

Berry exchange coordinate geometry in 3-methyl-2-hydroxycyclopenten-1-one tin esters

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Abstract

Three new penta- and hexacoordinated tin compounds (**1–3**) were prepared from PhSnCl_3 , Ph_2SnCl_2 and Ph_3SnOH and 3-methyl-2-hydroxy-2-cyclopenten-1-one (**L**). Compounds **1–3** were characterized by IR, mass spectra, elemental analysis, ^1H , ^{13}C , and ^{119}Sn NMR. The ligand acts as a bidentate giving the tin esters and coordinating the tin by the carbonyl group. Compound **1** ($\text{PhSnCl}_2\text{L} \cdot \text{EtOH}$) has an hexacoordinated tin atom, with an octahedral distorted geometry, which is a stereogenic center. Compounds **2** (Ph_2SnClL) and **3** (Ph_3SnL) have pentacoordinated tin atoms. The structures were determined by X-ray diffraction analyses. In the solid state **1** presents a racemic pair, linked by strong hydrogen bonds and **2** and **3** “Berry exchange coordinate” geometry.
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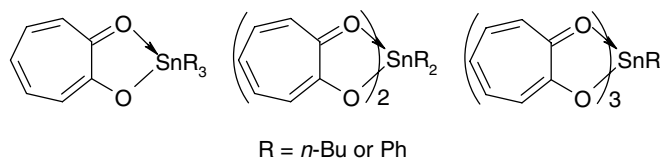
Keywords: Berry exchange coordinate geometry; 3-Methyl-2-hydroxycyclopenten-2-one tin compounds; Penta- and hexacoordinated tin derivatives

1. Introduction

We are interested in the structural analysis of hypervalent tin compounds and in the role of the coordination of oxygen atoms in expanding the tin valence. An important question in these studies is the understanding of the O–Sn bond nature. In this context, we have investigated the use of 3-methyl-2-hydroxy-cyclopenten-1-one as a versatile ligand for tin-organometallic compounds because it could act as a bidentate dione or ketoenol giving stable coordination structures. An additional interest in the α -hydroxyketones is their application as food additives [1] or ribonucleotide reductase inhibitor [2] or as antifungal or antibacterial agents [3]. Some α -hydroxyketones derived from Sn, Zn and Cu are used in oral care formulations [4–7]. And some others bonded to Sn(IV) are promising in the treatment of cancer [8,9].

We have reported a series of organotin tropolonate compounds, which demonstrate that the tropolone may give different tin derivatives, depending on the reagents ratio and on the number of organyl–tin bonds, **Scheme 1**. The reported derivatives containing from one to three tropolone molecules, and with tin coordination numbers varying from five to seven, were submitted to detailed NMR and X-ray diffraction studies [10]. It has been reported that the tin atom could extend its coordination number until eight by bonding to four tropolone molecules [11]. The tropolone ligand in tin compounds present two O–Sn bonds, almost similar in length (2.12–2.35 Å). In this context, the $\text{Ph}_3\text{Sn}(\text{tropolone})$, merits some comments, **Fig. 1**: it presents a *tbp* distorted geometry, the angle between the apical atoms (C8–Sn–O2) is 156.93° , whereas equatorial angles are C14–Sn–C20 117.67° , C20–Sn–O1 113.71° and O1–Sn–C14 123.37° and the ^{119}Sn NMR data correspond to a pentacoordinated compound [$\delta = -181.9$ ppm $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 668.3$ Hz]. Our interest to understand the bond between the carbonyl group and the

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Scheme 1. Reported tin compounds derived from 1,2-tropolone [10].

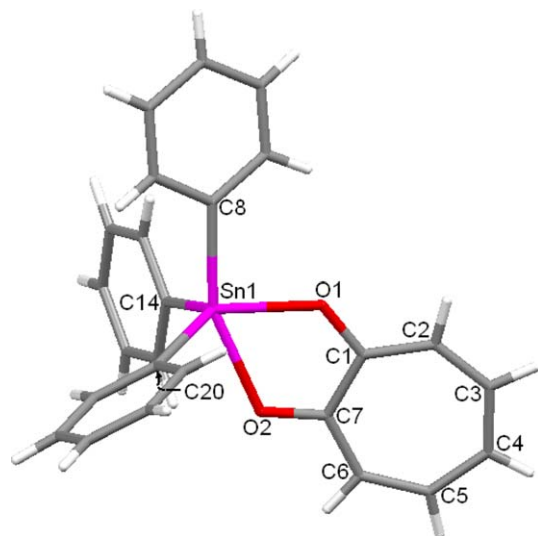


Fig. 1. X-ray data of triphenyltropolone compound [10] have been used for calculation of atomic charges [Sn, +0.98; O1, -0.60; O2, -0.59; C1, +0.30; C2, -0.13; C3, -0.17; C4, -0.15; C5, -0.18; C6, -0.14; C7, +0.31; C8, -0.02; C14, -0.02 and C20, -0.001]. Angles ($^{\circ}$) around tin atom inform about a distorted bpt geometry: O2–Sn–O1, 71.39 $^{\circ}$; O2–Sn–C14, 87.44 $^{\circ}$; O2–Sn–C20, 88.61 $^{\circ}$; O1–Sn–C8, 85.80 $^{\circ}$; C8–Sn–C14, 102.85 $^{\circ}$; C8–Sn–C20, 104.18 $^{\circ}$ and the C–C bond lengths of the tropolone ring show that it is a π -delocalized system C1–C2 1.394, C2–C3 1.381, C3–C4 1.378, C4–C5 1.397, C5–C6 1.368, C6–C7 1.414 and C7–C1 1.464 Å.

