Pergamon

PII: S0277-5387(97)00426-9

Polyhedron Vol. 17, Nos. 11–12, pp. 2087–2093, 1998

0277-5387/98 $19.00+0.00

Synthesis, molecular structure and reactivity of the first secondary carbaboranylbisphosphine 1,2-bis(phenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12)

Viktor P. Balema,[a] Maren Pink,[a] Joachim Sieler,[a] Evamarie Hey-Hawkins*[a] and Lothar Hennig[b]

[a] Institut für Anorganische Chemie der Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

[b] Institut für Organische Chemie der Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

(Received 1 September 1997; accepted 16 October 1997)

Abstract—The reaction of a diastereomeric mixture of 1,2-bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) with $LiAlH_4$, followed by hydrolysis with H_2O, gives a 4:1 mixture of *rac*- and *meso*-1,2-bis(phenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**2a, b**) or 1-phenylphosphino-1,2-dicarba-*closo*-dodecaborane(12) (**3**), depending on the stoichiometry employed. A mixture of **2a, b** reacts with sulfur in undecane at 190°C or without solvent at 105–110°C to give exclusively the cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithiodiphosphinic acid (**6**). **2, 3** and **6** were characterised spectroscopically (^1H, ^{31}P, ^{11}B, ^{13}C NMR, IR, MS) and X-ray structure determinations were carried out on the racemic isomers **2a** and **6**.

Keywords: secondary carbaboranylbisphosphine; cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithiodiphosphinic acid.

Organic or organo-element derivatives of dicarba-*closo*-dodecaboranes(12) have received increasing attention during the past decade as they exhibit interesting chemical and physical properties. Thus, these compounds have been employed as catalysts [1,2], as doping reagents in semiconductor materials [3], as precursors for ceramic materials [4], and in neutron-capture therapy of tumors (boron neutron capture therapy) [5] and other medical areas [6,7]. Hence applications in medicine can be envisioned for related carbaboranylphosphines and transition metal complexes thereof [8].

While tertiary phosphino derivatives of dicarba-*closo*-dodecaboranes(12), which were first reported in 1963 [9], have been employed as ligands in transition metal chemistry and as starting materials for the preparation of other *closo*-carbaborane(12)-containing organophosphorus compounds [10], their secondary analogues have remained largely unexplored. The only report on the attempted synthesis of secondary phosphinocarbaboranes, by A.V.Kasantsev *et al.* in 1971, claims that the reaction of 2-substituted 1-phenylchlorophosphino-1,2-dicarba-*closo*-dodecaboranes(12) with $LiAlH_4$ yields the corresponding 1-phenylphosphino-1,2-dicarba-*closo*-dodecaboranes (12), which, however, decompose under the reaction conditions with formation of C-substituted 1,2-dicarba-*closo*-dodecaboranes(12) and primary phosphines [11].

We now report the synthesis and spectroscopic properties of the first secondary bisphosphinocarbaboranes, *rac*- and *meso*-1,2-bis(phenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**2a, 2b**) and 1-phenylphosphino-1,2-dicarba-*closo*-dodecaborane(12) (**3**), as well as the separation of the diastereoisomers of **2** and the molecular structure of the *racemic* isomer **2a**. **2a, b** react with sulfur in boiling

* Author to whom correspondence should be addressed

undecane or at elevated temperature without solvent to give the cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl (12)-dithiodiphosphinic acid (**6**), which was also structurally characterised.

RESULTS AND DISCUSSION

Synthesis and properties of 2, 3 *and* 6

A mixture (4 : 1) of *rac*- and *meso*-1,2-bis(phenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**2a, 2b**) was obtained in 91% yield by reacting a diastereomeric mixture of *rac*- and *meso*-1,2-bis-(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) [9] (^{31}P: 80.54 and 80.62 ppm) with 1.1 eqv. $LiAlH_4$ in ether and subsequent hydrolysis with 10 eqv. H_2O (Scheme 1). It was observed previously [11] that the P—C bond is cleaved by an excess of $LiAlH_4$ and H_2O. Thus, when a 50% excess of $LiAlH_4$ and 50 eqv. of H_2O are employed, only 1-phenylphosphino-1,2-dicarba-*closo*-dodecaborane (12) (**3**) is obtained, in 42% yield, as well as insoluble boron- and phosphorus-containing products (Scheme 1).

