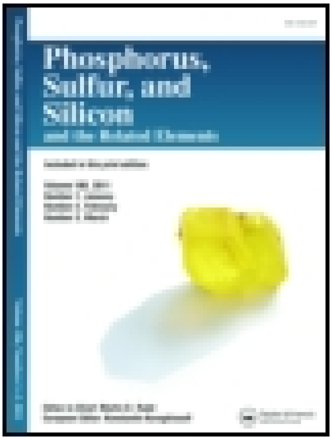

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New Phosph(V)azane Ligand as a Bidentate Donor in the Synthesis of One Novel Organometallic Tin(IV) Compound

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New Phosph(V)azane Ligand as a Bidentate Donor in the Synthesis of One Novel Organometallic Tin(IV) Compound

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The new ligand $\{[(C_6H_5NH)P(O)H](NC_6H_5)[(C_6H_5NH)P(O)H]\}$ *(**2**) was synthesized by heating bis(anilino)phosphine oxide* $(C_6H_5NH)2P(O)H$ *(**1**) at 110°C and elimination of aniline. The treatment of **2** with* $SnBu_2\ Cl_2$ *in the presence of triethylamine (TEA) in dry THF yielded the novel compound* $Bu^n_2Sn\{[Et_3NH(NPh)P(O)H](NPh)p(O)H]\}_2$ *(**3**) in which the phosphazane ligand acts as a bidentate ligand. The products have been characterized by means of elemental analysis, IR, MS, and multinuclear NMR* (^1H, ^{13}C, ^{31}P, *and* ^{119}Sn) *spectroscopy. The spectroscopic data are consistent with the bounding of the phosph(V)azane ligand through both oxygen and phosphorus atoms to Sn(IV) center in the final compound **3**. TEA is used as a base in order to deprotonate the phosphazane ligand and is separated as* $Et_3NH^+Cl^-$, *whereas* $HTEA^+$ *exists in the title product **3** and is acting as a charge balancing and H-bond structure directing agent.*

Keywords ^{119}Sn NMR; bidentatebidentate; charge charge balancing; H-bonding; phosph(V)azane; TEA

INTRODUCTION

Amino substituted phosphazanes, both phosph(III)azanes and phosph(V)azanes are potential intermediates for the synthesis of a wide variety of phosphazane compounds becaue of their N—H bond functionality.[1] In this way, phosphor(V)azans substituted with chalcogens (O, S, Se, or Te) have prompted inorganic chemists interest in studying their coordination chemistry.[2] We were interested in

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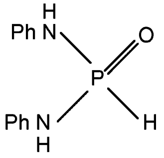
Address correspondence to Abbas Tarassoli, Chemistry Department, College of Science, Shahid Chamran University, Ahvaz, Iran. E-mail: tarassoli@scu.ac.ir studying those categories of these P(V)—N derivatives containing oxygen because of their ease of synthesis and stability.[3–6]

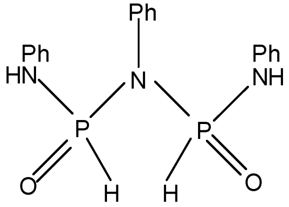
In our ongoing work, we have re-examined the formation reaction of bis(anilino)phosphine oxide ($(C_6H_5NH)_2P(O)H$ (**1**). This ligand has already been obtained by hydrolysis of $(PhNH)_2P$ which shown in Eq. 1.[7]

$$(PhNH)_3P + H_2O \longrightarrow (PhNH)_2\,P(O)H + PhNH_2 \qquad (1)$$



1

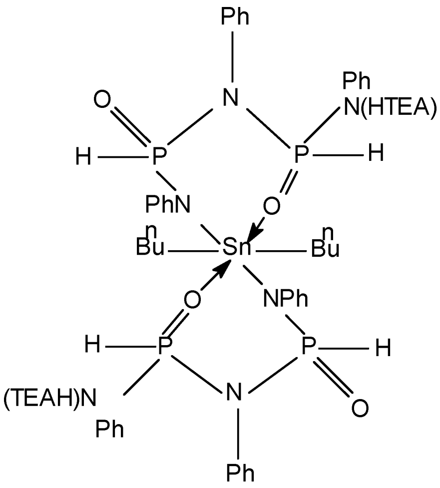
Oligomerization of **1** by thermal elimination of aniline yielded the new ligand $\{[(C_6H_5NH)P(O)H](NC_6H_5)[(C_6H_5NH)P(O)H]\}$ (**2**) that is reported here.



