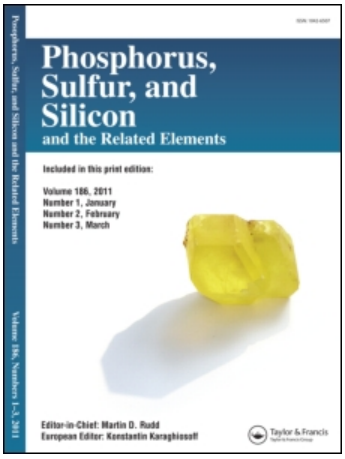

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Synthesis and Characterization of a Novel Phosph(V)azane-Tin(IV) Complex

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*The reaction of bis(anilino)phosphine oxide $(C_6H_5NH)_2P(O)H$, **1** with $Bu^n_2SnCl_2$ in the presence of an excess of triethylamine (TEA) in dry THF yields the novel N,O-bonded tin complex $Bu^n_2Sn[NPh(O)P(H)NPh(HNEt_3)]_2$, **2**. TEA is used as a base to deprotonate the phosphazane ligand and is separated as $Et_3NH^+Cl^-$, whereas $HTEA^+$ exists in the final product **2** and act as a charge balancing and H-bond structure–directing agent. This new compound has been fully characterized by means of IR, MS, and multinuclear (^1H, ^{31}P, and ^{119}Sn NMR) spectroscopy.*

Keywords ^{119}Sn NMR; bis(anilino)phosphine oxide; chelated compounds; substitution reactions; tin complexes

Phosphazanes are an established class of P–N compounds and are known for their stability and ease of synthesis.[1–3] The nature of the highly polar P–N bond with P- and N-donor sites makes a compound of this kind versatile in both coordination and organometallic chemistry.[4–7] Although a few phosphazanes have been used as ligands for main-group elements, their coordination chemistry is so far largely unexplored.[4,5] In particular the interaction between tin atom and P-containing ligands is not well established.[8]

Herein, bis(anilino)phosphine oxide, **1** is employed as a precursor which can form a dianionic ligand of type **3**.[5] We considered it of interest to synthesize a new organotin compound **2** containing this competitive P-, N-, and O-donor ligand.

These studies on the coordination chemistry of the phosph(V)azane oxide with both *soft* and *hard* coordination sites may help to unravel

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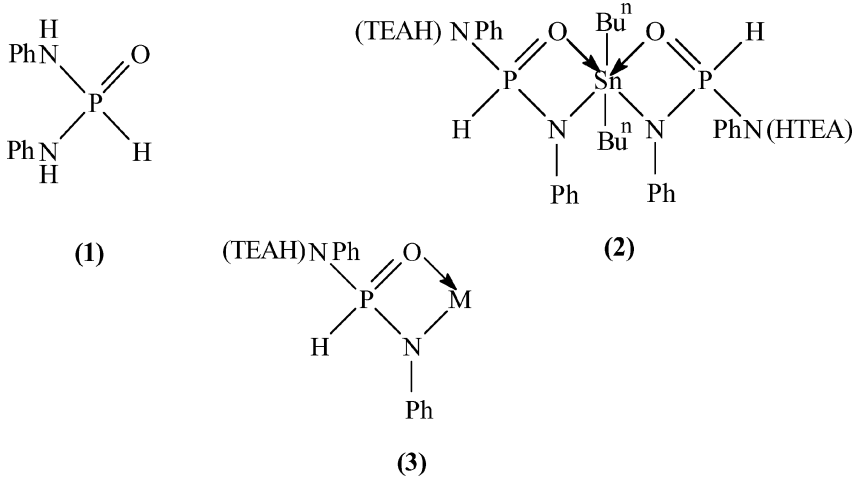

SCHEME 1

some interesting aspects of the mechanisms by which these complexes form and behave.

RESULTS AND DISCUSSION

$(C_6H_5NH)_2P(O)H$, **1** is prepared according to Eq. (1):

$$PCl_3 + 5PhNH_2 \rightarrow (PhNH)_2P(O)H + 3PhNH_3Cl \qquad (1)$$

The interaction of PCl_3 with $PhNH_2$ in a mole ratio of 1:5 results in the stepwise replacement of PhNH and finally formation of $(PhNH)_3P$, which is converted to $(PhNH)_2P(O)H$ upon addition of H_2O in a controlled hydrolysis reaction with the elimination of aniline (yield; 84%).

$(PhNH)_2P(O)H$ has already been obtained in excess of 60% yield by hydrolysis of $(PhNH)_3P$ or $[(PhNH)_2P]_2NPh$.[9] It seems that the direct hydrolysis of the product which is reported here (Eq. (1)) is more convenient and in a better yield than the previously reported one. The spectroscopic data are shown in the Experimental section.

