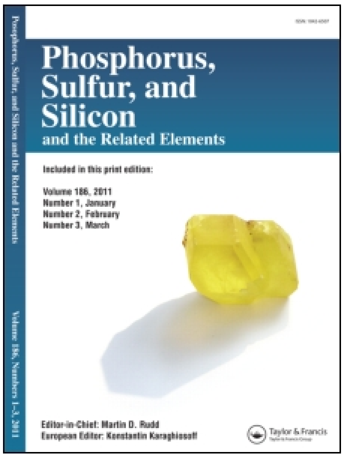

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CYCLOMETALLAPHOSPHAZENES OF ANTIMONY(III) AND BISMUTH(III): SYNTHESIS AND CHARACTERIZATION

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To cite this Article Pandey, Sushil K.(1996) 'CYCLOMETALLAPHOSPHAZENES OF ANTIMONY(III) AND BISMUTH(III): SYNTHESIS AND CHARACTERIZATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 113: 1, 255 — 258
To link to this Article: DOI: 10.1080/10426509608046396
URL: http://dx.doi.org/10.1080/10426509608046396

Phosphorus, Sulfur, and Silicon, 1996, Vol. 113, pp. 255–258
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CYCLOMETALLAPHOSPHAZENES OF ANTIMONY(III) AND BISMUTH(III): SYNTHESIS AND CHARACTERIZATION

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Dedicated to Professor H. W. Roesky on the occasion of his 60th birthday

(Received September 14, 1995; in final form February 2, 1996)

Cycloantimony(III) and bismuth(III) phosphazenes have been synthesized by the reactions of acyclic mono-(**1**), bis-(**2**) and tris-(**3**) silylated phosphazene ligands with $Sb(OOCMe)_3$ (**4**) and Bi(O)OOCMe (**5**). The reactions of (**2**) with (**4**) and (**3**) with (**4**) yielded cyclic compound $HN[P(NMe_2)_2N]_2$-SbOOCMe (**6**) and $N[P(Ph)_2NSiMe_3]_2Sb(OOCMe)_2$ (**7**), respectively. The compound $HN[P(NMe_2)_2N]_2BiOOCMe$ (**8**) and $Me_3SiN[P(NMe_2)_2N]_2BiOOCMe$ (**9**) have been obtained by reacting (**1**) with (**5**) and (**2**) with (**5**). These solid and fairly soluble compounds were characterized by elemental analysis, IR, mass and NMR spectroscopic studies.

Key words: Cyclometallaphosphazene, mono-, bis- and tris-silylated, X-ray.

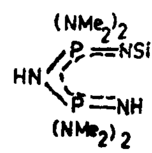
INTRODUCTION

We previously reported on the synthesis of mono-silylated phosphazene ligand (**1**) and an isomeric cycloantimony(III) phosphazene complex.[1] However, the success was limited only to an antimony(III) cyclophosphazene complex. The phosphazene-metal complexes exhibits some interesting facets concerning their structural and physical properties.[2,3] We have also investigated such species extensively in recent years.[4–8] It is evident from the literature that the development of cyclometallaphosphazene chemistry has created a versatile field of research.[9,14] A careful literature survey shows the paucity of informations on such derivatives particularly with antimony(III) and bismuth(III).[10–12]

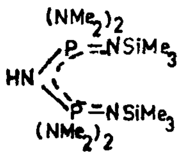
In contrast, the derivatives having Sb—O and Sb—S have been synthesized in recent years.[11–13] The synthesis and characterization of cycloantimony(III) and bismuth(III) phosphazene is reported in this paper by using $Sb(OOCMe)_3$ (**4**) and Bi(O)OOCMe (**5**) as starting materials.

RESULTS AND DISCUSSION

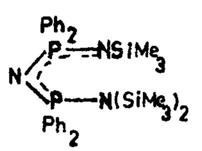
The following mono-(**1**), bis-(**2**) and tris-(**3**) silylated ligands have been used during the present course of investigations:



(1)

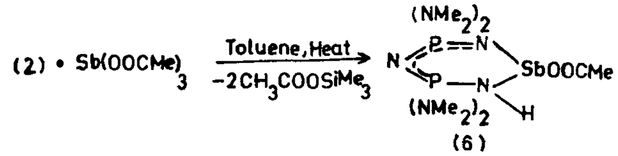


(2)



(3)

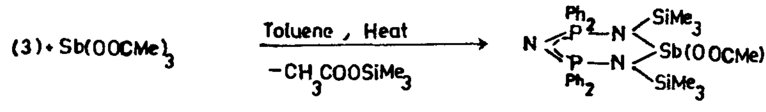
The compound (6) was obtained when the bis-silylated ligand (2) reacted with (4) in a 1:1 molar ratio in toluene. The cyclization takes place with the elimination of two moles of $MeCOOSiMe_3$ which can be easily removed in vacuo.



