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Communication

Reversible CO_2 fixation by intramolecularly coordinated diorganotin(IV) oxides

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ABSTRACT

The intramolecularly coordinated organotin(IV) oxides $[L(Ph)Sn(\mu\text{-}O)]_2$ (**1**) and $[L(Bu)Sn(\mu\text{-}O)]_2$ (**2**) readily absorb CO_2 yielding molecular organotin(IV) carbonates $L(Ph)SnCO_3$ (**3**) and $L(Bu)SnCO_3$ (**4**) with terminally bonded the carbonate moiety. The easy desorption and reversible CO_2 fixation was achieved.

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1. Introduction

The increasing emission of carbon dioxide into the atmosphere forced chemists to seek efficient solutions for the recovery of CO_2 [1]. What else, CO_2 being an inexpensive, nontoxic commodity, holds considerable potential as a C_1 feedstock for the preparation of key intermediates, such as urea and dimethyl carbonate (DMC) [2]. For this reason, the fixation of CO_2 is of current interest. The possible solution is the CO_2 fixation by organometallic species that play an important role for the activation of the C–O bonds in CO_2. Organometallic compounds with M–X bonds are able to react with CO_2 providing new M–O–C(O)X fragments as the result of the CO_2 insertion [3]. Interestingly, recent theoretical calculations suggested that the coordination of CO_2 to the metal atom is not the driving force and that the insertion of CO_2 is initiated by nucleophilic attack of X at the carbon atom of CO_2 with assistance of the metal center acting as a Lewis acid [4].

In contrast to the variety of transition-metal compounds that are able to form complexes with CO_2, examples of main group organometallic species known to bind CO_2 are rare [1,5]. The promising main group species are organotin(IV) oxides, $(R_3Sn)_2O$, hydroxides, R_3SnOH, or di- and triorganotin alkoxides, $R_nSn(OR')_{4-n}$ (R, R′ = organic group, $n = 2, 3$), which react with gaseous CO_2 providing polymeric triorganotin(IV) carbonates, $(R_3Sn)_2CO_3$ [6] or di- and triorganotin(IV) (alkoxy) carbonates, $R_3Sn(O_2COR')$ and $R_2Sn(OR')(O_2COR')$ [7].

We have found out that a solution of intramolecularly coordinated oxides, $[L(Ph)Sn(\mu\text{-}O)]_2$ (**1**) or $[L(Bu)Sn(\mu\text{-}O)]_2$ (**2**) (see Scheme 1), readily absorbs gaseous CO_2 at room temperature to produce the unprecedented molecular organotin(IV) carbonates $L(Ph)SnCO_3$ (**3**) and $L(Bu)SnCO_3$ (**4**) as air-stable crystalline materials. Compounds **3** and **4** are obtained when an excess of CO_2 is bubbled through the toluene solution of **1** or **2**. The final products **3** and **4** were also detected when CH_2Cl_2 solution of **1** or **2** was exposed for several days to air.

2. Result and discussion

The intramolecularly coordinated organotin(IV) oxides, $[LPhSn(\mu\text{-}O)]_2$ (**1**) and $[L(Bu)Sn(\mu\text{-}O)]_2$ (**2**) were prepared by reaction of the organotin(IV) chlorides $L(Ph)SnCl_2$ and $L(Bu)SnCl_2$ with KOH (Scheme 1) [8].

The molecular structures of **1** (Fig. 1) and **2** (Figure S1, see supporting information) [9] are similar and display an almost planar Sn_2O_2 core with the L ligands placed in mutually *trans* positions with the regard to Sn_2O_2 ring. The N–Sn bond lengths (range of 2.627(5)–2.819(6) Å for **2** and 2.742(2)–2.755(2) Å for **3**) suggest the presence of N → Sn coordination in both compounds. The structures of **1** and **2** are retained in C_6D_6 solution. The ^{119}Sn NMR spectrum of **1** showed a singlet resonance at δ −191.0 (δ −131.7 for **2**). The ^1H NMR spectrum of **1** revealed an AX-type resonance at δ_A 2.96 and δ_X 4.70 for the diastereotopic CH_2N protons in accordance with structure (δ_A 2.75 and δ_X 4.78 for **2**).