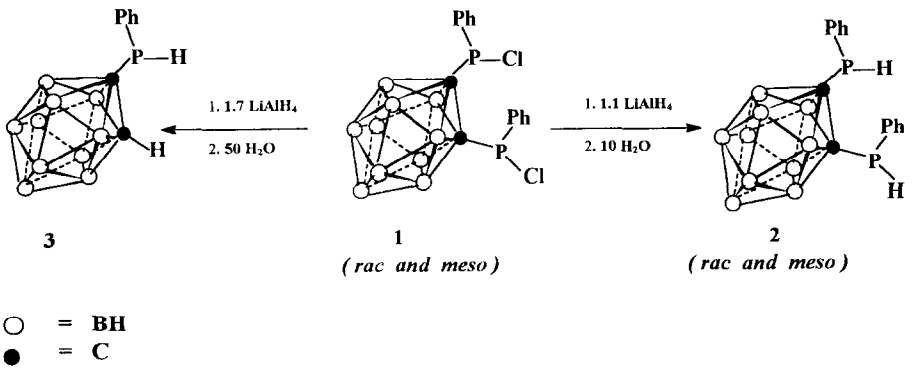
The carbaboranylphosphines **2** and **3** are obtained as air- and water-stable colourless solids, soluble in organic solvents, and purifiable by column chromatography. The better solubility of **2b** in hexane allows the diastereoisomers of **2** to be separated.

In the $^{31}P\{H\}$ NMR spectrum, the two diastereoisomers of **2** exhibit singlets at −15.15 for **2a** and −14.98 ppm for **2b**; for **3**, the resonance is shifted to low field (−2.67 ppm, $^1J_{PH}$ 229 Hz). On proton coupling, the HPC—CPH fragments in **2a** and **2b** show the signals of an AA′XX′ spin system. The coupling constants ($^1J_{PH}$ 244 Hz **2a**, 239 Hz **2b**; $^3J_{PP}$ 84 Hz **2a**, 87 Hz **2b**) were obtained from simulated ^{1}H NMR spectra [12]. However, the two signals of the diastereoisomers of *o*-phenylenebisphosphine, 1,2-$(PhPH)_2C_6H_4$ (−41.8, −42.4 ppm) [13], and 1,2-bis(phenylphosphino)ethane, $PhP(H)CH_2CH_2(H)$-PPh (−45.6, −45.9 ppm) [14], are observed in the same range as those of their corresponding monophosphines, Ph_2PH (−41 ppm) [15] and Ph(Et)PH (−46 ppm) [15]. The observation of no notable chemical shift difference in the ^{31}P NMR spectra indicates only minor magnetic interaction of the P atoms in these bisphosphines. Thus, the low-field shift of the resonance of **3** relative to **2** cannot be attributed to steric or electronic effects of the second PHPh group. Therefore, the observed difference in the chemical shifts of **2** and **3** must be due to the influence of the 1,2-dicarba-*closo*-dodecaborane(12) cluster. This assumption is supported by the observed difference in the ^{31}P chemical shifts of 1-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane(12) (25.6 ppm) [16] and 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (8.2 ppm) [17].

