electrons are placed at the equatorial positions. In 5, the Ge(1)-O(1) and Ge(1)–O(3) bond lengths (Table 2) are 2.226(19) and 2.2509(18) Å, respectively, which are understandably much longer than the reported Ge-alkoxide bonds because of their purely coordinative characteristic. Meanwhile, the respective bond lengths of Ge(1)-O(2) and Ge(1)-O(4) are 1.8931(18) and

1.9086(18) Å which are much closer to the reported Ge-O bond lengths in [(L)GeOC(H)₂(PhOMe-4)] (L = [N{C₆H₂(C-(H)Ph₂)₂^{*i*}Pr-2,6,4}(Si[/]Pr₃)]), 1.8120(19) Å,¹⁹ [(BDI)GeO^tBu] (BDI = [{N(2,6-[']Pr₂C₆H₃)C(Me)₂CH]), 1.8284(3) Å,²⁰ and [LGe(O[']Pr)(HO[']Pr)] (L = amine(trisphenolate)) 1.799(2) Å.²¹ Similarly, in complex 10, the respective bond lengths of Sn(1)-O(1) and Sn(1)-O(3) at 2.397(2) and 2.366(2)Å are longer than those of common Snalkoxide bonds; whereas, the bond lengths of Sn(1)-O(2) (2.110(2) Å) and Sn(1)-O(4) (2.099(2) Å) showed similar characteristics to those of previously reported complexes such $(BDI)SnO^{i}Pr$ and $(BDI)SnO^{i}Bu$ $(BDI = [{N(2,6 (Pr_2C_6H_3)C(Me))_2CH]$,²² with Sn–O lengths measuring 2.000(5) and 2.0179(16) Å, respectively and $[Sn(C_5H_7O_2)(C_2H_3O_2)]^{23}$ giving a Sn-O reading of 2.156(4) Å. The bond angles of O(1)-Ge(1)-O(3) (147.25(7)°) in 5 and O(1)-Sn(1)-O(3) (134.93(8)°) in 10 displayed (Table 2) a large deviation from the ideal 180° reading largely due to the presence of the lone pair of electrons in the outer orbital of the central metal atoms. The N(1)-C(2) and N(2)-C(10) bond lengths in 5 and 10 are 1.285(3) and 1.296(3) Å versus 1.295(4) and 1.294(4) Å, respectively. This shows that the C=N bond was formed as a result of ligand deprotonation during in the complex formation.

The FT-NMR data of the complexes confirmed that the reaction proceeded successfully and intended products were formed. In 1 and 6, the absence of the -NH/-OH protons indicated a successful reaction, and the differences in the solubility of the free ligand (mpaH) and the complexes compelled us to perform the NMR analysis in two different solvents. Therefore, the chemical shifts were not compared. In 2 and 7, the COCH(CH₃)₂, OCH₂CH₃, as well as OCH₂CH₃ protons at δ 1.15, 1.26, and 4.14 ppm (2) and δ 1.21, 1.26, and 4.15 ppm (7), respectively were shifted downfield compared to the empaH protons (5 1.14, 1.14, 3.95 ppm). Nontheless, the COCH(CH₃)₂ proton signals showed little change as a result of the coordination. In **3** and **8**, the $COC(CH_3)_3$ and OCH_3 protons appeared at δ 1.25 and 3.70 versus δ 1.32 and 3.67 ppm respectively. These signals were significantly shifted downfield from those in free the ligand (δ 1.09 and 3.59 ppm). In 4, the COC(CH₃)₃, OCH₂CH₃, and OCH₂CH₃ protons resonated at δ 1.25, 1.25, and 4.18 ppm, respectively, while the same set of protons appeared at δ 1.25, 1.33, and 4.15 ppm in 9. This large downfield shift with respect to the edpaH proton signals

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indicates strong bonds between the metal centers and the ligands. In **5** and **10**, the OCH₃ protons showed a large downfield shift (\bar{o} 3.85 (**5**) and \bar{o} 3.80 ppm (**10**)) compared to those of the free mbaH species (\bar{o} 3.59 ppm), whereas the aromatic protons were less affected by the coordination. The absence of the –NH protons in any of the products proved that all the complexes (**1-10**) were successfully formed.



Figure 1. Crystal structure of complex 5.



Figure 2. Crystal structure of complex ${\bf 10}.$

The elemental analysis of the complexes showed comparable values to those obtained via calculations considering their sensitive nature toward air and moisture. Despite our best efforts and a series of repeated experiments, we were unable to obtain better results, and this might be due to the decomposition of a small portion of the samples resulting from a short exposure to ambient air during the sampling of the complexes. The mass spectra of the samples verified the calculated values of the monomeric complexes in all cases (1-10) and we expect a similar monomeric structure for all the complexes, with four oxygen atoms coordinated to the central metal atom as in the case of **5** and **10**. The spectral data (especially the complexes' mass spectra) and the large NMR downfield shifts observed for

the protons adjacent to the coordinating oxygen atoms of the ligands supported the aforementioned observation.

