Preparation and Structure of 1,4-Dichloro-1,1,3,3-tetraphenyl-*catena*-di(boraphosphane), $BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl$

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The title compound has been isolated as an unexpected product of the reaction between $[NMe_4][B_3H_8]$ and PPh_2Cl, and has been examined by ^1H, ^{31}P, and ^{11}B n.m.r. spectroscopy and by single-crystal *X*-ray analysis. The compound crystallizes in colourless prisms in the triclinic space group $P\bar{1}$ with a = 12.15(5), b = 12.151(7), c = 9.523(4) Å, α = 92.60(4), β = 103.48(3), γ = 116.33(4)°, U = 1 207.4(9) Å^3, and Z = 2. The structure has been solved using diffractometer data on 2 028 independent reflections; all the atoms have been included in the refinement which gives a final R of 0.043 and R' of 0.053. Interatomic distances along the chain are Cl(1)–B(1) 1.877(7), B(1)–P(2) 1.953(6), P(2)–B(3) 1.959(6), B(3)–P(4) 1.907(6), and P(4)–Cl(4) 2.025(2) Å. The angles Cl(1)–B(1)–P(2) 110.1(3), B(1)–P(2)–B(3) 113.6(3), P(2)–B(3)–P(4) 117.1(2), and B(3)–P(4)–Cl(4) 113.5(2)° are all somewhat larger than tetrahedral, presumably due to non-bonded steric interaction.

BORAPHOSPHANES $(BH_2PR_2)_n$ which have a cyclic structure have been known for over a quarter of a century, and have thermal, hydrolytic, and oxidative stabilities which are said to be remarkable for compounds which have B–H bonds.[1-3] The origin of this stability is not as yet thoroughly understood, but is generally supposed to arise from steric hindrance to the reaction of nucleophiles,[4] or from hyperconjugative H–B–P interaction which will both reduce the hydridic character of the boron hydrogens and stabilize the boron–phosphorus bonding.[4,5] Evidence for the latter is generally taken from the molecular structure[5] of the trimer $(BH_2PMe_2)_3$, in which the B–P–B and P–B–P interbond angles of 118 and 112° respectively are somewhat larger than the tetrahedral angle, but it is not certain whether any delocalization extends to the whole ring system. It is important in this context to have structural data for an acyclic analogue, and we report here results obtained for the novel linear 1,4-dichloro-1,1,3,3-tetraphenyl-*catena*-di(boraphosphane) $(BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl)$ which we have isolated as an unexpected product from the reaction of chlorodiphenylphosphine with tetramethylammonium octahydrotriborate $[NMe_4][B_3H_8]$. Only two examples of linear boraphosphanes have previously been claimed:[6,7] these are polymers tentatively formulated as $(BH_2PR_2)_n$, where $R_2 = Me_2$ and MeEt and n = 80 and 20 respectively, but for which no further structural data are available.

EXPERIMENTAL

All the manipulations, apart from those involving the final air-stable crystalline sample of $BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl$, were carried out under dry nitrogen.

Nuclear Magnetic Resonance Spectra.—These were obtained at 27 °C in the Fourier-transform mode on a modified Bruker HX instrument operating at 90 MHz for ^1H, 36.4 MHz for ^{31}P, and 28.9 MHz for ^{11}B. Reference standards were $SiMe_4$(internal), 85% H_3PO_4(external), and $OEt_2{\cdot}BF_3$ in C_6D_6(external) respectively, and chemical shifts to high frequency of these are quoted as positive. It should be noted that this recently recommended sign convention[8] has the disadvantage that chemical shifts and nuclear shielding are of opposite sign. For comparison, $\delta(^{31}P)$ was also measured for $(PClPh_2)_2B_{10}H_{12}$ and for $Ph_2PB_{10}H_{13}$ (saturated solutions in CD_2Cl_2) and found to be $+81 \pm 1$ and -57 ± 1 p.p.m. respectively.

Infrared Spectra.—These were recorded using KBr discs and a Perkin-Elmer 457 instrument, and calibrated using a polystyrene film.

