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Synthesis and reactivity of tin amide complexes

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Dedicated to Robert G. Bergman.

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ABSTRACT

A terminal tin amide and a terminal tin anilide complex, (BDI)SnN(*i*Pr₂) and (BDI)SnN(H)Ar (Ar = 2.6^{-i} Pr₂C₆H₃), respectively, have been synthesized utilizing the bulky β -diketiminate ligand, $[{N(2,6^{-i}Pr_2C_6H_3)C(Me)}_2CH]^-$, or BDI, to stabilize the low coordinate divalent tin metal center. Only (BDI)SnN(iPr2) reacts with phenylacetylene to yield (BDI)SnCCPh, but both species react with methyl triflate to give (BDI)SnOTf and carbon dioxide, resulting in the formation of (BDI)SnOC(O)N(*i*Pr₂) and (BDI)SnOC(O)N(H)Ar.

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1. Introduction

Divalent β -diketiminate group 14 complexes have been the subject of several recent studies, including the synthesis and reactivity of germanium and tin hydrides [1,2], synthesis and reactivity of lead alkoxides [3,4], and the generation of unusual molecules such as a tin hydroxide stabilized by $Fe(CO)_4$ [5], and germanium and lead phosphides [6,7]. By far the most common β -diketiminate ligand used is $[{N(2,6-{}^{i}Pr_{2}C_{6}H_{3})C(Me)}_{2}CH]^{-}$, or BDI. The geometry of the ligands around the BDI-bound group 14 metal center, (BDI)MX, is always trigonal pyramidal, presumably due to the presence of a stereochemically active lone pair. The metal center for these neutral molecules lies outside the plane consisting of the BDI back-bone (NCCCN plane). This is consistent with fourcoordinate BDI-metal complexes, furthering the hypothesis that the presence of a stereochemically lone pair is influencing the geometry of the complex. However, the overall solid state geometry of the complex takes two different forms; one in which the metal center and X ligand are on the same side of the NCCCN plane, the X ligand lies in between the two N-aryl groups of the BDI ligand and the M-X bond is at an approximately 90° angle from the NCCCN plane ("endo" configuration) and the other configuration in which the metal center lies above the NCCCN plane and the X ligand points away from the (BDI)-M core ("exo" configuration, Fig. 1).

A number of tin complexes, (BDI)SnX, have been generated. For instance, Gibson synthesized a series of (BDI)Sn-alkoxide complexes and investigated them as potential catalysts for the polymerization of rac-lactide [8,9]. Only two (BDI)Sn-amide complexes have been synthesized, (BDI)SnN(SiMe₃)₂ and (BDI)SnNMe₂



Fig. 1. The two different configurations of (BDI)MX complexes, where M = Ge(II), Sn(II), Pb(II).

[9,10] and the reactivity of the latter towards electrophiles and weak acids has been examined [11]. This study aims to expand the reactivity of tin-amide complexes towards a wider variety of electrophiles as well as heterocumulenes.

2. Experimental

2.1. General considerations

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in an inert-atmosphere glovebox. Solvents were dried from the appropriate drying agent, distilled, degassed and stored over 4 Å sieves. The ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on a Varian 400, 500 or 600 MHz spectrometer. All spectrometers were equipped with X¹H broadband-observe probes. The ¹H and ¹³C NMR spectroscopy chemical shifts are given relative to residual solvent peaks and the ¹¹⁹Sn signals were externally referenced to SnMe₄. (BDI)SnCl (1) was prepared according to literature procedure [12], other reagents were purchased from Acros or Aldrich and purified according to standard procedures. Carbon dioxide was used as received (BOC, 100.000%).