tin atom, motivated us to use the reported X-ray diffraction data [10] of the $\text{Ph}_3\text{Sn}(\text{tropolone})$ in order to calculate its atomic charges, Fig. 1. The atomic charges and the C–C bond lengths indicated that coordination favored the delocalization of the positive charge affording a stable tin compound. Some reported metal derivatives of tropolonates ($\text{Na}(\text{trop})$, $\text{Ir}(\text{trop})_3$ and $\text{Rh}(\text{trop})_3$) studied by NMR showed that ^{13}C NMR spectra C1 and C2 are equivalent ($\delta^{13}\text{C}$, 184.7, 188.6 and 187.9 ppm, respectively) as a consequence of a delocalized aromatic system where both carbonyl groups show a partial double bond character [12].

Another example of a strong tin carbonyl coordination has been found in diphenol–oxalamide tin esters, where C=O–Sn bonds are very short (O1–Sn1 2.04; O2–Sn1 2.29 and O3–Sn2 2.21 Å), almost as covalent bonds (O1–Sn1 2.04 and O4–Sn2 2.06 Å) and the resulting positive charges are distributed in the oxalamide delocalized system [13], Fig. 2.

In order to continue with our research, we decided to investigate the 3-methyl-2-hydroxy-2-cyclopenten-1-one and to examine the tin carbonyl coordination. The pentacyclic ketoenol is the stable tautomer of the 3-methyl-1,2-

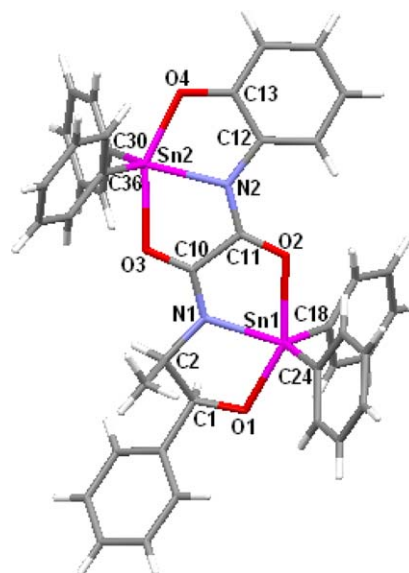


Fig. 2. X-Ray data of an oxalamide diphenyltin ester [13] have been used for atomic charges calculation [Sn1, +0.96; Sn2, +0.97; N1, -0.35; N2, -0.38; O1, -0.60; O2, -0.66; O3, -0.65; O4, -0.63; C10, +0.39; C11, +0.38; C12, +0.15; C13, +0.28; C18, +0.01; C24, +0.02; C30, +0.02 and C36, +0.03].

cyclopentadione as it was clear from examination of IR and NMR spectra in CDCl_3 , their data in Tables 1 and 2 were assigned by a ^1H – ^{13}C COLOC experiment.

2. Results and discussion

Three new Sn(IV) compounds (1–3) from 3-ethyl-2-hydroxy-2-cyclopenten-1-one and PhSnCl_3 , Ph_2SnCl_2 and Ph_3SnOH were synthesized, Scheme 2. The reactions were performed in ligand/tin molar ratios of 3/1, 2/1 and 1/1, respectively. The products were characterized by ^1H , ^{13}C , and ^{119}Sn NMR, IR, mass spectra and elemental analysis. Tin compounds were recrystallized from CH_2Cl_2 /ethanol and suitable crystals for their X-ray diffraction studies were obtained.

2.1. Spectroscopic analysis

Spectroscopic analyses have shown in compounds 1–3 that one chlorine or one OH group was substituted by one hydroxyketone molecule. In the IR spectra the stretching C=O bands indicate the tin coordination, the free ligand forms a strong hydrogen bond and it is also found in the same range of frequencies. [$\nu(\text{C}=\text{O})$: free ligand 1655.0; 1 1647.1; 2 1658.3 and 3 1679.2 cm^{-1}]. The trend indicate that C=O–Sn coordination becomes weaker in going from 1 to 3. The mass spectra of compounds 1–3 correspond to the proposed structures.

^1H , ^{13}C and ^{119}Sn NMR data of 1–3 are listed in Tables 1 and 2. The assignment of the resonances of the phenyl groups was based on their $nJ(^{13}\text{C}, ^{117/119}\text{Sn})$ coupling constants. In solution the ^{119}Sn chemical shifts of 1–3, the

Table 1
 ^{13}C and ^{119}Sn NMR data of compounds **1–3**, (δ , ppm) and [$^nJ(^{13}\text{C}, ^{119/117}\text{Sn})$, Hz] in CDCl_3 at 25 °C

