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# Rational syntheses and serendipity: the compounds $[LSnPtCl_2(SMe_2)]_2$ , [ $\{LSnPtCl(SMe_2)\}_2SnCl_2$ ], [ $(LSn)_3(PtCl_2)(PtClSnCl)\{LSn(Cl)OH\}$ ] and [ $O(SnCl)_2(SnL)_2$ ] with L = MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>

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#### Abstract

The syntheses and molecular structures of the novel dimeric tin–platinum complex  $[LSnPtCl_2(SMe_2)]_2$  (2), of the novel tin platinum clusters  $[\{LSnPtCl(SMe_2)\}_2SnCl_2)]$  (3), and  $[(LSn)_3(PtCl_2)(PtClSnCl)(LSnOHCl)]$  (6)  $[L = MeN(CH_2CMe_2O^-)_2]$  and of the unprecedented tin(II) aminoalkoxide–tin oxide chloride complex  $[O(SnCl)_2 \cdot (SnL)_2]$  (5) are reported. The compounds were characterized by multinuclear NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, <sup>195</sup>Pt), <sup>119</sup>Sn Mössbauer spectroscopy (1-3, 6), electrospray ionization mass spectrometry, elemental analyses and single crystal X-ray diffraction analyses (2·CH<sub>2</sub>Cl<sub>2</sub>, 3·2C<sub>4</sub>H<sub>8</sub>O, 5, 6·3CH<sub>2</sub>Cl<sub>2</sub>). The tin(II) aminoalkoxide [MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (1) behaves like a neutral ligand, inserts into a Pt–Cl bond, or is involved in rearrangement reactions with the different behavior

occurring even within one compound (3, 6). DFT calculations show that the tin-platinum compounds behave like electronic chameleons.

#### Keywords

Platinum, stannylene, NMR spectroscopy, <sup>119</sup>Sn Mössbauer spectroscopy, charge decomposition analysis

#### Introduction

Tin(II) aminoalkoxides of the type  $RN(CH_2CR'_2O)_2Sn$  (R = alkyl, Ph, H, Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>, MeOCH<sub>2</sub>CH<sub>2</sub>) show stannylene-like behaviour and behave as neutral donor ligands in reactions with transition metal carbonyl complexes to give the corresponding complexes RN(CH<sub>2</sub>CR'<sub>2</sub>O)<sub>2</sub>Sn $\rightarrow$ M(CO)<sub>n</sub> (M = W, Cr, Fe; n = 4, 5)<sup>1-4</sup>. Recently we reported the dimeric structure in solution and in the solid state of the model compound bis(2,8-dioxa-5aza-3,3,5,7,7-pentamethyl-1-stanna(II)bicyclo[3.3.0]octane),  $(LSn)_2$ (1, L MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>), and its transition metal complexes  $[LSn \rightarrow M(CO)_n]_2$  (M = W, Cr, Fe; n = 4, 5.<sup>4</sup> In this context we extend the chemistry of 1 to reactions with platinum(II) chloride, PtCl<sub>2</sub>, and its more soluble complex dichloridobis(dimethylsulfide)platinum(II), PtCl<sub>2</sub>(SMe)<sub>2</sub>, in order to prove whether it behaves as two electron  $\sigma$ -donor ligand or inserts into Pt–Cl bonds. It is well known from literature that divalent tin compounds are able to insert into Pt-Cl bonds but previous research was limited to tin(II)chloride<sup>5-10</sup> and stannylenes of the type  $SnR_2$  (R = CH(SiMe\_3)\_2, N{CH(SiMe\_3)\_2}\_2, N(SiMe\_3)\_2)^{11-14} and Me<sub>2</sub>Si(N-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>Sn.<sup>15</sup> In analogy, dichloridobis(dimethylsulfide)platinum(II) reacts with two molar equivalents of tin(II) chloride dihydrate give to tris[chloridotris(dimethylsulfide)platinum(II)]pentakis(trichloridostannyl)platinate(II), [PtCl(SMe<sub>2</sub>)<sub>3</sub>]<sub>3</sub>[Pt(SnCl<sub>3</sub>)<sub>5</sub>].<sup>7</sup> More recently, we demonstrated the intramolecularly coordinated heteroleptic organostannylenes RSnCl (R = 2.6-(Me2NCH2)2C6H3, 4-t-Bu-2,6-

 $[P(O)(O-i-Pr)_2]_2C_6H_2)$  to react towards  $PtCl_2$  as  $\sigma$ -donor ligand rather than under insertion into the Pt-Cl bond.<sup>16</sup>

Herein we report the tin(II) amino alcoholate 1 behaving towards Pt(II) salts either as neutral donor ligand, inserts into Pt–Cl bonds or takes part in rearrangement reactions giving products that range from the heterobimetallic complex [LSnPtCl<sub>2</sub>(SMe<sub>2</sub>)]<sub>2</sub> via the complex [{LSnPtCl(SMe<sub>2</sub>)}<sub>2</sub>SnCl<sub>2</sub>)] containing a Pt-SnCl<sub>2</sub>-Pt moiety to the heptanuclear cluster [(LSn)<sub>3</sub>(PtCl<sub>2</sub>)(PtClSnCl){LSn(Cl)OH}]. The novel compounds are characterized by standard analytical methods and state-of-the-art theoretical calculations including charge-decomposition analyses accompany the experimental work. These studies contribute to a further understanding of the nature of the Pt–Sn bond and help answering the question whether this bond should be interpreted as a dative bond or an electron-sharing bond with formulations such as Sn(II)→Pt(II), Sn(III)–Pt(I) or Sn(IV)←Pt(0), as it was discussed in previous works.<sup>[17, 18]</sup>

In course of the synthetic work, the unprecedented compound  $[O(SnCl)_2 \cdot (SnL)_2]$  [L = MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>] was also obtained. It proves the existence, in its stabilized form, of the yet unknown heteroleptic Sn(II) species ClSnOSnCl and holds potential for subsequent research.

#### **Results and discussion**

The reaction of compound  $1^4$  with two molar equivalents of PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> gave selectively the complex 2 in quantitative yield (Scheme 1).



Scheme 1. Synthesis of the compounds 2-4.

Compound 2 was obtained as yellow solid material that shows good solubility in dichloromethane, THF and hot toluene. Re-crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane gave single crystals of 2, as its dichloromethane solvate  $2 \cdot CH_2Cl_2$ . The molecular structure of compound  $2 \cdot CH_2Cl_2$ , determined by single crystal X-ray diffraction analysis, is presented in Figure 1, selected interatomic distances and angles are summarized in the figure caption.



Figure 1. Molecular structure of compound  $2 \cdot CH_2Cl_2$  (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Selected interatomic distances [Å]: Pt(1)–Sn(1) 2.5018(5), Pt(1)–Cl(1) 2.3078(14), Pt(1)–Cl(2) 2.3600(17), Pt(1)–S(1) 2.2583(15), Pt(2)–Sn(2) 2.4941(4), Pt(2)–Cl(3) 2.3647(13), Pt(2)–Cl(4) 2.3057(17), Pt(2)–S(2) 2.2597(17), Sn(1)–O(11) 2.089(3), Sn(1)–O(17) 1.958(3), Sn(1)–O(31) 2.147(4), Sn(1)–N(14) 2.324(4), Sn(2)–O(11) 2.134(3), Sn(2)–O(31) 2.065(3), Sn(2)–O(37) 1.968(3), Sn(2)–N(34) 2.286(4). Selected bond angles [°]: O(11)–Sn(1)–O(17) 101.81(14), O(11)–Sn(1)–Pt(1) 131.08(9), O(11)–Sn(1)–O(31) 70.00(13), O(11)–Sn(2)–O(31) 70.71(13), N(14)–Sn(1)–O(31) 141.75(16), O(17)–Sn(1)–Pt(1) 126.69(11), O(31)–Sn(2)–O(37) 106.60(14), O(31)–Sn(2)–Pt(2) 131.53(9), O(37)–Sn(2)–Pt(2) 121.74(10), N(34)–Sn(2)–O(11) 143.22(13), Sn(1)–O(11)–Sn(2) 109.43(15), Sn(2)–O(31)–Sn(1) 109.86(15).

