

803. Phosphorus–Boron Compounds. Part I. Cyclodiphosphinoborines.

By W. GEE, R. A. SHAW, and B. C. SMITH.

A series of phosphine–borane addition compounds and two cyclodiphosphinoborines have been prepared. The reactions of the latter have been studied and their structures are discussed.

CYCLOPHOSPHINOBORINES, $P_nR_{2n}B_nX_{2n}$, were first prepared by Burg and Wagner.¹ The remarkable stability of cyclotriphosphinoborines ($n = 3$)¹⁻⁴ and cyclotetraphosphinoborines ($n = 4$)^{1,3} attracted considerable attention; since then polyphosphinoborines,^{1,5} cyclodiphosphinoborines^{4,6} and monophosphinoborines^{7,8} have been reported. This Paper describes the preparation of some phosphine–borane addition compounds in which phenyl groups are attached to phosphorus, and the preparation and properties of 2,2,4,4-tetrahalogeno-1,1,3,3-tetraphenylcyclodiphosphinoborines, $P_2Ph_4B_2X_4$ ($X = Br, I$).

The molecular addition compounds Ph_3P, BBr_3 ,⁹ Ph_3P, BI_3 , Ph_2PH, BBr_3 , Ph_2PH, BI_3 , and Ph_3P, BPh_3 ¹⁰ have been prepared and characterised. Two of these compounds have been reported previously, and an addition compound $3Ph_3P, BI_3$ has also been described.¹¹ Other addition compounds required as intermediates, Ph_2PH, BCl_3 ⁸ and Ph_2PH, BPh_2I , were isolated but not characterised.

Phosphinoborines are prepared conveniently by elimination of *e.g.*, hydrogen, hydrogen halides, or trialkylsilyl derivatives from suitable phosphine–borane addition compounds. The products obtained depend on the method of preparation and on the nature of the substituents. The formation of cyclodiphosphinoborines appears to be favoured from addition compounds of boron tribromide or boron tri-iodide.

Reaction of triethylamine with a solution of diphenylphosphine–boron tribromide or tri-iodide in benzene gives a precipitate of triethylammonium halide, and almost quantitative yields of 2,2,4,4-tetrahalogeno-1,1,3,3-tetraphenylcyclodiphosphinoborines are obtained. Isolation of the intermediate addition compounds is not essential. No precipitate of triethylammonium chloride was observed on addition of an excess of triethylamine to diphenylphosphine–boron trichloride in benzene. Dehydroiodination of diphenylphosphine–diphenyliodoborane gives a stable insoluble product of empirical composition Ph_2P, BPh_2 . This compound has also been prepared by Coates and Livingstone,⁸ who consider that it may be monomeric or capable of dissociation into monomeric species.

The reactivity of boron–hydrogen bonds in phosphinoborines is considerably less than that observed in boron hydrides and borazoles. Similarly, there is a decrease in reactivity of boron–halogen bonds in halogenocyclodiphosphinoborines, particularly pronounced in the case of the iodide, when compared with those of the boron halides and halogenoborazoles. The iodide, $P_2Ph_4B_2I_4$, is stable in moist air. There is no reaction with ethanol at room temperature, diethylamine in boiling benzene, boiling methyl iodide, dinitrogen tetroxide in cyclohexane, phenylmagnesium bromide in boiling tetrahydrofuran–benzene, or potassium thiocyanate in acetone. The bromide, $P_2Ph_4B_2Br_4$,

¹ Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

² Biddulph, Brown, Cass, Long, and Silver, *J.*, 1961, 1822.

³ Burg and Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198.

⁴ Nöth and Schrägle, *Z. Naturforsch.*, 1961, **16b**, 473.

⁵ Wagner and Caserio, *J. Inorg. Nuclear Chem.*, 1959, **11**, 259.

⁶ Gee, Shaw, Smith, and Bullen, *Proc. Chem. Soc.*, 1961, 432.

⁷ Parry and Bissot, *J. Amer. Chem. Soc.*, 1956, **78**, 1524; Coates and Livingstone, *J.*, 1961, 5053; Nöth and Schrägle, *Angew. Chem. (Internat. Edn.)*, 1962, **1**, 457.