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2.2. Synthesis of $[{N(2,6-{}^{1}Pr_{2}C_{6}H_{3})C(Me)}_{2}CH}SnN(CH{CH_{3}}_{2})_{2}], 2$

Lithium diisopropylamide (2 M, 175 µL, 0.350 mmol) was added to a solution of (BDI)SnCl (1) (0.200 g, 0.350 mmol) in toluene (5 mL), resulting in an immediate color change to an orange solution, and the mixture was stirred for 1 h at room temperature. The solvent was filtered and the solution was slowly evaporated in vacuo and stored at -30 °C for 24 h yielding 2 (0.34 g, 32%, first crop) as orange crystals. ¹H NMR (C_6D_6 , 293 K): δ 7.14 (d, 2H, J = 1.9 Hz, m-H), 7.10 (s, 2H, p-H), 7.07 (d, 2H, J = 2.0 Hz, m-H), 4.85 (s, 1H, middle CH), 3.82 (septet, 2H, J = 6.9 Hz, CHMe₂), 3.75 (septet, 2H, J = 6.5 Hz, CHMe₂), 3.25 (septet, 2H, J = 6.7 Hz, CHMe₂), 1.57 (s, 6H, NCMe), 1.36 (d, 6H, J = 6.7 Hz, CHMe₂), 1.28 (d, 6H, J = 6.8 Hz, CHMe₂), 1.19 (d, 6H, J = 6.7 Hz, CHMe₂), 1.15 (s, 6H, CHMe₂), 1.12 (d, 12H, J = 6.8 Hz, CHMe₂). ¹³C{¹H} NMR (C₆D₆, 293 K): δ 166.61 (NCMe), 143.93 (ipso-C), 143.80 and 143.71 (ortho-C), 126.02 (para-C), 124.19 and 124.14 (meta-C), 98.36 (middle CH), 50.90, 28.48 and 27.76 (CHMe2), 27.53, 25.87, 24.99, 24.63 (CHMe₂), 24.40 (NCMe), 24.37 (CHMe₂). ¹¹⁹Sn NMR (C₆D₆, 293 K): δ -224 ppm. IR (Nujol, cm⁻¹) 1623 (s), 1552 (s), 1316 (s), 1169 (s), 1100 (s), 934 (s). Anal. Calc. for C₃₅H₅₅N₃Sn: C, 66.04; H, 8.71; N, 6.60. Found: C, 65.98; H, 8.64; N, 6.52%.

2.3. Synthesis of $[{N(2,6-{}^{i}Pr_{2}C_{6}H_{3})C(Me)}_{2}CH}SnNH({}^{i}Pr_{2}C_{6}H_{3})], 3$

Lithium 2,6-diisopropylanilide (0.064 g, 0.35 mmol) was added to a solution of (BDI)SnCl (1) (0.200 g, 0.350 mmol) in toluene (5 mL) and the mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum and the residue was extracted with pentane (2×2 mL). The combined extracts were filtered and the resulting orange solution was slowly evaporated in vacuo and stored at -30 °C for 24 h yielding **3** (0.095 g, 38%, first crop) as yellow crystals. ¹H NMR (C₆D₆, 293 K): δ 7.12–7.02 (8H, ArH), 6.78 (t, 1H, J = 7.6, p-H), 5.54 (s, 1H, NH), 4.96 (s, 1H, middle CH), 3.40 (septet, 2H, J = 6.8 Hz, CHMe₂), 3.28 (septet, 4H, J = 6.7 Hz, CHMe₂), 1.61 (s, 6H, NCMe), 1.21 (d, 6H, J = 6.9 Hz, CHMe₂), 1.20 (d, 12H, J = 6.4 Hz, CHMe₂), 1.10 (d, 6H, J = 6.8 Hz, CHMe₂), 0.92 (d, 6H, I = 6.8 Hz, CHMe₂), 0.90 (d, 6H, I = 6.7 Hz, CHMe₂). ¹³C{¹H} NMR (C₆D₆, 293 K): δ 164.49 (NCMe), 147.52, 145.09 (ipso-C), 142.55, 142.20 and 134.19 (ortho-C), 126.82 (meta-C), 124.60 (para-C), 123.72 and 122.98 (meta-C), 115.84 (para-C), 96.57 (middle CH), 28.81, 28.39 and 28.12 (CHMe₂) 25.70, 24.29, 24.25, 23.93, 23.54 $(CHMe_2)$, 23.40 (NCMe). ¹¹⁹Sn NMR (C₆D₆, 293 K): δ –745. IR (Nujol, cm⁻¹) 1623 (s), 1589 (s), 1552 (s), 1520 (s), 1283 (s), 1170 (s), 1098 (s), 935 (s), 841 (s), 793 (s), 747(s). Anal. Calc. for C₄₁H₅₉N₃Sn: C, 69.10; H, 8.34; N, 5.90. Found: C, 69.16; H, 8.50; N, 5.90%.

