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C,N-chelated organotin(IV) azides: Synthesis, structure and use within the click chemistry

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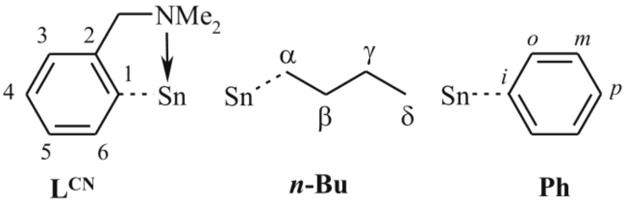


Scheme S1: General NMR numbering of organic substituents used in the full paper

Numbering of compounds corresponds with the numbering in the full paper.

Table S1: Important NMR parameters of **1-16** recorded in $CDCl_3$ (unless specified otherwise)

Compound	**$\delta(^{119}Sn)$** [ppm]	**$\Delta\delta(^{119}Sn)$** [ppm][a]	**$\delta(^{13}C)$** [ppm][b]	**$^{1}J(^{119/117}Sn, ^{13}C(1))$** [Hz]	**$^{3}J(^{119}Sn, ^{1}H(6))$** [Hz]
1	-84.2	-32.5	n/a	~ 655	64
2	-196.1	-19.0	n/a	812/775	73
3	-141.1	-23.0	n/a	728/694	~ 70
4	-194.6	-90.3	n/a	n/a	84
5	-243.5	-73.5	n/a	n/a	86
6	-312.6	-59.8	n/a	1219/1164	102
7	-87.5	-3.3	159.6	662/632	65 [c]
8	-222.0	-25.9	158.1	818/782	74
9	-88.4	-4.2	172.3	660/630	65
10	-220.0	-23.9	172.4	n/a	~ 70
11	-84.3	-0.1	163.7	660/631	65 [c]
12	-216.5	-20.4	163.6	n/a	71
13	-85.7	-1.5	161.2	661/633	65
14	-221.9	-25.8	160.4	808/773	~ 72
15	-98.2	-14.0	144.8 (br)	652/622	~ 63 [c]
16	-223.2	-27.1	144.1 (br)	770/740	74

[a] with respect to the starting *C,N*-chelated organotin(IV) chloride (for **1-6**) or azide (**7-16**); [b] chemical shift value of the tetrazolide or triazolide carbons; [c] measured in benzene-d_6

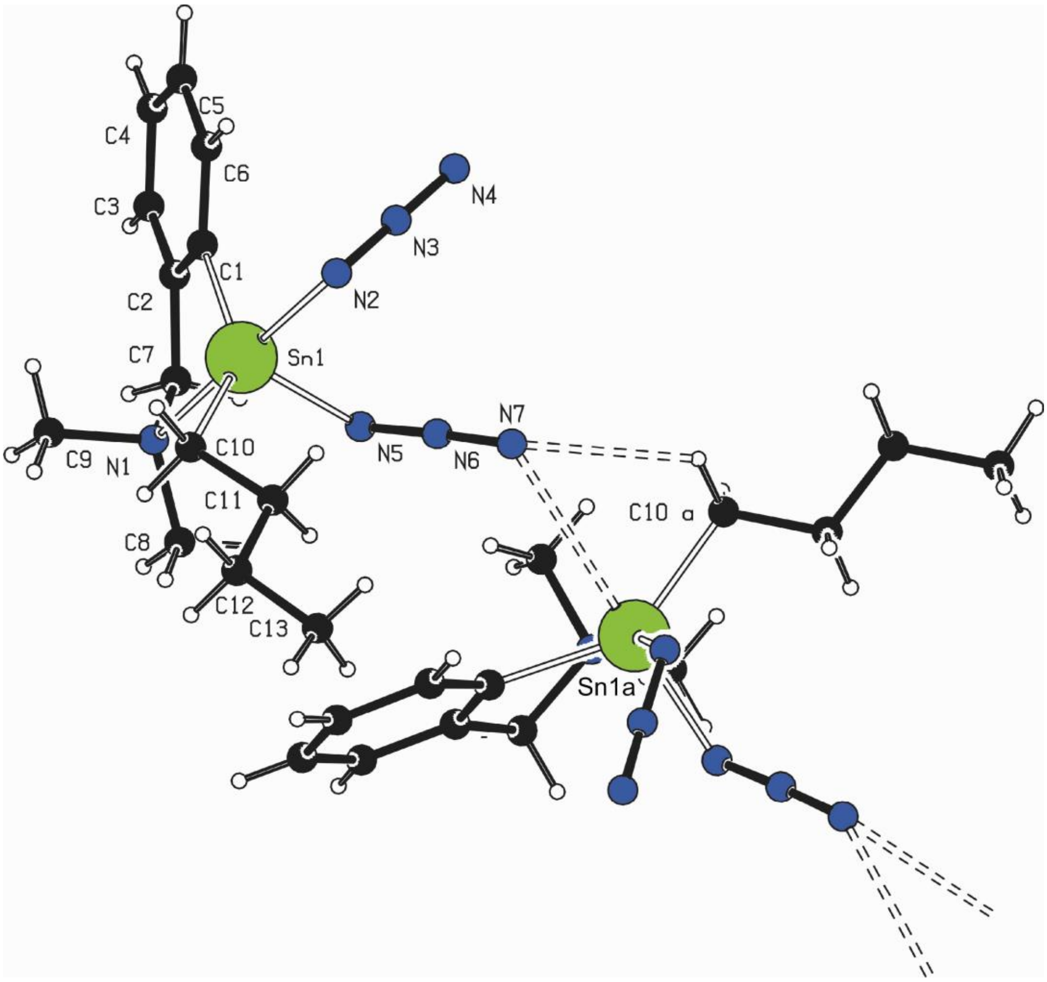


Fig. S1: Supramolecular architecture of **4** (PLUTON view). Selected interatomic distances [Å]: N7-Sn1a 3.278, N7-C10a 3.285. N7...H-C10a 122.74°.

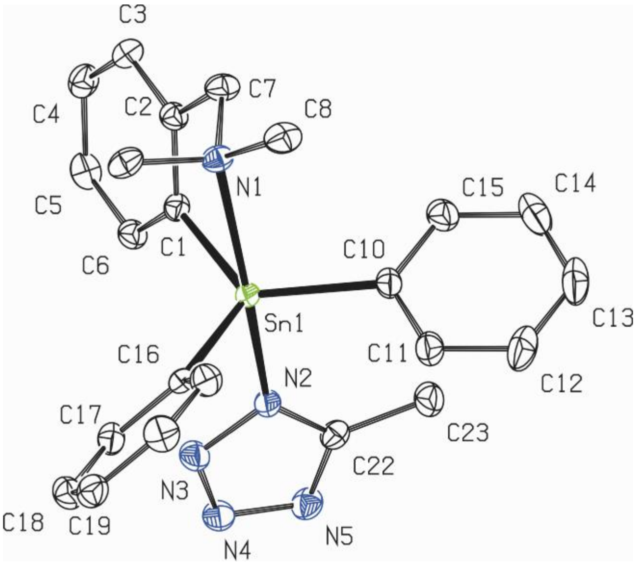


Fig. S2: Molecular structure of **8** (ORTEP presentation, 40% probability level). Solvating $CHCl_3$ and water molecules as well as all hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]; values in square brackets are given for another two independent molecules in the unit cell: Sn1-N1 2.466(5) [2.448(5), 2.468(4)], Sn1-N2 2.263(5) [2.254(5), 2.255(4)], N2-N3 1.361(6) [1.353(6), 1.365(6)], N3-N4 1.302(7) [1.304(7), 1.306(8)], N4-N5 1.358(6) [1.343(7), 1.349(8)], N2-C22 1.344(7) [1.341(7), 1.335(7)], N5-C22 1.315(8) [1.322(7), 1.325(7)], Sn1-C1 2.126(5) [2.134(5), 2.130(5)], Sn1-C10 2.126(5) [2.132(4), 2.123(5)], Sn1-C16 2.132(5) [2.121(5), 2.123(6)]; N1-Sn1-N2 169.33(13) [170.97(14), 167.68(15)], Sn1-N2-N3 116.7(3) [114.2(3), 116.2(4)], N2-N3-N4 108.5(4) [108.1(4), 107.0(5)], N3-N4-N5 109.6(4) [110.2(4), 110.9(5)], N4-N5-C22 105.8(4) [105.6(5), 105.1(5)], N2-C22-N5 110.8(4) [110.4(4), 110.7(5)], C22-N2-N3 105.4(4) [105.7(4), 106.3(4)], C1-Sn1-C10 122.89(18) [124.57(18), 112.69(19)], C1-Sn1-C16 123.09(18) [114.60(18), 127.37(18)], C10-Sn1-C16 112.57(19) [119.25(19), 118.4(2)].

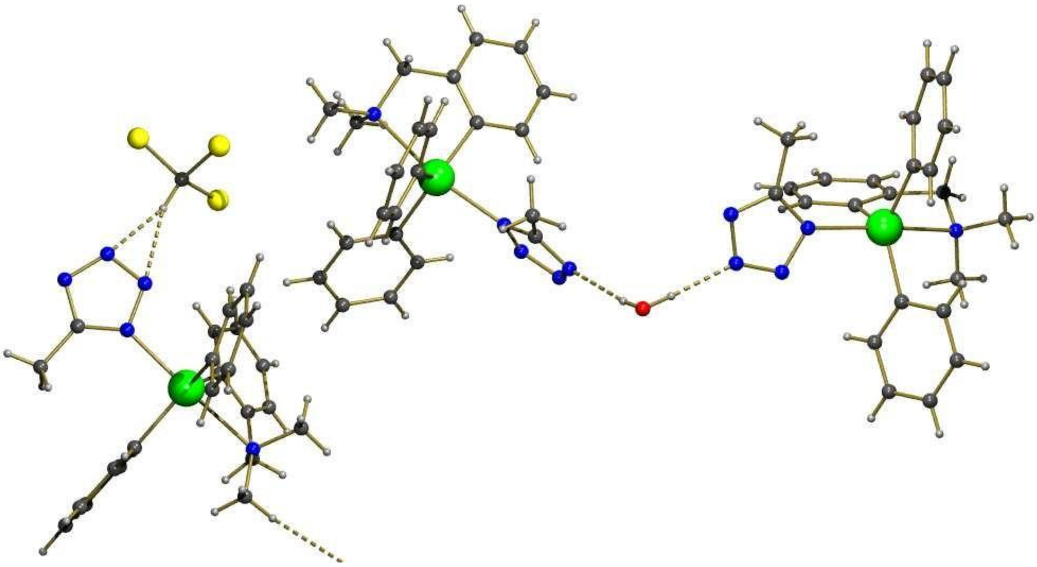


Fig. S3: Detail of selected part of the molecular structure of **8** (with solvating H_2O and $CHCl_3$ molecules) – presentation of the H-bonding. H-bonding: *i)* N...H-O 167.39° (2.872 Å), *ii)* N...H-O 169.51° (2.914 Å).

