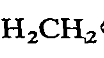
Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SYNTHESIS OF POLYPHOSPHINOBORANES BY THE REACTION OF SECONDARY BISPHOSPHINES WITH TRIETHYLAMINEBORANE

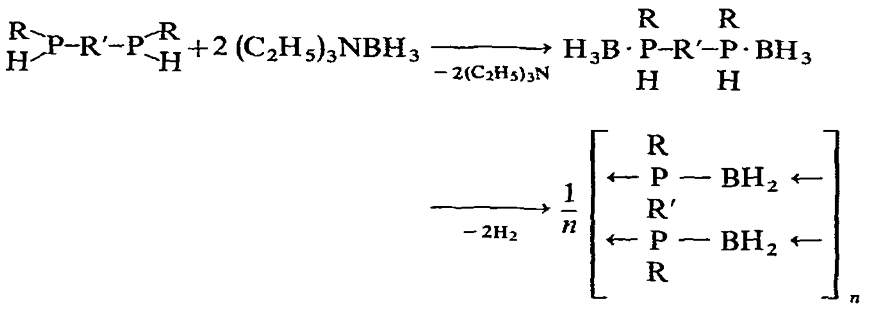
V. V. Korshak, V. A. Zamyatina, A. I. Solomatina, E. I. Fedin and P. V. Petrovskii
Institute of Organoelement Compounds, Vavilova Street, Moscow B 312 (U.S.S.R.)

(Received December 8th, 1968)

SUMMARY

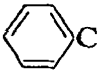
Secondary bisphosphines of general formula, $H(C_6H_5)P-R-P(C_6H_5)H$ $R = (CH_2)_{10}$; CH_2CH_2CH_2CH_2; $(CH_2)_3O(CH_2)_3$; $CH_2CH_2(CH_3)_2Si-O-Si-(CH_3)_2CH_2CH_2$ have been synthesized by the reaction of phenylphosphine with divinyl compounds. The corresponding polymeric phosphinoboranes have been prepared by heating bisphosphines with triethylamineborane. Polymer properties and molecular chain structures have been discussed.

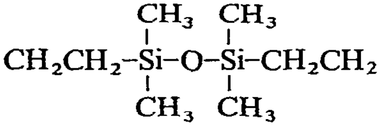
The patents of Hoffmann and Burg and Wagner[1,2] describe the synthesis of polyphosphino boranes from bisphosphines and a diborane and propose a polycyclic structure for the former, but the corresponding data for polymer structure and properties are not given. The present study therefore reports on the reaction of some secondary bisphosphines with triethylamine borane and the investigation of the resulting polymers. It is probable that the molecules of such polymers have a linear structure composed of phosphine borane chains bonded with cross-linking units, rather than a polycyclic structure:



$$\underset{H}{\overset{R}{>}}P-R'-P\underset{H}{\overset{R}{<}} + 2\,(C_2H_5)_3NBH_3 \xrightarrow[-2(C_2H_5)_3N]{} H_3B\cdot\underset{H}{\overset{R}{P}}-R'-\underset{H}{\overset{R}{P}}\cdot BH_3$$

$$\xrightarrow[-2H_2]{} \frac{1}{n}\left[\begin{array}{c} R \\ \leftarrow P - BH_2 \leftarrow \\ R' \\ \leftarrow P - BH_2 \leftarrow \\ R \end{array}\right]_n$$

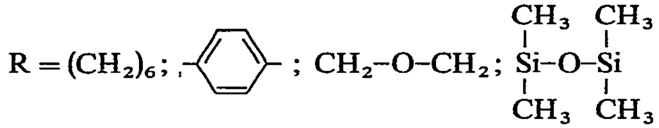
$R = C_6H_5$; $R' = (CH_2)_{10}$; CH_2CH_2CH_2CH_2; $(CH_2)_3-O-(CH_2)_3$;



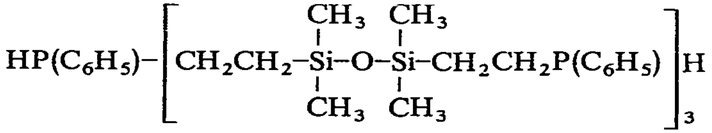
$$CH_2CH_2-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2CH_2$$

Bisphosphines were obtained by migration addition of phenylphosphine to the corresponding divinyl compounds in the presence of free-radical initiators, except for the reaction with divinylbenzene which was carried out without a catalyst.

$$2\,C_6H_5PH_2 + CH_2{=}CH\text{-}R\text{-}CH{=}CH_2 \rightarrow HP(C_6H_5)CH_2CH_2RCH_2CH_2(C_6H_5)PH$$



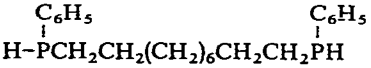
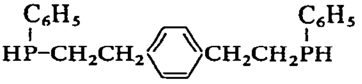
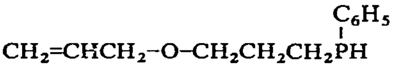
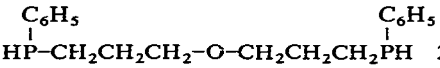
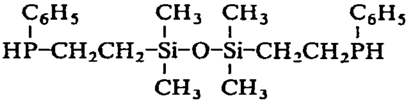
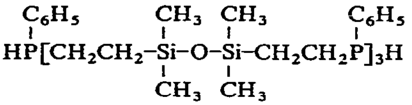
Diallyl ether gave also a secondary monophosphine: $CH_2{=}CH\text{-}CH_2\text{-}O\text{-}CH_2CH_2\text{-}CH_2P(C_6H_5)H$, and phenylphosphine with divinyltetramethyldisiloxane formed bisphosphine and a oligomeric linear phosphine:



$$HP(C_6H_5)\text{-}\left[CH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2CH_2P(C_6H_5)\right]_3H$$

