PERGAMON

Polyhedron 18 (1999) 545–552

POLYHEDRON

The reaction of phenylchlorophosphino-substituted 1,2-dicarba-*closo*-dodecaboranes(12) with elemental sulfur and molecular structures of *rac*-1,2-bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) and 1-phenylchlorothiophosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12)

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Received 10 June 1998; accepted 21 July 1998

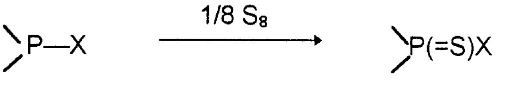
Abstract

rac-1,2-Bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) reacts with four equivalents of sulfur at 185–190°C in undecane to give the cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithiodiphosphinic acid (**2**). Under comparable conditions, 1-phenyl-chlorophosphino-1,2-dicarba-*closo*-dodecaborane(12) (**4**) and 1-phenyl-chlorophosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (**5**) react with sulfur to give 1-phenylchlorothiophosphino-1,2-dicarba-*closo*-dodecaborane(12) (**6**) and 1-phenylchlorothiophosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (**7**). Compounds **4**–**7** were characterized by ^{1}H, ^{31}P, ^{13}C and ^{11}B NMR spectroscopy and elemental analysis, and X-ray structure determinations were carried out on **1** and **7**.

Keywords: Carbaboranylchlorophosphines; Carbaboranylchlorothiophosphines

1. Introduction

The oxidation of organic derivatives of trivalent phosphorus by sulfur is probably the most widely investigated reaction in the chemistry of organophosphorus compounds after the Arbuzov reaction [1]. The sulfurization of compounds containing P(III)–halogen bonds has been extensively studied because of its importance for the synthesis of a wide range of organic derivatives of phosphorus [2, 3]. The reactions which have been reported in the literature proceed with retention of the P–X bond (X = halide) to give the corresponding thiophosphorus acids (eqn (1)).



(1)

Here we report on our studies of the reactions of *rac*-1,2-bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**), 1-phenylchlorophos-phino-1,2-dicarba-*closo*-dodecaborane(12) (**4**) and 1-phenylchlorophosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (**5**) with sulfur. Although **1** has been known for more than 30 years [4], its reaction with chalcogens has not yet been reported. While the reaction of **4** and **5** with sulfur forms carbaboranyl-chlorothiophosphines, **1** unexpectedly gives the cyclic anhydride of 1,2-bis(phenylthiophos-phoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithio-diphosphinic acid (**2**).

2. Results and discussion

1,2-Bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) is obtained as a mixture of diastereomers (*rac* and *meso*) [4], from which one isomer can be isolated by fractional crystallization from hexane/toluene. This was shown to be the *rac* isomer by X-ray structure analysis (vide infra).

rac-1,2-Bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) reacts with two equivalents of sulfur in undecane over 6 h at 185–190°C to give an inseparable mixture of products. The ^{31}P NMR spectrum of the reaction mixture exhibits several signals at 80.1 (d,

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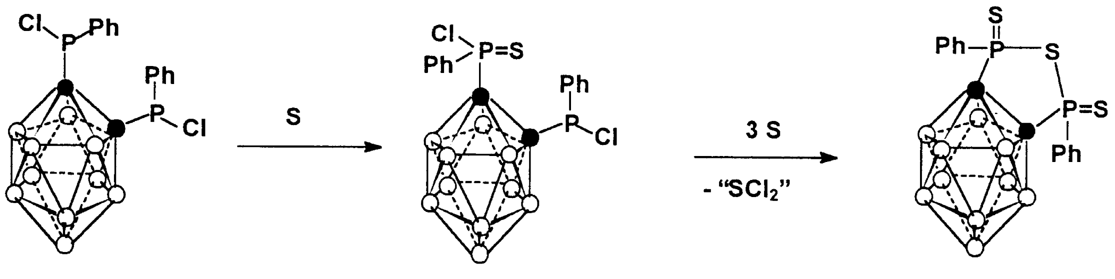
PII: S0277-5387(98)00330-1

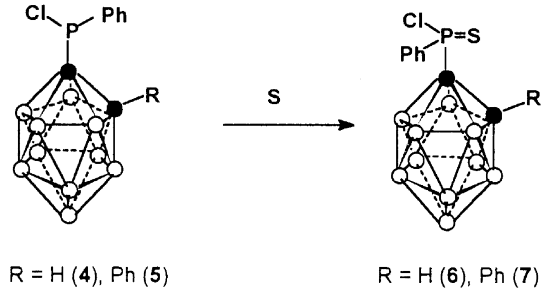
J_{PP} 10 Hz), 79.9 (d, J_{PP} 10 Hz), 72.4 (d, J_{PP} 10 Hz), 70.7 (d, J_{PP} 10 Hz) and 75.2 ppm (s). However, when four equivalents of sulfur are employed, one major product is formed (75.2 ppm, s) and can be isolated in 57% yield. Its spectroscopic data (^{31}P, ^{1}H, ^{11}B and ^{13}C NMR), melting point and elemental analyses are in agreement with the cyclic anhydride of 1,2-bis(phenylthiophos-phoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithiodiphosphinic acid (**2**), which was also obtained from 1,2-bis(phenylphosphino)-1,2-dicarba-*closo*-dodeca-borane(12) and sulfur [5]. The four doublets which are observed for the reaction mixture indicate the initial formation of *rac*- and *meso*-1-(phenylchlorothiophosphino)-2-phenylchlorophosphino-1,2-dicarba-*closo*-dodecaborane(12) (**3**) (eqn (2)) (see NMR data).



