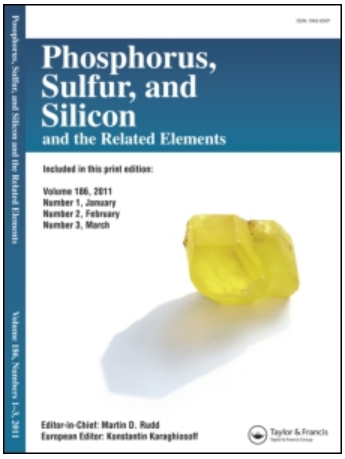

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Spirocyclic Phosphazene Complexes of Arsenic(III): Synthesis and Characterization

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Online publication date: 27 October 2010

To cite this Article Paul, Yash and Pandey, Sushil K.(2003) 'Spirocyclic Phosphazene Complexes of Arsenic(III): Synthesis and Characterization', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 1, 159 — 170
To link to this Article: DOI: 10.1080/10426500307773
URL: http://dx.doi.org/10.1080/10426500307773

Phosphorus, Sulfur and Silicon, 2003, Vol. 178:159–170

1042-6507/03 $12.00 + .00
DOI: 10.1080/10426500390170318

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SPIROCYCLIC PHOSPHAZENE COMPLEXES OF ARSENIC(III): SYNTHESIS AND CHARACTERIZATION

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(Received June 3, 2002; accepted July 27, 2002)

*A new acyclic phosphazene ligand, $[HN(PPh_2NPh)_2]$ (**A**) has been synthesized and characterized. Spirocyclic phosphazene-glycolate complexes of arsenic(III) with ligand (**A**) and $[HN(PPh_2NSiMe_3)_2]$ (**B**), having the general formula $[N(PPh_2NPh)_2\overline{AsOGO}]$ and $[N(PPh_2NSiMe_3)_2\overline{AsOGO}]$ (where G = $-CH_2CH_2-$, $-CHMeCH_2-$, $-CHMeCH_2CMe_2-$, $-CH_2CH_2CH_2-$, or $-CMe_2CMe_2-$) also have been synthesized by their reaction with chloro dioxarsolanes and -arsenanes in anhydrous medium. These moisture sensitive complexes are characterized by elemental analysis, IR, NMR (^1H, ^{13}C, and ^{31}P), and mass spectral data which have been discussed in relation to plausible structure for these arsenic(III) derivatives.*

Keywords: Dioxarsenane; dioxarsolane; heterometallacyclophosphazene; metallaphosphazene; phosphazene-glycolate

INTRODUCTION

Arsenic compounds find extensive use in agriculture as herbicides for weed control, such as MSMA (monosodium methylarsonate), DSMA (the disodium salt, Na_2MeAsO_3), and cacodylic acid. The use of organoarsenicals in medicine dates from the discovery in 1905 by H. W. Thomas that "atoxyl" cured experimental trypnosomiasis (e.g., sleeping sickness). A literature survey revealed that much work has been done on arsenic compounds containing As—O and As—S linkages,[1–7] but there is paucity of information on the arsenic derivatives of nitrogen

The authors are thankful to DST, New Delhi for financial assistance. Y. P. is grateful for JRF. We are also grateful to RRL, Jammu and CDRI, Lucknow for spectral studies.

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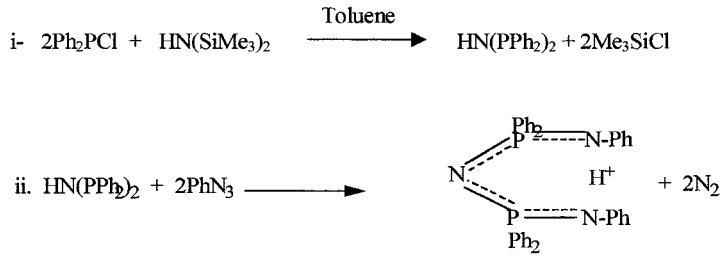
containing ligand. However, synthesis of Sb—N and Bi—N heterocycles has been reported.[8,9]

