J. Iran. Chem. Soc., Vol. 7, No. 2, June 2010, pp. 371-375.

JOURNAL OF THE
Iranian
Chemical Society

New Organotin(IV) Complexes with a Potentially Multi-Site Ligand Based on the Cyclotriphosphazene Platform: Synthesis and Spectral Studies

T. Sedaghat*, A. Tarassoli and A. Mojaddami
Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran

(Received 24 April 2009, Accepted 11 June 2009)

A functionalized cyclotriphosphazene with four pyrazolyl substituents, $N_3P_3(MeNC_2H_4O)(dmp)_4$ where dmp = 3,5-dimethyl-pyrazole, has been synthesized and characterized. The reaction of this potentially multi-site coordinating cyclotriphosphazene with diorganotin(IV) dichlorides, SnR_2Cl_2 (R = Ph, Me), leads to dinuclear $[(SnPh_2Cl_2)_2\{N_3P_3(MeNC_2H_4O)(dmp)_4\}]$ (**1**) and mononuclear $[(SnMe_2Cl_2)\{N_3P_3(MeNC_2H_4O)(dmp)_4\}]$ (**2**) complexes. These new compounds were characterized by elemental analysis and IR, ^1H, ^{31}P and ^{119}Sn NMR spectroscopy. On the basis of these data, in the complex **1** pyrazolylcyclotriphosphazene acts as a bis-bidentate ligand and coordinates to two $SnPh_2Cl_2$ molecules *via* two geminal pyrazolyl nitrogen atoms. As for complex **2**, coordination to one $SnMe_2Cl_2$ molecule occurs through two nongeminally substituted pyrazolyl nitrogens. The ^{119}Sn NMR data are consistent with the increasing of coordination number of tin(IV) in solution.

Keywords: Organotin, Cyclotriphosphazene, Pyrazolylcyclotriphosphazene, Tin

INTRODUCTION

Cyclophosphazenes are an important class of inorganic heterocyclic compounds containing alternate phosphorus and nitrogen atoms. Research on these compounds has expanded very rapidly over the time and covered several applicative domains [1]. Among this family of compounds, hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) is the best known and a suitable starting material for the design of many cyclic and poly-phosphazenes. The ease of nucleophilic substitution reactions at the P-Cl bonds provides a route for creating a variety of phosphazenes and tuning their properties [2,3]. Recently cyclotriphosphazenes with exocyclic donor groups attached to the phosphazene skeletal phosphorus have been used as multimodal ligands in coordination chemistry.

Nowadays the ligating behavior of the various multi-site ligands based on cyclophosphazene platforms is an extremely interesting area [4-9]. An interest in these ligands comes from their ability to readily extend the small molecule chemistry to appropriate high polymers such as corresponding polyphosphazenes [2,10-13]. These metal-rich phosphazene polymers have potentially desirable properties as, for example, catalysis, conductors or drug delivery systems [6,14-16]. To date, many different types of cyclophosphazene-based ligands have been designed and metal ions ranging from first row transition metals to lanthanides have been involved to prepare coordination and organometallic compounds [4]. However, no attempts have been made to synthesize organotin complexes with these ligands.

Recently we reported the first organotin adducts based on cyclotriphosphazene scaffolds with exocyclic pyrazolyl substituents [17]. Pyrazolylcyclophosphazenes are versatile multimodal ligand systems which bind to metals *via* both the ring nitrogen atoms of the cyclophosphazene and the pyridine

*Corresponding author. E-mail: tsedaghat@scu.ac.ir

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nitrogen atoms of pyrazolyl rings [3]. In continuation of our studies, we have been interested in the behavior of other pyrazolylcyclophosphazenes in coordination to tin. Organotin(IV) complexes present an interesting variety of structural possibilities, so that a remarkable diversity in structure may be observed even when only a small change in chemistry exists [18,19]. In view of the antitumor activity of various diorganotin(IV) complexes especially with bidentate nitrogen donor ligands [20-22], complexes of pyrazolyl substituted cyclophosphazenes with diorganotin compounds may be excellent candidates affording potential applications as antitumor drugs.

In this research work, we report the synthesis of 2,2-spiro(N-methylethanolamino)-4,4,6,6-tetrakis-(3,5-dimethyl-pyrazolyl) cyclotriphosphazene (Fig. 1) as a nonsymmetric functionalized cyclotriphosphazene and investigate the coordination behavior of this multisite ligand with diorganotins.