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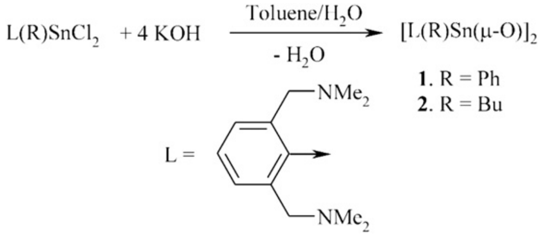


Scheme 1. Synthesis of the intramolecularly coordinated organotin(IV) oxides **1** and **2**.

The bubbling of an excess of CO_2 through the toluene solution of **1** and **2** provided organotin(IV) carbonates L(Ph)$SnCO_3$ (**3**) and L(Bu)$SnCO_3$ (**4**), respectively (see Scheme 2).

The molecular structures of **3** and **4** (Fig. 2) [10] display an almost planar SnO_2C core with a coordination of the carbonate moiety as a terminal ligand in a chelating fashion. This binding mode of the carbonate is very rare for main group metal compounds and to our knowledge there are few examples with terminally bonded carbonate group reported up to now [5b,11]. Structurally characterized main group carbonates usually possess the carbonate entity in a bridging position [12].

The carbonate CO_3 moiety is bonded to the tin atom by two oxygen atoms as a terminal ligand providing a four-membered $SnCO_2$ ring. The Sn(1)–O(1) and Sn(1)–O(2) bond lengths are similar (2.099(3) and 2.107(3) Å for **3**; 2.110(2) and 2.125(2) ≈ for **4**) proving nearly symmetrical coordination of the carbonate in **3** and **4**. The geometry of the tin atom can be described as a strongly distorted octahedron, where both carbon atoms are situated in the axial positions and two nitrogen atoms and two oxygen atoms define the equatorial plane. The distortion seems to originate from the chelating coordination mode of the carbonate.

The structures of **3** and **4** are retained in $CDCl_3$ solution. The ^{119}Sn NMR spectrum of **3** revealed a signal at δ −379.2 (δ −314.0 for **4**) that is consistent with the hexacoordinate tin atom. The presence of the carbonate moiety is evident from the ^{13}C NMR spectrum of **3**, where a signal at δ 163.5 was found (δ 163.9 for **4**). The intramolecular N → Sn coordination in compound **3** is retained

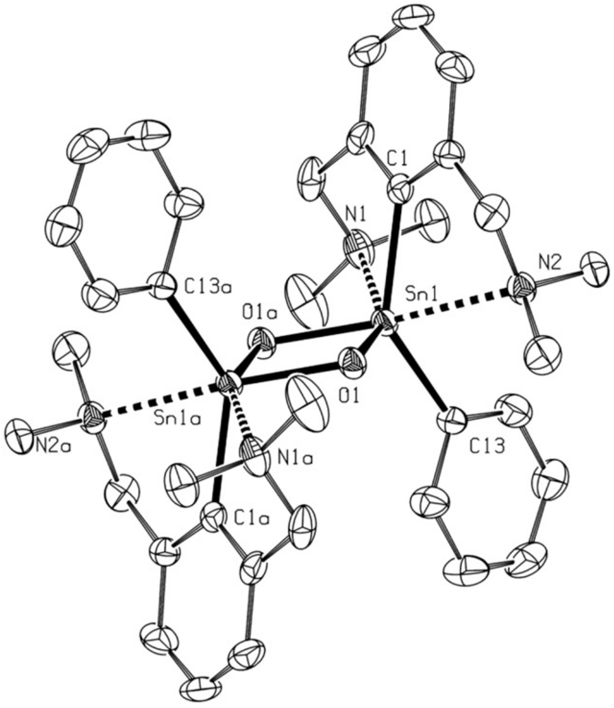
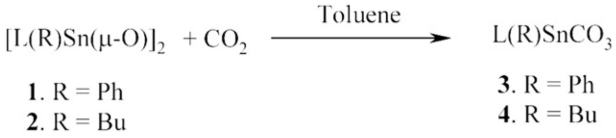


Fig. 1. ORTEP view of 1. The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)–O(1) 2.016(4), Sn(1)–O(1a) 2.023(4), Sn(1)–N(1) 2.819(6), Sn(1)–N(2) 2.627(5).



Scheme 2. Synthesis of organotin(IV) carbonates **3** and **4**.