2.4. Synthesis of $[{N(2,6-{}^{i}Pr_{2}C_{6}H_{3})C(Me)}_{2}CH}SnCC-(C_{6}H_{3})], 4$

Phenyl acetylene (35 µL, 0.315 mmol) was added to a solution of (BDI)Sn(NiPr₂) (**2**) (0.2 g, 0.315 mmol) in toluene (5 mL), and the mixture was stirred for 6 days at 70 °C. The solvent was filtered and the solution was slowly evaporated in vacuo and stored at -30 °C yielding **4** (0.19 g, 96%, first crop) as colorless crystals. ¹H NMR (C₆D₆, 293 K): δ 7.53 (dd, 2H, J = 7.53 Hz, 1.3 Hz, ortho-C), 712-6.92 (m, 9H, ArH), 5.01 (s, 1H, middle CH), 4.04 (septet, 2H, J = 6.8 Hz, CHMe₂), 3.35 (septet, 2H, J = 6.8 Hz, CHMe₂), 1.61 (s, 6H, NCMe), 1.41 (d, 6H, J = 6.7 Hz, CHMe₂), 1.25 (d, 6H, J = 7.0 Hz, $CHMe_2$), 1.25 (d, 6H, I = 7.0 Hz, $CHMe_2$) 1.12 (d, 6H, I = 6.8 Hz, CHMe₂). ¹³C{¹H} NMR (C₆D₆, 293 K): δ not found (CC), 166.28 (NCMe), 145.67, 142.60, 142.44, 131.64, 128.13, 126.68, 124.57, 123.97, 123.70 (Ar-C), 106.10 (CC), 99.97 (middle CH), 28.75, 27.85 (CHMe2), 27.77, 24.47, 24.17, 23.73 (CHMe2), 23.56 (NCMe). ¹¹⁹Sn NMR (C₆D₆, 293 K): δ –206. IR (Nujol, cm⁻¹) 1523 (s), 1316 (s), 1203 (s), 1171 (s), 1100 (s), 934 (s). Anal. Calc. for C₃₇H₄₆N₂Sn: C, 69.71; H, 7.27; N, 4.39. Found: C, 69.99; H, 7.32; N, 4.33%.