Compound	Free ligand	1 ^a	2	3	
				25 °C	–90 °C
C6	14.1	16.4	15.5	15.0	15.2
C4	27.1	28.8	28.5	27.1	27.1
C5	32.1	30.5 [30]	30.5	31.1	31.1
C3	149.3	156.6	153.3	152.3 [10]	151.3
C2	145.9	152.4 [70]	150.5 [30.5]	144.5 [21.3]	142.1
C1	203.7	210.0 [83.4]	210.7	206.4	207.4
<i>Ci</i>		137.2 [1230/1123]	141.0 [935/894]	142.2 [657/628]	142.1 [658/630]
<i>Co</i>		135.2 [63.5]	136.2 [60.5]	137.1 [48]	137.2 [45.3]
<i>Cp</i>		132.0 [31]	130.6 [17.7]	129.5 [12.8]	129.9
<i>Cm</i>		129.9 [84.5]	128.9 [89]	128.6 [62]	128.7 [61.4]
^{119}Sn	–	–407.6	–143.6	–114.1	–113.5

^a Ethyl group signals appear at: 58.9 and 18.5 ppm.

coordination number six is deduced for compound **1** (δ ^{119}Sn = –407.6 ppm), whereas for **2** and **3** (–143.6 and –114.1 ppm, respectively) the resonances are in between the tetra- and pentacoordination, this could indicate that a possible internal coordination does not have a significant effect [14,15]. However, an indication of the coordination

Table 2
 ^1H NMR data of compounds **1–3** (δ , ppm) [$^nJ(^1\text{H}, ^{119}\text{Sn})$, Hz], in CDCl_3 at 25 °C

Compound	Free ligand ^a	1 ^b	2	3	
				25 °C	–90 °C
H4	2.38 m	2.76 b ^c	2.54 b	2.38 s	2.32 b ^c
H5	2.34 m	2.70 b ^c	2.60 b	2.38 s	2.36 b ^c
H6	1.94 s	2.29 s	2.11 s	2.08 s	2.03 s
Ho		7.7 m [40]	7.95 m [78]	7.78 m [54]	7.75 m [57.8]
<i>Hm,p</i>		7.5 m	7.42 m	7.40 m	7.39 m

^a δ (ppm) Hydroxy group: 7.15 ppm s.

^b Ethyl group: 3.73 (q, 7.6), 1.25 ppm (t, 7.6).

^c Close to the slow exchange limit. Coupling constant in Hz $^nJ(^1\text{H}, ^{119}\text{Sn})$ in parentheses. Abbreviations: s, singlet; m, complex pattern; b, broad.

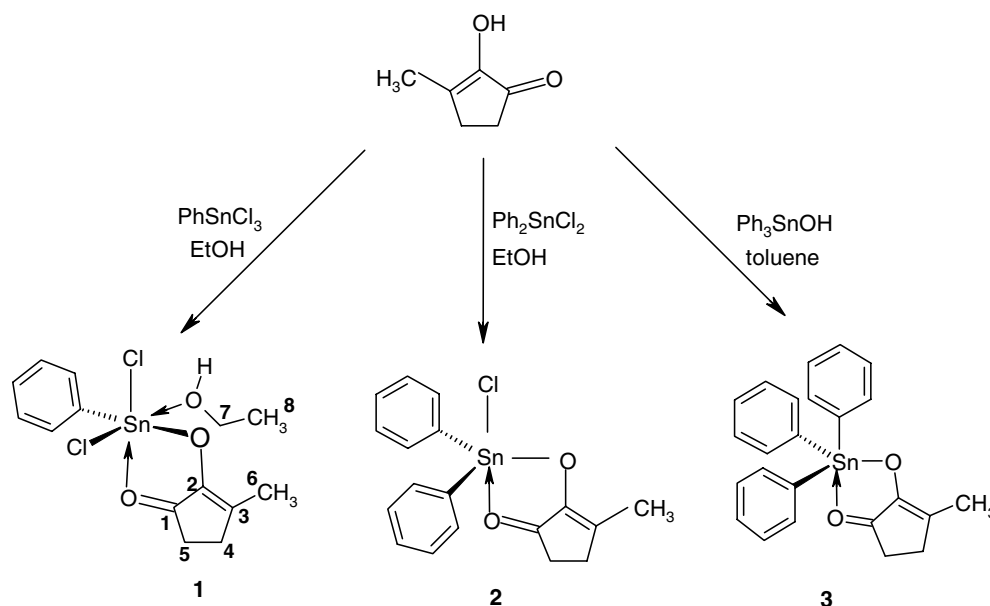
number can be found in the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ of the *ipso*-carbon of the phenyl groups, of **1** (1230 Hz), which is considered adequate for a six coordinated compound [for example, the $\text{Ph}_2\text{Sn}(\text{tropolone})_2$ has a coupling constant of 939.7 Hz [10,14,15]] whereas for compounds **2** and **3** their coupling constants (935 and 657 Hz) correspond to pentacoordinated compounds, as it can be validated by comparison with the coupling constant value (668.3 Hz) reported for the pentacoordinated $\text{Ph}_3\text{Sn}(\text{tropolone})$ [10].

The assignment of the proton resonances for **1–3** was based in ^1H – ^{13}C COLOC experiments, and the phenyl protons, in all cases, appear as complex patterns.

