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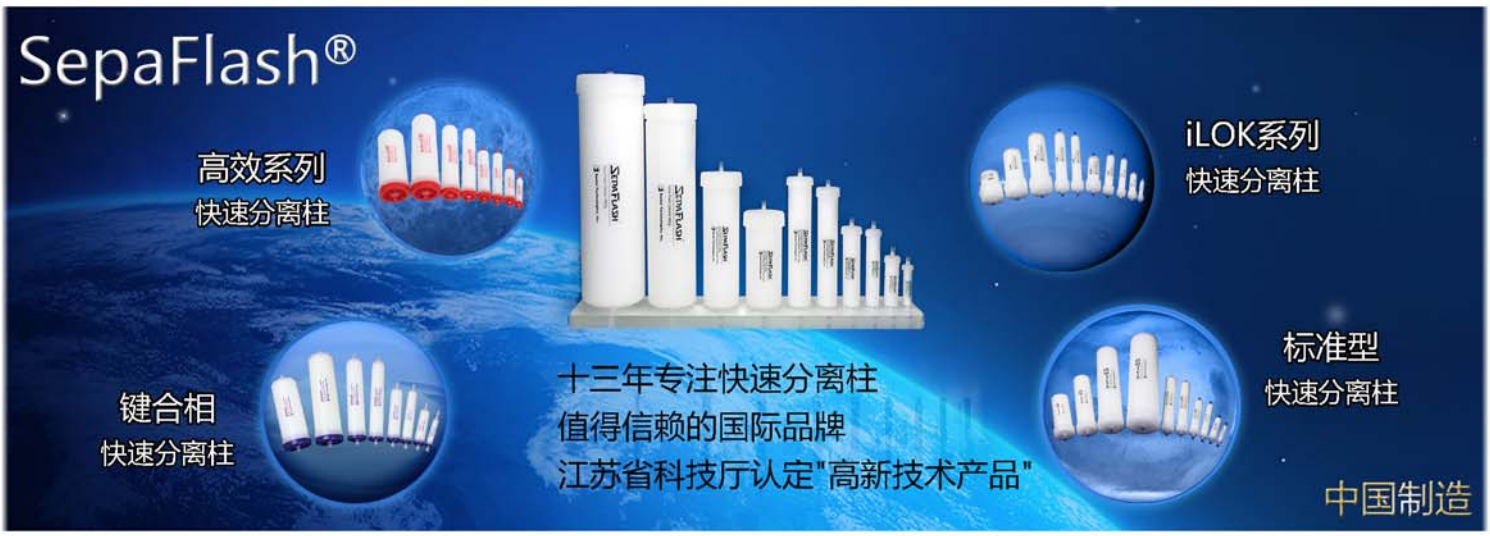

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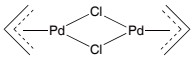

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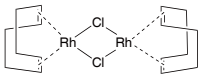

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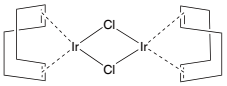

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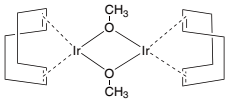

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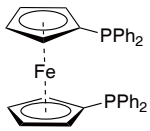

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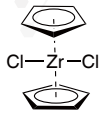

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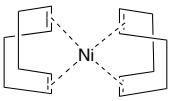

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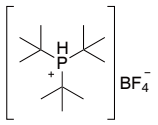

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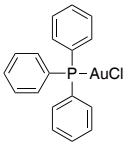

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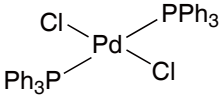

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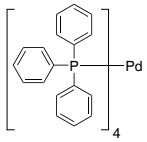

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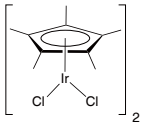

