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Inorganica Chimica Acta 361 (2008) 2792-2798

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Synthesis and structures of three, four, and six-coordinate monomeric tin(II) and tin(IV) compounds containing η^2 -ketiminate ligands

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Received 21 June 2007; received in revised form 28 January 2008; accepted 4 February 2008 Available online 8 February 2008

Abstract

A series of Sn(II) and Sn(IV) compounds containing ketiminate ligands were synthesized. Reactions of SnCl₂ with 1 or 2 equiv. Li[OCMeCHCMeNAr] (where Ar = 2,6-diisopropylphenyl) generate [OCMeCHCMeNAr]SnCl (1) and [OCMeCHCMeNAr]₂Sn (2) in moderate yield, respectively. Similarly, reacting SnCl₄ with 2 equiv. Li[OCMeCHCMeNAr] yields a six-coordinated [OCMeCHC-MeNAr]₂SnCl₂ (3). Divalent tin compound 2 can be oxidized with I₂ in diethyl ether to generate tetravalent tin compound [OCMeCHC-MeNAr]₂SnI₂ (4) in moderate yield. Compounds 1–4 have been characterized by ¹H and ¹³C NMR spectroscopy and have been analyzed by X-ray crystallography. Theoretical calculation found that the bonding of ketiminate ligands and tin atom in compound 2 has a strong ionic character.

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Keywords: Tin; Ketiminate; Oxidative addition

1. Introduction

Organotin compounds have been widely used in many fields such as organic synthesis and catalysis [1]. High valent tin(IV) compounds have long been used as biocides [2] and as homogeneous catalysts in industries [3]. Moreover, di- and tri-organotin compounds have been found to have in vitro activity against a large variety of tumor cell lines [4]. Therefore, the versatility of applications, oxidation states, and molecular structures for the tin metals has been attracting much attention. The structural diversity of organotin compounds is of interest and is reviewed periodically [5]. The molecular structures of these organotin compounds can be formed as monomers [6], dimers [7], trimers [8], or even oligomers [6b,9] depending on the steric bulkiness of coordinating ligands. The general method

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for synthesizing a monomeric organotin compound is increasing the bulkiness of ligands which results the stability of the tin metal coordination sphere. The strategy was to use bidentate ligands with bulky substituents on one side to protect the metal centers and open ends on the other side to increase the activity of the metal complexes. We are interested in using substituted ketiminate as ancillary ligands in chelating to group 13 and early transition metals [10] and we studied their reactivities towards small organic molecules. Here, we report the synthesis and characterization of a series of Sn(II) and Sn(IV) monomeric compounds incorporating ketiminate ligands.

2. Results and discussion

2.1. Synthesis and characterization of tin compounds

A series of tin(II) and tin(IV) complexes containing mono-anionic ketiminate ligand, [OCMeCHCMeNAr]⁻, has been synthesized as shown in Scheme 1. A

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three-coordinated tin compound 1, [OCMeCHCMeNAr]-SnCl, was isolated as a white solid in moderate yield from the metathesis reaction of SnCl₂ with 1 equiv. of Li-[OCMeCHCMeNAr] in diethyl ether. A small amount of ketimine ligand was presented in compound 1 even repeating recrystallization from a methylene chloride solution. The ¹H NMR spectra of 1 in CDCl₃ consisted of two singlet resonances at δ 2.32 and 1.80, indicating the existence of the ketiminate ligands. The resonance for the methine proton of ketiminate backbone was seen at δ 5.46 and the two methine protons of the isopropyl were found at δ 2.98 as a multiplet. The ¹³C NMR spectrum of 1 was consistent with the ¹H NMR data, and the methine carbon of the ketiminate backbone was observed at δ 101.3.

Similarly, while 2 equiv. of Li[OCMeCHCMeNAr] was used to react with SnCl₂ in THF solution, compound 2, [OCMeCHCMeNAr]₂Sn, can be obtained in 68% yield (Scheme 1). Pure white crystals of 2 were obtained by recrystallization from a methylene chloride solution at -20 °C. The ¹H NMR spectrum of **2** was very similar to that of 1. The methine protons of the ketiminate backbones showed a singlet at δ 5.06 and the methyl fragments appeared at δ 1.96 and 1.65. It is also worth noting that the methine protons of the isopropyl groups on the phenyl rings appeared as two septet at δ 3.58 and 2.81, indicating the slow rotation of the N-C (phenyl) bonds of the ketiminate ligands. Again, the methyl groups of isopropyl showed four doublets at δ 1.03, 1.06, and 1.19 (where two doublets accidentally overlapped; however, two doublets can be observed when the δ 1.19 resonances were expanded). This indicates the slow rotation of C-C (isopropyl-phenyl) bonds. The ¹³C NMR resonances for the methyl groups of the isopropyl fragments and the ketiminate backbone were verified by the ¹H⁻¹³C 2D HSQC (heteronuclear single quantum correlation) NMR spectrum which is shown in Fig. 1.

