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Synthesis and structural characterization of organotin(IV) complexes with ferrocenyldithiophosphonate ligands

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ABSTRACT

The reaction of ammonium salts of benzylferrocenyldithiophosphonate ligands [NH_4][$S_2P(OR)(Fc)$] [R = Bz (**1**), 4-(^{i}Pr)-Bz (**2**), 4-(^{t}Bu)-Bz (**3**), 4-(Ph)-Bz (**4**), 3-(OBz)-Bz (**5**); Bz = benzyl, Fc = ferrocenyl] with organotin(IV) chlorides Ph_2SnCl_2, $^{n}Bu_2SnCl_2$ and Ph_3SnCl, gave the corresponding organotin(IV) benzylferrocenyldithiophosphonates [$Ph_2Sn\{S_2P(OR)(Fc)\}_2$] [R = Bz (**6**), 4-(^{i}Pr)-Bz (**7**), 4-(^{t}Bu)-Bz (**8**), 4-(Ph)-Bz (**9**), 3-(OBz)-Bz (**10**)], [$^{n}Bu_2Sn\{S_2P(OR)(Fc)\}_2$] [R = Bz (**11**), 4-(Ph)-Bz (**12**)] and [$Ph_3Sn\{S_2P(OBz)(Fc)\}$] (**13**). Compounds **6**–**13** were characterized by elemental analyses, infrared, ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{119}Sn\{^{1}H\}$NMR spectroscopy and ESI mass spectrometry, while complexes **6**, **11** and **13** were also characterized by single-crystal X-ray diffraction studies. The dithiophosphonate ligands display an anisobidentate coordination mode upon interaction with the metal center. The solid-state structures of the disubstituted complexes **6** and **11** exhibit a *trans* arrangement for the ferrocenyl groups from the dithiophosphonate ligands.

1. Introduction

Organotin (IV) complexes are important due to their potential applications as antitumor agents, as reagents or catalysts in organic reactions [1–3]. Furthermore, organotin 1,1-dithiolates, namely ditiocarbamates, dithiophosphates and dithiophosphinates, have been extensively studied revealing a broad diversity of coordination patterns due to their ability to engage in intra- or intermolecular bonds [4–6]. Nonetheless, tin (IV) complexes bearing dithiophosphonate ligands remain scarce with only a handful of fully structurally characterized examples [7,8].

In this regard, we recently reported on the first example of organotellurium (IV) dithiophosphonate complexes with the electron-rich benzylferrocenyldithiophosphonate ligands [9]. These sterically-demanding ligands promote the formation of discrete molecular arrangements in the solid state, exhibiting only weak intramolecular contacts.

Following up on our studies on *p*-block elements bearing 1,1-dithiolates, we now report on the use of benzylferrocenyldithiophosphonate ligands for the preparation of organotin(IV) complexes.

2. Results and discussion

Reaction of the ammonium salts [NH_4][$S_2P(OR)(Fc)$] [R = Bz (**1**), 4-(^{i}Pr)-Bz (**2**), 4-(^{t}Bu)-Bz (**3**), 4-(Ph)-Bz (**4**), 3-(OBz)-Bz (**5**); Bz = benzyl, Fc = ferrocenyl] with Ph_2SnCl_2 in ethanol in a 2:1 M ratio gave the organotin complexes **6**–**10** in moderate to good yields. In a similar manner, the reaction of $^{n}Bu_2SnCl_2$ with **1** and **4** gave the dibutyltin complexes **11** and **12**, respectively. Interestingly, the disubstituted complexes **6**–**12** were obtained regardless of the metal:ligand ratio used in the reaction (1:2, 1:1 or 2:1). On the other hand, the equimolar reaction of **1** and Ph_3SnCl gave complex **13** albeit in low yield (Scheme 1).

Compounds **6**–**13** were isolated as yellow to orange air-stable solids soluble in CH_2Cl_2 and THF but exhibit limited stability in chlorinated solvents. All complexes were characterized by analytical and spectroscopic methods and in the case of **6**, **11** and **13**, also by X-ray diffraction studies.