TABLE 1

SECONDARY PHOSPHINES OBTAINED BY THE REACTION OF DIENES WITH PHENYLPHOSPHINE

Compound	B.p. (°C) (mm Hg)	Element composition (%)					Yield (%)
			C	H	P	Si	
 $H\text{-}\overset{C_6H_5}{P}CH_2CH_2(CH_2)_6CH_2CH_2\overset{C_6H_5}{P}H$	244–245(3)	Calcd.	73.72	9.00	17.28	—	26.7
		Found	74.79	9.15	16.54		
			74.56	9.39	16.54		
	210–220(2)	Calcd.	75.36	6.89	17.62	—	32
		Found	75.54	7.08	17.00		
			75.67	7.13			
 $CH_2{=}CHCH_2\text{-}O\text{-}CH_2CH_2CH_2\overset{C_6H_5}{P}H$	99–101(2)	Calcd.	69.24	8.71	14.87	—	18.1
		Found	68.43	8.76	14.78		
			68.50	8.77	14.90		
 $H\overset{C_6H_5}{P}\text{-}CH_2CH_2CH_2\text{-}O\text{-}CH_2CH_2CH_2\overset{C_6H_5}{P}H$	205–207(2)	Calcd.	67.91	7.59	19.46	—	19.3
		Found	68.32	7.85	17.27		
			68.33	7.74	17.30		
 $H\overset{C_6H_5}{P}\text{-}CH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2CH_2\overset{C_6H_5}{P}H$	223–228(3)	Calcd.	59.56	7.93	15.23	13.81	51.7
		Found	58.44	8.07	14.35	12.34	
 $H\overset{C_6H_5}{P}[CH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2CH_2\overset{C_6H_5}{P}]_3H$	viscous mass	Calcd.	57.67	8.28	12.39	16.86	41.3
		Found	56.60	8.22	11.94	16.55	

The properties of the resulting compounds are given in Table 1.

Although the literature data indicate that the free-radical addition of phosphines to a terminal double bond proceeds according to the Farmer rule, we considered it necessary to investigate this further, if only on one example. For this purpose a bisphosphine(I) prepared by the addition of phenylphosphine to 1,9-decadiene, having two non-conjugated and non-activated terminal double bonds was used. For identification purposes, we also synthesized decamethylene-1,10-bis(phenylphosphine)(II) from potassium monophenylphosphide and 1,10-dibromodecane:

$$2\,H(C_6H_5)PK + Br(CH_2)_{10}Br \xrightarrow[-2KBr]{} H(C_6H_5)P\text{–}(CH_2)_{10}\text{–}P(C_6H_5)H$$

These two bisphosphines of similar elemental composition have similar physical properties (Table 2).

TABLE 2

PROPERTIES OF DECANEBISPHENYLPHOSPHINES

Compound	M.p. (°C)	B.p. (°C) (mm Hg)	d_4^{46}	n_D^{46}
I	37–38	244–245 (3)	0.9940	1.5530
II	40–40.5	220–221 (1)	0.9944	1.5582

The infrared spectra of the two bisphosphines are identical (Fig. 1). Characteristic asymmetric (2930 cm^{-1}) and symmetric (2857 cm^{-1}) CH-stretching in the CH$_2$-group is clearly seen; CH$_3$ absorption bands are absent.

The high resolution proton magnetic resonance (PMR) indicates a nonbranched structure of the aliphatic species of the 1,10-bis(phenylphosphino)decane molecule. The PMR spectrum shows a doublet with a chemical shift of 4.30 ppm in

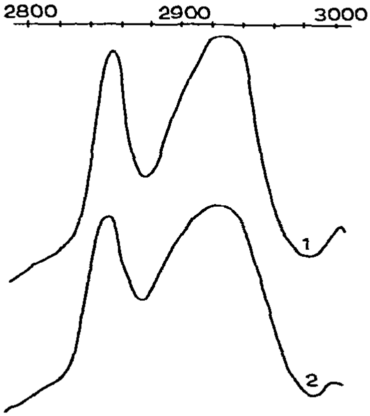


Fig. 1. Infrared spectra of decanebis(phenylphosphine) synthesized by: (1) phenylphosphine addition to 1,9-decadiene; (2) the reaction of potassium monophenylphosphide with 1,10-dibromodecane (two liquids).

the δ-scale and spin–spin coupling, $J(\text{P–H}) \approx 200$ cps, characteristic of the interaction of the hydride hydrogen proton with the phosphorus atom nucleus. Every doublet line is split into three components due to interaction with the protons of CH_2-groups confined between phosphorus atoms. Furthermore, if the aliphatic bonding groups were branched, a doublet with splitting near 7 cps would appear in the PMR spectrum in the iso-configuration due to the methyl group signals. The absence of such a doublet in the aliphatic range of the spectrum testifies to an unbranched bond (Fig. 2).