In the last five decades, a substantial amount of work has been carried out on phosphazene derivatives,[10–15] particularly by using $(NPCl_2)_3$. But the present work is motivated by a recent development of heterometallacyclophosphazenes in which one of the phosphorus atoms is substituted by another hetero atom. The phosphazene is isoelectronic to siloxane moiety that has shown many interesting aspects in view of their utility as inorganic polymer and ceramics. Similarly, metallacyclophosphazenes have shown interesting structural features and physical properties.[16–18] These compounds have been employed as precursors in inorganic polymer chemistry and also in generating new materials. In the past, we also have contributed to this field by synthesizing new heterometallacyclophosphazenes[19–22] of various elements, so it was thought worthwhile to insert arsenic into the P—N ring system. Here, we report on the synthesis of heterometallacyclophosphazene by using acyclic phosphazene ligand (**A**) and (**B**) with arsenic(III)glycolates. We have used chlorodioxarsolanes and -arsenanes as reacting species because they already have been well characterized and their application as starting materials serve many purposes. Moreover, it is expected that these phosphazene-arsolane/-arsenane derivatives may get their applications as precursors for metal oxides and materials for "high-tech" purposes.

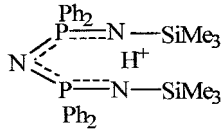
RESULTS AND DISCUSSION

The phenylated acyclic phosphazene ligand (**A**) was obtained in about 65–70% yield as pale yellow powder (m.p. 156–159°C) in a two step synthesis (i and ii). The reaction of chlorodiphenylphosphine with hexamethyldisilazene in 2:1 molar ratio in toluene formed compound $HN(PPh_2)_2$, which on treatment with phenylazide resulted in the formation of **A**.



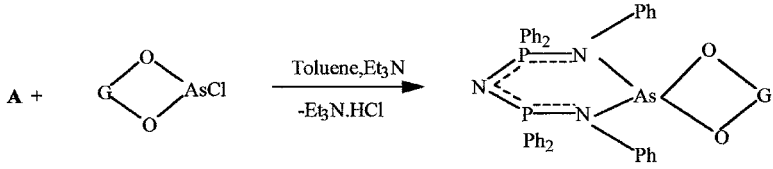
(A)

This bis-phenylated acyclic ligand (**A**) has shown the characteristic pattern in the IR spectrum. The bands for νP—N have been found in the region 1228–1176 cm^{-1} and νNH at 3345 cm^{-1}. The ^1H NMR has given a chemical shift as two multiplet in the region δ 6.6–7.9 ppm, the multiplet in high field region (δ 6.7–7.0 ppm) may be attributed to 20H of phenyl groups attached to the phosphorus while the multiplet toward low field region (δ 7.0–7.9 ppm) has been assigned to the 10H of phenyl groups attached to the nitrogen. The ^{31}P NMR has shown chemical shift as singlet at δ 7.1 ppm, which indicates the equivalence of phosphorus nuclei in the molecule. The mass spectrum of ligand (**A**) has revealed the presence of molar (M^+) ion at m/z 566 (20%) [M-H^+], suggesting the monomeric nature of ligand. Another ligand, bis-silylated acyclic phosphazene (**B**), also used here for complexation, was prepared as described in the literature.[23–24]

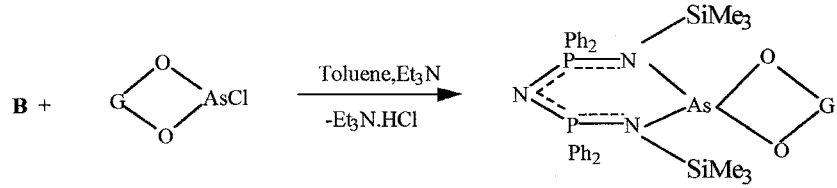


(B)

Various chlorodioxarsolanes and -dioxarsenanes, $\overline{OGO}AsCl$, have reacted with ligand (**A**) and (**B**) in toluene in equimolar ratio which resulted spirocyclic phosphazene-arsolane/-arsenane complexes.