1 **3** **2**

(2)

To understand the course of the reaction between **1** and sulfur, we also studied the reaction of 1-phenylchlorophosphino-1,2-dicarba-*closo*-dodecaborane (12) (**4**) and 1-phenyl-2-phenylchlorophosphino-1,2-dicarba-*closo*-dodecaborane(12) (**5**), both of which were prepared from Li derivatives of the corresponding *o*-carbaboranes and PhPCl$_2$[1]. Compounds **4** and **5** react with sulfur over 6 h at 185–190°C in undecane to give the carbaboranylphenyl-chlorothiophosphines **6** and **7*** [6] (eqn (3)), which were characterized by NMR spectroscopy and elemental analysis. Additionally, an X-ray structure determination was carried out on **7**. The same products were obtained with an excess of sulfur (two equivalents).



(3)

The fact that different sulfurization products are obtained on reacting **1** or **4** and **5** with sulfur under comparable reaction conditions is not readily explained. The possibility that **2** is formed from **1** and H$_2$S, a possible pyrolysis product of undecane in the presence of sulfur [7], can be excluded as the products that would be expected here are not obtained in the reactions of **4** and **5** with sulfur. Apparently, the electron-withdrawing properties of the 1,2-dicarba-*closo*-dodecaboranyl(12) fragment [8–10] and the presence of a second phosphine group determine the reactivity of carbaboranylphosphines. The most likely first step in the reaction of **1** with sulfur, which is also supported by NMR studies, is the oxidation of one phosphine group to give **3** (eqn (2)), while the further steps in the formation of **2** are unclear. Abstraction of Cl atoms from **3** by sulfur and an addition of further sulfur atoms to intermediate compounds seems likely but could not be proved spectroscopically. The assistance of the second PhPCl group in **1** seems to be crucial for the abstraction of chlorine, similar to the abstraction of halogen from hydrocarbon halides [7], since for **4** and **5** the reaction stops at the stage of the carbaboranylphenylchlorothiophosphines **6** and **7**. Similarly, 1,2-bis(phenylphosphino)-1,2-dicarba-*closo*dodecaborane(12) reacts with sulfur to give a carbaboranylphenylthiophosphine intermediate, which yields **2** as the final product [5].

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[1] Although the synthesis of **5** was reported earlier [6], no spectroscopic data were given and the published melting point is 20°C lower than that determined by us for **5**. Similarly, differences between our results and those reported previously [6] were also observed for 1-phenylchlorothiophos-phine-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (**7**).

2.1. *NMR spectra*

Table 1 lists ^{1}H, ^{31}P, ^{13}C and ^{11}B NMR spectroscopic data for **1**, **2** and **4**–**7**, as well as ^{31}P NMR data of **3**. The NMR spectra of **2** have been discussed earlier [5,10]. Compounds **1** and **4**–**7** exhibit singlets in their ^{31}P NMR spectra at 80.9, 91.3, 81.1, 79.5 and 71.5 ppm, respectively. For the *rac* and *meso* isomers of the intermediate **3**, doublets are observed at 80.1, 79.9, 72.4 and 70.7 with J_{PP} 10 Hz. The first two signals can be assigned to the PhPCl group, and the latter to the PhP(S)Cl group by comparison with **1** and **4**–**7**. While similar chemical shifts are observed in the ^{31}P NMR spectra of **1** and **5**, the corresponding signal of **4** is shifted to low field by about 10 ppm. The signals for the thiophosphine groups of **3**, **6** and **7** are shifted to high field by *ca*. 10–12 ppm compared with the corresponding phosphine groups in **1**, **4** and **5**.

In the ^{13}C NMR spectra, the signals of the cluster carbon atoms of **1**, **2**, **5** and **7** are observed in the range 82–86 ppm, while **4** and **6** exhibit these signals at 74–76 ppm. This phenomenon of low-field shift of ^{31}P NMR signals together with high-field shift of the ^{13}C NMR signals of the cluster carbon atoms in the spectra of 1-substituted *o*-carbaboranyl(12)-phosphorus compounds compared with 1,2-disubstituted *o*-carbaboranyl(12)-phosphorus compounds is apparently a general trend for phosphorus derivatives of *o*-carbaborane(12) (cf.[5]). As expected, the $^{1}J_{CP}$ coupling constant of the thiophosphine derivatives **6** and **7** (51 and 44 Hz) is smaller than that of the corresponding phosphine derivatives **4** and **5** (97 and 94 Hz).