Similarly, reacting tetravalent $SnCl_4$ with 2 equiv. of ketiminate lithium salts in methylene chloride yielded a six-coordinate Sn(IV) compound [OCMeCHCMeNAr]₂- $SnCl_2$ (3) in 72% yield. The patterns of ¹H and ¹³C NMR spectra for 3 were similar to those of 2. The methine groups of the ketiminate backbones show their ¹H and ¹³C NMR



Fig. 1. The ¹H–¹³C 2D HSQC NMR spectrum for the range of isopropyl and methyl fragment of the ketiminate backbone.

signal at δ 5.19 and 98.3, respectively. However, due to the sterically crowded of **3**, the isopropyl–phenyl bonds rotated slowly, causing the methyl groups of isopropyl fragments to exhibit four distinguished doublets at δ 1.02, 1.08, 1.16, and 1.33.

The divalent tin compound 2 reacted with 1 equiv. of iodine to generate tetravalent *cis*-diiodo-diketiminate–tin compound [OCMeCHCMeNAr]₂SnI₂ (4) in 73% yields through oxidative addition (Scheme 2). Compound 4 has been characterized by 1D ¹H and ¹³C NMR and 2D HSQC NMR spectroscopy and elemental analysis. Again, the ¹H and ¹³C NMR spectra of 4 were similar to those of 3; however, the ¹H NMR spectra show that all the resonances are



Scheme 2.

| Table 1 | | | |
|-------------|---------------------|----------|-----------------|
| The summary | of crystallographic | data for | compounds $1-4$ |

upfield shifted in comparison to those of compound **3** due to the less electronegative and more electron donating ability of iodine. It is worthy to note that the carbon resonances of methyl groups are all appearing within the range of δ 25.1–29.0 and some of them are overlapping. However, the assignment for all carbon atoms can be completed by using 2D HSQC NMR spectra (see Section 4).

¹¹⁹Sn NMR spectra in a CDCl₃ solution at room temperature have been measured for compounds 1–4 which show a resonance at δ –590.6, –587.4, –626.9, and –916.5, respectively. The ¹¹⁹Sn chemical shifts agree with those reported in the literature [11]. However, the chemical shift for compound 4 is in a much higher field than that for compounds 1–3, presumably due to the iodide atoms contributing a large amount of electron density to shield the tin metal.

2.2. Molecular structures of compounds 1-4

The molecular structures of 1-4 have been characterized by single crystal X-ray diffraction analyses. The summary of data collections and the selected bond lengths and angles for compounds 1-4 are listed in Tables 1 and 2, respectively. The molecular structures of 1-4 are shown in Figs. 2-5. The ketiminate backbone of the chelating ligands for compounds 1-4 is essentially planar and the tin is out of the plane at 0.6684 Å for 1, 0.6891 Å for 2, 0.1128 Å for