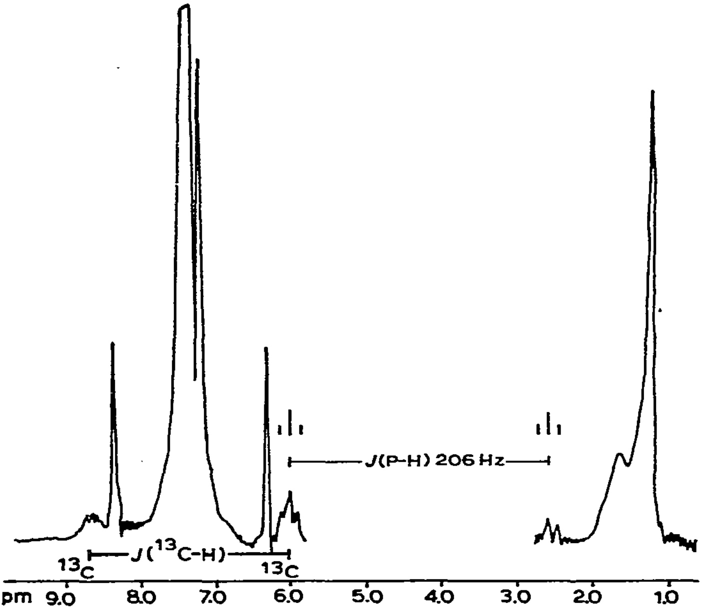


Fig. 2. PMR spectrum of decanebis(phenylphosphine).

Polyphosphinoboranes were obtained by heating bisphosphines with a small excess of triethylamine borane at increasing temperature of 300° followed by removal under vacuum of the material of low molecular weight. Since all polymers were solid glassy substances insoluble in aliphatic and aromatic hydrocarbons, alcohol, ether, cresol, dimethylformamide and dimethylsulfoxide, their molecular weights and intrinsic viscosities of their solutions could not be determined. Thermostability is appreciably related to the chemical nature of bonding groups (Fig. 3a). The temperature interval of the high elastic state is 240–300° for polymers with a decamethylene bonding chain, and is shorter for polyphosphinoborane with aryl groups. Its shift towards lower temperatures is probably explained by a somewhat lower molecular weight. The ether bond of the polyphosphinoborane from 3,3′-bis(phenylphosphino)-propyl ether seems to result in a longer high elastic state: 180–340°. The polymer with siloxane groups proved to be rather low melting (flows at *ca.* 240°). This is consistent with the nature of Si–O–Si bonds.

Thermogravimetric studies of the resulting polymers showed that the polymer from decadiene is more stable to thermal and thermo-oxidative destruction. When heated in air or an inert gas, it did not change up to 380–390° (Fig. 3b). The same

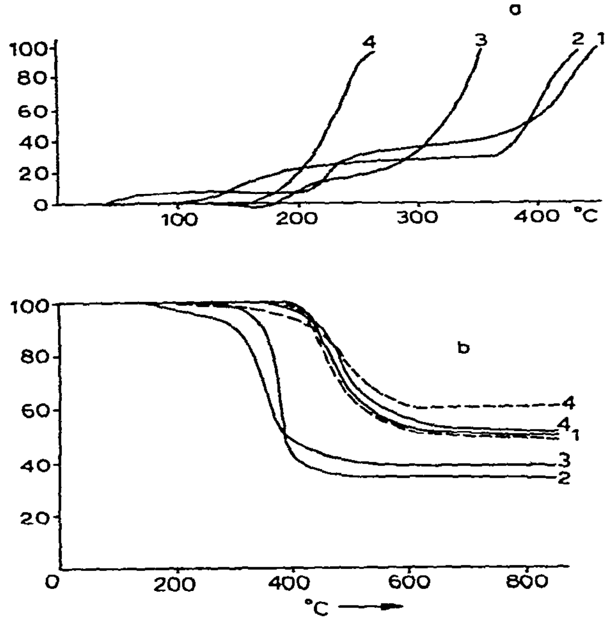
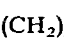
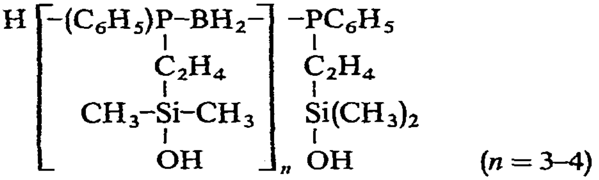


Fig. 3. Thermomechanical (a) and thermogravimetric (b) curves of polyphosphinoboranes with following bonding groups: (1) $-(CH_2)_{10}$; (2) $-(CH_2)_3-O-(CH_2)_3$; (3) $-(CH_2)_2-$$-(CH_2)_2$; (4) $-(CH_2)_2-Si-(CH_3)_2-O-Si(CH_3)_2-(CH_2)_2$.

thermogravimetric analysis data were obtained with an identical polymer prepared from a bisphosphine formed in the reaction of dibromodecane with potassium phenylphosphide. The polymer with an aromatic cycle in the bonding group was less stable. On heating in an inert atmosphere at 300° it lost 7% in weight. While the ether bond in the molecule of an organic polymer does not impair its thermostability, in our case it is this bond which is responsible for the fact that the polyphosphinoborane containing this group in the bonding group shows indications of disintegration as low as 250°. The strong tendency of boron to coordinate with oxygen at high temperatures leads probably to the interaction of the C–O–C bond with the boron atom, thus initiating polymer destruction. The weight loss of the polymer with siloxane groups begins above 350° in an inert gas, but in air, signs of thermo-oxidative destruction appear at 200°.