2

In order to investigate the coordinating ability and the behavior of this new ligand towards organotin(IV) moieties, **2** was lead let to react with $SnBu_2{}^nCl_2$ to obtain the new organometallic tin(IV) derivative **3**.

In recent years, there has been considerable interest in the coordination chemistry of Sn(IV) derivatives and continues to receive attention mainly due to the reactivity, interesting structural features and anticancer activity of some organotin(IV) compounds. For instance, they have been known as having a specific action on mitochondrial oxidative phosphorylation, and also, in recent years many triorgano- and diorganotin compounds have been tested for their in vitro activity against a large variety in vitro activity against a large variety of tumor lines.[8–14] Among the interesting tin-coordinative derivatives are phosphorus-based acids containing Sn—O bond.[13] Our oxygen oxygen-containing phosph(V)azane ligand that can bond to dibutyldichlorotin precursor through both donor atoms N and O simultaneously is as one of the attractive cases in this field in which the unprecedented compound **3** has been formed.



3

The resulting products were characterized by elemental analysis, as well as MS, IR and multinuclear NMR (^{1}H, ^{13}C, ^{31}P, ^{119}Sn) spectroscopy.

EXPERIMENTAL

Materials and Methods

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. $CHCl_3$ and CH_2Cl_2 were distilled from P_4O_{10}. Phosphorus trichloride and $Bu_2{}^{n}SnCl_2$ were used as purchased from Merck Co. NMR spectra were recorded on a Bruker Avance 500 MHz at ambient temperature. ^{1}H (500.13 MHz) and ^{13}C NMR (125.77 MHz) were recorded using DMSO as a solvent with TMS as an external standard for ^{1}H NMR and DMSO for ^{13}C NMR. ^{31}P spectra (202.45 MHz) and ^{119}Sn spectrum (195.50 MHz) were referenced to external H_3PO_4 85% and Me_4Sn respectively. IR spectra were measured on a Bomem FT-IR spectrophotometer. FAB(+) mass spectra were recorded using a JEOL SX-102A instrument. Elemental analysis (C, H, N) was performed by the microanalytical service of N.I.O.C. Research Institute of Petroleum Industry.

Preparation of $(PhNH)_2P(O)H$ (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 from the hot reaction mixture. The solvent was removed, and the white product was washed with cold toluene, then recrystallized from ethanol (yield 84%), m.p. 160°C. Anal. Calc. for $C_{12}H_{13}N_2PO$: C, 62.07; H, 5.64; N, 12.06%. Found: C, 62.09; H, 5.58; N, 12.02%.

Synthesis of {[(PhNH)P(O)H](NPh)[(PhNH)P(O)H]} (2)

$(PhNH)_2P(O)H$ (0.5 g, 2.115 mmol) was dissolved in 100 ml of dry toluene under N_2 atomsphere and then was refluxed at 110°C for 3 h. The mixture was filtered from the hot reaction mixture. The solvent was removed and the white product was washed with cold toluene. Then the remaining solid was recrystallized from CH_2Cl_2 (yield 52%), m.p. 165°C. Anal. Calc. for $C_{18}H^{19}N_3P_2O_2$: C, 58.22; H, 5.15; N, 11.31%. Found: C, 58.28; H, 5.12; N, 11.29%.