Reaction of Chlorodiphenylphosphine with Thallium Octahydrotriborate.—Following some preliminary unpublished work in this Department by I. M. Ward, $Tl[B_3H_8]$ (0.74 g, 3.0 mmol) was added to a solution of PPh_2Cl (0.67 g, 3.0 mmol) in CH_2Cl_2 (18 cm^3) and stirred for 25 h at room temperature (21 °C). Hydrogen (1.8 mmol) was evolved. The mixture was filtered, and the volatile components were removed from the filtrate at 0.01 mmHg,† yielding a translucent viscous syrup. The ^{31}P-$\{^1H$(broad-band)$\}$ n.m.r. spectrum of this showed at least 20 resonance lines (50% v/v in CD_2Cl_2; δ ±0.5 p.p.m.; relative intensities as percentages of the total phosphorus are given in parentheses): +94.5(3.2), +93.0(2.5), +92.0(3.1), +91.5(0.9), +90.0(2.5), +89.5(1.9), +87.5(3.0), +83.0(0.4), +32.5 (4.1); +26.0(7.3), +21.5(11.6), +14.5(11.3), +12.5(10.7), +9.5(11.0); +7.5(10.3), +5.0(1.6), +2.0(1.3), −6.0(6.3), −21.5(6.0), and −26.0(0.4). The ^{11}B n.m.r. spectrum had two broad envelopes of overlapping resonances in the regions δ −5 to −20 and −30 to −55 p.p.m. This complex mixture could not be separated into identifiable components.

Preparation of 1,4-*Dichloro*-1,1,3,3-*tetraphenyl*-catena-*di*(*boraphosphane*), $BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl$.—A solution of PPh_2Cl (2.0 g, 9.1 mmol) in CH_2Cl_2 (30 cm^3) was stirred with a 1 : 2 w/w mixture of $[NMe_4][B_3H_8]$ and $[NMe_4]I$ (1.0 g, containing *ca.* 2.9 mmol of $[B_3H_8]^-$) for 28 h and filtered. The volatile components were removed from the filtrate under reduced pressure (0.01 mmHg, 20 °C, 15 h). The resulting colourless viscous syrup was shaken vigorously with OEt_2 (20 cm^3) for *ca.* 2 min, and rapidly decanted. The ether was removed from the decantate (0.1 mmHg,

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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20 °C, 2 h) and the resulting semi-solid dissolved in the minimum amount of warm C_6H_6 (*ca.* 5 cm^3 at 50 °C). Hexane was added dropwise until a faint turbidity persisted, and the solution was briefly warmed and then allowed to cool, yielding a small quantity of crystalline material. Recrystallization from benzene–hexane afforded a mixture of fused crystalline clusters, m.p. 118—120 °C (minor component) and isolated prisms of the title compound, m.p. *ca.* 210 °C (decomp.) (major component). These two components were separated by hand and found to have identical i.r. spectra in the 250—4 000 cm^{-1} region, with principal peaks as follows: $\nu_{max.}$ at 3 050mw, 2 430s, 2 395s, 2 380(sh), 1 585mw, 1 485m, 1 435s, 1 310mw, 1 190mw, 1 145m, 1 105s, 1 020s, 1 000m, 985mw, 755m, 750m, 730m, 720m, 695s, 655m, 600m, 530m, 490m, 480m, 445mw, 400mw, and 350mw cm^{-1} (KBr disc; ± 5 cm^{-1}). Microanalysis of a small sample of mixed crystals showed the presence of chlorine and iodine in an atomic ratio of *ca.* 4.5 : 1 which suggests that the compounds may differ only in the nature of one of the halogen atoms. A solution of the prisms in $CDCl_3$ had the following n.m.r. parameters: $\delta(^{11}B)$ -15.5 ($w_{\frac{1}{2}}$ *ca.* 350 Hz) and -31 p.p.m. ($w_{\frac{1}{2}}$ *ca.* 250 Hz) ($w_{\frac{1}{2}}$ in each case decreased by a factor of *ca.* 1.5 on broadband ^1H irradiation); δ (^{31}P) -26 and $+83$ p.p.m., $^2J(^{31}P-^{31}P)$ *ca.* 80 Hz; and δ (^1H) $+1.1$ ($w_{\frac{1}{2}}$ *ca.* 120 Hz) and $+3.0$ p.p.m. ($w_{\frac{1}{2}}$ *ca.* 150 Hz), together with aromatic proton resonance lines. The solid-phase structure and constitution of this compound (*i.e.* the major component) were found by single-crystal *X*-ray diffraction analysis (see below). The compound is quite stable, our remaining crystals being unchanged after storage in air for 13 months.

