



# Synthesis, spectroscopic characterization and solution behavior of new tin tetrachloride adducts with $\gamma$ -keto allyl phosphonates



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## ABSTRACT

Four new octahedral complexes of the type  $[\text{SnCl}_4\text{L}_2]$  ( $\text{L} = \gamma$ -keto allyl phosphonate) (**1–4**) were prepared and characterized by multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>119</sup>Sn) NMR, IR spectroscopy and elemental analysis. The NMR data show, as expected, that these complexes exist in solution as mixtures of *cis* and *trans* isomers. More importantly, the solution structure was confirmed by <sup>119</sup>Sn NMR spectra which show two triplets corresponding to the two isomers. In addition, the solution behavior of these complexes in the presence of excess ligand was studied by variable temperature NMR using the coalescence temperature method. The metal-ligand exchange activation energies were therefore determined and found to be in the range 57–60 kJ/mol. The effect of remote substituents on the metal-ligand interaction was studied and compared with closely related tin-phosphoryl complexes.

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## 1. Introduction

The ability of the strong Lewis acid tin tetrachloride to form 1:2 adducts with a variety of neutral ligands is well-known [1–5]. For instance, phosphoramides show strong affinity to this Lewis acid and produce hexacoordinate, 2:1, *cis*- or *trans*-complexes. These complexes have been characterized in solution and in the solid state [6,7]. The tin complex with hexamethylphosphoramide,  $[\text{SnCl}_4(\text{HMPA})_2]$ , has been found to exist as a *trans*-adduct in the solid by X-ray diffraction [8] and in solution as a mixture of *cis* and *trans* isomers by IR and NMR spectroscopy [9,10], whereas the complex with trimethylphosphate (TMPA) was shown to be predominantly a *cis*-adduct [11]. This difference in reactivity towards the tin center could be explained in terms of the nature of the substituents on the phosphorus atom of the ligand [6,12–14].

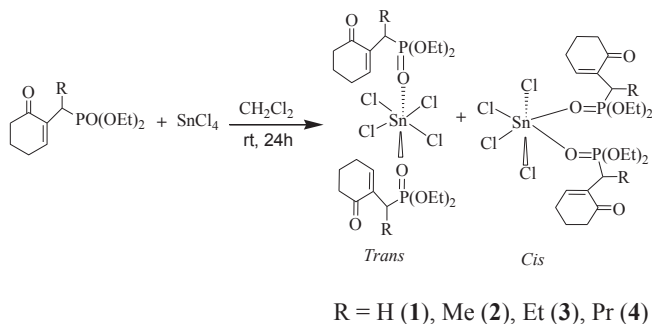
On the other hand, phosphonates containing functional groups are attracting considerable attention due to their potential application in medicinal bioorganic and organic chemistry [15,16]. The coordination chemistry of these molecules could represent another venue towards a further understanding of their chemistry.

In our previous works [17–21], we studied tin(IV) complexes containing the ligands  $(\text{R}_2\text{N})_2\text{P}(\text{O})\text{F}$  and  $\text{R}_2\text{NP}(\text{O})\text{F}_2$  using multinuclear NMR in solution and showed that whilst the *cis* isomer predominates with the former, the latter ligand forms almost exclusively the *cis*-complex [17,18]. In a more recent work, we have also shown that when the fluorine atom in these ligands was substituted by a fluoroalkoxy ( $\text{OCH}_2\text{CF}_3$ ) group the isomer distribution in the adduct formed with  $\text{SnCl}_4$  reversed and the *trans*-complex becomes the major isomer observed in solution [19–21]. This straightforward dependence of stereochemistry on the nature of the substituents on the phosphorus atom of the ligand inspired us to investigate the solution structure of tin complexes with bulkier phosphonate ligands containing a carbonyl group. We were also interested to see if the carbonyl oxygen would coordinate to the tin center in the presence of a phosphoryl group.

Herein, we report on the synthesis and characterization of  $\text{SnCl}_4$  complexes with four  $\gamma$ -keto allyl phosphonates of Bayllis Hilman adducts type [22]. The solution behavior of these new tin complexes in the presence of excess ligand is also investigated using variable temperature NMR spectroscopy.

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**Scheme 1.** Synthesis of complexes **1–4**.

**Table 1**  
IR data ( $\nu/\text{cm}^{-1}$ ) for the complexes **1–4** and their ligands (L).

Compound	$\nu_{\text{P=O}}$ L	$\nu_{\text{P=O}}$ ( $\Delta\nu_{\text{PO}}$ ) Complex	$\nu_{\text{C=O}}$ L	$\nu_{\text{C=O}}$ ( $\Delta\nu_{\text{CO}}$ ) Complex	$\nu_{\text{Sn-O}}$
<b>1</b>	1250	1171 (79)	1682	1675 (7)	507
<b>2</b>	1225	1167 (58)	1679	1682 (3)	523
<b>3</b>	1249	1169 (80)	1684	1683 (1)	544
<b>4</b>	1243	1158 (85)	1684	1682 (–2)	536

## 2. Experimental

### 2.1. General experimental procedures

All reactions were carried out under a nitrogen atmosphere in solvents dried by standard techniques [23] and stored over molecular sieves. The NMR spectra were recorded on a Bruker AC-300 spectrometer in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  solution;  $^1\text{H}$  at 300 MHz (TMS),  $^{13}\text{C}$  at 75.4 MHz (TMS),  $^{31}\text{P}$  at 121 MHz (85%  $\text{H}_3\text{PO}_4$ ) and  $^{119}\text{Sn}$  at 111.8 MHz ( $\text{SnCl}_4$ ).  $^{119}\text{Sn}$  NMR spectra were recorded in 10 mm NMR tubes containing 15–20% deuterated solvent. IR spectra were measured on a Perkin–Elmer Paragon 1000 PC spectrometer. The elemental analyses were performed on a SHIMADZU TOC5000A instrument.