⁸ Coates and Livingstone, *J.*, 1961, 1000.

⁹ Heal and Madden, *Nature*, 1962, **195**, 280.

¹⁰ Wittig and Haag, *Chem. Ber.*, 1955, **88**, 1654.

¹¹ Muetterties, *J. Inorg. Nuclear Chem.*, 1960, **15**, 182.

decomposes in moist air and reacts with diethylamine in benzene to give trisdiethylamino-borane and diphenylphosphine. There is no reaction with ethanol at room temperature or with phenylmagnesium bromide in boiling ether-benzene, but reaction occurs with phenyl-lithium in boiling benzene and subsequent hydrolysis gives a low yield of triphenyl-boroxole, $B_3Ph_3O_3$; no phosphinoborine was recovered. It is not clear whether reaction occurs first with the B-P or B-Br bonds. The above contrasts with the vigorous reactions of alcohols and Grignard reagents with boron halides and halogenoborazoles. The rapid cleavage of ethers by boron tribromide¹² and the replacement of halogen by pseudo-halides in boron-nitrogen compounds¹³ have been observed recently.

We have drawn attention elsewhere¹⁴ to the behaviour of compounds of the biacyl type, Y-Y', where Y and Y' are the same or different acid residues including acyl, triazinyl, and phosphino. We consider that the diphosphinoborines are compounds of this type: reaction of the bromide, $P_2Ph_4B_2Br_4$, with diethylamine is analogous to that of the acylphosphine, $PhCO \cdot PET_2$, with phenylhydrazine giving N-anilinobenzamide, $PhCO \cdot NH \cdot NHPH$, and diethylphosphine.¹⁵

X-Ray-crystallographic data show that the bromo- and iodo-compounds are isomorphous and that the possibility of a trimeric structure can be rejected.⁶ This is further confirmed by the chemical and physical properties of the dimeric bromide, $P_2Ph_4B_2Br_4$, which are different from those of the trimeric bromide, $P_3Ph_6B_3Br_6$, which has been prepared from the cyclotriphosphinoborine, $P_3Ph_6B_3H_6$, by substitution.¹⁶ The corresponding hexaiodocyclotriphosphinoborine is so far unknown. Chemical arguments (see below) show that a monomeric structure is unlikely. Ebullioscopic measurements over the concentration range 0—3% w/v establish that the compounds are dimeric.

It has been suggested that the diphosphinoborine, $P_2Bu_4B_2Br_4$, contains a four-membered phosphorus-boron ring.⁴ This structure is more probable than the alternative four-membered boron-halogen ring with exocyclic PR_2 groups, and our findings are in agreement with this. Halogen bridges are unlikely in boron chemistry, although they are known in compounds of aluminium and gallium, as well as elsewhere in the periodic table.¹⁷

The donor properties of phosphino-groups in the biacyl species, Y-Y', discussed elsewhere,¹⁴ are reduced but are sufficiently pronounced for reaction to occur with methyl iodide or oxidising agents. The iodide, $P_2Ph_4B_2I_4$, is neither quaternised by methyl iodide nor oxidised by dinitrogen tetroxide, presumably because the lone pair of electrons of phosphorus participates in dative bonding to boron. Ready quaternisation by methyl iodide has been found for the monomeric 2,2-diaryl-1,1-diethylphosphinoborines.⁸

Methyl iodide and dinitrogen tetroxide would be expected to react with the lone pair of electrons of the phosphorus atom which here is involved in dative bonding to the boron atom. The nitrogenous bases probably react by nucleophilic attack on the atom bonded to phosphorus, boron in this case, and carbonyl carbon in the example mentioned above.¹⁵

The infrared spectra of the two cyclodiphosphinoborines, and of the addition compounds reported here, resemble the spectrum of triphenylphosphine. We are unable to assign particular bands to the P-B bond. It has been suggested⁸ that the peak at 1440 cm^{-1} , which occurs in a number of monophosphinoborines with P-Ph or B-Ph groups, can be assigned to the P-B bond. Compounds containing P-Ph groups invariably show an intense band at $1445\text{--}1440 \text{ cm}^{-1}$ and this is accompanied by a well-resolved peak

¹² McOmie and Watts, *Chem. and Ind.*, 1963, 1658; Manson and Musgrave, *J.*, 1963, 1101; Bonner, Bourne, and McNally, *J.*, 1960, 2929; Amonoo-Neizer, Shaw, and Smith, unpublished results.