In the ^{11}B NMR spectra, the signals of compounds **1**, **2** and **4**–**7** are observed in the expected range of −1 to 14 ppm with coupling constants J_{BH} of 136–183 Hz. In the ^{1}H NMR spectrum, the signals of the Ph groups are observed between 7.6 and 6.6 ppm and overlap partially.

Table 1
NMR data for compounds **1**–**7**

Compound	^{31}P (ppm)/ J_{PP} (Hz)	^{11}B (ppm)/J_{BH} (Hz)	^{1}H (ppm)	^{13}C (ppm)/J_{CP} or J_{CH} (Hz)
1 (*rac*)	80.9	0.0/147 (2B), −6.6/153 (2B), −10.2/144 (4B), −11.9/145 (2B)	7.55 (m, 2H, Ph), 6.96 (m, 3H, Ph), 3.5–1.9 (m, v br, 10H, B–H)	134.3, 133.4, 133.2, 129.7 (Ph); 85.0 (m, $C_{cluster}$–P)
2 [5] (*rac*)	75.2	−2.7/167 (2B), −4.3/166 (2B), −10.3 (6B)	8.18 (m, 2H, Ph), 6.91 (m, 3H, Ph), 3.5–1.9 (m,v br, 10H, B–H)	136.3, 133.4, 130.2, 128.6 (Ph); 85.8 (m, $C_{cluster}$–P)
3	80.1 (d)/10, 79.9 (d)/10, 72.4 (d)/10, 70.7 (d)/10			
4	91.3	−1.3/136 (1B), −1.9/140 (1B), −7.3/152 (2B), −11.2/169 (2B), −12.5/171 (2B), −13.9/183 (2B),	7.30 (m, 2H, Ph), 6.97 (m, 1H, Ph), 6.92 (m, 2H, Ph), 3.29 (s, v br, 1H, C–$H_{cluster}$), 3.1–1.8 (m, v br, 10H, B–H)	133.4, 132.5/30, 129.7, 129.6 (Ph); 74.6/97 ($C_{cluster}$–P), 63.4/194 ($^{1}J_{CH}$)/10 ($^{3}J_{CP}$) ($C_{cluster}$–H)
5	81.1	−0.6/148 (1B), −3.4/153 (1B), −7.9/160 (2B), −9.2/156 (4B), −11.8 (1B), −12.9 (1B),	7.45 (m, 2H, Ph), 7.30 (m, 2H, Ph), 6.97 (m, 2H, Ph), 6.90 (m, 4H, Ph), 3.4–1.8 (m, v br, 10H, B–H)	134.5/33, 133.1/8, 132.8, 132.4, 131.7, 131.6 (Ph); 87.3/17 ($^{3}J_{CP}$) ($C_{cluster}$–Ph), 85.0/94 ($^{1}J_{CP}$) ($C_{cluster}$–P)
6	79.5	−1.1/149 (1B), −3.5/150 (1B), −6.7/138 (1B), −7.7/141 (1B), −11.6 (2B), −12.9 (2B), −13.8 (2B)	7.67 (m, 2H, Ph), 6.96 (m, 1H, Ph), 6.86 (m, 2H, Ph), 4.33 (s, 1H, C–$H_{cluster}$), 3.5–1.8 (m, v br, 10H, B–H)	134.8, 133.5, 132.6, 130.8 (Ph); 75.4/51 ($^{1}J_{CP}$) ($C_{cluster}$–P), 65.4
7	71.5	0.8/150 (1B), −1.9/155 (1B), −7.6/174 (2B), −10.0/147 (6H)	7.44 (m, 2H, Ph), 7.22 (m, 2H, Ph), 6.90 (m, 2H, Ph), 6.74 (m, 4H, Ph), 3.4–1.9 (m, v br, 10H, B–H)	134.1/4, 133.9/12, 133.0, 132.3, 131.6, 130.5 (Ph), 87.2 ($C_{cluster}$–Ph), 82.5/44 ($^{1}J_{CP}$) ($C_{cluster}$–P)

2.2. X-ray structure analyses of rac-1,2-bis(phenylchlorophosphino)-1,2-dicarba-closo-dodecaborane(12) (1) and 1-phenylchlorothiophosphino-2-phenyl-1,2-di-carba-closo-dodecaborane(12) (7)

Crystals of **1** were obtained from hexane/toluene and crystals of **7** from hexane at room temperature. In both compounds, the P atoms are chiral centers. **1** crystallizes in the centrosymmetric space group $P\bar{1}$ (No. 2). Due to the crystallographic center of inversion, both enantiomers (*R*,*R*) and (*S*,*S*) are present in the unit cell (Fig. 1). **7** crystallizes in the orthorhombic space group *Pbca* (No. 61) with eight formula units in the unit cell. Due to the crystallographic center of inversion, both enantiomers (*R*) and (*S*) are present in the unit cell (Fig. 2).