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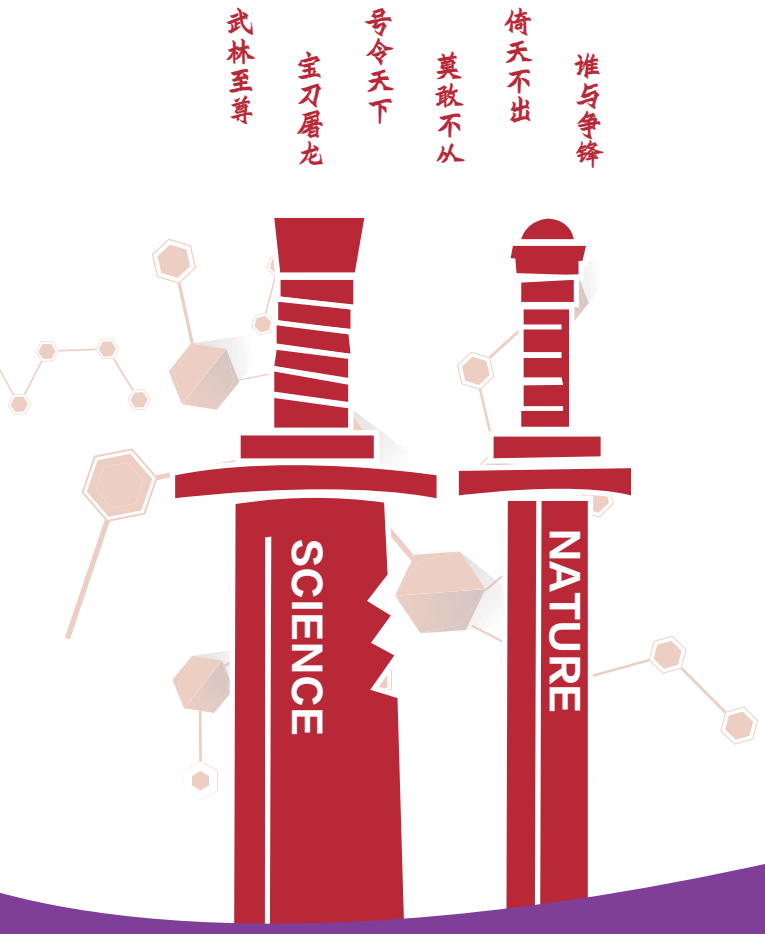

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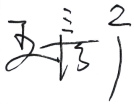
前　言

中国化学会第十九届全国金属有机化学学术讨论会于2016年10月28～31日在浙江大学紫金港校区体育馆成功举行。本届会议由中国化学会主办，浙江大学化学系、浙江省化学会和中国科学院上海有机化学研究所金属有机化学国家重点实验室共同承办，并得到国家自然科学基金委与浙江省科协的资助。本届会议云集了我国金属有机化学界的著名专家学者以及广大研究生约1500人，其中包括8位院士、25位国家杰青等著名专家学者，另外，还邀请了美国、香港以及新加坡的著名化学家。与会代表围绕金属有机化学研究的前沿科学问题展开热烈交流，展示最新研究成果、展望学科未来，极大地促进了我国金属有机化学研究的进一步发展。

本届会议共收到会议论文549篇，参会代表们围绕金属有机化学研究的前沿科学问题，以大会报告、邀请报告、口头报告和墙报展等进行了形式多样、丰富多彩的交流。会议共安排了5个大会报告、1个黄耀曾金属有机化学终身成就奖获奖报告、2个黄耀曾金属有机化学奖获奖报告、25个邀请报告、24个口头报告以及317个墙报展。会议的成功举办，也获得中国化学会的赞誉，并授予本次会议承办单位“优秀学术交流组织奖”。本届会议还得到了国家自然科学基金委员会、浙江省科协和26家相关领域企业和公司的赞助与支持，在此表示衷心地感谢！

为了支持我国金属有机化学的发展，集中展示我国金属有机化学研究的最新成果，《有机化学》编辑部于2017年5月出版一期“金属有机化学专辑”。该专辑共录用稿件29篇，其中综述与进展8篇，研究论文14篇，研究简报6篇，研究通讯1篇。感谢《有机化学》编辑部对本专辑按时出版所付出的辛劳！萨恩化学技术(上海)有限公司、苏州欣家园化学科技有限公司、江苏欣诺科催化剂有限公司、三泰科技(常州)有限公司对本专辑印刷出版提供了大力支持，在此也深表感谢！



中国化学会第十九届全国金属有机化学学术讨论会组委会主席

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Chinese Journal of Organic Chemistry NOTE

两种 β-二亚胺锡化合物的合成与表征

马小莉* 邓紫嫣† 姚苗苗† 钟明东 李文玲 杨 智*
(北京理工大学化学与化工学院 北京 100081)

摘要 *N*,*N*-二(2,6-二异丙基苯基)-2,4-戊二亚胺的锂盐与二甲基二氯化锡的反应以及 *N*,*N*-二(2,6-二乙基苯基)-2,4-戊二亚胺的锂盐与三甲基氯化锡的反应均以物质的量比为 1∶1 在室温下进行, 分别得到了新化合物 N(Ar)=C(Me)CH=C(NHAr)CH_2SnMe_2Cl•C_7H_8 (**1**) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) 和 [N(Ar')C(Me) = CHC(= NAr')CH_2SnMe_2]$_2$•CH_2Cl_2 (**2**) (Ar' = 2,6-Et$_2$C$_6$H$_3$). 通常来说, β-二亚胺配体与金属卤化物反应容易形成氮-金属-氮键, 而化合物 **1** 和 **2** 中由于 $SnMe_2Cl$ 与 $SnMe_3$ 基团的路易斯酸性使得锡-氮键断裂和锡-碳键的生成得到了少见的氮-锡-碳键. 化合物 **2** 是罕见的具备两个共振结构式的锡二聚体. 通过核磁共振、元素分析及 X 射线单晶衍射分析鉴定了这两种化合物的结构. 通过这两个结构的对比探讨了二聚体 **2** 的形成机理.