Like the related compounds  $RN(CH_2CH_2O)_2SnM$  (R = Me, *t*Bu, Me\_2NCH\_2CH\_2, MeOCH\_2CH\_2; M = lone pair, Cr(CO)\_5, W(CO)\_5],<sup>[1-4]</sup> complex **2** forms a *cis*-configured dimer by means of intermolecular O $\rightarrow$ Sn coordination to give four-membered Sn<sub>2</sub>O<sub>2</sub> rings with

intracyclic Sn–O distances that range between 2.065(3) [Sn(2)–O(31)] and 2.147(4) Å [Sn(1)–O(31)]. The Sn(1)–O(17) [1.958(3) Å] and Sn(2)–O(37) [1.968(3) Å] distances involving two-coordinated oxygen atoms are shorter. The tin atoms are pentacoordinated and, as one possible interpretation, adopt each a strongly distorted trigonal bipyramidal environment with the N(14), O(31) (at Sn1) and N(34), O(11) (at Sn2) atoms occupying the axial positions. The equatorial positions at Sn(1) are taken by O(11), O(17), and Pt(1), those at Sn(2) by O(31), O(37), and Pt(2). The distortion from the ideal geometry is especially expressed by the N(14)–Sn(1)–O(31) and N(34)–Sn(2)–O(11) angles of 141.75(16) and 143.22(13), respectively, deviating considerably from the ideal value of 180°. The Sn(1)–N(14) [2.324(4) Å] and Sn(2)–N(34) [2.286(4) Å] distances are slightly different and comparable to those in compound **6**·3CH<sub>2</sub>Cl<sub>2</sub>. The chlorido ligands at the square planar platinum centers are *cis*. The Pt(1)–Cl(2) [2.3600(17) Å] and Pt(2)–Cl(3) [2.3647(13) Å] distances are longer as compared to the Pt(1)–Cl(1) [2.3078(14) Å] and Pt(2)–Cl(4) [2.3057(17) Å] ones reflecting a superior *trans*-effect of the tin(II) aminoalkoxide **1** over dimethylsulfide, Me<sub>2</sub>S.

A <sup>119</sup>Sn Mössbauer spectrum of complex 2 at 78 K is presented in Figure 2 together with a transmission integral fit.



Figure 2. Experimental and simulated <sup>119</sup>Sn Mössbauer spectrum of 2 at 78 K.

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In agreement with the solid state structure the spectrum could be well reproduced with a single signal at  $\delta_{lS} = 1.23(1) \text{ mms}^{-1}$  which is subjected to quadrupole splitting of  $\Delta E_Q = 2.03(1) \text{ mm/s}$ . The refined experimental line width is  $\Gamma = 0.85(1) \text{ mms}^{-1}$ . The isomer shift is considerably smaller than that of the tin(II) aminoalkoxide  $\mathbf{1}$  ( $\delta_{lS} = 2.62(1) \text{ mms}^{-1}$ , Figure S1) while the quadrupole splitting is close to that of  $\mathbf{1}$  ( $\Delta E_Q = 2.16(1) \text{ mms}^{-1}$ ). The data for the latter compound are close to those reported for the parent tin(II) aminoalkoxides [RN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (R = Me<sup>19</sup>:  $\delta_{lS} = 2.75 \text{ mms}^{-1}$ ,  $\Delta E_Q = 1.97 \text{ mms}^{-1}$ ; R = *t*-Bu<sup>19</sup>:  $\delta_{lS} = 2.87 \text{ mms}^{-1}$ ,  $\Delta E_Q = 1.73 \text{ mms}^{-1}$ ; R = Et<sup>20</sup>:  $\delta_{lS} = 2.64 \text{ mms}^{-1}$ ,  $\Delta E_Q = 2.66 \text{ mms}^{-1}$ ). Notably, the decrease of the isomer shift ( $\Delta \delta_{lS} = 1.39 \text{ mms}^{-1}$ ) for the platinum complex  $\mathbf{2}$  with respect to the stannylene  $\mathbf{1}$  is much more pronounced than the differences between [RN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (R = Me, *t*-Bu) and their complexes [RN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SnM]<sub>2</sub> (M = Cr(CO)<sub>5</sub>, Mo(CO)<sub>5</sub>, W(CO)<sub>5</sub>,  $\Delta \delta_{lS} = 0.90$ -0.99 mms<sup>-1</sup>).<sup>19</sup> Apparently, in the platinum complex  $\mathbf{2}$  the degree of electron density perturbation between the Sn and Pt atoms is higher than between the Sn and Cr/Mo/W atoms in the transition metal pentacarbonyl complexes mentioned above.

A <sup>1</sup>H NMR spectrum of complex **2** shows a singlet resonance for the NCH<sub>3</sub> protons at  $\delta$  2.79 with unresolved <sup>117/119</sup>Sn satellites of 15.9 Hz. The NCH<sub>2</sub> protons appear as AB-type resonance [ $\delta$  2.55, 2.90; <sup>2</sup>J(<sup>1</sup>H-<sup>1</sup>H) 13.0 Hz] while two equally intense singlet resonances are observed for the CCH<sub>3</sub> protons. The SCH<sub>3</sub> protons appear as singlet that show <sup>3</sup>J(<sup>1</sup>H-<sup>195</sup>Pt) satellites of 49.3 Hz. A <sup>13</sup>C NMR spectrum shows single resonances for the NCH<sub>3</sub>, NCH<sub>2</sub>, CCH<sub>3</sub>, and SCH<sub>3</sub> carbon atoms. Two equally intense resonances are found for the CCH<sub>3</sub> carbon atoms. Most remarkably, except for the SCH<sub>3</sub> carbon resonances, <sup>117/119</sup>Sn satellites are observed for all these resonances. The <sup>195</sup>Pt and <sup>119</sup>Sn NMR spectra show single resonances at  $\delta$ (<sup>195</sup>Pt) –4393 [s, <sup>1</sup>J(<sup>195</sup>Pt-<sup>119</sup>Sn) = 25831 Hz, <sup>1</sup>J(<sup>195</sup>Pt-<sup>117</sup>Sn) = 24685 Hz] and  $\delta$ (<sup>119</sup>Sn) –482 (s, <sup>1</sup>J(<sup>119</sup>Sn-<sup>195</sup>Pt) = 25899 Hz), respectively. The NMR spectra (except <sup>195</sup>Pt) resemble those of the parent stannylene [MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> at room temperature.<sup>4</sup>

However, they differ from the related compounds [MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>SnM(CO)<sub>5</sub>] $2^{1b}$  for which even at room temperature two sets of OCH<sub>2</sub> and NCH<sub>2</sub> <sup>13</sup>C NMR resonances were observed and which showed  $J(^{119}$ Sn-O- $^{117}$ Sn) satellites.

The NMR data indicate for compound 2 (i) the intramolecular N $\rightarrow$ Sn coordination being retained in solution, (ii) the dimer being kinetically labile on the <sup>1</sup>H and <sup>13</sup>C NMR time scales at ambient temperature and rather likely involved in a monomer  $\rightleftharpoons$  dimer equilibrium, and (iii) the Sn–Pt bond being kinetically inert. An ESI-MS spectrum (positive mode) shows mass clusters centered at m/z = 857.3, 682.1 and 646.0 which are assigned to [0.5(2) + SMe<sub>2</sub> + LH<sub>2</sub> + H]<sup>+</sup>, [0.5(2) + SMe<sub>2</sub> + H]<sup>+</sup> and [0.5(2) + SMe<sub>2</sub>–Cl]<sup>+</sup>, respectively. In the negative mode, a mass cluster centered at m/z = 656.0 is present that is assigned to [0.5(2) + Cl]<sup>-</sup>. Neither in the positive nor negative mode mass clusters were observed representing dimers.

As shown in Scheme 1, the reaction of compound **1** with only one molar equivalent of PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> gave a crude reaction mixture a <sup>119</sup>Sn NMR spectrum (Supporting Information, Figures S12, S13) of which is complex. It showed major resonances at  $\delta = -477$  (s, <sup>1</sup>*J*(<sup>119</sup>Sn-<sup>195</sup>Pt) = 25707 Hz, **2**),  $\delta = -413$  ppm (<sup>1</sup>*J*(<sup>119</sup>Sn-<sup>195</sup>Pt) = 27724 Hz, *J*(<sup>119</sup>Sn-<sup>117/119</sup>Sn) = 1446 Hz), and  $\delta = -368$  ppm (<sup>1</sup>*J*(<sup>119</sup>Sn-<sup>195</sup>Pt) = 24599 Hz, *J*(<sup>119</sup>Sn-<sup>117/119</sup>Sn) = 1439 Hz), respectively. Furthermore, there are minor intense resonances at  $\delta = -329$  ppm (<sup>1</sup>*J*(<sup>119</sup>Sn-<sup>195</sup>Pt) = 25730 Hz, *J*(<sup>119</sup>Sn-<sup>117</sup>Sn) = 1278 Hz),  $\delta = -478$  ppm, <sup>1</sup>*J*(<sup>119</sup>Sn-<sup>195</sup>Pt) = 29918 Hz,  $\delta = -83.0$  ppm (<sup>1</sup>*J*(<sup>119</sup>Sn-<sup>195</sup>Pt) = 18400 Hz), and  $\delta = -439$  (s, **4**). A <sup>195</sup>Pt NMR spectrum (Supporting Information, Figures S14, S16)of the same solution showed a major resonance at  $\delta = -4379$  (s, <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>117/119</sup>Sn) = 24570/25709 Hz, **2**), and minor intense signals at  $\delta = -4690$  ppm (s, <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>117/119</sup>Sn) = 26748/28080 Hz and 24614/23570 Hz),  $\delta = -4686$  ppm, and  $\delta = -4626$  ppm. From this reaction mixture, the novel tin–platinum cluster **3** was obtained as yellow crystalline material. Recrystallization from THF provided single crystals of the THF solvate

been isolated, showed rather poor solubility in common organic solvents precluding further NMR measurements.