Ge(mba) ₂ (5)		Sn(mba) ₂ (10)	
	(Å)		(Å)
Ge(1)-O(1)	2.2226(19)	Sn(1)-O(1)	2.397(2)
Ge(1)-O(2)	1.8931(18)	Sn(1)-O(2)	2.110(2)
Ge(1)-O(3)	2.2509(18)	Sn(1)-O(3)	2.366(2)
Ge(1)-O(4)	1.9086(18)	Sn(1)-O(4)	2.099(2)
N(1)-C(2)	1.285(3)	N(1)-C(2)	1.295(4)
N(2)-C(10)	1.296(3)	N(2)-C(10)	1.294(4)
	(°)		(°)
O(2)-Ge(1)-O(4)	95.68(8)	O(2)-Sn(1)-O(4)	92.26(9)
O(2)-Ge(1)-O(1)	74.61(7)	O(2)-Sn(1)-O(1)	68.17(7)
O(4)-Ge(1)-O(1)	83.92(7)	O(4)-Sn(1)-O(1)	79.09(8)
O(2)-Ge(1)-O(3)	83.84(7)	O(2)-Sn(1)-O(3)	81.66(8)
O(4)-Ge(1)-O(3)	73.84(7)	O(4)-Sn(1)-O(3)	69.17(8)
O(1)-Ge(1)-O(3)	147.25(7)	O(1)-Sn(1)-O(3)	134.93(8)

Thermogravimetric analyses of the complexes 1-10 were conducted in the temperature range between room temperature and 600 °C. Prior to that, sampling was carried out in an argonfilled glove box and data were collected under a constant flow of nitrogen to avoid any air contact. Among complexes 1-5 (Figure 3), 1 and 5 showed step wise decomposition characteristics in their TG curve, indicating the unstable nature of the complexes at higher temperatures. Both the complexes displayed an initial mass loss of 47% and 53% in the temperature range of 50-210 °C, followed by a second mass loss of 21% and 15% in the 210-400 °C region. Meanwhile, Ge(empa)₂ (2), displayed a sharp mass loss of 71% in the region 50-150 °C and a further loss of 7% up to 300 °C. Ge(mdpa)₂ (3) and Ge(edpa)₂ (4) turned out to be the most stable species among the complexes and both displayed a single step in their respective TGA curve with mass losses of 89% (3) and 79% (4) in the temperature region of 50-180 °C. The final residual mass obtained for the complexes 1-5 were 32%, 22%, 10%, 20%, and 32%, respectively. The TGA plot of the complexes 6-10 are shown in Figure 4, where Sn(mpa)₂ (6) and Sn(empa)₂ (7) displayed 56% and 65% mass losses in the temperature range of 50-170°C and 50-185 °C, respectively. A further mass loss of 8% was observed for 6 (170-250 °C) and 7% for 7 (185-250 °C). Similar to the germanium complexes, the $Sn(mdpa)_2$ (8) and $Sn(edpa)_2$ (9) are the most stable species among the Sn complexes; both showing single step TGA curves with the respective mass losses of 80% (50-200 °C) and 91% (50-210°C). The complex 10 showed stepwise dissociation characteristics at higher temperatures with mass losses of 45% (80-240 °C) and 17% (240-400°C). Final residual masses of 36%, 28%, 20%, 9%, and 38% were observed for 6-10 at the end of the analyses.

To better understand the volatility and stability of the complexes, they subjected to distillation/sublimation experiments. Complex 1 was distilled at 120 °C/10⁻¹ Torr to afford its purified form however showed highly unstable characteristics at elevated temperature and at longer period of time in room temperature. It decomposed into a brown liquid and an insoluble solid over time. Attempts to identify the decomposed components were unsuccessful owing to complicated nature of the data obtained. Nevertheless, the TGA data of the complex agreed with the aforementioned observation of a high residual mass and step wise decomposition characteristics. Complexes 2 (distilled at 100 °C/10⁻¹ Torr), 3 (sublimed at 60 °C/10⁻¹ Torr), and 4 (distilled

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Figure 3. TGA plot of complexes 1-5, black (1), red (2), blue (3), pink (4), and green (5).



Figure 4. TGA plot of complexes 6-10, black (6), red (7), blue (8), pink (9), and green (10).

at 80 °C/10⁻¹ Torr), all showed good volatility but, 2 and 4 did experience partial decomposition at elevated temperatures (indicated by the presence of excess residue in their respective thermogravimetric analyses). On the other hand. demonstrated good stability and had minimal residual amount according to its TGA reading. Complex 5 was not volatile and showed unstable characteristics at elevated temperatures, thus supporting the postulate of a stepwise decomposition as observed in the TG analysis. Among the tin complexes, 6 and 7 showed good volatility and were distilled over at 85 °C/10⁻¹ Torr and 100 °C/10⁻¹ Torr, respectively. However, high residual amounts in their TGA plots indicate partial decomposition of the compounds at high temperatures. Complexes 8 and 9 also showed good volatile characteristics; 8 sublimed at 60 °C/10⁻¹ Torr whereas, **9** distilled over at 90 °C/10⁻¹ Torr. Both complexes displayed good stability at high temperatures with 20% and 9% residues in their respective thermogravimetric analyses. Complex 10 showed an identical behavior to its germanium analogue, being nonvolatile and underwent step wise decomposition at elevated temperatures. The thermogavimetric analysis and volatility study showed that, Ge(mdpa)₂ (3) and $Sn(edpa)_2$ (9) are the most volatile and stable complexes with the least amount of residues. Complexes 5 and 10 are the only nonvolatile complexes with unstable characteristics. The remaining complexes all displayed good volatility, but exhibited partial decomposition at elevated temperatures, thus showing their relatively unstable characteristics compared to 3 and 9. The nonvolatile residue obtained during the TG analyses of 5 and 10 was thought to be the combination of germanium oxide (GeO₂) and tin oxide (SnO or SnO₂) as well as nonvolatile carbon fragments resulting from the ligand decomposition. In general, complexes 1, 2, 4, 6, 7, and 8 are volatile, and have varying degree of temperature instability. This suggests that, part the complexes are initially vaporized before they undergo decomposition at higher temperatures to GeO₂. SnO. or SnO₂ and nonvolatile carbon fragments.