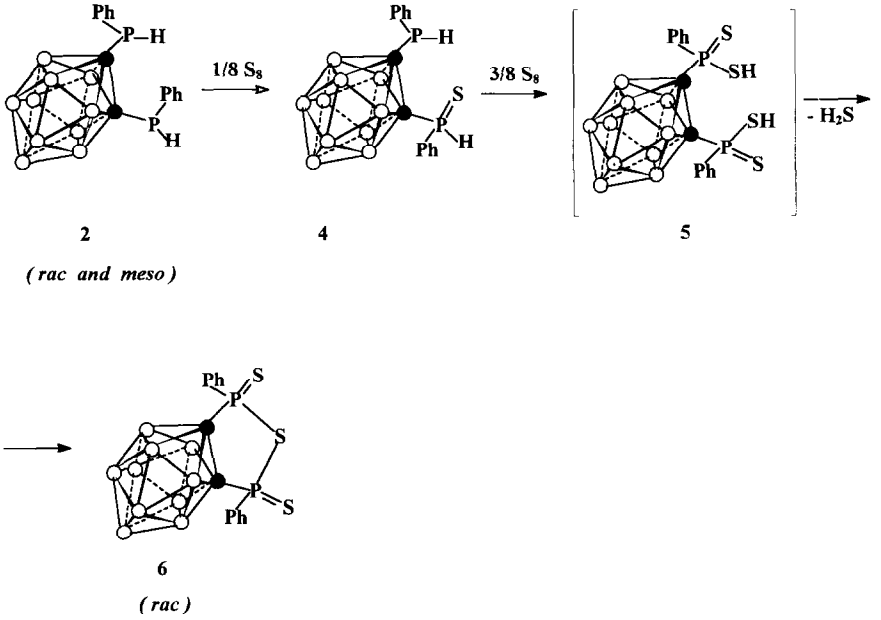
To investigate the chemical reactivity of **2a, b,** its reaction with sulfur was studied (Scheme 2). No reaction was observed on heating a *racemic* mixture of **2a, b** (4 : 1) and sulfur in THF or toluene under refluxing conditions. However, when the reaction was carried out in undecane at 190°C or without solvent at 105–110°C, the cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl-(12)-dithiodiphosphinic acid (**6**) was obtained in 67 (undecane) or 44% (without solvent) yield.

The course of the reaction, followed by ^{31}P NMR spectroscopy, indicated that the reactivity of **2a, b** is rather different to that of other secondary 1,2-diphosphines [18–20]. **2a, b** were heated with sulfur without solvent and samples were taken after 10 min, 1 h, 2 h, 5 h and 6 h, dissolved in C_6D_6 and studied by ^{31}P NMR spectroscopy.

After 10 *min*. A very intense signal for the starting material **2a, b** is observed at ca −15 ppm and several very weak singlets in the range of +64 to +90 ppm, which could not be assigned. In addition, signals for the two diastereoisomers of **4** [doublets at −13.4 ppm (J_{PP} 59 Hz) and −12.3 ppm (J_{PP} 45 Hz) and doublets at +32.2 ppm (J_{PP} 58 Hz) and +33.4 ppm (J_{PP} 45 Hz)] were observed. On proton coupling, the signals



Scheme 1.



Scheme 2.

at low field show additional P—H coupling [J_{PH} 572 Hz (δ 32.2 ppm) and J_{PH} 513 Hz (δ 33.4 ppm)], indicating the presence of a P(=S)H group [15], while those at high field exhibit coupling constants of 240 and 210 Hz, characteristic of secondary phosphines. The ^{31}P NMR data indicate that this compound is the intermediate 1-phenylphosphino-2-phenylthiophosphoryl-1,2-dicarba-*closo*-dodecaborane(12) (**4**) shown in Scheme 2.

After 1 *h*, 2 *h*, 5 *h and* 6 *h*. Samples taken after 1–6 h show decreased intensity of the signals of **2a, b** and **4**, while a singlet at +75 ppm increases in intensity, indicating the formation of **6**. A crystal structure determination (*vide infra*) showed that **6** consists of the *racemic* isomer only. Surprisingly, no signals for the proposed intermediate, the bis(phosphinesulfide) derivative, are observed. In contrast, the reaction of related 1,2-diphosphines, $H(Ph)P(CH_2)_nP(Ph)H$ (n = 2–6), with sulfur gave the corresponding disulfides, $H(S)(Ph)P(CH_2)_nP(Ph)(S)H$, as the only reaction products [19].

Molecular structure of **2a** *and* **6**

Crystal structure determinations were carried out on the *racemic* isomer **2a** (Fig. 1) and on **6**. The latter proved to be the *racemic* isomer (Fig. 2). To our knowledge, **2a** is the first structurally characterised secondary 1,2-dicarba-*closo*-dodecaboranyl(12)-bisphosphine, and **6** the first structurally characterised cyclic 1,2-bis(thiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithiodiphosphinic acid anhydride.

2a crystallises in the centrosymmetric monoclinic space group $C2/c$, and the molecule is located on a crystallographic C_2 axis which bisects the C(1)—C(1)′ and B(2)—B(2)′ bonds. The cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl(12)-dithiodiphosphinic acid (**6**) crystallises in the centrosymmetric monoclinic space group $P2_1/n$. Of the two possible diastereomers, the *racemic* form is present. Due to the presence of an inversion centre in both space groups, both enantiomeric forms of **2a** and **6** (*R,R*) and (*S,S*), are present in the unit cell. Selected bond lengths and bond angles are given in Tables 1 and 2.