EXPERIMENTAL

Materials and Methods

All chemicals and solvents were purchased from commercial sources. 2,2-Spiro(N-methylethanolamino)-4,4,6,6-tetrachlorocyclotriphosphazene, $N_3P_3(MeNC_2H_4O)Cl_4$, was prepared applying the literature method [23]. The IR spectra were obtained using an FT BOMEM MB102 spectrophotometer. The ^1H and ^{31}P NMR spectra were recorded with a Bruker Avance DPZ500 spectrometer at 500.130 MHz and 202.456 MHz using TMS and H_3PO_4 (85%) as references, respectively. The $^{119}Sn\{^1H\}$ NMR spectra were recorded with a Brucker Avance DPZ400 spectrometer at 149.211 MHz using $SnMe_4$ 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.

Synthesis of 2,2-Spiro(N-methylethanolamino)-4,4,6,6-tetrakis-(3,5-dimethylpyrazolyl)cyclotriphosphazene, $N_3P_3(MeNC_2H_4O)(dmp)_4$

3,5-Dimethylpyrazole (dmp) (0.59 g, 6.0 mmol) dissolved in benzene (5 ml) was added dropwise to a stirred solution of the $N_3P_3(MeNC_2H_4O)Cl_4$ (0.52 g, 1.5 mmol) in benzene (20 ml). Then triethylamine (6 mmol) was added and the solution

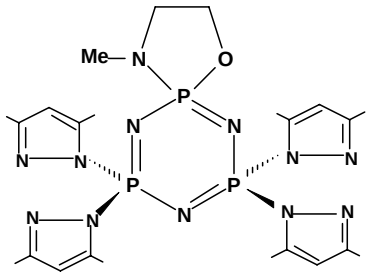

Fig. 1. Structure of $N_3P_3(MeNC_2H_4O)(dmp)_4$.

was refluxed for 18 h. The mixture was filtered to remove triethylamine hydrochloride. Evaporation of the solvent *in vacuo* afforded an oily residue which was powdered in diethylether (5 ml). The solid was washed with water (3 × 5 ml) and diethylether (3 × 4 ml) and dried under vacuum. Yield 0.50 g (87%), m.p.: 140-142 °C. FT-IR (KBr, cm^{-1}): ν(P=N), 1195, 1245. ^1H NMR ($CDCl_3$): δ 2.17 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.33 (s, 6H, CH_3), 2.67 (d, 3H, NCH_3, $^3J_{PH}$ = 12.0 Hz), 3.41 (dt, 2H, NCH_2, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 6.3 Hz), 4.37 (dt, 2H, OCH_2, $^3J_{PH}$ = 9.4 Hz, $^3J_{HH}$ = 6.3 Hz), 5.89 (s, 4H, CH). ^{31}P NMR ($CDCl_3$): δ = 2.7 (d, ^2J (P-N-P) = 60 Hz), 28.6 (tq, Pspiro, $^3J_{PH}$ = 11 Hz).

Synthesis of $[(SnPh_2Cl_2)_2\{N_3P_3(MeNC_2H_4O)(dmp)_4\}]$ (1)

A mixture of $SnPh_2Cl_2$ (0.25 g, 0.72 mmol) and $N_3P_3(MeNC_2H_4O)(dmp)_4$ (0.14 g, 0.24 mmol) in acetone was stirred for 48 h at room temperature. The solvent was evaporated *in vacuo* and the residue was washed with petroleum ether (3 × 5 ml) to remove excess $SnPh_2Cl_2$. Then the product was dried under vacuum. Yield 0.39 g (95% based on the ligand), m.p.: 118-120 °C. Anal. Calcd. for $C_{47}H_{55}N_{12}OP_3Cl_4Sn_2$ (%): C, 44.2; H, 4.3; N, 13.1. Found: C, 43.7; H, 4.4; N, 12.6. FT-IR (KBr, cm^{-1}): ν(P=N), 1195, 1244. ^1H NMR ($CDCl_3$): δ 2.00 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 2.29 (s, 6H, CH_3), 2.40 (s, 6H, CH_3), 2.53 (s, 3H, NCH_3), 3.05 (br, 2H, NCH_2), 4.19 (br, d, 2H, OCH_2, $^3J_{PH}$ = 12.8), 5.95 (s, 4H, CH), 7.40-7.44 [m, 6H, $H_{3,4,5}(SnPh_2)$], 7.98 (d, 4H, $^3J(^{119}Sn-^1H)$ = 100.0 Hz), ^{31}P NMR ($CDCl_3$): δ = -1.9 (d, ^2J (P-N-P) = 61 Hz), 0.83 (t, br, Pspiro). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ = -198.0 (br).

