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胍基配体的五核锡(Ⅱ)化合物的合成、结构及其对*N*,*N*′-二异丙基碳二亚胺加成苯胺反应的催化活性

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摘要:通过苯胺的衍生物三甲基硅基取代的苯胺基锂与无水二氯化锡按物质的量之比1∶1.25在无水无氧的条件下反应,合成了基于胍基配体的五核锡化合物[PhNC(NMe)$_2$N(H)SnCl]$_2$[PhNC(NMe)$_2$NSnCl]$_2$Sn (**1**)。其结构分别用核磁共振氢谱、碳谱、元素分析和X射线单晶衍射技术进行了表征。化合物**1**在催化苯胺与碳二亚胺加成生成胍的反应中表现出较好的活性,以高收率得到了胍化合物。

关键词:锡(Ⅱ);胍;结构;催化加成
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Pentanuclear Sn(Ⅱ) Guanidinate Complex: Synthesis, Structure, and Catalytic Activity for Addition of Arylamines into *N*,*N*′-Diisopropylcarbodiimide

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Abstract: A pentanuclear Sn(Ⅱ) guanidinate complex [PhNC(NMe)$_2$N(H)SnCl]$_2$[PhNC(NMe)$_2$NSnCl]$_2$Sn (**1**) was synthesized via the reaction of PhN(Li)SiMe$_3$ and anhydrous tin(Ⅱ) chloride. It was well structurally characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, and X-ray single crystal crystallography techniques. Complex **1** is an active catalyst in the addition reaction of arylamines into *N*,*N*′-diisopropylcarbodiimide giving guanidinates. CCDC: 1954650.

Keywords: tin(Ⅱ); guanidinate; structure; catalytic addition

0 Introduction

Guanidinate ligands as one of the important non-cyclopentadienyl ancillary ligands have received increasing attention in organometallic chemistry and synthetic chemistry. They are useful in stabilizing a variety of main group, transition metal, and *f*-block element complexes[1-3]. Some of these derivatives have been found to be efficient catalysts or pre-catalysts in organic and polymerization reaction[4-6]. The synthetic access for the preparation of most of these ligand species rely on the insertion reaction of carbodiimides RN=C=NR into a metal alkyl amide bond[7-10]. The non-symmetric guanidinato ligands were prepared via the nucleophilic reactions of N-centered anions to nitriles free from α-hydrogen, migrations of SiMe$_3$ group and isomerization[4-5,11]. Both the tin(Ⅱ) and cyclo-Sn(Ⅳ)S$_4$ complexes bearing symmetric amidinato ligands, much similar to the guanidinato ligands, were outstanding catalysts for the cyclotrimerization of phenyl isocya-

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nates to triaryl isocynnurates[12-13]. Sn (Ⅱ) guanidinate complexes have been limited to a handful of systems which typically contain sterically bulky groups[14-17]. Recently, some Sn (Ⅱ) guanidinate complexes were proved to be potential to act as single source precursors to the deposited thin films[18]. Very recently, homo- and hetero- mononuclear 1,3,5-triazapentadienyltin(Ⅱ) complexes and organotin (Ⅳ) complexes were synthesized and some of them were efficient catalysts for the catalytic addition of arylamine to *N*,*N*′-diisopropylcarbodiimide giving guanidine[19-20]. Here we report the synthesis and structural features of pentanuclear Sn (Ⅱ) guanidinate complex **1**. Its catalytic behaviors towards addition reaction of arylamines into *N*, *N*′-diisopropylcarbodiimide have been investigated and it is active as a catalyst to give a guanidinate.

1 Experimental

1.1 Reagents general procedures

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purchased from commercial sources. Deuterated solvent $CDCl_3$ was dried over activated molecular sieves (0.4 nm) and vacuum transferred before use. THF was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. $PhN(Li)SiMe_3$ was synthesized according to literature procedures[4]. Glassware was oven-dried at 150 ℃ overnight. The NMR spectra were recorded on Bruker AVANCE Ⅲ-600MHz spectrometer and recorded in $CDCl_3$. The chemical shifts were reported in δ values relative to external $SiMe_4$ for ^1H and ^{13}C. Melting points were measured in sealed capillaries and uncorrected. Elemental analyses were carried out using a Vario EL-Ⅲ analyzer (Germany).