关键词 β-二亚胺配体; 金属卤化物; 锡二聚体; 氮-锡-碳键

Synthesis and Characterization of Two β-Diketiminato Tin(IV) Compounds

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(*School of Chemistry and Chemical Engineering*, *Beijing Institute of Technology*, *Beijing 100081*)

Abstract The reactions of L^{1}Li [L^1=HC(CMeNAr)$_2$, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$] with Me_2SnCl_2, and L^{2}Li [L^2=HC(CMeNAr')$_2$, Ar'=2,6-Et$_2$C$_6$H$_3$] with Me_3SnCl in a molar ratio of 1∶1 were carried out at room temperature and acquired two new compounds, N(Ar)=C(Me)CH=C(NHAr)CH_2SnMe_2Cl•C_7H_8 (**1**) and [N(Ar')C(Me)=CHC(=NAr')CH_2SnMe_2]$_2$•CH_2Cl_2 (**2**), respectively. Different from regular nitrogen-metal-nitrogen bonds generated by the reactions of β-diketiminato ligands with metal halides, uncommon nitrogen-tin-carbon bonds in compounds **1** and **2** were obtained by Sn—N bond cleavage and concomitant Sn—C bond formation due to the Lewis acidity of $SnMe_3$ and $SnMe_2Cl$ group. Compound **2** is a rare tin dimer with two resonant structures . Two compounds have been confirmed by ^{1}H NMR, ^{13}C NMR, elemental analysis, and single crystal X-ray structural analysis. Through the comparison of compounds **1** and **2**, the formation mechanism of dimer **2** has been investigated.

Keywords β-diketiminato ligands; metal halides; tin dimer; nitrogen-tin-carbon bonds

There has been continued research aimed at the discovery of metal compounds with *N*-aryl substituted β-diketiminato ligand L^{1}H [L^1 = HC(CMeNAr)$_2$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$] as some of these compounds can be used as precursors in reactions with various small molecule substrates at the center[1] and efficient homogeneous catalysts.[2] In these researches, most coordination modes of L^{1}H can be summarized in four activated modes,[3] including normal N—H activation,[4] backbone Me C—H activation,[5] backbone γ-CH ligation or γ-C—H activation,[6] and a combination of backbone Me and γ-CH C—H activation.[4a,6a] Among which, N—H activation was common due to the relatively rigid N,N-chelation backbone and the demanding *N*-substituents,[3] while N,C-bonded β-diketiminato compounds were rarely reported. With these two modes, compounds containing phosphorus,[5a] antimony,[7] bismuth[3] and germanium[8] have been reported. Possible reasons for the formation of N,C-bonded mode instead of N,N-bonded mode are summed up as follows: the ease of breakage of center atom-nitrogen bond, the control of thermodynamic conditions, and the steric demand of metal group. In the reactions of phosphorus halides, antimony(III) halides and

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† 这些作者对该研究贡献相等(These authors contributed equally to this work).

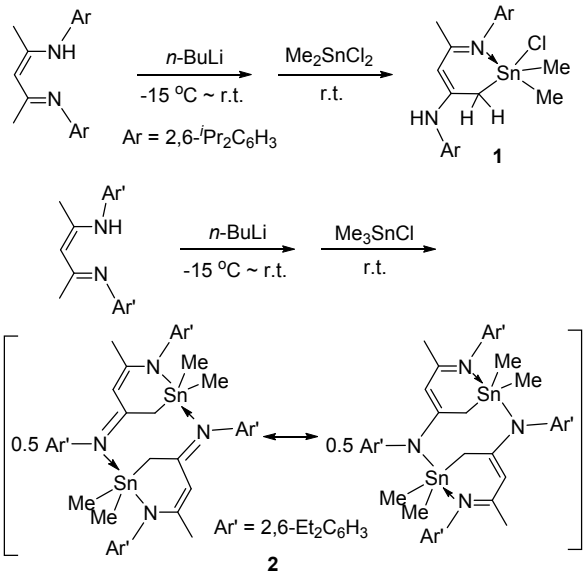
bismuth halides with *β*-diketiminato ligands, the intramolecular C—H activations were thought to be attributed to the presence of the reactive P—X (X=halide), Sb—X, Bi—N and the reaction conditions.[3,5a,7] The compounds consisting of amino group and Lewis pairs with MMe_3 (M=Si, Ge, Sn) group undergo dipolar addition reactions with alkyne molecules to form heterocyclic intermediates which rearrange through a N—M bond cleavage and concomitant N—P double bond formation due to the Lewis acidity of the MMe_3 group being weaker than that of the MCl_3 groups.[9,10] Thus, it indicates that the reactivity of center atom-nitrogen bond depends on the Lewis acidity of the $MCl_{3-n}Me_n$ (n= 0, 3) group. In 2011, Zhu and his co-workers[3] found that temperature was the main factor to cause versatile L ligation modes of Bi(III) compounds. The reaction of $BiCl_3$ with L^1Li was carried out under various temperature conditions and afforded three ligation modes of Bi (III) compounds. Alkaline-earth metal complexes can also undergo intramolecular C—H activation process: series similar N,C-bonded dimers could be produced from two molecules of N,N-chelation mode of L at metal through the elimination of small molecules[11]. Thus, under proper operation condition, N,N-chelation mode can be transformed to N,C-bonded mode in the reactions of halides with *β*-diketiminato ligands.