Synthesis of $Bu_2^nSn\{[Et_3NH(NPh)P(O)H](NPh)[(PhN)P(O)H]\}_2$ (3)

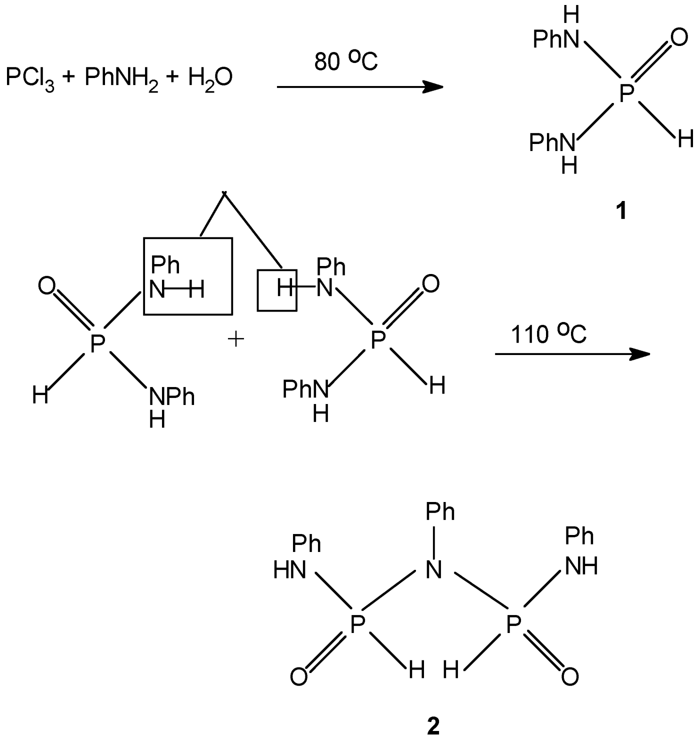
$SnBu_2{}^nCl2$ (0.081 gr, 0.269 mmol) was dissolved in 10 ml of dry THF, and added dropwise to a mixture of **2**, (0.2 g, 0.539 mmol) and 1 ml of NEt_3 (excess) in 50 ml of dry THF under N2 at 25°C. Then the mixture was stirred for 48 h. $NEt_3H^+Cl^-$ was filtered off. The solvent was removed and 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 **3** (yield 70.6%), m.p. 210°C dec. Anal. Calc. for $C_{56}H_{84}N_8P_4O_4Sn$: C, 57.1; H, 7.1; N, 9.5%. Found: C, 56.6; H, 6.7; N, 8.9%.

All attempts in growing single crystal of **3** suitable for X-ray crystallography were unsuccessful at this stage.

RESULTS AND DISCUSSION

In this workarticle, we prepared bis(anilino)phosphine oxide $(C_6H_5NH)_2P(O)H$ (**1**) according to an improved procedure with a better yield than that previously reported, one[15] that which is shown in scheme Scheme 1.

The new phosph(V)azane ligand **2** reported here was synthesized as shown in Scheme 1. As we have suggested, the reaction proceeds via an aniline elimination between two monophosphazane **1** by heating at 110°C to form the dinuclear phosphazane $\{[(C_6H_5NH)P(O)H](NC_6H_5)[(C_6H_5NH)P(O)H]\}$ (**2**). This compound is moderately soluble in a few solvents such as THF, DMSO, CH_2Cl_2 and slightly soluble in $CHCl_3$, EtOH and $(CH_3)_2CO$. It is very stable solid and no decomposition was observed, even when it was exposed to the air for one week. It was also stable in the above solvents.



SCHEME 1

In continuation, **2** was reacted with $SnBu^n_2Cl_2$ to obtain the unprecedented product **3** (Eq. 2) in the ratio of 2:1 in the presence of an excess of triethylamine (TEA). The reaction was carried out at 25°C in dry THF

TABLE I Infrared Data for Compounds 1–3

Compound	ν (HNEt3)	ν (N—H)	ν (P—H)	ν (P=O)	ν (Sn—O)	ν (Sn—N)
1		3191	2369	1175		
2		3334	2365	1150–1091		
3	3462		2355	1114–1071	563	433

and the pale-yellow product was obtained.