1.2 Preparation

1.2.1 Synthesis of $[PhNC(NMe)_2N(H)SnCl]_2[PhNC(NMe)_2NSnCl]_2Sn$ (**1**)

$(CH_3)_2NCN$ (0.24 mL, 2.92 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.50 g, 2.92 mmol) in THF (30 mL) at −78 ℃. The resulting mixture was warmed to *ca.* 20 ℃ and stirred overnight. $SnCl_2$ (0.68 g, 3.65 mmol) was added at −78 ℃. The resulting mixture was warmed to *ca.* 20 ℃ and stirred overnight. The solution was concentrated *in vacuo* and stored at −20 ℃ for one month, affording colorless crystals of **1** (0.256 g, 28.4%). m. p. 138~141 ℃. Anal. Calcd. for $C_{36}H_{46}Cl_4N_{12}Sn_5\cdot 2THF$(%): C, 34.62; H, 4.09; N, 11.01. Found(%): C, 34.59; H, 4.07; N, 11.03. ^1H NMR ($CDCl_3$): δ 1.695 (s, THF), 2.565 (s, 12 H, $N(CH_3)_2$), 3.209 (s, 12 H, $N(CH_3)_2$), 3.764 (s,THF), 4.105 (s, 2 H, N*H*) 7.015~7.379 (m, 20 H, Ph). ^{13}C NMR ($CDCl_3$): δ 25.61 (THF), 40.02, 42.52 ($N(CH_3)_2$), 68.00 (THF), 122.18 (*p*-*C*Ph), 122.37 (*m*-*C*Ph), 129.71 (*o*-*C*Ph), 148.00 (*C*ipso-Ph), 169.51 (N*C*N).

1.2.2 General addition reaction procedures

A 30 mL Schlenk tube in a dried argon atmosphere was charged with **1** (0.015 g, 0.01 mmol). To the flask were added *N*,*N*′-diisopropylcarbodiimide (0.31 mL, 2.00 mmol) and arylamines (2.00 mmol). The resulting mixture was stirred at 25, 60 or 80 ℃ for the desired time. The reaction mixture was then hydrolyzed with water (0.5 mL), extracted with dichloromethane (3×10 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the residue was recrystallized in hexane to give the final product as a white solid.

1.2.3 X-ray crystallography

The single crystals of **1** suitable for X-ray diffraction studies were obtained. Data collection was performed with Mo *Kα* radiation (λ =0.071 073 nm) on a D8 Venture diffractometer using the Ω scan mode yielding a total of N reflections. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS)[21]. The structure was solved by the direct method (SHELXS-97)[22]. The remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using riding modes (SHELXTL)[23]. Crystal data and details of data collection and refinements for **1** are summarized in Table 1.

CCDC: 1954650.

Table 1 Crystallographic data and structural refinement for 1

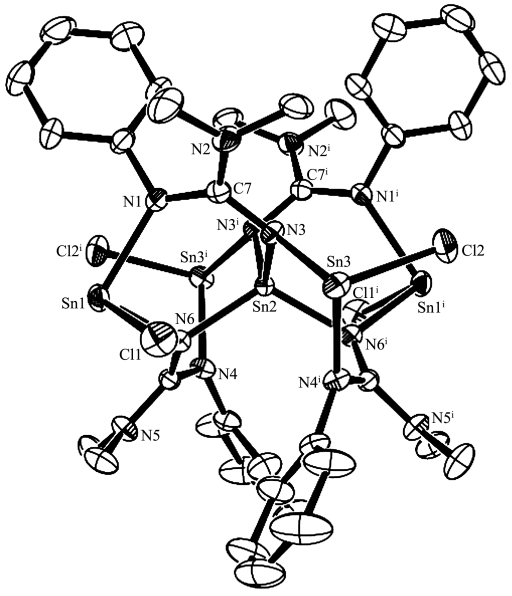
Formula	$C_{44}H_{62}Cl_4N_{12}O_2Sn_5$	D_c / (g·cm^{-3})	1.78
Formula weight	1 526.3	μ / mm^{-1}	0.025 8
Crystal system	Orthorhombic	F(000)	2 976
Space group	*Pbcn*	Reflection collected	30 424
a / nm	2.190 96(15)	Independent reflection	5 015
b / nm	1.230 31(9)	Parameter	311
c / nm	2.113 31(15)	R_1, wR_2 [$I>2\sigma(I)$]	0.029 8, 0.061 5
V / nm^3	5.696 6(7)	R_1, wR_2 (all data)	0.033 9, 0.064 0
Z	4	Goodness of fit on F^2	1.207