It is worth noting that, in scanty reports of *β*-diketiminato compounds of tin[4b,6b,12], there is a special dinuclear N,C-bonded structure[12a] with chair configuration, which is similar to that of the N,C-bonded Yb[13] and alkaline-earth metal complexes[11]. However, only two uncertain intermediates have been given in the formation of the tin dimer and the definite formation mechanism has not been reported. By careful control of the reaction and isolation conditions, two new tin compounds **1** and **2** were prepared, which were structurally characterized and exhibited C,N-bonded L ligation modes. In this paper, these results are reported and the formation mechanism for $[N(Ar')C(Me)=CHC(=NAr')CH_2SnMe_2]_2{\bullet}CH_2Cl_2$ (**2**) is discussed.

1 Results and discussion

Compound **1** was prepared from the reactions of L^1H with *n*-BuLi and Me_2SnCl_2 (Scheme 1), while compound **2** was prepared from L^2H with *n*-BuLi and Me_3SnCl. Compounds **1** and **2** were isolated after growing colorless crystals from the concentrated toluene and dichloromethane solution, respectively. They are soluble in toluene, ether, tetrahydrofuran, and trichloromethane. **1** was characterized by ^1H NMR investigation in $CDCl_3$ solution as well as elemental analysis. **2** was characterized by ^1H NMR, ^{13}C NMR investigation in $CDCl_3$ solution as well as elemental analysis. The structures of **1** and **2** (Figure 1) were unequivocally established using X-ray crystallography.

The single-crystal X-ray structural analysis of **1** unambiguously discloses a C,N-chelation bonding mode, which is completely different to those regular *N*,*N*-chelation bonding mode. A series of Bi(III)[3] and Sb(III)[7] com-



Scheme 1 Preparation of compounds **1** and **2**

pounds with versatile L-ligation modes were prepared by careful control of the reaction and isolation conditions, especially the temperature. To reduce *N*,*N*-chelation byproducts, the operation of adding *n*-BuLi solution at −15 ℃ to the solution of L^1H was completed in about three minutes and finally the ice-salt bath was removed and the temperature was allowed to increase rapidly from −15 ℃ to room temperature. Furthermore, in the second step, Me_2SnCl_2 solution was added at room temperature, and the reaction was kept for at least 48 h. The same reaction condition was applied in the synthesis of compound **2**.

In a ^1H NMR spectrum, the singlet peaks at δ 8.93 and 2.05 are assignable to the NH and $SnCH_2$ protons, respectively in compound **1**. It indicates that intramolecular C—H activation rather than N—H activation occurred in the reaction. Two single peaks at δ 0.78 and 0.76, and a single peak at δ 2.05 in ^1H NMR spectrum are assignable to the protons of $SnMe_2Cl$ and CH_2Sn, respectively. It reveals that the tin atom of **1** exhibits penta-coordination, and it is coordinated by one nitrogen atom of the ligand, three carbon atoms and one chloride atom. The ^1H NMR spectrum of **2** exhibits the backbone methyl (CMe), methane (γ-CH), and methane ($SnCH_2$) proton resonances as singlets at δ 1.61, 4.79 and 1.73, respectively, which also shows a N,C-chelation mode of ligand to Sn. Similarly, $[N(Ar)=C(Me)CH=C(NHAr)CH_2BiCl(\mu\text{-}Cl)]_2$ was thought to undergo intramolecular C—H activation due to the presence of the active Bi—N bond.[3,14] It is reasonable to deduce that such activation may be induced from structural isomerization[15], which is probably due to the active Sn—N bond.[9,15,16] In the formation of **1** and **2**, L^1Li and L^2Li may act like $HC(CPhNPh)_2Li$ to form the C_3N_2Sn-heterocycle intermediate $HC(CMeNAr)_2SnMe_2Cl$ (**A**) and $HC(CMeNAr')_2SnMe_3$ (**B**),[12b] respectively. Since the Lewis acidity of the $SnMe_2Cl$ and $SnMe_3$ group is weaker than that of the SnX_3 (X=Cl, Br) groups, the as-formed heterocycles **A** and **B** are not stable.[9,10] These heterocycles would further rearrange