No detailed mechanistic studies concerning the synthesis of complex 3 have been performed. Likely, the first step is the formation of compound 2 by the reaction of the tin(II) aminoalkoxide 1 with two molar equivalents of dichloridobis(dimethylsulfide)platinum(II) under release of dimethylsulfide. The redox-type reaction of complex 2 with a second molar equivalent of 1 takes place under intermolecular rearrangement and generates the [{PtCl(SMe<sub>2</sub>)}<sub>2</sub>SnCl<sub>2</sub>] moiety and the tin(IV) compound *spiro*-[MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>Sn (4). The identity of the latter compound in the crude reaction mixture was confirmed by addition of an authentic sample of 4 that had been prepared by the reaction of tin(IV) tetra-tertbutoxide, 1,1'-(methylazanediyl)bis(2-methylpropan-2-ol),  $Sn(OtBu)_4$ , with MeN(CH<sub>2</sub>CMe<sub>2</sub>OH)<sub>2</sub>.<sup>4</sup> Small amounts of crystalline material of 3·2C<sub>4</sub>H<sub>8</sub>O could even be isolated from a solution of 2 in dry THF upon storage for several weeks at 4 °C. This indicates kinetic lability of complex 2 in THF solution and confirms the formation of 3 by the reaction of 2 with compound 1.

The molecular structure of compound  $3.2C_4H_8O$ , as determined by single crystal X-ray diffraction analysis, is presented in Figure 3. Selected interatomic distances and angles are given in the figure caption.



**Figure 3.** Molecular structure of compound  $3.2C4H_{8O}$  (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The solvent molecules were removed by the squeeze routine of the program Platon.<sup>21</sup> Selected interatomic distances [Å]: Pt(1)–Sn(1) 2.5416(4), Pt(1)–Sn(2) 2.5042(7), Pt(1)–Cl(2) 2.392(2), Pt(1)–S(1) 2.344(2), Sn(1)–Cl(1) 2.430(2), Sn(2)–O(11) 2.098(5), Sn(2)–O(11A) 2.197(5), Sn(2)–O(17) 1.979(5), Sn(2)–N(14) 2.331(6). Selected interatomic angles [°]: Sn(1)–Pt(1)–Sn(2) 92.49(2), Sn(1)–Pt(1)–Cl(2) 176.82(6), S(1)–Pt(1)–Sn(2) 178.07(7), Pt(1)–Sn(1)–Pt(1A) 140.58(4), Cl(1)–Sn(1)–Cl(1A) 97.15(13), O(11A)–Sn(2)–N(14) 139.3(2), O(11)–Sn(2)–O(17) 109.2(2), O(11)–Sn(2)–Pt(1) 120.94(14), O(17)–Sn(2)–Pt(1) 129.88(15), O(11)–Sn(2)–O(11A) 70.9(2), Sn(2)–O(11)–Sn(2A) 104.0(2). Symmetry code A: *y*–2/3, *x*+2/3, –*z*+1/6.

Similar to compound **2**, two tin(II) aminoalkoxide molecules form a *cis*-configured dimer via intermolecular  $O(11A) \rightarrow Sn(2)/O(11) \rightarrow Sn(2A)$  interactions at a distance of 2.197(5) Å and complex the Pt(1) and Pt(1A) atoms, respectively. The Sn(2) atom is pentacoordinated and

exhibit a similar geometric environment as the tin atoms in 2·CH<sub>2</sub>Cl<sub>2</sub>. Therefore it is not discussed in more detail. The intramolecular Sn(2)–N(14) distance of 2.331(6) Å is close to the corresponding distances found for 2 and indicates a strong N→Sn interaction. The two Pt atoms are bridged by the Sn(1) atom at a Sn(1)–Pt(1) distance of 2.5416(4) Å being slightly longer than the Pt(1)–Sn(2) distance of 2.5042(7) Å and of the Sn–Pt distances in 2 [2.5018(5)/2.4941(4) Å]. The Sn(1) atom shows a distorted tetrahedral geometry. The strong deviation from ideal tetrahedral geometry is expressed by the Pt(1)–Sn(1)–Pt(1A) and Cl(1)–Sn(1)–Cl(1A) angles of 140.58(4)° and 97.15(13)°, respectively. The Pt(1) atom exhibits a square planar environment in which the 2,8-dioxa-5-aza-1-stanna(II)bicyclooctane is trans to the dimethylsulfide ligand. Compound 3·2C4H<sub>8</sub>O is a rare case for a Pt–SnCl<sub>2</sub>–Pt bonding pattern. Such motif was realized before by the oxidative addition of SnCl<sub>2</sub> into Pt–Pt bonds, coordination of SnCl<sub>2</sub> onto platinum networks or oxidative addition of platinum complexes into Sn–Cl bonds of trichloridostannyl platinum complexes.<sup>22-26</sup>

A  $^{119}$ Sn Mössbauer spectrum of **3** at 78 K is presented in Figure 4 together with a transmission integral fit.



Figure 4. Experimental and simulated <sup>119</sup>Sn Mössbauer spectrum of 3 at 78 K.

The spectrum was well reproduced by a superposition of two sub-spectra with fixed area ratios (1:2). The isomer shifts of 1.41(1)/1.45(1) mms<sup>-1</sup> are almost identical and indicate

similar electron density at the tin atoms, but the signals show slightly different quadrupole splitting values of 1.85(2) (Sn1) and 2.24(1) (Sn2) mms<sup>-1</sup>.

### Serendipitous formation of [O(SnCl)<sub>2</sub>(SnL)<sub>2</sub>] and [(LSn)<sub>3</sub>(PtCl<sub>2</sub>)(PtClSnCl){LSn(Cl)OH}]

The synthesis of tin(II)methoxide, Sn(OMe)<sub>2</sub>, being employed for the synthesis of compound **1**, is well established<sup>[20b]</sup> and became routine in our laboratory. Stannous chloride, SnCl<sub>2</sub>, is treated with dry methanol in the presence of dry triethyl amine, NEt<sub>3</sub>, giving Sn(OMe)<sub>2</sub> as white precipitate that is filtered and carefully washed with dry methanol in order to remove residual amounts of NHEt<sub>3</sub>Cl. In one case, we attempted the synthesis of compound **1** by employing a batch of Sn(OMe)<sub>2</sub> that apparently had not been prepared carefully according to the procedure mentioned above and contained a considerable amount of tin(II) hydroxide chloride, Sn(Cl)OH (Scheme 2).



Scheme 2. Serendipitous formation of a mixture consisting of compounds 1 and 5.

As result, we obtained a mixture of crystalline material consisting of compound 1 (major) and the novel tetranuclear tin compound  $[O(SnCl)_2(LSn)_2]$ , 5 (minor). Of the latter, some quantity of colorless crystals could be separated manually and proved being suitable for single crystal

X-ray diffraction analysis. The molecular structure of compound **5** is shown in Figure 5, selected interatomic distances and angles are given in the figure caption.



**Figure 5.** Molecular structure of compound **5** (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). Selected interatomic distances [Å]: Sn(1)–O(1) 2.3200(13), Sn(1)–O(11) 2.094(2), Sn(1)–O(17) 2.101(2), Sn(1)–N(14) 2.514(3), Sn(2)–Cl(2) 2.4749(8), Sn(2)–O(1) 2.1503(13), Sn(2)–O(11) 2.324(2), Sn(2)–O(17A) 2.273(2). Selected interatomic angles [°]: O(11)–Sn(1)–O(17) 93.98(8), O(1)–Sn(1)–N(14) 131.67(9), O(11)–Sn(2)–O(17A) 144.63(7), O(1)–Sn(2)–Cl(2) 89.44(7), Sn(1)–O(1)–Sn(1A) 126.07(12), Sn(2)–O(1)–Sn(2A) 128.12(14). Symmetry code A: -x+1, y, -z+1/2.