The $B_{10}H_{10}C_2P_2Ph_2$ fragments of **6** and **2a** are similar. A comparison of the P—C and C—C bond lengths of **2a** and **6** with the related phosphino-1,2-dicarba-*closo*-dodecaboranes(12), 1-diphenylphosphino-2-thioisopropyl-1,2-dicarba-*closo*-dodecaborane(12) **7** [21], 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane(12) **8** [22], and 1,2 bis(diisopropylphosphino)-1,2-dicarba-*closo*-dodecaborane (12) **9** [23], shows only a small shortening of the $C_{carbaborane}$—$C_{carbaborane}$ bond length in **2a** [1.683(2) Å] and **6** [1.658(3)] compared with **7** [1.747(5) Å], **8** [1.702(6) Å] and **9** [1.719(3) Å]. The P—$C_{carbaborane}$ [1.8727(13) for **2a**, 1.870(2), 1.862(2) for **6**, 1.884(4) for **7**, 1.884(4) for **8** and 1.891(3), 1.894(3) Å for **9**] and P—C_{Ph} bond lengths [1.8244(14) for **2a**, 1.807(3), 1.805(2) for **6**, 1.832(5) Å, 1.822(5) Å for **7**, and 1.829(4) Å, 1.832(4) Å for **8**] remain largely unchanged.

Dithiodiphosphinic acid anhydrides structurally related to **6** are rare. A similar (S)P—S—P(S) frame-

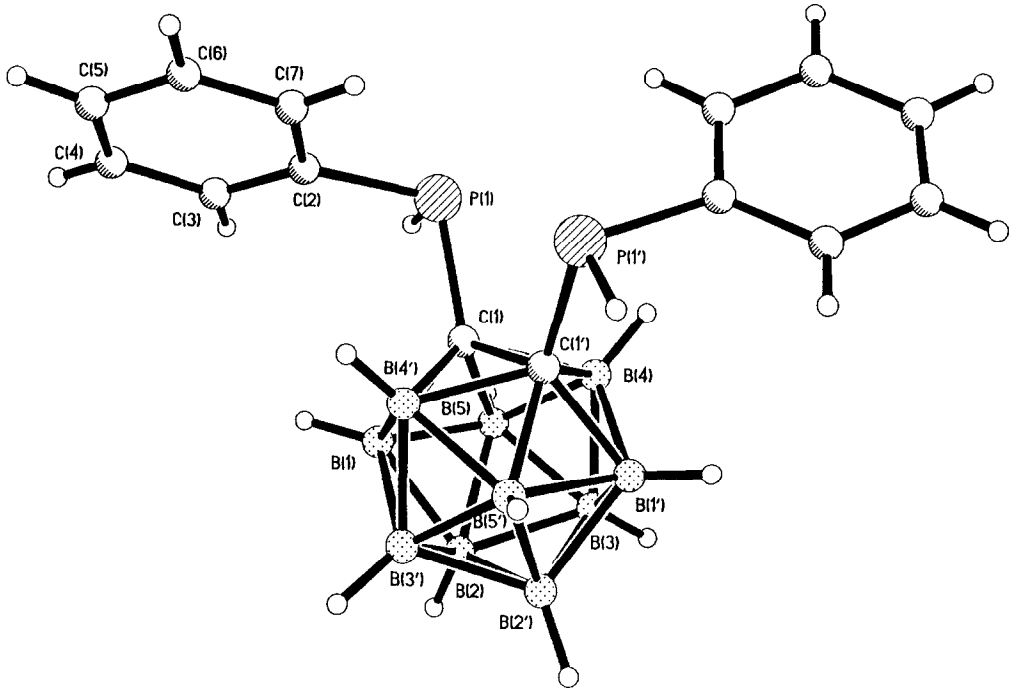


Fig. 1. Molecular structure of **2a** showing the atom numbering scheme employed (SHELXTL PLUS; XP) [26].