[*Where* G = -CH_2CH_2-(**1**), -$CHMeCH_2$-(**2**), -$CHMeCH_2CMe_2$-(**3**), -$CH_2CH_2CH_2$-(**4**) or –CMe_2CMe_2-(**5**)].



[*Where* G= -CH_2CH_2-(**6**), -$CHMeCH_2$-(**7**), -$CH_2CH_2CH_2$-(**8**), -CMe_2CMe_2-(**9**) or -$CHMeCH_2CMe_2$-(**10**)]

TABLE I Synthetical and Analytical Data of Compounds $[N(PPh_2NPh)_2AsOGO]$ and $[N(PPh_2NSiMe_3)_2AsOGO]$

S. no.	Reactants: *$HN(PPh_2NR)_2$ (g)	Reactants: $OGOAsCl$ (g)	Product (Yield %)	Physical state	Analysis of As (%) found (calcd.)
1	1.36 (2.39 mmol)	OCH_2CH_2OAsCl 0.41 (2.39 mmol)	$[N(PPh_2NPh)_2AsOCH_2CH_2O]$ (78)	Yellow Viscous	10.45 (10.68)
2	1.46 (2.57 mmol)	$OCH(CH_3)CH_2OAsCl$ 0.47 (2.57 mmol)	$[N(PPh_2NPh)_2AsOCH(CH_3)CH_2O]$ (97)	Yellow Viscous	11.02 (10.47)
3	1.14 (2.01 mmol)	$OCH(CH_3)CH_2CMe_2OAsCl$ 0.45 (2.01 mmol)	$[N(PPh_2NPh)_2AsOCH(CH_3)CH_2CMe_2O]$ (95)	Yellow Viscous	9.71 (9.89)
4	1.13 (1.99 mmol)	$OCH_2CH_2CH_2OAsCl$ 0.37 (1.99 mmol)	$[N(PPh_2NPh)_2AsOCH_2CH_2CH_2O]$ (88)	Yellow Viscous	9.08 (10.47)
5	0.94 (1.6 mmol)	$OCMe_2CMe_2OAsCl$ 0.38 (1.6 mmol)	$[N(PPh_2NPh)_2AsOCMe_2CMe_2O]$ (92)	Yellow Viscous	9.10 (9.89)
6	1.34 (2.39 mmol)	OCH_2CH_2OAsCl 0.41 (2.39 mmol)	$[N(PPh_2NSiMe_3)_2AsOCH_2CH_2O]$ (84)	Light yellow Semi-solid	10.75 (10.81)
7	0.90 (1.61 mmol)	$OCHCH_3CH_2OAsCl$ 0.30 (1.61 mmol)	$[N(PPh_2NSiMe_3)_2AsOCHCH_3CH_2O]$ (73)	Light yellow Semi-solid	10.59 (11.51)
8	1.02 (1.82 mmol)	$OCH_2CH_2CH_2OAsCl$ 0.33 (1.82 mmol)	$[N(PPh_2NSiMe_3)_2AsOCH_2CH_2CH_2O]$ (89)	Light yellow Semi-solid	10.40 (10.59)
9	1.50 (2.68 mmol)	$OCMe_2CMe_2OAsCl$ 0.60 (2.68 mmol)	$[N(PPh_2NSiMe_3)_2AsOCMe_2CMe_2O]$ (83)	Yellow Semi-solid	9.61 (10.53)
10	1.0 (1.78 mmol)	$OCH(CH_3)CH_2CMe_2OAsCl$ 0.40 (1.78 mmol)	$[N(PPh_2NSiMe_3)_2AsOCH(CH_3)CH_2CMe_2O]$ (85)	Yellow Semi-solid	9.53 (9.89)

*R = —Ph (**1–5**) or —$SiMe_3$ (**6–10**).