2.5. Synthesis of $[{N(2,6-{}^{i}Pr_{2}C_{6}H_{3})C(Me)}_{2}CH}SnOCON(C{CH_{3}}_{2})_{2}], 6$

Compound 2 (0.2 g, 0.315 mmol) was dissolved in toluene (5 mL) and loaded into an ampule. The reaction vessel was connected to a Schlenk line and a cylinder of high-purity CO₂. The vessel was submerged in a dry ice/acetone bath, and after three pump/ refill cycles, CO₂ was introduced at a pressure of 1.5 and the mixture was stirred for 3 days at room temperature. The yellow solution was concentrated in vacuo and stored at -30 °C yielding 6 (14%, first crop) as colorless crystals. ¹H NMR (C₆D₆, 293 K): δ 7.13 (s, 1H, ArH), 7.12 (s, 1H, ArH), 7.11 (s, 1H, ArH), 7.05 (d, 1H, J = 2.7 Hz, ArH), 7.04 (d, 1H, J = 2.7 Hz, ArH), 4.96 (s, 1H, middle CH), 3.91 (septet, 2H, *J* = 6.7 Hz, CHMe₂), 3.67 (septet, 2H, *J* = 6.8 Hz, CHMe₂), 3.14 (septet, 2H, *J* = 6.9 Hz, CHMe₂), 1.58 (s, 6H, NCMe), 1.43 (d, 6H, J = 6.7 Hz, CHMe₂), 1.26 (d, 6H, J = 6.8 Hz, CHMe₂), 1.18 (d, 12H, J = 6.8 Hz, CHMe₂), 1.15 (d, 6H, J = 6.9 Hz, CHMe₂), 1.08 (d, 6H, I = 6.8 Hz, CHMe₂). ¹³C{¹H} NMR (C₆D₆, 293 K): § 164.85 (NCMe), 161.75 (OCO), 144.59 (ipso-C), 142.86 and 142.18 (ortho-C), 126.59 (para-C), 124.46 and 123.69 (meta-C), 99.71 (middle CH), 45.34 (CHMe₂), 28.58 and 27.66 (CHMe₂), 26.23, 24.82 (CHMe₂), 24.13 and 23.37 (CHMe₂), 21.19 (NCMe). 119 Sn NMR (C₆D₆, 293 K): δ –394. IR (Nujol, cm $^{-1}$) 1595 (s), 1575 (s), 1552 (s), 1524 (s), 1337 (s), 1262 (s), 1097 (s), 1050 (s), 1019 (s) 791 (s). Anal. Calc. for C₃₆H₅₅N₃O₂Sn: C, 63.53; H, 8.15; N, 6.17. Found: C, 63.59; H, 8.26; N, 5.98%.

2.6. Synthesis of $[{N(2,6^{-i}Pr_2C_6H_3)C(Me)}_2CH}SnOCONH(^{i}Pr_2C_6H_3)]$, 7

Compound 3 (0.2 g, 0.280 mmol) was dissolved in toluene (5 mL) and loaded into an ampule. The reaction vessel was connected to a Schlenk line and a cylinder of high-purity CO₂. The vessel was submerged in a dry ice/acetone bath, and after three pump/ refill cycles, CO₂was introduced at a pressure of 1.5 and the mixture was stirred for 4 h at room temperature. The yellow solution was concentrated in vacuo and stored at -30 °C yielding 7. ¹H NMR (C_6D_6 , 293 K): δ 7.14 (d, 1H, J = 1.5 Hz, m-H), 7.13 (s, 1H, ArH), 7.11 (t, 2H, J = 4.1 Hz, p-H), 7.08 (d, 1H, J = 3.1 Hz, m-H), 7.05 (s, 1H, ArH), 7.03 (s, 2H, ArH), 7.01 (s, 1H, ArH), 5.91 (s, 1H, NH), 4.85 (s, 1H, middle CH), 3.61 (septet, 2H, J = 6.8 Hz, CHMe₂), 3.29 (septet, 2H, J = 6.8 Hz, CHMe₂), 3.11 (septet, 2H, J = 6.9 Hz, CHMe₂), 1.57 (s, 6H, NCMe), 1.31 (d, 6H, J = 6.7 Hz, CHMe₂), 1.24 (d, 6H, J = 6.8 Hz, CHMe₂), 1.17 (d, 6H, J = 6.9 Hz, CHMe₂), 1.10 (d, 12H, J = 6.8 Hz, CHMe₂), 1.06 (d, 6H, J = 6.8 Hz, CHMe₂). ¹³C{¹H} NMR (C₆D₆, 293 K): δ 165.23 (NCMe), 161.59 (OCO) 145.25 (ipso-C), 142.52 (ipso-C), 141.67 (ortho-C), 133.36 and 126.82 (ortho-C), 126.48 (meta-C), 124.48 (para-C) 123.77 and 122.96 (meta-C) 115.84 (para-C), 99.01 (middle CH), 28.75 (CHMe2), 28.32 and 27.82 (CHMe2) 25.75 (CHMe2), 24.87 (CHMe2), 24.32, 24.23 and 23.76 (CHMe₂) 23.70 (NCMe). ¹¹⁹Sn NMR (C_6D_6 , 293 K): δ –398. IR (Nujol, cm⁻¹) 3413 (s), 1624 (s), 1554 (s), 1526 (s), 1517 (s), 1238 (s), 1172 (s), 1099 (s), 1058 (s), 1022 (s), 891 (s), 793 (s).