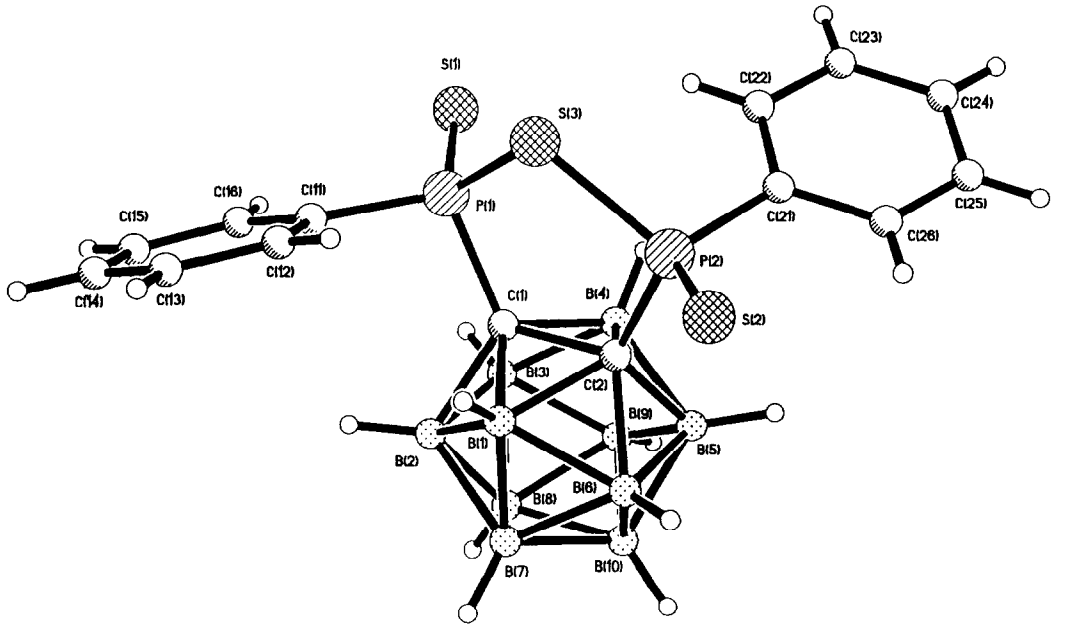


Fig. 2. Molecular structure of **6** showing the atom numbering scheme employed (SHELXTL PLUS; XP) [26].

work is observed in **6** [P=S 1.9154(9), 1.9218(9), P—S 2.1106(9), 2.1211(9) Å], *rac*-[Me(Bu^t)P(S)]$_2$S (**10**) [24] [P=S 1.939(1), 1.941(1), P—S 2.126(1), 2.123(1) Å], and 3,5-di-*tert*-butyl-1,8-epithio-1λ^5,8λ^5-naphthol-[1,8-*cd*][1,7,2,6]benzodioxadiphosphonine-1,8-dithione (**11**) [25] [P=S 1.917(2), 1.905(2), P—S 2.074(2), 2.087(2) Å]. The latter is, however, obtained as the *meso* form only, due to the presence of two fused rings [$C_3P(=S)_2S$ and $C_2O_2P(=S)_2S$]. The P—S—P [**6**: 103.44(4), **10**: 104.78(5)°] and S—P—S

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

P(1)—C(1)	1.8727(13)	P(1)—C(2)	1.8244(14)
P(1)—H(1P)	1.32(2)	C(1)—C(1)′	1.683(2)
B(1)—C(1)	1.712(2)	B(4)—C(1)′	1.714(2)
B(4)—C(1)	1.737(2)	B(5)—C(1)	1.712(2)
B—B from 1.769(2) to 1.792(2)		B—H from 1.05(2) to 1.09(2)	
C(2)—P(1)—C(1)	104.58(6)	C(2)—P(1)—H(1P)	98.6(8)
C(1)—P(1)—H(1P)	92.4(8)	C(1)—B(1)—B(3)′	105.2(1)
C(1)—B(1)—B(4)′	58.78(8)	C(1)—B(1)—B(2)	105.1(1)