Table 2. The physical properties of complexes 1-10.

Complex	State at 25 °C	Mp (°C)	Sublimation/ Distillation Temperature at 10 ⁻¹ T (°C)
Ge(mpa) ₂ (1)	liquid	-	120
Ge(empa) ₂ (2)	liquid	-	100
Ge(mdpa) ₂ (3)	solid	47	60
Ge(edpa) ₂ (4)	liquid	-	80
Ge(mba) ₂ (5)	solid	132	-
Sn(mpa) ₂ (6)	liquid	-	85
Sn(empa) ₂ (7)	liquid	-	100
Sn(mdpa) ₂ (8)	solid	53	60
Sn(edpa) ₂ (9)	liquid	-	90
Sn(mba) ₂ (10)	solid	145	-

Our study reveals the suitability of carboxylamidate ligands as the stabilizing ligands for tin and germanium complexes. Moreover, it provided good stability and volatile characteristics to the corresponding complexes which make it suitable as precursors for thin film depositions. The germanium complex $[Ge(mdpa)_2]$ (3) exhibits low melting point (mp 47 °C) and sublimation temperatures (60 °C) (table 2) which are appreciated characteristics for metal precursors. Whereas, the complex [Sn(edpa)₂] (9) displays superior properties compared to that of most of the oxygen coordinated commercially available tin precursors; eg: Sn(thd)₂ (solid), Sn(acac)₂ (liquid; decomposes below its bp at ambient pressure), $Sn(OC_2H_5)_2$ (solid; mp 145 °C and decomposes at high temperatures), Sn(hfac)₂ (solid; mp 75 °C and decomposes at high temperatures). To ensure the stability of the above complexes and the absence of fragmentation during sublimation and distillation procedures, the obtained products were analyzed by FTIR, FT-NMR, and elemental analysis, which confirmed that both compounds were intact and there was no decomposition.

Conclusions

We have demonstrated the feasibility of the carboxyl amides as stabilizing ligands in precursor chemistry by synthesizing a series of new tin and germanium complexes stabilized by Nalkoxy-functionalized carboxylamidate ligands. These complexes were synthesized by substitution reactions using Sn(btsa)₂, Ge(btsa)₂, and their corresponding carboxylamides. The crystal structure of complexes 5 and 10 showed that they were formed as monomers and the central metal atoms are in a tetra-coordinate state with a trigonal bipyramidal geometry. The complexes 2-4 and 6-9 showed good volatility and thermal stability as proven by the thermal characterization. The germanium complexes 3 and the tin complex 9, in particular, exhibited excellent characteristics which is better than many commercially available precursors. Their appealing volatility and thermal stability with a clean single step TGA curve and low nonvolatile residual mass make them good candidates for thin film deposition techniques. Thin film deposition experiments carried out using complex 3 and 9 via the ALD technique are currently in the final stages of study and will be published separately.

Experimental Section

Materials and methods

NMR spectra were recorded on a Bruker 400 MHz spectrometer with either C₆D₆ or CDCl₃ as the solvent and the standard. IR spectra were obtained from a Nicolet Nexus FT-IR spectrophotometer using a 4 mm KBr window or KBr pellet. The KBr pellets of the samples were prepared using a standard pellet technique inside a glove box. Elemental analyses were carried out on a ThermoScientific OEA Flash 2000 analyzer. Thermo-gravimetric analyses were conducted on a SETARAM 92-18 TG-DTA instrument with a constant flow of nitrogen throughout the experiment. Mass spectra were recorded using a JEOL JMS-700 spectrometer operating in the electron ionization (EI) mode. All reactions except ligand preparations were carried out under inert and dry conditions using standard Schlenk techniques or in an argon-filled glove box. The ligands were prepared according to a modified literature method.²⁴ Hexane and toluene were purified using an Innovative Technology PS-MD-4 solvent purification system. All chemicals were purchased from Aldrich and used as received.