2.7. X-ray data

Data collection parameters for complexes **2**, **3**, **4** and **6** are listed in Table 1. Crystals were covered in an inert oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97 [13] Details specific to individual datasets are outlined below:

Compound **2**. A residual peak of 1.90 electrons is present close to the Sn atom.

Compound **3**. The hydrogen atom on N3 was located and refined; all others were placed in calculated positions.

Compound **4**. The unit cell contains a toluene solvate molecule which has been treated as diffuse contribution to the overall

Table 1						
Crystallographic dat	a for	3,	4,	5	and	6.

	(BDI)SnN(<i>i</i> Pr) ₂ (2)	(BDI)SnNH(Ar) (3)	(BDI)SnCCPh (4)	$(BDI)Sn\{OC(O)N(iPr_2)\}$ (6)
Chemical formula	C35H55N3Sn	C41H59N3Sn	$C_{37}H_{46}N_2Sn \cdot C_7H_8$	C ₃₆ H ₅₅ N ₃ O ₂ Sn
Formula weight	636.51	712.60	729.58	680.54
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm ³)	$0.28\times0.22\times0.08$	$0.19 \times 0.13 \times 0.10$	$0.20\times0.20\times0.16$	$0.29 \times 0.20 \times 0.14$
Crystal system	$P 2_1/c$ (no. 14)	triclinic	<i>I</i> 4/ <i>m</i> (no. 87)	<i>P</i> 1̄ (no. 2)
Space group	monoclinic	<i>P</i> 1̄ (no. 2)	tetragonal	triclinic
a (Å)	10.3140(2)	9.2335(2)	18.4398(4)	11.4858(3)
b (Å)	20.2436(4)	11.4606(2)	18.4398(4)	13.1637(4)
c (Å)	17.9140(3)	19.1522(4)	21.2276(6)	13.4152(4)
α (°)	90	100.622(1)	90	91.601(2)
β (°)	114.056(1)	102.355(1)	90	107.273(2)
γ (°)	90	99.208(1)	90	114.822(4)
$V(Å^3)$	3415.45(11)	1903.40(7)	7217.9(3)	1730.45(11)
Ζ	4	2	8	4
$\rho_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.24	1.24	1.34	1.31
Absorption coefficient (mm ⁻¹)	0.77	0.70	0.74	0.772
θ range for data collection (°)	3.53-26.74	3.44-27.10	3.45-26.73	3.45-27.50
Measured/independent reflections/R _(int)	37 640/6909/0.065	30 546/8358/0.055	11 847/3941/0.036	25 911/7847/0.044
Reflections with $l > 2\sigma(l)$	5886	7414	3335	7182
Data/restraints/parameters	6909/0/366	8358/0/412	3941/0/173	7847/0/381
Goodness-of-fit on (GOF) F ²	1.052	1.028	1.082	1.070
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.036, wR_2 = 0.080$	$R_1 = 0.031, wR_2 = 0.064$	$R_1 = 0.038, wR_2 = 0.104$	$R_1 = 0.0326, wR_2 = 0.078$
R indices (all data)	$R_1 = 0.048, wR_2 = 0.085$	$R_1 = 0.039, wR_2 = 0.066$	$R_1 = 0.048, wR_2 = 0.108$	$R_1 = 0.037, wR_2 = 0.081$
Largest difference in peak and hole ($e Å^3$)	1.90 and -0.80	0.42 and -0.55	0.80 and -0.77	3.17 and -0.86

scattering without specific atom positions by SQUEEZE/PLA-TON. The phenyl group of the acetylide ligand is disordered across a mirror plane and was refined as a rigid body with atoms at half occupancy and isotropic carbon atoms.

Compound **6**. There is residual electron density of \sim 3 electrons located at the inversion center. This is believed to be an artifact of the data.