The bond lengths and angles of the $C_2B_{10}H_{10}$ fragment (Table 2 and Table 3) show no remarkable deviations from comparable structures [5,11–15]. The P–Cl bond lengths in **1** and **7** [**1**: P(1)–Cl(1) 2.051(1), P(2)–Cl(2) 2.058(1) Å; **7**: P(1)–Cl(1) 2.0104(8) Å] and the P–S bond length in **7** [P(1)–S(1) 1.9207(8) Å] lie in the range observed for P–Cl bonds in P(O)Cl [1.991(2) and 2.04(4) Å] [16] or P(S)Cl groups [2.071–2.03(1) Å] [17, 18] and P═S bonds in comparable compounds [**2**: P═S 1.9154(9), 1.9218(9) Å] [5].

3. Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. NMR spectra: Avance DRX 400 (Bruker), standards: ^{1}H NMR (400 MHz): traces of protonated solvent, C_6D_6, ^{13}C NMR (100.6 MHz): internal solvent, ^{31}P NMR (162 MHz): external 85% H_3PO_4, ^{11}B NMR: external $BF_3 \cdot Et_2O$. The IR spectra were recorded as KBr mulls on a Perkin–Elmer System 2000 FT–IR spectrometer in the range 350–4000 cm^{-1}. Melting points were determined in capillaries and are uncorrected. $PhPCl_2$ is commercially available (Aldrich).

3.1. Synthesis of rac-1,2-bis(phenylchlorophosphino)-1,2-dicarba-closo-dodecaborane(12) (1)

1 was prepared according to the literature procedure [4] from 5.0 g (34.7 mmol) 1,2-dicarba-*closo*-dodecaborane(12) and 12.5 g (69.4 mmol) $PhPCl_2$ in ether. The diastereomers were separated by recrystallization of the reaction product from a hexane/toluene mixture at room temperature. Yield of *rac*-1,2-bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) 7.2 g (56%). m.p. 159–161°C. IR (cm^{-1}): 3075, 3059, 3005 (*ν*CH); 2625, 2609, 2596, 2578, 2551 (*ν*BH); 1959, 1884, 1806, 1757 (*ν*Ph); 1584, 1572, 1481, 1435, 1383, 1335, 1305, 1275, 1185, 1160, 1090, 1069, 1025, 999, 970, 934, 902, 876, 838, 798, 743, 724, 699, 689, 674, 622, 561, 507, 485, 421.

3.2. Synthesis of 1-phenylchlorophosphino-1,2-dicarba-closo-dodecaborane(12) (4)

At 8°C, a suspension of 1-lithio-1,2-dicarba-*closo*-dodecaborane(12) in benzene, obtained from 3.0 g (20.8 mmol) of 1,2-dicarba-*closo*-dodecaborane(12) and BuLi (21 mmol, 1.6 M in hexane) in benzene (25 cm^{-3}) was added to a solution of 5.9 g (33.3 mmol) $PhPCl_2$ in benzene (25 cm^{-3}). The reaction mixture was kept at room temperature for 12 h, then the solvent was removed and the remaining solid was dissolved in pentane and filtered. Recrystallization from pentane gave 3.6 g (60%) of **4** (at room temperature). m.p. 58–61°C. IR (cm^{-1}): 3056 (*ν*CH), 2594 (*ν*BH), 1589, 1482, 1436, 1307, 1261, 1221, 1175, 1117, 1090, 1070, 1022, 999, 961, 878, 849,

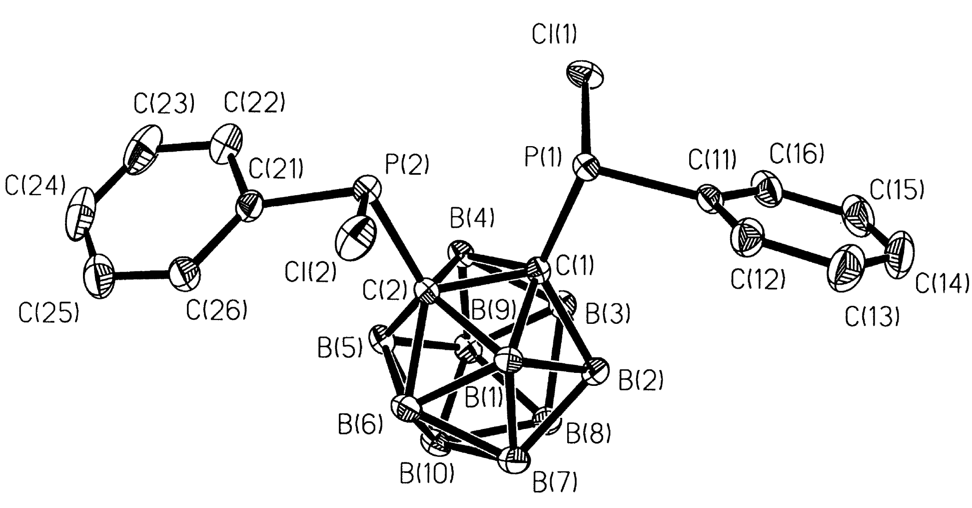

Fig. 1. Molecular structure of **1**. Only one of the enantiomers with its atom numbering scheme is shown (ORTEP, 50% probability, SHELXTL PLUS; XP) [19]. Hydrogen atoms omitted for clarity.