In the ^{31}P NMR spectrum a signal at δ-4.07 occurs, which is in the region associated with P(V) oxide species. The relatively large $^1J_{PH}$ coupling constant (590–610 Hz) also is consistent with that of a directly bonded hydrogen. δ_P and $^1J_{PH}$ data agree well with those reported for $(C_6H_5NH)_2P(O)H$,[9] also characterized as the phosphine oxide. Further

characterization by IR and ^{1}H NMR spectroscopic techniques was made for **1**.

Compound **1** was allowed to react with di-n-butyltin dichloride in the ratio of 2:1 in presence of an excess of TEA to form $Bu^n_2Sn[(NPh)(O)P(H)NPh(HNEt_3)]_2$ **2** (Eq. (2)). The reaction was carried out at 25°C in dry THF and the resulting pale yellow product was extensively studied by MS and IR spectrometry as well as ^{1}H, ^{31}P, and ^{119}Sn NMR techniques (cf. Experimental section). It is notable that quantitative determination of chloride in **2** showed the lacking of chloride in the product.

$$2(C_6H_5NH)_2\,P(O)H + SnBu_2Cl_2 \xrightarrow[THF,\ 25^{\circ}C]{NEt_3}$$

$$SnBu_2[NPhP(O)HNPh(HNEt_3)]_2 + Et_3NH^+Cl^-$$

The P═O stretching vibrations in IR spectrum shifted by almost 100 cm^{-1} to lower frequencies is coordination as a result of decrease in the P═O bond order. The appearance of two new bands at 529 and 476 cm^{-1} which is assigned to Sn—O and Sn—N, respectively, supports the bonding of the central tin atom to oxygen and nitrogen. The IR spectrum also clearly showed the absence of the ligand N—H band at 3191 cm^{-1} and exhibited the presence of a new broad band centered at 3438 cm^{-1} which is attributed to protonated triethylamines.

The ^{1}H NMR spectrum of **2** shows that the butyl protons attached with tin as a complex multiplet are in the range of δ 0.85–1.60 ppm. The presence of $HTEA^+$ protons at 1.18, 3.04, and 10.28 ppm, with the absence of the characteristic NH signal of the ligand, suggested the occurrence of protonated $HTEA^+$ cations.

Triethylamine was applied to deprotonate NH groups of the ligand but based on the above IR and ^{1}H NMR evidences TEA exists in the final product **2**. It may be assumed that $HTEA^+$ cation has a charge-balancing role and is acting as a H-bond structure–directing agent. Similar situation is reported in the synthesis of conventional zeolites such as phosphates[10,11] and triethylammonium benzene-1,3,5- tricarboxylato (pyridine) zinc (II).[12]

In the $^{31}P\{^1H\}$ NMR spectrum of **2**, only one signal is seen at 0.87 ppm in the region associated with P(V) environment, which is flanked by Sn satellites ($^2J_{PSn}$ = 125 Hz). ^{31}P NMR coupled with proton displays one doublet ($^1J_{PH}$ = 633 Hz), which is consistent with the presence of the P—H bond. We obtained no evidence for the involvement of this bond during the course of reaction under the conditions of our experiment.

$^{119}Sn\{^{1}H\}$ NMR spectrum of **2** contains only one sharp singlet at −182 ppm indicating the formation of a single species, with the tin-119 resonance appearing at lower frequency than that of its dibutyltin dichloride precursor (+122 ppm in CH_2Cl_2).[13] The coordination number of six around the tin atom in **2** is also supported by its ^{119}Sn NMR chemical shift.[14–17]

The MS spectrum of **2** was recorded with FAB-positive source. The mass data are easily related to the proposed structure, with the normal loss of n-Bu, $HNEt_3^+$, and fragments arising from the Bu_2Sn entity and the ligand.

All attempts in growing single crystal of **2** suitable for X-ray crystallography were unsuccessful at this stage.

In conclusion, we have shown that the reaction of **1** with dibutyltin dichloride in the presence of an excess of triethylamine has exclusively led to the novel N,O-chelated complex **2**, as the only isolable product with $HTEA^+$ which is residing in the interlayer space and playing an important role as structural directing agent. More research work is currently in progress to develop these types of chemistry.