3. Results and discussion

3.1. Synthesis of tin-amide complexes

Addition of a lithium diisopropylamide solution to (BDI)SnCl (1) results in an immediate color change to an orange solution of tin diisopropyl amide **2** (Eq. (1)). The ¹H NMR spectrum of isolated tin-amide 2 revealed three resonances in a 1:1:1 ratio, corresponding to three different isopropyl CH environments, two from the BDI N-aryl isopropyl groups, and one from the N-diisopropyl ligand. A ¹¹⁹Sn NMR spectroscopic signal was observed at δ –224 ppm, which is only slightly upfield to that found for (BDI)SnNMe₂ (δ -172 ppm) [9], but significantly upfield to that of (BDI)Sn{N $(SiMe_3)_2$ (δ 112 ppm) [10]. X-ray quality crystals were grown by cooling a saturated toluene solution of tin amide 2 to -30 °C. The ORTEP diagram is shown in Fig. 2 and selected bond lengths and angles are listed in Table 2. As with most other (BDI)-Sn complexes, the ligands around the metal center are in a pyramidal arrangement, presumably due to the presence of a stereochemically active lone pair. The tin metal center is displaced from the N(1)-C(1)-C(2)-C(3)-N(2) (NCCCN) plane by 1.359 Å, significantly further than any other (BDI)Sn complex reported. This is presumably due to the inability of the bulky *N*-isopropyl ligand to lie in between the two N-aryl groups of the BDI ligand (endo configuration); instead, this planar N-isopropyl ligand must point away from the rest of the molecule (exo configuration). This is in contrast to both (BDI)SnNMe₂ and (BDI)Sn{N(SiMe₃)₂}; the trigonal planar amide ligands of these latter structures lie in between the N-aryl groups of the BDI ligand, and one of the N-Me or N-SiMe₃ groups lies directly below the NCCCN plane (endo configuration). The Sn-N bond

length of 2.070(2) Å is slightly longer than the Sn–N bond length of the (BDI)SnNMe₂ complex (2.038(6) Å), but shorter than the Sn–N bond length of the (BDI)SnN(SiMe₃)₂ complex (2.159 Å).

Tin anilide **3** was generated by treating a toluene solution of tin chloride **1** with lithium-(2,6-di-isopropyl)anilide (Eq. (2)). The ¹H NMR spectrum revealed the presence of three septets in a 1:1:1 ratio, corresponding to the isopropyl CH protons; two of these correspond to the BDI ligand, the other correspond to the (2,6-diisopropyl)anilide ligand. A single ¹¹⁹Sn spectroscopic signal was observed at δ -745 ppm, significantly upfield to the tin amide complexes. The solid state structure reveals the expected trigonal pyramidal arrangement of the ligands around the metal center, with the tin atom displaced from the NCCCN plane by 0.721 Å, and a Sn–N bond length of 2.1000(17) Å (Fig. 3, Table 2). The latter is slightly shorter than the terminal anilide tin complex, {(MA-NH)Sn-(μ -HN-MA)₂Li·2THF} (MA = 2-MeO-C₆H₄) of 2.118(8) Å and the terminal anilide ligands of $Sn_2{N(H)Ar}_4$ (Ar = 2,6-*i*Pr₂C₆H₃) (2.117(3) and 2.120(4) Å) [14,15]. An endo configuration of the complex is found, presumably due to smaller bulk at the N-aryl nitrogen relative to the amide ligand of 2. No evidence of hindered rotation around the Sn-N3 bond was found by ¹H NMR spectroscopy.





Fig. 2. ORTEP diagram of tin amide 2, showing two different orientations of the complex; "front-view" (left), with H atoms omitted and "side-view" (right) with H atoms omitted and BDI C atoms minimized for clarity. The ellipsoid probability is shown at 30%.

Table 2Selected bond lengths and angles for compounds 2 and 3.