Synthetic procedures

N-Methoxypropanamide (mpaH): Pyridine (14.6 mL, 180 mmol) was added dropwise to a constantly stirred dichloromethane (150 mL) solution of O-methyl hydroxylamine hydrochloride (5.26 g, 63.0 mmol) in a two-neck flask fitted with a reflux condenser. The mixture was cooled to 0 °C in an ice bath and propionyl chloride (5.55 g, 60.0 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for another 12 hours. Upon reaction completion, the reaction mixture was quenched with ice cold water and the organic layer was separated. Subsequently, the aqueous layer was extracted with methylene chloride (MC) (20 mL \times 3). The combined organic layers were dried over anhydrous MgSO₄, filtered, and solvents were removed under reduced pressure. The pure product was obtained as a colorless liquid via distillation (70 °C /10⁻¹Torr). Yield: 5.01 g (81%). ¹H NMR (CDCl₃, 400 MHz): δ_H 1.13 (t, 3H, COCH₂CH₃), 2.12 (br, 2H, COCH₂CH₃), 3.71 (s, 3H, OCH₃), 9.75(s, 1H, NH). ¹³C NMR (CDCl₃, 100 MHz) δ_C 9.7 (COCH2CH3), 26.4 (COCH2CH3), 64.1 (OCH3), 172.1 (COCH2CH3). FT-

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IR (ν_{max}/cm^{-1}) 3191s, 2980s, 2941s, 2817w, 1664s, 1512m, 1463m, 1440m, 1376w, 1229w, 1148w, 1097m, 1048s, 1004w, 945m, 914w, 803w, 684w. Anal. Calcd for C₄H₉NO₂: C, 46.59; H, 8.80; N, 13.58. Found: C, 46.55; H, 8.78; N, 13.22. EI-MS: m/z calcd for [mpaH]: 103 [M]⁺; found 103 (15%), 57 [EtCO]⁺ (100%).

N-Ethoxy-2-methylpropanamide (empaH): Triethylamine (25.0 mL, 180 mmol) was added dropwise to a constantly stirred THF (150 mL) solution of O-ethyl hydroxylamine hydrochloride (6.15 g, 63.0 mmol) in a two-neck flask fitted with a reflux condenser. The mixture was cooled to 0 °C in an ice bath and isobutyryl chloride (6.39 g, 60.0 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and refluxed for another12 hours. Upon reaction completion, the reaction mixture was quenched with ice cold water and the organic layer was separated. Subsequently, the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous MgSO₄, filtered, and solvents were removed under reduced pressure. The pure product was obtained as a colorless viscous liquid via distillation (110 °C/ 10⁻¹ Torr). Yield: 5.20 g (67%). ¹H NMR (C₆D₆, 400 MHz) δ_H 1.14 (br, m, 9H, COCH(CH₃)₂ OCH₂CH₃), 2.62 (br, 1H, COCH), 3.95 (q, 2H, OCH₂CH₃), 11.33 (br, 1H, NH). ¹³C NMR (C₆D₆, 100 MHz) δ_C 13.6 (OCH₂CH₃), 19.6 (COCH(CH₃)₂), 32.1 (COCH), 71.5 (OCH₂CH₃), 175.5 (COCH(CH₃)₂). FT-IR (v_{max}/cm⁻¹) 3196s, 2975s, 2935m, 2878m, 1661s, 1517m, 1470m, 1384m, 1236w, 1158w, 1122w, 1096m, 1050s, 987w, 952w, 880w, 850w, 802w, 668w. Anal. Calcd for C₆H₁₃NO₂: C, 54.94; H, 9.99; N, 10.68. Found: C, 54.77; H, 9.87; N, 10.64. EI-MS: m/z calcd for [empaH]: 131 [M]⁺; found 131 (35%), 116 [M-CH₃]⁺ (30%), 71 [ⁱPrCO]⁺ (100%).

N-Methoxy-2,2-dimethylpropanamide (mdpaH): Triethylamine (25.0 mL, 180 mmol) was added dropwise to a constantly stirred THF (150 mL) solution of O-methyl hydroxylamine hydrochloride (5.26 g, 63.0 mmol) in a two-neck flask fitted with a reflux condenser. The mixture was cooled to 0 °C in an ice bath and pivaloyl chloride (7.24 g, 60.0 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and refluxed for another 12 hours. Upon reaction completion, the reaction mixture was quenched with ice cold water and the organic layer was separated. Subsequently, the aqueous layer was extracted with ethyl acetate (20 mL X 3). The combined organic layers were dried over anhydrous MgSO₄, filtered, and solvents were removed under reduced pressure. The pure product was obtained as a colorless liquid via distillation (70 °C/ 10^{-1} Torr). Yield: 5.35 g (68%). ¹H NMR (C₆D₆, 400 MHz) δ_H 1.09 (s, 9H, COC(CH₃)₃), 3.59 (s, 3H, OCH₃), 9.30 (s, 1H, NH). ${}^{13}C \text{ NMR } (C_6D_6, \text{ 100 } \text{ MHz}) \ \ \delta_C \ \ 27.2(\text{COC}(CH_3)_3), \ \ 37.8(\text{COC}(CH_3)_3),$ 63.5(OCH₃), 175.8(COC(CH₃)₃). FT-IR (ν_{max} /cm⁻¹): 3228s, 2967s, 2873m, 2813m, 2813w, 1653s, 1506s, 1482s, 1440w, 1400m, 1368 m, 1294w, 1226m, 1060s, 1021m, 941m, 917m, 811w, 622w, 586w. Anal. Calcd for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 54.45; H, 9.87; N, 10.42. EI-MS: m/z calcd for [mdpaH]: 131 [M]+; found 131 (10%), 116 [M-CH₃]⁺ (8%), 85 [^tBuCO]⁺ (20%), 57 [^tBu]⁺ (100%).