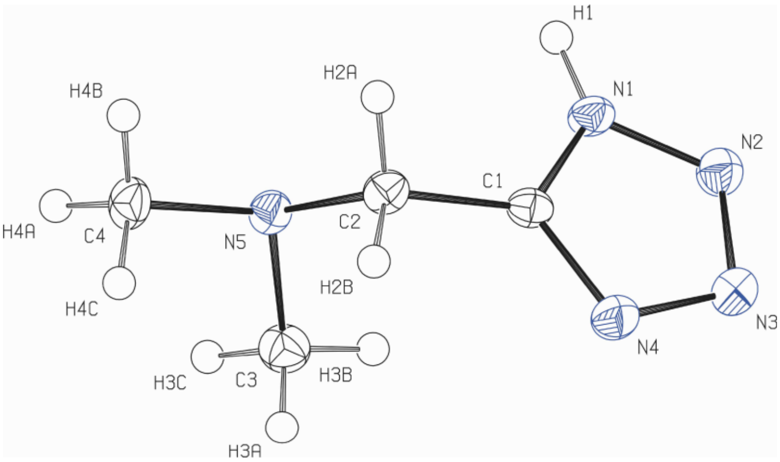


Fig. S4: Molecular structure of the monomeric unit of 5-*N*,*N*-dimethylaminomethyl-*1H*-tetrazole (**14a**) (ORTEP presentation, 50% probability level). Selected interatomic distances [Å] and angles [°]: N1-N2 1.344(3), N2-N3 1.309(3), N3-N4 1.353(3), N4-C1 1.328(3), N4-C10 1.346(3), N5-C10 1.332(3), Sn1-C1 2.138(2), Sn1-C17 2.144(2), N1-C1 1.330(3); N1-N2-N3 108.82(17), N2-N3-N4 109.56(17), N3-N4-C1 104.72(17), N1-C1-N4 111.37(17), N2-N1-C1 105.52(16).

Selected crystallographic data of **14a**:

Empirical formula: $C_4H_9N_5$; formula weight 127.16; crystal system: monoclinic; Space group: *C*2/c; a = 16.2012(4) Å; b = 6.1332(5) Å; c = 12.7070(2) Å; β = 97.423(5)°; Z = 8; V = 1252.05(11) Å^3; D_c = 1.349 g.cm^{-3}; crystal size: 0.23 x 0.13 x 0.06 mm; crystal shape: block; μ = 0.096 mm^{-1}; F(000) = 544; h k l range: -20,18; -7,7; -16,16; θ range: 2.536 – 27.497°; 4919 reflections measured (1416 independent, 1074 observed); 82 parameters refined; max/min τ (eÅ^{-3}): 0.659 / -0.746; GOF = 1.117; R = 0.0520.

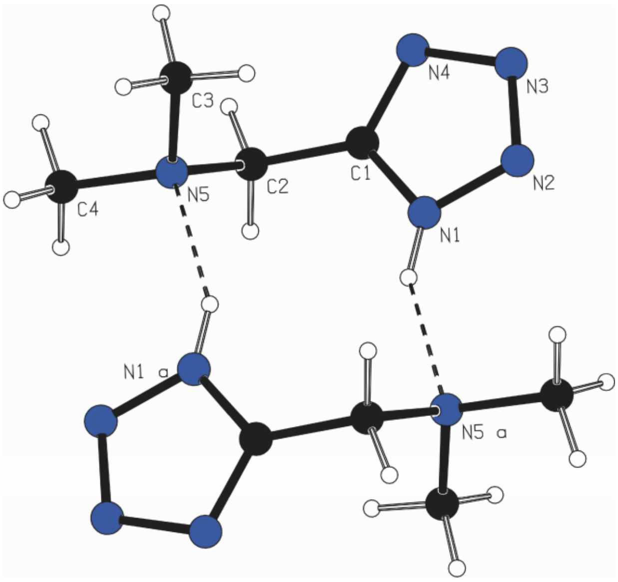


Fig. S5: Dimeric presentation of the molecular structure of **14a** (PLUTON view). Hydrogen bond N1-N5a = N5-N1a = 2.761 Å and N1-H¨N5a = N5-H¨N1a = 148.54°. Other selected interatomic distances [Å]: N1-N2 1.344(3), N2-N3 1.309(3), N3-N4 1.353(3), N1-C1 1.330(3), 1.328(3).

Experimental part – preparation and spectroscopic characterization of **1-16**

Preparation of $L^{CN}(n\text{-}Bu)_2SnN_3$ (***1***)

$L^{CN}(n\text{-}Bu)_2SnCl$ (403 mg, 1.0 mmol) was dissolved in diethyl ether (10 mL) and NaN_3 (325 mg, 5.0 mmol) in distilled water (10 mL) was added. The resulting biphasic system was stirred overnight at ambient temperature. The water phase was then separated and washed with diethyl ether (2x 10 mL). The combined organic phases were dried over $MgSO_4$. After filtration, the clear diethyl ether solution of the title product was evaporated to dryness in vacuo giving pure **1** as yellowish oil. Isolated yield 348 mg (85%). ^1H NMR ($CDCl_3$, 295 K, ppm): 7.90 (d, 1H, H(6), $^3J(^1H, ^1H) = 6$ Hz, $^3J(^{119}Sn, ^1H) = 64$ Hz); 7.30 (m, 2H, H(4, 5)); 7.13 (d, 1H, H(3), $^3J(^1H, ^1H) = 7$ Hz, $^4J(^{119}Sn, ^1H) = 29$ Hz); 3.56 (s, 2H, CH_2N); 2.31 (s, 6H, NMe_2); 1.67 (m, 4H, α-CH_2); 1.38-1.29 (m, 8H, β- and γ-CH_2); 0.90 (t, 6H, δ-CH_3, $^3J(^1H, ^1H) = 5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): 142.4 (C(2), $^2J(^{119/117}Sn, ^{13}C) = 37$ Hz); 139.7 (C(1), $^1J(^{119/117}Sn, ^{13}C) \approx 655$ Hz, tin satellites are partially overlapped by resonances of C(2) and C(6)); 137.3 (C(6), $^2J(^{119/117}Sn, ^{13}C) = 33$ Hz); 129.4 (C(4)); 127.9 (C(5), $^3J(^{119/117}Sn, ^{13}C) = 59$ Hz); 127.0 (C(3), $^3J(^{119/117}Sn, ^{13}C) = 55$ Hz); 65.2 (CH_2N); 45.4 (NMe_2); 28.2 (β-C, $^2J(^{119/117}Sn, ^{13}C) = 31$ Hz); 26.9 (γ-C, $^3J(^{119/117}Sn, ^{13}C) = 81$ Hz); 15.2 (α-C, $^1J(^{119/117}Sn, ^{13}C) = 497/475$ Hz); 13.7 (δ-C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): -84.2. ^1H NMR (C_6D_6, 295 K, ppm): 8.32 (d, 1H, H(6), $^3J(^1H, ^1H) = 6$ Hz, $^3J(^{119}Sn, ^1H) = 65$ Hz); 7.20-7.10 (m, 2H, H(4, 5)); 6.84 (d, 1H, H(3), $^3J(^1H, ^1H) = 7$ Hz, $^4J(^{119}Sn, ^1H) = 29$ Hz); 2.89 (s, 2H, CH_2N); 1.80-1.70 (m, 4H, α-CH_2); 1.57 (s, 6H, NMe_2); 1.38 (m, 4H, β-CH_2); 1.22-1.12 (m, 4H, γ-CH_2); 0.92 (t, 6H, δ-CH_3, $^3J(^1H, ^1H) = 6$ Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 295 K, ppm): -88.8. $^{119}Sn\{^1H\}$ NMR (THF-d8, 295 K, ppm): -92.6. IR-ATR (cm^{-1}, selected bands only): 2055 (vs, ν(N=N=N) stretching vibration). Elemental analysis (%): found C, 50.1; H, 7.6; N, 13.6. Calc. for $C_{17}H_{30}N_4Sn$ (409.14): C, 49.91; H, 7.39; N, 13.69.

Preparation of $L^{CN}Ph_2SnN_3$ (***2***)

$L^{CN}Ph_2SnCl$ (443 mg, 1.0 mmol) was dissolved in dichloromethane (15 mL) and NaN_3 (325 mg, 5.0 mmol) in distilled water (10 mL) was added. The resulting biphasic system was stirred overnight at ambient temperature. The water phase was then separated and washed with dichloromethane (2x 10 mL). The combined organic phases were dried over $MgSO_4$. After filtration, the clear dichloromethane solution of the title product was evaporated to dryness *in vacuo* giving pure **2** as a crystalline solid. Isolated yield 270 mg (60%). Single crystals of **2** were obtained from its $CHCl_3$ solution by the slow evaporation of the solvent in the air. M.p. 188-189°C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.17 (d, 1H, H(6), ^{3}J(^{1}H, ^{1}H) = 7 Hz, ^{3}J(^{119}Sn, ^{1}H) = 73 Hz); 7.62 (d, 4H, *o*-Ph, ^{3}J(^{1}H, ^{1}H) = 7 Hz, ^{3}J(^{119}Sn, ^{1}H) = 68 Hz); 7.45-7.30 (m, 8H, L^{CN} and Ph moieties); 7.18 (d, 1H, H(3), ^{3}J(^{1}H, ^{1}H) = 7 Hz, ^{4}J(^{119}Sn, ^{1}H) = 32 Hz); 3.51 (s, 2H, CH_2N); 1.88 (s, 6H, NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K, ppm): 143.0 (C(2), ^{2}J($^{119/117}$Sn, ^{13}C) = 42 Hz); 138.0 (*i*-Ph, ^{1}J($^{119/117}$Sn, ^{13}C) = 768/727 Hz); 137.9 (C(6), ^{2}J($^{119/117}$Sn, ^{13}C) = 39 Hz); 136.2 (C(1), ^{1}J($^{119/117}$Sn, ^{13}C) = 812/775 Hz); 135.8 (*o*-Ph, ^{2}J($^{119/117}$Sn, ^{13}C) = 43 Hz); 130.3 (C(4)); 129.8 (*p*-Ph)); 129.1 (*m*-Ph), ^{3}J($^{119/117}$Sn, ^{13}C) = 66 Hz); 128.3 (C(5), ^{3}J($^{119/117}$Sn, ^{13}C) = 68 Hz); 127.5 (C(3), ^{3}J($^{119/117}$Sn, ^{13}C) = 64 Hz); 64.5 (CH_2N, ^{2}J($^{119/117}$Sn, ^{13}C) = 31 Hz); 45.7 (NMe_2). ^{119}Sn{^{1}H} NMR ($CDCl_3$, 295 K, ppm): -196.1. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.56 (d, 1H, H(6), ^{3}J(^{1}H, ^{1}H) = 7 Hz, ^{3}J(^{119}Sn, ^{1}H) = 73 Hz); 7.56 (m, 4H, *o*-Ph, ^{3}J(^{119}Sn, ^{1}H) = 68 Hz); 7.27 (m, 1H, H(4)); 7.19 (m, 7H, L^{CN} and Ph moieties); 6.84 (d, 1H, H(3), ^{3}J(^{1}H, ^{1}H) = 8 Hz, ^{4}J(^{119}Sn, ^{1}H) = 33 Hz); 2.87 (s, 2H, CH_2N); 1.31 (s, 6H, NMe_2). ^{119}Sn{^{1}H} NMR (C_6D_6, 295 K, ppm): -195.7. ^{119}Sn{^{1}H} NMR (THF-d8, 295 K, ppm): -199.9. IR-ATR (cm^{-1}, selected bands only): 2050 (vs, ν(N=N=N) stretching vibration). Elemental analysis (%): found C, 56.4; H, 5.1; N, 12.3. Calc. for $C_{21}H_{22}N_4Sn$ (449.12): C, 56.16; H, 4.94; N, 12.47.