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Synthesis of [($SnMe_2Cl_2$){$N_3P_3(MeNC_2H_4O)(dmp)_4$}] (2)

Complex **2** was synthesized as described for compound **1** from $SnMe_2Cl_2$ (0.11 g, 0.504 mmol) and $N_3P_3(MeNC_2H_4O)(dmp)_4$ (0.102 g, 0.168 mmol) in chloroform and after 16 h reflux. Yield 0.080 g (60% based on the ligand), m.p.: 112-115 °C. Anal. Calcd. for $C_{25}H_{41}N_{12}OP_3Cl_2Sn$ (%): C, 37.1; H, 5.1; N, 20.8. Found: C, 36.5; H, 5.2; N, 20.3. FT-IR (KBr, cm^{-1}): ν(P=N), 1196, 1240; ν_{as}(Sn-C), 581; ν_s(Sn-C), 526. ^1H NMR ($CDCl_3$): δ 1.17 (s, 6H, $^2J(^{119}Sn\text{-}^1H)$ = 76.2 Hz), 2.15 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.28 (s,6H, CH_3), 2.35 (s, 6H, CH_3), 2.82 (s, 3H, NCH_3), 3.37 (s, br, 2H, NCH_2), 4.27 (s, br, 2H, OCH_2, $^3J_{PH}$ = 12.8), 5.95, 6.00 (s, 4H, CH). ^{31}P NMR ($CDCl_3$): δ -0.4 (d, ^2J (P-N-P) = 66 Hz), 2.8 (br, Pspiro). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ = -116.0 (sh).

RESULTS AND DISCUSSION

Pyrazolyl substituted cyclophosphazene, $N_3P_3(MeNC_2H_4O)(dmp)_4$, was prepared from the reaction of $N_3P_3(MeNC_2H_4O)(dmp)_4$ with 3,5-dimethylpyrazole (dmp) in the presence of triethylamine as HCl acceptor in benzene. Then the organotin(IV) adducts were synthesized by the reaction of $N_3P_3(MeNC_2H_4O)(dmp)_4$ with the excess of $SnPh_2Cl_2$ and $SnMe_2Cl_2$. Stoichiometry of the adducts was confirmed by the analytical data and the integrated ^1H NMR spectra were consistent with the empirical formulae. The nature of bonding was established by the spectroscopic investigations.

For the free ligand P=N stretching band was observed at 1195 and 1245 cm^{-1} which occured at the same position in the spectra of adducts without splitting, indicative of phosphazene ring nitrogen not participating in the coordination. It is known that metallation of the ring nitrogen atoms in cyclophosphazenes leads to a splitting of ring P-N stretching frequency. On the contrary, if the coordination is exclusively through exocyclic nitrogen atoms, the ring P-N stretching frequency remains largely unaffected [24,25]. The presence of both ν_s(Sn-C) and ν_{as}(Sn-C) in the IR spectrum of **2** is consistent with a nonlinear Me-Sn-Me configuration.

In the ^1H NMR spectra of complexes, the ratio of the integrals of the signals from protons of the ligand to those of the organic groups on the tin provides a reliable measure of the metal to ligand ratio in the synthesized adducts. The ^1H NMR spectrum of $N_3P_3(MeNC_2H_4O)(dmp)_4$ shows four peaks for the pyrazolyl methyl protons because of the two types of pyrazolyl rings. This is due to the spatial differences that arise as a result of the orientation of the spiro-$MeNC_2H_4O$ group with OCH_2 group on one side and the $MeNCH_2$ on the other side of the plane of the phosphazene ring. The ^1H NMR spectra of the adducts also show four peaks for the methyl groups which are slightly shifted with respect to the free ligand. These data are consistent with the coordination of the pyrazolyl nitrogen atoms to the metal and the equivalence of two $P(dmp)_2$ fragments in the complexes.

The signal at 7.98 ppm in the diphenyltin derivative is assigned to the *ortho* protons in the phenyl rings of the organometallic fragment. This signal has ^{119}Sn satellites with $^3J(^{119}Sn\text{-}^1H)$ larger than uncomplexed $SnPh_2Cl_2$ (81.7 Hz). The increasing of coupling constant indicates the higher coordination number of tin [26]. The highfield region in the spectrum of dimethyltin derivative shows signal at 1.17 ppm due to the methyl groups in the organometallic fragment. This signal once again has satellites due to coupling with tin. $^2J(^{119}Sn\text{-}^1H)$ for this compound (76.2 Hz) is larger than the original $SnMe_2Cl_2$ (68.7 Hz). The substitution of $^2J(^{119}Sn\text{-}^1H)$ in the Lockhart-Manders equation [27] (an empirical relationship between the coupling constant and C-Sn-C bond angle) affords a value of 126.3° for Me-Sn-Me angle in chloroform. This value is in agreement with nonlinear C-Sn-C in the solid state.