All polymers have good chemical resistance; they do not change on prolonged exposure to air, while polymers containing oxygen in the bonding group show some hygroscopicity with a weight increase of 2–3%. They are not affected by boiling water and dilute hydrochloric acid or alkali. The polyphosphinoborane with siloxane groups is an exception; it gradually degradates in boiling aqueous alkali. First, Si–O–Si bond rupture would occur and the boron content of the residue would decrease compared with the calculated value and boric acid would be present in the aqueous solution. The molecular weight of the hydrolysis product could not be determined because of its insolubility in the solvents used. Nevertheless, using the significant decrease in boron content and increase in phosphorus content of the product we attempted to calculate the average molecular weight of the resulting fragments and obtained good agreement between found and calculated values for boron, phosphorus and silicon content for a linear molecule.



$$\mathrm{H}\left[\begin{array}{c}-(C_6H_5)P-BH_2-\\ |\\ C_2H_4\\ |\\ CH_3-Si-CH_3\\ |\\ OH\end{array}\right]_n\begin{array}{c}-PC_6H_5\\ |\\ C_2H_4\\ |\\ Si(CH_3)_2\\ |\\ OH\end{array}\qquad (n=3\text{–}4)$$

These molecules can be considered as segments of longer chains composed of alternating boron and phosphorus atoms linked coordinatively:

$$\rightarrow B - P \rightarrow B - P \rightarrow B - P \rightarrow$$

Figure 4 shows the infrared spectra of the resulting polyphosphinoboranes and several secondary phosphines. The intense absorption maximum at 2280 cm^{-1} observed in the bisphosphine spectra and characteristic of P–H stretching, is absent in the polymer spectra, but a new strong absorption band appears at 2440–2380 cm^{-1} corresponding to B–H stretching in the BH_2-group. P–B deformation vibrations usually absorb at 700–500 cm^{-1} and are considered by some authors as pulsation of a phosphinoborane cycle[6]. In the spectra of our polymers there is only a weak absorp-

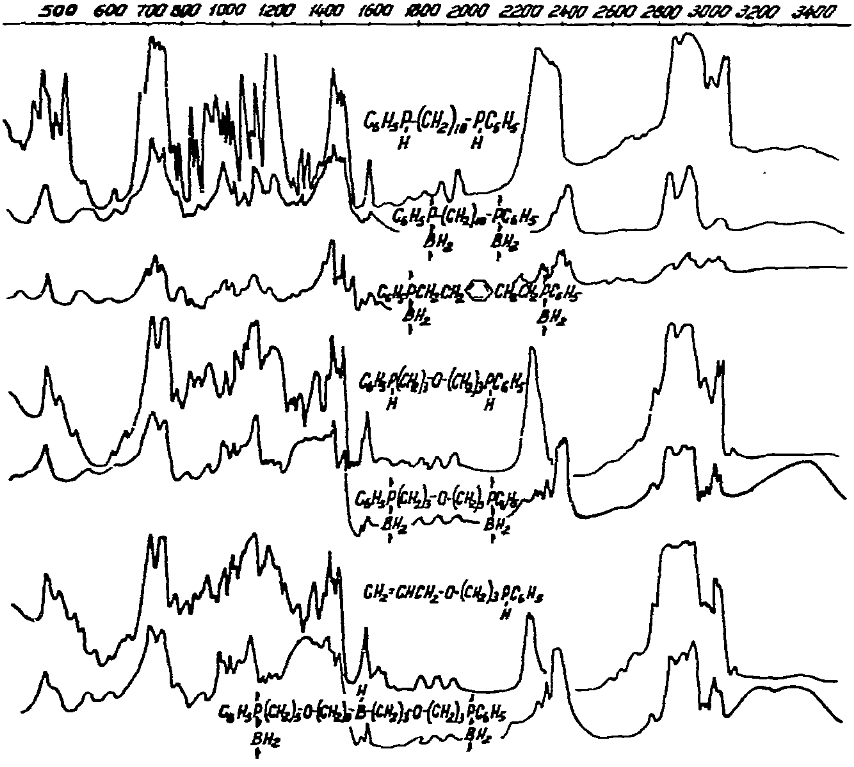


Fig. 4. Infrared spectra of secondary bisphosphines (liquids) and polyphosphinoboranes (KBr pellets).

tion band in this range, which could not be taken as evidence of a cyclic structure of the phosphinoborane part of the molecule.

The synthesis of a polymer from 3-allyloxypropylphenylphosphine is characterized by some specific features.

Although the double bond could not be hydroborated at lower temperatures with triethylamineborane[7], the reaction proceeds at higher temperatures (180–200°). We therefore carried out the reaction in 1 : 2 molar ratio according to the scheme:

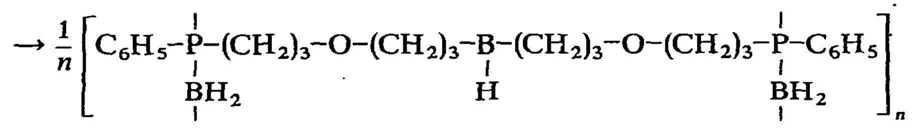
$$CH_2{=}CHCH_2OCH_2CH_2CH_2P(C_6H_5)H + (C_2H_5)_3NBH_3 \xrightarrow[-(C_2H_5)_3N;\ -H_2]{}$$

$$\rightarrow CH_2{=}CHCH_2OCH_2CH_2CH_2P(C_6H_5)BH_2 \xrightarrow[-(C_2H_5)_3N]{+(C_2H_5)_3NBH_3}$$

$$\rightarrow H_2B(CH_2)_3{-}O{-}(CH_2)_3P(C_6H_5)BH_2$$

However, the reaction at 240° resulted in a polymer corresponding to a disproportionation product with a boron content lower then calculated for the formula:

$$2\,H_2B(CH_2)_3{-}O{-}(CH_2)_3P(C_6H_5)BH_2 \xrightarrow[-BH_3]{240^\circ}$$



$$\rightarrow \frac{1}{n}\left[\begin{array}{c} C_6H_5{-}\overset{|}{\underset{\underset{|}{BH_2}}{P}}{-}(CH_2)_3{-}O{-}(CH_2)_3{-}\underset{\underset{H}{|}}{B}{-}(CH_2)_3{-}O{-}(CH_2)_3{-}\overset{|}{\underset{\underset{|}{BH_2}}{P}}{-}C_6H_5 \end{array}\right]_n$$