	(BDI)SnN(<i>i</i> Pr) ₂ (2)	(BDI)SnNH(Ar) (3)
M-N(1)	2.227(2)	2.2143(17)
M-N(2)	2.290(2)	2.2250(17)
M-N(3)	2.070(2)	2.1000(17)
N(3)-C(30)	1.458(4)	1.403(3)
N(3)-C(33)	1.477(4)	
N(3)-H		
N(1)-M-N(2)	81.28(8)	83.72(6)
N(1)-M-N(3)	99.27(8)	86.08(7)
N(2)-M-N(3)	104.59(9)	94.17(7)
M-N(3)-C(30)	127.81(18)	131.85(15)
M-N(3)-C(33)	117.27(18)	
C(30)-N(3)-C(33)	114.9(2)	
Sum of angles	285.14	263.97
DOP	83.2	106.7
M-NCCCN plane	1.359	0.721
NR2-NCCCN	0.564	2.615

3.2. Reactivity of tin-amide complexes

There are only a few studies exploring the reactivity of terminal tin amide complexes. For instance, Gibson examined the use of (BDI)SnNMe₂ as a potential catalyst for the polymerization of *rac*-lactide [9]. Roesky performed a small reactivity study with (BDI)SnNMe₂ and found that this compound acts as a nucleophile towards reactive ketones, such as 2-benzoylpyridine and 2,2,2-tri-fluoroacetophenone, and deprotonates terminal acetylenes, such as methyl- and ethyl propiolate, to yield terminal tin-acetylide complexes [11].

Tin amide **2** is generally more reactive than tin anilide **3**. For instance tin amide **2** reacts with phenylacetylene to form (BDI)SnCCPh **4** after heating to 70 °C for 3 days; however, no reactivity was observed between tin anilide **3** and phenylacetylene, even after prolonged heating. X-ray quality crystals of acetylide **4** were grown by slow cooling a toluene solution of **4** to -30 °C (Fig. 4, Table 3). The solid state structure reveals the typical pyramidal arrangement of the ligands around the metal center, and an *endo* configuration of the complex. The Sn is displaced from the NCCCN plane by 0.805 Å, and the acetylide ligand is perpendicular to the NCCCN plane (Table 4). Both the Sn–C16 bond length of 2.196(4) Å and the C–C triple bond length of 1.190(6) Å are slightly shorter than the Sn–C bond length of Roesky's (BDI)SnCC(CO₂Et) complex of 2.214(2) Å and the C–C triple bond length of 1.213(3) Å. A ¹¹⁹Sn spectroscopic signal was observed at δ

-206 ppm, upfield to that observed for Roesky's (BDI)SnCC(-CO₂Et) complex (δ 187 ppm).



Both tin amide and anilide complexes, **2** and **3**, exhibit reactivity with methyl triflate (Eq. (3)). However, divergent reactivity was observed with these systems; for instance, addition of methyl triflate to anilide **3** results in 100% conversion to known (BDI)SnOTf (**5**); however with amide **2**, a complex mixture of products is formed. Addition of the less reactive electrophile, methyl iodide, to the tin amide **2** results in the formation of a complex mixture of products after 1 day at room temperature, and the tin-anilide complex **3** does not react with methyl iodide, even upon heating to 75 °C for several days.



No reactivity was observed between the amide and anilide complexes, 2 and 3, with benzophenone. Addition of benzaldehyde to complexes 2 and 3 resulted in the formation of a complex mixture of products in both cases. However, both tin complexes 2 and 3 do react cleanly with one atmosphere of carbon dioxide to yield the corresponding metal carbamates 6 and 7 after four hours at room temperature (Eq. (5)). The ¹³C NMR spectrum of *N*-diisopropyl carbamate **6** shows a resonance at δ 161.8 ppm, indicative of a carbamate carbon. The $^{119}\mathrm{Sn}$ spectroscopic signal shifts upfield to δ -394 ppm. The IR spectrum reveals a new stretch at 1595, 1575 and 1524 cm⁻¹; unfortunately, conclusive assignment of the IR stretching frequencies was prevented due to overlap of the NCO₂ moiety stretching frequencies with the β -diketiminate stretching frequencies [16,17]. X-ray quality crystals were grown by slowly cooling a pentane solution of **6** to $-30 \degree C$ (Fig. 4, Table 4). Although transition metal carbamates are not unusual, this is the first example



Fig. 3. ORTEP diagram of tin anilide 3, showing two different orientations of the complex; "front-view" (left), with H atoms omitted and "side-view" (right) with H atoms omitted and BDI C atoms minimized for clarity. The ellipsoid probability is shown at 30%.



