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Synthesis and spectroscopic studies of diorganotin(IV) adducts based on cyclotriphosphazene scaffolds with exocyclic pyrazolyl substituents

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Functionalized cyclotriphosphazenes with four pyrazolyl substituents have been employed for the synthesis of two new organotin complexes. These new compounds have been characterized by elemental analysis and IR, $^1$H, $^{31}$P and $^{119}$Sn NMR spectroscopy. On the basis of these data, pyrazolylcyclotriphosphazene is bis-bidentate neutral ligand coordinating to two SnMe$_2$Cl$_2$ molecules in the resulting adducts. Coordination occurs only via the pyrazolyl nitrogens; cyclotriphosphazene ring nitrogens are not involved in coordination. The $^{119}$Sn NMR data are consistent with increasing of coordination number of tin(IV) in solution.

Keywords: Organotin; Cyclotriphosphazene; Pyrazolylcyclotriphosphazene; Tin

1. Introduction

Cyclotriphosphazenes are one of the most well studied inorganic ring systems, largely due to development of polymeric materials. The chemistry of cyclophosphazenes has developed on three themes: (1) nucleophilic substitution reactions of halogenocyclophosphazenes [1], (2) ring-opening polymerization to linear polymers [2, 3] and (3) using these ring compounds as ligands in coordination and organometallic chemistry. The third facet of chemistry of cyclophosphazenes has received much attention recently [4, 5]. Cyclotriphosphazenes with pendant donor groups attached to the phosphorus atoms exhibit diverse behavior as multimodal ligands. A goal for this research is preparation of metal-rich phosphazene polymers as catalysis, conductors, or drug delivery systems; it is advantageous to use substituted cyclotriphosphazenes as small molecule model compounds [6–9]. Metal ions ranging from first row transition metals to lanthanides have been involved in complex formation utilizing cyclophosphazene-based ligands [5].

No attempts have been made to synthesize organotin complexes with these ligands. In continuation of our studies on the interaction of organotin species with multi-site coordination ligands [10–13], we report here the synthesis of new organotin adducts with pyrazolyl substituted cyclotriphosphazenes. Pyrazolylcyclotriphosphazenes are

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versatile multimodal ligands which bind to metals via both the ring nitrogens of the cyclophosphazene and the pyridine nitrogens of pyrazolyl rings [4]. Coordination behavior of pyrazoles as ligands in general, and poly(pyrazolyl)borates and poly(pyrazolyl)alkanes in particular, towards organotin compounds [14–16] has prompted us to investigate the ligating behavior of multipyrazolyl cyclophosphazenes with organotin compounds. The results of these studies are reported herein.

2. Experimental

All chemicals and solvents were purchased from commercial sources. N₃P₃(O₂C₁₂H₈)Cl₄ was prepared by literature method [17]. IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. The ¹H and ³¹P NMR spectra were recorded with a Bruker Avance DPZ500 spectrometer at 500.130 MHz and 202.456 MHz using TMS and H₃PO₄ (85%) as references, respectively. ¹¹⁹Sn NMR were recorded with a Bruker Avance DPZ400 spectrometer at 186.496 MHz using SnMe₄ as reference. The C, H and N analyses were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

2.1. Synthesis of substituted cyclotriphosphazenes

2.1.1. 2,2-spiro(1,3-propanediamino)-4,4,6,6-tetrakis-(3,5-dimethylpyrazolyl) cyclotriphosphazene, N₃P₃(HNC₃H₆NH)(dmp)₄ (1). Compound 1 was prepared by the literature method [18]. ¹H NMR (CDCl₃): δ = 5.87 (s, 4H, CH), 3.71 (s, br, 2H, NH), 3.37 (dt, 4H, ³J (P–H) = 14.6 Hz, ³J (H–H) = 5.8 Hz, NCH₂), 2.20 (s, 12H, CH₃), 2.08 (s, 12H, CH₃), 1.86 (quin, 2H, ³J(H–H) = 5.6 Hz, CH₂). ³¹P NMR: δ 13.08 (t, P spiro), 2.28 (d), ²J (P–N–P) = 51.8 Hz.