(6)

The compound (6) is a white solid and soluble in polar organic solvent. The IR spectrum shows the presence of νC═O frequency at 1690 cm^{-1}. The ^1H NMR show the absence of the —$SiMe_3$ group which indicates the elimination of two moles of $MeCOOSiMe_3$. The acetate protons found at δ1.90 ppm. In the ^{31}P NMR, two singlets have been found at δ20.8 ppm and δ27.35 ppm for the phosphorus nuclei in the molecule.

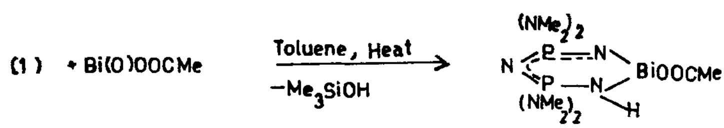
When the tris-silylated ligand (3) reacted with (4) in a 1:1 molar stoichiometry in toluene, the elimination of only one mole of $MeCOOSiMe_3$ group has taken place and the cyclic compound (7) is thus formed.



(7)

The compound (7) is a cream color solid, melts at 110°C and fairly soluble in organic solvents. In the IR spectra the νC═O bond is found at 1700 cm^{-1}. The electron impact mass spectra indicate the monomeric nature of species in gaseous phase. The ^1H NMR spectrum has shown the presence of two acetyl and two silyl groups in the compound. One singlet was found in the ^{31}P NMR spectrum of this compound which indicates the equivalent nature of phosphorus nuclei in the molecule.

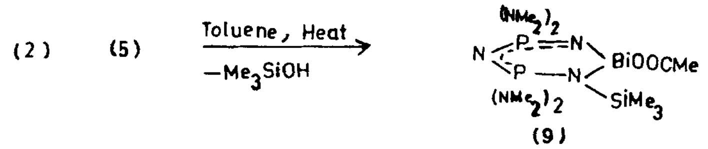
The reaction of (1) with Bi(O)OOCMe (5) in a 1:1 molar ratio in toluene at 80°C yielded a yellow solid compound (8) with the elimination of Me_3SiOH. The reaction can be depict as below:



(8)

This compound melts at 85°C and has the same solubility as the antimony derivatives. The peak for molecular ion in the mass spectrum was found at m/z 549 (30%). The band for νC═O was present in the IR spectrum. The ^1H NMR spectrum does not have the signal for —$SiMe_3$ protons while the signal for acetyl protons was present at δ1.82 ppm. In the ^{31}P NMR spectrum two singlets were found at δ21.3 ppm and δ32.35 ppm for the phosphorus nuclei, showing the presence of two types of nuclei in the molecule.

Similar to the compound (**8**), the phosphazene ligand (**2**) reacted with (**5**) in a 1:1 molar stoichiometry in toluene. The elimination of Me_3SiOH was again found.



(**9**)

The compound (**9**) was a cream color solid and the solubility was similar to the compounds (**6**), (**7**) and (**8**). A peak for the molecular ion was found at m/z 597 (35%) in the electron impact mass spectrum. The other studies such as elemental analysis, IR, ^1H and ^{31}P NMR were found in accordance to the compound. The relevant data are given in the experimental section.

In general, the above compounds were sufficiently pure for spectroscopic and other studies but these can be further purified by washing with *n*-hexane. These compounds were non-volatile even under reduced pressure and sensitive to moisture but can be kept unchanged for long period in an anhydrous medium. In view of the failure to obtain suitable single crystals for X-ray analysis it is difficult to predict the structural geometry of these compounds at this juncture. However, the efforts in this direction are still continued.

Conclusively, the versatility in the bonding mode as bi-, tri or penta-dentate is unique feature of these ligands.[2,4] A number of methods have been developed for the preparation of 6 and 8 membered metallacyclophosphazenes starting from open chain phosphazene derivatives and metal halides.[2] The metallacyclophosphazenes may have possibilities of their applications in the development of "high-tech" materials[2,9,14] similar to the siloxanes derivatives, so it worthy to go ahead in this field of research.

EXPERIMENTAL

All the synthesis and the subsequent manipulations were conducted under nitrogen by using Schlenk, vacuum line and glove box techniques. Mono-(**1**), bis-(**2**) and tris-(**3**) silylated ligands[1,15] and $Sb(OOCMe)_3$[16] were prepared as described in the literature. Bi(O)OOCMe was used as supplied. IR (nujol mulls) and NMR spectra were recorded on Bio-Rad FTS7 spectrophotometer and Bruker AM250 spectrometer, respectively. The mass spectrometric analysis were performed with a Finnigan MAT8230 instrument. Elemental analyses were obtained from the Analytical Laboratory, Göttingen University, Germany.