It should be noted that the above conditions for the isolation of this product are very critical; furthermore, a number of attempts to prepare it from $Tl[B_3H_8]$, or from $[NMe_4][B_3H_8]$ in the absence of $[NMe_4]I$, were unsuccessful, as were attempts to isolate the other components of the reaction mixture. Viscous syrups, semi-solids, and gels were generally obtained, of which the ^{31}P n.m.r. spectra were similar to that described above, resonances in the region δ (^{31}P) $+80$—$+100$ p.p.m. being broadly associable with the chlorodiphenylphosphine moiety bonded to boron, and those in the region $+30$ to -30 p.p.m. with the diphenylphosphine group bonded to electropositive atoms such as B, P, and H.

X-*Ray Diffraction Experiments.—Crystal data.* $C_{24}H_{24}B_2Cl_2P_2$, $M = 466.93$, Triclinic, $a = 12.151(5)$, $b = 12.151(7)$, $c = 9.523(4)$ Å, $\alpha = 92.60(4)$, $\beta = 103.48(3)$, $\gamma = 116.33(4)°$, $U = 1\,207.4(9)$ Å^3, $Z = 2$, $D_c = 1.284$ g cm^{-3}, $F(000) = 484$. Space group $P\bar{1}$. Mo-K_α radiation, graphite-monochromatized, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 4.07 cm^{-1}.

Structure determination. Preliminary photographs showed the crystals to be triclinic and subsequent measurements were made on a Syntex $P2_1$ diffractometer. The crystal used was an irregular fragment of mean diameter *ca.* 0.4 mm. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40°$. Intensities of all the independent reflections with $5 < 2\theta < 40°$ were measured in the θ—2θ scan mode, using scans from 1.0° below K_{α_1} to 1.0° above K_{α_2}. The structure analysis used the 2 028 independent reflections having $I > 3\sigma(I)$, where $\sigma(I)$ was calculated from counting statistics; another 242 reflections were considered 'unobserved'. Absorption corrections were not made.

Non-hydrogen atoms were located from Patterson and electron-density syntheses, and least-squares refinement converged at R 0.072. A difference map then showed the hydrogen atoms as the 24 highest peaks (0.73—0.88 e Å^{-3}), and they are included as fixed contributions with $U_{iso.}$ 0.05 Å^2. Further refinement of the non-hydrogen atoms led to convergence at R 0.043 and R' 0.053. The function minimized was $\Sigma w(F_o - |F_c|)^2$, with $w^{-1} = \sigma^2(F_o) = \sigma^2(I)/4LpI$. Use of weights based on the errors due to counting statistics gave a fairly uniform distribution of $w\Delta^2$ as a function of F_o, although the final value of $[\Sigma w\Delta^2/(n-m)]^{\frac{1}{2}} = 4.98$ indicates a substantial contribution to the errors from other sources. Further refinement in which the hydrogen-atom parameters were also allowed to vary converged at R 0.035

