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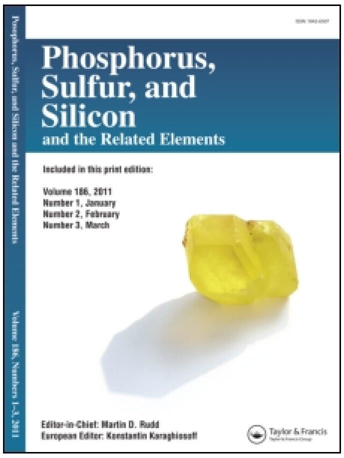

Phosphorus, Sulfur, and Silicon and the Related Elements

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Alkoxo-Bridged Heterobinuclear Derivatives of Arsenic(III) and Boron Based on Dithiophosphate Ligands: Synthesis and Characterization

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To cite this Article Sharma, Pankaj Kumar and Singh, Yashpal(2009) 'Alkoxo-Bridged Heterobinuclear Derivatives of Arsenic(III) and Boron Based on Dithiophosphate Ligands: Synthesis and Characterization', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 2, 471 — 479

To link to this Article: DOI: 10.1080/10426500802177034

URL: http://dx.doi.org/10.1080/10426500802177034

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Phosphorus, Sulfur, and Silicon, 184:471–479, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802177034

Alkoxo-Bridged Heterobinuclear Derivatives of Arsenic(III) and Boron Based on Dithiophosphate Ligands: Synthesis and Characterization

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The heterobinuclear derivatives of arsenic(III) and boron of the general formula $[(RO)_2P(S)S]_2As(\mu\text{-}OPr^i)_2B(OPr^i)_2$ *{where R = Me*(**1**)*; Et* (**2**)*;* Pr^i (**3**)*;* Pr^n (**4**)*; and* Bu^n (**5**)*] have been synthesized by the reactions of chlorobis(dialkyldithiophosphato)arsenic (III) compounds,* $[(RO)_2P(S)S]_2AsCl$ *with sodium tetraisopropoxoborate,* $NaB(OPr^i)_4$ *in 1:1 molar ratio in refluxing benzene solution. All these new nonvolatile, moisture-sensitive, light-yellow colored, viscous liquid derivatives have been characterized by elemental analyses and molecular weight measurements. Their FT IR, multinuclear NMR* (^1H, ^{13}C, ^{31}P, *and* ^{11}B), *and FAB mass spectral studies have been discussed.*

Keywords Bidentate ligands; chlorobis(dialkyldithiophosphato)arsenic(III); heterobinuclear derivatives; tetra-coordinated boron

INTRODUCTION

Although during the last two decades there has been significant development in the chemistry of heterobimetallic alkoxides of heavier group 15 elements,[1–17] except for two examples,[18] there is a dearth of analogous studies concerning arsenic(III), though homodinuclear derivatives[19] of arsenic(III) containing deprotonated dithiophosphates and an isopropoxoarsenate group as well as mixed ligand dialkyldithiophosphate derivatives of arsenic(III) have already been reported earlier[20–22] in the literature. In view of the previous statement, we report the synthesis and characterization of heterobinuclear alkoxide derivatives of arsenic(III) with boron.

Received 3 March 2008; accepted 2 May 2008.

One of the authors (P.K.S.) is grateful to University Grants Commission, New Delhi for the award of a Senior Research Fellowship.

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RESULTS AND DISCUSSION

The reactions of freshly prepared sodium tetraisopropoxoborate, $NaB(OPr^i)_4$ with chlorobis(dialkyldithiophosphato)arsenic(III) compounds, $[(RO)_2P(S)S]_2AsCl$, in 1:1 molar ratio in refluxing benzene solution for ~4 h yields the corresponding heterobinuclear alkoxide derivatives of arsenic(III), **1–5**:

$$[(RO)_2P(S)S]_2AsCl + NaB(OPr^i)_4 \xrightarrow[\text{Reflux}]{C_6H_6} [(RO)_2P(S)S]_2As(\mu{-}OPr^i)_2B(OPr^i)_2 + NaCl\downarrow \qquad \mathbf{1-5}$$

where, R = Me(**1**); Et (**2**); Pr^i (**3**); Pr^n (**4**); and Bu^n (**5**).