2 Results and discussion

2.1 Synthesis and molecular structure of [PhNC(NMe)$_2$N(H)SnCl]$_2$[PhNC(NMe)$_2$NSnCl]$_2$Sn (1)

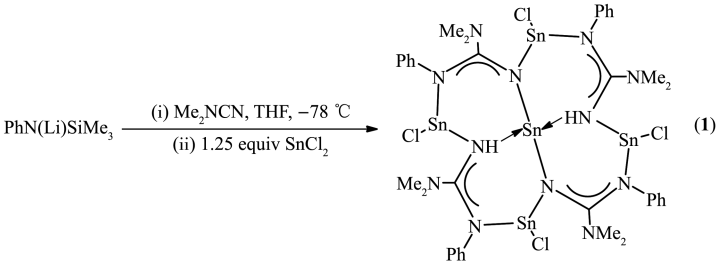
Compound **1** was prepared according to Scheme 1. Thus, treatment of PhN(Li)SiMe$_3$ with one equivalent of Me$_2$NCN in THF at low temperature, and then 1.25 equiv of $SnCl_2$, afforded the Sn compound. The likely course of reaction was successive insertion of Me$_2$NCN into the Li-N(SiMe$_3$)Ph bond, elimination of Me$_3$SiCl molecules, hydrolysis, and metathesis with $SnCl_2$, thus featuring both monoanionic and dianionic guanidinate ligands in **1**. Complex **1** has been characterized by ^{1}H and ^{13}C NMR and elemental analysis. Suitable crystals for X-ray diffraction analysis can be obtained by slowly cooling the saturated THF solution to −20 ℃ for one month.

The molecular structure of compound **1** is shown in Fig.1. It crystallizes in the orthorhombic space group *Pbcn*. In **1**, there are two mono- and two dianionic guanidinato ligands. The tetra-coordinated central Sn(Ⅱ) ion bonded to four terminal nitrogen atoms from each of mono- or dianionic guanidinato ligand, located in a tetrahedral environment with a dihedral angle of 89.6° between planes N3Sn2N3^i and N6Sn2N6^i (Fig.1). Each



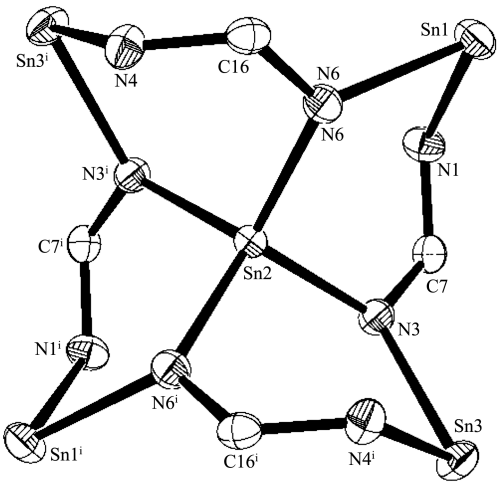
Thermal ellipsoids are drawn at 50 % probability level; Hydrogen atoms are omitted for clarity; Selected bond lengths (nm) and angles (°): N(1)-C(7) 0.136 6(5), N(2)-C(7) 0.135 4(5), N(3)-C(7) 0.133 3(5), N(4)-C(16) 0.137 2(5), N(5)-C(16) 0.134 9(5), N(6)-C(16) 0.133 5(5), Sn(1)-N(1) 0.221 5(3), Sn(1)-N(6) 0.218 9(3), Sn(1)-Cl(1) 0.249 0(1), Sn(2)-N(3) 0.202 8(3), Sn(2)-N(6) 0.202 1(3), Sn(3)-N(3) 0.216 5(3), Sn(3)-N(4^i) 0.220 9(3), Sn(3)-Cl(2) 0.249 5(1); N(1)-C(7)-N(3) 120.8(3), N(4)-C(16)-N(6) 120.5(3), N(1)-Sn(1)-N(6) 89.43(12), N(1)-Sn(1)-Cl(1) 89.84(9), N(6)-Sn(1)-Cl(1) 90.34(9), N(3)-Sn(2)-N(6) 106.49(13), N(3)-Sn(3)-N(4^i) 89.86(12), N(3)-Sn(3)-Cl(2) 90.82(9), N(4^i)-Sn(3)-Cl(2) 88.71(9); Symmetry code: ^{i} 1−*x*, *y*, 1/2−*z*