| | 1 | 2 | 3 | 4 |
|---|------------------------------|----------------------------|----------------------------|----------------------------|
| Formula | C17H24ClNOSn | C34H48N2O2Sn | C34H48Cl2N2O2Sn | C34H48I2N2O2Sn |
| Formula weight | 412.51 | 635.43 | 706.33 | 889.23 |
| Temperature (K) | 150 | 150 | 150 | 150 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | C2/c | $P2_1/c$ | $P2_1/n$ |
| a (Å) | 8.7981(4) | 9.2184(4) | 11.9338(3) | 12.9602(4) |
| b (Å) | 10.1224(4) | 15.5961(4) | 16.7790(3) | 16.3356(5) |
| <i>c</i> (Å) | 11.7124(5) | 23.2357(11) | 16.9388(4) | 17.0852(5) |
| α (°) | 107.4765(14) | | | |
| β (°) | 109.2478(15) | 91.5070(10) | 99.9791(6) | 103.6370(6) |
| γ (°) | 99.850(2) | | | |
| Volume $(Å^3)/Z$ | 896.08(7), 2 | 3339.5(3), 4 | 3339.5(3), 4 | 3515.18(18), 4 |
| D^{calc} (Mg/m ³) | 1.529 | 1.264 | 1.404 | 1.680 |
| Absorption coefficient (mm^{-1}) | 1.574 | 1.574 | 0.957 | 2.514 |
| F(000) | 416 | 1328 | 1464 | 1752 |
| Crystal size (mm) | $0.20\times 0.15\times 0.15$ | 0.35 	imes 0.29 	imes 0.26 | 0.25 	imes 0.25 	imes 0.20 | 0.45 	imes 0.41 	imes 0.30 |
| θ Range (°) | 1.99-27.50 | 1.75-27.51 | 1.72-27.50 | 1.75-29.05 |
| Number of reflections collected | 14565 | 10477 | 29864 | 39740 |
| Number of independent reflections $[R_{int}]$ | 4065 [0.0663] | 3800 [0.0255] | 7640 [0.0532] | 9378 [0.0193] |
| Maximum and minimum transmission | 0.775 and 0.630 | 0.9486 and 0.7580 | 0.859 and 0.663 | 0.5192 and 0.3975 |
| Number of data/restraints/parameters | 4065/0/197 | 3800/0/183 | 7640/0/371 | 9378/0/382 |
| Goodness-of-fit on F^2 | 1.088 | 1.048 | 1.058 | 1.073 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$, R_1^{a} | $R_1 = 0.0493$ | $R_1 = 0.0282$ | $R_1 = 0.0431$ | $R_1 = 0.0246$ |
| wR_2^{b} | $wR_2 = 0.1096$ | $wR_2 = 0.0738$ | $wR_2 = 0.1072$ | $wR_2 = 0.0604$ |
| R indices (all data), R_1^{a} | $R_1 = 0.0874$ | $R_1 = 0.0316$ | $R_1 = 0.0663$ | $R_1 = 0.0301$ |
| wR_2^{b} | $wR_2 = 0.1537$ | $wR_2 = 0.0753$ | $wR_2 = 0.1186$ | $wR_2 = 0.0618$ |
| Largest difference in peak and hole ($e \mathring{A}^{-3}$) | 1.131 and -1.143 | 0.701 and -0.309 | 1. 729 and -0.821 | 1.109 and -1.576 |

 $^{a} R_{1} = \sum |F_{o}| - |F_{c}| / \sum |F_{o}|.$

^b $wR_2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2} \right].$

164.46(5)

85.69(7)

85.81(5)

106.036(8)

O(1) - Sn(1) - I(2)

O(1)-Sn(1)-N(1)

O(2) - Sn(1) - I(2)

I(1)-Sn(1)-I(2)

| | | HM. Kao et a | l. Inorganica C |
|---------------------------------|-------------------|----------------------|-------------------|
| Table 2 Selected bond length | and angles for | r compounds 1-4 | |
| Compound 1 | is and angles for | | |
| Sn(1) = O(1) | 2.087(4) | Sn(1) = N(1) | 2 227(5) |
| Sn(1)-Cl(1) | 2.4637(17) | O(1)-C(2) | 1.311(7) |
| C(2)-C(3) | 1.359(9) | C(3)-C(4) | 1.419(8) |
| N(1)–C(4) | 1.319(7) | | |
| O(1)-Sn(1)-Cl(1) | 90.66(12) | N(1)-Sn(1)-Cl(1) | 93.92(12) |
| O(1)–Sn(1)–N(1) | 84.63(16) | | |
| Compound 2 | | | |
| Sn(1)-O(1) | 2.0944(15) | Sn(1)-N(1) | 2.4092(15) |
| O(1)–C(2) | 1.304(3) | C(2)–C(3) | 1.366(3) |
| C(3)–C(4) | 1.426(2) | N(1)–C(4) | 1.303(3) |
| N(1)-Sn(1)-N(1A) | 152.38(8) | O(1)-Sn(1)-O(1A) | 91.16(9) |
| O(1)-Sn(1)-N(1) | 79.62(5) | O(1)-Sn(1)-N(1A) | 81.14(5) |
| Compound 3 | | | |
| Sn(1)-O(1) | 2.074(2) | Sn(1)-O(2) | 2.073(2) |
| Sn(1)-N(1) | 2.224(3) | Sn(1)-N(2) | 2.224(3) |
| Sn(1)-Cl(1) | 2.3713(8) | Sn(1)-Cl(2) | 2.3708(8) |
| O(1) - C(2) | 1.281(4) | C(2) - C(3) | 1.365(4) |
| C(3) - C(4) | 1.408(4) | N(1)-C(4) | 1.324(4) |
| O(2) - C(19) | 1.292(4) | C(19)-C(20) | 1.361(4) |
| O(2) - C(19) | 1.292(4) | C(19)–C(20) | 1.361(4) |
| C(20)-C(21) | 1.413(4) | O(2) - C(19) | 1.292(4) |
| N(2)-Sn(1)-N(1) | 174.33(9) | O(1)-Sn(1)-Cl(1) | 172.80(7) |
| O(2) - Sn(1) - Cl(2) | 173.11(7) | O(1) - Sn(1) - N(1) | 88.00(8) |
| O(2) - Sn(1) - N(2) | 88.12(8) | O(2)-Sn(1)-Cl(1) | 89.50(8) |
| O(1) - Sn(1) - O(2) | 83.61(11) | O(1) - Sn(1) - Cl(2) | 89.76(8) |
| Cl(1)-Sn(1)-Cl(2) | 97.18(3) | | |
| Compound 4 | | | |
| Sn(1)–O(1) | 2.0784(18) | Sn(1)–O(2) | 2.0650(18) |
| Sn(1)-N(1) | 2.246(2) | Sn(1)-N(2) | 2.261(2) |
| Sn(1)-I(1) | 2.7683(2) | Sn(1)-I(2) | 2.7841(2) |
| O(1) - C(2) | 1.295(3) | C(2) - C(3) | 1.370(4) |
| C(3) - C(4) | 1.420(4) | N(1)-C(4) | 1.325(3) |
| O(2) - C(19) | 1.305(3) | C(19) - C(20) | 1.359(4) |
| C(20)-C(21) | 1.422(4) | O(2) - C(19) | 1.305(3) |