TABLE II IR Spectral Data of Compounds $[N(PPh_2NPh)_2\overline{AsOGO}]$ and $[N(PPh_2NSiMe_3)_2\overline{AsOGO}]$ (in cm^{-1})

S. no.	Compound	νP═N	νP─N─P (Ring vibration)	νC─O	νAs─O	νAs─N
1	$[N(PPh_2NPh)_2\overline{AsOCH_2CH_2O}]$	1610, vs	1130–1270	1030, s	640, w	520, w
2	$[N(PPh_2NPh)_2\overline{AsOCH(CH_3)CH_2O}]$	1610, vs	1230–1120	1030, m	700, s	530, m
3	$[N(PPh_2NPh)_2\overline{AsOCH(CH_3)CH_2CMe_2O}]$	1600, s	1270–1130	1030, m	590, m	510, m
4	$[N(PPh_2NPh)_2\overline{AsOCH_2CH_2CH_2O}]$	1600, s	1290–1120	1030, m	600, m	520, m
5	$[N(PPh_2NPh)_2\overline{AsOCMe_2CMe_2O}]$	1600, s	1260–1120	1035, m	700, m	510, m
6	$[N(PPh_2NSiMe_3)_2\overline{AsOCH_2CH_2O}]$	1610, s	1240–1130	1040, m	650, m	520, m
7	$[N(PPh_2NSiMe_3)_2\overline{AsOCHCH_3CH_2O}]$	1610, s	1230–1120	1030, m	550, w	510, m
8	$[N(PPh_2NSiMe_3)_2\overline{AsOCH_2CH_2CH_2O}]$	1600, m	1280–1110	1020, s	610, m	510, w
9	$[N(PPh_2NSiMe_3)_2\overline{AsOCMe_2CMe_2O}]$	1600, s	1260–1120	1030, s	630, m	500, w
10	$[N(PPh_2NSiMe_3)_2\overline{AsOCH(CH_3)CH_2CMe_2O}]$	1610, s	1260–1130	1040, s	630, m	490, m

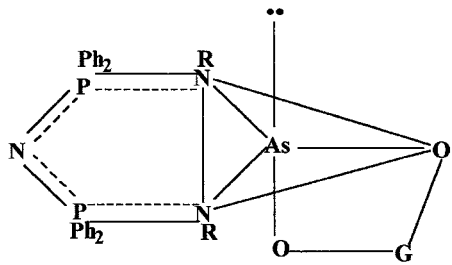
s = strong; vs = very strong; m = medium; and w = weak.

These compounds obtained almost in quantitative yield, soluble in common organic solvents, and appear to be susceptible to moisture but can be kept unchanged for a long time under a dry and nitrogen atmosphere. The derivatives of ligand (**A**) are yellow viscous while the derivatives of ligand (**B**) are light yellow semi-solids. They were obtained as sufficiently pure for spectral and other studies. The synthetic and analytical data are given in Table I.

The mass spectra of few represented compounds such as (**7**) and (**8**) have shown molar ion (M^+) peak at m/z 706 (14%) beside the usual fragmentation pattern that occurs for phosphazene complexes. The peak for M^+-$\overline{OGOA}$s fragement was found at m/z 149, 11% in complex (**7**) and 41% in complex (**8**). The base peak for both cases was occurring for phenyl group at m/z 77 (100%). The characteristic absorptions for νP═N bonds were found in the region 1290–1100 cm^{-1} in the IR spectra of these complexes which are in accordance with the symmetric nature of νP–N–P system. Further, disappearance of νN-H (3345 cm^{-1}) and appearance of νAs-N in the region 520–490 cm^{-1} is suggestive of formation of bond between arsenic and nitrogen. The νC–O and νAs–O occurs in the region 1040–1020 cm^{-1} and 700–590 cm^{-1}, but νC–O found with slight shift. All the relevant IR data are given in the Table II. ^{1}H NMR chemical shift of these complexes were recorded in $CDCl_3$. The signal for –NH proton in the region δ 4.5–5.0 ppm have not been observed in all these compound. The phenyl protons for –PPh_2 and –NPh in the complexes with ligand (**A**) are found in the region δ 6.7–7.0 ppm and δ 7.2–8.1 ppm respectively, as two multiplet, while in the complexes with ligand (**B**), the protons for –PPh_2 found as one multiplet in the region δ 6.9–8.0 ppm. The chemical shift for –NPh and –$NSiMe_3$ have been observed in the ^{1}H NMR spectra of these compounds. However, it was observed earlier that in some cases the –$SiMe_3$ has been substituted.[9.25] Various protons of glycol moiety have appeared in their usual pattern but with a slight chemical shift toward the downfield, which is indicative of complexation. The ^{13}C NMR spectra have shown the characteristic chemical shift with slight downfield shift compared to the phosphazene ligands, dioxarsolanes, and dioxarsenanes. In the cases of ligand (**A**) derivatives, signals for phenyl carbons were observed as multiplets in the range δ 127–138 ppm and the carbons of trimethylsilyl were found in the region δ 8.0–8.5 ppm. The derivatives of ligand (**B**) have shown three multiplet for phenyl carbons, the signal for –NPh appearing as one multiplet in the region δ 115–125 ppm and for –PPh_2 two multiplet in the region δ 127–132 ppm. The other carbons of glycoxy moiety were present in their characteristic range (Table III). In ^{31}P NMR, one singlet was found in the complexes of both ligand (**A**) and (**B**) with a downfield