Chemical shifts in ^{13}C spectra indicate that the tin atom is bonded to the enol tautomer, C2 signals [152.4 (**1**), 150.5 (**2**) and 144.5 ppm (**3**)] are characteristic for an enol C–O bond. All compounds exhibit a double C=O bond [210.0 (**1**), 210.7 (**2**) and 206.5 ppm (**3**)]. A ^{119}Sn variable temperature experiment was performed on compound **3**, in order to check if at low temperature the tin resonance would change to lower frequencies, due to a better Sn–O coordination; however, we have not found evidence of any difference in the tin chemical shift at –80 °C, this result indicates that coordination cannot be stronger.

2.2. X-ray diffraction structures

Compounds **1** and **2** crystallized in the orthorhombic system, space groups $Pcab$ and $P2_1/cn$, respectively. The crystals of compound **3** were monoclinic with space group Cc . Relevant structural parameters are summarized in Table 3.



Scheme 2. Synthesis of compounds 1–3.

The X-ray diffraction structures of compounds 1–3 show that the ligand combines a single bond Sn–O2 [2.109(3) Å 1, 2.032(4) and 2.034(4) Å 2, 2.032(3) Å 3] and a coordinative bond C=O1 → Sn [2.349(3) Å 1, 2.342(3) and 2.359(3) Å 2, 2.630(3) Å 3], Tables 4–6. It could be consid-

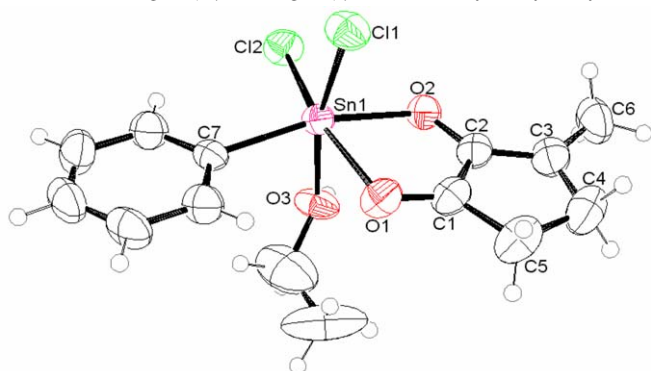
ered that the coordination bond in compound 3 is too long, but literature search showed data for apical O–Sn bonds with monodentate ligands, in pentacoordinated compounds, which present bonds as long as 2.48–2.51 Å [16–18]. Therefore, the distance found for O–Sn in compound

Table 3
Crystal and data collection parameters of compounds 1–3

Compound	1	2	3
Empirical formula	C ₁₄ H ₁₇ Cl ₂ O ₃ Sn	C ₁₈ H ₁₇ ClO ₂ Sn	C ₂₄ H ₂₂ O ₂ Sn
Formula weight	422.87	419.46	461.11
Crystal size (mm)	0.25 × 0.28 × 0.30	0.12 × 0.28 × 0.4	0.12 × 0.28 × 0.42
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pcab</i>	<i>P2₁cn</i>	<i>Cc</i>
<i>a</i> (Å)	14.400(3)	9.22850(10)	15.754(3)
<i>b</i> (Å)	13.445(3)	12.90250(10)	16.847(3)
<i>c</i> (Å)	16.760(3)	29.9390(4)	8.105(2)
α (°)	90.00	90.00	90.00
β (°)	90.00	90.00	104.63(3)
γ (°)	90.00	90.00	90.00
<i>V</i> (Å ³)	3244.9(11)	3564.86(7)	2081.4(7)
<i>Z</i>	8	8	4
ρ_{calc} (mg/m ³)	1.731	1.563	1.471
μ (mm ⁻¹)	1.907	1.587	1.242
<i>F</i> (000)	1672	1664	928
Index range	−16 ≤ <i>h</i> ≤ 14, −17 ≤ <i>k</i> ≤ 17, −20 ≤ <i>l</i> ≤ 20	−9 ≤ <i>h</i> ≤ 11, −16 ≤ <i>k</i> ≤ 13, −37 ≤ <i>l</i> ≤ 36	−18 ≤ <i>h</i> ≤ 18, −19 ≤ <i>k</i> ≤ 21, −9 ≤ <i>l</i> ≤ 10
2 θ (°)	56.02	52.72	52.70
Temperature (K)	293(2)	293(2)	293(2)
Reflections collected	16426	32177	6557
Reflections unique	3295	6454	3596
Reflections observed (4 σ)	2451	4373	3231
<i>R</i> _{int}	0.0723	0.0626	0.0355
Variables	182	398	210
Weighting scheme ^a <i>x/y</i>	0.02970/3.35490	0.03060/0.00	0.03260/0.85150
Goodness-of-fit	1.074	0.980	1.058
Final <i>R</i> (4 σ)	0.0354	0.0351	0.0320
Final <i>wR</i> ₂	0.0743	0.0604	0.0765
Largest res. peak (e/Å ⁻³)	0.609	0.663	0.600

^a $1/w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

Table 4
Selected bond lengths (Å) and angles (°) determined by X-ray analysis of **1**



Bond lengths		Bond angles	
Sn1–O1	2.349(3)	O1–Sn1–Cl1	82.51(9)
Sn1–O2	2.109(3)	O1–Sn1–Cl2	165.66(8)
Sn1–Cl1	2.313(1)	O1–Sn1–O3	86.4(1)
Sn1–Cl2	2.474(1)	O2–Sn1–C7	166.1(1)
Sn1–C7	2.183(4)	O2–Sn1–Cl1	85.87(8)
C1–C2	1.432(6)	O2–Sn1–O3	83.3(1)
C2–C3	1.419(6)	O3–Sn1–Cl1	166.1(1)
C3–C4	1.543(7)	O3–Sn1–C7	86.6(1)
C4–C5	1.539(8)	C7–Sn1–Cl1	102.4(1)
C5–C1	1.563(7)	C7–Sn1–Cl2	98.5(1)
C1–O1	1.286(5)	Cl1–Sn1–Cl2	101.1(4)
C2–O2	1.418(5)		