3, and 0.6450 Å for 4. The geometry of 1 can be described as a distorted three-coordinated tetrahedral with one apical position filled with a pair of electrons. Due to the large lone pair electrons repulsion with bonding electrons pushing the coordinating atoms together, the bond angles around the tin atom are close to 90°. The bond length of Sn-Cl 2.4637(17) Å is at the average length of normal Sn(II)-chloride. The geometry of **2** contains a C_2 symmetry and can be described as a distorted trigonal bipyramidal with lone pair electrons occupying at equatorial position. The two nitrogen atoms from ketiminate ligands occupy the axial positions and again the bonding electrons are pushed away from the lone pair electrons and the axial axis is bended at 152.38(8)°. The ketiminate ligands bind to the central tin atom with an acute angle of 79.62(5)°. The six-coordinate compound 3 features a distorted octahedral geometry

N(1)-Sn(1)-N(2)

O(2)-Sn(1)-I(1)O(2)-Sn(1)-N(2)

O(1)–Sn(1)–O(2) O(1)–Sn(1)–I(1) 176.53(8)

167.93(5)

86.59(7)

78.90(7)

89.36(5)



Fig. 2. The molecular structure of compound 1, thermal ellipsoids drawn at the 50% probability level.



Fig. 3. The molecular structure of compound $\mathbf{2}$, thermal ellipsoids drawn at the 50% probability level.

with the two oxygen atoms of the ketiminate ligands trans to the two chloro atoms and the two nitrogen atoms of the ketiminate ligands occupy opposite positions. The bond lengths of Sn–Cl in 3 (av. 2.37 Å) are shorter than that of 1 due to the stronger interaction of high valent Sn(IV) with chloro atoms. Similarly, the geometry of compound 4 is the same as that of 3 with the two oxygen atoms of the ketiminate ligands trans to the two iodo atoms and the two nitrogen atoms of the ketiminate ligands occupy opposite directions.

2.3. Bonding models of the Sn(II)

It is interesting to compare the bonding nature of Sn(II) in the complexes. For this purpose, we performed



Fig. 4. The molecular structure of compound **3**, thermal ellipsoids drawn at the 50% probability level.



Fig. 5. The molecular structure of compound **4**, thermal ellipsoids drawn at the 50% probability level.

theoretical studies on SnCl₂, Sn(N–O)Cl, and Sn(N–O)₂, where (N–O) = OCMeCHCMeNAr. We used the gradient-corrected hybrid density functional theory (DFT), B3LYP. The approach is a hybrid method, which consists of the three-parameter mixing of gradient-corrected exchange functional of Becke [12] and correlation functional of Lee, Yang, and Parr [13]. For H, C, N, and O atoms we used the 6-31G basis sets. For Sn, we used the DGDZVP basis set [14]. At the optimized structure, natural bond orbital (NBO) analysis was performed [15]. All calculations were carried out using the GAUSSIAN 03 program [16].