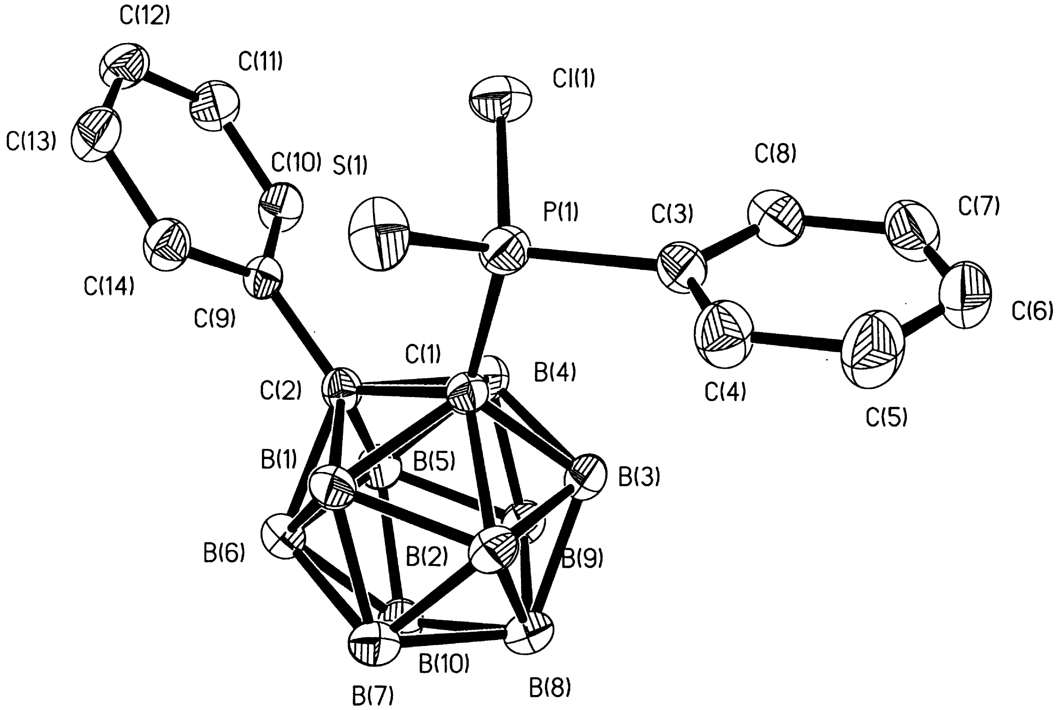

Fig. 2. Molecular structure of **7**. Only one of the enantiomers with its atom numbering scheme is shown (ORTEP, 50% probability, SHELXTL PLUS; XP) [19]. Hydrogen atoms omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

P(1)–C(11)	1.821(2)	P(1)–C(1)	1.879(2)
P(1)–Cl(1)	2.051(1)	P(2)–C(21)	1.815(3)
P(2)–C(2)	1.886(2)	P(2)–Cl(2)	2.058(1)
B(1)–C(2)	1.726(3)	B(1)–C(1)	1.728(3)
B(2)–C(1)	1.715(3)	B(3)–C(1)	1.706(3)
B(4)–C(2)	1.730(3)	B(4)–C(1)	1.732(3)
B(5)–C(2)	1.711(3)	B(6)–C(2)	1.709(3)
C(1)–C(2)	1.702(3)	C(11)–C(12)	1.385(3)
C(11)–C(16)	1.395(3)	C(12)–C(13)	1.393(4)
C(13)–C(14)	1.374(5)	C(14)–C(15)	1.370(5)
C(15)–C(16)	1.379(4)	C(21)–C(22)	1.395(4)
C(21)–C(26)	1.396(4)	C(22)–C(23)	1.388(5)
C(23)–C(24)	1.385(6)	C(24)–C(25)	1.372(6)
C(25)–C(26)	1.370(4)		
C(11)–P(1)–C(1)	100.48(10)	C(11)–P(1)–Cl(1)	101.53(8)
C(1)–P(1)–Cl(1)	100.71(7)	C(21)–P(2)–C(2)	101.39(10)
C(21)–P(2)–Cl(2)	101.68(8)	C(2)–P(2)–Cl(2)	101.03(7)
C(2)–C(1)–P(1)	112.89(13)	B(3)–C(1)–P(1)	128.9(2)
B(2)–C(1)–P(1)	122.2(2)	B(1)–C(1)–P(1)	109.96(14)
B(4)–C(1)–P(1)	120.21(14)	C(1)–C(2)–P(2)	112.19(13)
B(6)–C(2)–P(2)	130.0(2)	B(5)–C(2)–P(2)	121.6(2)
B(1)–C(2)–P(2)	121.2(2)	B(4)–C(2)–P(2)	108.37(13)
C(12)–C(11)–C(16)	119.6(2)	C(12)–C(11)–P(1)	115.2(2)
C(16)–C(11)–P(1)	125.2(2)	C(11)–C(12)–C(13)	119.9(3)
C(14)–C(13)–C(12)	119.6(3)	C(15)–C(14)–C(13)	120.8(3)
C(14)–C(15)–C(16)	120.3(3)	C(15)–C(16)–C(11)	119.8(3)
C(22)–C(21)–C(26)	119.3(3)	C(22)–C(21)–P(2)	114.8(2)
C(26)–C(21)–P(2)	125.8(2)	C(23)–C(22)–C(21)	119.8(3)
C(24)–C(23)–C(22)	119.7(3)	C(25)–C(24)–C(23)	120.4(3)
C(26)–C(25)–C(24)	120.5(4)	C(25)–C(26)–C(21)	120.2(3)