Fig.1 Molecular structure of **1**



Scheme 1 Synthetic route for compound **1**

of other four Sn(Ⅱ) ions coordinates with two terminal nitrogen atoms from each of mono- and dianionic guanidinato ligand and a chlorine ligand in a pyramidal manner. The Sn(Ⅱ) ions are almost in a plane with the mean deviation of 0.007 50 nm. The central of molecule **1** is a tin atom (Sn2) surrounded by four fused six-membered Sn_2N_3C rings. The 16-membered macrocycle $(SnNCN)_4$ may be regarded as a star containing $Sn_5N_8C_4$ that four N atoms with respect to the central tin atom Sn2 (Fig. 2). The structure of **1** is different from those clusters or cages, that polynuclear tin complexes possessing N and O donor groups normally have, such as tin(Ⅱ) imido cubanes, distorted cubanes or boat with $[SnN]_4$ motif, mix-oxidation-state Sn(Ⅱ)/Sn(Ⅳ) double cubanes with Sn_7N_8 (two Sn_4N_4 cubanes which share a central Sn(Ⅳ) ion)[19,24-26], and a ladder-like or drum structures for the higher oxidative state of organooxotin clusters[27-28].



Symmetry code: i 1−*x*, *y*, 1/2−*z*

Fig.2 Core of **1**

For the C7N1N2N3 and C16N4N5N6 frameworks, the three C-N bond distances in the guanidinate ligands are in a range of 0.133 5(5)~0.136 6(5) nm and 0.133 5(5)~0.137 2(5) nm, respectively. These are comparable to C(sp^2)-N(sp^2) bonds (*ca*. 0.136 nm)[29], indicating of lone pair donation from the nitrogen atom (dimethylamido group) to the central carbon and concomitant electron delocalization involving all three nitrogen atoms of the chelating ligands. The bond distance of N3-Sn3 (0.216 5(3) nm) is slightly shorter than that of N6-Sn1 (0.218 9(3) nm). The Sn-Cl bond distances of Sn1-Cl1 (0.248 98(12) nm) and Sn3-Cl2 (0.249 50(12) nm) are comparable to that of tri-coordinated tin(Ⅱ) triazapentadienyl complex (0.250 97(9) nm)[19], shorter than that in [(*i*-Pr)$_2$ATI]SnCl ([(*i*-Pr)$_2$ATI]=*N*-isopropyl-2-(isopropylamino)troponimine) (0.254 2(2) nm)[30], and in $[C_5H_5]$SnCl (0.268 nm)[31].

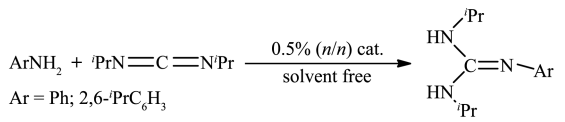
The bond angles of N1-Sn1-N6, N3-Sn2-N6 and N3-Sn3-N4^i are 89.43(12)°, 106.49(13)° and 89.86(12)°, respectively. The bond angles of N-C-N in the CN_3 frameworks are in a range of 119.0(3)°~120.8(3)°. The Sn1…Sn2, Sn1…Sn3 and Sn2…Sn3 separations are 0.352 4, 0.491 4 and 0.351 0 nm, respectively, suggesting the weak tin-tin bonding (Sn-Sn 0.368 nm)[32] between Sn1 and Sn2, Sn2 and Sn3, respectively.

2.2 Catalytic behaviors of the catalyst

The catalytic activity of **1** for catalytic addition of arylamines to *N*,*N*′-diisopropylcarbodiimide to guanidinates was evaluated. The optimum conditions and results are listed in Table 2. For comparison, $SnCl_2$ was also used in the addition reaction of arylamines to *N*,*N*′-diisopropylcarbodiimide (Table 3). All reactions were performed under solvent free condition.

The reaction of aniline with *N*,*N*′-diisopropylcarbodiimide was performed at 25 ℃ in the presence of **1**.

Table 2 Addition of $ArNH_2$ to ^{i}PrNCN^{i}Pr by complex 1[a]



Entry	*T* / ℃	*t* / h	Yield / %[c]
1	25	0.25	16.8
2	25	0.50	40.3
3	25	1.0	80.4
4	25	2.0	84.6
5	60	0.25	76.8
6	60	0.50	91.0
7	80	0.25	95.9
8	80	0.50	97.3
9[b]	25	0.25	10.5
10[b]	60	0.25	28.5
11[b]	80	0.25	40.3
12[b]	80	0.50	51.5

[a] Arylamines (2.00 mmol), *N*, *N*′-diisopropylcarbodiimide (2.00 mmol); [b] Ar=2,6-^{i}PrC$_6$H$_3$; [c] Isolated yields.