The natural charge of Sn and its ligands, Wiber bond index, and natural electron configuration of Sn are summa-

| Та | ble | 3 |
|----|-----|---|
| | | |

The natural charges of Sn and its ligands, Wiber bond index, and natural electron configurations of Sn

| | SnCl ₂ | Sn(N–O)Cl | Sn(N-O)2 |
|------------------|-------------------|---------------|--------------|
| Natural charges | 1.142 (Sn) | 1.243 (Sn) | 1.428 (Sn) |
| | -0.570 (Cl) | -0.643(Cl), | -0.714 (N-O) |
| | | -0.600 (N-O) | |
| Wiber bond | 0.733 (Sn-Cl) | 0.582 (Sn-Cl) | 0.680 |
| index | | 0.680 | (Sn-(N-O)) |
| | | (Sn-(N-O)) | |
| Natural electron | 5s(1.89), | 5s(1.80), | 5s(1.79), |
| configuration | 5p(0.93), | 5p(0.94), | 5p(0.77), |
| (Sn) | 6s(0.01), | 6s(0.01), | 6s(0.01), |
| | 5d(0.01) | 5d(0.01) | 5d(0.01) |

(N-O) = OCMeCHCMeN.



Fig. 6. DFT calculation depicted that the nonbonding Sn electrons of $SnCl_2$, Sn(N-O)Cl, and $Sn(N-O)_2$ are all located in 5s orbitals forming the geometries of V-shape, trigonal pyramidal, and sea-saw.

rized in Table 3. We can see that substitution of a chloride ion from $SnCl_2$ by the $(N-O)^-$ ligand increases the positive charge on the Sn center. Natural electron configuration at Sn shows that the valence electrons reside mostly on its 5s orbital. A schematic drawing of the geometries of SnCl₂, Sn(N–O)Cl, and Sn(N–O)₂ is depicted in Fig. 6 reveals the nonbonding character of Sn. The tendency to place nonbonding Sn electrons in 5s orbital has resulted the geometries of SnCl₂, Sn(N-O)Cl, and Sn(N-O)₂ as V shape, trigonal pyramid, and sea-saw, respectively. Natural bond orbital analysis resolves Sn-natural bond orbitals only in SnCl₂, while for Sn(N–O)Cl and Sn(N–O)₂ no natural bond involving Sn has been resolved. These observations suggest that Sn-(N-O) bond has a stronger ionic character. Despite its ionic bonding nature, $Sn(N-O)_2$ is not a very polar compound, however. The dipole moments of SnCl₂, Sn(N–O)Cl and Sn(N–O)₂ are 3.876, 5.972, and 2.559 Debyes, respectively. Despite the ionic character of the Sn-(N-O) bond, an attempt to further study the reaction of NaBPh₄ and Sn(N–O)₂ in d^8 -THF at 80 °C results an decomposition.

3. Conclusions

In conclusion, we have synthesized a series of divalent and tetravalent tin compounds containing mono-anionic ketiminate ligands. The divalent tin compound 2 can be easily oxidized with iodine to form a tetravalent tin compound 4. DFT calculation shows that the nonbonding electrons of Sn(II) are mainly localized on the 5s orbitals and the Sn-(N-O) bond has strong ionic character. Further study of the activity of these Sn compounds toward lactone and lactide polymerization is undergoing.

4. Experimental

4.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. Toluene, diethyl ether, and tetrahydrofuran were dried by refluxing over sodium benzophenone ketyl. CH₂Cl₂ was dried over P₂O₅. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts for ¹H and ¹³C spectra were recorded in ppm relative to the residual protons and ¹³C of CDCl₃ (δ 7.24, 77.0) and C₆D₆ (δ 7.15, 128.0). ¹¹⁹Sn chemical shifts are reported in ppm from an external SnMe₄ standard. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. OCMeCHCMeNHAr was prepared according to a previously reported procedure. SnCl₂ and SnCl₄ (Strem) were used as received.

4.2. Synthesis of (OCMeCHCMeNAr)SnCl (1)

A 50 mL Schlenk flask charged with (OCMeCHCMeN-Ar)Li (0.50 g, 1.89 mmol) and SnCl₂ (0.36 g, 1.90 mmol) was cooled to -78 °C and CH₂Cl₂ (20 mL) was added. The solution was then warmed to room temperature and was stirred for 30 min. The solution was filtered through Celite and the filtrate was dried under vacuum. The solid was recrystallized from a saturated methylene chloride solution to yield the final product. A small amount of compound 2 and ketimine ligand was presented in the final product even after repeating recrystallization. ¹H NMR (CDCl₃):1.14 (d, 6H, Me), 1.19 (d, 6H, Me), 1.80 (s, 3H, Me), 2.32 (s, 3H, Me), 2.93 (m, 2H, Me), 5.45 (s, 1H, CMeCHCMe), 7.15–7.32 (m, 3H, phenyl CH). ¹³C NMR (CDCl₃): 23.5 (Me), 24.0 (Me), 25.0 (Me), 27.1 (Me), 28.5 (CHMe₂), 101.3 (CMeCHCMe), 124.5 (phenyl), 127.1 (phenyl), 138.8 (phenyl), 167.0 (phenyl), 171.2 (s, CN), 179.7 (s, CO). ¹¹⁹Sn NMR (CDCl₃): -590.6.