Table 3
Selected bond lengths (Å) and angles (°) for **7**

Cl(1)–P(1)	2.0104(8)	P(1)–C(3)	1.805(2)
P(1)–C(1)	1.874(2)	P(1)–S(1)	1.9207(8)
C(1)–B(2)	1.703(3)	C(1)–C(2)	1.716(2)
C(1)–B(3)	1.722(3)	C(1)–B(4)	1.730(3)
C(1)–B(1)	1.737(3)	C(2)–B(5)	1.711(3)
C(2)–B(6)	1.716(3)	C(2)–B(1)	1.737(3)
C(2)–B(4)	1.752(3)	B–B	1.765(3)–1.790(4)
C(9)–C(14)	1.390(3)	C(9)–C(10)	1.397(3)
C(9)–C(2)	1.505(2)	C(10)–C(11)	1.385(3)
C(13)–C(12)	1.378(3)	C(13)–C(14)	1.391(3)
C(12)–C(11)	1.380(3)	C(4)–C(3)	1.391(3)
C(4)–C(5)	1.391(3)	C(3)–C(8)	1.395(3)
C(6)–C(5)	1.376(4)	C(7)–C(6)	1.375(4)
C(7)–C(8)	1.380(3)		

C(3)–P(1)–C(1)	105.91(8)	C(3)–P(1)–S(1)	113.80(7)
C(1)–P(1)–S(1)	112.27(6)	C(3)–P(1)–Cl(1)	104.72(7)
C(1)–P(1)–Cl(1)	104.37(6)	S(1)–P(1)–Cl(1)	114.85(4)
B(2)–C(1)–P(1)	117.42(13)	B(3)–C(1)–P(1)	120.39(13)
B(4)–C(1)–P(1)	120.73(12)	B(1)–C(1)–P(1)	116.31(13)
C(2)–C(1)–P(1)	121.22(12)	C(4)–C(3)–P(1)	118.3(2)
C(8)–C(3)–P(1)	121.8(2)	C(14)–C(9)–C(2)	122.0(2)
C(10)–C(9)–C(2)	118.9(2)	C(9)–C(2)–C(1)	120.68(15)
C(14)–C(9)–C(10)	119.1(2)	C(11)–C(10)–C(9)	120.5(2)
C(12)–C(11)–C(10)	120.1(2)	C(12)–C(13)–C(14)	120.8(2)
C(9)–C(14)–C(13)	119.7(2)	C(7)–C(6)–C(5)	120.3(2)
C(5)–C(4)–C(3)	119.6(2)	C(4)–C(3)–C(8)	119.8(2)
C(6)–C(7)–C(8)	120.6(2)	C(7)–C(8)–C(3)	119.6(2)
C(6)–C(5)–C(4)	120.1(2)		

795, 745, 722, 690, 628, 551, 510, 486, 424. Found: C, 34.35; H, 5.48; Cl, 12.68. Calc.: for $C_8H_{16}B_{10}PCl$ (286.5): C, 33.51; H, 5.58; Cl, 12.39%.

*3.3. Synthesis of 1-phenylchlorophosphino-2-phenyl-1,2-dicarba-closo-dodecaborane(12) (**5**)*

At 0°C, a solution of 1-lithio-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12), obtained from 1.23 g (5.5 mmol) 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12) and BuLi (6 mmol, 1.6 M in hexane) in ether (25 cm^{-3}) was added to a solution of 0.99 g (5.6 mmol) $PhPCl_2$ in ether (25 cm^{-3}). The reaction was kept at 0°C for 1 h and then for 12 h at room temperature. The solvent was removed, and the remaining solid dissolved in hexane and filtered. Recrystallization from hexane at room temperature gave 0.8 g (41%) of **5**. m.p. 158–159°C. IR (cm^{-1}): 3439, 3064, 2925 (νCH); 2667, 2655, 2602, 2574, 2561, 2546 (νBH); 1954, 1887, 1812 (νPh); 1585, 1493, 1480, 1447, 1435, 1332, 1306, 1283, 1246, 1232, 1195, 1158, 1106, 1090, 1072, 999, 919, 886, 848, 835, 803, 774, 746, 689, 670, 625, 575, 515, 497, 475, 432, 418. Found: C, 47.02; H, 5.81; Cl, 9.41. Calc.: for $C_{14}H_{20}B_{10}PCl$ (362.5): C, 46.35; H, 5.52; Cl, 9.79%.

