ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 10, pp. 2027–2030. © Pleiades Publishing, Ltd., 2014.

Synthesis and Thermal Properties of Aminopyrimidine Ge(II) Precursors for CVD/ALD Technology[1]

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Received August 1, 2014

Abstract—Derivatives of aminopyrimidine had been used as ligands in various metals complexes but not as precursors for PRAM. A series of aminopyrimidine Ge(II) precursors has been synthesized for the first time. The diamine germanium (II) precursors were tested by TG and demonstrated excellent volatilization.

Keywords: Ge(II) precursors, CVD/ALD, synthesis, aminopyrimidine, thermal properties

DOI: 10.1134/S1070363214100284

INTRODUCTION

The use of Ge(II) precursors [1–5] for chemical vapor deposition (CVD) or atomic layer deposition (ALD) of phase-change chalcogenide alloy films with the prototype of GeTe or GeSbTe (GST) undergo a thermally induced crystalline-amorphous phase transition for data storage [6–17]. Recently it has been applied to the next-generation nonvolatile phase-change random access memory (PRAM) as a means to replace conventional dynamic and flash random access memory technologies [18–22]. However, there are limitations associated with germanium precursors for the CVDs of Ge alloy films such as high deposition temperatures that result in poor film conformance and morphology, hazardous process conditions, and premature decomposition [23–28].

The foregoing gave us an impulse to design and synthesize an appropriate ligand of volatile, thermally robust Ge precursors as potential sources for low-temperature CVD processes.

The research was focused on nitrogen containing heterocycles. Derivatives of aminopyrimidine had been used as the ligands in various metals complexes [29–30] but not the precursors for PRAM (Scheme 1). Aminopyrimidine due to its conjugated system can make complexes stable. Substituents can facilitate stability and certain thermal properties of metal compounds. Herein we report synthesis of a series of aminopyrimidine germanium complexes and characterize thermal stability and volatility of those as an early approach to their application as precursors of the PRAM.

RESULTS AND DISCUSSION

Synthesis of Ge(II) complexes. *N*-Butylpyrimidin-2-amine was chosen as the model substrate for reaction optimization. To start with LiMe was used as a base in THF, wherein the desired product was accumulated with a low yield. Application of LiMe as a base and ether as a solvent appeared to be most efficient and led to high yield of a product (Table 1).

The optimized conditions of the reaction of secondary amine salts with $GeCl_2$·dioxane (Table 2) were applied to a variety of substrates to determine the scope and limitations of the method. Aliphatic substituents on the nitrogen atom were beneficial for the reaction (60–70% yield). The aromatic substituent in the product **IIc** led to the lower yield probably due to poor solubility in dichloromethane, ether and hexane.

Thermal properties. Volatilization of Ge(II) precursors was tested by TGA. The temperatures of 50% mass (T_{50}) loss derived from TGA in simultaneous thermal analyses (STA) experiments for the secondary amine complexes **IIa**–**IId** are listed in Table 3.

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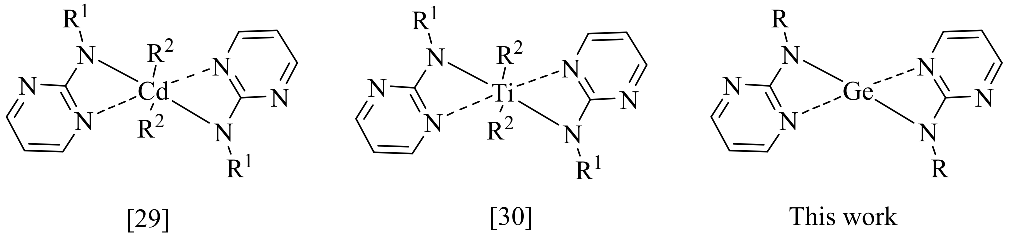
[1] The text was submitted by the authors in English.