4.3. Synthesis of $(OCMeCHCMeNAr)_2Sn(2)$

A 100 mL Schlenk flask charged with $SnCl_2$ (0.72 g, 3.79 mmol) and 20 mL THF was cooled to 0 °C. To the $SnCl_2/THF$ solution, a solution of (OCMeCHCMeNAr)Li (2.00 g, 7.55 mmol) in 20 mL THF was added and the solution was stirred at room temperature for 8 h. Volatiles were removed under vacuum and the resulting solid was extracted with 40 mL CH₂Cl₂ in three portions. The extraction was filtered through Celite and the solvent was removed to yield 1.47 g of **2** (68% yield). ¹H NMR (CDCl₃):1.03 (d, 6H, CHMe₂), 1.06 (d, 6H, CHMe₂), 1.19 (d, 12H, CHMe₂), 1.65 (s, 6H, CMe), 1.96 (s, 6H, CMe), 2.81 (m, 2H, CHMe₂), 3.58 (m, 2H, CHMe₂), 5.06 (s, 2H, CMeCHCMe), 7.10–7.18 (m, 6H, phenyl CH).

¹³C NMR (CDCl₃): 23.1 (q, $J_{CH} = 127$ Hz, CH Me_2), 23.8 (q, $J_{CH} = 126$ Hz, CMe), 23.9 (q, $J_{CH} = 125$ Hz, CH Me_2), 24.6 (q, $J_{CH} = 127$ Hz, CMe), 26.2 (q, $J_{CH} = 126$ Hz, CH Me_2), 26.3 (q, $J_{CH} = 126$ Hz, CH Me_2), 27.1 (d, $J_{CH} = 127$ Hz, CHM e_2), 28.0 (d, $J_{CH} = 127$ Hz, CHM e_2), 27.1 (d, $J_{CH} = 127$ Hz, CHM e_2), 28.0 (d, $J_{CH} = 127$ Hz, CHM e_2), 98.8 (d, $J_{CH} = 157$ Hz, CMeCHCMe), 123.2 (d, $J_{CH} = 156$ Hz, phenyl CH), 123.8 (d, $J_{CH} = 157$ Hz, phenyl CH), 141.2 (s, phenyl CH), 125.0 (d, $J_{CH} = 159$ Hz, phenyl CH), 141.2 (s, phenyl C_{ipso}), 141.8 (s, phenyl C_{ipso}), 143.6 (s, phenyl C_{ipso}), 167.6 (s, CN), 175.3 (s, CO). ¹¹⁹Sn NMR (CDCl₃): -587.4. Anal. Calc. for C₃₄H₄₈N₂O₂Sn: C, 64.26; H, 7.61; N, 4.41.

4.4. Synthesis of $(OCMeCHCMeNAr)_2SnCl_2$ (3)

Found: C, 64.06; H, 7.40; N, 4.18%.

A solution of (OCMeCHCMeNAr)Li (1.00 g, 1.88 mmol) in CH₂Cl₂ (20 mL) was added dropwise to a stirred solution of SnCl₄ (0.49 g, 3.83 mmol) in CH₂Cl₂ (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and was stirred for additional 12 h. The precipitate was filtered, and the volatiles were removed to afford 3(0.96 g, 72%). Colorless crystals were obtained from a saturated THF solution of **3** at -20 °C. ¹H NMR (CDCl₃): 1.02 (d, 6H, CHMe2), 1.08 (d, 6H, CHMe2), 1.16 (d, 6H, CHMe2), 1.33 (d, 6H, CHMe2), 1.78 (s, 6H, CMe), 2.06 (s, 6H, CMe), 3.40 (m, 2H, CHMe₂), 3.65 (m, 2H, CHMe₂), 5.19 (s, 2H, CMeCHCMe), 7.12–7.24 (m, 6H, phenyl CH). ¹³C NMR (CDCl₃): 25.1 (q, $J_{CH} = 126$ Hz, CH Me_2), 25.31 $(q, J_{CH} = 127 \text{ Hz}, CHMe_2), 25.34 (q, J_{CH} = 127 \text{ Hz},$ CH Me_2), 25.4 (q, $J_{CH} = 127$ Hz, CH Me_2), 26.6 (q, $J_{\rm CH} = 128$ Hz, CMe), 27.1 (q, $J_{\rm CH} = 128$ Hz, CMe), 27.2 (d, $J_{CH} = 128$ Hz, CHMe₂), 27.7 (d, $J_{CH} = 130$ Hz, CHMe₂), 98.3 (d, $J_{CH} = 160$ Hz, CMeCHCMe), 124.1 (d, $J_{\rm CH} = 156$ Hz, phenyl CH), 124.5 (d, $J_{\rm CH} = 156$ Hz, phenyl CH), 127.4 (d, $J_{CH} = 160$ Hz, phenyl CH), 141.4 (s, phenyl C_{ipso}), 144.1 (s, phenyl C_{ipso}), 144.3 (s, phenyl C_{ipso}), 177.4 (s, CN), 181.1 (s, CO). ¹¹⁹Sn NMR (CDCl₃): -626.9. Anal. Calc. for C₃₄H₄₈N₂O₂SnCl₂: C, 57.81; H, 6.85; N, 3.96. Found: C, 58.00; H, 6.82; N, 4.87%.