Compound 5 can be interpreted as being composed of two molecules of 2 that coordinate the hitherto unknown central tin chloride oxide moiety, ClSnOSnCl, via O $\rightarrow$ Sn interactions at Sn(1)–O(1), Sn(2)–O(11), and Sn(2)–O(17A) distances of 2.3200(13), 2.324(2), and 2.273(2) Å, respectively. The Sn(2)–O(1) [2.1503(13) Å] and Sn(1)–O(11) [2.094(2) Å] distances are considerably shorter. The Sn(1)–N(14) distance of 2.514(3) Å is comparable to those in the parent tin(II) aminoalkoxides [MeN(CH<sub>2</sub>CM<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (2.494(2), 2.524(2) Å),<sup>4</sup> [MeN(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (2.447(10), 2.413(10) Å),<sup>1</sup>

[HOCMe<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (2.561(3), 2.552(3) Å),<sup>27</sup> [MeN(CH<sub>2</sub>CMe<sub>2</sub>O){(*S*)-CHMe-(*R*)-CHPhO}Sn]<sub>2</sub> (2.523(2) Å) and [CH<sub>2</sub>NMe-(*S*)-CHMe-(*R*)-CHPhO]<sub>2</sub>Sn (2.540(2), 2.416(2) Å).<sup>28</sup> The coordination environment about the Sn(1) and Sn(2) atoms might be with caution described as being pseudo-trigonal bipyramidal with O(1), N(14) (at Sn1) and O(11), (O17A) (at Sn2), respectively, occupying the axial and O(11), O(17), lone electron pair (at Sn1) and O(19, Cl(2), lone electron pair (at Sn2) occupying the equatorial positions.

Notably, organotin analogues ArSnOSnAr [Ar = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)<sub>2</sub>, as co-crystallite with (ArSnOH)<sub>2</sub><sup>29a</sup>; 4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub><sup>29b</sup>] of ClSnOSnCl have also been reported. In contrast to the *trans* bent geometry of the aryl ligands in ArSnOSnAr, the chlorido ligands in compound **5** are *cis*. The Sn(2)–O(1)–Sn(2A) angle of 128.12(14)° is smaller than the corresponding angle in the organotin analogues [154.7(3),<sup>[29a]</sup> 180 °<sup>[29b]</sup>].

A <sup>119</sup>Sn NMR spectrum of **5** in CD<sub>2</sub>Cl<sub>2</sub> solution (Figure S2) shows three rather broad resonances at  $\delta = -250$  ( $\Delta v_{1/2} = 558$  Hz), -263 ( $\Delta v_{1/2} = 560$  Hz) and -278 ( $\Delta v_{1/2} = 523$  Hz). At 193 K (Figure S3) two equally intense resonances at  $\delta = -246(v_{1/2} = 102$  Hz),  $\delta = -276$  ( $v_{1/2} =$ 118 Hz) are observed. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the same sample show one set of signals for compound **5** with an AB type pattern for the NC*H*<sub>2</sub> protons and with slightly broadened resonances for the <sup>13</sup>C signals. Also present are sharp resonances of low intensity assigned to MeN(CH<sub>2</sub>CMe<sub>2</sub>OH)<sub>2</sub> (LH<sub>2</sub>). The NMR data indicate compound **5** being kinetically labile on the NMR time scales at room temperatur but kinetically inert at 193 K on the <sup>119</sup>Sn NMR time scale. No detailed studies concerning the identity of the species being involved in the equilibrium were performed.

An electrospray ionization mass spectrum (positive mode) of **5** shows a mass cluster centered at m/z = 873.0 which is assigned to  $[5-C1]^+$ . Also present are mass clusters centered at m/z = 585.2 and 294.2 that are assigned to the protonated monomeric and dimeric 3,3,5,7,7-pentamethyl-(2,8-dioxa-5-aza-1-stannabicyclo[3.3.0]octane) [MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn + H]<sup>+</sup> and  $[1 + H]^+$ , respectively.

The reaction of compound **1** that contained tin(II) hydroxochloride, SnClOH, with PtCl<sub>2</sub> in dry THF gave the tin–platinum cluster **6** (Scheme 3).



Scheme 3. Serendipitous formation of the tin–platinum cluster 6.

Recrystallization from  $CH_2Cl_2$ /hexane gave single crystals of **6** as its dichloromethane solvate **6**·3CH\_2Cl\_2. The molecular structure of compound **6**·3CH\_2Cl\_2, determined by single crystal X-ray diffraction analysis, is presented in Figure 6, selected interatomic distances and angles are given in the figure caption.

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Figure 6. Molecular structure of compound  $6 \cdot 3 \text{CH}_2 \text{Cl}_2$  (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). The solvent molecules were removed by the squeeze routine of the program Platon.<sup>21</sup> Selected interatomic distances [Å]: Pt(1)–Sn(1) 2.5290(8), Pt(1)–Sn(2) 2.5422(8), Pt(1)–Sn(4) 2.5211(8), Pt(1)–Cl(1) 2.387(3), Pt(2)–Sn(1) 2.5274(8), Pt(2)–Sn(3) 2.4759(7), Pt(2)–Cl(3) 2.371(2), Pt(2)–Cl(4) 2.392(3), Sn(1)–Cl(2) 2.433(3), Sn(1)–O(1) 2.159(6), Sn(2)–O(20) 1.986(6), Sn(2)–O(21) 2.070(7), Sn(2)–O(30) 2.179(6), Sn(2)–N(2) 2.316(8), Sn(3)–O(21) 2.191(6), Sn(3)–O(30) 2.091(7), Sn(3)–O(31) 1.991(7), Sn(3)–N(3) 2.325(8), Sn(4)–O(40) 1.972(7), Sn(4)–O(41) 2.172(6), Sn(4)–O(50) 2.180(7), Sn(4)–N(4) 2.334(9), Sn(5)–O(1) 2.067(6), Sn(5)–O(41) 2.063(7), Sn(5)–O(50) 2.061(6), Sn(5)–O(51) 2.009(7), Sn(5)–N(5) 2.250(10), Sn(5)–Cl(5) 2.380(3). Selected interatomic angles [°]: Sn(1)–Pt(1)–Cl(1) 178.57(7), Sn(2)–Pt(1)–Sn(4) 178.33(3), Sn(1)–Pt(2)–Cl(3) 90.90(7), Sn(1)–Pt(2)–Cl(4) 178.70(7), Pt(1)–Sn(1)–Pt(2) 137.43(3), Pt(1)–Sn(1)–Cl(2) 105.58(7), Pt(1)–Sn(1)–O(1) 110.13(19), O(21)–Sn(2)–O(30) 71.0(2), O(21)–Sn(3)–O(30) 70.3(3), Sn(2)–O(21)–Sn(3) 105.9(3) O(41)–Sn(4)–O(50) 69.3(2),

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$$O(41)-Sn(5)-O(50)$$
 73.7(3),  $Sn(4)-O(41)-Sn(5)$  105.8(3),  $O(1)-Sn(5)-Cl(5)$  82.77(19),  
 $O(41)-Sn(5)-N(5)$  152.1(3).