N-Ethoxy-2,2-dimethylpropanamide (edpaH): Triethylamine (25.0 mL, 180 mmol) was added dropwise to a constantly stirred THF (150 mL) solution of *O*-ethyl hydroxylamine hydrochloride (6.15 g, 63.0 mmol) in a two-neck flask fitted with a reflux condenser. The mixture was cooled to 0 °C in an ice bath and pivaloyl chloride (7.24 g, 60.0 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and refluxed for another 12 hours. After completion of the reaction, the reaction mixture was quenched with ice cold water and the organic layer was separated. Subsequently, the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous MgSO₄, filtered, and solvents were removed under reduced pressure. The pure product was obtained as a colorless viscous liquid via distillation (120 °C/ 10⁻¹ Torr). Yield: 6.01 g (69%). ¹H

NMR (C_6D_6 , 400 MHz) δ_H 1.10 (s, 9H, COC(CH₃)₃), 1.16 (t, 3H, OCH₂CH₃), 3.84 (q, 2H, OCH₂CH₃), 8.20(s, 1H, NH). ¹³C NMR (C_6D_6 , 100 MHz) δ_C 13.7 (OCH₂CH₃), 27.4 (COC(CH₃)₃), 37.9 (COC(CH₃)₃), 71.4 (OCH₂CH₃), 176.0 (COC(CH₃)₃). FT-IR (ν_{max}/cm^{-1}): 3226s, 2979s, 1652s, 1506s, 1483s, 1462m, 1399w, 1386w, 1368w, 1294w, 1229w, 1159w, 1123w, 1091w, 1057s, 1029m, 1009m, 933m, 863w, 812w, 598w. Anal. Calcd for C₇H₁₅NO₂: C, 57.90; H, 10.41; N, 9.65. Found: C, 57.88; H, 10.38; N, 9.61. EI-MS: m/z calcd for [edpaH]: 145 [M]⁺; found 145 (30%), 130 [M-CH₃]⁺ (30%), 85 [^tBuCO]⁺ (75 %), 57 [^tBu]⁺ (100%).

N-Methoxybenzamide (mbaH): O-methyl hydroxylamine hydrochloride (5.26 g, 63.0 mmol) was added to a solution of K₂CO₃ (24.9 g, 180 mmol) in an ethyl acetate/water mixture (150 mL, 2:1). The above mixture was cooled to 0 °C in an ice bath and benzoyl chloride (8.43 g, 60.0 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for another 12 hours. Upon reaction completion, the reaction mixture was guenched with ice cold water and the organic layer was separated. Subsequently, the aqueous layer was extracted with ethyl acetate (20 mL X 3). The combined organic layers were dried over anhydrous MgSO₄, filtered, and solvents were removed under reduced pressure. The pure product was obtained as a colorless liquid via distillation at 90 °C/ 10⁻¹Torr, and solidified as a white solid after cooling. Yield: 7.26 g (80%). ¹H NMR (C₆D₆, 400 MHz) δ_H 3.59 (s, 3H, OCH₃), 7.06 (m, 3H, Ph), 7.83 (d, 2H, Ph), 10.18 (s, 1H, NH).¹ ¹³C NMR (CDCl₃, 100 MHz) δ_C 63.9 (OCH₃), 127.2 (Ph-C), 128.4 (Ph-C), 131.8 (Ph-C), 166.3 (CO). FT-IR (ν_{max} /cm⁻¹): 3202s, 2978s, 2937m, 2815w, 1654s, 1601w, 1579s, 1516s, 1482s, 1438m, 1308s, 1190w, 1152m, 1075w, 1044s, 1025s, 943m, 880s, 798m, 713s, 692s, 674s, 608m. Anal. Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.55; H, 5.96; N, 9.22. EI-MS: m/z calcd for [mbaH]: 151 [M]+; found 151 (30%), 105 [PhCO]⁺ (100%), 77 [Ph]⁺ (45%).

Germanium Complexes

Ge(mpa)₂ (1): A solution of *N*-methoxypropanamide (mpaH) (0.50 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Ge(btsa)₂ (1.0 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* and the crude product was distilled (10⁻¹ Torr) to afford the pure complex as a colorless liquid at 120 °C. Yield: 0.22 g (33%). ¹H NMR (C₆D₆, 400 MHz) δ_{*H*} 1.02 (t, 3H, COCH₂CH₃), 2.11 (q, 2H, COCH₂CH₃), 3.69 (s, 3H, OCH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_{*C*} 10.9 (COCH₂CH₃), 23.6 (COCH₂CH₃), 59.5 (OCH₃), 166.0 (COCH₂CH₃). FT-IR (ν_{max}/cm^{-1}): 2979m, 2942m, 2829w, 1615m, 1464m, 1438m, 1379m, 1355m, 1288m, 1270m, 1191w, 1042s, 999m, 902m, 845m, 623w, 474w. Anal. Calcd for C₈H₁₆GeN₂O₄: C, 34.71; H, 5.83; N, 10.12. Found: C, 34.12; H, 5.73; N, 9.91. EI-MS: m/z calcd for [Ge(mpa)₂]: 278 [M]⁺; found 278 (20%), 176 [Ge(mpa)]⁺ (25%), 57 [EtCO]⁺ (100%).