Preparation of $(L^{CN})_2$*(n-Bu)SnN*$_3$ *(**3**)*

3 was prepared in the same way as **1** using $(L^{CN})_2$(*n*-Bu)SnCl (480 mg, 1.0 mmol) and NaN_3 (325 mg, 5.0 mmol). Yellowish oil. Isolated yield 403 mg (83%). ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.67 (br, 2H, H(6), ^{3}J(^{119}Sn, ^{1}H) ≈ 70 Hz); 7.25 (m, 4H, H(4, 5)); 7.16 (d, 2H, H(3), ^{3}J(^{1}H, ^{1}H) = 7 Hz); 3.57 and 3.28 (br, 2x 2H, anisochronous CH_2N moieties); 2.09 (br, 12H, NMe_2); 1.63 (br, 2H, α-CH_2); 1.55 (br, 2H, β-CH_2); 1.38 (m, 2H, γ-CH_2); 0.86 (t, 3H, δ-CH_3, ^{3}J(^{1}H, ^{1}H) = 6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K, ppm): 143.7 (br, C(2), ^{2}J($^{119/117}$Sn, ^{13}C) could not be read); 140.6 (C(1), ^{1}J($^{119/117}$Sn, ^{13}C) = 728/694 Hz); 136.6 (C(6), ^{2}J($^{119/117}$Sn, ^{13}C) = 39 Hz); 129.1 (C(4), ^{4}J($^{119/117}$Sn, ^{13}C) = 13 Hz); 128.4 (br, C(5), ^{3}J($^{119/117}$Sn, ^{13}C) could not be read); 127.3 (C(3), ^{3}J($^{119/117}$Sn, ^{13}C) = 65 Hz); 65.7 (CH_2N, ^{n}J($^{119/117}$Sn, ^{13}C) = 25 Hz); 45.5 (NMe_2); 28.2 (β-C, ^{2}J($^{119/117}$Sn, ^{13}C) = 30 Hz); 26.8 (γ-C, ^{3}J($^{119/117}$Sn, ^{13}C) = 97 Hz); 16.7 (br, α-C, ^{1}J($^{119/117}$Sn, ^{13}C) could not be read); 13.6 (δ-C). ^{119}Sn{^{1}H} NMR ($CDCl_3$, 295 K, ppm): -141.1. IR-ATR (cm^{-1}, selected bands only): 2056 (vs, ν(N=N=N) stretching vibration). Elemental analysis (%): found C, 54.5; H, 6.9; N, 14.3. Calc. for $C_{22}H_{33}N_5Sn$ (486.23): C, 54.35; H, 6.84; N, 14.40.

Preparation of L^{CN}*(n-Bu)Sn(N*$_3$*)*$_2$ *(**4**)*

4 was prepared in the same way as **2** using L^{CN}(*n*-Bu)SnCl$_2$ (381 mg, 1.0 mmol) and NaN$_3$ (650 mg, 10.0 mmol). Yellowish oil which slowly solidifies on standing. Isolated yield 295 mg (75%). Single crystals of **4** were obtained from its CHCl$_3$ solution by the slow evaporation of the solvent in the air. M.p. 74-76°C. ^{1}H NMR (CDCl$_3$, 295 K, ppm): 7.87 (d, 1H, H(6), $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H)$ = 84 Hz); 7.42-7.35 (m, 2H, H(4, 5)); 7.20 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 7 Hz, $^4J(^{119}Sn, ^1H)$ = 38 Hz); 3.66 (s, 2H, CH$_2$N); 2.39 (s, 6H, NMe$_2$); 1.83 (m, 2H, α-CH$_2$); 1.70 (m, 2H, β-CH$_2$); 1.44 (m, 2H, γ-CH$_2$); 0.95 (t, 6H, δ-CH$_3$, $^3J(^1H, ^1H)$ = 7 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 295 K, ppm): 141.5 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 47 Hz); 136.6 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 56 Hz); 131.0 (C(4)); 128.6 (C(5), $^3J(^{119/117}Sn, ^{13}C)$ = 82 Hz); 127.6 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 71 Hz); 63.5 (CH$_2$N); 45.0 (NMe$_2$); 27.3 (β-C, $^2J(^{119/117}Sn, ^{13}C)$ = 42 Hz); 26.5 (γ-C, $^3J(^{119/117}Sn, ^{13}C)$ = 100 Hz); 20.6 (α-C, $^1J(^{119/117}Sn, ^{13}C)$ = 682/651 Hz); 13.7 (δ-C); C(1) resonance was not observed. ^{119}Sn{^{1}H} NMR (CDCl$_3$, 295 K, ppm): -194.6. IR-ATR (cm^{-1}, selected bands only): 2066 (vs, ν(N=N=N) stretching vibration). Elemental analysis (%): found C, 39.8; H, 5.5; N, 24.7. Calc. for $C_{13}H_{21}N_7Sn$ (394.05): C, 39.62; H, 5.37; N, 24.88.

*Preparation of L^{CN}PhSn(N$_3$)$_2$ (**5**)*

5 was prepared in the same way as **2** using L^{CN}PhSnCl$_2$ (401 mg, 1.0 mmol) and NaN$_3$ (650 mg, 10.0 mmol). Yellowish oil. Isolated yield 253 mg (61%). ^{1}H NMR (CDCl$_3$, 295 K, ppm): 8.03 (br d, 1H, H(6), $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H) \approx$ 86 Hz); 7.61 (br, 2H, *o*-Ph); 7.55-7.40 (m, 5H, L^{CN} and Ph moieties); 7.25 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 7 Hz); 3.67 (s, 2H, CH$_2$N); 2.23 (s, 6H, NMe$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 295 K, ppm): 141.6 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 58 Hz); 137.2 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 56 Hz); 136.6 (br, *i*-Ph); 134.8 (*o*-Ph, $^2J(^{119/117}Sn, ^{13}C)$ = 55 Hz); 130.8 (br, C(4)); 129.5 (br, *p*-Ph); 129.1 (br, *m*-Ph); 128.8 (br, C(5)); 127.9 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 41 Hz); 63.2 (CH$_2$N, $^2J(^{119/117}Sn, ^{13}C)$ = 45 Hz); 45.3 (NMe$_2$); C(1) resonance was not observed. ^{119}Sn{^{1}H} NMR (CDCl$_3$, 295 K, ppm): -243.5. IR-ATR (cm^{-1}, selected bands only): 2055 (vs, ν(N=N=N) stretching vibration). Elemental analysis (%): found C, 43.6; H, 4.2; N, 23.5. Calc. for $C_{15}H_{17}N_7Sn$ (414.04): C, 43.51 H, 4.14; N, 23.68.

*Preparation of (L^{CN})$_2$Sn(N$_3$)$_2$ (**6**)*

6 was prepared in the same way as **2** using (L^{CN})$_2$SnBr$_2$ (274 mg, 0.5 mmol) and NaN$_3$ (650 mg, 10.0 mmol). Yellowish oil that very slowly crystallizes on standing. Isolated yield 120 mg (51%). Single crystals of **6** were obtained from its CHCl$_3$ solution by the slow evaporation of the solvent in the air. M.p. 169-171°C. ^{1}H NMR (CDCl$_3$, 295 K, ppm): 7.97 (m, 2H, H(6),

$^{3}J(^{119}\text{Sn}, ^{1}\text{H})$ = 102 Hz); 7.45-7.40 (m, 4H, H(4, 5)); 7.21 (m, 2H, H(3), $^{4}J(^{119}\text{Sn}, ^{1}\text{H})$ = 48 Hz); 3.77 and 3.49 (AX spin system, 2x 2H, CH_2N, Δδ = 142 Hz, $^{2}J(^{1}\text{H}, ^{1}\text{H})$ = 14 Hz); 2.40 and 2.01 (br, 2x 6H, anisochronous NMe_2 groups). $^{13}\text{C}\{^{1}\text{H}\}$ NMR ($CDCl_3$, 295 K, ppm): 141.1 (C(2), $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 61 Hz); 136.7 (C(1), $^{1}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 1219/1164 Hz); 136.0 (C(6), $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 50 Hz); 130.7 (C(4), $^{4}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 18 Hz); 128.5 (C(5), $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 98 Hz); 128.2 (C(3), $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 94 Hz); 64.1 (CH_2N, $^{n}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 43 Hz); 46.6 and 46.4 (br, anisochronous NMe_2 groups). $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR ($CDCl_3$, 295 K, ppm): -312.6. IR-ATR (cm^{-1}, selected bands only): 2055 (vs, ν(N=N=N) stretching vibration). Elemental analysis (%): found C, 46.1; H, 5.3; N, 23.6. Calc. for $C_{18}H_{24}N_8Sn$ (471.13): C, 45.89; H, 5.13; N, 23.78.