The reaction may be interpreted in terms of a redox-type reaction of compound 1 with ClSnOH and PtCl<sub>2</sub>. The first step might be the insertion of a tin(II) aminoalkoxide molecule (1) into the Pt–Cl bond followed by disproportionation and rearrangement with tin(II) hydroxochloride to form the ClSnPtCl moiety and MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn(Cl)OH. The latter are stabilized by a  $PtCl_2$  and three tin(II) aminoalkoxide molecules (1), whose tin atoms are pentacoordinated and adopt square-pyramidal environments with the platinum atoms occupying the axial position. Two tin(II) aminoalkoxide molecules (1) form a cis-configured dimer via  $O \rightarrow Sn$  interactions at distances ranging between 2.070(7) [Sn(2)–O(21)] and 2.191(6) Å [Sn(3)-O(21)]. The dimer complexes the Pt(1) and Pt(2) centers [Pt(1)-Sn(2)]2.5422(8), Pt(2)–Sn(3) 2.4759(7) Å]. The third tin(II) aminoalkoxide molecule (1) interacts with the MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn(Cl)OH moiety via intermolecular O→Sn coordination at distances of 2.063(7) [Sn(5)–O(41)] and 2.180(7) Å [Sn(4)–O(50)] and complexes the Pt(1) center [Pt(1)–Sn(4) 2.5211(8) Å]. The central tetra-coordinated Sn(1) atom symmetrically bridges the platinum centers at Pt(1)-Sn(1) and Pt(2)-Sn(1) distances of 2.5290(8) and 2.5274(8) Å, respectively, and adopts a strongly distorted tetrahedral environment. The strong deviation from ideal tetrahedral geometry is expressed by the Pt(1)-Sn(1)-Pt(2) and O(1)-Sn(1)-Cl(2) angles of 137.43(3)° and 91.9(2)°, respectively. The Sn(5) atom is hexacoordinated and shows a distorted octahedral environment with O(1)-Sn(5)-O(51), O(41)-Sn(5)-N(5), and O(50)-Sn(5)-Cl(5) angles of 172.1(3), 152.1(3), and 166.0(2)°, respectively. The PtCl<sub>2</sub> moiety is *cis* configured, while the tin(II) aminoalkoxide molecules (1) at Pt(2) are mutually trans configured. The Sn-N distances vary between 2.250(10) [Sn(5)-N(5)] and 2.325(8) Å [Sn(3)–N(3)] with the shortest one involving the more Lewis acidic tin(IV) atom. The hydroxyl oxygen atom O(1) bridges the Sn(1) and Sn(5) atoms unsymmetrically at distances of 2.159(6) and 2.067(6) Å, respectively. The O(1)···Cl(3) distance of 2.968(8) Å hints at O–H···Cl hydrogen bonding. The corresponding proton could not be unambiguously localized from the X-ray diffraction data because of nearby heavy atoms, but its presence was independently verified by both FT-IR (v/cm<sup>-1</sup> = 3487, 3218) and <sup>1</sup>H NMR spectroscopy [ $\delta$  7.78 ppm (s, <sup>2</sup>J(<sup>1</sup>H-<sup>119/117</sup>Sn) = 20.2 Hz, 1H, SnO*H*). Similar chemical shifts and coupling constants were reported for SnO*H* protons in [(2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Sn)8( $\mu$ 4-O)<sub>2</sub>( $\mu$ <sub>2</sub>-O)<sub>4</sub>( $\mu$ <sub>2</sub>-OH)<sub>8</sub>{Sn(OH)}<sub>4</sub>]<sup>[30]</sup> ( $\delta$  = 8.83 (s, <sup>2</sup>J(<sup>1</sup>H-<sup>119/117</sup>Sn) = 17 Hz), 4.93 (s, <sup>2</sup>J(<sup>1</sup>H-<sup>119/117</sup>Sn) = 58 Hz) and Sn<sub>12</sub>O<sub>8</sub>(OH)<sub>4</sub>(OEt)<sub>28</sub>(HOEt)<sub>4</sub><sup>[31]</sup> ( $\delta$  = 8.05 (s, <sup>2</sup>J(<sup>1</sup>H-<sup>119/117</sup>Sn) = 3.9 Hz, 17.3 Hz, Sn- $\mu$ <sub>2</sub>-OH), 7.89 (s, <sup>2</sup>J(<sup>1</sup>H-<sup>119/117</sup>Sn) = 16.6 Hz, 11.0 Hz, Sn- $\mu$ <sub>2</sub>-OH).

A <sup>119</sup>Sn Mössbauer spectrum of compound **6** recorded at 78 K is presented in Figure 7 together with a transmission integral fit.



Figure 7. Experimental and simulated <sup>119</sup>Sn Mössbauer spectrum of 6 at 78 K. The subspectra of the tin atoms Sn(1), Sn(2)–(4), and Sn(5) are drawn in orange, green, and blue colour.

The corresponding fitting parameters are listed in Table 1.

The complex spectrum was well reproduced by a superposition of three sub-spectra. The main component arises from the three tin atoms Sn(2)-Sn(4) of the 2,8-dioxa-5-aza-1-stanna(II)bicyclooctane molecules, [Sn(OCMe<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe]. This signal arises at an isomer shift  $\delta_{IS} = 1.407(2)$  mms<sup>-1</sup> and is subjected to strong quadrupole splitting of  $\Delta E_Q = 2.691(5)$ 

mms<sup>-1</sup>. These tin centres might be considered as being Sn(II). The strong decrease of the isomer shift compared to compound **1** is the result of  $\sigma$ -donation and  $\pi$ -backbonding. The latter should also be the reason for the slightly increase of the quadrupole splitting. The major signal in the spectrum of **6** is superimposed by two less intense ones. The Sn(5) atom with a SnO4NCl coordination pattern occurs at  $\delta_{IS} = 0.58(3)$  mms<sup>-1</sup> with  $\Delta E_Q = 0.40(5)$  mms<sup>-1</sup>. The isomer shift clearly indicates Sn(IV). The third signal at  $\delta_{IS} = 1.95(3)$  mms<sup>-1</sup> with  $\Delta E_Q = 3.11(5)$  mms<sup>-1</sup> corresponds to the central Sn(1) atom that is bridging the platinum atoms. The isomer shift observed nicely fits with the calculated 5s population. Comparable values occur for platinum stannides, e. g.  $\delta_{IS} = 1.857$  mms<sup>-1</sup> in Ca[PtSn]<sup>[32]</sup> or  $\delta_{IS} = 2.10-2.18$  in Ca<sub>2</sub>[Pt<sub>3</sub>Sn<sub>5</sub>].<sup>[33]</sup>

The three sub-spectra have then been refined with free parameters, leading to the area ratio given in Table 1, in very good agreement with the 1:3:1 multiplicity in the crystal structure. The <sup>119</sup>Sn Mössbauer spectrum nicely underlines the presence of three electronically different tin atoms in compound **6**. The isomer shift for compound **2** [1.23(1) mms<sup>-1</sup>] is slightly smaller than those of comparable moieties in complex **6** [1.407(2) mms<sup>-1</sup>], indicating slightly higher electron density at the tin nuclei in the latter complex.

A <sup>1</sup>H NMR spectrum shows a single resonance for the hydroxyl proton, 14 + (1+1) singlets for the CCH<sub>3</sub> and four singlets for the NCH<sub>3</sub> protons. The signals for the NCH<sub>2</sub> protons are not resolved. Similarly, the <sup>13</sup>C NMR spectrum shows respectively eight singlets for the C(CH<sub>3</sub>)<sub>2</sub>O and NCH<sub>2</sub>, four singlets for the NCH<sub>3</sub> and 8 + 4(1+1) singlets for the CCH<sub>3</sub> carbon atoms. An ESI-MS spectrum shows four major mass clusters centered at m/z = 1838.4, 1798.4 and 1490.1 which are assigned to [6–Cl]<sup>+</sup>, [6–HCl–Cl]<sup>+</sup>, and [6–ClPtSnCl+H]<sup>+</sup>, respectively.

#### Elucidation of the nature of the Sn–Pt bond by DFT calculations

Compounds containing a direct Pt–Sn bond offer various interpretations. Especially when stannylenes are coordinated to Pt(II) centres, the bond can be interpreted as  $Sn(II) \rightarrow Pt(II)$  or

as Pt(0) $\rightarrow$ Sn(IV), with the arrow indicating the direction of electron density transfer. In fact, the Sn–Pt bond is covalent to a great extent and consequently, an electron-sharing Sn(III)-Pt(I) formalism was discussed as well.<sup>[17, 18, 34, 35, 36]</sup> In order to elucidate the situation in the compounds **2**, **3** and **6**, we performed DFT calculations using NBO theory.<sup>[37,38]</sup> Since the formal charges do not accord with NBO charges due to chemical bonds and charge transfer effects, it is useful to take the stannylene **1**, the *spiro*-type compound **4**, and the multi-cyclic derivative **5** into account. Then, formal assignments can be made based on the comparison of NBO charges, <sup>119</sup>Sn and <sup>195</sup>Pt NMR, and <sup>119</sup>Sn Mössbauer spectroscopic data.

For the DFT calculations, Gaussian09<sup>[39]</sup> with the pure functional BP86<sup>[40]</sup> and the def2-TZVP basis set<sup>[41]</sup> was used for the geometry optimisation. This combination has already successfully been employed for similar compounds.<sup>[17, 18, 42]</sup> The NBO analyses were performed with NBO6.0<sup>[43]</sup> with BP86/def2-SVP since double-zeta basis sets give more reliable results for these types of compounds.

Tables S1-S3 show, by using the BP86/def2-TZVP combination that the calculated geometric parameters for the compounds **2**, **3**, and **5** fit well with the experimentally obtained values. Table 2 collects the NBO charges for all except hydrogen and carbon atoms of compounds **1**-**6** together with the isomer shifts and quadrupole splitting values obtained from <sup>119</sup>Sn Mössbauer spectroscopic measurements, and the corresponding <sup>119</sup>Sn and <sup>195</sup>Pt NMR chemical shifts.

The NBO charges of  $\pm 1.35$  for the tin atom in compound **1** and of  $\pm 2.43$  for the tin atom in compound **4** can be taken as reference values for Sn(II) and Sn(IV), respectively.