2.1.2. 2,2-spiro(2’2”-dioxy-1’1”-biphenyllyl)-4,4,6,6-tetrakis-(3,5-dimethyl pyrazolyl)cyclotriphosphazene, N₃P₃(O₂C₁₂H₈)(dmp)₄ (2). A solution of N₃P₃(O₂C₁₂H₈)Cl₄ (0.39 g, 0.846 mmol) in benzene (10 mL) was added dropwise to a stirring solution of 3,5-dimethylpyrazole (0.338 g, 3.39 mmol) and triethylamine (3.50 mmol) in benzene (20 mL) at room temperature. The temperature was slowly raised to 80°C and the reaction mixture was refluxed for 20 h, cooled and filtered. The precipitate was washed with water (2 × 10 mL) and ether (3 × 5 mL) and dried under vacuum. Yield 0.293 g (50%), m.p. 198–200°C. ¹H NMR (CDCl₃): δ 7.33–7.57 (m, 8H, Ph), 6.05 (s, 4H, CH), 2.31 (s, 12H, CH₃), 2.26 (s, 12H, CH₃). ³¹P NMR: δ 20.30 (t), 1.5 (d), ²J (P–N–P) = 72.8 Hz.

2.2. Synthesis of adducts

2.2.1. [(SnMe₂Cl₂)₂{N₃P₃(HNC₃H₆NH)(dmp)₄}] (3). A mixture of SnMe₂Cl₂ (0.20 g, 0.9 mmol) and N₃P₃(HNC₃H₆NH)(dmp)₄ (0.18 g, 0.3 mmol) in CH₂Cl₂ (100 mL) was refluxed for 18 h. The solvent was evaporated in vacuo and the oily residue washed with
Et₂O (3 × 20 mL) and hexane (20 mL). A white solid obtained was dried over CaCl₂. Yield 0.12 g (40% based on the ligand). Anal. Calcd for C₂₇H₄₈N₁₃P₃Sn₂Cl₄ (%): C, 31.5; H, 4.7; N, 17.7. Found: C, 31.9; H, 5.1; N, 18.0. FT-IR (KBr, cm⁻¹): ν(P=N), 1251; ν₅(Sn–C), 579; ν₆(Sn–C), 523; ν(Sn–N), 470. ¹H NMR (CDCl₃): 5.91 (s, 4H, CH), 3.70 (s, 2H, NH), 3.37 (dt, 4H, NCH₂), 2.37 (s, 12H, CH₃), 2.09 (s, 12H, CH₃), 1.85 (quin, 2H, –CH₂–), 1.22 (s, 12H, SnCH₃, 2J(¹¹⁹Sn–H) = 80.0 Hz). ³¹P NMR: δ 13.37 (t), 1.25 (d), 2J (P–N–P) = 50.29 Hz. ¹¹⁹Sn NMR: δ = −116.3.

2.2.2. [(SnMe₂Cl₂)₂{N₃P₃(O₂C₁₂H₈)(dmp)₄}] (4). Complex 4 was synthesized as described for 3 from SnMe₂Cl₂ (0.20 g, 0.9 mmol) and N₃P₃(O₂C₁₂H₈)(dmp)₄ (0.21 g, 0.3 mmol). Yield 0.19 g (56% based on the ligand). Anal. Calcd for C₃₆H₄₈N₁₁O₂P₃Sn₂Cl₄ (%): C, 37.9; H, 4.2; N, 13.5. Found: C, 38.3; H, 4.2; N, 13.3. FT-IR (KBr, cm⁻¹): ν(P=N), 1220; ν₅(Sn–C), 600; ν₆(Sn–C), 521; ν(Sn–N), 417. ¹H NMR (CDCl₃): 7.20–7.48 (m, 8H, Ph), 5.87 (s, 4H, CH), 2.23 (s, 12H, CH₃), 2.12 (s, 12H, CH₃), 1.16 (s, 12H, SnCH₃, 2J(¹¹⁹Sn–H) = 78.4 Hz). ³¹P NMR: δ 21.09 (t), 1.7 (d), 2J (P–N–P) = 71.8 Hz, ¹¹⁹Sn NMR: δ = −15.9.