*Preparation of C,N-chelated di-n-butyltin(IV) 5-methyltetrazol-1-ide (**7**)*

1 (205 mg, 0.50 mmol) was dissolved in toluene (10 mL) and MeCN (10 mL, excess) was added. The solution was heated to reflux for 150 hours. Volatiles were then removed *in vacuo* giving pure oily **7** in a quantitative yield (225 mg). ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.27 (m, 1H, H(L^{CN})); 7.20 (m, 1H, H(L^{CN})); 7.15 (m, 2H, H(L^{CN})); 3.67 (s, 2H, CH_2N); 2.51 (s, 3H, CH_3); 2.42 (s, 6H, NMe_2); 1.70-1.45 (m, 8H, α- and β-CH_2); 1.34 (m, 4H, γ-CH_2); 0.83 (t, 6H, δ-CH_3, $^{3}J(^{1}\text{H}, ^{1}\text{H})$ = 6 Hz). $^{13}\text{C}\{^{1}\text{H}\}$ NMR ($CDCl_3$, 295 K, ppm): 159.6 (N_4C ring); 142.4 (C(2), $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 35 Hz); 138.8 (C(1), $^{1}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 662/632 Hz); 137.5 (C(6), $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 35 Hz); 129.5 (C(4), $^{4}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 13 Hz); 128.0 (C(5), $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 62 Hz); 127.0 (C(3), $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 56 Hz); 65.4 (CH_2N, $^{n}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 26 Hz); 45.6 (NMe_2); 28.1 (β-C, $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 31 Hz); 26.9 (γ-C, $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 90 Hz); 15.6 (α -C, $^{1}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 501/480 Hz); 13.5 (δ-C); 10.9 (CH_3). $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR ($CDCl_3$, 295 K, ppm): -87.5. ^{1}H NMR (C_6D_6, 295 K, ppm): 7.81 (d, 1H, H(6), $^{3}J(^{1}\text{H}, ^{1}\text{H})$ = 7 Hz, $^{3}J(^{119}\text{Sn}, ^{1}\text{H})$ = 65 Hz); 7.08 (m, 1H, H(4)); 6.98 (m, 1H, H(5)); 6.90 (d, 1H, H(3), $^{3}J(^{1}\text{H}, ^{1}\text{H})$ = 8 Hz, $^{4}J(^{119}\text{Sn}, ^{1}\text{H})$ = 28 Hz); 3.11 (s, 2H, CH_2N); 2.57 (s, 3H, CH_3); 1.78 (s, 6H, NMe_2); 1.53-1.43 (m, 8H, α- and β-CH_2); 1.33 (m, 4H, γ-CH_2); 0.82 (t, 6H, δ-CH_3, $^{3}J(^{1}\text{H}, ^{1}\text{H})$ = 6 Hz). $^{13}\text{C}\{^{1}\text{H}\}$ NMR (C_6D_6, 295 K, ppm): 160.8 (N_4C ring); 143.4 (C(2), $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 37 Hz); 140.0 (C(1), $^{1}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 666/636 Hz); 138.8 (C(6), $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 35 Hz); 130.0 (C(4), $^{4}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 13 Hz); 128.7 (C(5)); 127.6 (C(3), $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 55 Hz); 65.5 (CH_2N, $^{n}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 25 Hz); 45.4 (NMe_2); 28.9 (β-C, $^{2}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 31 Hz); 27.7 (γ-C, $^{3}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 88 Hz); 16.3 (α -C, $^{1}J(^{119/117}\text{Sn}, ^{13}\text{C})$ = 507/485 Hz); 14.1 (δ-C); 11.6 (CH_3). $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (C_6D_6, 295 K, ppm): -94.1. Elemental analysis (%): found C, 51.0; H, 7.6; N, 15.3. Calc. for $C_{19}H_{33}N_5Sn$ (450.20): C, 50.69; H, 7.39; N, 15.56.

*Preparation of C,N-chelated diphenyltin(IV) 5-methyltetrazol-1-ide (**8**)*

8 was prepared similarly as described for **7** using **2** (225 mg, 0.50 mmol) and MeCN (10 mL, excess). Overall reflux time 70 hours. White crystalline solid. Isolated yield 240 mg (98%). M.p. 69-71°C (valid for single crystals with solvating H_2O and $CHCl_3$ molecules). ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.85 (d, 4H, *o*-Ph, $^3J(^1H, ^1H)$ = 6 Hz, $^3J(^{119}Sn, ^1H)$ = 68 Hz); 7.59 (d, 1H, H(1), $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H)$ = 74 Hz); 7.50-7.35 (m, 8H, L^{CN} and Ph substituents); 7.28 (m, 1H, H(3)); 3.70 (s, 2H, CH_2N); 2.00 (s, 3H, CH_3); 1.96 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): 158.1 (N_4C ring); 143.0 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 42 Hz); 138.2 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 42 Hz); 137.9 (*i*-Ph, $^1J(^{119/117}Sn, ^{13}C)$ = 785/751 Hz); 136.1 (*o*-Ph, $^2J(^{119/117}Sn, ^{13}C)$ = 44 Hz); 135.0 (C(1), $^1J(^{119/117}Sn, ^{13}C)$ = 818/782 Hz); 130.4 (C(4), $^4J(^{119/117}Sn, ^{13}C)$ = 14 Hz); 130.0 (*p*-Ph, $^4J(^{119/117}Sn, ^{13}C)$ = 13 Hz); 129.1 (*m*-Ph, $^3J(^{119/117}Sn, ^{13}C)$ = 69 Hz); 128.4 (C(5), $^3J(^{119/117}Sn, ^{13}C)$ = 71 Hz); 127.6 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 65 Hz); 64.4 (CH_2N, $^nJ(^{119/117}Sn, ^{13}C)$ = 30 Hz); 45.5 (NMe_2); 10.2 (CH_3). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): -222.0. Elemental analysis (%): found C, 56.6; H, 5.4; N, 14.1. Calc. for $C_{23}H_{25}N_5Sn$ (490.18): C, 56.36; H, 5.14; N, 14.29.

*Preparation of C,N-chelated di-n-butyltin(IV) 5-tert-butyltetrazol-2-ide (**9**)*

9 was prepared similarly as described for **7** using **1** (205 mg, 0.50 mmol) and *t*-BuCN (2 mL, excess). Overall reflux time 8 days. Yellowish oil. Isolated yield 234 mg (95%). ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.46 (d, 1H, H(6), $^3J(^1H, ^1H)$ = 8 Hz, $^3J(^{119}Sn, ^1H)$ = 65 Hz); 7.31 (m, 1H, H(4)); 7.18 (m, 1H, H(5)); 7.13 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 8 Hz); 3.66 (s, 2H, CH_2N); 2.41 (s, 6H, NMe_2); 1.67-1.54 (m, 4H, α-CH_2); 1.46 (s, 9H, $C(CH_3)_3$); 1.36-1.29 (m, 8H, β- and γ-CH_2); 0.83 (t, 6H, δ-CH_3, $^3J(^1H, ^1H)$ = 6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): 172.3 (N_4C ring); 142.4 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 37 Hz); 139.3 (C(1), $^1J(^{119/117}Sn, ^{13}C)$ = 660/630 Hz); 138.0 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 35 Hz); 129.3 (C(4)); 127.9 (C(5), $^3J(^{119/117}Sn, ^{13}C)$ = 61 Hz); 126.9 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 55 Hz); 65.5 (CH_2N, $^nJ(^{119/117}Sn, ^{13}C)$ = 25 Hz); 45.6 (NMe_2); 31.2 ($\mathit{C}(CH_3)_3$); 30.1 ($C(\mathit{CH}_3)_3$); 28.1 (β-C, $^2J(^{119/117}Sn, ^{13}C)$ = 26 Hz); 26.9 (γ-C, $^3J(^{119/117}Sn, ^{13}C)$ = 88 Hz); 15.7 (α-C, $^1J(^{119/117}Sn, ^{13}C)$ = 500/481 Hz); 13.5 (δ-C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): -88.4. Elemental analysis (%): found C, 53.9; H, 8.2; N, 14.0. Calc. for $C_{22}H_{36}N_5Sn$ (492.28): C, 53.68; H, 7.99; N, 14.23.

*Preparation of C,N-chelated diphenyltin(IV) 5-tert-butyltetrazol-2-ide (**10**)*

10 was prepared similarly as described for **7** using **2** (225 mg, 0.50 mmol) and *t*-BuCN (2 mL, excess). Overall reflux time 14 days. Isolated yield 240 mg (96%). Single crystals of **10** were obtained from its $CDCl_3$ solution by the slow evaporation of the solvent from the NMR tube. M.p. 158-159°C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.84 (d, 4H, *o*-Ph, $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H)$ = 71 Hz); 7.78 (d, 1H, H(6), $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H) \approx$ 70 Hz); 7.48-7.38 (m, 8H, L^{CN} and Ph substituents); 7.34 (m, 1H, H(5)); 7.21 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 7 Hz); 3.64 (s, 2H, CH_2N); 1.98 (s, 6H, NMe_2); 1.36 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): 172.4 (N_4C ring); 143.1 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 41 Hz); 138.9 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 41 Hz); 138.3 (*i*-Ph, $^1J(^{119/117}Sn, ^{13}C)$ = 788/754 Hz); 136.6 (*o*-Ph, $^2J(^{119/117}Sn, ^{13}C)$ = 44 Hz); 136.2 (C(1), due to the low intensity of the resonance the tin satellites were not observed); 130.4 (C(4), $^4J(^{119/117}Sn, ^{13}C)$ = 14 Hz); 129.8 (*p*-Ph, $^4J(^{119/117}Sn, ^{13}C)$ = 13 Hz); 128.9 (*m*-Ph, $^3J(^{119/117}Sn, ^{13}C)$ = 69 Hz); 128.5 (C(5), $^3J(^{119/117}Sn, ^{13}C)$ = 71 Hz); 127.5 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 65 Hz); 64.9 (CH_2N, $^nJ(^{119/117}Sn, ^{13}C)$ = 31 Hz); 45.9 (NMe_2); 31.3 ($C(CH_3)_3$); 30.1 ($C(CH_3)_3$). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): -220.0. Elemental analysis (%): found C, 59.0; H, 6.0; N, 13.0. Calc. for $C_{26}H_{31}N_5Sn$ (532.26): C, 58.67; H, 5.87; N, 13.16.