4.5. Synthesis of $(OCMeCHCMeNAr)_2SnI_2$ (4)

A solution of **2** (0.70 g, 1.10 mmol) in diethyl ether (20 mL) was added dropwise to a stirred solution of I₂ (0.28 g, 1.10 mmol) in diethyl ether (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and was stirred for additional 2 h. Volatiles were removed under vacuum and the resulting solid was recrystallized from a saturated CH₂Cl₂ solution at -20 °C to afford yellow crystals of **4** (0.72 g, 73%). ¹H NMR (CDCl₃): 1.02 (d, 12H, CH*Me*₂), 1.24 (d, 6H, CH*Me*₂), 1.34 (d, 6H, CH*Me*₂), 1.87 (s, 6H, C*Me*), 2.04 (s, 6H, C*Me*), 3.59 (m, 2H, C*HMe*₂), 3.72 (m, 2H, C*HMe*₂), 5.29 (s, 2H, CMeC*H*CMe),7.14–7.25 (m, 6H, phenyl C*H*). ¹³C NMR (CDCl₃): 25.1 (q, *J*_{CH} = 121 Hz, CH*Me*₂), 25.2 (q, *J*_{CH} = 121 Hz, C*Me*), 25.3 (q, *J*_{CH} = 121 Hz, CH*Me*₂), 27.1 (q, *J*_{CH} = 127 Hz, C*Me*), 27.1 (d, *J*_{CH} = 126 Hz, CH*Me*₂) (Two peaks are overlapped. This can be differentiated by 2D HSQC NMR spectra), 27.3 (q, $J_{CH} = 126$ Hz, CH Me_2), 28.2 (d, $J_{CH} = 130$ Hz, CHMe₂), 29.0 (q, $J_{CH} = 128$ Hz, CHMe₂), 97.7 (d, $J_{CH} = 160$ Hz, CMeCHCMe), 124.1 (d, $J_{CH} = 165$ Hz, phenyl CH), 124.8 (d, $J_{CH} = 153$ Hz, phenyl CH), 127.5 (d, $J_{CH} = 160$ Hz, phenyl CH), 142.0 (s, phenyl CH), 127.5 (d, $J_{CH} = 160$ Hz, phenyl CH), 142.0 (s, phenyl C_{ipso}), 144.4 (s, phenyl C_{ipso}), 145.4 (s, phenyl C_{ipso}), 175.7 (s, CN), 180.0 (s, CO). ¹¹⁹Sn NMR (CDCl₃): -916.5. Anal. Calc. for C₃₄H₄₈N₂O₂SnI₂: C, 45.92; H, 5.44; N, 3.15. Found: C, 45.93; H, 5.53; N, 3.13%.

4.6. Crystallographic structural determination of compounds 1-4

Crystal data collection, refinement parameter and bond length and angles are listed in Tables 1 and 2, respectively. The crystals were mounted on capillaries and transferred to a goniostat and were collected at 150 K under nitrogen stream. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo K α radiation. Structure determinations were performed using the SHELXTL package of programs. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are included in calculated positions into the refinements.

5. Supplementary material

CCDC 638775, 638776, 638777, and 638778 contain the supplementary crystallographic data for 1, 2, 3, and 4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a-c.uk/data_request/cif.

Acknowledgements

We are grateful to the National Science Council of Taiwan for support of this research. We also thank the National Changhua University of Education for support of the X-ray facility.