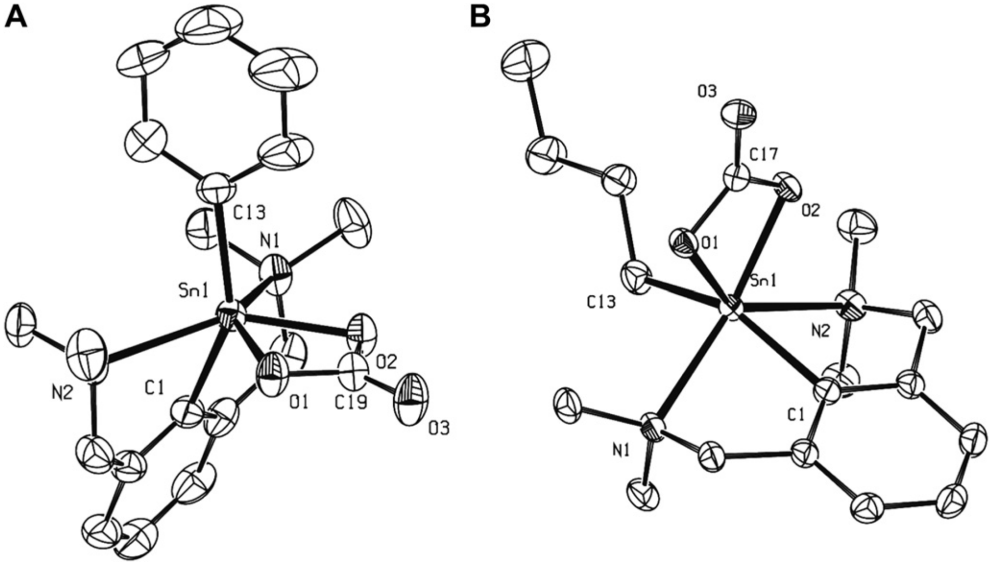


Fig. 2. ORTEP view of 3 (A) and 4 (B). The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): for 3: Sn(1)–O(1) 2.099(3), Sn(1)–O(2) 2.107(3), C(19)–O(1) 1.331(6), C(19)–O(2) 1.322(6), C(19)–O(3) 1.221(5), Sn(1)–N(1) 2.456(5), Sn(1)–N(2) 2.538(4), O(1)–Sn(1)–O(2) 62.47(14), C(1)–Sn(1)–C(13) 145.83(17), N(1)–Sn(1)–N(2) 133.20(14). For 4: Sn(1)–O(1) 2.110(2), Sn(1)–O(2) 2.125(2), C(17)–O(1) 1.333(4), C(17)–O(2) 1.325(4), C(17)–O(3) 1.223(4), Sn(1)–N(1) 2.453(3), Sn(1)–N(2) 2.513(3), O(1)–Sn(1)–O(2) 62.55(8), C(1)–Sn(1)–C(13) 148.98(14), N(1)–Sn(1)–N(2) 131.07(9).

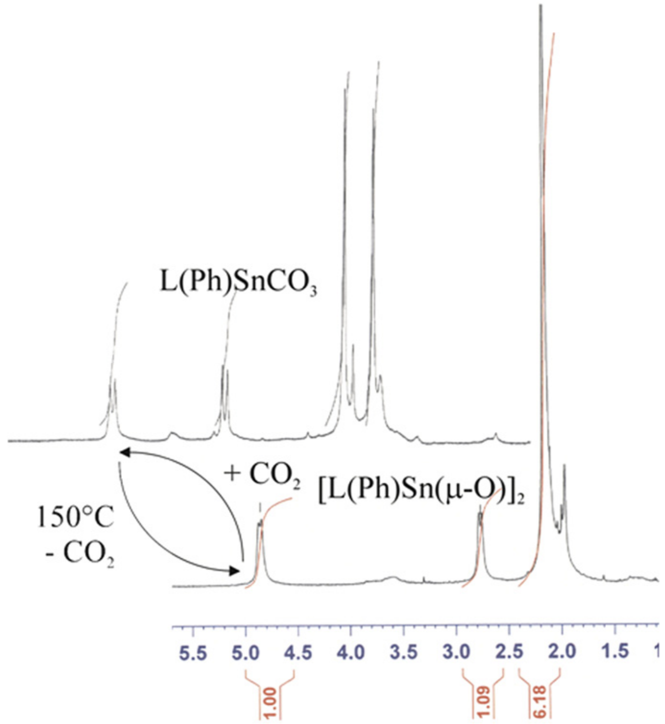


Fig. 3. The reversible CO_2 absorption process monitored by the ^1H NMR spectroscopy of compounds 1 and 3.