shift in the range δ 7–12 ppm and δ 9–10 ppm. The singlet was observed in the region δ 14.4–18.9 ppm and δ 20.8 to δ 21.0 ppm for the complexes with ligand (**A**) and (**B**) respectively. The occurrence of one singlet with downfield shift in ^{31}P NMR compare to ligands, (**A** = δ 7.1 ppm and **B** = δ 11.1 ppm), showing the equivalence of phosphorus nuclei in the molecule and the formation of As—N bond. The ^{1}H, ^{31}P, and ^{13}C NMR data of all the compounds are summarized in Table III respectively.

Since, we could not get the crystals in order to get them analyzed by x-ray, so we relied on the basis of the above observations and a comparison of relevant data from literature to propose a plausible geometry for these complexes. These acyclic phosphazene ligands behaved in bidentate manner in most of the cases.[17–23] Analogus cyclophosphazene antimony(III) complex also has shown a bidentate mode of bonding by two terminal nitrogen atoms with antimony as determined by single crystal x-ray diffraction analysis (Sb—N bond lengths are 202.7 pm and 203.2 pm).[25] As(III) is not a strong Lewis acid, therefore it may presumed that the anisobidentate mode of bonding exists in these complexes with one sigma bond (Sb—N) and a very weak electrostatic attraction to the second nitrogen atom. Considering the above details, a distorted Ψ-trigonal bipyramidal geometry around arsenic (lone pair of electron at equatorial position) may be suggested.



Ψ - Trigonal bipyramidal geometry of spirocyclic phosphazene-glycolate complexes (where G = -CH_2CH_2-(1), -$CHMeCH_2$-(2), -$CHMeCH_2CMe_2$-(3), -$CH_2CH_2CH_2$-(4) or –CMe_2CMe_2-(5) and R= -Ph or –$SiMe_3$).

EXPERIMENTAL

These heterometallacyclophosphazenes of As(III) are extremely susceptible to moisture. Therefore, stringent precautions have been taken to maintain anhydrous conditions during the syntheses of these

TABLE III NMR Spectral Data of Complexes $[N(PPh_2NPh)_2\overline{AsOGO}]$ and $[N(PPh_2NSiMe_3)_2\overline{AsOGO}]$