These reactions are quite facile and quantitative. All the newly synthesized heterobinuclear derivatives, **1–5** are hygroscopic, light-yellow colored, nonvolatile, viscous liquids that are soluble in common organic solvents. Molecular weight measurements reveal their monomeric nature in freezing benzene solution.

IR Spectra

The tentative assignments of the important characteristic bands in the IR spectra of the new heterobinuclear derivatives have been made by comparing them with the IR spectral data reported earlier.[20–24] A strong band present in the region 620–690 cm^{-1} due to $\nu(P{=}S)$ vibrations in the IR spectra of free dialkyldithiophosphoric acid ligands or their sodium salts have shifted towards lower wave numbers by ~30 cm^{-1} in the IR spectra of these new derivatives, **1–5**. This shifting may be attributed to the strong bidentate chelation of dithiophosphate moieties with arsenic. The medium intensity bands present in the region 505–615 cm^{-1} may be due to symmetric and asymmetric P—S stretching vibrations. The medium intensity broad bands present in the regions 800–825 and 970–995 cm^{-1} have been assigned to [P—O—(C)] and [(P)—O—C] stretching modes, respectively. These heterobinuclear derivatives also show additional bands in the regions 665–680 and 1250–1475 cm^{-1} due to As—O and B—O stretching vibrations, respectively.

^{1}H NMR Spectra

^{1}H NMR spectral data of these derivatives, **1–5**, have been summarized in Table I. The ^{1}H NMR spectra of all the new compounds exhibit

TABLE I ^{1}H NMR Spectral Data (δ ppm) of New Heterobinuclear Derivatives, 1–5

S. No.	Compound R =	^{1}H NMR chemical shifts (δ, ppm)* and coupling constants (J, Hz)	
1	Me	1.34, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{T}$
		1.40, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{B}$
		3.72, d, 12H; $J_{\mathrm{P-O-CH3}} = 13.55$	$(\mathrm{O}\mathbf{CH}_3)_\mathrm{dtp}$
		4.60, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{T}$
		4.80, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{B}$
2	Et	1.19, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{T}$
		1.32, t, 12H; $J_{\mathrm{CH3CH2}} = 6.25$	$(\mathrm{C}\mathbf{H}_3)_\mathrm{dtp}$
		1.40, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{B}$
		4.06, dq, 8H; $J_{\mathrm{P-O-CH2}} = 10.45$, $J_{CH3-CH2} = 6.25$	$(\mathrm{OC}\mathbf{H}_2)_\mathrm{dtp}$
		4.23, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{T}$
		4.72, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{B}$
3	Pr^i	1.20,d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{T}$
		1.31,d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{B}$
		1.38, d, 24H; $J_{\mathrm{CH3CH}} = 6.22$	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{dtp}$
		4.20, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{T}$
		4.78, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{B}$
		4.93, m, 4H; $J_{\mathrm{P-O-CH}} = 11.0$, $J_{\mathrm{CH3-CH}} = 6.22$	$(\mathrm{OC}\mathbf{H})_{dtp}$
4	Pr^n	0.98, t, 12H; $J_{\mathrm{CH3CH2}} = 7.32$	$(\mathrm{C}\mathbf{H}_3)_\mathrm{dtp}$
		1.21, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{T}$
		1.39, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{B}$
		1.75, m, 8H; $J_{\mathrm{CH3-CH2}} = 7.32$	$(\mathrm{C}\mathbf{H}_2\mathrm{CH}_3)_\mathrm{dtp}$
		4.13, dt, 8H; $J_{\mathrm{P-O-CH2}} = 8.52$, $J_{\mathrm{CH2-CH2}} = 7.32$	$(\mathrm{OC}\mathbf{H}_2)_\mathrm{dtp}$
		4.60, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{T}$
		4.89, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{B}$
5	Bu^n	0.91, t, 12H; $J_{\mathrm{CH3-CH2}} = 5.76$	$(\mathrm{C}\mathbf{H}_3)_\mathrm{dtp}$
		1.20, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{T}$
		1.36, d, 12H;	$(\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2)_\mathrm{B}$
		1.42, m, 8H; $J_{\mathrm{CH3-CH2}} = 5.76$	$(\mathrm{C}\mathbf{H}_2\mathrm{CH}_3)_\mathrm{dtp}$
		1.69, m, 8H; $J_{\mathrm{CH3-CH2}} = 5.76$	$(\mathrm{OCH}_2\mathrm{C}\mathbf{H}_2)_\mathrm{dtp}$
		2.98, dt, 8H; $J_{\mathrm{P-O-CH2}} = 7.68$, $J_{\mathrm{CH2-CH2}} = 5.76$	$(\mathrm{OC}\mathbf{H}_2)_\mathrm{dtp}$
		4.59, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{T}$
		4.86, m, 2H;	$(\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2)_\mathrm{B}$