$$2\{[(PhNH)P(O)H](NPh)[(PhNH)P(O)H]\} + SnBu^n_2Cl_2 + NEt_3 \rightarrow$$
$$Bu^n_2Sn\{[Et_3NH(NPh)P(O)H](NPh)[(PhN)P(O)H]\}_2 + NEt_3H^+Cl^- \quad (2)$$

The adduct compound **3** is moderately soluble in THF and DMSO and slightly soluble in $CHCl_3$, EtOH and $(CH_3)_2CO$; and it is also is stable in when exposure exposed of to air for at least one day. The title compounds **1–3** were characterized by IR (Table I), Mass and multinuclear NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn) spectroscopy (Tables II–IV) and elemental analysis (C, H, N).

Infrared spectra data given in Table II indicate that ligand **2** shows strong bands in the regions 3334, 2365, 1635–1497, and 1150–1091 cm^{-1}, assigned to N—H, P—H, C=C and P=O vibrations, respectively. IR spectrum for **3** shows that the P=O stretching shifted by almost 30 cm^{-1} to the lower frequency upon coordination, as a result of decrease in the P=O bond order. The appearance of two new bands at 563 and 433 cm^{-1}, which are assigned to Sn—O and Sn—N, respectively, supports the bonding of central tin atom to oxygen and nitrogen. The IR spectrum also clearly showed the absence of the ligand N—H band at 3334 cm^{-1} and exhibited the presence of a new broad band centered at 3462 cm^{-1}, which is attributed to protonated triethylamines. These information proves the binding through N and O from dinuclear ligand to Sn(IV) center.

The mass spectrum of **3** was recorded with FAB positive source. The mass data (m/z 57, 102, 269, 155, 212, 459, 539) are easily related to the proposed structures, with the normal loss of n-Bu, $HNEt_3^+$, and fragments arising from the Bu_2Sn moities and the ligand.

Tables II–IV list ^1H, ^{13}C, ^{31}P, and ^{119}Sn chemical shifts and coupling constants for **1–3** compounds. The ^1H and ^{13}C NMR spectra of **2** and **3** confirmed the identity of the compounds, showing the expected integration and multiplicities (Table II). The ^1H NMR of **2** exhibits phenyl protons in the region of δ 6.62–7.33 ppm (complex multiplet, area 15) and P—H protons appears as a doublet at δ 6.71 ppm (doublet, area 2). $^1J_{PH} = 633$ Hz for **2** and $^1J_{PH} = 635$ Hz for **3** are characteristic coupling

TABLE II **^{1}H NMR Data of Compounds 1–3 in Me_2SO-d_6**

Compound	P—H	NPh	N—H	$HNEt_3$	Sn—Bu
1	7.28 (d, $^1J_{PH}$ = 596 Hz, 1H)	6.5–7.5 (m, 10H)	8.09 (d, $^2J_{PNH}$ = 8.92 Hz, 2H)		
2	6.71 (d, $^1J_{PH}$ = 633 Hz, 2H)	6.62–7.33 (m, 15H)	8.31 (broad 2H)		
3	7.05 (d, $^1J_{PH}$ = 635 Hz, 4H)	6.44–7.49 (m, 30H)		1.15 (t, ^3J = 7.24 Hz, 18H, CH_3)	0.85(t, $^3J_{HH}$ =7.21 Hz, 6H, CH_3, δ)
				2.97 (m, ^3J = 5.7 Hz, 12H, CH_2)	1.28 (m, $^3J_{HH}$ = 7.38 Hz, 4H, CH_2, γ)
				10.18 (broad, NH)	1.53 (m, $^3J_{HH}$ = 7.40 Hz, 4H, CH_2, β)
					1.64 (m, $^3J_{HH}$ = 7.49 Hz, 4H, CH_2, α)

constants for these types of compounds. The spectrum of **3** shows that the butyl protons attached to tin appear as a complex signal (multiplet, area 6) in the range of δ 0.85–1.64 ppm and the phenyl protons (multiplet, area 30) at δ 6.44–7.49 ppm.