*Preparation of C,N-chelated di-n-butyltin(IV) 5-phenyltetrazol-2-ide (**11**)*

11 can be prepared by two methods using **1** and PhCN: *i)* **1** (205 mg, 0.50 mmol) is mixed with PhCN (1 mL, excess) in toluene (5 mL) and the reaction mixture is then heated to reflux for ten days. Afterwards, excess of PhCN is distilled off *in vacuo* (*ca.* 150°C, 100-200 Pa) giving pure **11** as a yellowish oil in a quantitative yield (256 mg); *ii)* **1** (102 mg, 0.25 mmol) is mixed with PhCN (26 µL, 0.25 mmol) in C_6D_6 (0.6 mL) and the mixture is sealed in the NMR tube under vacuum. The NMR tube is then heated to 100°C for two weeks which results in the quantitative conversion of reagents to pure **11**. The sample may be remeasured in $CDCl_3$. Single crystals of **11** were obtained by the slow evaporation of its dichloromethane solution in the air. M.p. 116-118°C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.23 (d, 2H, *o*-Ph, $^3J(^1H, ^1H)$ = 8 Hz); 7.47-7.40 (m, 3H, H(6) and *m*-Ph); 7.34 (m, 1H, H(4)); 7.24 (m, 1H, H(5)); 7.13 (t, 1H, *p*-Ph, $^3J(^1H, ^1H)$ = 7 Hz); 7.10 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 7 Hz); 3.63 (s, 2H, CH_2N); 2.38 (s, 6H, NMe_2); 1.72-1.62 (m, 4H, α-CH_2); 1.57 (m, 4H, β-CH_2); 1.34 (m, 4H, γ-CH_2); 0.83 (t, 6H, δ-CH_3, $^3J(^1H, ^1H)$ = 7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): 163.7 (N_4C ring); 142.4 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 37 Hz); 139.1 (C(1), $^1J(^{119/117}Sn, ^{13}C)$ = 660/631 Hz); 138.0 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 36 Hz); 130.1 (*i*-Ph); 129.5 (C(4)); 128.8 (*p*-Ph); 128.6 (*o*-Ph); 128.2 (C(5), $^3J(^{119/117}Sn, ^{13}C)$ = 60 Hz); 127.0 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 54 Hz); 126.9 (*m*-Ph); 65.6 (CH_2N, $^nJ(^{119/117}Sn, ^{13}C)$ = 29 Hz); 45.7 (NMe_2); 28.3 (β-C, $^2J(^{119/117}Sn, ^{13}C)$ = 31 Hz); 27.1 (γ-C, $^3J(^{119/117}Sn, ^{13}C)$ = 90 Hz); 15.9 (α-C, $^1J(^{119/117}Sn, ^{13}C)$ = 501/478 Hz); 13.6

(δ-C). ^{119}Sn{^{1}H} NMR ($CDCl_3$, 295 K, ppm): -84.3. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.62 (d, 2H, *o*-Ph, ^{3}J(^{1}H, ^{1}H) = 8 Hz); 7.82 (d, 1H, H(6), ^{3}J(^{1}H, ^{1}H) = 7 Hz, ^{3}J(^{119}Sn, ^{1}H) = 65 Hz); 7.32 (m, 2H, *m*-Ph); 7.32 (m, 2H, *m*-Ph); 7.19 (m, 1H, H(4)); 7.12 (m, 1H, H(5)); 7.01 (t, 1H, *p*-Ph, ^{3}J(^{1}H, ^{1}H) = 7 Hz); 6.91 (d, 1H, H(3), ^{3}J(^{1}H, ^{1}H) = 8 Hz, ^{4}J(^{119}Sn, ^{1}H) = 28 Hz); 3.12 (s, 2H, CH_2N); 1.82 (s and m, 8H, NMe_2 and α-CH_2); 1.70-1.50 (m, 6H, α- and β-CH_2); 1.38 (m, 4H, γ-CH_2); 0.89 (t, 6H, δ-CH_3, ^{3}J(^{1}H, ^{1}H) = 7 Hz). ^{119}Sn{^{1}H} NMR (C_6D_6, 295 K, ppm): -88.1. Elemental analysis (%): found C, 56.5; H, 7.1; N, 13.5. Calc. for $C_{24}H_{35}N_5Sn$ (512.27): C, 56.27; H, 6.89; N, 13.67.

*Preparation of C,N-chelated diphenyltin(IV) 5-phenyltetrazol-2-ide (**12**)*

12 can be prepared similarly as described for **11** using **2** [*i)* 225 mg, 0.50 mmol; *ii)* 60 mg, 0.13 mmol] and PhCN [*i)* 1 mL, excess; *ii)* 14 µL, 0.13 mmol]. *i)* overall reflux time ten days or *ii)* two weeks at 100°C. Quantitative yield of a white solid **12** is achieved upon evaporation of all volatiles *in vacuo*. M.p. 53-55°C. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 8.07 (d, 2H, *o*-Ph of the tetrazolide ring, ^{3}J(^{1}H, ^{1}H) = 7 Hz); 7.83 (d, 5H, H(6) and *o*-Ph, ^{3}J(^{1}H, ^{1}H) = 8 Hz, ^{3}J(^{119}Sn, ^{1}H) = 71 Hz, signals are completely overlapped by coincidence); 7.35-7.25 (m, 4H, L^{CN} and Ph substituents); 7.18 (d, 1H, H(3), ^{3}J(^{1}H, ^{1}H) = 7 Hz); 3.61 (s, 2H, CH_2N); 1.94 (s, 6H, NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K, ppm): 163.6 (N_4C ring); 143.0 (C(2), ^{2}J($^{119/117}$Sn, ^{13}C) = 41 Hz); 138.8 (C(6), ^{2}J($^{119/117}$Sn, ^{13}C) = 41 Hz); 138.1 (*i*-Ph, ^{1}J($^{119/117}$Sn, ^{13}C) = 787/753 Hz); 136.5 (*o*-Ph, ^{2}J($^{119/117}$Sn, ^{13}C) = 43 Hz); 135.8 (C(1), due to the low intensity of the resonance the tin satellites were not observed); 130.5 (C(4), ^{4}J($^{119/117}$Sn, ^{13}C) = 14 Hz); 130.0 (*p*-Ph, ^{4}J($^{119/117}$Sn, ^{13}C) = 14 Hz); 129.9 (*i*-Ph of the tetrazolide ring); 129.1 (*m*-Ph, ^{3}J($^{119/117}$Sn, ^{13}C) = 69 Hz); 128.8 (*p*-Ph of the tetrazolide ring); 128.7 (C(5)); 128.5 (*o*-Ph of the tetrazolide ring); 127.6 (C(3), ^{3}J($^{119/117}$Sn, ^{13}C) = 64 Hz); 127.0 (*m*-Ph of the tetrazolide ring); 64.8 (CH_2N, ^{n}J($^{119/117}$Sn, ^{13}C) = 32 Hz); 45.9 (NMe_2). ^{119}Sn{^{1}H} NMR ($CDCl_3$, 295 K, ppm): -216.5. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.48 (d, 2H, *o*-Ph of the tetrazolide ring, ^{3}J(^{1}H, ^{1}H) = 7 Hz); 8.22 (d, 1H, H(6), ^{3}J(^{1}H, ^{1}H) = 7 Hz, ^{3}J(^{119}Sn, ^{1}H) = 74 Hz); 7.72 (m, 4H, *o*-Ph, ^{3}J(^{119}Sn, ^{1}H) ≈ 70 Hz); 7.15-6.99 (m, 11H, L^{CN} and Ph substituents); 6.82 (d, 1H, H(3), ^{3}J(^{1}H, ^{1}H) = 7 Hz); 2.95 (s, 2H, CH_2N); 1.32 (s, 6H, NMe_2). ^{119}Sn{^{1}H} NMR (C_6D_6, 295 K, ppm): -219.1. Elemental analysis (%): found C, 61.1; H, 5.0; N, 12.5. Calc. for $C_{28}H_{27}N_5Sn$ (552.25): C, 60.90; H, 4.93; N, 12.68.

*Preparation of C,N-chelated di-n-butyltin(IV) 5-(N,N-dimethylaminomethyl)tetrazol-1-ide **(13)***

The synthesis was carried out under an argon atmosphere because of the sensitivity of the product towards the moist air. **13** can be prepared similarly as described for **11** using **1** [*i)* 205 mg, 0.50 mmol; *ii)* 102 mg, 0.25 mmol] and Me_2NCH_2CN [*i)* 1 mL, excess; *ii)* 24 µL, 0.25 mmol]. *i)* overall reflux time ten days or *ii)* 20 days at 100°C. Quantitative yield of an oily yellowish **12** is achieved after evaporation of all volatiles *in vacuo*. ^1H NMR ($CDCl_3$, 295 K, ppm): 7.32 (d, 1H, H(6), $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H)$ = 65 Hz); 7.27 (m, 1H, H(4)); 7.19-7.10 (m, 2H, H(5) and H(3)); 3.86 (s, 2H, CH_2N of the tetrazolide ring); 3.67 (s, 2H, CH_2N of the L^{CN} ligand); 2.42 (s, 6H, NMe_2 of the tetrazolide ring); 2.30 (s, 6H, NMe_2 of the L^{CN} ligand); 1.64-1.44 (m, 8H, α- and β-CH_2); 1.33 (m, 4H, γ-CH_2); 0.82 (t, 6H, δ-CH_3, $^3J(^1H, ^1H)$ = 7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): 161.2 (N_4C ring); 142.3 (C(2), $^2J(^{119/117}Sn, ^{13}C)$ = 36 Hz); 139.2 (C(1), $^1J(^{119/117}Sn, ^{13}C)$ = 661/633 Hz); 137.8 (C(6), $^2J(^{119/117}Sn, ^{13}C)$ = 36 Hz); 129.5 (C(4), $^4J(^{119/117}Sn, ^{13}C)$ = 13 Hz); 128.1 (C(5), $^3J(^{119/117}Sn, ^{13}C)$ = 61 Hz); 127.0 (C(3), $^3J(^{119/117}Sn, ^{13}C)$ = 55 Hz); 65.6 (CH_2N, $^nJ(^{119/117}Sn, ^{13}C)$ = 26 Hz); 53.5 (CH_2N of the tetrazolide ring); 45.7 and 45.1 (NMe_2 moieties); 28.2 (β-C, $^2J(^{119/117}Sn, ^{13}C)$ = 31 Hz); 27.0 (γ-C, $^3J(^{119/117}Sn, ^{13}C)$ = 91 Hz); 15.8 (α-C, $^1J(^{119/117}Sn, ^{13}C)$ = 500/477 Hz); 13.6 (δ-C). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): -85.7. ^1H NMR (C_6D_6, 295 K, ppm): 7.85 (d, 1H, H(6), $^3J(^1H, ^1H)$ = 7 Hz, $^3J(^{119}Sn, ^1H)$ = 65 Hz); 7.08 (m, 1H, H(4)); 7.00 (m, 1H, H(5)); 6.90 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 7 Hz); 4.02 (s, 2H, CH_2N of the tetrazolide ring); 3.10 (s, 2H, CH_2N of the L^{CN} ligand); 2.33 (s, 6H, NMe_2 of the tetrazolide ring); 1.77 (s, 6H, NMe_2 of the L^{CN} ligand); 1.60-1.40 (m, 8H, α- and β-CH_2); 1.33 (m, 4H, γ-CH_2); 0.83 (t, 6H, δ-CH_3, $^3J(^1H, ^1H)$ = 7 Hz). $^{119}Sn\{^1H\}$ NMR (C_6D_6, 295 K, ppm): -93.0. Elemental analysis (%): found C, 51.4; H, 7.9; N, 16.9. Calc. for $C_{21}H_{38}N_6Sn$ (493.27): C, 51.14; H, 7.77; N, 17.04.