$_\mathrm{T}$ = terminal, $_\mathrm{B}$ = bridging, $_\mathrm{dtp}$ = dialkyldithiophosphate, d = doublet, m = multiplet, t = triplet, dq = doublet of quartets, dt = doublet of triplets.

two sets of signals for terminal and bridging isopropoxy groups in the regions 1.19–1.34, 1.31–1.40 ppm (doublets) $\{\mathrm{CH}(\mathrm{C}\mathbf{H}_3)_2\}$, and 4.20–4.60, 4.72–4.89 ppm (multiplets) $\{\mathrm{C}\mathbf{H}(\mathrm{CH}_3)_2\}$, respectively. All alkyl protons of the (RO) group attached to P atom are observed at their expected positions. Splitting due to coupling between α-protons and phosphorus nuclei has been observed in the signals of these alkyl groups attached to OP(S)S group (Table I).

^{13}C NMR Spectra

A comparative study of ^{13}C NMR spectra (proton decoupled) of these new derivatives, **1–5**, with the spectra of parent chloro-bis(dialkyldithiophosphato)arsenic(III) compounds provides some useful information about the mode of bonding in these derivatives. In the ^{13}C NMR spectra (Table II) of these heterobinuclear derivatives, **1–5**, an upfield shift (~5–7 ppm) has been observed in the positions of the signals of different alkyl group carbons of the dialkyldithiophosphate moieties as compared to their positions in corresponding parent chloro-bis(dialkyldithiophosphato)arsenic(III) compounds. This upfield shift may be due to the fact that the coordination number of arsenic has increased from five to six. ^{13}C–^{31}P NMR coupling has been observed up to three bond lengths in the signals due to carbon atoms of dialkyldithiophosphate moieties. No further splitting of the ^{13}C signals of the alkyl groups, attached to P-O group, has been observed.

Two sets of signals due to terminal and bridging isopropoxy groups have been observed in the spectra of all these new derivatives, **1–5**, in the range 23.29–26.23, 25.18–30.25 ppm $\{CH(\mathbf{C}H_3)\}$ and 63.90–71.88, 73.34–73.92 ppm $\{\mathbf{C}H(CH_3)_2\}$, respectively.

^{31}P NMR Spectra

Some important information about the complexation behavior of dialkyldithiophosphate ligands with central arsenic atom and the geometry of these new derivatives has been obtained from ^{31}P NMR spectral data (Table II). The proton decoupled ^{31}P NMR spectra exhibit only one signal in the spectra of each new derivative in the range 87.04–91.67 ppm. The presence of ^{31}P NMR signals in this range has been interpreted in terms of bidentate nature of the dialkyldithiophosphate ligands[25] in these derivatives, **1–5**.

^{11}B NMR Spectra

^{11}B NMR spectra of these new derivatives also exhibit only one signal for each compound, **1–5**, in the range −18.14 to −19.36 ppm (Table II). Presence of ^{11}B NMR signal in this range is indicative of a tetrahedral environment around boron atom[26,27] in these heterobinuclear derivatives.