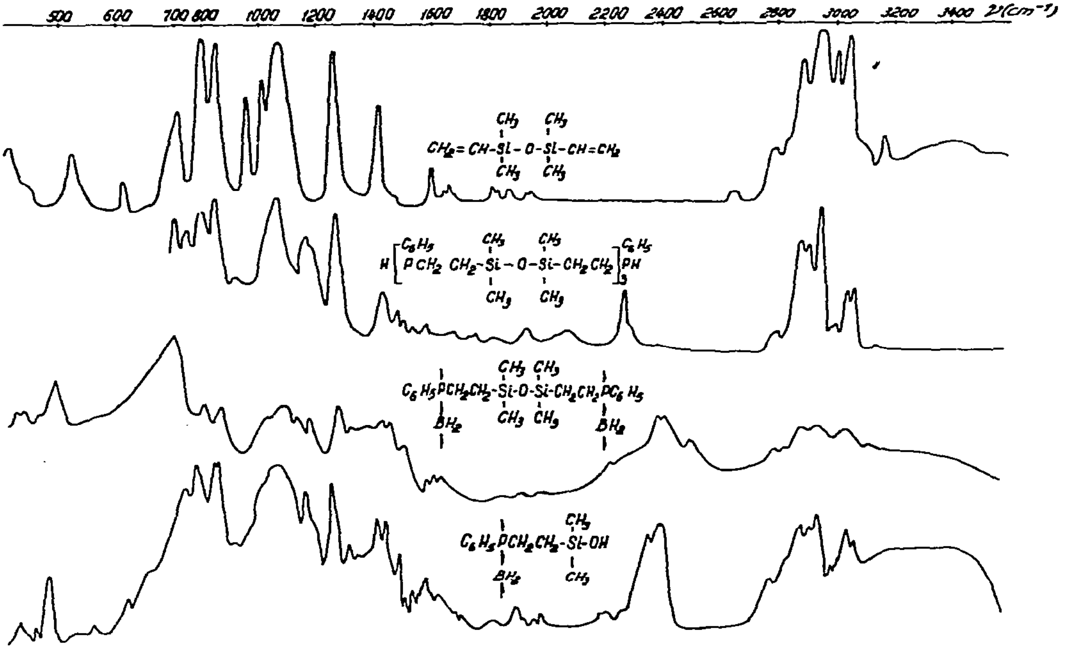


Fig. 5. Infrared spectra of divinyltetramethyldisiloxane (liquid), the oligomeric product from its reaction with phenylphosphine (film), and polyphosphinoborane (KBr pellets).

The terminal double bond absorption bands at 1650 and 1005 cm^{-1} present in phosphine spectra are therefore absent in polyphosphinoborane but in other respects, the spectra of two phosphines with ether bonds and of their polymers are very similar (Fig. 4).

Fig. 5 shows the infrared spectra of divinyltetramethyldisiloxane, an oligomeric product from the reaction of this with phenylphosphine, the polyphosphinoborane, and a residue after alkali hydrolysis of the polymer. Characteristic frequencies of 1412, 1250, 800 and 700 cm^{-1} in $Si(CH_3)_2$ and absorption at 1065 cm^{-1} corresponding to Si–O–Si stretching are common to all spectra. In the spectrum of the polymer hydrolysis product the maximum of this frequency occurs at 1050 cm^{-1} and characterizes the Si–O group. Deformation vibrations of this bond occur in the original monomer at 515 and 410 cm^{-1}, in the polymer as a singlet at 485 cm^{-1} and a doublet at 425–415 cm^{-1} and in the spectrum of the hydrolysis product at 470 and 425 cm^{-1}, respectively. Characteristic absorption bands of the vinyl groups of tetramethyldivinyldisiloxane at 3050 cm^{-1}, 3010 cm^{-1}, 1610 cm^{-1} and 960 cm^{-1} [8] are absent from the spectrum of the oligomeric phosphine and it may be suggested that the two terminal groups in it are phosphine which is consistent with the phosphorus content of the product. New bands in the oligomer spectra are caused by the phenyl group, the frequency of 1435 cm^{-1} being characteristic of p-C_6H_5. The spectrum of the polyphosphinoborane is typical of polymeric substances, the B–H absorption band of the BH_2-group (2400 cm^{-1}) is, nevertheless, clearly defined. The infrared spectrum of the solid residue after alkali hydrolysis of the polymer shows that the hydrolytic scission begins primarily at the Si–O–Si bond. The hydroxyl groups linked with the silicon atom are probably associated; the characteristic absorption band is found at 3400–3200 cm^{-1}. BH_2-groups are represented by frequencies of 2400 and 2360 cm^{-1} (asymmetric and symmetric BH vibrations).