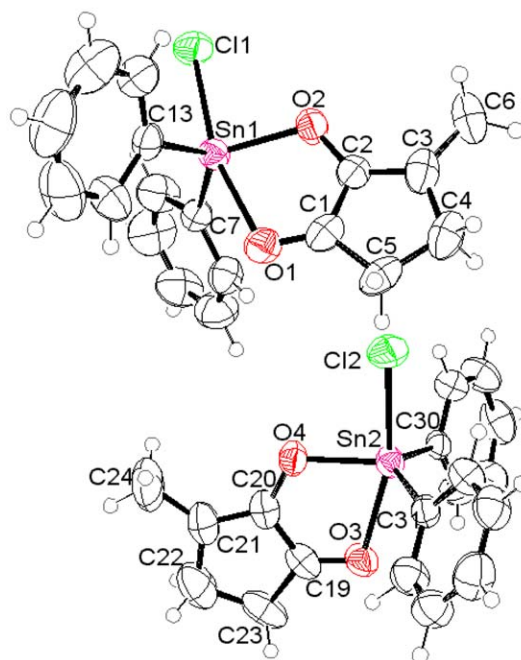
3 could be considered as a weak coordination bond, but nevertheless with a physical meaning.

In compound **1**, the tin atom is six-coordinated, it is linked to one ligand molecule, two Sn–Cl bonds, a Sn–Ph group and a Sn-coordinated ethanol molecule, Fig. 3. A similar tin connectivity was also reported in hexacoordinated oxalamide tin esters [19]. The distorted octahedral tin geometry is a consequence of the five membered ring chelate, the atoms in *anti* position have angles smaller than 180° [O1–Sn1–Cl2 165.66(8)°, O2–Sn1–C7 166.1(1)° and O3–Sn1–Cl1 166.1(1)°].

The tin atom in compound **1** is a stereogenic center and therefore 12 possible isomers could be expected, however only two enantiomers were found in the solid state. The enantiomers form a racemic pair through very strong hydrogen bonds (1.96 Å) between the proton of the ethanol and the oxygen O2, the distance between both oxygen atoms (O2–O3') is 2.67 Å. The hydrogen bonds linking the dimer are forming an eight membered ring [O2–Sn–O3–H]₂, Fig. 3. One Sn–Cl bond (2.313 Å) is in *trans* position to the Sn–OHET bond (2.122 Å) both are the shortest bonds, whereas the longest are the O1–Sn (2.349 Å) and Sn–Cl2 (2.474(2) Å). The phenyl group is in the plane formed by the tin atom, the ligand and Cl2; this fact is attributed to two intramolecular hydrogen bonds O1–H12 (2.561 Å) and Cl2–H8 (3.020 Å). Cl1 atom has two intermolecular hydrogen bonds with H4A (2.923 Å) and with H14A (2.774 Å).

Compounds **2** and **3** have pentacoordinate tin atoms, their geometry can be considered as a distorted trigonal

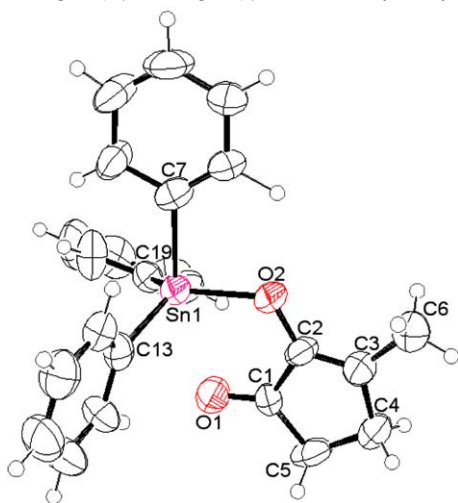
Table 5
Selected bond lengths (Å) and angles (°) determined by X-ray analysis of **2**



Bond lengths		Bond angles	
Cl1–Sn1	2.412(1)	O2–Sn1–Cl13	118.1(2)
C1–O1	1.243(7)	O2–Sn1–C7	113.7(2)
C2–O2	1.357(7)	C13–Sn1–C7	125.6(3)
C7–Sn1	2.113(6)	O2–Sn1–O1	76.6(1)
C13–Sn1	2.112(7)	C13–Sn1–O1	86.0(2)
O1–Sn1	2.342(3)	C7–Sn1–O1	90.9(2)
O2–Sn1	2.032(4)	O2–Sn1–Cl1	88.1(1)
Cl2–Sn2	2.418(1)	C13–Sn1–Cl1	97.6(2)
C19–O3	1.243(6)	C7–Sn1–Cl1	99.2(1)
C20–O4	1.329(7)	O1–Sn1–Cl1	164.2(1)
C30–Sn2	2.104(7)	O4–Sn2–C30	116.9(2)
C31–Sn2	2.133(6)	O4–Sn2–C31	112.8(2)
O3–Sn2	2.359(3)	C30–Sn2–C31	127.7(2)
O4–Sn2	2.034(4)	O4–Sn2–O3	76.0(1)
		C30–Sn2–O3	86.6(2)
		C31–Sn2–O3	90.3(2)
		O4–Sn2–Cl2	88.0(1)
		C30–Sn2–Cl2	98.5(2)
		C31–Sn2–Cl2	98.5(2)
		O3–Sn2–Cl2	163.8(1)