¹³ Lappert and Pyszora, *Proc. Chem. Soc.*, 1960, 350; *J.*, 1963, 1744; Turner and Warne, *Proc. Chem. Soc.*, 1962, 69; Turner, personal communication.

¹⁴ Hewertson, Shaw, and Smith, *J.*, 1964, 1020.

¹⁵ Issleib and Priebe, *Chem. Ber.*, 1959, 92, 3183.

¹⁶ Gee, Shaw, and Smith, submitted for publication.

¹⁷ Cf. Hayter, *J. Amer. Chem. Soc.*, 1962, 84, 2004, 3046.

at 1000 cm^{-1} .^{18,19} Similarly, compounds with B-Ph or Si-Ph groups show intense absorption at 1440—1430 or 1430—1425 cm^{-1} , respectively.¹⁸

EXPERIMENTAL

Many of the starting materials and intermediates are unstable to oxidation and hydrolysis, and most of the reactions were conducted in an atmosphere of purified nitrogen. "Oxygen-free" nitrogen was passed through two columns (30 \times 2.5 cm.) of manganous oxide (prepared by heating manganous oxalate, supported on calcium sulphate, in a stream of nitrogen at 400°) and two similar columns of phosphorus pentoxide. Glass apparatus was baked at 120° (5 hr.), assembled hot, evacuated, flushed with purified nitrogen three times, and allowed to cool under a slight positive pressure of nitrogen.

Melting points of stable compounds were observed on a Reichert-Kofler micro-heating apparatus fitted with a polarising microscope. A Gallenkamp electric melting-point apparatus with sealed tubes was used for unstable materials. Molecular weights were measured in a modified Gallenkamp ebulliometric apparatus.

Solvents.—Benzene, ether, light petroleum (b. p. 60—80°), and pentane were dried with sodium wire. Chloroform and carbon tetrachloride were dried by distillation from phosphorus pentoxide. Ethanol was dried by distillation from sodium and dibutyl phthalate, and was stored in a molecular-sieve column. Amines were dried by distillation from potassium hydroxide and barium oxide, triethylamine being purified first by distillation from acetic anhydride.

Phosphines.—Triphenylphosphine, m. p. 79.5°, was recrystallised from ethanol. Diphenylphosphine, b. p. 103°/1 mm., was prepared from triphenylphosphine by reaction with sodium in liquid ammonia,²⁰ and was stored in sealed ampoules under nitrogen. Diphenyliodoborane, b. p. 140°/1.2 mm., was prepared²¹ by the action of boron tri-iodide on diphenylboronous anhydride.

Molecular Addition Compounds.—Phosphine-borane addition compounds were prepared from their components in pentane solution and the precipitates were recrystallised from chloroform-light petroleum. Preparative details and analytical data are recorded in the Table.

Preparation of phosphine-boranes.

| Phosphine | | | | | Compound | No. | M. p. | Yield | | |
|-------------------------|------|--------|------------------|--------|----------|--------------------------------------|-------|----------|------|----|
| | (g.) | (mole) | Borane (g.) | (mole) | | | | (g.) | (%) | |
| PPh ₃ | 0.54 | 0.002 | BPh ₃ | 0.5 | 0.002 | Ph ₃ P, BPh ₃ | 1 | 212—213° | 0.95 | 91 |
| PPh ₃ | 8.3 | 0.030 | BBr ₃ | 8.0 | 0.030 | Ph ₃ P, BBr ₃ | 2 | 194—195 | 14.0 | 86 |
| PPh ₃ | 6.7 | 0.025 | BI ₃ | 10.0 | 0.025 | Ph ₃ P, BI ₃ | 3 | 168—169 | 12.8 | 77 |
| PHPh ₂ | 12.8 | 0.063 | BBr ₃ | 17.2 | 0.067 | Ph ₂ PH, BBr ₃ | 4 | 133—134 | 25.0 | 83 |
| PHPh ₂ | 4.75 | 0.025 | BI ₃ | 10.0 | 0.025 | Ph ₂ PH, BI ₃ | 5 | 137—139* | 14.0 | 95 |

* Decomp.