Ge(empa)₂ (2): A solution of *N*-ethoxy-2-methylpropanamide (empaH) (0.64 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Ge(btsa)₂ (1.0 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* and the crude product was distilled (10⁻¹ Torr) to afford the pure complex as a colorless liquid at 100 °C. Yield: 0.38 g (47%). ¹H NMR (C₆D₆, 400 MHz) δ_H 1.15 (d, 6H, COCH(CH₃)₂), 1.26 (t, 3H, OCH₂CH₃), 2.57 (m, 1H, COC*H*(CH₃)₂), 4.14 (m, 2H, OCH₂CH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_C 15.2 (OCH₂CH₃), 20.1 (COCH(CH₃)₂), 30.3 (COCH(CH₃)₂), 69.6 (OCH₂CH₃), 168.0 (COCH(CH₃)₂). FT-IR (ν_{max}/cm^{-1}): 2973s, 2935m, 2876m, 1600s, 1471m, 1386m, 1341m, 1288m, 1262m, 1165m, 1122m, 1095m, 1076m, 1043s, 966w, 906m, 883m, 848w, 816w, 680w, 620w, 526w, 486w. Anal. Calcd for C₈H₁₆GeN₂O₄: C, 43.29; H, 7.27; N, 8.41. Found: C, 43.75; H, 7.71; N, 8.58. EI-MS: m/z calcd for

 $[Ge(empa)_2]:$ 334 $[M]^{\ast};$ found 334 (60%), 204 $[Ge(empa)]^{\ast}$ (65%), 71 $[{}^{i}PrCO]^{\ast}$ (75%).

Ge(mdpa)₂ (3): A solution of *N*-Methoxy-2,2-dimethylpropanamide (mdpaH) (0.64 g, 4.84 mmol) in hexane (10 mL) was added dropwise to a stirring hexane solution (20 mL) of Ge(btsa)₂ (1.0 g, 2.42 mmol). After being left to react overnight rat room temperature, the volatiles were removed *in vacuo* and the crude product was sublimed at (60 °C /10⁻¹ Torr) to afford the pure complex as a white solid. Yield: 0.40 g (49%). Mp 47 °C. ¹H NMR (C₆D₆, 400 MHz) δ_H 1.25 (s. 9H, COC(CH₃)₃), 3.70 (s, 3H, OCH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_C 28.1 (COC(CH₃)₃), 35.3 (COC(CH₃)₃), 59.5 (OCH₃), 170.3 (COC(CH₃)₃). FT-IR (ν_{max} /cm⁻¹): 2976m, 2941m, 2869w, 1588s, 1480m, 1460w, 1394w, 1367w, 1328m, 1224w, 1186s, 1036s, 943w, 846w, 788w, 731w, 632w, 613w, 535w, 484w. Anal. Calcd for C₁₂H₂₄GeN₂O₄: C, 43.29; H, 7.27; N, 8.41. Found: C, 43.15; H, 7.41; N, 8.38. EI-MS: m/z calcd for [Ge(mdpa)₂]: 334 [M]⁺; found 334 (47%), 204 [Ge(mdpa)]⁺ (35%), 57 [^tBu]⁺ (100%).

Ge(edpa)₂ (4): A solution of N-Ethoxy-2,2-dimethylpropanamide (edpaH) (0.70 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Ge(btsa)₂ (1.0 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed in vacuo and the crude product was distilled $(10^{-1} \, \text{Torr})$ to afford the pure product as a colorless liquid at 80 °C. Yield: 0.45 g (51%). ¹H NMR (C₆D₆, 400 MHz) δ_H 1.25 (m, br, 12H, OCH₂CH₃ & COC(CH₃)₃), 4.18 (q, 2H, OCH₂CH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_{C} 15.3 (OCH₂CH₃), 28.1 (COCH(CH₃)₃), 35.5 (COCH(CH₃)₃), 69.6 (OCH₂CH₃), 169.7 (COCH(CH₃)₃). FT-IR (ν_{max} /cm⁻¹): 2977s, 2932w, 2870w, 1589s, 1482m, 1458w, 1395m, 1386m, 1359w, 1329s, 1292w, 1224w, 1188s, 1121m, 1092w, 1041s, 960w, 938w, 905m, 854w, 811w, 792w, 778w, 729 w, 633m, 614m, 530w, 477w, 445w. Anal. Calcd for C14H28GeN2O4: C, 46.58; H, 7.82; N, 7.76. Found: C, 46.52; H, 7.78; N, 7.72. EI-MS: m/z calcd for [Ge(edpa)₂]: 362 [M]⁺; found 362 (7%), 218 [Ge(edpa)]⁺ (7%), 145 [edpaH]⁺ (17%), 57 [^tBu]⁺ (100%).