Table 3 Addition of $ArNH_2$ to $^{i}PrNCN^{i}Pr$ by $SnCl_2$[a]

Entry	*T* / ℃	*t* / h	Yield / %[c]
1	25	0.25	trace
2	25	0.50	2.4
3	25	1.0	7.3
4	25	2.0	28.6
5	60	0.25	10.2
6	60	0.50	34.8
7	80	0.25	13.7
8	80	0.50	51.3
9	80	1.0	70.5
10[b]	25	0.25	0
11[b]	60	0.25	trace
12[b]	60	0.50	trace
13[b]	80	0.25	trace
14[b]	80	0.50	3.6

[a] Arylamines (2.00 mmol), *N*, *N*′ - diisopropylcarbodiimide (2.00 mmol), 0.5%(*n*/*n*) catalyst loading; [b] Ar=2,6-$^{i}PrC_6H_3$; [c] Isolated yields.

With the increase of the reaction time from 0.25 to 2 h, the yields increased from 16.8% to 84.6% (Table 2, Entry 1~4). At 60 and 80 ℃, the yields in 0.25 h were 76.8% and 95.9 %, respectively (Table 2, Entry 5 and 7), much higher than that of 16.8% at 25 ℃ (Table 2, Entry 1). In 0.5 h, the higher temperature will proceed the transformation and give a higher yield of guanidinate (Table 2, Entry 6 and 8). By comparison, both the complex **1** and $SnCl_2$ can accelerate the addition reaction with the increase of the reaction temperature and reaction time in a similar manner, but the catalytic activities of **1** are much higher than those of $SnCl_2$ (Table 3). For instance, the reaction with $SnCl_2$ afforded guanidinate in only 28.6% (Table 3, Entry 4), 34.8% (Table 3, Entry 6), and 51.3% (Table 3, Entry 8) isolated yields, respectively, whereas the yields were 84.6% (Table 2, Entry 4), 91.0% (Table 2, Entry 6) and 97.3% (Table 2, Entry 8), respectively, when complex **1** was used. However, the activity of **1** at 80 ℃ in 0.5 h (Entry 8, 97.3%) was lower than those of some Lewis acids such as $GaCl_3$, which can afford the product in the yield of 99% in only 2 min at 10 ℃ (5%(*n*/*n*) catalyst loading)[33]; but comparable to that of anhydrous $AlCl_3$ (97%), regardless of the reaction time and reaction temperature[34]. When complex **1** was used in the addition reaction of bulky amine and *N*,*N*′-diisopropylcarbodiimide, the lower yields were found and neither the higher reaction temperature nor the prolong reaction time can be helpful to the catalytic reaction (Table 2, Entry 9~12). The much less active situation of $SnCl_2$ was shown in Table 3 (Entry 10~14). The less efficient with lower yields because of the larger steric hindrance of the substrate was also documented in the lanthanide aryloxide complexes[35] and organotin (Ⅳ) complexes[20] reported previously.

The proposed pathway involved the amination of **1** by aniline giving an intermediate, then the nucleophilic addition reaction to a carbodiimide yielding an active species, protonolysis by aniline affording the product and the intermediate. The four tri-coordinated tin(Ⅱ) ions(Sn1, Sn1^{i}, Sn3, and Sn3^{i}) having sterically active lone pair, would have been relevant to the catalytic activity of **1**. The experimental data on the reaction pathway and the isolation of the intermediate and the active species are worth expecting in the future.

3 Conclusions

In conclusion, a pentanuclear Sn(Ⅱ) guanidinate complex $[PhNC(NMe)_2N(H)SnCl]_2[PhNC(NMe)_2NSnCl]_2Sn$ (**1**) was readily prepared via the reaction of PhN(Li)$SiMe_3$ with Me_2NCN, and further $SnCl_2$. The structural features were determined by X-ray diffraction study. This complex exhibits good activity for the catalytic addition of aniline to *N*,*N*′-diisopropylcarbodiimide. Further studies on the synthesis of new metal guanidinate complexes and use in the reactions of various primary and secondary aromatic amines to carbodiimide are pursuing in our laboratory.

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