To define more exactly the structure of the polymeric chains, we decided to synthesize a polymer, the bonding groups of which would have more easily hydrolyzed groups than siloxane groups. We thus prepared 3-oxypropylphenylphosphine, not previously reported, and carried out its condensation with triethylamineborane. It is known that the reaction of alcohols with diborane, even in excess of the latter, give, almost without exception, dialkoxyboranes[9,10]. We should therefore obtain a bisphosphine with the dialkoxyborane group in the bonding chain and a polyphosphino-

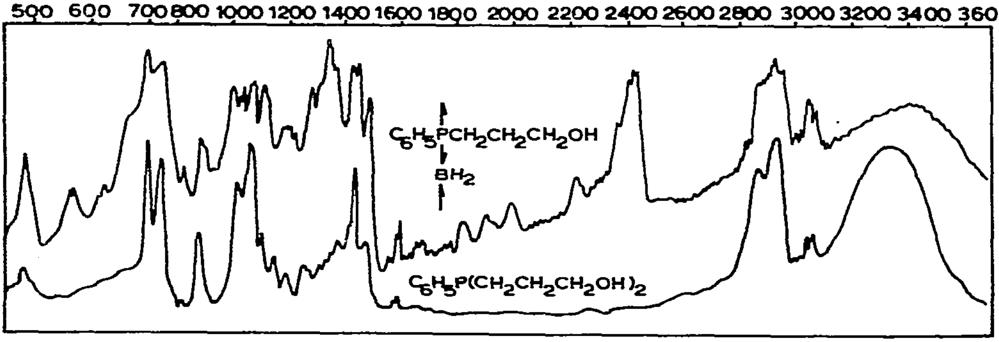
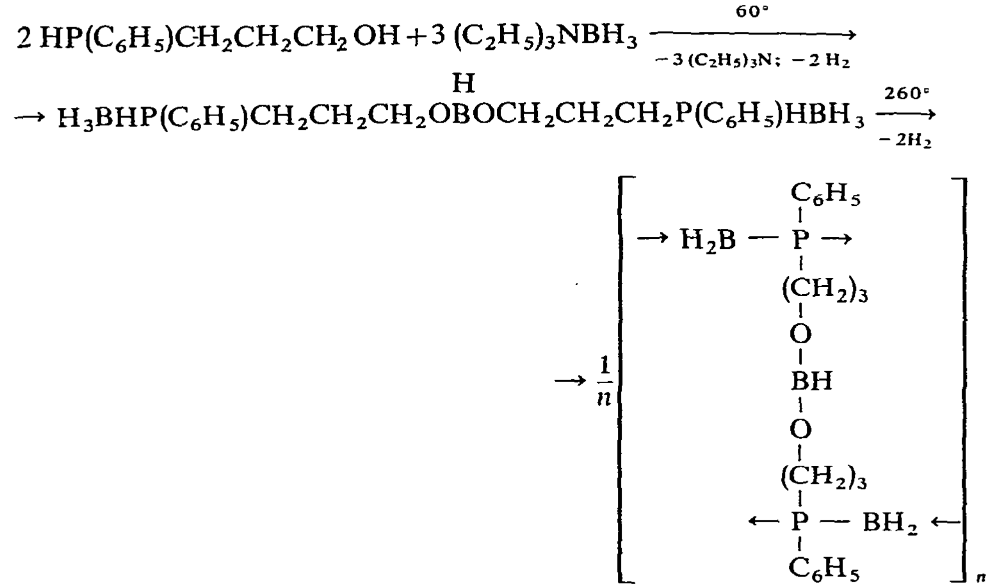


Fig. 6. Infrared spectra of polyphosphinoborane hydrolysis product (KBr pellet) and dioxypropylphenylphosphine (liquid).

borane with a molecular structure similar to that of the above polymers.

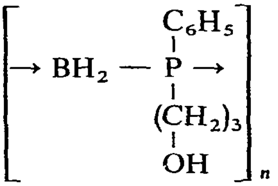
The study made supported our suggestion. At the first stage the reaction of 3-oxypropylphenylphosphine with excess triethylamineborane yielded a diborane complex of bis(3-phenylphosphinopropoxy)borane. Its pyrolysis resulted in a yellow polymeric substance somewhat sensitive to air moisture:



$$2\,HP(C_6H_5)CH_2CH_2CH_2OH + 3\,(C_2H_5)_3NBH_3 \xrightarrow[-3(C_2H_5)_3N;\ -2\,H_2]{60^\circ}$$

$$\rightarrow H_3BHP(C_6H_5)CH_2CH_2CH_2O\overset{H}{B}OCH_2CH_2CH_2P(C_6H_5)HBH_3 \xrightarrow[-2H_2]{260^\circ}$$

Hydrolytic scission of this polymer gave a linear polymer of corresponding elemental composition which was readily soluble in organic solvents (mol.wt. 2700, $n=15$).



Its infrared spectrum corresponds fully to the suggested structure. B–H stretching in the BH_2-group is presented in the spectrum by a very strong band with a maximum at 2415 cm^{-1}. The presence of the oxypropyl group is confirmed by the 3500–3200 cm^{-1} absorption, as well as by characteristic frequencies of 1330 and 995 cm^{-1} (O–H plane deformation vibration and C–O stretching).

The addition of the phosphorus atom to the terminal carbon atom of allyl alcohol was evidenced by the infrared spectrum of the tertiary di(3-oxypropyl)phenylphosphine isolated as the second fraction in the synthesis of 3-oxypropylphenylphosphine (Fig. 6). Aliphatic C–H stretching frequencies have only two absorption maxima at 2940 and 2880 cm^{-1} assigned as asymmetric and symmetric CH-stretching in the CH_2-group. The absence of the methyl group was corroborated by the PMR spectrum of this tertiary phosphine.

Polyphosphinoboranes obtained from bisphosphines and diborane appear to be interesting substances stable to heating, hydrolysis, and chemical action. Their molecules are composed of linear chains of alternating boron and phosphorus atoms linked with coordinative bonds. These chains are bonded with organic cross-links or organo-element groups. However, as they are completely insoluble in organic solvents, there must be cross-links, to a greater or lesser degree, between ladder molecules and the structure of these polymers is, therefore, almost three-dimensional.

EXPERIMENTAL

All experiments were conducted in argon.