bipyramid, which can be depicted as a “Berry exchange coordinate” [20], because the geometry distortion is formed by the approach of the carbonyl oxygen atom to the tin atom in order to form a *tbp*; however, a perfect trigonal bipyramid is not reached because of the ring tension and the Lewis acid character of the tin atom. For compound **2** the apical positions are occupied by the oxygen of the carbonyl and a chlorine atom [O1–Sn1–Cl1 164.2(1)° and O3–Sn2–Cl2 163.8(1)°], Fig. 4. One oxygen atom and two phenyl groups are in equatorial, they form angles not far from 120° [O4–Sn2–C30 116.9(2)°, C30–Sn2–C31 127.7(2)° and O4–Sn2–C31 112.8(2)°]. The angles formed by the carbonyl oxygen O3 and the equatorial atoms are lesser than 90° [O3–Sn2–O4 76.0(1)°, O3–Sn2–C30

Table 6
Selected bond lengths (Å) and angles (°) determined by X-ray analysis of 3



Bond lengths		Bond angles	
Sn1–O1	2.630(3)	O2–Sn1–C19	116.65(2)
Sn1–O2	2.032(3)	C19–Sn1–C13	118.91(1)
Sn1–C7	2.163(4)	C19–Sn1–C7	104.9(2)
Sn1–C13	2.146(4)	O2–Sn1–C7	91.9(2)
Sn1–C19	2.139(4)	O2–Sn1–C13	112.9(2)
C1–C2	1.441(1)	C13–Sn1–C7	106.9(2)
C2–C3	1.318(9)	O1–Sn1–C7	162.69
C3–C4	1.496(1)		
C4–C5	1.479(1)		
C5–C1	1.510(1)		
C1–O1	1.238(9)		
C2–O2	1.346(7)		

86.6(2)° and O3–Sn2–C31 90.3(2)°], whereas the angles formed between the chlorine and the equatorial atoms are more open than 90° [Cl2–Sn2–O4 88.0(1)°, Cl2–Sn2–C30 98.5(2)° and Cl2–Sn2–C31 98.5(2)°], Table 5.

The unit cell of compound 2 contains two independent molecules, the bond lengths and angles in both molecules do not differ beyond experimental error. The molecules

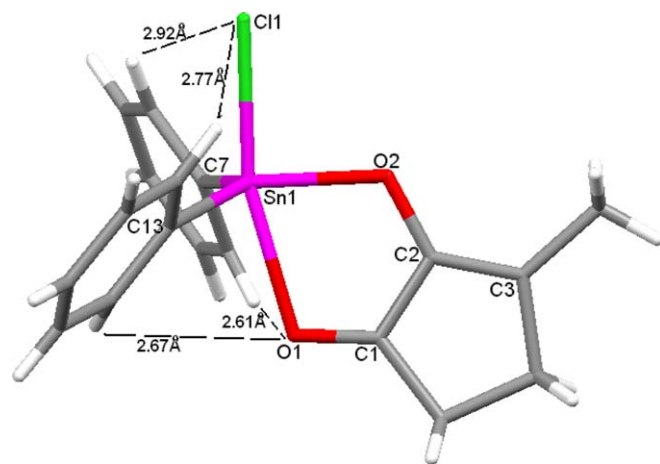


Fig. 4. One structure of compound 2 and the intramolecular hydrogen bonds.

of 2 are associated in the solid state by forming weak coordinative hydrogen bonds via the atoms C11H–O4 (2.705 Å). In both molecules the planes of the phenyl groups are oriented in order to approach the *ortho* aromatic protons to the apical oxygen and chlorine atoms giving four hydrogen bonds.

Compound 3 has three phenyl groups and one ligand, its geometry is similar to that found in 2, Fig. 5. The oxygen O1 and a phenyl groups are in apical positions (O1–Sn–C7 is 162.69°) and the angles for the three equatorial substituents are O2–Sn–C13 112.9(2)°, C13–Sn–C19 118.91(1)° and C19–Sn–O2 116.65(2)°. As expected, the angles formed between the apical oxygen O1 and three equatorial atoms [O1–Sn–O2 71.84°, O1–Sn–C13 83.42°, O1–Sn–C19 80.27°] are smaller than 90°, whereas the angles with the apical atom C7 [C7–Sn–C13 106.9(2)°, C7–Sn–O2 91.9(2)° and C7–Sn–C19 104.9(2)°] are larger than 90°, Table 6. In compound 3, the phenyl group in apical is aligned with the plane of the ligand in order to form a hydrogen bond O2–H8 (2.38 Å), another phenyl group in