References

- [1] (a) P. Espinet, A.M. Echavarren, Angew. Chem., Int. Ed. 43 (2004) 4704;
 - (b) A. Orita, A. Sakamoto, Y. Hamada, A. Mitsutome, J. Otera, Tetrahedron 55 (1999) 2899;
- (c) A. Orita, A. Mitsutome, J. Otera, J. Org. Chem. 63 (1998) 2420. [2] (a) M. Gielen, Appl. Organomet. Chem. 16 (2002) 481;
- (b) K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann, J.J. Zuckerman, Organometallics 5 (1986) 85.
- [3] C.J. Evans, in: P.J. Smith (Ed.), Chemistry of Tin, Blackie Academic and Professional, London, 1998.
- [4] (a) S. Tabassum, C. Pettinari, J. Organomet. Chem. 691 (2006) 1761;
 (b) N. Hoeti, J. Ma, S. Tabassum, Y. Wang, M. Wu, J. Biochem. 134 (2003) 521;
 - (c) M. Gielen, Coord. Chem. Rev. 151 (1996) 41;

(d) R. Willem, H. Dalil, P. Broekaert, M. Biesemans, L. Gyhs, K. Nooter, D. de Vos, F. Ribot, M. Gielen, Main Group Met. Chem. 20 (1997) 535.

- [5] (a) V. Chandrasekhar, S. Nagendran, V. Baskar, Coord. Chem. Rev. 235 (2002) 1;
 - (b) J. Beckmann, K. Jurkschat, Coord. Chem. Rev. 215 (2001) 267;
 - (c) R.R. Holmes, Acc. Chem. Res. 22 (1989) 190.
- [6] (a) Y. Ding, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Organometallics 20 (2001) 1190;
 (b) Y. Tang, A.M. Felix, L.N. Zakharov, A.L. Rheingold, R.A. Kemp, Inorg. Chem. 43 (2004) 7239;
 (c) M. Kemmer, L. Ghys, M. Gielen, M. Biesemans, E.R.T. Tiekink,
- R. Willem, J. Organomet. Chem. 582 (1999) 195.
- [7] (a) R.W. Chorley, P.B. Hitchcock, B.S. Jolly, M.F. Lappert, G.A. Lawless, J. Chem. Soc., Chem. Commun. (1991) 1302;
 (b) J. Beckmann, K. Jurkschat, M. Schürmann, J. Organomet. Chem. 626 (2001) 49;

(c) K. Sakamoto, Y. Hamada, H. Akashi, A. Orita, J. Otera, Organometallics 18 (1999) 3555;

(d) S.P. Narula, S. Kaur, R. Shankar, S. Verma, P. Venugopalan, S.K. Sharma, R.K. Chadha, Inorg. Chem. 38 (1999) 4777.

- [8] (a) H. Puff, W. Schuh, R. Sievers, R. Zimmer, Angew. Chem., Int. Ed. Engl. 20 (1981) 591;
 (b) F. Kayser, M. Biesemans, M. Bouâlam, E.R.T. Tiekink, A.E. Khloufi, J.M. Piret, A. Bouhdid, K. Jurkschat, M. Gielen, R. Willem, Organometallics 13 (1994) 1098;
 (c) F.A.G. Mercier, A. Meddour, M. Gielen, M. Biesemans, R. Willem, E.R.T. Tiekink, Organometallics 17 (1998) 5933.
- [9] (a) V. Chandrasekhar, M.G. Muralidhara, K.R. Justin Thomas, E.R.T. Tiekink, Inorg. Chem. 31 (1992) 4707;
 (b) S.W. Ng, V.G.K. Das, G. Pelizzi, F. Vitali, Heteroatom. Chem. 1 (1990) 433.
- [10] (a) P.-C. Kuo, I.-C. Chen, H.M. Lee, C.-H. Hung, J.-H. Huang, Inorg. Chim. Acta 358 (2005) 3761;
 (b) P.-C. Kuo, I.-C. Chen, J.-C. Chang, M.-T. Lee, C.-H. Hu, C.-H. Hung, H.M. Lee, J.-H. Huang, Eur. J. Inorg. Chem. (2004) 4898;
 (c) S.-H. Hsu, J.-C. Chang, C.-L. Lai, C.-H. Hu, H.M. Lee, G.-H. Lee, S.-M. Peng, J.-H. Huang, Inorg. Chem. 43 (2004) 6786.
- [11] H. Jing, S.K. Edulji, J.M. Gibbs, C.L. Stern, H. Zhou, S.T. Nguyen, Inorg. Chem. 43 (2004) 4315.
- [12] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [13] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [14] N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, Can. J. Chem. 70 (1992) 560.
- [15] J.E. Carpenter, F. Weinhold, J. Mol. Struct. (Theochem) 169 (1988) 41.
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Verven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, T. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.