in solution resulting in an AX-type ^1H NMR resonance at δ_A 3.33 and δ_X 4.17 for the diastereotopic CH_2N protons and two resonances at δ 2.19 and δ 2.41 for the NCH_3 protons (δ_A 3.26 and δ_X 4.17; δ 2.13 and δ 2.70 for **4**).

The reversibility of the absorption process is required, preferably at a low temperature, to be suitable organometallic species for the fixation and recovery of CO_2 [1]. A thermogravimetric analysis (TGA) of **3** and **4** showed mass loss between 140 and 195 °C (10.8% found, 9.8% calculated) in the first step of TGA for **3** and mass lost between 100 and 150 °C (8.0% found, 10.3% calculated) in the first step of TGA for **4** associated with the liberation of CO_2 (see Supporting information).

The heating of 200 mg of **3** and **4** at 150 °C for 2 h under argon atmosphere resulted to the released of CO_2 and the residual material was identified by the ^1H and ^{119}Sn NMR spectroscopy as the starting organotin(IV) oxides **1** and **2**, respectively (for **1** see Fig. 3). The residual organotin(IV) oxides **1** and **2** were dissolved in toluene and used for the reabsorption of CO_2. The ^1H and ^{119}Sn NMR spectra of the crude products indicated the renewed quantitative formation of **3** and **4**, respectively (for **3** Fig. 3). This procedure was repeated for 3 times without any loss of mass of the starting material.

3. Conclusion

We have shown that the intramolecularly coordinated organotin(IV) oxide $[L(Ph)Sn(\mu\text{-}O)]_2$ (**1**) and $[L(Bu)Sn(\mu\text{-}O)]_2$ (**2**) readily absorb CO_2 producing air-stable molecular organotin(IV) carbonates $L(Ph)SnCO_3$ (**3**) and $L(Bu)SnCO_3$ (**4**), respectively. Compounds **3** and **4** contain planar SnO_2C core due to an unusual coordination of the carbonate moiety. The easy desorption of CO_2 from compounds **3** and **4** gave the starting organotin(IV) oxides **1** and **2**. This desorption process was achieved at rather low temperatures, following by successful reabsorption of CO_2.

4. Experimental

4.1. General methods

The starting compounds $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](Ph)SnCl_2$, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](Bu)SnCl_2$ were prepared according to the literature [8]. Solvent was used as received without any drying. The ^1H, ^{13}C, ^{119}Sn NMR spectra were recorded on a Bruker Avance500 spectrometer at 300 K in C_6D_6 or $CDCl_3$. The ^1H, ^{13}C, ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to external Me_4Sn (^{119}Sn), Me_4Si (^{13}C, ^1H). Elemental analyses were performed on an LECO-CHNS-932 analyzer. The thermogravimetric analysis was done using a homemade apparatus constructed of a computer-controlled oven and a Sartorius BP210S balance. The measurements were carried out in air between 30 and 450 °C at a heating rate of 5 °C min^{-1}.

4.2. Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(Ph)Sn(\mu\text{-}O)]_2$ (**1**)

A solution of KOH (0.4 g, 6.7 mmol) in H_2O (15 mL) was added to a suspension of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](Ph)SnCl_2$ (0.3 g, 0.7 mmol) in toluene (15 mL) at room temperature. The resulting mixture was stirred for further 2 h at room temperature. After separation of the mixture toluene-water, the toluene phase was evaporated in vacuo to leave a solid residue. The solid was recrystallized from hexane to give **1** as a white powder. Yield: 0.1 g (40%). Mp. 216–218 °C. Anal. calcd for $C_{36}H_{48}N_4O_2Sn_2$ (805.40 g mol^{-1}): C, 53.64; H, 6.00. Found: C, 54.03; H, 6.22. ^1H NMR (C_6D_6, 500.13 MHz): δ 2.21 (s, 12H, CH_3), 2.96 (AX system, 2H, CH_2), 4.70 (AX system, 2H, CH_2), 7.11–7.40 (m, 6H, ArH), 7.55 (d, 2H, ArH). ^{13}C NMR (C_6D_6, 125.77 MHz): δ 44.7 (CH_3), 64.2 (CH_2), 125.9 (C (3,5)), 127.0 (C'(3,5)Ph), 127.3 (C'(4)Ph), 127.9 (C(4)), 135.2 (C'(2,6)Ph), 144.4 (C'(1)Ph), 146.2 (C(2,6)), 147.9 (C(1)). ^{119}Sn NMR (C_6D_6, 186.49 MHz): δ −191.0.