The ^{31}P NMR spectrum of $N_3P_3(MeNC_2H_4O)(dmp)_4$ is of the A_2X type with a doublet for $P(dmp)_2$ and a triplet of quartet for P(spiro) at 2.71 and 28.66 ppm (2:1), respectively. Similarly, the ^{31}P NMR spectra of complexes show a doublet and a triplet for $P(dmp)_2$ and P(spiro), respectively, both being shielded. The chemical shift of the phosphorus nucleus is influenced by several factors and the shifting of these peaks to both up and down fields upon complexation has been reported [28-30]. These data are consistent with the two equivalent $P(dmp)_2$ phosphorus nuclei in organotin adducts.

The $^{119}Sn\{^1H\}$ NMR spectrum of **1** shows one broad singlet at -198 ppm. This resonance appears significantly at lower frequency than that of $SnPh_2Cl_2$ (-27 ppm), which is in agreement with the increase in the coordination number of tin. On the basis of the chemical shift ranges proposed empirically

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for organotin(IV) derivatives, δ(^{119}Sn) moves upfield by 60-150 ppm with a change of the coordination number of tin from 4 to 5 and by 130-200 ppm from 5 to 6 [31,32]. Therefore it appears reasonable to assume that for the adduct **1** the coordination number of the tin atom is six in solution. However, the value of this resonance is at the low field limit of this range for six-coordinate adducts. Broadening and deshielding of this signal indicates that the adduct is partially dissociated in chloroform and the free and coordinated ligand are involved in the interchanging processes. Unlike the ^{119}Sn NMR spectrum, the ^{1}H NMR spectrum shows sharp lines. This observation indicates that the rate of exchange processes is between the time scales associated with ^{119}Sn NMR and ^{1}H NMR. Similar dissociation of organotin adducts with pyrazolyl ligands in chlorinated solvents has been also reported earlier [33-35,17]. The ^{119}Sn{^{1}H} NMR spectrum of **2** shows one sharp singlet at -116 ppm which is significantly at higher field than that of $SnMe_2Cl_2$ (+137 ppm). The chemical shift for this adduct is within the expected range for a coordination number of six.

CONCLUSIONS

On the basis of the analytical and spectral data, $N_3P_3(MeNC_2H_4O)(dmp)_4$ reacts with $SnPh_2Cl_2$ in 1:2 ratio and two geminally pyrazolyl nitrogens are coordinated to the tin, while the cyclotriphosphazene ring nitrogen atoms are not involved in the coordination to the tin (Fig. 2). The reaction of $N_3P_3(MeNC_2H_4O)(dmp)_4$ with $SnMe_2Cl_2$ occurs in 1:1 ratio and the two non-geminally pyrazolyl nitrogens are involved in the coordination to the tin (Fig. 3). However, there may be a weak interaction between the cyclophosphazene ring nitrogen and the metal atom.

In view of the structural variety of organotin(IV) complexes and numerous possible co-substituents at the phosphazene backbone, it was deemed worthwhile to synthesize variable organotin complexes based on cyclophosphazene scaffolds. We believe this work will open up new avenues to the study of the structural chemistry of these interesting compounds with potential surprising applications.

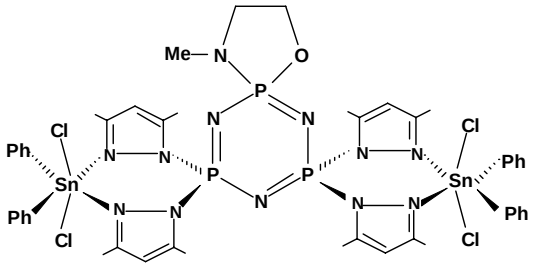

Fig. 2. The suggested structure for $[(SnPh_2Cl_2)_2\{N_3P_3(MeNC_2H_4O)(dmp)_4\}]$ (**1**).

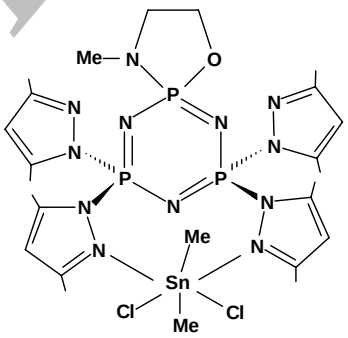

Fig. 3. The suggested structure for $[(SnMe_2Cl_2)\{N_3P_3(MeNC_2H_4O)(dmp)_4\}]$ (**2**).

ACKNOWLEDGMENTS

The financial support of this work by Shahid Chamran University, Ahvaz, Iran (Grant No. 1387) is hereby gratefully acknowledged.

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