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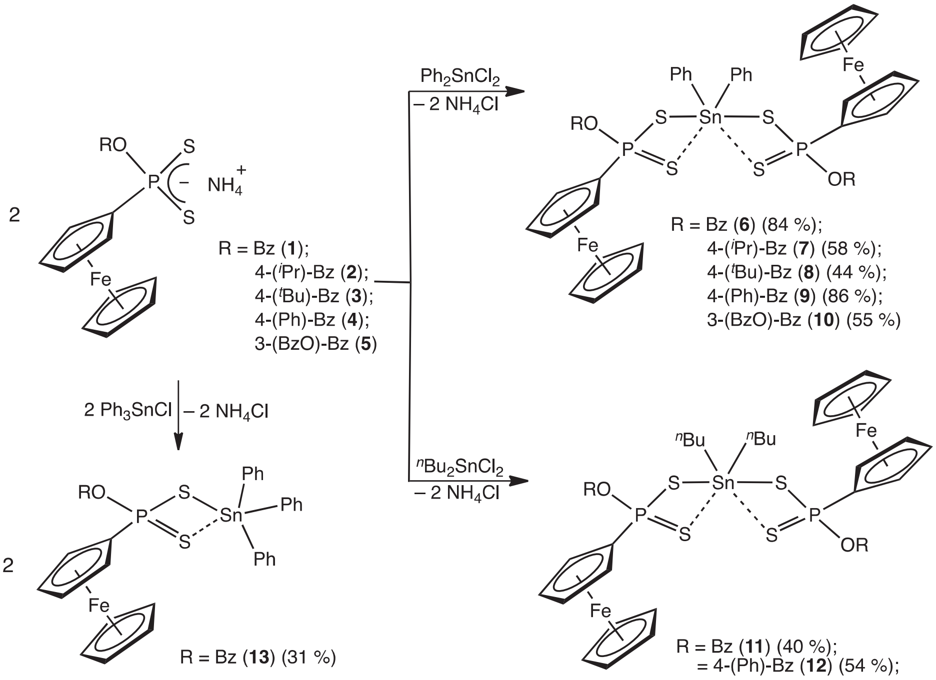

Scheme 1. Preparation of compounds **6**–**13**.

The IR spectra of these compounds exhibit characteristic absorption bands for ν (P–C) (1431–1487 cm^{-1}), ν (P–O) (977–1033 cm^{-1}) and ν (C–O) (1105–1269 cm^{-1}) bonds. The coordination patterns of PS_2 based ligands can be assessed by the difference between the asymmetric and symmetric ν (PS_2) vibrations [10]. Consequently, the coordination behavior of the ligands in **6**–**13** ($\Delta\tilde{\nu}_{sys/asym}$ 80–130 cm^{-1}) can be described as anisobidentate (90–100 cm^{-1}). A similar behavior has been observed in organotellurium(IV) complexes bearing the same dithiophosphonate ligands [9].

It is noteworthy that due to the potential coordination mode of the ligands, it is possible to have *cis* or *trans*-like isomers for the disubstituted complexes. In this regard, the ^1H NMR spectra of **6**–**12** show only a single set of signals for both ligand units. Moreover, the $^{31}P\{^1H\}$ NMR spectra of **6**–**12** show signals corresponding to one type of phosphorus atom in the range of δ 95.0–99.4 ppm. This suggests the presence of only one type of isomer in solution or the existence of a fluxional behavior.