4.3. Synthesis of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(Bu)Sn(\mu\text{-}O)]_2$ (**2**)

A solution of KOH (1.0 g, 18 mmol) in H_2O (15 mL) was added to a suspension of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](Bu)SnCl_2$ (0.8 g, 1.8 mmol) in toluene (15 mL) at room temperature. The consequent mixture was stirred for further 2 h at room temperature. After separation of the mixture toluene–water, the toluene phase was evaporated in vacuo to leave a solid residue. The solid was recrystallized from hexane to give **2** as a white powder. Yield: 0.3 g (40%). Mp. 242–244 °C. Anal. calcd for $C_{34}H_{56}N_4O_2Sn_2$ (765.38 g mol^{-1}): C, 46.46; H, 6.93. Found: C, 46.03; H, 6.52. ^1H NMR (C_6D_6, 500.13 MHz): δ 0.73–1.35 (m, 9H, Bu), 2.21 (s, 12H, CH_3), 2.75 (AX system, 2H, CH_2), 4.78 (AX system, 2H, CH_2), 6.70–7.20 (m, 3H, ArH). ^{13}C NMR (C_6D_6, 125.77 MHz): δ 13.8 (C'(4)Bu), 19.7 (C'(1)Bu), 23.0 (C'(1)Bu), 27.7 (C'(3)Bu), 27.8 (C'(3)Bu), 29.9 (C'(2)Bu), 31.2 (C'(2)Bu), 44.4 (CH_3), 64.2 (CH_2), 125.9 (C(3,5)), 129.0 (C(4)), 137.5 (C(1)), 145.9 (C(2,6)).^{119}Sn NMR (C_6D_6, 186.49 MHz): δ −131.7.

4.3. Synthesis of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](Ph)SnCO_3$ (**3**)

Carbon dioxide was bubbled through toluene solution (20 mL) of **1** (0.2 g, 0.45 mmol) for 1 h at room temperature [Alternatively, the toluene solution (20 mL) of **1** (0.2 g, 0.45 mmol) and dry ice was stirred in an autoclave under the pressure 2 bar for 2 h]. After the solid was precipitated from the solution, the solvent was decanted and solid residue was washed with hexane to give **3** as a white powder. Yield: 0.2 g (72%). Mp. 280–283 °C. Anal. calcd for $C_{19}H_{23}N_2O_3Sn$ (447.01 g mol^{-1}): C, 51.00; H, 5.40. Found: C, 50.73; H, 5.22. ^1H NMR ($CDCl_3$, 500.13 MHz): δ 2.19 (s, 6H, CH_3), 2.41 (s, 6H, CH_3), 3.33 (AX system, 2H, CH_2), 4.17 (AX system, 2H, CH_2), 7.15–7.50 (m, 6H, ArH), 7.79 (d, 2H, ArH). ^{13}C NMR ($CDCl_3$, 125.77

MHz): δ 45.2 (CH_3), 62.1 (CH_2), 126.9 (*C* (3,5)), 128.9 (*C*′(3,5)Ph), 130.5 (*C*′(4)Ph), 131.4 (*C*(4)), 133.5 (*C*′(1)Ph), 135.2 (*C*′(2,6)Ph), 136.7(*C*(1)), 143.3 (*C*(2,6)), 163.5 (*C*O). ^{119}Sn NMR ($CDCl_3$, 186.49 MHz): δ −379.2.