Ge(mba)₂ (5): A solution of *N*-Methoxybenzamide (mbaH) (0.73 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Ge(btsa)₂ (1.0 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* to yield the crude product as a white solid. The pure product was obtained via recrystallization from a hexane solution at 0 °C as colorless crystals. Yield: 0.38 g (42%). Mp 132 °C. ¹H NMR (C₆D₆, 400 MHz) δ_H 3.85 (s, 3H, OCH₃), 7.00 (m, 3H, Ph), 8.01 (m, 2H, Ph). ¹³C NMR (CDCl₃, 100 MHz) δ_C 60.9 (OCH₃), 127.2 (Ph), 128.3 (Ph). 130.4 (CPh), 130.5 (Ph), 161.7 (CO). FT-IR (ν_{max}/cm^{-1}): 3065w, 3003w, 2940m, 2816w, 1595m, 1558s, 1518w, 1352s, 1306w, 1185w, 1116m, 1043w, 1026s, 1015m, 908w, 830w, 780w, 703m, 691s, 680s, 584w, 564w, 506w, 440w. Anal. Calcd for C₁₆H₁₆GeN₂O₄: C, 51.53; H, 4.32; N, 7.51. Found: C, 51.15; H, 4.25; N, 7.42. EI-MS: m/z calcd for [Ge(mba)₂]: 374 [M]⁺; found 374 (50%), 224 [Ge(mba)]⁺ (10%), 105 [PhCO]⁺ (100%), 77 [Ph]⁺ (50%).

Tin Complexes

Sn(mpa)₂ (6): A solution of *N*-methoxypropanamide (mpaH) (0.50 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Sn(btsa)₂ (1.1 g, 2.4 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* and the crude product was distilled (10⁻¹ Torr) to afford the pure complex as a colorless liquid at 85 °C. Yield: 0.35 g (45%). ¹H NMR (C₆D₆, 400 MHz) δ_{*H*} 1.13 (t, 3H, COCH₂CH₃), 2.24 (q, 2H, COCH₂CH₃), 3.66 (s, 3H, OCH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_{*C*} 11.2 (COCH₂CH₃), 24.7 (COCH₂CH₃), 59.6 (OCH₃), 167.8 (COCH₂CH₃). FT-IR (ν_{max} /cm⁻¹): 2971m, 2939m, 2818w, 1585s, 1468m, 1384w, 1353m, 1288m, 1271m, 1190w, 1077w, 1038s, 1001w, 930w, 826w, 798w, 672w, 603w, 496w,

462w. Anal. Calcd for $C_8H_{16}N_2O_4Sn$: C, 29.75; H, 4.99; N, 8.67. Found: C, 29.55; H, 4.84; N, 8.59. EI-MS: m/z calcd for $[Sn(mpa)_2]$: 324 $[M]^+$; found 324 (30%), 222 $[Sn(mpa)]^+$ (37%), 103 $[mpaH]^+$ (62%), 57 $[EtCO]^+$ (100%).

Sn(empa)₂ (7): A solution of N-ethoxy-2-methylpropanamide (empaH) (0.64 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Sn(btsa)₂ (1.1 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed in vacuo and the crude product was distilled (10⁻¹ Torr) to afford the pure complex as a colorless liquid at 100 °C. Yield: 0.52 g (57%). ¹H NMR (C₆D₆, 400 MHz) δ_H 1.21 (d, 6H, COCH(CH₃)₂), 1.26 (t, 3H, OCH₂CH₃), 2.71 (m, 1H, COCH(CH₃)₂), 4.15 (q, 2H, OCH₂CH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_C 15.7 (OCH₂CH₃), 20.3 (COCH(CH₃)₂), 30.1 (COCH(CH₃)₂), 69.5 (OCH₂CH₃), 169.9 (COCH(CH₃)₂). FT-IR (v_{max}/cm⁻¹): 2972m, 2933w, 2873w, 1589s, 1470m, 1385m, 1349m, 1284w, 1268m, 1168w, 1123w, 1092w, 1077m, 1045s, 969w, 900w, 879w, 810w, 729w, 670w, 601w, 517w. Anal. Calcd for C10H20N2O4Sn C, 38.03; H, 6.38; N, 7.39. Found: C, 37.90; H, 6.31; N, 7.28. EI-MS: m/z calcd for [Sn(empa)₂]: 380 [M]⁺; found 380 (32%), 250 [Sn(empa)]⁺ (35%), 131 [empaH]⁺ (63%), 71 [ⁱPrCO]⁺ (100%).

Sn(mdpa)₂ (8): A solution of *N*-methoxy-2,2-dimethylpropanamide (mdpaH) (0.64 g, 4.84 mmol) in hexane (10 mL) was added dropwise to a stirring hexane solution (20 mL) of Sn(btsa)₂ (1.1 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* and the crude product was sublimed at (60 °C /10⁻¹ Torr) to afford the pure complex as a white solid. Yield: 0.59 g (64%). Mp 53 °C. ¹H NMR (C₆D₆, 400 MHz) δ_H 1.32 (s, 9H, COC(CH₃)₃), 3.67 (s, 3H, OCH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_C 28.3 (COC(CH₃)₃), 36.0 (COC(CH₃)₃), 59.6 (OCH₃), 172.1 (COC(CH₃)₃). FT-IR (ν_{max}/cm^{-1}): 2970m, 2957m, 2904w, 2865w, 1579s, 1480m, 1437w, 1421w, 1395w, 1358w, 1324m, 1224w, 1188s, 1028s, 931m, 844m, 785w, 734w, 599m, 527w, 467m. Anal. Calcd for C₁₂H₂₄N₂O₄Sn: C, 38.28; H, 7.36; N, 7.37. Found: C, 38.03; H, 7.29; N, 7.32. EI-MS: m/z calcd for [Sn(mdpa)₂]: 380 [M]⁺; found 380 (32%), 250 [Sn(mdpa)]⁺ (17%), 57 [¹Bu]⁺ (47%).