Fig. 4. ORTEP diagram of tin acetylide **4** (left) and tin carbamate **6** (right), with H atoms omitted and BDI C atoms minimized for clarity. The ellipsoid probability is shown at 30%.

Table 3

Selected bond lengths and angles for compound 4.

	(BDI)SnCCPh (4)
Sn–N	2.179(2)
Sn-C(16)	2.196(4)
C(16)-C(17)	1.190(6)
C(17)-C(18)	1.435(6)
N–Sn–N'	86.42
N-Sn-C(16)	90.57(10)
N'-Sn-C(16)	90.57(10)
Sn-C(16)-C(17)	170.7(4)
C(16)-C(17)-C(18)	174.2(4)
Sum of angles	267.56
DOP	102.7
Sn-NCCCN plane	0.805
C(30)-NCCCN plane	2.724

 Table 4

 Selected bond lengths and angles for compound 6.

Selected bond lengths and angles for compound 6 .		
$(BDI)Sn\{OC(O)N(iPr_2)\}$ (6)		
2.2051(18)		
2.2012(19)		
2.1346(16)		
1.304(3)		
1.238(3)		
2.839		
1.366(3)		
1.474(3)		
1.481(3)		
84.78(7)		
87.43(7)		
87.41(7)		
109.65(15)		
121.7(2)		
116.6(2)		
121.7(2)		
122.0(2)		
120.2(2)		
117.8(2)		
259.62		
111.5		
0.546		
2.514		
$\begin{array}{c} 2.839\\ 1.366(3)\\ 1.474(3)\\ 1.481(3)\\ 84.78(7)\\ 87.43(7)\\ 87.41(7)\\ 109.65(15)\\ 121.7(2)\\ 116.6(2)\\ 121.7(2)\\ 122.0(2)\\ 122.0(2)\\ 120.2(2)\\ 117.8(2)\\ 259.62\\ 111.5\\ 0.546\\ 2.514\end{array}$		

of a group 14 metal carbonate bound through the oxygen atom of the carbamate ligand [18]. The tin center is displaced from the NCCCN plane by 0.546 Å, and an *endo* configuration is observed in which the Sn–O bond is approximately 90° to the of the NCCCN plane. The Sn–O(1) bond length of 2.1346(16) Å is longer than that of Gibson's (BDI)SnOiPr (2.000(5) Å) [8]. The Sn \cdots O(2) of 2.839 Å is smaller than the sum of the van der Waals radii for oxygen and tin (3.69 Å).



Tin amide carbamate **6** is formed quantitatively as observed by ¹H NMR spectroscopic analysis; however, tin anilide carbamate **7**

only forms in 90% conversion and a second product is observed in the ¹H NMR spectrum. The ¹³C NMR spectrum of **7** shows a indicative carbamate carbon resonance at δ 161.6 ppm, and the ¹¹⁹Sn NMR spectrum revealed a resonance at δ 398 ppm, significantly downfield to that of tin anilide **3**. The IR spectrum shows a shift of the stretching frequencies from the tin anilide complex **3** to 1554, 1526 and 1517 cm⁻¹. As with the carbamate **6**, the β -diketiminate stretching frequencies overlap with that expected for the NCO₂ moiety, preventing conclusive assignment of the IR stretching frequencies [16,17]. Unfortunately, despite repeated attempts, we have been unable to grow X-ray quality crystals of this species. In contrast to what is observed for (BDI)-tin- and lead-alkoxides [3,19], no reversion back to amide **2** or anilide **3** is observed, even under reduced pressure.

4. Conclusions

Two new tin-amide and -anilide complexes have been synthesized and their reactivity was explored. The amide complex was found to be more reactive than the anilide complex, a trend that mirrors reactivity studies performed on transition metal analogs [20], and is presumably due to the higher nucleophilic character of the amide nitrogen versus the anilide nitrogen. Addition of carbon dioxide to both tin-amide and -anilide complexes **2** and **3** resulted in insertion of carbon dioxide into the tin-nitrogen bond.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.009.

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