The presence of $HTEA^+$ protons at 1.15, 2.97, and 10.18 ppm, together 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 on the basis of IR and ^{1}H NMR evidence it exists in the final product **3**. It may be assumed that $HTEA^+$ cation has a charge-balancing role and is acting as an H-bond structure-directing agent. Similar situation is reported

TABLE III **$^{13}C\{^1H\}$ NMR Data of Compounds 1–3 in Me_2SO-d_6**

Compound	Ph	$HNEt_3$	Sn—Bu
1	146.0 (Ci) 129.4 (C_o), 118.3 (C_m), 115.9 (C_p)		
2	146.7, 140.8, 130.1, 129.3, 123.8, 118.4, 117.8, 115.6		
3	146.6, 130.1, 129.3, 122.6, 121.2, 118.4, 117.4, 115.3	45.9 (CH_2), 39.5(CH_3)	9.3 (C_δ), 14.2 (C_γ), 26.0 (C_β), 28.0 (C_α)

TABLE IV $^{119}Sn\{^1H\}$, ^{31}P and $^{31}P\{^1H\}$ NMR data of compounds 1–3 in Me_2SO-d_6

Compound	δ (^{31}P) (ppm)	δ ^{31}P(^{1}H) (ppm)	δ (^{119}Sn) (ppm)
1	−4.07 $^2J_{PNH} = 9.11$ Hz $^1J_{PH} = 590$ Hz	−4.07	
2	1.34 $^1J_{PH} = 631$ Hz	1.38	
3	1.52 $^1J_{PH} = 637$ Hz	1.52	−218.22

in the synthesis of conventional zeolites such as phosphate[16−−17] and triethylammonium benzenne-1,3,5-tricarboxylato (pyridine) zinc(II).[18]

The $^{13}C^1H$ spectrum of **2** showed eight signals characteristic of terminal and bridging phenyl groups which appeared also in the spectrum of **3**. In addition, there are six signals that related to butyl and TEA groups in compound **3**. The $^{13}C^1H$ NMR results show that terminal phenyls are similar to those in compound **3**.

In the ^{31}P NMR spectrum of **2** only one signal occurs as a doublet at δ 1.34 ppm, which is in the region associated with P(V) oxide species. The relatively large $^1J_{PH}$ coupling constant (631 Hz) is also consistent with that of a directly directly-bonded hydrogen. In the $^{31}P\{^1H\}$ NMR spectrum of **3**, only one signal is seen at 1.52 ppm in the region associated with P(V) environment. ^{31}P NMR coupled with proton displays one doublet ($^1J_{P\text{–}H} = 637$ 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. It is interesting to note that, ^{31}P NMR data exhibit identical chemical environment for both phosphorus atoms and these data along with ^{13}C NMR data reveal that some type of mechanism is involved which equalize phosphorus atoms. We suggest that this is related to $HNEt_3$ moiety, which is being intrachangedinterchanged on nitrogen atoms in donor ligands.

$^{119}Sn\{^1H\}$ NMR spectrum of **3** contains only one sharp singlet at −218 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).[19] The coordination number of six around the tin atom in **3** is also supported by its ^{119}Sn NMR chemical shift.[12,20−23] The NMR spectra were also recorded in $CDCl_3$ as a non-coordinative solvent, and interestingly the results were the same with the data in DMSO and only the intensity of peaks were lower because of less solubility. The quantitative determination of chloride in **3** showed the lacking of chloride in the product.

CONCLUSION

It is concluded, from MS, IR and NMR studies that the new phosph(V)azane ligand $[(C_6H_5NH)P(O)H](NC_6H_5)[(C_6H_5NH)P(O)H]$ (**2**) in the presence of an excess of triethylamine acts as a bidentate ligand bonding through oxygen and nitrogen atoms to give $Bu^n{}_2Sn\{[Et_3NH(NPh)P(O)H](NPh)[(PhN)P(O)H]\}_2$ (3). This is the only isolable product with $HTEA^+$which is playing an important role by intrachanginginterchanging between nitrogen atoms.

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