4.4. Synthesis of [2,6-($Me_2NCH_2)_2C_6H_3$](Bu)SnCO$_3$ (4)

Carbon dioxide was bubbled through toluene solution (20 mL) of **2** (0.3 g, 0.7 mmol) for 1 h at room temperature [Alternatively, the toluene solution (20 mL) of **2** (0.3 g, 0.7 mmol) and dry ice was stirred in an autoclave under the pressure 2 bar for 2 h]. After the solid was precipitated from solution, the solvent was decanted and solid residue was washed with hexane to give **4** as a white powder. Yield: 0.2 g (61%). Mp. 238–240 °C. Anal. calcd for $C_{17}H_{28}N_2O_3Sn$ (427.012 g mol^{-1}): C, 41.9; H, 5.8. Found: C, 41.53; H, 5.42. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 1.00 (t, 3H, Bu), 1.52 (m, 2H, Bu), 1.59 (m, 2H, Bu), 1.95 (m, 2H, Bu), 2.13 (s, 6H, CH_3), 2.70 (s, 6H, CH_3), 3.26 (AX system, 2H, CH_2), 4.17 (AX system, 2H, CH_2), 7.12 (d, 2H, ArH), 7.36 (t, 1H, ArH). ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ 13.8 (C′(4)Bu), 18.2 (C′(1)Bu), 26.7 (C′(3)Bu), 26.9 (C′(2)Bu), 43.5 (CH_3), 46.6 (CH_3), 63.0 (CH_2), 126.6 (*C*(3,5)), 131.4 (*C*(4)), 135.3 (*C*(2,6)), 143.4 (*C*(1)), 163.9 (CO). ^{119}Sn NMR ($CDCl_3$, 186.49 MHz): δ −314.0.

4.5. X-ray structure determination

Compounds **1** and **2** were dissolved in hexane and slow diffusion of prepared solutions gave X-ray quality material. Compound **3** and **4** were dissolved in CH_2Cl_2 and slow diffusion of prepared solutions gave X-ray quality material. The X-ray data for colorless crystals of **1**–**4** (see Table S1 in supporting information) were obtained at 150 K using Oxford Cryostream low temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN [13]. The absorption was corrected by integration methods [14]. Structures were solved by direct methods (Sir92) [15] and refined by full matrix least-square based on F^2 (SHELXL97) [16]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings moiety, respectively.

Acknowledgment

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.11.006.

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[9] **1**: $C_{36}H_{48}N_4O_2Sn_2$, triclinic, P_{-1}, $a = 9.8670(6)$, $b = 11.0989(6)$, $c = 18.7191(12)$, $\alpha = 77.892(5)^\circ$, $\beta = 77.300(6)^\circ$, $\gamma = 65.238(4)^\circ$, $V = 1799.9(2)$ Å^3, $Z = 2$, $R1$ (obsd data) = 0.0554, $wR2$ (all data) = 0.1112. CCDC 835082.**2**: $C_{32}H_{56}N_4O_2Sn_2$, triclinic, P_{-1}, $a = 9.8370(4)$, $b = 9.9380(3)$, $c = 10.2931(4)$, $\alpha = 69.179(3)^\circ$, $\beta = 65.041(3)^\circ$, $\gamma = 84.333(3)^\circ$, $V = 851.14(6)$ Å^3, $Z = 1$, $R1$ (obsd data) = 0.0220, $wR2$ (all data) = 0.0532. CCDC 835514.
[10] **3**: $C_{19}H_{24}N_2O_3Sn$, monoclinic, $P_{21/c}$, $a = 9.2780(2)$, $b = 14.8611(11)$, $c = 16.2460(13)$, $\alpha = 90.0^\circ$, $\beta = 122.122(4)^\circ$, $\gamma = 90.0(4)^\circ$, $V = 1897.1(2)$ Å^3, $Z = 4$, R_1 (obsd data) = 0.0424, $wR2$ (all data) = 0.1217. CCDC 835515. **4**: (2 × 4), CH_2Cl_2: $C_{35}H_{52}N_4Cl_2O_6Sn$, triclinic, P_{-1}, $a = 9.5980(11)$, $b = 12.1691(18)$, $c = 18.2560(10)$, $\alpha = 91.480(7)^\circ$, $\beta = 101.821(8)^\circ$, $\gamma = 103.742(9)^\circ$, $V = 2021.1(4)$ Å^3, $Z = 2$, $R1$ (obsd data) = 0.0324, $wR2$ (all data) = 0.0776. CCDC 835513.
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