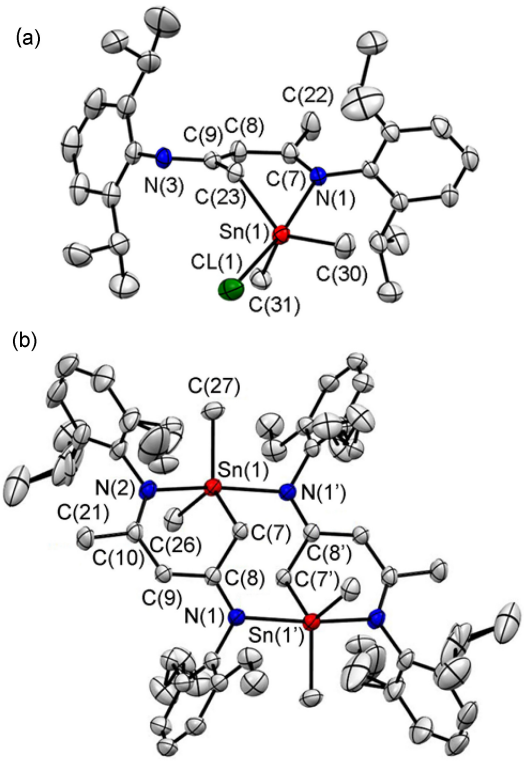


Figure 1 An ORTEP representation of compounds **1** (a) and **2** (b) with atom labeling scheme

C-bound hydrogen atoms are omitted for clarity. A molecule of CH_2Cl_2 is omitted from the diagram

through a N—Sn bond cleavage and concomitant C—Sn bond formation (as shown in Scheme 2).[9] However, we tried to isolate such heterocycles by controlling the reaction temperature and/or time but failed. This probably suggests a very fast transformation to **1** and intermediate **C** that is confirmed by referring to the structure of **1**.

However, the reaction of L^2Li and Me_3SnCl was not stopped here because of the active Sn—CH_3 bond.[12b,12c] The elimination of methane occurred between $SnMe_3$ moiety of intermediate **C** and NH proton of adjacent molecule with symmetrical arrangement (Scheme 2), which resulted in an eight-membered ring. The reaction was kept at the room temperature for a long time for the release of methane. At the same time, the electrons of conjugated double bonds in six-membered ring of SnCCCCN were affected by the deprotonation of N—H and dispersed in original NCCCN plane, resulting in two resonant structures which make dimer **2** more energetically favored. The molecule of **2** shows a dinuclear dimer arrangement with both intramolecular and intermolecular bondings which make the tin atom coordinated by two nitrogen atoms and three carbon atoms. Moreover, the two resonant structures of **2** could be drawn according to its crystal structure shown in Figure 2 and confirmed by the analysis of crystallographic data.

All selected geometrical parameters of the two compounds are presented in Figure 2. Based on the above analysis, the backbone of the ligand in compounds **1** and **2** had undergone an intramolecular C—H activation, resulting in a similar six-membered ring of NSnCCCC in **1** and **2**. The related bond lengths and bond angles of the two compounds are broadly similar. For example, 2.152(2) Å (Sn(1)—C(23)) in **1** is comparable to 2.153(3) Å (Sn(1)—C(7)) in **2**, 78.98(8)° (N(1)—Sn(1)—C(23)) in **1** is comparable to 77.32(9)° (N(2)—Sn(1)—C(7)) in **2**. However, there are subtle differences in bond lengths between them because of different positions of conjugated double bonds. The bond lengths of C(10)—N(2) (1.328(4) Å) and C(8)—C(9) (1.413(4) Å) in **2** are longer than those pure double bond lengths of C(7)—N(1) (1.313(3) Å) and C(8)—C(9) (1.381(3) Å) in compound **1**, while the bond lengths of C(8)—N(1) (1.330(4) Å) and C(9)—C(10) (1.407(4) Å) in **2** are shorter than those pure single bond lengths of C(9)—N(3) (1.349(3) Å) and C(7)—C(8) (1.424(3) Å) in compound **1**. Moreover in compound **2**, the two C—N bond lengths are almost the same and also do the two C—C bond lengths. These phenomena of longer and shorter average bond lengths have been found in the typically energetically favored NCCCNH ring of *β*-diimine tautomer. This demonstrates that in compound **2** the electrons are flexibly dispersed in the approximate plane N(2)C(10)C(9)-C(8)N(1) and the two resonant structures of **2** obtained are reasonable. The two resonant structures transform to each other, making **2** more stable.