TABLE II ^{13}C, ^{31}P, and ^{11}B NMR Spectral Data (δ ppm) of New Heterobinuclear Derivatives, 1–5

S. No.	Compound R =	^{13}C NMR chemical shift (ppm) and coupling constnt (J, Hz)		^{31}P NMR chemical shift (ppm)	^{11}B NMR chemical shift (ppm)
1	Me	26.23;	$(CH(\mathbf{C}H_3)_2)_T$;	97.04	−18.14
		29.26;	$(CH(\mathbf{C}H_3)_2)_B$;		
		54.55, d; $^2J_{PC} = 5.28$	$(O\mathbf{C}H_3)_{dtp}$;		
		71.13;	$(\mathbf{C}H(CH_3)_2)_T$;		
		73.56;	$(\mathbf{C}H(CH_3)_2)_B$;		
2	Et	15.86, d; $^3J_{PC} = 7.91$	$(CH_2\mathbf{C}H_3)_{dtp}$;	89.51	−19.36
		23.61;	$(CH(\mathbf{C}H_3)_2)_T$;		
		25.32;	$(CH(\mathbf{C}H_3)_2)_B$;		
		63.78, d; $^2J_{PC} = 8.30$	$(O\mathbf{C}H_2)_{dtp}$;		
		64.29;	$(\mathbf{C}H(CH_3)_2)_T$;		
		73.92;	$(\mathbf{C}H(CH_3)_2)_B$;		
3	Pr^i	23.35;	$(CH(\mathbf{C}H_3)_2)_T$;	86.30	−18.90
		24.71, d; $^3J_{PC} = 6.79$	$(CH(\mathbf{C}H_3)_2)_{dtp}$;		
		25.18;	$(\mathbf{C}H(CH_3)_2)_B$;		
		63.90;	$(\mathbf{C}H(CH_3)_2)_T$;		
		73.05, d; $^2J_{PC} = 7.54$	$(\mathbf{C}H(CH_3)_2)_{dtp}$;		
		73.34;	$(\mathbf{C}H(CH_3)_2)_B$;		
4	Pr^n	10.16;	$(\mathbf{C}H_3)_{dtp}$;	90.21	−18.50
		23.29;	$(CH(\mathbf{C}H_3)_2)_T$;		
		23.61, d; $^3J_{PC} = 5.28$	$(\mathbf{C}H_2CH_3)_{dtp;}$		
		25.36;	$(CH(\mathbf{C}H_3)_2)_B$;		
		64.48;	$(\mathbf{C}H(CH_3)_2)_T$;		
		69.73, d; $^2J_{PC} = 6.04$	$(O\mathbf{C}H_2)_{dtp}$;		
		73.92;	$(\mathbf{C}H(CH_3)_2)_B$;		
5	Bu^n	13.24;	$(\mathbf{C}H_3)_{dtp}$;	91.67	−18.85
		20.18;	$(\mathbf{C}H_2CH_3)_{dtp}$;		
		23.74;	$(CH(\mathbf{C}H_3)_2)_T$;		
		30.25;	$(CH(\mathbf{C}H_3)_2)_B$;		
		34.11, d; $^3J_{PC} = 4.35$	$(OCH_2\mathbf{C}H_2)_{dtp}$;		
		66.93, d; $^2J_{PC} = 5.28$	$(O\mathbf{C}H_2)_{dtp}$;		
		71.88;	$(\mathbf{C}H(CH_3)_2)_T$;		
		73.79;	$(\mathbf{C}H(CH_3)_2)_B$;		

$_T$ = terminal, $_B$ = bridging, $_{dtp}$ = dialkyldithiophosphate, d = doublet.