Analyses of phosphine-boranes.

| No. | Found (%) | | | | | M | Formula | Calc. or required (%) | | | | | M |
|-----|-----------|-----|------|------|-----|-----|--|-----------------------|------|------|-------|-----|-----|
| | C | H | B | Hal | P | | | C | H | B | Hal | P | |
| 1 | 84.7 | 6.3 | 2.05 | — | 6.6 | — | C ₃₆ H ₃₀ BP | 85.7 | 6.0 | 2.1 | — | 6.1 | — |
| 2 | 42.0 | 2.8 | 2.0 | 44.3 | 5.5 | 527 | C ₁₆ H ₁₅ BBr ₃ P | 42.15 | 2.95 | 2.1 | 46.75 | 6.0 | 513 |
| 3† | 32.8 | 2.1 | 1.7 | 57.6 | 4.7 | 729 | C ₁₈ H ₁₅ BI ₃ P | 33.1 | 2.3 | 1.65 | 58.2 | 4.7 | 654 |
| 4† | 32.8 | 2.6 | 2.1 | 54.6 | — | 439 | C ₁₂ H ₁₁ BBr ₃ P | 33.0 | 2.5 | 2.5 | 54.9 | — | 437 |
| 5† | 25.05 | 2.1 | 1.85 | 66.1 | 6.1 | — | C ₁₂ H ₁₁ BI ₃ P | 24.9 | 1.9 | 1.9 | 65.9 | 5.4 | — |

† New compound.

2,2,4,4-Tetrahalogeno-1,1,3,3-tetraphenylcyclophosphinoboranes.—*Preparation.* Diphenylphosphine (11.8 g., 0.064 mole) in benzene (50 ml.) was added to a stirred solution of boron

¹⁸ Cross, "Introduction to Practical Infrared Spectroscopy," Butterworths, London, 1960; Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958.

¹⁹ Daesch and Smith, *Analyt. Chem.*, 1951, **23**, 853.

²⁰ Hewertson and Watson, *J.*, 1962, 1490; Müller, Thesis, Tübingen, 1957, quoted in Gilman and Wittenberg, *J. Org. Chem.*, 1958, **23**, 1063; Gee, Hewertson, Shaw, and Smith, unpublished results.

²¹ Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

tribromide (15.9 g., 0.063 mole) in benzene (150 ml.) at room temperature. Triethylamine (6.4 g., 0.063 mole) dissolved in benzene (30 ml.), was added slowly to the reaction mixture and a copious white precipitate formed immediately. The stirred mixture was heated under reflux on an oil bath at $<110^\circ$ (2 hr.), cooled to room temperature, and crystalline triethylammonium bromide (21.8 g., 96%), m. p. $183\text{--}184^\circ$, was removed by filtration. The filtrate was evaporated to dryness and the solid residue was extracted with cold dry ethanol. Recrystallisation from benzene gave colourless laths of 2,2,4,4-tetrabromo-1,1,3,3-tetraphenylcyclodiphosphinoborine (18.5 g., 85%), m. p. $183\text{--}184^\circ$ (decomp.) (Found: C, 40.9; H, 3.0; B, 2.75; Br, 43.5; P, 9.0%; *M*, 740, 738, 677 in benzene, toluene, and carbon tetrachloride, respectively. $\text{C}_{24}\text{H}_{20}\text{B}_2\text{Br}_4\text{P}_2$ requires C, 40.5; H, 2.8; B, 3.0; Br, 44.9; P, 8.7%; *M*, 712).