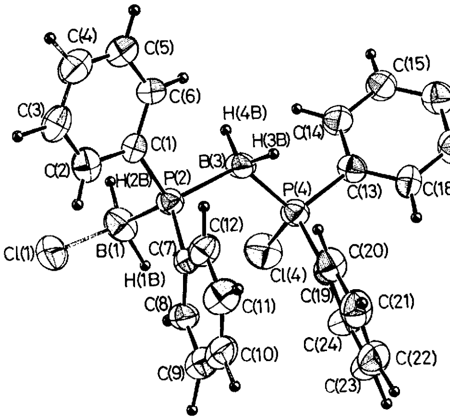
TABLE 1

Atomic fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
B(1)	0.310 8(5)	0.709 4(5)	0.414 7(6)
P(2)	0.395 9(1)	0.771 9(1)	0.263 7(1)
B(3)	0.402 9(5)	0.930 1(5)	0.218 2(6)
P(4)	0.244 6(1)	0.927 4(1)	0.124 3(1)
Cl(1)	0.321 8(1)	0.565 5(1)	0.461 3(1)
Cl(4)	0.113 7(1)	0.862 3(1)	0.238 3(1)
C(1)	0.562 0(4)	0.802 4(4)	0.324 6(4)
C(2)	0.590 3(4)	0.703 8(4)	0.341 1(5)
C(3)	0.716 6(4)	0.726 0(5)	0.394 8(5)
C(4)	0.813 9(4)	0.846 7(5)	0.429 9(5)
C(5)	0.786 9(4)	0.944 0(4)	0.414 1(5)
C(6)	0.661 7(4)	0.922 6(4)	0.362 2(5)
C(7)	0.324 7(4)	0.657 7(4)	0.096 6(4)
C(8)	0.198 5(4)	0.567 6(4)	0.065 3(5)
C(9)	0.137 7(4)	0.487 2(4)	−0.068 8(5)
C(10)	0.204 5(5)	0.496 3(4)	−0.169 4(5)
C(11)	0.330 8(5)	0.583 3(5)	−0.137 8(5)
C(12)	0.391 7(4)	0.665 1(4)	−0.005 5(5)
C(13)	0.271 4(4)	1.085 3(4)	0.116 4(4)
C(14)	0.335 3(4)	1.172 6(4)	0.243 4(5)
C(15)	0.358 2(4)	1.294 7(4)	0.239 1(5)
C(16)	0.319 5(4)	1.329 4(4)	0.109 5(5)
C(17)	0.255 9(4)	1.241 6(4)	−0.017 1(5)
C(18)	0.232 5(4)	1.120 1(4)	−0.014 6(5)
C(19)	0.159 7(4)	0.837 5(4)	−0.057 0(4)
C(20)	0.228 8(4)	0.821 1(4)	−0.145 5(5)
C(21)	0.165 2(5)	0.752 3(5)	−0.284 5(5)
C(22)	0.035 1(5)	0.700 4(5)	−0.334 3(5)
C(23)	−0.033 3(5)	0.718 1(5)	−0.249 8(5)
C(24)	0.027 6(4)	0.785 7(5)	−0.111 4(5)
H(2)	0.522	0.618	0.304
H(3)	0.740	0.642	0.407
H(4)	0.903	0.859	0.478
H(5)	0.855	1.035	0.448
H(6)	0.646	0.997	0.359
H(8)	0.156	0.564	0.148
H(9)	0.038	0.398	−0.090
H(10)	0.160	0.436	−0.274
H(11)	0.381	0.592	−0.220
H(12)	0.494	0.735	0.024
H(14)	0.370	1.153	0.344
H(15)	0.401	1.353	0.330
H(16)	0.328	1.421	0.095
H(17)	0.232	1.268	−0.115
H(18)	0.183	1.050	−0.107
H(20)	0.323	0.858	−0.106
H(21)	0.217	0.747	−0.351
H(22)	−0.012	0.650	−0.445
H(23)	−0.139	0.677	−0.296
H(24)	−0.014	0.813	−0.033
H(1B)	0.454	0.964	0.112
H(2B)	0.446	0.993	0.331
H(3B)	0.378	0.786	0.513
H(4B)	0.193	0.679	0.364

and R' 0.042, but produced a systematic shortening of the C–H distances by *ca.* 0.2 Å, accompanied by some shortening of the C–C distances. We consider the results of the ' fixed-hydrogen ' refinement (with the hydrogen positions held at their accurately interpolated difference-map positions) to be more reliable, and the atomic co-ordinates and estimated standard deviations listed in Table 1 are from that refinement. The vibrational parameters and the observed and calculated structure factors are listed in Supplementary Publication No. SUP 22131 (18 pp.).* Atomic-scattering factors were calculated from the analytical approximation and values given in ref. 9, those for hydrogen being the spherically bonded values of Stewart *et al.*[10]

The molecular structure and atomic numbering are shown in the Figure.



ORTEP drawing of the title compound $BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl$

DISCUSSION

In solution, the four unique atoms of the boraphosphane chain are identifiable from the n.m.r. spectra. The nuclei of atoms B(1), B(3), P(2), and P(4) are assigned to the resonances at $\delta(^{11}B)$ −15.5 and −31 p.p.m. and $\delta(^{31}P)$ −26 and +83 p.p.m. respectively by comparison both with literature data[11,12] and with additional ^{31}P n.m.r. measurements from these laboratories (the general lack of ^{31}P n.m.r. data for the many phosphorus–boron compounds reported in the literature is surprising). The ^{31}P resonances were broad because of the effect of the adjacent boron nuclei with spin quantum number $I > \frac{1}{2}$, and any coupling $^{1}J(^{31}P-^{11}B)$ was unresolved. However, doublet structure was discernable with $^{2}J(^{31}P-^{31}P)$ *ca.* 80 Hz, which is within the range expected for geminal phosphorus–phosphorus coupling *via* an sp^3-hybridized first-row element with no lone pair of electrons.[13]

The compound $BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl$ is expected to have approximately tetrahedral geometry about the boron and phosphorus atoms, and the results of the single-crystal X-ray diffraction analysis confirm the butane-like open-chain structure. Interatomic distances and angles are in Table 2. The conformation adopted by the molecule has a *ca.* 60° torsion angle in the BPBP chain, the P(2)- and P(4)-phenyl groups are all *gauche* to the B(3)-hydrogen atoms, and the large PPh_2Cl moiety is *trans* to phenyl rather than BH_2Cl. These dispositions suggest that steric interactions and intermolecular contacts dictate the preferred conformation.