S. no.	Compound	^{1}H chemical shift (δ ppm)	^{31}P chemical shift (δ ppm)	^{13}C chemical shift (δ ppm)
1	$[N(PPh_2NPh)_2\overline{AsOCH_2CH_2O}]$	3.62, s, 4H (—OCH_2) 7.04–7.64, m, 20H (—PPh_2) 7.74–8.12, m, 10H (—NPh)	14.47, s	60.50, s (—$CH_2CH_2^-$) 120–127, m (—NPh) 128–134, m (—PPh_2)
2	$[N(PPh_2NPh)_2\overline{AsOCH(CH_3)CH_2O}]$	0.90–1.16, d, 3H(—Me) 3.16–3.60, m, 2H (—OCH_2) 3.70–3.90, m, 1H (—OCH) 7.14–7.70, m, 20H (—PPh_2) 7.80–8.08, m, 10H (—NPh)	14.51, s	20.50, s (—CH_3) 46.85, s (—OCH_2) 66.00, s (—OCH) 120–127, m, (—NPh) 128–134, m (—PPh_2)
3	$[N(PPh_2NPh)_2\overline{AsOCH(CH_3)CH_2CMe_2O}]$	1.00–1.42, t, 9H (—Me) 3.60, s, 2H (—CH_2) 4.0–4.4, m, 1H (—OCH) 7.16–7.64, m, 20H (—PPh_2) 7.80–8.08, m, 10H (—NPh)	15.16, s	23.25, s (—Me_2) 28.08, d (—CH_3) 34.90, s (—CH_2) 44.86, d (—OCH_2) 120–127, m (—NPh) 128–134, m (—PPh_2)
4	$[N(PPh_2NPh)_2\overline{AsOCH_2CH_2CH_2O}]$	3.20, m, 2H (—CH_2) 3.68–3.92, t, 4H (—OCH_2) 7.12–7.64, m, 20H (—PPh_2) 7.80–8.08, m, 10H (—NPh)	15.13, s	33.50, s (—CH_2) 61.10, s (—OCH_2) 120–127, m (—NPh) 128–134, m (—PPh_2)
5	$[N(PPh_2NPh)_2\overline{AsOCMe_2CMe_2O}]$	1.20, s, 12H (—CMe_2) 6.80–7.60, m, 20H (—PPh_2) 7.68–8.00, m, 10H (—NPh)	18.98, s	25.50, s (Me_2) 79.58, d (—OC) 120–127, m (—NPh) 128–134, m (—PPh_2)
6	$[N(PPh_2NSiMe_3)_2\overline{AsOCH_2CH_2O}]$	0.14, s, 18H (—$SiMe_3$) 3.62, s, 4H (—OCH_2) 7.00–8.08, m, 20H (—Ph)	20.94, s	8.25, s (—$SiMe_3$) 61.10, s (—OCH_2) 127–138, m (—PPh_2)

7	$[N(PPh_2NSiMe_3)_2\overline{AsOCHCH_3CH_2O}]$	0.12, s, 18H (—$SiMe_3$) 3.12–3.50, m, 2H (—OCH_2) 3.60–3.80, m, 1H (—OCH) 7.12–7.60, m, 20H (—PPh_2) 7.75–8.08, m, 10H (—NPh)	20.94, s	8.48, s (—$SiMe_3$) 18.76, s (—CH_3) 45.50, s (—OCH_2) 65.60, s (—OCH) 127–138, m (—PPh_2)
8	$[N(PPh_2NSiMe_3)_2\overline{AsOCH_2CH_2CH_2O}]$	0.10, s, 18H (—$SiMe_3$) 3.62–3.68, m, 2H (—CH_2) 4.00–4.52, m, 4H (—OCH_2) 6.96–8.04, m, 20H (—Ph)	20.95, s	8.42, s (—$SiMe_3$) 34.90, s (—CH_2) 60.80, s (—OCH_2) 127–138, m (—PPh_2)
9	$[N(PPh_2NSiMe_3)_2\overline{AsOCMe_2CMe_2O}]$	0.10, s, 18H (—$SiMe_3$) 1.32, s, 12H (—CMe_2) 7.04–7.96, m, 20H (—Ph)	20.85, s	8.45, s (—$SiMe_3$) 24.55, s (Me_2) 78.60, d (—OC) 127–138, m (—PPh_2)
10	$[N(PPh_2NSiMe_3)_2\overline{AsOCH(CH_3)CH_2CMe_2O}]$	0.12, s, 18H (—$SiMe_3$) 1.08–1.40, s, 9H (—CMe) 3.5–4.5, t, 1H (—OCH) 6.96–8.00, m, 20H (—Ph)	21.00, s	8.42, s (—$SiMe_3$) 23.25, s (Me_2) 28.02, d (—CH_3) 34.90, s (—CH_2) 44.86, d (—OCH) 127–138, m (—PPh_2)