Tin tetrachloride was used as received. The allyl phosphonate ligands were prepared as very recently described [22].

### 2.2. General procedure for the preparation of complexes **1–4**

A solution of allylic phosphonates (4 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) was slowly added to  $\text{SnCl}_4$  (2 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) and the mixture stirred under  $\text{N}_2$  for ca. 24 h. The volatiles were then removed in vacuo and the complex  $[\text{SnCl}_4\text{L}_2]$  washed with anhydrous hexane and dried in vacuo to give the complex **1** as a yellow oil and **2–4** as white solids.

**1**: Yield: 86%;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 16.0, 22.7, 24.9, 26.4, 37.8, 65.8, 65.9, 127.9, 152.6, 197.4. Anal. calcd for  $\text{C}_{22}\text{H}_{38}\text{Cl}_4\text{O}_8\text{P}_2\text{Sn}$ : C, 35.09; H, 5.09 (%); Found: C, 34.88; H, 5.24 (%).

**2**: Yield: 91%; mp 244–245 °C  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 16.0, 16.1, 22.5, 26.3, 28.5, 37.9, 65.9, 66.4, 133.8, 151.7, 197.4; Anal.

**Table 2**  
NMR data ( $\delta/\text{ppm}$ ) for complexes **1–4** in  $\text{CDCl}_3$ .

Compound	$\delta_{^{31}\text{P}}$ ( $^2J_{\text{P-Sn}}$ )		$\delta_{^{119}\text{Sn}}$ ( $^2J_{\text{P-Sn}}$ )	
	Cis	Trans	Cis	Trans
<b>1</b>	24.43 (s, 154)	24.76 (s, 206)	–551(t, 156)	–571(t, 213)
<b>2</b>	24.36 (s, 210)	25.27(s, 259)	–552(t, 207)	–573(t, 257)
<b>3</b>	23.67 (s, 204)	24.44(s, 259)	–552(t, 219)	–573(t, 258)
<b>4</b>	23.37 (s, 195)	24.12(s, 258)	–552(t, 193)	–573(t, 257)

calcd for  $\text{C}_{24}\text{H}_{42}\text{Cl}_4\text{O}_8\text{P}_2\text{Sn}$ : C, 36.91; H, 5.42 (%). Found: C, 36.86; H, 5.15 (%).

**3**: Yield: 93%; mp 261–262 °C;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 11.8, 16.0, 16.1, 22.0, 22.5, 26.4, 34.2, 37.8, 65.8, 66.4, 131.9, 152.0, 198.2; Anal calcd for  $\text{C}_{26}\text{H}_{46}\text{Cl}_4\text{O}_8\text{P}_2\text{Sn}$ : C, 38.60; H, 5.73 (%); Found: C, 38.38; H, 5.51 (%).

**4**: Yield 90%; mp 273–274 °C;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 16.0, 16.1, 20.2, 22.5, 26.4, 30.3, 30.4, 37.9, 65.8, 66.4, 132.1, 151.8, 197.7; Anal calcd for  $\text{C}_{28}\text{H}_{50}\text{Cl}_4\text{O}_8\text{P}_2\text{Sn}$ : C, 40.17; H, 6.02 (%); Found: C, 40.17; H, 5.99 (%).

## 3. Results and discussion

### 3.1. Synthesis

$\text{SnCl}_4$  reacts with the ligands (L =  $\gamma$ -keto allyl phosphonates [22]) in anhydrous dichloromethane to produce white solids (**2–4**) or an oil (**1**) with the composition  $[\text{SnCl}_4\text{L}_2]$ . The solids are soluble in dichloromethane and chloroform. The complexes were characterized by elemental analysis and particularly by their NMR data and comparison with the corresponding data for the free ligands. The possible structures of complexes **1–4** are shown in Scheme 1.

### 3.2. Spectroscopic characterization

The infrared spectra (Table 1) show strong bands within the range 1230–1250  $\text{cm}^{-1}$  attributed to  $\nu_{\text{P=O}}$ . The  $\nu_{\text{P=O}}$  stretching vibration is shifted towards lower wave numbers on coordination to the tin atom compared with its value in the free ligands. The coordination shift is consistent with phosphoryl coordination to the tin atom. This shift is in the range 58–85  $\text{cm}^{-1}$  explaining the relative similarity in the basicity strength of these ligands. The absorption band at 507–544  $\text{cm}^{-1}$  corresponds to the stretching vibration of the Sn–O group, in good agreement with literature data for related complexes [21,10]. Interestingly, the C=O stretching vibration of complexes **1–4** displaying strong absorptions in the range 1675–1683  $\text{cm}^{-1}$  remains approximately unchanged compared to that in the free ligands (1679–1684  $\text{cm}^{-1}$ ) (see Table 1). This clearly confirms that the C=O group was not involved in coordination to the tin center which occurs only through the P=O group as also detailed below.

The NMR spectra of the four complexes were recorded in  $\text{CDCl}_3$  solutions and the data obtained from these spectra are summarized in Table 2.

At room temperature, the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of complexes **2** and **4** showed only one signal, whilst two resonances were observed for **1** and **3**; the high frequency resonance was flanked with Sn satellites (Fig. 1). These signals are shifted to lower frequency compared with that of the free ligand. Such a behavior is interpreted in terms of inductive effects resulting from a decrease in the electron density at phosphorus upon coordination of the phosphoryl oxygen of the ligand to the tin atom.

The corresponding  $^{119}\text{Sn}$  NMR spectra for each of complexes **1–4**

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