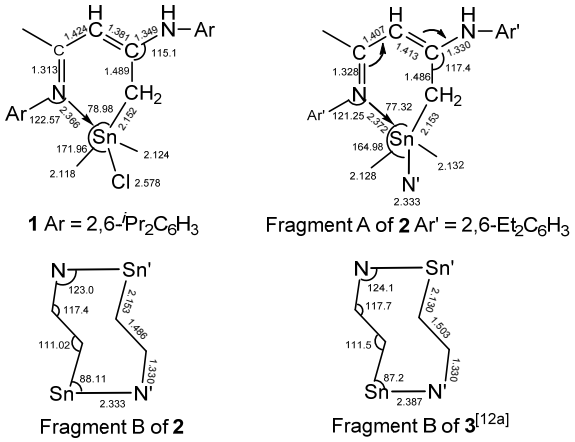
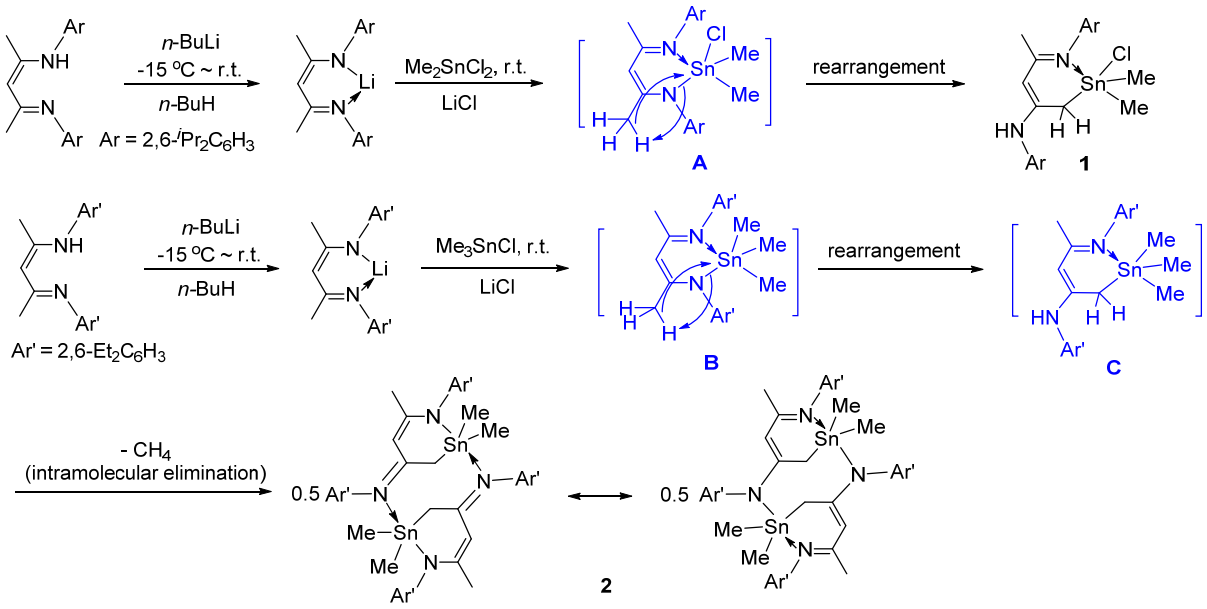


Figure 2 Selected bond lengths (Å) and angles (°) of selected fragments of compounds **1**, **2** and **3**

In the fragment A of compound **2** (Figure 2), the Sn(1)—N(2) bond length (2.372(2) Å) is a little longer than that of the Sn(1)—N(3) (2.333(3) Å) and closer to that in compound **1** (2.366(19) Å). Compound **2** is somewhat unusual in that the eight-membered ring formed by the elimination of methane between two "monomers" and being chair-shaped. This ring (fragment B of **2**) containing three approximate planes, N(1)C(8)C(7')Sn(1'), C(8)C(7')C(8')-C(7), and C(7)Sn(1)N(1')C(8'), looks like the chair- shaped ring of cyclohexane with two planes folded in ver-tically opposite directions. The chair configuration that conforms to the minimum energy principle makes **2** more stable. The similar structural feature has been found only in compounds of Yb,[13] group 2 alkyls,[11] and [N(Ar')C(Me)=CHC-