Di-1,4-(2-phenylphosphinoethyl)benzene

1,4-Divinylbenzene (5.05 g, 0.038 mole) dissolved in 10 ml of ether was dropped on to 14.6 g (0.13 mole) of phenylphosphine at room temperature with stirring. The reaction mixture was stirred for 18 h. Low boiling fractions were isolated by water pump vacuum and the residue was fractionated. After a fourfold distillation, 4.35 g (32%) of a colourless liquid, b.p. 210–220° (2 mm Hg) were obtained.

1,10-Bis(phenylphosphine)decane

1,9-Decadiene (5.08 g, 0.036 mole) was dropped to 15.15 g (0.137 mole) of phenylphosphine and 0.07 g of the dinitrile of azodiisobutyric acid with stirring at 40–50°. The reaction mixture was heated for 5 h at 40–100° and 10 h at 100°. Low boiling fractions were isolated by water pump vacuum. The residue was fractionated. After double distillation, 32 g (26.7%) of a colourless liquid, b.p. 244–245° (3 mm Hg) were obtained. On standing the liquid crystallized, m.p. 37–38°.

The syntheses of other secondary bisphosphines were carried out similarly.

Reaction of potassium phenylphosphide with 1,10-dibromodecane

1,10-Dibromodecane (7.6 g, 0.025 mole) in 20 ml of benzene were added to a hot suspension of 8 g (0.053 mole) of potassium phenylphosphide, prepared by the method described[11], in 70 ml of benzene. The reaction mixture was boiled until decolourized. The precipitate of potassium bromide was filtered off and washed on the filter with benzene. The benzene solution was fractionated under vacuum. A fraction with b.p. 220–221° (1 mm Hg) was isolated in 8.9 g (91.1%) yield. The liquid crystallized during distillation; m.p. of crystals, 40–40.5°. (Found: C, 73.56; 73.37; H, 9.23, 9.08; P, 17.30, 17.15. $C_{22}H_{32}P_2$ calcd.: C, 73.72; H, 9.00; P, 17.28%.)

Reaction of 1,10-bis(phenylphosphine)decane with triethylamineborane.

A mixture of 1.97 g (0.005 mole) of 1,10-bis(phenylphosphine)decane and 1.4 g (0.012 mole) of triethylamineborane was heated, with gradual increase of temperature to 300° for 24 h. Hydrogen evolution began at 80° and the total amount evolved was 246 ml (1.1 mole). A transparent solid was obtained after additional heating for 3 h at 290–300° and 3 mm Hg in 1.7 (81.3%) yield. (Found: C, 68.01; H, 8.92; B, 5.67; P, 15.72. $C_{22}H_{34}B_2P_2$ calcd.: C, 69.15; H, 8.96; B, 5.67; P, 16.21%.)

Reaction of 1,4-bis(2-phenylphosphinoethyl)benzene with triethylamineborane

Bisphosphine (2.6 g, 0.0074 mole) and 1.85 g (0.016 mole) of triethylamineborane were heated under the above conditions and 2.55 g (92%) of a glassy substance were obtained. (Found: C, 69.34; H, 7.16; B, 5.32; P, 15.41. $C_{22}H_{26}B_2P_2$ calcd.: C, 70.63; H, 7.06; B, 5.78; P, 16.56%.)

Reaction of di(3-phenylphosphino)propyl ether with triethylamineborane

An opaque solid (0.97 g, 100%) was obtained from 0.9 g (0.0028 mole) of di(3-phenylphosphino)propyl ether and 0.75 g (0.0065 mole) of triethylamine borane. (Found: B, 6.60; P, 17.38. $C_{18}H_{26}B_2P_2O$ calcd.: B, 6.33; P, 18.12%.)

Reaction of 3-allyloxypropylphenylphosphine with triethylamineborane

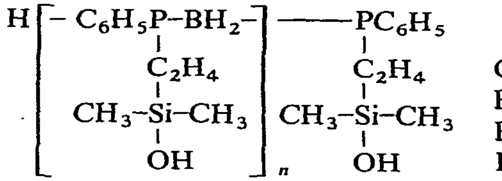
From 2.35 g (0.0113 mole) of phosphine and 2.7 g (0.0234 mole) of triethylamine borane, a glassy polymer was obtained in 2.45 g (96.1%) yield, m.p. 110–113°. (Found: C, 63.27; H, 8.04; B, 7.00; P, 12.50. $C_{24}H_{37}B_3O_2P_2$ calcd.: C, 63.78; H, 8.25; B, 7.18; P, 13.68%.)

Reaction of tetramethyldi(2-phenylphosphinoethyl)disiloxane with triethylamineborane

Bisphosphine (1.14 g, 0.0028 mole) and 0.75 g (0.0065 mole) of triethylamine-borane were heated together with a gradual increase of temperature to 150°, for 3 h and then at 150–200° for 4 h. After additional heating for 3 h at 200° (3 mm Hg) a colourless transparent solid was obtained in 1.25 g (104%) yield. (Found: C, 53.56; H, 7.41; B, 4.92. $C_{20}H_{34}B_2P_2Si_2O$ calcd.: C, 55.76; H, 7.95; B, 5.02%.)