FAB Mass Spectra

The FAB mass spectral data, recorded for one representative compound **(3)**, have been summarized in Table III. These data provide evidence for its discrete monomeric nature in the gas phase, as there is no fragment of mass higher than the monomeric species (m = 749) should give. It is also evident from Table III that there are two preferable modes of frag-

TABLE III FAB Mass Spectral Data of the New Heterobinuclear Derivative (3), $[\{(CH_3)_2CHO\}_2P(S)S]_2As\{\mu\text{-}OCH(CH_3)_2\}_2B\{OCH(CH_3)_2\}_2$

Sr. No.	Mass No.	Rel. Abundance	Assignment
1.	749*	—	$[\{(CH_3)_2CHO\}_2P(S)S]_2As\{\mu\text{-}OCH(CH_3)_2\}_2B\{OCH(CH_3)_2\}_2^+$
2.	691	8.3	$[\{(CH_3)_2CHO\}_2P(S)S]_2As\{\mu\text{-}OCH(CH_3)_2\}_2B(H)\{OCH(CH_3)_2\}^+$
3.	649*	—	$[\{(CH_3)_2CHO\}_2P(S)S]_2As\{\mu\text{-}OCH(CH_3)_2\}_2B(H)(OH)^+$
4.	591	8.3	$[\{(CH_3)_2CHO\}_2P(S)S]_2As\{\mu\text{-}OCH(CH_3)_2\}B(H)_2(OH)^+$
5.	577	12.5	$[\{(CH_3)_2CHO\}_2P(S)S]_2As\{OCH(CH_3)_2\}(O)^+$
6.	549	12.5	$[\{(CH_3)_2CHO\}_2P(S)S]_2As\{\mu\text{-}OH\}B(H)_2(OH)^+$
7.	535	33.3	$[\{(CH_3)_2CHO\}_2P(S)S]As\{\mu\text{-}OCH(CH_3)_2\}_2B\{OCH(CH_3)_2\}_2^{2+}$
8.	475*	—	$[\{(CH_3)_2CO\}P(S)_2]As\{\mu\text{-}OCH(CH_3)_2\}_2B\{OCH(CH_3)_2\}_2\bullet^+$
9.	460	95.8	$[\{CH_3CO\}P(S)_2]As\{\mu\text{-}OCH(CH_3)_2\}_2B\{OCH(CH_3)_2\}_2^+$
10.	418	100.0	$[\{CH_3CO\}P(S)_2]As\{\mu\text{-}OCH(CH_3)_2\}_2B(OH)\{OCH(CH_3)_2\}^+$
11.	376	87.5	$[\{CH_3CO\}P(S)_2]As\{\mu\text{-}OCH(CH_3)_2\}_2B(OH)_2^+$
12.	334	87.5	$[\{CH_3CO\}P(S)_2]As\{\mu\text{-}OH\}\{\mu\text{-}OCH(CH_3)_2\}B(OH)_2^+$
13.	316	8.3	$[\{CH_3CO\}P(S)_2]As\{\mu\text{-}OH\}\{\mu\text{-}OCH(CH_3)_2\}B(O)^+$
14.	139	10.4	$CH_3OAs(OH)O\ ^-/AsS_2^-$
15.	107	14.6	AsO_2^-/AsS^+
16.	91	7.9	AsO^+

*These peaks have not been observed.

mentation for this compound, viz. one through the loss from isopropoxy moieties and another through the loss of one dithiophosphate ligand moiety. This compound does not show the molecular ion peak but the highest mass fragment observed arises from the loss of one acetone molecule from the isopropoxy groups.

In view of the presence of two bidentate dialkyldithiophosphate ligands around the arsenic atom, the presence of two types of isopropoxy (terminal and bridging) groups, tetracoordination around the boron atom, and considering the monomeric nature of all these new derivatives, a structure having hexacoordination around the arsenic(III) center and tetracoordination around the boron center appears to be most probable for all these new heterodinuclear derivatives, **1–5**, in which the two central atoms As and B appear to be joined by bridging isopropoxy groups.