Scheme 2 Formation mechanism of compounds **1** and **2**

(=NAr')$CH_2SnMe_2]_2$•C_7H_8 (**3**).[12a]

The bond angles in the fragment B of **2** are 88.11(10)° (C(8')—Sn(1')—N(1)), 111.0(19)° (C(8)—C(7)—Sn(1)), 117.4(2)° (N(1)—C(8)—C(7)), and 123.0(2)° (Sn(1')—N(1)—C(8)). The fragment B in **2** is very similar to that in **3**: the latter having Sn(1)—N(2'), Sn(1)—C(17), C(3)—C(17) and N(2)—C(3) bond lengths of 2.387(6), 2.130(6), 1.503(9) and 1.330(9) Å, respectively, and C(17)—Sn(1)—N(2'), C(3)—C(17)—Sn(1), N(2)—C(3)—C(17) and C(3)—N(2)—Sn(1') bond angles of 87.2(2)°, 111.5(5)°, 117.7(6)° and 124.1(4)°, respectively.

As clearly presented in Figure 1, surprisingly, ethyl in **2** is not given single definite localization but two, while isopropyl in **1** or **3** is fixed as normal. In the process of molecular stacking, ethyl could be rotated more flexibly than isopropyl and arranged in two possible localizations. Furthermore, ^{1}H NMR spectra of **1** and **2** exhibit isopropyl ($CHMe_2$) or ethyl (CH_2Me) proton resonances as a heptet peak at δ 2.57 for **1** or two quartet peaks at δ 2.38～2.54 for **2**, illustrating the above phenomenon. Such difference between **2** and **3** has no influence on the whole backbone, thus the formation of mechanism of **3** is considered similar to **2**.

2 Conclusions

In summary, the synthesis of two new β-diketiminato tin(IV) compounds **1** and **2** by reacting β-diketiminato ligands with different alkyl tins is successfully accomplished. By ^{1}H NMR, ^{13}C NMR, and single crystal X-ray structural analysis, two N,C-bonded tin compounds have been confirmed. Of these compounds, **2** is a dimer with chair-shaped eight-membered ring. The formation mechanism of these two compounds is also discussed by comparing one against the other. As a result, both compounds undergo intramolecular C—H activation process.

3 Experimental section

3.1 Instruments and reagents

All manipulations of air- and moisture-sensitive materials were carried out under nitrogen by using Schlenk line and glovebox techniques. Organic solvents including toluene, *n*-hexane, and tetrahydrofuran (THF) were dried by refluxing with sodium/potassium benzophenone under nitrogen prior to use. CH_2Cl_2 was heated with CaH_2 for 12 h before use. Deuterated $CDCl_3$ was degassed, dried with CaH_2, and filtered before use. NMR spectra were recorded with a Bruker Avance II 400 spectrometer. Elemental analyses were performed by the Analytical Instrumentation Center of the Beijing Institute of Technology. Commercially available reagents were purchased from Energy Chemical and used as received. L^1H and L^2H were prepared according to published procedures.[17]

3.2 Experiment method

3.2.1 Synthesis of [N(Ar)=C(Me)CH=C(NHAr)-CH_2SnMe_2Cl•C_7H_8] (**1**)

n-BuLi (2.10 mL, 2.5 mol•L^{-1} in *n*-hexane, 5.25 mmol) was added dropwise to a precooled (−15 ℃) solution of L^1H (2.09 g, 5.00 mmol) in THF (25 mL). The first addition was completed in about 3 min. The mixture was stirred and warmed to room temperature. After stirring for 5 h, a solution of Me_2SnCl_2 (1.10 g, 5.00 mmol) in THF (10 mL) was added dropwise to the L^1Li solution. After the addition was complete, stirring of the reaction mixture was continued for at least 48 h at room temperature. Then the solvent was removed *in vacuo*. The solid was extracted with toluene (20 mL), and the extract was stored at −8 ℃ for 3 d to afford **1** as colorless crystals. An additional crop of **1** was obtained from the mother liquor. Total yield: 0.149 g (43%). ^{1}H NMR (400.18 MHz, $CDCl_3$) δ: 8.93 (s, 1H, NH), 7.13～7.22 (m, 4H, C_6H_3), 6.94, 6.92 (s, 2H, C_6H_3), 4.37 (s, 1H,

γ-CH), 2.69 (s, 3H, CMe), 2.57 (hept, J=6.4 Hz, 4H, C**H**Me$_2$), 2.05 (s, 2H, CH$_2$Sn), 1.01～1.28 (m, 24H, C**H**Me$_2$), 0.78, 0.76 (s, SnMe$_2$Cl). Anal. calcd for $C_{38}H_{55}ClN_2Sn$: C 65.76, H 7.99, N 4.04; found C 65.52, H 7.93, N 3.98.