*Preparation of C,N-chelated diphenyltin(IV) 5-(N,N-dimethylaminomethyl)tetrazol-1-ide **(14)***

14 was prepared under an argon atmosphere similarly as described for **11** using **2** [*i)* 225 mg, 0.50 mmol; *ii)* 67 mg, 0.15 mmol] and Me_2NCH_2CN [*i)* 1 mL, excess; *ii)* 15 µL, 0.15 mmol]. *i)* overall reflux time eight days or *ii)* 18 days at 100°C. Quantitative yield of an oily yellowish **14** is achieved after evaporation of all volatiles *in vacuo*. ^1H NMR ($CDCl_3$, 295 K, ppm): 7.80 (m, 5H, H(6) and *o*-Ph, $^3J(^{119}Sn, ^1H) \approx 72$ Hz, signals are completely overlapped by coincidence); 7.47-7.37 (m, 7H, L^{CN} and Ph substituents); 7.34 (m, 1H, H(5)); 7.22 (d, 1H, H(3), $^3J(^1H, ^1H)$ = 7 Hz); 3.63 (s, 2H, CH_2N of the L^{CN} ligand); 3.41 (s, 2H, CH_2N of the tetrazolide ring); 1.93 (br, 12H, NMe_2 fragments, signals are completely overlapped by coincidence). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 295 K, ppm): 160.4 (N_4C ring); 143.2 (C(2), $^{2}J(^{119/117}Sn, ^{13}C)$ = 42 Hz); 139.1 (C(6), $^{2}J(^{119/117}Sn, ^{13}C)$ = 41 Hz); 138.6 (*i*-Ph, $^{1}J(^{119/117}Sn, ^{13}C)$ = 791/758 Hz); 136.5 (*o*-Ph, $^{2}J(^{119/117}Sn, ^{13}C)$ = 44 Hz); 136.1 (C(1), $^{1}J(^{119/117}Sn, ^{13}C)$ = 808/773 Hz); 130.4 (C(4), $^{4}J(^{119/117}Sn, ^{13}C)$ = 13 Hz); 130.0 (*p*-Ph, $^{4}J(^{119/117}Sn, ^{13}C)$ = 14 Hz); 129.1 (*m*-Ph, $^{3}J(^{119/117}Sn, ^{13}C)$ = 69 Hz); 128.6 (C(5)); 127.6 (C(3), $^{3}J(^{119/117}Sn, ^{13}C)$ = 63 Hz); 65.0 (CH_2N of the L^{CN} ligand, $^{n}J(^{119/117}Sn, ^{13}C)$ = 31 Hz); 53.0 (CH_2N of the tetrazolide ring); 45.9 and 45.0 (NMe_2 moieties). $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$, 295 K, ppm): -221.9. ^{1}H NMR (C_6D_6, 295 K, ppm): 8.30 (d, 1H, H(6), $^{3}J(^{1}H, ^{1}H)$ = 6 Hz, $^{3}J(^{119}Sn, ^{1}H)$ = 71 Hz); 7.70 (m, 4H, *o*-Ph, $^{3}J(^{119}Sn, ^{1}H) \approx 68$ Hz); 7.20-7.10 (m, 8H, L^{CN} and Ph substituents); 6.85 (m, 1H, H(3)); 3.60 (br, 2H, CH_2N of the tetrazolide ring); 2.97 (s, 2H, CH_2N of the L^{CN} ligand); 1.96 (br, 6H, NMe_2 of the tetrazolide ring); 1.33 (s, 6H, NMe_2 of the L^{CN} ligand). $^{119}Sn\{^{1}H\}$ NMR (C_6D_6, 295 K, ppm): -225.3. Elemental analysis (%): found C, 56.5; H, 5.8; N, 15.6. Calc. for $C_{25}H_{30}N_6Sn$ (533.25): C, 56.31; H, 5.67; N, 15.76.

*Preparation of C,N-chelated di-n-butyltin(IV) 4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazol-1-ide (**15**)*

1 (102 mg, 0.25 mmol), cycloctyne (31 µL, 0.25 mmol) and benzene-d_6 (0.6 mL) were sealed under vacuum in the NMR tube. The tube was heated to 100°C for two days in order to achieve a complete conversion of reagents to **15**. Quantitative yield of an oily yellowish **15** is obtained after evaporation of all volatiles *in vacuo*. The sample was remeasured in $CDCl_3$ in the air. ^{1}H NMR ($CDCl_3$, 295 K, ppm): 7.21 (m, 2H, H(6) and H(4)); 7.11 (m, 1H, H(5)); 7.06 (d, 1H, H(3), $^{3}J(^{1}H, ^{1}H)$ = 7 Hz); 3.56 (s, 2H, CH_2N); 2.87 (t, 4H, $H_2CC{=}CCH_2$ fragment of the C_8 ring); 2.32 (s, 6H, NMe_2); 1.72 (br, 4H, CH_2 fragments of the C_8 ring); 1.65-1.45 (m, 12H, α- and β-CH_2 and CH_2 fragments of the C_8 ring); 1.32 (m, 4H, γ-CH_2); 0.83 (t, 6H, δ-CH_3, $^{3}J(^{1}H, ^{1}H)$ = 7 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 295 K, ppm): 144.8 (N_3C_2 ring); 142.9 (C(2), $^{2}J(^{119/117}Sn, ^{13}C)$ = 37 Hz); 140.6 (C(1), $^{1}J(^{119/117}Sn, ^{13}C)$ = 652/622 Hz); 138.0 (C(6), $^{2}J(^{119/117}Sn, ^{13}C)$ = 33 Hz); 129.0 (C(4), $^{4}J(^{119/117}Sn, ^{13}C)$ = 13 Hz); 127.8 (C(5), $^{3}J(^{119/117}Sn, ^{13}C)$ = 59 Hz); 126.9 (C(3), $^{3}J(^{119/117}Sn, ^{13}C)$ = 56 Hz); 65.6 (CH_2N, $^{n}J(^{119/117}Sn, ^{13}C)$ = 24 Hz); 45.7 (NMe_2); 29.4 (CH_2 of the C_8 ring); 28.3 (β-C, $^{2}J(^{119/117}Sn, ^{13}C)$ = 28 Hz); 27.1 (γ-C, $^{3}J(^{119/117}Sn, ^{13}C)$ = 87 Hz); 25.9 (CH_2 of the C_8 ring); 24.1 (CH_2 of the C_8 ring); 15.4 (α-C, $^{1}J(^{119/117}Sn, ^{13}C)$ = 503/481 Hz); 13.7 (δ-C). $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$, 295 K, ppm): -98.2.

^{1}H NMR (C_6D_6, 295 K, ppm): 8.05 (d, 1H, H(6), $^{3}J(^{1}H, ^{1}H)$ = 7 Hz, $^{3}J(^{119}Sn, ^{1}H) \approx 63$ Hz); 7.12 (m, 2H, H(5) and H(4)); 6.88 (d, 1H, H(3), $^{3}J(^{1}H, ^{1}H)$ = 7 Hz); 3.10 (t, 4H, $H_2CC{=}CCH_2$

fragment of the C_8 ring); 3.04 (s, 2H, CH_2N); 1.91 (m, 2H, α-CH_2); 1.78 (br, 6H, α-CH_2 and CH_2 fragments of the C_8 ring); 1.70 (s, 6H, NMe_2); 1.65-1.55 (m, 4H, β-CH_2); 1.51 (br, 4H, CH_2 fragments of the C_8 ring); 1.51 (br, 4H, CH_2 fragments of the C_8 ring); 1.43 (m, 4H, γ-CH_2); 0.92 (t, 6H, δ-CH_3, $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7 Hz). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (C_6D_6, 295 K, ppm): -101.9. Elemental analysis (%): found C, 58.2; H, 8.30; N, 10.7. Calc. for $C_{25}H_{42}N_4Sn$ (517.33): C, 58.04; H, 8.18; N, 10.83.

*Preparation of C,N-chelated diphenyltin(IV) 4,5,6,7,8,9-hexahydrocycloocta[d][1,2,3]triazol-1-ide (**16**)*

2 (112 mg, 0.25 mmol), cycloctyne (31 µL, 0.25 mmol) and benzene-d6 (1.0 mL) were sealed under vacuum in the NMR tube. The tube was heated to 100°C for two days in order to achieve a complete conversion of reagents to **16**. Quantitative yield of an oily yellowish **16** is obtained after evaporation of all volatiles *in vacuo*. The sample was remeasured in $CDCl_3$ in the air. $^{1}\mathrm{H}$ NMR ($CDCl_3$, 295 K, ppm): 7.83 (d, 4H, *o*-Ph, $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7 Hz, $^{3}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ = 69 Hz); 7.50 (d, 1H, H(6), $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7 Hz, $^{3}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ = 74 Hz); 7.48-7.30 (m, 7H, L^{CN} and Ph moieties); 7.26 (m, 1H, H(4)); 7.15 (d, 1H, H(3), $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 8 Hz); 3.57 (s, 2H, CH_2N); 2.65 (br, 4H, $H_2CC{=}CCH_2$ fragment of the C_8 ring); 1.80 (s, 6H, NMe_2); 1.51 (br, 4H, CH_2 fragments of the C_8 ring); 1.31 (br, 4H, CH_2 fragments of the C_8 ring). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($CDCl_3$, 295 K, ppm): 144.1 (br, N_3C_2 ring); 143.5 (C(2), $^{2}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 43 Hz); 139.1 (C(1), $^{1}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 770/740 Hz); 138.8 (C(6), $^{2}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 39 Hz); 136.6 (*o*-Ph, $^{2}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 43 Hz); 136.0 and 135.9 (*i*-Ph, due to the low intensities of both signals the tin satellites could not be read); 130.0 (C(4), $^{4}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 13 Hz); 129.5 (*p*-Ph), $^{4}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 14 Hz); 128.8 (*m*-Ph), $^{3}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 67 Hz); 128.3 (C(5), $^{3}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 68 Hz); 127.5 (C(3), $^{3}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 65 Hz); 64.8 (CH_2N, $^{2}J(^{119/117}\mathrm{Sn}, ^{13}\mathrm{C})$ = 32 Hz); 45.6 (NMe_2); 29.0 (CH_2 of the C_8 ring); 25.7 (CH_2 of the C_8 ring); 23.8 (CH_2 of the C_8 ring). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR ($CDCl_3$, 295 K, ppm): -223.2.

$^{1}\mathrm{H}$ NMR (C_6D_6, 295 K, ppm): 8.36 (d, 1H, H(6), $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7 Hz, $^{3}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ = 72 Hz); 7.86 (d, 4H, *o*-Ph, $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7 Hz, $^{3}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ = 67 Hz); 7.23 (m, 1H, H(4)); 7.19-7.10 (m, 7H, L^{CN} and Ph moieties); 6.86 (d, 1H, H(3), $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 8 Hz, $^{4}J(^{119}\mathrm{Sn}, ^{1}\mathrm{H})$ = 29 Hz); 2.98 (s, 2H, CH_2N); 2.98 (t, 4H, $H_2CC{=}CCH_2$ fragment of the C_8 ring); 1.58 (br, 4H, CH_2 fragments of the C_8 ring); 1.35 (s, 6H, NMe_2); 1.31 (br, 4H, CH_2 fragments of the C_8 ring). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (C_6D_6, 295 K, ppm): -225.2. Elemental analysis (%): found C, 62.7; H, 6.2; N, 10.0 Calc. for $C_{29}H_{34}N_4Sn$ (557.31): C, 62.50; H, 6.15; N, 10.05.