Table 2. Selected bond lengths (Å) and angles (°) for **6**

S(1)—P(1)	1.9154(9)	S(2)—P(2)	1.9218(9)
S(3)—P(2)	2.1106(9)	S(3)—P(1)	2.1211(9)
P(1)—C(11)	1.807(3)	P(1)—C(1)	1.870(2)
P(2)—C(21)	1.805(2)	P(2)—C(2)	1.862(2)
C(1)—C(2)	1.658(3)	C(1)—B(3)	1.709(4)
C(1)—B(2)	1.713(3)	C(1)—B(1)	1.731(4)
C(1)—B(4)	1.731(4)	C(2)—B(5)	1.709(4)
C(2)—B(6)	1.724(4)	C(2)—B(1)	1.727(4)
C(2)—B(4)	1.736(4)		
B—B from 1.764(4) to 1.791(5)			
P(2)—S(3)—P(1)	103.44(4)	C(11)—P(1)—C(1)	104.05(11)
C(11)—P(1)—S(1)	115.38(9)	C(1)—P(1)—S(1)	113.61(8)
C(11)—P(1)—S(3)	105.62(9)	C(1)—P(1)—S(3)	99.95(8)
S(1)—P(1)—S(3)	116.42(4)	C(21)—P(2)—C(2)	106.71(11)
C(21)—P(2)—S(2)	115.40(9)	C(2)—P(2)—S(2)	113.13(8)
C(21)—P(2)—S(3)	107.02(9)	C(2)—P(2)—S(3)	101.01(8)
S(2)—P(2)—S(3)	112.39(4)	C(2)—C(1)—P(1)	116.6(2)
C(1)—C(2)—P(2)	116.2(2)		

[**6**: 116.42(4), 112.39(4), **10**: 115.68(5), 117.36(5)°] bond angles of **6** and **10** are in the same range, while those of **11** are much smaller [P—S—P 97.21(6), S—P—S 109.90(8), 110.51(8)°] as the P—S—P group is part of two strained fused cyclic systems.

CONCLUSION

The results presented here show that the secondary carbaboranylphosphines **2** and **3** are readily accessible, air- and water-stable solids. The diastereoisomers **2a** and **2b** can be separated by fractional crystallisation. The reaction of **2a, b** with sulfur indicates that the reactivity of secondary carbaboranylphosphines differs significantly from that of secondary alkyl- or arylbisphosphines. Further studies of the reactivity of **2** are under way.

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): trace amounts 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 FT-IR spectrometer System 2000 in the range 350–4000 cm^{-1}. The melting points were determined in sealed

capillaries under argon and are uncorrected. *Rac*- and *meso*-1,2-bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**1**) were prepared by literature procedures [9] and obtained in 80% yield.

Synthesis of rac- and meso-1,2-bis(phenylphosphino)-1,2-dicarba-*closo*-dodecaborane(12) (**2a**), (**2b**)

A suspension of $LiAlH_4$ (0.5 g, 13 mmol) in 25 cm^3 ether was added to a solution of **1** (5.1 g, 11.8 mmol) in 125 cm^3 ether at 0 °C over 1.5 h. The reaction was kept at 0 °C for 1 h, then for 1 h at 16 °C; finally, the mixture was refluxed for 1 h. After cooling to r.t., 2.1 cm^3 H_2O was added, the mixture filtered and the solution dried over $NaHSO_4$. The ether was removed *in vacuo* to give 3.9 g (91%) **2**. The diastereoisomers were separated by fractional crystallisation from hexane. After 6 crystallisations, 0.8 g of pure **2a** or, after 10 crystallisations, 0.06 g of **2b** were obtained. M.p. 148–149 °C, **2a**; 120–124 °C, **2b**. Found: C, 46.93; H, 6.01; P, 16.49. Calc.: for $C_{14}H_{22}B_{10}P_2$: C, 46.68; H, 6.10; P, 17.16%. IR for **2a, 2b** (KBr) cm^{-1}: 3072 (C—H); 2626, 2606, 2583, 2561 (B—H); 2323 (P—H); 1957, 1814 (Ph); 1584; 1483; 1436; 1310; 1276; 1113; 1079; 1026; 1000; 941; 919; 876; 813; 741; 728; 689; 483; 407.