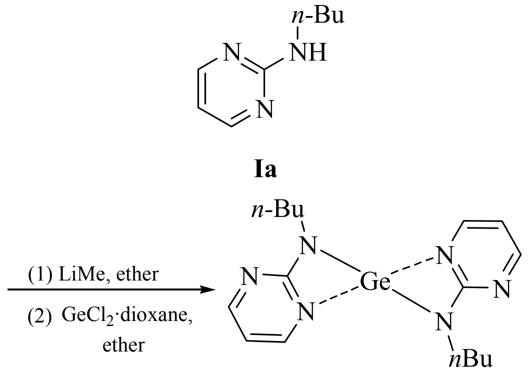
Scheme 1. Complexes with aminopyrimidine ligand



T_{50} values correlated with volatility of the sample and were used for comparing relative volatilities. Those were stable up to vaporization temperatures with minimal mass residuals that were far below those calculated in regard to the elemental germanium content. This discrepancy was due to weight loss from the intact transportation of the precursors prior to pyrolytic decomposition. It indicated clean transport characteristics and substantial vapor-phase stability.

Only 83% of the precursor **IIa** was transported up to 450°C. The complex **IIa** yielded multi-step transport TGA curves with corresponding endothermic peaks in the DSC plot thus suggesting thermal decomposition.

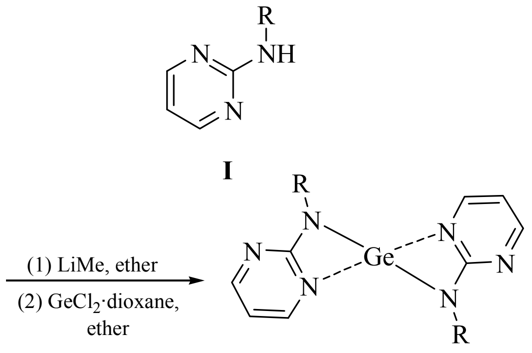
Table 1. Screening of reaction conditions[a]

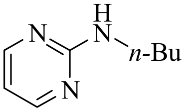
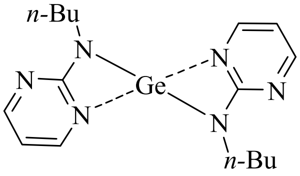
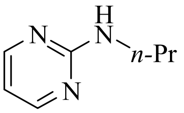
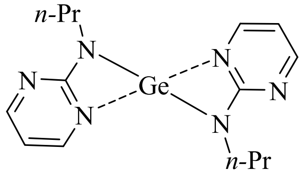
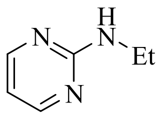
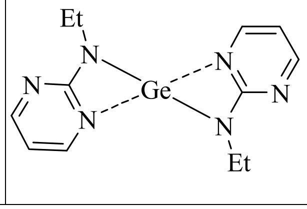


Entry	Base	Solvent	Time, h	Yield, %[b]
1	K_2CO_3	Ether	24	–
2	*t*-BuOK	Ether	24	–
3	LiMe	Ether	24	68
4	*n*-BuLi	Ether	24	60
5	LiMe	THF	24	<5
6	LiMe	Hexane	24	16
7	LiMe	Toluene	24	32
8	LiMe	Ether	12	48
9	LiMe	Ether	36	58
10	none	Ether	24	–

[a] Conditions: **Ia** (1 mmol), LiMe (1 mmol), ether, *RT* ~ –78°C, 3 h, in N_2, $GeCl_2$·dioxane (0.5 mmol), ether, 24 h, *RT* ~ –78°C, in N_2. [b] Isolated yields.

Table 2. Substrate expansion[a]



Entry	Substrate	Product	Yield, %[b]
IIa			50
IIb			62
IIc			40

[a] Conditions: **I** (1.0 mmol), LiMe (1 mmol), ether, *RT* ~ –78°C, 3 h, in N_2, $GeCl_2$·dioxane (0.5 mmol), ether, 24 h, *RT* ~ –78°C, in N_2. [b] Isolated yields by recrystallization based on **I**.