ESI-MS measurements of selected compounds

1	$C_{17}H_{30}N_4SnNa^+$	calc. 433.1387[M+Na]$^+$	found	433.1383	(3.94%);
	$C_{17}H_{30}NSn^+$	calc. 368.1397 [M-N$_3$]$^+$	found	368.1397	(100%).
2	$C_{21}H_{22}N_4SnNa^+$	calc. 473.0762 [M+Na]$^+$	found	473.0750	(2.87%);
	$C_{21}H_{22}NSn^+$	calc. 408.0772 [M-N$_3$]$^+$	found	408.0770	(100%).
3	$C_{22}H_{33}N_5SnNa^+$	calc. 510.1653 [M+Na]$^+$	found	510.1638	(9.26%);
	$C_{22}H_{33}N_2Sn^+$	calc. 445.1664 [M-N$_3$]$^+$	found	445.1653	(100%).
4	$C_{13}H_{21}N_7SnNa^+$	calc. 418.0774 [M+Na]$^+$	found	418.0772	(7.00%);
	$C_{26}H_{42}N_2O_2Sn_2H^+$	calc. 653.1367 [2M-4(N$_3$)+O$_2$+H]$^+$	found	653.1355	(100%).
5	$C_{15}H_{17}N_7SnNa^+$	calc. 438.0461 [M+Na]$^+$	found	438.0461	(8.24%);
	$C_{30}H_{34}N_2O_2Sn_2H^+$	calc. 693.0742[2M-4(N$_3$)+O$_2$+H]$^+$	found	693.0736	(100%).
6	$C_{18}H_{24}N_8SnNa^+$	calc. 495.1041 [M+Na]$^+$	found	495.1045	(19.20%);
	$C_{18}H_{24}N_5Sn^+$	calc. 430.1051 [M-N$_3$]$^+$	found	430.1042	(100%).
7	$C_{19}H_{33}N_5SnNa^+$	calc. 474.1653 [M+Na]$^+$	found	474.1673	(10.56%);
	$C_{17}H_{30}NSn^+$	calc. 368.1397 [M-C$_2$H$_3$N$_4$]$^+$	found	368.1395	(100%).
8	$C_{23}H_{25}N_5SnH^+$	calc. 492.1208 [M+H]$^+$	found	492.1202	(1.07%);
	$C_{21}H_{22}NSn^+$	calc. 408.0772 [M-C$_2$H$_3$N$_4$]$^+$	found	408.0772	(100%).
10	$C_{26}H_{31}N_5SnNa^+$	calc. 556.1498 [M+Na]$^+$	found	556.1500	(0.74%);
	$C_{21}H_{22}NSn^+$	calc. 408.0772 [M-C$_5$H$_9$N$_4$]$^+$	found	408.0772	(100%).
11	$C_{24}H_{35}N_5SnNa^+$	calc. 536.1810 [M+Na]$^+$	found	536.1804	(4.33%);
	$C_{17}H_{30}NSn^+$	calc. 368.1397 [M-C$_7$H$_5$N$_4$]$^+$	found	368.1398	(100%).

MS spectra in the positive mode exhibit [M+Na]$^+$ peaks with characteristic isotopic tin envelope. In the compounds containing one azido group (**1-3)** (even after the incorporation of nitriles - compounds **7**, **8**, **10** and **11**) very stable cations of [M-N$_3$]$^+$ or [M-RCN$_4$]$^+$, respectively, are formed. The formation of dimeric cationic species with coordination of oxygen or carbon dioxide molecules (*i.e.* [RL$_2$Sn-O-SnL$_2$R+H]$^+$) is common. In the MS spectra of compounds containing two azido groups (**4-6**), the preferential loss of -N$_3$ was observed only in the case of **6**. In **4** and **5**, except [M+Na]$^+$ peaks, the dimeric structures with coordination of various neutral species are more pronounced.

The MS/MS studies revealed, that after release of -N_3/-RCN_4 group, in the *n*-butyltin derivatives (**1**, **3**, **4**, **7** and **11**, respectively) the butyl group is lost first leading to the formation of $L^{CN}Sn^+$ cations. When two ligands are present (**3**), L^{CN}SnTropylium$^+$ cation can be observed. In the phenyltin derivatives (**2**, **5**, **8** and **10**), after the loss of the -N_3/-RCN_4 group, the loss of dimethylamine and formation of the PhSnTropylium$^+$ species is preferred. In the case of compound **6**, similar ionisation mechanism (*via* the release of the dimethylamine group) was observed.

Table S2: Selected crystallographic data of **2**, **4** and **6**

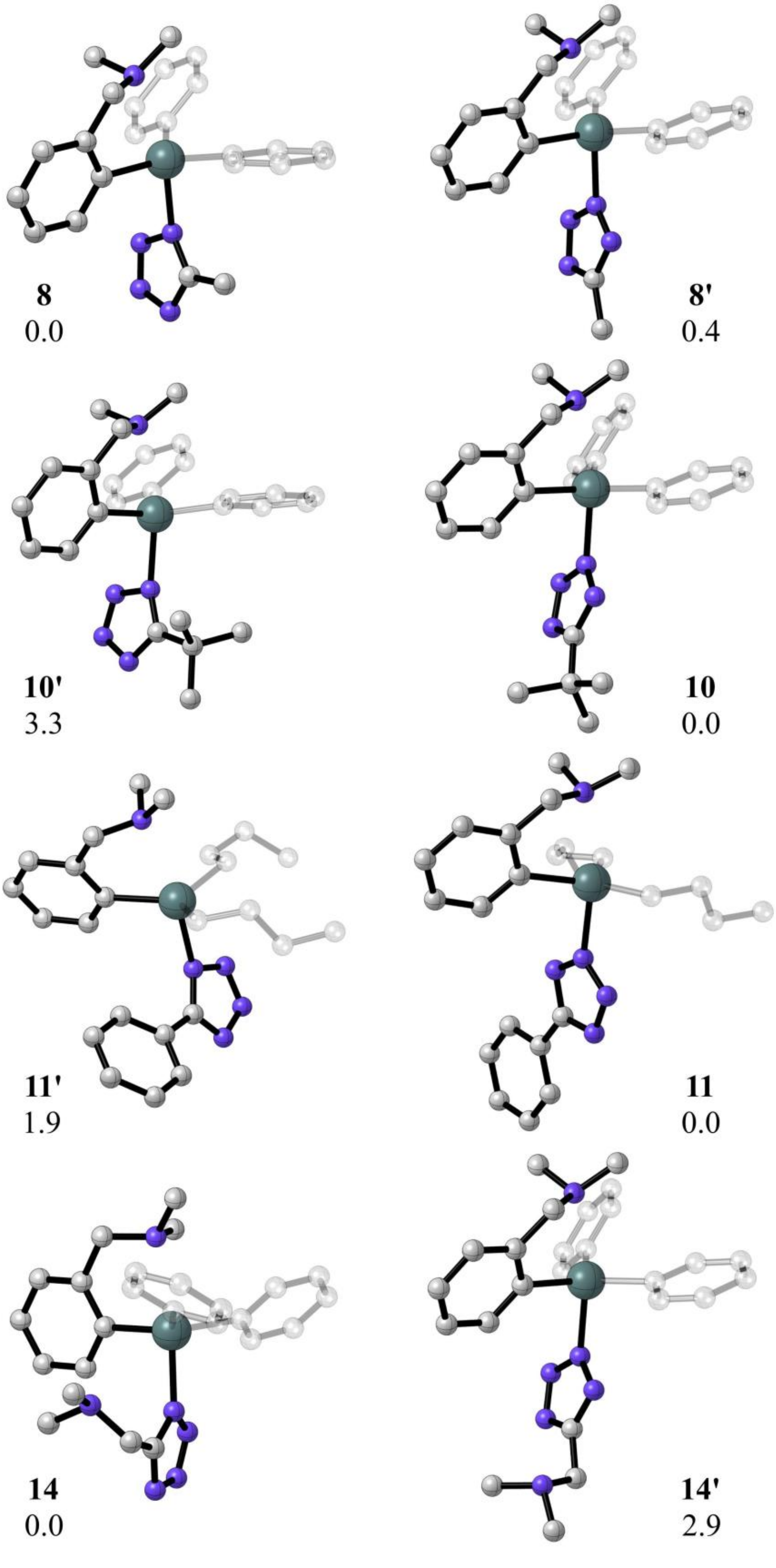
Compound	$L^{CN}Ph_2SnN_3$ ·(**2**)	L^{CN}(*n*-Bu)$Sn(N_3)_2$ ·(**4**)	$(L^{CN})_2Sn(N_3)_2$ ·(**6**)
Empirical formula	$C_{21}H_{22}N_4Sn$	$C_{13}H_{21}N_7Sn$	$C_{18}H_{24}N_8Sn$
Crystal system	monoclinic	orthorhombic	monoclinic
Formula weight	449.12	394.06	471.14
Space group	$P2_1$/c	*P*bca	$P2_1$/c
a (Å)	8.7010(5)	13.3890(9)	9.9650(6)
b (Å)	14.8150(6)	15.3861(13)	14.0700(6)
c (Å)	17.4601(9)	15.9340(7)	16.8031(11)
α (°)	90	90	90
β (°)	118.559(5)	90	120.993(6)
γ (°)	90	90	90
Z	4	8	4
V ($Å^3$)	1976.9(2)	3282.5(4)	2019.6(2)
D_c ($g.cm^{-3}$)	1.509	1.595	1.550
Crystal size (mm)	0.58 x 0.44 x 0.27	0.46 x 0.10 x 0.10	0.57 x 0.40 x 0.32
Crystal shape	block	needle	block
μ (mm^{-1})	1.304	1.562	1.285
F(000)	904	1584	952
h; k; l range	-11, 11; -19, 17; -22, 20	-15, 17; -19, 18; -20, 17	-11, 12; -18, 17; -21, 20
θ range (°)	2.99 - 27.48	2.39 - 27.50	2.02 - 27.50
Reflections measured	23121	20863	16394
- independent (R_{int}) [a)]	4442	3739	4568
- observed [I>2σ(I)]	3974	2724	4049
Parameters refined	235	190	244
Max/min τ ($eÅ^{-3}$)	0.598 / -0.524	0.887 / -0.847	1.325 / -0.646
GOF [b)]	1.216	1.168	1.195
R [c)] / wR [c)]	0.0189 / 0.0441	0.0246 / 0.0486	0.0298 / 0.0691

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, [b] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$, [c] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$