Synthesis of $HN[P(NMe_2)_2N]_2SbOOCMe$ (**6**): A toluene solution (20 ml) of 0.69 g (2.3 mmol) of (**3**) was added slowly to the toluene solution (20 ml) of 1.0 g (2.3 mmol) of phosphazene ligand (**2**) with stirring at room temperature. No physical change was at this stage. The contents were heated about 70–80°C and stirred for overnight; a light yellow solution was obtained. The volatiles were evaporated under reduced pressure. A white colored solid compound was obtained in the yield of 0.9 g (90%). M.P. 90°C. Elemental analysis for $C_{10}H_{28}N_7P_2O_2Sb$ (461.75 g/mol) Found (Calcd.): C 25.6 (25.9), H 5.8 (6.0), N 20.9 (21.2). EI-MS: m/z (%): 462 (28) [M]. IR (nujol mulls, ν, cm^{-1}): 1690m, 1620s, 1560m, 1465vs, 1290mb, 1260m, 1193m, 1064m, 980vs, 804m, 745vs, 672s, 620m, 490m and 460m. ^1H NMR ($CDCl_3$): δ 1.9 ppm (s, 3H, —OOCMe) δ 2.5 ppm (t, 24H, —NMe_2, J = 10.2 Hz). ^{31}P NMR ($CDCl_3$): δ 20.8 ppm and δ 27.35 ppm (s).

Synthesis of $N[P(Ph_2)NSiMe_3]_2Sb(OOCMe)_2$ (**7**): Mixed a 1.0 g (1.6 mmol) of tris-silylated phosphazene ligand (**3**) with 0.48 g (1.6 mmol) of $Sb(OOCMe)_3$ (**4**) in a 100 ml flask containing 45 ml toluene. The contents of the flask were heated to 80°C with stirring for overnight. A light yellow solution was formed. All the volatiles were removed under reduced pressure. The cream color solid compound was obtained; yield 1.0 g (77%). M.P. 110°C. Elemental analysis for $C_{34}H_{44}N_3O_4P_2Si_2Sb$ (797.5 g/mol) Found (Calcd.): C 50.96 (51.14), H 5.43 (5.51), N 5.38 (5.26). EI-MS: Mz (%): 797 (15) [M]. IR (nujol mulls, ν, cm^{-1}): 1700m, 1610s, 1565m, 1470vs, 1290b, 1262m, 1198m, 1170m, 1044m, 980vs, 804m, 756vs, 675s, 622m, 490m, and 469m. ^1H NMR ($CDCl_3$): δ 7.3–8.0 ppm (m, 24H, —Ph), δ 2.0 ppm (s, 6H, —OOCMe), δ 0.1–0.2 ppm (s, 18H, —$SiMe_3$). ^{31}P NMR ($CDCl_3$): δ 25.3 ppm(s).

Synthesis of $HN[P(NMe_2)_2N]_2BiOOCMe$ (**8**): 1.5 g (4.2 mmol) of mono-silylated phosphazene ligand (**1**) and 1.2 g (4.2 mmol) of Bi(O)OOCMe (**5**) was used and the rest of experimental manipulations were same as used for the compound (**7**). A yellow solid compound (**8**) was obtained and the yield was 2.1 g (91%). M.P. 85°C. Elemental analysis for $C_{10}H_{27}N_7P_2O_2Bi$ (548.98 g/mol) Found (Calcd.): C 21.5 (21.8), H 4.9 (5.1), N 17.7 (17.8). EI-MS: M/z (%): 549 (30) [M], 490 [M—OAc] (40), 283 [M—BiOAc] (60). IR (nujol mulls, ν, cm^{-1}): 1680m, 1630m, 1548s, 1462s, 1280mb, 1250m, 1198m, 1175m, 1074m, 980vs, 802m, 750vs, 665m, 498m and 450m. ^1H NMR ($CDCl_3$): δ 2.5 ppm (d, 24H, —NMe_2), δ 1.8 ppm (s, 3H, —OOCMe). ^{31}P NMR ($CDCl_3$): δ 21.3 ppm (s) and δ 32.3 ppm (s).

Synthesis of $Me_3SiN[P(NMe_2)_2N]_2BiOOCMe$ (**9**): 1.0 g (2.3 mmol) of (**2**) and 0.6 g (2.3 mmol) of (**5**) were used and the rest of method was same as adopted in the case of compound (**8**). A cream color solid compound was obtained in the yield of 1.1 g (92%). M.P. 75°C. Elemental analysis for $C_{13}H_{36}N_7P_2SiBi$ (596.98 g/mol) Found (Calcd.): C 22.2 (22.1), H 5.8 (6.0), N 16.2 (16.4). EI-MS: m/z (%): 597 (50) [M]. IR (nujol mulls, ν, cm^{-1}): 1680m, 1625m, 1560s, 1470s, 1272mb, 1248m, 1192m, 1170m, 990vs, 805m, 760vs, 662m, 490m and 454m, ^1H NMR ($CDCl_3$): δ 5.7 ppm (d, 9H, —$SiMe_3$), δ 1.8 ppm (s, 3H, —OOCMe), δ 2.5 ppm (d, 24H, —NMe_2, J = 10.2 Hz). ^{31}P NMR ($CDCl_3$): δ 20.9 ppm (s) and δ 32.4 ppm (s).

ACKNOWLEDGEMENT

Financial support in the form of a Pool Scientist from CSIR, New Delhi is gratefully acknowledged. The author thanks Prof. R. C. Mehrotra for his suggestions.

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