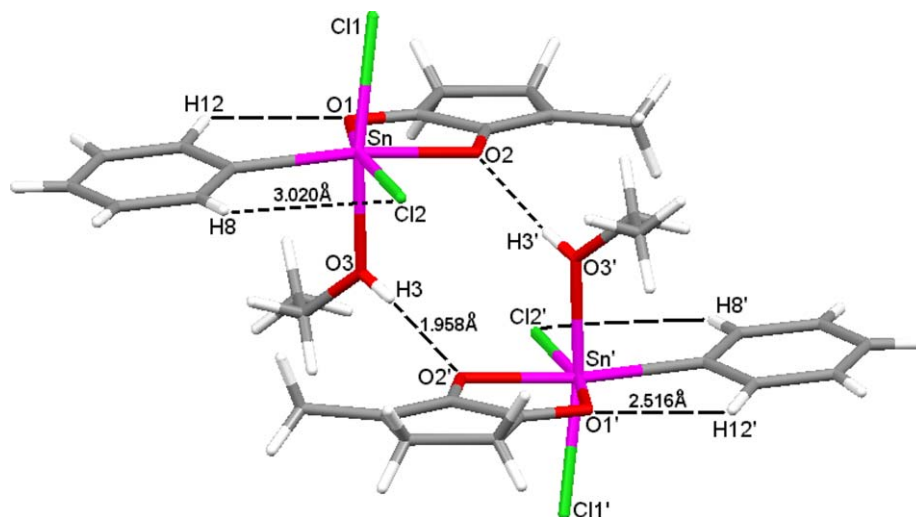


Fig. 3. Racemic pair of compound 1 is shown as well as the hydrogen bonds between them.

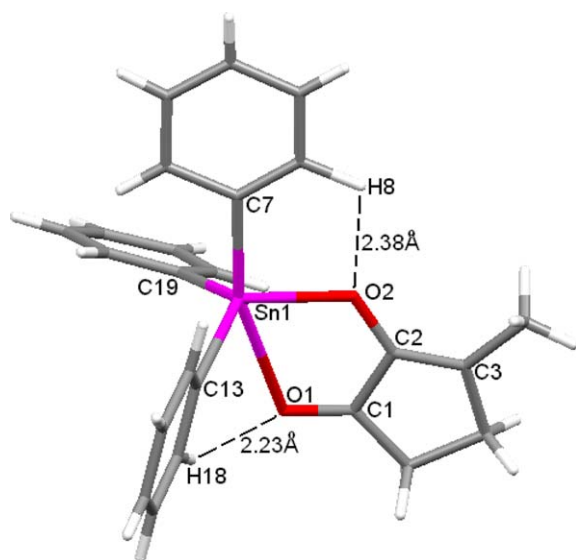


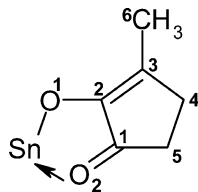
Fig. 5. Structure of compound **3** and the intramolecular hydrogen bonds.

equatorial is also aligned with the bond O1–Sn1 and a hydrogen bond is formed between H18 and O1 2.23 Å, Fig. 5.

For compound **1** the C1–O1 is more likely a double bond [1.286(5) Å], whereas the C2–O2 a single bond [1.418(5) Å]. C1–C2 [1.432(6) Å] and C2–C3 [1.419(6) Å] are delocalized bonds. For **3** where the O–Sn coordination is weaker, the bond lengths values are C1–O1 1.238(9), C2–O2 1.346(7), C1–C2 1.441(1) and C2–C3 1.318(9) Å.

Using the X-ray diffraction data we have calculated the atomic charges of molecules **1–3** and the corresponding to the ligand which are described in Table 7. The molecules are neutral, the tin and C1 and C2 atoms have an important positive charge, whereas the oxygen atoms bear the negative charges. It is interesting that C3 does not share the positive charge in an allylic delocalization.

Table 7
Atomic charges calculated of the ketoenol ligand and the tin compounds **1–3**



Ligand	1	2	3		
Sn	–	+1.514	+1.154	+1.115	+0.900
O1	–0.416	–0.559	–0.609	–0.630	–0.613
O2	–0.649	–0.467	–0.539	–0.548	–0.617
C1	+0.434	+0.312	+0.325	+0.292	+0.312
C2	+0.341	+0.343	+0.329	+0.327	+0.326
C3	–0.045	–0.039	–0.013	–0.032	–0.015
C4	–0.347	–0.345	–0.363	–0.382	–0.384
C5	–0.293	–0.331	–0.299	–0.338	–0.326
C6	–0.382	–0.470	–0.470	–0.474	–0.481

3. Conclusion

Three new penta- and hexacoordinated tin compounds (**1–3**) were obtained and characterized. The three compounds present a weak dative Sn ← O bond that produces hypervalent tin atoms. The weak coordination was mainly established in the solid state, where the geometry implicates the dative bond. Compound **1** has an hexacoordinate tin atom, which is a stereogenic center. In the solid state it displays a racemic pair linked by strong hydrogen bonds. For compounds **2** and **3** the tin atom is pentacoordinate. Compound **3** has a long dative Sn ← O bond. Even if the ^{119}Sn chemical shift is not an argument for pentacoordination in solution, the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ of the tin atom and the *ipso*-carbon of the phenyl group is characteristic for pentacoordinate tin and the Sn ← O is without question in the solid state. All compounds present the distorted *tbp* geometry with the carbonyl group in apical position and pointing at the tin atom. Geometrical distortion is generated by the ring tension. Compounds **2** and **3** showed a “Berry exchange coordinate” geometries according to X-ray diffraction analysis.