*3.4. Reaction of **1**, **4** and **5** with sulfur: general procedure*

1 was reacted with four, and **4** and **5** with one or two equivalents of sulfur in undecane at 185–190°C for 6 h. Then undecane was removed, and the remaining solid dissolved in hexane and filtered. Compounds **2**, **6** and **7** were obtained by recrystallization from hexane at room temperature.

*3.5. Synthesis of the cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-closo-dodecaboranyl(12)-dithiodiphosphinic acid (**2**)*

2 was obtained from 1.0 g (2.3 mmol) **1** and 0.3 g (9.3 mmol) sulfur in undecane (20 cm^{-3}). Yield: 0.6 g (57%), m.p. 226–229°C (lit. 229–232°C [5]). NMR and IR spectroscopic data are in agreement with those reported earlier [5].

*3.6. Synthesis of 1-phenylchlorothiophosphino-1,2-dicarba-closo-dodecaborane(12) (**6**)*

6 was obtained from 0.86 g (3.0 mmol) **4** and 0.3 g (6.2 mmol) sulfur in undecane (20 cm^{-3}). Yield: 0.82 g (86%), m.p. 118–119°C. IR (cm^{-1}): 3058, 3041, 2961, (νCH); 2608, 2580 (νBH), 1581, 1474, 1437, 1383, 1337, 1309, 1262, 1189, 1163, 1126, 1097, 1069, 1024, 999, 937, 917, 904, 868, 855, 796, 741, 683, 630, 614, 591, 560, 550, 528, 486, 421. Found: C, 30.14; H, 5.02; S, 10.04. Calc.: for $C_8H_{16}B_{10}PSCl$ (286.5): C, 30.65; H, 5.24; S, 9.89%.

3.7. Synthesis of 1-phenylchlorothiophosphino-2-phenyl-1,2-dicarba-closo-dodecaborane(12) (7)

7 was obtained from 0.54 g (1.5 mmol) **5** and 0.09 g (3.0 mmol) sulfur in undecane (15 cm^{-3}). Yield: 0.4 g (66%), m.p. 177–178°C (lit. 162–163°C [6]). IR (cm^{-1}): 3061, 2963 (νCH); 2674, 2639, 2608, 2593, 2583, 2570, 2549 (νBH), 1956, 1898, 1810 (νPh); 1580, 1494, 1481, 1471, 1448, 1436, 1340, 1309, 1286, 1262, 1197, 1095, 1078, 1028, 1004, 998, 921, 905, 885, 851, 801, 744, 709, 684, 624, 615, 574, 520, 509, 494, 483, 436. Found: C, 42.38; H, 5.01. Calc.: for $C_{14}H_{20}B_{10}PCl$ (394.5): C, 42.58; H, 5.07%.

3.8. Data collection and structure refinement of **1**

Experimental data (a total of 4405 reflections) were collected at $T = 220 \pm 2$ K on a Siemens CCD (SMART) diffractometer in the range $2.9 < 2\Theta < 49.4°$ with monochromated MoKα radiation ($\lambda = 0.71073$ Å). This includes a total of 2979 unique reflections ($R_{int} = 0.0127$). All observed reflections were used for determination of the unit cell parameters. The studied specimen was a white single crystal with the dimensions 0.5 × 0.4 × 0.2 mm. Crystal data for **1** are as follows: $C_{14}H_{20}B_{10}Cl_2P_2$, $M = 429.24$, space group $P\bar{1}$ (No. 2), $a = 6.740(2)$ Å, $b = 11.372(3)$ Å, $c = 15.317(2)$, $\alpha = 106.83(2)°$, $\beta = 100.00(2)°$, $\gamma = 102.49(2)°$, $V = 1061.6(4)$ Å^3, at $T = 220(2)$ K, $Z = 2$, $D_c = 1.343$ Mg m^{-3}, $F(000) = 436$, $\mu(\mathrm{MoK}\alpha) = 0.455\ mm^{-1}$, no absorption correction.

Positions of P, C, Cl and B atoms were located by using direct methods (SHELXTL PLUS) [19]. Subsequent least-squares refinement and difference electron density map calculations revealed the positions of the H atoms. Final full-matrix least-squares refinement of 333 parameters with a unit weighting scheme (P, C, Cl and B atoms anisotropic approximation, H atoms isotropic approximation) converged to $R1 = 0.0319$, $wR2 = 0.0872$ [for reflections with $I > 2\sigma(I)$], $R1 = 0.0340$, $wR2 = 0.912$ (all data).