3. Results and discussion

The new organotin adducts, [(SnMe₂Cl₂)₂{N₃P₃(HNC₃H₆NH)(dmp)₄}] (3) and [(SnMe₂Cl₂)₂{N₃P₃(O₂C₁₂H₈)(dmp)₄}] (4), were obtained by reaction of pyrazolyl substituted cyclotriphosphazenes with excess SnMe₂Cl₂ in CH₂Cl₂. Stoichiometry of the adducts has been confirmed by analytical data and the integrated ¹H NMR spectra are consistent with the empirical formulas. The nature of bonding was established by spectroscopic investigations.

The P–N stretching band at 1249 and 1218 cm⁻¹ in the IR spectra of the free 1 and 2, respectively, is at the similar position in the spectra of the adducts without splitting, indicating that the ring nitrogens are not involved in coordination to tin. Metallation of ring nitrogens in cyclophosphazenes leads to splitting of ring P–N stretching frequency; if coordination is exclusively through exocyclic nitrogens the ring P–N stretching frequency remains largely unaffected [19, 20].

The ¹H NMR spectra of 3 and 4 show a singlet around 1.20 ppm for SnMe₂ protons accompanied by satellites due to ¹H–¹¹⁹Sn coupling with 2J(¹¹⁹Sn–¹H), larger than in SnMe₂Cl₂ [2J(¹¹⁹Sn–¹H) = 68.7 Hz]. Increasing coupling constant indicates higher coordination number of tin. Substitution of the coupling constants in the Lockhart-Manders equation [21] gives a value ~130° for the C–Sn–C angle, consistent with a nonlinear Me–Sn–Me configuration.

¹¹⁹Sn{¹H} NMR spectrum of 3 shows a singlet at −116 ppm, significantly lower frequency than that of SnMe₂Cl₂ (+137 ppm). ¹¹⁹Sn chemical shift is strongly dependent on the coordination number of tin and an increase in coordination number produces a large upfield shift, by 60–150 ppm with a change in the coordination number of tin from 4 to 5 and by 130–200 ppm from 5 to 6 [22, 23]. Therefore, it appears that in 3 coordination number of the tin is six in solution. In the ¹¹⁹Sn NMR spectrum of 4 a broad singlet at −15 ppm indicates an increase in coordination number but not in the range for six-coordinate complexes. Broadening and deshielding of
this signal indicate the adduct is partially or completely dissociated after standing in chloroform and the free and coordinated ligand are involved in interchange. Unlike the $^{119}\text{Sn}$ NMR spectrum, the $^1\text{H}$ NMR spectrum shows sharp lines, indicating that the rate of exchange is between the time scales associated with $^{119}\text{Sn}$ NMR and $^1\text{H}$ NMR. Similar dissociation of organotin derivatives of pyrazolylalkanes in chlorinated solvents has been reported [16].

The $^{31}\text{P}$ NMR spectra of both the ligands and the adducts show an $A_2X$ pattern with only slight shifts in the spectra of the adducts with respect to the ligands. This means that the ring nitrogen is not involved in bonding with tin. If this bond was formed, there would have been noticeable shifts in the spectra of resulting complexes.

Thus, the two geminally substituted pyrazolyl ring nitrogens are involved in coordination to the tin with no sign of interaction of the cyclophosphazene ring nitrogens (scheme 1).

4. Conclusion

We have demonstrated the utility of substituted cyclotriphosphazenes for synthesis of organotin adducts. A variety of diorganotin(IV) adducts containing nitrogen donor ligands have antitumor activity [24, 25] and complexes of pyrazolyl substituted cyclophosphazenes with diorganotin compounds may be excellent candidates as antitumor drugs. Structural variety of organotin(IV) complexes and numerous possible co-substituents at the phosphazene backbone may allow synthesis of new organotin compounds with interesting structures and applications.

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