4. Experimental

4.1. General comments

All chemicals were reagent grade and were used without further purification. Solvents were purified by usual methods. Melting point were obtained in Mel-Temp II apparatus and are uncorrected. IR (KBr, disc) were determined on a Perkin–Elmer 16 FPC spectrometer. All ^1H , ^{13}C and ^{119}Sn NMR spectra were run in CDCl_3 on a Jeol Eclipse 400 spectrometer. δ (ppm) being referenced to TMS for ^1H and ^{13}C and to Me_4Sn for ^{119}Sn . For ^1H , ^{13}C -COLOC pulse sequence method used see Ref. [21,22]. Elemental analyses were performed in Thermofinnigan Flash EA 1112 instrument. Atomic charges were calculated with the MS Modeling program v3.2.0.0 from data of X-ray diffraction of the ketoenol ligand and compounds **1–3**.

4.2. Syntheses

4.2.1. [(O–Sn)-Ethanol]-(3-methyl-2-oxo-cyclopentanen-1-one-dichlorophenyltin) (**1**)

A mixture of 3-methyl-1,2-cyclopentanedione (6 mmol, 670 mg), SnPhCl_3 (2 mmol, 604 mg) in ethanol (4 mL) is stirred, at r.t. for 48 h. The white crystalline product was filtered off. The tin compound was purified by recrystallization from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ [3/1]. Yield: 754 mg, 89%. M.p. 102–104 °C. IR (KBr) ν (cm^{-1}): 3075 m, 1647 s, 1560 s, 1479 w, 1414 s, 1391 s, 1357 m, 1245 m, 1202 m, 1068 w, 1032 m, 871 w, 745 s, 699 m, 548 w, 521 w, 455 w. MS (EI, 20 eV), m/z (%): 424 $[\text{M}]^+$, 377 (35), 301 (100), 266 (37). Anal. Calc. for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Cl}_2\text{Sn}$: C, 39.62; H, 4.27. Found: C, 39.20; H, 4.09%.

4.2.2. 3-Methyl-2-oxo-cyclopentanen-1-one-chlorodiphenyltin (2)

A mixture of 3-methyl-1,2-cyclopentanedione (**1**) (4 mmol, 450 g), SnPh₂Cl₂ (2 mmol, 690 mg) and Et₃N (1 mmol) in ethanol (4 mL) was stirred at r.t. for 48 h. A crystalline colorless product was filtered off and purified by recrystallization from CH₂Cl₂/EtOH [3/1]. Yield: 750 mg, 89%. M.p. 116–118 °C. IR (KBr) ν (cm⁻¹): 3049 w, 2911 w, 1658 s, 1583 s, 1480 w, 1432 s, 1409 s, 1357 s, 1309 w, 1248 m, 1203 m, 1150 s, 1069 m, 996 w, 806 w, 743 s, 694 s, 542 w, 472 w, 498 w, 445 m. MS (EI, 20 eV), m/z (%): 419 [M]⁺ (3), 385 (18), 343 (100), 154 (54). Anal. Calc. for C₁₈H₁₇O₂ClSn: C, 51.53; H, 4.09. Found: C, 51.66; H, 4.14%.

4.2.3. 3-Methyl-2-oxo-cyclopentanen-1-one-triphenyltin (3)

A mixture of 3-methyl-1,2-cyclopentanedione (4 mmol, 450 mg), Ph₃SnOH (4 mmol, 1.47 g) in toluene (8 mL) was refluxed in a 50-mL flask equipped with a Dean Stark funnel. After 5 h, the 50% of the initial solvent was distilled off and the remaining solution was filtered. The solvent was evaporated under vacuum and the crystalline colorless product was purified by recrystallization from CH₂Cl₂/EtOH [3/1]. Yield: 1.61 g, 88 %. M.p. 132–134 °C. IR (KBr) ν (cm⁻¹): 3055 m, 2904 m, 1679 s, 1622 s, 1478 m, 1428 s, 1401 s, 1343 s, 1307 m, 1247 s, 1208 s, 1138 s, 1071 s, 995 m, 851 w, 811 w, 729 s, 697 s, 535 w, 441 s. MS (EI, 20 eV), m/z (%): 385 (100), 351 (14), 231 (15). Anal. Calc. for C₂₄H₂₂O₂Sn: C, 62.51; H, 4.81. Found: C, 62.78; H, 4.93%.

4.3. X-ray structural analysis of 1–3

X-ray diffraction studies of compounds **1–3** were performed with an Enraf–Nonius CAD4 diffractometer [$\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$]. Structure solution and refinement were performed with the program SHELXL 1997. Absorption correction (semiempirical for **1–3**). For compound **1** ethanol C–H hydrogen atoms were calculated as well as the protons of the methyl C-6, the other hydrogen atoms were found and refined with isotropic thermal parameters and for **2** (H12, H18, H25 and H32) and **3** (H8 and H18) protons were found and refined with isotropic thermal parameters.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for compounds **1–3** have been deposited with the Cambridge Crystallographic Data as supplementary Publications Nos. CCDC-289015. Copies of the data can be obtained free of charge on application to CCDC-289127 (**1**), CCDC-289125 (**2**), CCDC-289126 (**3**), 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2005.12.036.

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