Diphenylphosphine (9.5 g., 0.05 mole) reacted similarly with boron tri-iodide (20.0 g., 0.05 mole) and triethylamine (5.1 g., 7.0 ml., 0.05 mole) in benzene solution. The product was isolated by extraction with dry alcohol and recrystallisation of the residue from chloroform-light petroleum gave colourless 2,2,4,4-tetraiodo-1,1,3,3-tetraphenylcyclodiphosphinoborine (20.7 g., 91%), m. p. $194\text{--}195^\circ$ (decomp.) (Found: C, 31.7; H, 2.5; B, 2.6; I, 55.8; P, 7.3%; *M*, 862, 929 in benzene, 962 in carbon tetrachloride. $\text{C}_{24}\text{H}_{20}\text{B}_2\text{I}_4\text{P}_2$ requires C, 32.0; H, 2.2; B, 2.4; I, 56.4; P, 6.9%; *M*, 900).

A solution of diphenylphosphine-boron trichloride (19 g., 0.063 mole), prepared by the reaction of boron trichloride with diphenylphosphine, was treated with an excess of triethylamine (7 g., 0.07 mole) in benzene. The mixture was heated under reflux, but no precipitate of triethylammonium chloride was observed on cooling.

Reactions.—Diethylamine. Diethylamine (15.2 g., 0.020 mole) in benzene was added to a solution of 2,2,4,4-tetrabromo-1,1,3,3-tetraphenylcyclodiphosphinoborine (18.6 g., 0.025 mole) in benzene (150 ml.). A precipitate formed and the stirred mixture was boiled under reflux (2 hr.). The solvent was evaporated and the residual oil triturated with benzene (30 ml.). The solid residue was removed by filtration, and recrystallisation from ethanol-ether gave diethylammonium bromide (12.0 g., 68%), m. p. 213° . Fractional distillation of the filtrate gave (a) benzene, b. p. 80° , (b) trisdiethylaminoborane, b. p. $45^\circ/1$ mm. (lit.,²² $50\text{--}53^\circ/0.4$ mm.) (Found: B, 4.7. Calc. for $\text{C}_{12}\text{H}_{30}\text{BN}$: B, 4.8%), hydrolysis gave diethylamine which was characterised by formation of the picrate, m. p. and mixed m. p. $73\text{--}74^\circ$, and (c) diphenylphosphine, b. p. $103^\circ/1$ mm. (lit.,²³ $100\text{--}102^\circ/1.5$ mm.). This was characterised further by the preparation of dimethyldiphenylphosphonium iodide, m. p. and mixed m. p. $258\text{--}260^\circ$.

Phenyl-lithium. A solution of phenyl-lithium, prepared from lithium (7 g., 1 mole) and bromobenzene (78 g., 0.5 mole) in pentane, was filtered and added to a solution of 2,2,4,4-tetrabromo-1,1,3,3-tetraphenylcyclodiphosphinoborine (18.6 g., 0.025 mole) in benzene (400 ml.). The mixture was boiled under reflux (2 hr.), concentrated to ca. 100 ml., diluted with ether (100 ml.), and hydrolysed with 2*N*-hydrochloric acid (1 l.). The organic layer was washed with water, 5% sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), filtered, and evaporated to dryness under reduced pressure. Recrystallisation of the residue from benzene-cyclohexane gave a trace of triphenylboroxole, m. p. and mixed m. p. $217\text{--}218^\circ$.

1,1,2,2-Tetraphenylphosphinoborine.—Diphenylphosphine-diphenyliodoborane (5 g., 0.01 mole) in benzene (150 ml.) reacted with an excess of triethylamine (9 ml.) to give a colourless crystalline precipitate from which triethylammonium iodide (3.0 g., 98%) was extracted with alcohol. The residue, 1,1,2,2-tetraphenylphosphinoborine (3.6 g., 99%), m. p. 234° , was insoluble in common organic solvents (Found: C, 82.0; H, 5.6; B, 2.8; P, 9.0. Calc. for $\text{C}_{24}\text{H}_{20}\text{BP}$: C, 82.3; H, 5.8; B, 3.1; P, 8.85%).

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DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
MALET STREET, LONDON W.C.1.

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²² Gerrard, Lappert, and Pearce, *J.*, 1957, 381.

²³ Kuchen and Buchwald, *Chem. Ber.*, 1958, **91**, 2871.