Alkali hydrolysis of polyphosphinoborane with siloxane groups

The substance prepared in the above experiment (0.38 g) was boiled in 2.5 *N* NaOH solution for 6 h. The solution was decanted and the residue washed to neutral reaction and dried. A white brittle substance was obtained in 0.25 g (65.8%) yield. (Found: B, 3.87, 3.75; P, 14.29, 14.21, Si, 12.44, 12.55. $C_{10}H_{18}BPSiO$ unit calcd.: B, 4.82; P, 13.82; Si 12.53%.) For the molecule



$$\mathrm{H}\left[\begin{array}{c} -C_6H_5P-BH_2- \\ | \\ C_2H_4 \\ | \\ CH_3-Si-CH_3 \\ | \\ OH \end{array}\right]_n \begin{array}{c} -PC_6H_5 \\ | \\ C_2H_4 \\ | \\ CH_3-Si-CH_3 \\ | \\ OH \end{array}$$

$C_{40}H_{70}B_3P_4Si_4O_4$ calcd. at $n=3$: B, 3.67; P, 14.02; Si, 12.71%. $C_{50}H_{88}B_4P_5Si_5O_5$ calcd. at $n=4$: B, 3.90; P, 13.98; Si, 12.67%.

Synthesis of 3-oxypropylphenylphosphine

Allyl alcohol (6.72 g, 0.115 mole) was dropped on to 14.0 g (0.127 mole) of phenylphosphine with stirring and heating to 40–50°. The reaction mixture was then heated to 100° and kept at this temperature for 8 h. A fraction with b.p. 107–108° (3 mm Hg) was isolated by distillation, in 9.09 g (46.8%) yield. (Found: C, 63.50, 63.25; H, 7.74, 7.90; P, 18.12, 18.19. $C_9H_{13}OP$ calcd.: C, 64.27; H, 7.79; P, 18.42%.)

Reaction of 3-oxypropylphenylphosphine with triethylamineborane

3-Oxypropylphenylphosphine (3.1 g, 0.018 mole) and 4.5 g (0.039 mole) of triethylamineborane were heated for 14 h, the temperature being gradually increased from 20 to 100°. Hydrogen evolution began at 40°, and was most vigorous at 50–60°, the total amount of hydrogen evolved being 387 ml (0.94 mole). Triethylamine and excess triethylamineborane were removed under vacuum at the bath temperature of 90–95°. A tough opaque mass was obtained in 3.49 g (101.1%) yield. (Found: B, 8.00, 8.02; P, 15.90, 16.09. $C_{18}H_{31}B_3O_2P_2$ calcd.: B, 8.69; P, 16.57%.)

3.21 g of the resulting substance were heated at 260° for 8 h, 337 ml (0.91 mole) of hydrogen being evolved. 3.18 g (100.3%) of a white solid were obtained. (Found: B, 8.90; P, 16.75, 16.53. $C_{18}H_{27}B_3O_2P_2$ calcd.: B, 8.78; P, 16.75%.)

0.9942 g of the resulting substance was boiled in water for 3 h and 25.3 ml of 0.1 *N* alkali solution was used to neutralize the boric acid found in the aqueous solution. The equivalent weight of the substance was 393. The calculated equivalent weight of the $C_{18}H_{27}B_3O_2P_2$ unit was 369.91.

The solid residue of hydrolyzed substance after drying at 110–120° (3 mm Hg) weighed 0.8555 g of 86% of the starting material. (Found: C, 60.90, 60.89; H, 7.80, 7.74; B, 6.20; 6.38; P, 17.37, 17.46. $C_9H_{14}BOP$ calcd.: C, 60.05; H, 7.84; B, 6.01; P, 17.19%.)

The molecular weight of the resulting monomeric compounds was determined by the cryoscopic method in benzene, and that of the polymers by the ebullioscopic method in ethyl alcohol. Infrared spectra were determined using a UR-20-type spectrophotometer using KBr, NaCl and LiP prisms. PMR spectra were determined using the Hitachi H-60 and Perkin–Elmer R-12 spectrophotometers (operating frequency, 60 Mcps at 34°) in benzene using tetramethylsilane as external standard. Thermomechanical curves were obtained by the pulver method. Operating pressure was 0.8 kg/cm^2. Thermogravigrams were determined by means of McBen balances. The temperature increase rate was 200°/h.

CONCLUSIONS

1. A number of polyphosphinoboranes stable on heating to 300–400° in air, and chemically inert, have been prepared by the reaction of secondary bisphosphines with triethylamineborane.
2. It has been shown that polyphosphinoborane molecules are composed of linear B–P chains bonded with organic or organo-element bonding groups.
3. Secondary phosphines and bisphosphines used in polymer synthesis were first prepared by the reaction of phenylphosphine with organic or organo-element vinyl and divinyl compounds.

REFERENCES

1 E. Hofmann, *Brit. Patent*, 941556 (1963); 941557 (1963); *Chem. Abstr.*, 60 (1964) 4305; 4184.
2 A. B. Burg and R. I. Wagner, *U.S. Patent*, 2948689 (1960).
3 M. M. Rauhut, H. A. Currier, A. M. Semsel and V. P. Wystrach, *J. Org. Chem.*, 26 (1961) 5138.
4 H. Niebergall, *Makromol. Chem.*, 52 (1962) 218.
5 H. Niebergall and K. Gutweiler, *BRD Patent*, 1103590 (1961); *Chem. Abstr.*, 55 (1961) 24102.
6 H. Nöth and W. Schrägle, *Chem. Ber.*, 98 (1965) 352.
7 E. C. Ashby, *J. Amer. Chem. Soc.*, 81 (1959) 4791.
8 J. Knizek, M. Horák and V. Chvalovský, *Collection Czech. Chem. Commun.*, 28 (1963) 3079.
9 W. J. Lehmann, H. F. Weiss and I. Shapiro, *J. Chem. Phys.*, 30 (1959) 1226.
10 H. Steinberg, *Organoboron Chemistry*, Vol. I, Interscience, New York, 1964, p. 486.
11 K. Issleib and D. Jacob, *Chem. Ber.*, 94 (1961) 107.