In addition to the NBO charges, NBO theory yields the Wiberg indices (Table 3) which give a measure for the degree of covalence of the corresponding bonds. The N $\rightarrow$ Sn dative bonds all show Wiberg indices of approximately 0.15 whereas the normal Sn–O bonds involving two-coordinate oxygen atoms are stronger with Wiberg indices of 0.32-0.43. The bridging Sn–O interactions involving three-coordinate oxygen atoms show Wiberg indices of 0.13-0.26. The

Sn–Pt bonds show high covalence with Wiberg indices of about 0.71. This is in accordance with the values calculated for comparable PtSn<sub>2</sub>-containing compounds.<sup>[16]</sup>

In compound 2, the tin atom has a NBO charge of +1.83. Together with the charge for Pt of +0.12, this is indicative for the Sn(IV)←Pt(0)-type situation. The Wiberg index supports a covalent bond between Sn and Pt and thus, the interpretation as Sn(III)–Pt(0) is valid as well. However, the <sup>119</sup>Sn Mössbauer isomer shift supports the Sn(IV)←Pt(0)-type interpretation.<sup>[44]</sup> In order to get deeper insight into this exciting electronic situation we performed a charge-decomposition analysis.<sup>[45]</sup> Figure 8 shows the fragmentation schemes for compound 2 covering all three possibilities ranging from (a) total charge-transfer Sn(IV)←Pt(0) via (b) the electron-sharing version Sn(III)–Pt(I) to (c) the Sn(II)→Pt(II) description. By using the AOMix wave function methodology following an energy decomposition analysis,<sup>[46]</sup> the orbital interaction energy E<sub>orbital</sub> can be calculated. According to this method, the smallest absolute value for E<sub>orbital</sub> indicates the best chemical description of a chemical bond originating from the interacting moieties.<sup>[46]</sup> The results obtained clearly suggest for compound 2 the Sn(II)→Pt(II) description to be the best, although it does not go along with the NBO charges.



**Figure 8**. Fragmentation schemes of compound **2** (simplified drawing) for CDA/EDA analyses.  $E_{orbital}$  is by definition a negative value which denotes the difference between the sum of the wave function energies of the fragments before and after interaction. A less

negative value indicates a smaller change in the wave function; hence, the orbital guess is closer to reality. The colour code of the frames denotes the specific fragment whereas the filling illustrates the oxidation states.

In compound 3, the situation can be interpreted as a formal substitution of the chlorido ligands at the platinum centre by a bridging  $[SnCl_2]^{2-}$  moiety. This former Sn(0) adds its electrons to the tin-platinum system where all bonds can be described as being covalent. The NBO analysis reveals that this bridging Sn possesses a charge of +0.88 which is apparently lower than that of the tin centres in the two intramolecularly N $\rightarrow$ Sn-coordinated stannylene compounds 1. In the latter, the tin atoms have both a charge of +1.88 indicative for Sn(IV) $\leftarrow$ Pt(0) or Sn(III)–Pt(I) interpretations. Since the bridging tin moiety adds one electron the resulting charge at the platinum atoms is lowered to -0.17. This shows that the platinum centre in compound 3 has gained more net electrons than in compound 2. This is reflected in the larger <sup>195</sup>Pt NMR chemical shift. The differing Sn NBO charges are in line with the <sup>119</sup>Sn NMR chemical shifts. However, the orbital interaction energy (Figure 9) reveals that this method favours the case d) with Sn(II) in the binuclear fragment donating to the Pt centre. Since the bridging Sn atom is here assigned as Sn(II) the Pt now gains the charge of I. This is in contrast to the NBO prediction and the <sup>119</sup>Sn NMR data and shows that compound 3 can be regarded as electronic chameleon.



**Figure 9.** Fragmentation scheme for compound **3** (simplified drawing) for CDA/EDA analyses. The colour code of the frames denotes the specific fragment whereas the filling illustrates the oxidation states.

In compund **6**, the bonding situation appears at first sight more complex but can be dissected into  $Sn(IV) \leftarrow Pt(O)$  or Sn(III)-Pt(I) interpretation cases and one inorganic Sn(IV) (with a NBO charge of +2.34). The two Pt atoms do not display the same NBO charge since one Pt atom is bound to three Sn atoms (-0.42) and one only to two Sn atoms (-0.07). The charge transferred from the former stannylene seems to add up at the Sn atom. The <sup>119</sup>Sn Mössbauer data support this interpretation.<sup>[36]</sup>

For the sake of comparison, we performed benchmarking calculations on the fragmentation of SnCl<sub>2</sub>, SnMe<sub>2</sub>, SnCl<sub>4</sub> and SnMe<sub>4</sub> which are summarised in Table S5 (Supporting Information). The table reveals that the tin chlorides as well as SnMe<sub>2</sub> are predicted in their ionic structures whereas the SnMe<sub>4</sub> compound is already a borderline case between a semi-ionic form and the full ionic interpretation. This shows that the CDA fragmentation favours ionic interpretations although charge-transfer effects are taken into account.

#### Conclusion

The dimeric tin(II) aminoalkoxide **1** reacts with  $PtCl_2$  as well as with  $PtCl_2(SMe_2)$  under formation of Pt–Sn bonds. In contrast to the reactions with some transition metal carbonyl complexes  $M(CO)_n$  (M = W, Cr, Fe; n = 4, 5) the tin(II) aminoalkoxide **1** may either act as a  $\sigma$ -donor ligand, or react by insertion into Pt–Cl bonds followed by rearrangement to form  $PtSnCl_nPt$  (n = 1, 2) coordination patterns. <sup>119</sup>Sn Mössbauer spectroscopic data for compounds **1-3** and **6** gave additional information about the electronic density and oxidation states at the tin atoms. Furthermore, the 2,8-dioxa-5-aza-3,3,5,7,7-pentamethyl-1-stanna(II)bicyclo-[3.3.0]octane ligands are suitable to stabilize molecular tin(II) species such as tin oxy chloride ClSnOSnCl which, to the best of our knowledge, is not known so far. Although the synthesis is still serendipitous, it illustrates in principle the potential that structurally modified amino alcohols hold for tin oxocluster chemistry and beyond. By careful hydrolysis of Sn(Cl)NR<sub>2</sub><sup>[46b, c]</sup> under appropriate kinetically controlled conditions (low temperature, stoichiometric amounts of water) it should even be possible to obtain the Sn(Cl)OH and/or ClSnOSnCl without stabilization by Sn(OCMe<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NMe moieties. Such compounds could serve as reactive starting materials for the synthesis of tin-containing oxoclusters including even heterometallic ones. Such metal oxoclusters continue to receive attraction.<sup>[46d, e]</sup>

With respect to the bonding situation, compound **3** can be regarded as a chameleon since the  $^{195}$ Pt and  $^{119}$ Sn NMR spectroscopic data as well as the NBO analyses point towards a  $Sn(IV) \leftarrow Pt(0)$  or Sn(III)-Pt(I) interpretation with large covalence of the Sn-Pt bonds whereas the CDA analysis on basis of the wave functions supports a fragmentation with Sn(II) in the binuclear fragment donating to the Pt(I) ions. This demonstrates that experimentally observed new bonding motifs challenge the different bonding schemes consistently anew.

#### **Experimental**

*General.* All experimental manipulations were carried out under argon atmosphere using Schlenk technique. All solvents were purified by distillation under argon from appropriate drying agents according to standard procedures.<sup>[47]</sup> Bis(2,8-dioxa-5-aza-3,3,5,7,7pentamethyl-1-stannabicyclo[3.3.0]octane)<sup>[4]</sup> **1** and dichloridobis(dimethylsulfide)platinum(II)<sup>[48]</sup> were prepared according to literature methods. Elemental analyses were performed on a LECO CHNS-932 analyzer. Solvate molecules of **6**·CH<sub>2</sub>Cl<sub>2</sub> were removed under reduced pressure ( $10^{-3}$  mbar). The electrospray mass spectra were recorded on a Thermoquest Finnigan instrument using CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> as a mobile phase. FTIR spectra were recorded on a PerkinElmer Spectrum Two Fourier Transform Infrared Spectrometer. Solution NMR spectroscopy. The NMR spectra were recorded on Bruker DRX 500, Bruker DRX 400 and Bruker DPX 300 spectrometers. Chemical shifts  $\delta$  are given in ppm and are referenced to the solvent peaks with the usual values calibrated against tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C), tetramethylstannane (<sup>119</sup>Sn) and sodiumhexachloridoplatinate (<sup>195</sup>Pt).