3.9. Data collection and structure refinement of **7**

Experimental data (a total of 20,073 reflections) were collected at $T = 220 \pm 2$ K on a Siemens CCD (SMART) diffractometer between $3.0 < 2\Theta < 56.0°$ with monochromated MoKα ($\lambda = 0.71073$ Å) radiation. This includes a total of 4429 unique reflections ($R_{int} = 0.0351$). All observed reflections were used for determination of the unit cell parameters. The studied specimen was a white single crystal of dimensions 0.4 × 0.3 × 0.2 mm. Crystal data for **7** are as follows: $C_{14}H_{20}B_{10}ClPS$, $M = 394.88$, space group *Pbca* (No. 61), orthorhombic, $a = 16.669(3)$ Å, $b = 8.556(2)$ Å, $c = 27.690(6)$ Å, $V = 3949.2(14)$ Å^3, at $T = 220(2)$ K, $Z = 8$, $D_c = 1.328$ Mg m^{-3}, $F(000) = 1616$, $\mu(\mathrm{MoK}\alpha) = 0.377\ mm^{-1}$, no absorption correction.

Positions of P, C, Cl, S and B atoms were located by using direct methods (SHELXTL PLUS) [19]. Subsequent least-squares refinement and difference electron density map calculations revealed the positions of the H atoms. Final full-matrix least-squares refinement of 324 parameters with a unit weighting scheme (P, C, Cl, S and B atoms anisotropic approximation, H atoms isotropic approximation) converged to $R1 = 0.0360$, $wR2 = 0.0945$ [for reflections with $I > 2\sigma(I)$], $R1 = 0.0562$, $wR2 = 0.1180$ (all data).

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (**1**: CSD 410159, **7**: CSD 410160).

Acknowledgements

We gratefully acknowledge support from the Fonds der Chemischen Industrie. Chemetall GmbH has provided a generous donation of lithium alkyls. V. P. B. thanks the Sächsisches Ministerium für Wissenschaft und Kunst (SMWK) for financial support (Az. 4-7531.50-04-0361-98/8).

References

[1] Corbridge DEC. Phosphorus: an Outline of its Chemistry, Biochemistry and Technology Elsevier, Amsterdam–New York, 1980.

[2] Bhattacharys AK, Roy NK. In: The Chemistry of Organophosphorus Compounds, Vol. 2, Hartley FR, editor. John Wiley and Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1992, p. 195.

[3] Edmunson RS. In: The Chemistry of Organophosphorus Compounds, Vol. 4, Hartley FR, editor. John Wiley and Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1996, p. 397.

[4] Alexander RP, Schroeder H. Inorg Chem 1963;2:1107.

[5] Balema VP, Pink M, Sieler J, Hey-Hawkins E, Hennig L. Polyhedron 1998;17:2087.

[6] Kasantsev AV, Zhubekova MN, Zakharkin LI. Zh Obshch Khim 1971;41:2027.

[7] Mayer R. In: Organic Chemistry of Sulfur, Oae S, editor. Plenum Press, New York and London, 1977, p 33.

[8] Grimes RN. Carboranes Academic Press, New York, 1970.

[9] Hawthorne MF, Berry TE, Wegner, PA. J Am Chem Soc 1965;87:4746.

[10] Fox MA, MacBride JAH, Peace RJ, Wade K. J Chem Soc Dalton Trans 1998;401.

[11] Balema VP, Blaurock S, Hey-Hawkins E, Pecharsky VK, Rys EG. Polyhedron 1998, in press.

[12] SHELXTL PLUS, Siemens Analyt X-ray Inst Inc 1990, XS: Pro-

gram for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactiv Molecular Graphics.

[13] Balema VP, Somoza F Jr, Hey-Hawkins E. Europ J Inorg Chem 1998;651.

[14] Sillanpää R, Kivekäs R, Teixidor F, Viñas C, Nuñez R. Acta Crystallogr 1996;C52:2223.

[15] McWhannell MA, Rosair GM, Welch AJ, Teixidor F, Viñas C. Acta Crystallogr 1996;C52:3135.

[16] Yanovskij AI, Furmanova NG, Struchkov, Yu T, Shemjakin NF, Zakharkin LI. Izv Akad Nauk SSSR Ser Khim 1979;1523.

[17] Furmanova NG, Struchkov, Yu T, Degtjarev AN, Bregadze VI, Godovikov NN, Kabachnik MI. Izv Akad Nauk SSSR Ser Khim 1980;845.

[18] Boese R, Hägele G, Kückelhaus W, Tossing G. Phosphorus and Sulfur 1985;25:103.

[19] Tasz MK, Cremer SE, Fanwick PE. Phosphorus and Sulfur 1995;104:223.