[a] NMR in $CDCl_3$, s = singlet, d = doublet, t = triplet, and m = multiplet.

complexes as well as ligands. All the syntheses and subsequent manipulations were conducted under an inert atmosphere and anhydrous conditions using standard Schelenk techniques, solvents were dried prior to use and were kept under nitrogen atmosphere. The bis-silylated phosphazene ligand (**B**),[24] arsolanes and arsenanes[26–27] were synthesized by using literature methods. Phenyl azide was prepared by diazotization reaction as described in the literature.[28] The glycols, triethylamine were supplied commercially, but distilled prior to use. The percentage of arsenic in the complexes was determined by iodometric titration.[29]

IR spectra were recorded in KBr mulls on Perkin Elemer-377 spectrophotometer in the range 4000–400 cm^{-1}. The ^{1}H and ^{13}C NMR were recorded on a Jeol FX90 Q MHz using TMS as external reference, ^{31}P-NMR were done on BurkerDRX 300(120 MHz) using 85% H_3PO_4 as external reference. The mass spectrophotometer analysis (EI) was carried out on ESQUIRE-3000 (BRUKER-DALTONICS) using LC-MS n technique.

Synthesis of [HN(PPh$_2$NPh)$_2$]

To a toluene solution of 3.42 g (21.1 mmol) of hexamethyldisilazene, $HN(SiMe_3)_2$ was added drop wise a toluene solution of Ph_2PCl 9.33 g (42.3 mmol) under nitrogen atmosphere. The contents were stirred at 80°C for 3 h and the thus formed trimethylsilylchloride (Me_3SiCl), was distilled off under reduced pressure. After removal of trimethylsilylchloride, 5.03 g (42.3 mmol) of phenyl azide (PhN_3) was added drop wise at 60°C which resulted in the evolution of nitrogen gas. The contents were refluxed till the evolution of nitrogen gas (about 2 h). Finally, the solvent was removed under vacuo, when a pale-yellow solid was obtained. Washing with n-hexane can further purify this. Yield 7.2 g (65%), m.p. 156–159°C. IR (KBr, cm^{-1}): 3345 m, 3050 m, 1600 s, 1580 vs, 1485 vs, 1430 s, 1315 vs, 1280 vs, 1260 vs, 1220 vs, 1170 s, 1040 s, 1020 s, 990 s, 935 s, 750 vs, 720 vs, 695 vs, 595 s, 545 s, 520 vs and 500 s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.9–6.6, m, –Ph (30H) and δ 5.0–4.5,s br., –NH (1H). ^{31}P NMR ($CDCl_3$, ppm): δ 7.1, s.

Synthesis of Complexes of Arsenic(III), [N(PPh$_2$NR)$_2$$\overline{\text{AsOGO}}$] (R = –Ph/–SiMe$_3$)

Chloro dioxarsolanes/arsenanes, $\overline{\text{OGO}}$AsCl, in toluene was added dropwise to a toluene solution of phenylated (**A**) or bis-silylated (**B**) phosphazene ligand, [$HN(PPh_2NR)_2$]; R = –Ph(**A**) and –$SiMe_3$(**B**), in an equimolar (1:1) ratio containing a stoichiometric amount of triethylamine at room temperature. An immediate reaction takes place which

is indicated by the formation of white precipitates of triethylaminehydrochloride, $Et_3N{\cdot}HCl$, and the contents were also turned to yellow. The reaction mixture was continuously stirred at moderate temperature (about 60°C) for 2–4 h for the sake of completion. Using an alkoxy funnel triethylaminehydrochloride was filtered. The solvent was removed under vacuo, which yielded the products quantitatively. The complexes were yellow viscous products incase of ligand (**A**) while light yellow semi-solid for ligand (**B**).

This methodology was applied to synthesize all the complexes using stoichiometric weights except for a slight difference in stirring time. The relevant synthetic and analytical data for all the complexes are given in Table I.

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