<sup>119</sup>Sn Mössbauer spectroscopy. A Ca<sup>119m</sup>SnO<sub>3</sub> source was used for the <sup>119</sup>Sn Mössbauer spectroscopic investigation. The sample was placed within a thin-walled glass container at a thickness of about 10 mg Sn/cm<sup>2</sup>. A palladium foil of 0.05 mm thickness was used to reduce the tin K X-rays concurrently emitted by this source. The measurement was conducted in the usual transmission geometry at 78 K with a total counting time of one day.

*Crystallography*. All intensity data were collected with an XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-Kα radiation at 110 K. Crystal data and structure refinement parameters are given in the Supporting Information (Table S4). The structures were solved with Direct Methods using SHELXS-2014<sup>[49]</sup> and refinements were carried out against  $F^2$  by using SHELXL-2014.<sup>[49]</sup> All non-hydrogen atoms were refined using anisotropic displacement parameters. The C–H hydrogen atoms were positioned with idealized geometry and refined using a riding model. In compound **3**·2C<sub>4</sub>H<sub>8</sub>O and **6**·3CH<sub>2</sub>Cl<sub>2</sub> solvate molecules were found severely disordered and removed by the Squeeze routine of the program Platon<sup>24</sup> to improve the main part of the structure. CCDC 988380 (**2**), CCDC 988381 (**3**·2C<sub>4</sub>H<sub>8</sub>O), CCDC 988382 (**5**), and CCDC 988383 (**6**·3CH<sub>2</sub>Cl<sub>2</sub>) contain the supplementary crystallographic data. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

*Computational Details*. The geometry optimizations were started from the geometry of the solid-state structures using the BP86 pure functional<sup>[40]</sup> and with the Ahlrichs type basis set def2-TZVP<sup>[41]</sup> basis set as implemented in Gaussian 09.<sup>[39]</sup> The program AOMix<sup>[50]</sup> was used

as a post-processing tool for charge decomposition analysis. NBO calculations were accomplished using the program suite NBO 6.0.<sup>[43]</sup>

#### Reaction of [MeN(CH<sub>2</sub>CMe<sub>2</sub>O)<sub>2</sub>Sn]<sub>2</sub> (1) with two molar equivalents of cis/trans-

#### **PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>.**

To a stirred solution of **1** (0.254 g, 0.435 mmol) in dry dichloromethane (4 mL) was added *cis/trans*-PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> (0.339 g, 0.869 mmol). The yellow solution was stirred for 16 h at room temperature. The volatiles were removed under reduced pressure giving almost quantitatively compound **2** (0.539 g, 0.435 mmol) as yellow solid. Single crystals of **2** suitable for X-ray diffraction analysis were obtained as its dichloromethane solvate **2**·CH<sub>2</sub>Cl<sub>2</sub> by recrystallisation from dichloromethane/hexane.

<sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  2.90 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 13.0 Hz, 2H, NCH–*H*<sub>4</sub>), 2.79 (s, 3H, *J*(<sup>1</sup>H-<sup>119/117</sup>Sn) = 15.9 Hz, NCH<sub>3</sub>), 2.70 (s, 6H, <sup>3</sup>*J*(<sup>1</sup>H-<sup>195</sup>Pt) = 49.3 Hz, SCH<sub>3</sub>), 2.55 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 12.9 Hz, 2H, NCH–*H*<sub>B</sub>), 1.31 (s, 6H, CCH<sub>3</sub>), 1.25 (s, 6H, CCH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  71.4 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 26.9 Hz, *C*(CH<sub>3</sub>)<sub>2</sub>), 71.1 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 34.5 Hz, NCH<sub>2</sub>), 50.4 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 30.1 Hz, NCH<sub>3</sub>), 31.1 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 31.8 Hz, CCH<sub>3</sub>), 31.1 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 31.8 Hz, CCH<sub>3</sub>), 31.1 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 31.8 Hz, CCH<sub>3</sub>), 23.4 (s, SCH<sub>3</sub>). <sup>119</sup>Sn{<sup>1</sup>H} NMR (111.87 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 294 K):  $\delta$  –482 (s, <sup>1</sup>*J*(<sup>19</sup>Sn-<sup>195</sup>Pt) = 25899 Hz). <sup>195</sup>Pt{<sup>1</sup>H} NMR (64.23 MHz, CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>D<sub>6</sub>, 294 K):  $\delta$  –4393 (s, <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>119</sup>Sn) = 25831 Hz, <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>117</sup>Sn) = 24685 Hz). Mp. 141 °C. Anal. Calcd. For C<sub>22</sub>H<sub>50</sub>Cl4N<sub>2</sub>O<sub>4</sub>Pt<sub>2</sub>S2Sn<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (%): C 20.9, H 4.0, N 2.1. Found: C 20.8, H 3.9, N 2.0. MS (ESI +): *m/z* = 857.3 [0.5(**2**) + SMe<sub>2</sub> + LH<sub>2</sub> + H]<sup>+</sup>, 682.1 [0.5(**2**) + SMe<sub>2</sub> + H]<sup>+</sup>, 646.0 [0.5(**2**) + SMe<sub>2</sub> - Cl]<sup>+</sup>. MS (ESI -): *m/z* = 656.0 [0.5(**2**) + Cl]<sup>-</sup>.

Reaction of  $[MeN(CH_2CMe_2O)_2Sn]_2$  (1) with one molar equivalent of cis/trans-PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>. The reaction of **1** (2.366 g, 4.05 mmol) with one molar equivalent  $PtCl_2(SMe_2)_2$  (1.581 g, 4.05 mmol) gave **3** (1.382 g, 1.017 mmol, 50 %) as yellow crystalline solid. Recrystallization from THF afforded crystals of **3**, as its THF solvate **3**·2THF, as yellow columns. The rather poor solubility of the crystalline material precluded NMR measurements.

Mp. 180–182 °C (decomposition). Anal. Calcd. For C<sub>22</sub>H<sub>50</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>4</sub>Pt<sub>2</sub>S<sub>2</sub>Sn<sub>3</sub> (%): C 19.5, H 3.7, N 2.1. Found: C 19.6, H 3.5, N 1.9.

#### Reaction of Sn(OMe)<sub>2</sub>/Sn(OH)Cl with MeN(CH<sub>2</sub>CMe<sub>2</sub>OH)<sub>2</sub> giving a mixture of 1 and 5.

To a suspension of 3.70 g Sn(OMe)<sub>2</sub> containing an unknown quantity of Sn(OH)Cl (3.70 g) in dry toluene (250 mL) was added a solution of MeN(CH<sub>2</sub>CMe<sub>2</sub>OH)<sub>2</sub> (3.59 g, 20.48 mmol) in dry toluene (40 mL). The reaction mixture was heated to reflux for 30 min giving a clear solution. Its volume was reduced to about 50 mL by azeotropic distillation. From this solution, compounds **1** and **5** crystallized as colorless columns and blocks, respectively, (total amount 3.61 g) that were separated manually.

The analytical data obtained for compound **1** were consistent with those reported previously.<sup>4</sup> Compound **5**:

<sup>1</sup>H NMR (300.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K):  $\delta$  3.11 (s, 0.25H, OH, LH<sub>2</sub>), 2.90 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 13.2 Hz, 2H, NCH–*H*<sub>4</sub>, **5**), 2.65 (s, 3H, NC*H*<sub>3</sub>, **5**), 2.64 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 13.0 Hz, 2H, NCH–*H*<sub>B</sub>, **5**), 2.50 (s, 0.56H, NC*H*<sub>2</sub>, LH<sub>2</sub>), 2.46 (s, 0.42H, NC*H*<sub>3</sub>, LH<sub>2</sub>), 1.45 (s, 6H, CC*H*<sub>3</sub>, **5**), 1.41 (s, 6H, CC*H*<sub>3</sub>, **5**), 1.15 (s, 1.75H, CC*H*<sub>3</sub>, LH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  75.8 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 19.2 Hz, *C*(CH<sub>3</sub>)<sub>2</sub>, **5**), 72.6 (s, NCH<sub>2</sub>, **5**), 72.3 (s, NCH<sub>2</sub>, LH<sub>2</sub>), 71.6 (s, *C*(CH<sub>3</sub>)<sub>2</sub>, LH<sub>2</sub>), 48.9 (s, NCH<sub>3</sub>, LH<sub>2</sub>), 48.8 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 48.0 Hz, NCH<sub>3</sub>, **5**), 32.6 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 24.0 Hz, CCH<sub>3</sub>, **5**), 30.8 (s, *J*(<sup>13</sup>C-<sup>119/117</sup>Sn) = 41.9 Hz, CCH<sub>3</sub>, **5**), 28.0 (s, CCH<sub>3</sub>, LH<sub>2</sub>). <sup>119</sup>Sn{<sup>1</sup>H} NMR (111.87 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 294 K):  $\delta$  -250 (s,  $\Delta v_{1/2} = 558$  Hz), -263 (s,  $\Delta v_{1/2} = 560$  Hz), -278 (s,  $\Delta v_{1/2} = 523$  Hz). Mp. 242 °C (decomposition). Anal. Calcd. For C<sub>18</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>Sn<sub>4</sub> (%): C 23.8, H 4.2, N 3.1. Found: C 23.6, H 4.3, N 2.8. MS (ESI +):