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

Cl(1)–B(1)	1.877(7)	Cl(1)–B(1)–P(2)	110.1(3)
B(1)–P(2)	1.953(6)	B(1)–P(2)–B(3)	113.6(3)
P(2)–B(3)	1.959(6)	P(2)–B(3)–P(4)	117.1(2)
B(3)–P(4)	1.907(6)	B(3)–P(4)–Cl(4)	113.5(2)
P(4)–Cl(4)	2.025(2)	B(1)–P(2)–C(1)	110.2(2)
P(2)–C(1)	1.820(5)	B(1)–P(2)–C(7)	111.9(2)
P(2)–C(7)	1.816(4)	B(3)–P(2)–C(1)	105.5(2)
P(4)–C(13)	1.807(5)	B(3)–P(2)–C(7)	109.8(2)
P(4)–C(19)	1.799(4)	B(3)–P(4)–C(13)	109.2(2)
B(1)–H(1B)	1.14	B(3)–P(4)–C(19)	117.4(3)
B(1)–H(2B)	1.27	Cl(2)–P(4)–C(13)	103.5(2)
B(3)–H(3B)	1.30	Cl(2)–P(4)–C(19)	104.1(2)
B(3)–H(4B)	1.15		
C–C	1.356—1.394(8)	average 1.379 Å	
C–C–C	118.5—120.6(4)	average 120.0°	
C–H	0.97—1.19	average 1.06 Å	

The interatomic distances (Table 2) generally fall within the expected ranges. The B(1)–P(2) and B(3)–P(2) bond lengths [1.953(6) and 1.959(6) Å respectively] are marginally less than the distance (1.98 Å) calculated from popular values of covalent radii, but compare well with measurements for other B–P bonds (1.92—1.95 Å).[5,14-16] The slightly shorter B(3)–P(4) bond length [1.907(6) Å] is to be expected in view of the general shortening of B–P bonds observed in other systems on increasing electronegative substitution on the phosphorus atom.[17-20]

The B(1)–P(2)–B(3) and P(2)–B(3)–P(4) interatomic angles of 113.6 and 117.1° respectively (Table 2) are interesting in that they tend towards trigonal from tetrahedral, and are similar to the values of 118 and 112° respectively measured for the cyclic compound $(BH_2{-}PMe_2)_3$.[5] Whether this indicates some deviation from simple formal two-electron two-centre B–P bonding is a

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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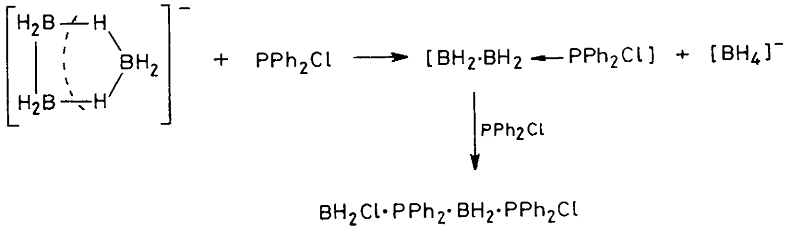
moot point, particularly as the changes are in the direction expected from non-bonded interaction between the substituents on the boraphosphane chains.

The formation of $BH_2Cl{\cdot}PPh_2{\cdot}BH_2{\cdot}PPh_2Cl$ in the reaction between $[NMe_4][B_3H_8]$ and PPh_2Cl is surprising and may result from the ' unsymmetrical ' cleavage of $[B_3H_8]^-$ by PPh_2Cl to give a phosphine–diborane fragment, followed by further reaction with a second mole of ligand as shown below:



Bis(ligand)diborane species such as $B_2H_4(PPh_3)_2$ are known to result from the reaction of $(NMe_3)B_3H_7$ with an excess of triphenylphosphine.[21] However, neither of the analogous chlorodiphenylphosphine adducts were

$$(NMe_3)B_3H_7 + 3PPh_3 \xrightarrow{C_6H_6,\ 50^{\circ}C} PPh_3{\cdot}BH_2{\cdot}BH_2{\cdot}PPh_3 + (PPh_3)BH_3 + NMe_3$$

isolated in the present work. In view of the very large number of products evident from the ^{31}P n.m.r. spectra of the reaction mixture it is clear that further mechanistic discussion would be purely speculative at this stage.

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[7/951 *Received, 2nd June, 1977*]

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