3.2.2 Synthesis of [N(Ar')C(Me)=CHC(=NAr')CH$_2$-SnMe$_2$]$_2$•CH$_2$Cl$_2$ (**2**)

Compound **2** was prepared by the procedure described for **2**, using 1.82 g of L^{2}H (5.00 mmol) in THF (25 mL, −15 ℃) and 1.00 g of Me$_3$SnCl (5.00 mmol) in THF (10 mL). The final solid was extracted with CH$_2$Cl$_2$ (20 mL), and the extracted liquid in CH$_2$Cl$_2$ solution was stored at −8 ℃ for 4 d to afford **2** as colorless crystals. An additional crop of **2** was obtained from the mother liquor. Total yield: 0.108 g (39%). ^{1}H NMR (400.18 MHz, CDCl$_3$) δ: 6.93～7.01 (m, 6H, C$_6$H$_3$), 4.79 (s, 1H, γ-CH), 2.38～2.54 (dq, J=7.6 Hz, 8H, C**H**$_2$Me), 1.73 (s, 2H, CH$_2$Sn), 1.61 (s, 3H, CMe), 1.09 (t, J=7.6 Hz, 12H, CH$_2$**Me**), 0.42 (s, 3H, SnMe$_2$), 0.25 (s, 3H, SnMe$_2$); ^{13}C NMR (100.63 MHz, CDCl$_3$) δ: 169.22 (C=N), 162.82 (CN), 159.74, 146.57, 142.85, 141.81, 138.36, 133.75, 128.03 127.71, 127.31, 125.55 (C of Ar'), 95.22 (γ-C), 26.93, 26.85 (**C**H$_2$Me), 22.40 (C**Me**), 16.66, 16.37 (CH$_2$**Me**), 3.10 (CH$_2$Sn), −5.11 (SnMe$_2$), −6.31 (SnMe$_2$). Anal. calcd for $C_{55}H_{78}Cl_2N_4Sn_2$: C 59.92, H 7.04, N 5.08; found C 59.87, H 7.10, N 5.13.

3.2.3 X-ray structures determination of **1** and **2**

Suitable crystals of **1** and **2** were mounted on a glass fiber and coated with paraffin oil. Crystal size of **1** was 0.54 mm×0.43 mm×0.38 mm. It was collected at 163(2) K on the Rigaku AFC10 Saturn 724+(2×2 bin mode) diffractometer equipped with graphite-monochromated Mo Kα radiation (μ=0.757, λ=0.71073 Å). 2θ range for data collection was 4.4° to 63.02°. Empirical absorption correction was applied using the SADABS program.[18] 45971 reflections were collected in **1** and out of which 12763 (R_{int}=0.0264) were independent reflections. The structures were solved by direct methods[19] and refined by full-matrix least squares on F^2 using the SHELXL-97 program.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms connected to carbon atoms were included at geometrically calculated positions and refined by using a riding model. Molecular formula of **1** is $C_{38}H_{55}ClN_2Sn$ (M_r=693.98), and it belongs to monoclinic(crystal system) and $P2_1/n$ (space group). Its unit cell parameters: a=12.4467(16) Å, b=16.704(2) Å, c=18.656(2), α=γ=90°, β=95.919(2)°, V=3858.0(9) Å^3, D_c=1.195 g/cm^3, Z=4, F(000)=1456, Goodness-of-fit on F^2=1.001.

Crystal data of **2**, with a size of 0.54 mm×0.43 mm×0.38 mm, was collected at 293(2) K. Its graphite-monochromated Mo Kα radiation parameters were chosen as: μ=1.075, λ=0.71073 Å. 2θ range for data collection was 4.02° to 63.08°. 26027 reflections were collected and out of which 8691 were independent reflections (R_{int}=0.0325). The structure was also solved and refined by the same methods as above. Molecular formula of **2** is $C_{55}H_{78}Cl_2N_4Sn_2$, M_r=1103.49, and it belongs to monoclinic (crystal system) and $C2/c$ (space group). Its unit cell parameters: a=29.515(6) Å, b=8.9121(15) Å, c=23.428(5) Å, α=γ=90°, β=120.045(2)°, V=5334.3(17) Å^3, D_c=1.195 g/cm^3, Z=4, F(000)=1456, Goodness-of-fit on F^2=0.999.

The crystallographic data of **1** and **2** were obtained from Analysis & Testing Center, Beijing Institute of Technology and saved in the Cambridge Crystallographic Data Centre, and the CCDC numbers are 1504606 (**1**) and 1504694 (**2**).

Supporting Information Crystal data and NMR spectra of **1** and **2**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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