Sn(edpa)₂ (9): A solution of *N*-ethoxy-2,2-dimethylpropanamide (edpaH) (0.70 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Sn(btsa)₂ (1.1 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* and the crude product was distilled (10⁻¹ Torr) to afford the pure complex as a colorless liquid at 90 °C. Yield: 0.57 g (58%). ¹H NMR (C₆D₆, 400 MHz) δ_H 1.25 (t, 3H, OCH₂CH₃), 1.33 (s, 9H, COC(CH₃)₃), 4.15 (q, 2H, OCH₂CH₃). ¹³C NMR (C₆D₆, 100 MHz) δ_C 15.7 (OCH₂CH₃), 28.3 (COC(CH₃)₃), 36.2 (COC(CH₃)₃), 69.5 (OCH₂CH₃), 171.5 (COC(CH₃)₃). FT-IR (ν_{max} /cm⁻¹): 2976s, 2902w, 2870w, 1581s, 1481m, 1457w, 1393m, 1358w, 1330s, 1197s, 1122w, 1092w, 1044s, 960w, 937w, 899w, 852w, 789w, 775w, 733w, 605m, 509w, 467w. Anal. Calcd for C₁₄H₂₈N₂O₄Sn: C, 41.31; H, 6.90; N, 6.88. Found: C, 41.13; H, 6.88; N, 6.75. EI-MS: m/z calcd for [Sn(edpa)₂]: 408 [M]⁺; found 408 (54%), 264 [Sn(edpa)]⁺ (47%), 145 [edpaH]⁺ (18%), 57 [^tBu]⁺ (100%).

Sn(mba)₂ (**10**): A solution of *N*-methoxybenzamide (mbaH) (0.73 g, 4.84 mmol) in diethyl ether (10 mL) was added dropwise to a stirring diethyl ether solution (20 mL) of Sn(btsa)₂ (1.1 g, 2.42 mmol). After being left to react overnight at room temperature, the volatiles were removed *in vacuo* to yield the crude product as a white solid. The pure product was obtained via recrystallization from an ether solution at 0 °C as colorless crystals. Yield: 0.64 g (63%). Mp 145 °C. ¹H NMR (C₆D₆, 400 MHz) δ_H 3.80 (s, 3H, OC*H*₃), 7.05 (m, 3H, Ph), 8.10 (d, br, 2H, Ph). ¹³C NMR (CDCl₃, 100 MHz) δ_C 61.0 (OCH₃), 127.2 (Ph-C), 128.3 (Ph-C), 130.1 (Ph-C), 132.0 (Ph-C), 163.3 (CO). FT-IR (ν_{max} /cm⁻¹): 3059w, 2963w, 2935w, 2894w, 1594m, 1556s, 1494w, 1461m, 1355s, 1329m, 1309w,

1128w, 1104w, 1050m, 1026w, 927w, 776w, 699s, 684w, 674w, 542w, 483w, 457w. Anal. Calcd for $C_{16}H_{16}N_2O_4Sn$: C, 45.56; H, 3.85; N, 6.69. Found: C, 45.27; H, 3.73; N, 6.65. EI-MS: m/z calcd for [Sn(mba)₂]: 420 [M]⁺; found 420 (52%), 270 [Sn(mba)]⁺ (6%), 105 [PhCO]⁺ (100%), 77 [Ph]⁺ (71%).

X-ray crystallography

Single crystals of all synthesized complexes were grown from saturated ether or hexane solutions at 0 °C. A specimen of suitable size and guality was coated with Paratone oil and mounted onto a glass capillary. Reflection data were collected on a Bruker Apex II-CCD area detector diffractometer, with graphite-monochromated MoK α radiation (λ = 0.71073 Å). The hemisphere of reflection data was collected as ω scan frames with 0.3° per frame and an exposure time of 10 s per frame. The SAINT²⁵ software was used for cell refinement and data deduction. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.²⁶ The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F2 using the SHELXTL/PC package.27 Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. CCDC 1481816-1481817 for complexes 5 and 10 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_- request/cif.

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Keywords: carboxylamide • germanium • tin • precursor • thinfilm

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Entry for the Table of Contents

Layout 1:

FULL PAPER

The alkoxy functionalized carboxylamides act as excellent stabilizing ligands for germanium and tin complexes and the physciochemical properties of these complexes prove their potential as precursors for thin film deposition.



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N-Alkoxy Carboxylamide-Stabilized Tin(II) and Germanium(II) Complexes for Thin Film Applications