Table S3: Selected crystallographic data of **8**, **10** and **11**

Compound	*C*,*N*-chelated diphenyltin(IV) 5-methyltetrazol-1-ide (**8**)	*C*,*N*-chelated diphenyltin(IV) 5-*tert*-butyltetrazol-2-ide (**10**)	*C*,*N*-chelated di-*n*-butyltin(IV) 5-phenyltetrazol-2-ide (**11**)
Empirical formula	$3(C_{23}H_{25}N_5Sn)\cdot 2CHCl_3\cdot H_2O$	$C_{26}H_{31}N_5Sn$	$C_{24}H_{35}N_5Sn$
Crystal system	triclinic	monoclinic	monoclinic
Formula weight	1727.26	532.25	512.26
Space group	*P*-1	*C*2/c	$P2_1$/c
a (Å)	10.9088(9)	32.4123(5)	10.0490(3)
b (Å)	13.3100(7)	9.6582(3)	13.4371(12)
c (Å)	28.147(3)	16.3820(3)	18.4539(10)
α (°)	81.282(7)	90	90
β (°)	80.812(8)	103.131(2)	103.310(4)
γ (°)	68.233(8)	90	90
Z	2	8	4
V ($Å^3$)	3727.8(6)	4994.2(2)	2424.9(3)
D_c ($g.cm^{-3}$)	1.539	1.416	1.403
Crystal size (mm)	0.54 x 0.36 x 0.25	0.33 x 0.24 x 0.20	0.25 x 0.25 x 0.22
Crystal shape	block	block	block
μ (mm^{-1})	1.266	1.045	1.073
F(000)	1740	2176	1056
h; k; l range	-14, 14; -17, 17; -36, 36	-41, 42; -12, 12; -20, 21	-13, 11; -15, 17; -23, 23
θ range (°)	1.473 - 27.499	2.21 - 27.50	1.89 - 27.48
Reflections measured	68944	20709	24210
- independent (R_{int}) a)	16321	5625	5443
- observed [I>2σ(I)]	15203	4845	4517
Parameters refined	868	289	271
Max/min τ ($eÅ^{-3}$)	3.743 / -3.528	0.979 / -0.878	0.524 / -0.546
GOF b)	1.054	1.142	1.146
R c) / wR c)	0.0548 / 0.1229	0.0244 / 0.0539	0.0256 / 0.0506

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, [b] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$, [c] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$



8
0.0

8′
0.4

10′
3.3

10
0.0

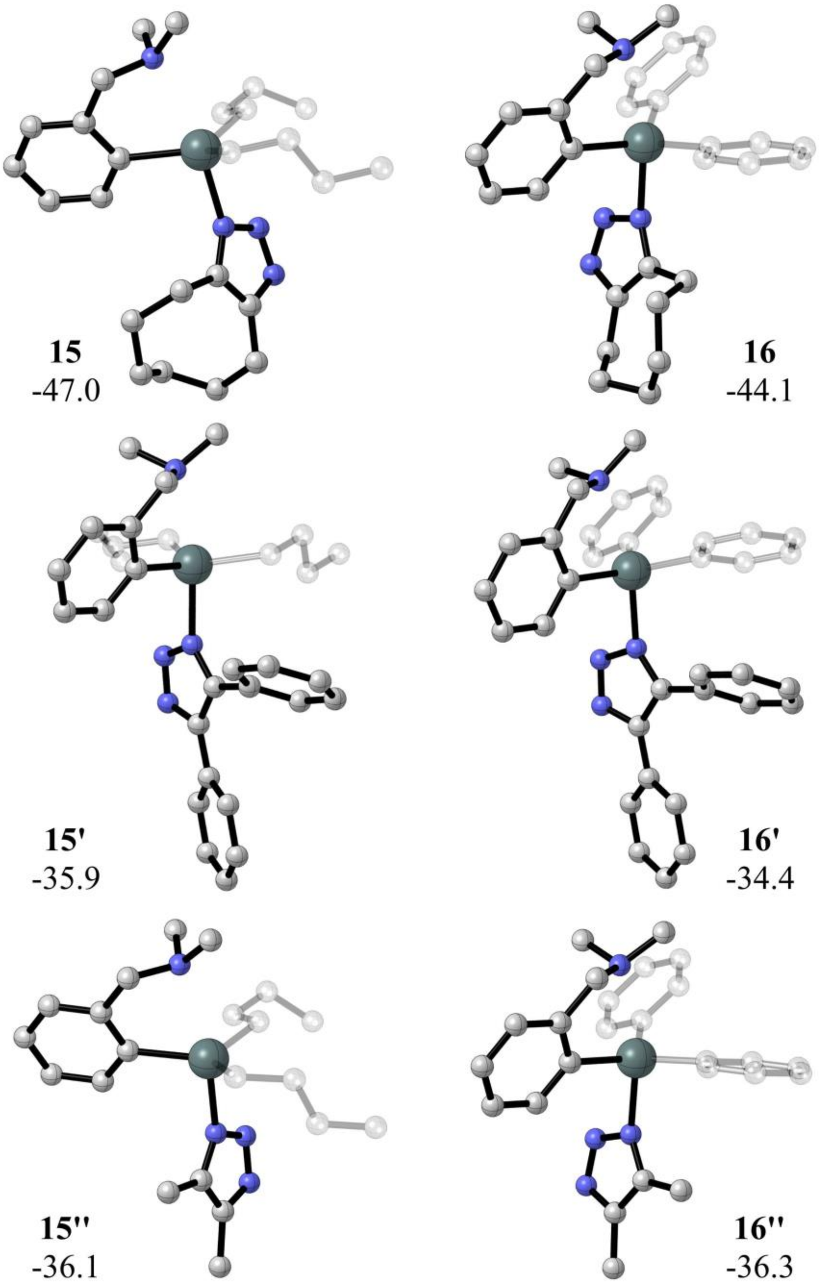
11′
1.9

11
0.0

14
0.0

14′
2.9

Fig. S6: M06 /cc-pVDZ(-pp) optimized geometries of compounds **8**, **10**, **11** and **14** along with relative Gibbs free energies (kcal mol^{-1}) for different regioisomers.



15
-47.0

16
-44.1

15'
-35.9

16'
-34.4

15''
-36.1

16''
-36.3

Fig. S7: M06 /cc-pVDZ(-pp) optimized geometries of compounds **15** and **16** along with corresponding Gibbs free energy of its formation (kcal mol^{-1}).

Table S4: Energy and Gibbs free energy differences for reaction steps displayed in Scheme 2 and Scheme 3

	ΔE (cc-pVDZ) [kcal·mol^{-1}]	**ΔE^{solv}** (cc-pVDZ) [kcal·mol^{-1}]	**ΔE** (cc-pVTZ) [kcal·mol^{-1}]	**ΔG** (cc-pVTZ) [kcal·mol^{-1}]	**ΔG^{solv}** (cc-pVTZ) [kcal·mol^{-1}]
2⓪8	-26.1	-27.2	-18.0	-0.6	-1.7
2⓪8’	-27.3	-27.2	-18.7	-1.4	-1.3
2⓪10	-29.3	-28.8	-20.5	-2.5	-2.0
2⓪10’	-26.6	-26.5	-18.5	1.3	1.3
1⓪11	-33.3	-33.9	-24.2	-4.6	-5.2
1⓪11’	-29.1	-30.0	-21.2	-2.3	-3.2
2⓪14	-33.2	-33.0	-24.7	-5.4	-5.3
2⓪14’	-29.5	-29.5	-20.7	-2.3	-2.3
14⓪14a	-11.0	-13.4	-12.3	-13.6	-16.0
14’⓪14a‘	-14.7	-15.4	-15.5	-16.0	-16.7
1⓪15	-75.4	-75.5	-67.3	-46.9	-47.0
1⓪15’	-64.8	-63.8	-56.0	-36.9	-35.9
1⓪15’’	-61.9	-62.2	-53.6	-35.8	-36.1
2⓪16	-72.7	-72.4	-63.6	-44.4	-44.1
2⓪16’	-64.6	-63.8	-54.7	-35.3	-34.4
2⓪16’’	-62.6	-62.8	-53.6	-36.1	-36.3

Table S5: Comparison of theoretical and experimental values of the relevant geometrical data for compounds **8**, **10** and **11**.

	Distance [Å] / Angle [°]				**Distance [Å] / Angle [°]**		
		Exp.	**Calc.**			**Exp.**	**Calc.**
8	Sn1-N1	2.448(5)	2.648		N1-Sn1-N2	167.50(7)	164.219
	Sn1-N2	2.254(5)	2.183		Sn1-N2-N3	126.52(15)	126.16
	N2-N3	1.353(6)	1.355		N2-N3-N4	107.59(18)	107.64
	N3-N4	1.304(7)	1.292		N3-N2-N5	111.43(18)	112.01
	N4-N5	1.343(7)	1.348		N3-N4-C10	105.82(18)	105.76
	N2-C22	1.341(7)	1.349		N2-N5-C10	103.41(18)	102.75
	N5-C22	1.322(7)	1.325		C1-Sn1-C15	123.10(8)	123.25
	Sn1-C1	2.134(5)	2.150		C1-Sn1-C21	117.80(9)	116.70
	Sn1-C10	2.132(4)	2.140		C15-Sn1-C21	116.66(9)	115.50
	Sn1-C16	2.121(5)	2.145		N1-Sn1-N2	167.50(7)	164.22
	N1-Sn1-N2	170.97(14)	165.79				
	Sn1-N2-N3	114.2(3)	113.92	**11**	Sn1-N1	2.480(2)	2.634
	N2-N3-N4	108.1(4)	107.92		Sn1-N2	2.280(2)	2.220
	N3-N4-N5	110.2(4)	110.64		N2-N3	1.319(3)	1.322
	N4-N5-C22	105.6(5)	105.69		N3-N4	1.332(3)	1.310
	N2-C22-N5	110.4(4)	109.55		N2-N5	1.344(3)	1.331
	C22-N2-N3	105.7(4)	106.19		N4-C10	1.346(3)	1.352
	C1-Sn1-C10	124.57(18)	127.19		N5-C10	1.332(3)	1.335
	C1- Sn1-C16	114.60(18)	113.81		Sn1-C1	2.138(2)	2.155
	C10-Sn1-C16	119.25(19)	114.407		Sn1-C17	2.144(2)	2.164
					Sn1-C21	2.141(2)	2.159
10	Sn1-N1	2.522(2)	2.684		N1-Sn1-N2	166.37(7)	169.21
	Sn1-N2	2.2218(19)	2.193		Sn1-N2-N3	123.29(15)	125.43
	N2-N3	1.321(3)	1.326		N2-N3-N4	108.21(19)	107.75
	N3-N4	1.331(3)	1.310		N3-N2-N5	111.22(19)	112.13
	N2-N5	1.343(3)	1.333		N3-N4-C10	105.20(19)	105.76
	N4-C10	1.345(3)	1.354		N2-N5-C10	103.21(18)	102.65
	N5-C10	1.329(3)	1.330		C1-Sn1-C17	126.61(9)	117.53
	Sn1-C1	2.123(2)	2.151		C1-Sn1-C21	117.30(8)	117.41
	Sn1-C15	2.126(2)	2.143		C17-Sn1-C21	119.85(9)	122.67
	Sn1-C21	2.119(2)	2.139				