The $^{119}Sn\{^1H\}$ NMR spectra of these compounds were measured in non-coordinating solvent ($CDCl_3$) exhibiting sharp single signals shifted upfield with regard to their parent compounds: Ph_2SnCl_2 (−29.0 ppm, $CDCl_3$), $^nBu_2SnCl_2$ (122 ppm, $CDCl_3$) and Ph_3SnCl (−48 ppm, $CDCl_3$). Compounds **6**–**10** exhibit a single signal in the range of δ −265.2 to −311.5 ppm, while the dibutyltin complexes **11** and **12** show signals at δ −176.8 and −175.4 ppm, respectively. The $^{119}Sn\{^1H\}$ NMR spectrum of **13** exhibits a single signal at δ −94.7 ppm for the triphenyltin complex. According to Otera's range for $^{119}Sn\{^1H\}$ NMR chemical shifts for organotin chelates [11], compounds **6**–**12** correspond to six-coordinate species, whereas **13** is considered a five-coordinate complex, thus, confirming the bidentate nature the benzylferrocenyldithiophosphonate ligands in solution for these compounds.

The electrospray ionization mass spectrometry (ESI-MS) for **6**–**12** in methanol shows the cationic fragment owing to the organometallic moiety with one unit of the ligand $[R_2Sn\{S_2P(OR)(Fc)\}]^+$ and the anionic fragment corresponding to the ligand unit $[\{S_2P(OR)(Fc)\}]^-$. In the case of compound **13**, the cationic fragment $[Ph_3Sn]^+$ was identified together with the anionic ligand unit.

2.1. Crystal structures of 6, 11 and 13

Single-crystals of the tin complexes **6** and **11** were obtained from CH_2Cl_2/hexane mixtures, while **13** was obtained from a THF/CH_2Cl_2/hexane mixture. Compounds **6** and **11** crystallized in the monoclinic space groups $P2/n$ and $C2/c$, respectively, with one half of the molecules in the asymmetric unit. Compound **13** crystallized in the triclinic $P\bar{1}$space group with one half of the compound in the asymmetric unit. The crystal data and refinement details for these compounds are listed in Table 1 and selected bond lengths and angles for these complexes are presented in Table 2.

The tin atoms in **6** and **11** are covalently bonded to two carbon atoms and to two units of the dithiophosphonate ligand in an anisobidentate fashion with no intermolecular contacts (Figs. 1 and 2). The Sn–S bond lengths in **6** [2.512(3) Å] and **11** [2.495(1) Å] are comparable to those in the organotin(IV) dithiophosphonates $[Me_2Sn\{S_2P(OR)(4\text{-}MeOC_6H_2)\}_2]$ [R = Me (2.506(1) Å), ^{i}Pr (2.503(1) Å)] [7], dithiophosphates $[Me_2Sn\{S_2P(OCMe_2)_2\}_2]$ [2.495(1) Å] [12], $[Me_2Sn\{S_2P(O(2\text{-}MeC_6H_4))_2\}_2]$ [2.508(1) Å] [13] and $[R_2Sn\{S_2P(OMen)_2\}_2]$ [Men = menthyl; R = Me (2.489(1) Å), Ph (2.510(1) and 2.512(1) Å)] [14], and dithiophosphinates $[Me_2Sn\{S_2P(R)_2\}_2]$ [R = Me (2.482(2) Å) [15], Ph (2.482(1) and 2.499(1) Å)] [16].

Furthermore, the Sn···S distances [3.223(1) Å for **6** and 3.302(1) Å for **11**] are longer than the sum of the covalent radii [Σr_{cov} (Sn, S) = 2.44 Å] [17] but shorter than the sum of the van der Waals radii [Σ_{vdW} (Sn, S) = 3.97 Å] [18] and thus, influence the local geometry. In this regard, the calculated Pauling-type bond orders [19] suggest weak Sn···S contacts for these compounds, 0.079 for **6** and 0.061 for **11**. The asymmetric bonding of the PS_2 unit to the tin atom is further supported by the difference in the P–S bond lengths, 1.940(2) and 2.028(1) Å for **6** and, 1.944(1) and 2.049(1) Å for **11**. Therefore, the coordination geometry around the tin atom can be described as skew-trapezoidal bipyramid with C–Sn–C angles of 136.3(4) and 125.2(2)° for **6** and **11**, respectively. The two apical Sn–C bonds are