At the same time, the mass residuals exceed the calculation for the elemental germanium content meaning that the actual process was decomposition but not volatilization.

The result indicated low effect of the alkyl substituent on thermal properties of the complexes. Although the complexes had different substituents, the onset temperatures were close and differences between them and T_{50} very small.

Isothermal TGA experiments were carried out to study transport properties of the most volatile candidate **IIc** in which the temperature of the STA furnace was held at various temperatures for 6 h. At 200°C which was between the onset temperature and T_{50}, volatilization was slow and incomplete while the process was much faster at 300°C. At 400°C the complex was volatilized fully and quickly. The experiment indicated that the thermostability and volatilization of samples would be suitable for potential membrane materials.

EXPERIMENTAL

NMR spectra were recorded by Bruker Avance III 400 Spectrometers at 400 MHz (^{1}H) and 101 MHz (^{13}C) in DMSO-d_6 or $CDCl_3$ at 25°C.

General procedure. A solution of lithium salt of respective aminopyrimidine ligands (1.0 mmol) was added dropwise to a stirred solution of $GeCl_2$·dioxane (0.5 mmol) in diethyl ether (40 mL) at –78°C. The reaction mixture was warmed up to room temperature and stirred for 24 h. After removal of all volatiles the residue was extracted with dichloromethane (30 mL). Storage of the extract in a –29°C freezer over night afforded yellow powder of the corresponding product.

Compound IIa. White needle crystals. ^{1}H NMR spectra (400 MHz, DMSO), δ, ppm: 8.23 d (J = 4.7 Hz, 4H), 6.51 t (J = 4.7 Hz, 2H), 3.24 d.t (J = 7.1, 6.0 Hz, 4H), 1.54–1.45 m (4H), 1.32 d.q (J = 14.3, 7.3 Hz, 4H), 0.88 t (J = 7.3 Hz, 6H). ^{13}C NMR spectra (101 MHz, DMSO), δ, ppm: 162.31, 157.83, 109.58, 54.92, 31.05, 19.62, 13.76.

Compound IIb. White needle crystals. ^{1}H NMR spectra (400 MHz, DMSO), δ 8.55 d (J = 5.2 Hz, 4H), 6.88 t (J = 5.2 Hz, 2H), 3.31 t (J = 7.2 Hz, 4H), 1.57 d.t (J = 14.1, 7.1 Hz, 4H), 0.91 t (J = 7.1 Hz, 6H). ^{13}C NMR spectra (101 MHz, $CDCl_3$) δ 162.16, 157.41, 110.42, 41.34, 22.41, 10.40.

Table 3. STA data of complexes **IIa**–**IIc**[a]

Entry	Comp. no.	T_{50}, °C	Onset temperature, °C	Residual mass, %
1	**IIa**	298	170	0.0
2	**IIb**	288	172	3.4
3	**IIc**	289	170	4.2

[a] Gas atmosphere: argon, sample size, mg: 7.57 (**IIa**); 8.03 (**IIb**); 7.57 (**IIc**).

Compound IIc. White needle crystals. ^{1}H NMR spectra (400 MHz, DMSO), δ, ppm: 8.31 d.d (J = 52.1, 4.7 Hz, 4H), 6.52 t (J = 4.7 Hz, 2H), 3.31–3.22 m (4H), 1.12–1.08 m (6H). ^{13}C NMR spectra (101 MHz, $CDCl_3$), δ, ppm: 162.41, 158.00, 110.25, 36.22, 14.90.

CONCLUSIONS

In conclusion, an efficient method was developed for synthesis of aminopyrimidine derivatives of Ge(II) precursors with good yields. The Ge(II) precursors were tested by TG and the curves showed little difference from one another (**IIb** and **IIc** showed high volatilization). Collectively, the experiments provided some data for the empirical correlation between structure and properties of complexes and thermostability and volatilization of those indicated their potential as membrane materials.

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (no. 21371080), the Natural Science Foundation of Jiangsu Province (BK20130125) and 333 Talent Project of Jiangsu Province (BRA2012165).

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