EXPERIMENTAL

All reactions were carried out under moisture-free atmosphere. Solvents (E. Merck) were carefully dried by standard methods before use. Mixed chlorobis(dialkyldithiophosphato)arsenic(III) compounds were

TABLE IV Synthetic, Physical, and Analytical Data of the Heterobinuclear Derivatives, 1–5

	Reactants, g (mmol)					Analysis (%) Found (Calculated)					
Compound	$[(RO)_2P(S)S]_2AsCl$	$NaB(OPr^i)_4$	Empirical Formula and Yield (%)	NaCl (g) Found (Calculated)	Color/ Physical State	As	B	S	C	H	Mol. Wt. Found (Calculated)
1	1.03	0.65	$C_{16}H_{40}O_8P_2S_4BAs$	0.14	Light yellow/	11.65	1.68	20.09	30.02	6.27	631
	(2.42)	(2.41)	86	(0.14)	Viscous liquid	(11.77)	(1.70)	(20.16)	(30.19)	(6.35)	(636.42)
2	1.40	0.79	$C_{20}H_{48}O_8P_2S_4BAs$	0.17	Light yellow/	10.77	1.57	18.44	34.28	6.92	688
	(2.91)	(2.92)	88	(0.17)	Viscous liquid	(10.82)	(1.56)	(18.52)	(34.68)	(7.00)	(692.52)
3	1.54	0.77	$C_{24}H_{56}O_8P_2S_4BAs$	0.16	Light yellow/	9.92	1.42	17.06	38.37	7.49	743
	(2.87)	(2.85)	85	(0.17)	Viscous liquid	(10.01)	(1.44)	(17.14)	(38.50)	(7.56)	(748.63)
4	1.49	0.75	$C_{24}H_{56}O_8P_2S_4BAs$	0.16	Light yellow/	9.95	1.39	17.09	38.62	7.48	7423
	(2.77)	(2.78)	87	(0.16)	Viscous liquid	(10.01)	(1.44)	(17.14)	(38.50)	(7.56)	(748.63)
5	1.39	0.63	$C_{28}H_{64}O_8P_2S_4BAs$	0.13	Light yellow/	9.24	1.30	15.82	41.62	7.97	798
	(2.34)	(2.33)	91	(0.14)	Viscous liquid	(9.31)	(1.34)	(15.94)	(41.79)	(8.03)	(804.73)

prepared by the reactions of arsenic(III) chloride with sodium salts of corresponding dilakyldithiophosphoric acids in 1:2 molar ratio in refluxing benzene solution.[21] Sodium tetraisopropoxoborate, $NaB(OPr^i)_4$, was prepared by the reported method.[18] Arsenic and boron were determined by the iodometric[28] and methylborate[28] methods, respectively. Sulfur was estimated by Messenger's[28] method.

Elemental analyses (C and H) were carried out on a Perkin Elmer Series II 2400 C, H, N analyzer. Molecular weights were determined cryoscopically in freezing benzene solution using a Beckmann's thermometer. The IR spectra were recorded on a FT IR spectrophotometer Model 8400S Shimadzu as liquid films on a KBr optics in the range 4000–400 cm^{-1}. ^1H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were recorded in $CDCl_3$ solution on a JEOL FT AL 300 MHz spectrometer; chemical shift values of ^1H and ^{13}C NMR have been expressed in ppm relative to TMS as an internal reference and those of ^{31}P and ^{11}B NMR in ppm relative to H_3PO_4 and $B(OCH_3)_3$ as external references.

Synthesis of Heterobinuclear Derivative 1

A ~20 mL benzene solution of freshly prepared sodium tetraisopropoxoborate, $NaB(OPr^i)_4$, (0.65 g, 2.41 mmol) was mixed with ~25 mL benzene solution of $[(MeO)_2P(S)S]_2AsCl$ (1.03 g, 2.42 mmol) and the resulting reaction mixture, after stirring at room temperature for ~3 h, was refluxed for ~1 h. The precipitated NaCl (0.14 g, 2.40 mmol) was removed by filtration. Removal of volatile components from filtrate under reduced pressure yielded 1.42 g (92.21%) derivative **1**, which was further purified by a 1:2 mixture of benzene and n-hexane at 0°C to obtain the analytically pure compound **1** in 85.71% (1.32 g) yield.

A similar procedure was adopted for the synthesis of all other new heterobinuclear derivatives, **2–5**. The synthetic, physical, and analytical data of these derivatives have been summarized in Table IV.

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