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 $m/z = 873.0 [\mathbf{5} - \text{Cl}]^+, 585.2 [\mathbf{1} + \text{H}]^+, 476.3 [\text{L}_2\text{Sn}(\text{IV}) + \text{H}]^+, 294.1 [\text{LSn} + \text{H}]^+, 176.2 [\text{LH}_2 + \text{H}]^+, 158.2 [\text{LH}_2 - \text{OH}]^+.$ 

#### Reaction of compound 1 containing Sn(OH)Cl with PtCl<sub>2</sub>.

A dry THF solution (20 mL) of 0.760 g **1** that contained an unknown quantity of Sn(OH)Cl was added to a stirred suspension of PtCl<sub>2</sub> (0.346 g, 1.30 mmol) in dry THF (15 mL). The reaction mixture was stirred for 18 h at room temperature and filtrated. From the red filtrate yellowish crystals were obtained within several hours. After the supernatant solution had been decanted, the crystals were washed with dry THF (5 mL) giving compound **6** (0.372 g, 0.20 mmol, 15%) as yellowish columns. Crystals of the dichloromethane solvate **6**·3CH<sub>2</sub>Cl<sub>2</sub> suitable for single crystal X-ray diffraction analysis were obtained by recrystallization from dichloromethane/hexane.

<sup>1</sup>H NMR (500.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 303 K):  $\delta$  7.78 (s, <sup>2</sup>*J*(<sup>1</sup>H-<sup>119/117</sup>Sn) = 20.2 Hz, 1 H, SnO*H*), 3.81 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 12.6 Hz, 1 H, NCH–*H*), 3.68 (m, THF), 3.43 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 12.8 Hz, 1 H, NCH–*H*), 3.11, 3.06, 3.04 (each s, 3 H, NCH<sub>3</sub>), 3.00–2.85 (m, 8 H, NC*H*<sub>2</sub>), 2.83 (s, 3 H, NCH<sub>3</sub>), 2.80–2.69 (m, 4 H, NC*H*<sub>2</sub>), 2.65 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 3.3 Hz, 1 H, NCH–*H*), 2.63 (d, <sup>2</sup>*J*(<sup>1</sup>H-<sup>1</sup>H) = 3.4 Hz, 1 H, NCH–*H*), 2.16, 1.74, 1.70, 1.68, 1.64, 1.62, 1.56, 1.44, 1.43, 1.42 (each s, 3 H, CC*H*<sub>3</sub>), (1.82 m, THF), 1.39 (s, 6 H, CC*H*<sub>3</sub>), 1.28, 1.26, 1.24, 1.23 (each s, 3 H, CC*H*<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  77.7, 76.6, 74.2, 73.8, 73.8, 73.7, 73.6, 73.0, 71.9, 71.4, 70.3, 69.9, 69.5, 69.3, 69.2, 69.0 (each s, NCH<sub>2</sub>, C(CH<sub>3</sub>)<sub>2</sub>), 68.1 (THF), 50.6, 49.7, 49.5, 49.4 (each s, NCH<sub>3</sub>), 33.0, 32.6, 32.4, 32.4, 32.1, 31.8, 31.1, 31.0, 30.5, 30.4, 30.1, 29.8 (each s, CCH<sub>3</sub>). ATR-FTIR (v/cm<sup>-1</sup>) 3487, 3218 (SnOH). Mp. 203–204 °C (decomposition). Anal. Calcd. For C<sub>36</sub>H<sub>77</sub>Cl<sub>5</sub>N<sub>4</sub>O<sub>9</sub>Pt<sub>2</sub>Sn<sub>5</sub> (%): C 23.1, H 4.2, N 3.0. Found: C 23.1, H 4.2, N 2.7. MS (ESI +): *m/z* = 1838.4 [**6** – Cl]<sup>+</sup>, 1798.4 [**6** – HCl – Cl]<sup>+</sup>, 1527.0 [not assigned]<sup>+</sup>, 1490.1 [**6** – ClPtSnCl + H]<sup>+</sup>.

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<b>Table 1</b> . Fitting parameters of the <sup>119</sup> Sn Mössbauer spectroscopic measurements
for compound <b>6</b> at 78 K. $\delta_{IS}$ isomer shift; $\Delta E_Q$ , electric quadrupole splitting; $\Gamma$ ,
experimental line width.

tin atoms	$\delta_{IS} / \mathrm{mm} \cdot \mathrm{s}^{-1}$	$\Delta E_{\rm Q} / \mathrm{mm}\cdot\mathrm{s}^{-1}$	$\Gamma / \mathrm{mm} \cdot \mathrm{s}^{-1}$	Area / %	
Sn(1)	1.95(3)	3.11(5)	0.84(2)	22(2)	
Sn(2)–Sn(4)	1.407(2)	2.691(5)	0.896(7)	63(2)	
Sn(5)	0.58(3)	0.40(5)	0.69(2)	15(2)	

	1	2	3	4	5	6
NBO charges						
SnL	1.35	1.83	1.88		1.48	1.89/1.86/1.84
SnCl <sub>2</sub>			0.84			
$SnO_4$				2.43		
ClSnO					1.32	
SnCl						1.03
SnO2(OH)Cl						2.34
Pt		0.12	-0.17			-0.42/-0.07
N	-0.45	-0.49	-0.50	-0.45	-0.46	-0.49
0	-0.93	-0.95/-1.04	-0.95	-0.90/		-0.95
				-0.87		
μ2-Ο	-0.97	-1.03	-1.05		-1.02	-1.00
μ4-Ο					-1.54	
ОН						-1.23
SnCl			-0.56		-0.60	-0.56
PtCl		-0.47/-0.50	-0.59			-0.49/-0.54
S		-0.47/-0.50	0.42			
<sup>119</sup> Sn						
Mössbauer						
spectroscopy						
δ	2.62	1.23	1.41/1.45			3.19/1.47/0.3
$\Delta E_{ m Q}$	2.16	2.03	1.85/2.24			0.65/2.45/0.8
<sup>119</sup> Sn NMR	-235	-482	-365/-415	-439	-250/-	
					263/-276	
<sup>195</sup> Pt NMR		-4393	-4704			-4133/-4657

**Table 2.** NBO charges (in e<sup>-</sup> units) for selected atoms (*italic*), <sup>119</sup>Sn Mössbauer spectroscopicdata (in units of mms<sup>-1</sup>), and <sup>119</sup>Sn and <sup>195</sup>Pt NMR chemical shifts for **1-6** 

	1	2	3	4	5	6
Sn–N	0.160	0.148	0.146	0.172	0.120	0.140
Sn–Pt		0.702	0.712			0.712
Sn–O	0.428	0.336	0.334	0.420		0.320
Sn-µ <sub>3</sub> O	0.195 /	0.145 /	0.170 /		0.175 /	0.130 /
	0.260	0.176	0.133		0.217	0.166
PtCl		0.644 /	0.543			0.573
		0.678				
µSn–Cl			0.590		0.561	0.499
μSn–OH						0.207
µSn–Pt			0.675			0.688 /
						0.706
Sn–OH						0.309
Sn-µO						0.263
Sn-O						0.439
Sn–N						0.239
SnCl						0.644
Pt–S		0.680	0.544			
Pt–µS			0.675			

Table 3.	Wiberg	indices	(Gaussian09.	BP86.	def2-TZVP).
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Depending on the ratio of the reactants, the reaction of  $[MeN(CH_2CMe_2O)_2Sn]_2$  (1) with  $PtCl_2(SMe_2)_2$  gives either the complex  $[MeN(CH_2CMe_2O)_2SnPtCl_2(SMe_2)_2]_2$  (2) or an equimolar mixture consisting of the unprecedented pentanuclear heterometallic cluster  $[MeN(CH_2CMe_2O)_2SnPtCl(SMe_2)]_2SnCl_2$  (3) and *spiro*- $[MeN(CH_2CMe_2O)_2]_2Sn$  (4). The unprecedented compound  $[O(SnCl)_2 \cdot (SnL)_2] [L = MeN(CH_2CMe_2O)_2]$  was also obtained.