EXPERIMENTAL

All experiments were performed under nitrogen using standard Schlenk techniques. The solvents were purified and dried as indicated: Tetrahydrofurane was treated with KOH and freshly distilled twice from sodium before use, diethyl ether and n-hexane were treated with calcium chloride and distilled over sodium, aniline was distilled from CaH_2 and stored over molecular sieves, NEt_3 was distilled over $MgSO_4$, toluene was distilled over sodium, chloroform was distilled from P_4O_{10}, and phosphorus trichloride, $Bu^n_2SnCl_2$ and absolute ethanol were used as purchased from Merck Co.

NMR spectra were recorded on a Bruker Avance 500 MHz at ambient temperature. The chemical shifts were referenced to external TMS for ^{1}H NMR (500.13 MHz), H_3PO_4 85% for ^{31}P NMR (202.45 MHz) and Me_4Sn was used as an external standard in ^{119}Sn NMR (186.50 MHz). IR spectra were measured on a Bomem FT-IR spectrophotometer. FAB(+) mass spectrum was recorded using a JEOL SX-102A instrument.

Preparation of $(C_6H_5NH)_2P(O)H$ (1)

PCl_3 (5 mL, 0.057 mol) in 10 mL toluene was added slowly under N_2 to a stirred solution of $PhNH_2$ (26.02 mL, 0.285 mol) in 60 mL of dry

toluene at 0°C. The reaction mixture was warmed up slowly to 25°C. After 2 h water (0.057 mol) in an H_2O-$CHCl_3$ solution was added slowly to the mixture. Then the mixture was stirred at 80°C for another 2 h. $PhNH_3^+Cl^-$ was filtered off the hot reaction mixture. The solvent was removed and the white product was washed with cold toluene, then recrystallized from ethanol (yield 84%), mp 160°C.

IR (KBr): 3191 (s, NH), 3032–3092 (Ph), 2369 (m, sh, P—H), 1175 (P═O), 749–690 (CH) cm^{-1}. ^1H NMR (25°C, $(CD_3)_2$ SO, ppm): 7.50–6.50 (m, 10H, Ph), 8.09 (d, $^2J_{PNH} = 8.92$ Hz, 2H, NH), and 7.28 (d, $^1J_{PH} = 596$ Hz, 1H, P—H). ^{31}P NMR (25°C, $(CD_3)_2SO$, ppm): −4.07 (doublet of triplet, $^1J_{PH} = 612$ Hz, $^2J_{PNH} = 9.19$ Hz).

Synthesis of Bu^n_2 Sn [NPh (O)P(H) NPh ($HNEt_3$)]$_2$ (2)

$Bu^n_2SnCl_2$ (0.130 gr, 0.431 mmol) was dissolved in 10 mL of dry THF, and added dropwise to a mixture of $(C_6H_5NH)_2P(O)H$, **1**, (0.2 gr, 0.862 mmol) and 1 mL of NEt_3 (excess) in 50 mL of dry THF under N_2 at 25°C. Then the mixture was stirred for 48 h. $NEt_3H^+Cl^-$was filtered off. The solvent was removed and the pale yellow residue was washed twice with diethyl ether, hexane and 1 mL of cold THF and dried under vacuum for 24 h to yield essentially pure **2**. (yield 67%), mp 223°C dec.

IR (KBr): 3438 (broad, NH), 3053 (Ph), 2359 (m, sh, P—H), 1093 (P═O), 749–683 (Ph), 598 (Sn—C), 529 (SnP—O), 476 (Sn—N) cm^{-1}. MS: *m/z* 463, 269, 102, 57, 31.

^1H NMR (25°C, $(CD_3)_2SO$, ppm): 0.85 (t, $^3J_{HH} = 7.37$ Hz, 6H, Bu), 1.18 (t, $^3J_{HH} = 7.29$ Hz, 18H, $HNEt_3$), 1.25 (m, $^3J_{HH} = 7.29$ Hz, 4H, Bu), 1.56 (m, $^3J_{HH} = 7$ Hz, 4H, Bu), 1.60 (m, $^3J_{HH} = 7$ Hz, 4H, Bu), 3.04 (quartet, $^3J_{HH} = 6.64$ Hz, 12H, $HNEt_3$), 6.70 (d, $^1J_{PH} = 633$ Hz, 2H, P—H), 6.45–7.30 (m, 20H, Ph), 10.28 (s, broad, 2H, $HNEt_3$). $^{119}Sn\{^1H\}$ NMR (25°C, $(CD_3)_2SO$, ppm): −182 (s). $^{31}P\{^1H\}$ NMR (25°C, $(CD_3)_2SO$, ppm): 0.87(s, $^2J_{PSn} = 125$ Hz). ^{31}P NMR: 0.87 (d, $^1J_{PH} = 637$ Hz).

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