Spectroscopic data for **2a** (C_6D_6, 25 °C). ^1H NMR (400 MHz): δ 7.30 (m, 4H, Ph), 7.00 (m, 6H, Ph), 4.78 (dt, 2H, P—H, $^1J_{PH}$ 244 Hz, $^3J_{PP}$ 82 Hz), 3.5–1.6 ppm (br, m, B—H); ^{31}P (161.9 MHz): $\delta -15.15$ ppm (dt, $^1J_{PH}$ 246 Hz, $^3J_{PP}$ 84 Hz); ^{13}C (100.6 MHz): δ 136.8 (m, *ipso*-C, Ph), 131.0, 130.9, 129.0 (Ph), 76.3 ppm (m, $C_2B_{10}H_{10}$); ^{11}B (128.4 MHz): $\delta -0.9$ (2B, $^1J_{BH}$ 142 Hz), -7.2 (4B, $^1J_{BH}$ 144 Hz), -9.4 (2B, $^1J_{BH}$ 225 Hz), -11.3 ppm (2B).

Spectroscopic data for **2b** (C_6D_6, 25 °C). ^1H NMR (400 MHz): δ 7.30 (m, 4H, Ph), 7.00 (m, 6H, Ph), 4.78 (dt, 2H, P—H, $^1J_{PH}$ 239 Hz, $^3J_{PP}$ 87 Hz), 3.5–1.6 ppm (br, m, B—H); ^{31}P (161.9 MHz): $\delta -14.98$ ppm (dt, $^1J_{PH}$ 239 Hz, $^3J_{PP}$ 87 Hz); ^{13}C (100.6 MHz): δ 136.8 (m, *ipso*-C, Ph), 131.0, 130.9, 129.0 (Ph), 77.6 ppm (m, $C_2B_{10}H_{10}$); ^{11}B (128.4 MHz): $\delta -0.9$ (2B, $^1J_{BH}$ 142 Hz), -7.2 (4B, $^1J_{BH}$ 144 Hz), -9.4 (2B, $^1J_{BH}$ 225 Hz), -11.3 ppm (2B).

Synthesis of 1-phenylphosphino-1,2-dicarba-*closo*-dodecaborane(12) (**3**)

3 was prepared analogously to **2** from **1** (5.7 g, 13.3 mmol) in 125 cm^3 ether, 0.8 g (21 mmol) $LiAlH_4$ in 30 cm^3 ether and 10.5 cm^3 H_2O. **3** was purified by column chromatography (hexane/acetone 4:1), yield 1.4 g (42%). M.p. 33–36 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 7.05, 7.00, 6.92 (m, 5H, Ph), 4.57 (d, 1H, $^1J_{PH}$ 229 Hz, P—H), 3.5–1.6 ppm (br, m, B—H); ^{31}P (161.9 MHz, C_6D_6, 25 °C): $\delta -2.67$ ppm (d, $^1J_{PH}$ 229 Hz); ^{11}B (128.4 MHz, C_6D_6, 25 °C): $\delta -1.2$ (1B, $^1J_{BH}$ 160 Hz), -2.7 (1B, $^1J_{BH}$ 170 Hz), -7.6 (2B, $^1J_{BH}$ 152 Hz), -9.5 (1B, $^1J_{BH}$ 182 Hz), -11.0 (1B, $^1J_{BH}$ 200 Hz), -12.8 ppm (4B); ^{13}C (100.6 MHz, C_6D_6, 25 °C): δ 136.7 (d, $^1J_{CP}$ 18 Hz, *ipso*-C, Ph), 131.8, 130.6, 129.8 (Ph), 69.0 (d, $^1J_{CP}$ 60 Hz, $C_2B_{10}H_{11}$), 63.8 ppm (d, $^1J_{CH}$ 196 Hz, $C_2B_{10}H_{11}$); IR (KBr) cm^{-1}: 3058, 2957, 2927 (C—H); 2586 (B—H); 2320 (P—H); 1957, 1884 (Ph); 1585; 1483; 1437; 1308; 1275; 1172; 1115; 1091; 1072; 1025; 1001; 944; 918; 900; 827; 795; 739; 720; 692; 628; 481; 408. Found: C, 39.07; H, 6.77; P, 11.50. Calc.: for $C_8H_{17}B_{10}P$: C, 38.14; H, 6.75; P, 12.28%.

Synthesis of the cyclic anhydride of 1,2-bis(phenylthiophosphoryl)-1,2-dicarba-*closo*-dodecaboranyl-(12)-dithiodiphosphinic acid (**6**)

In undecane. A racemic mixture of **2a, b** (0.72 g, 2.0 mmol) and sulfur (0.07 g, 9.0 mmol) were heated in undecane (20 cm^3) at 190–200 °C for 5 h. The solvent was distilled off *in vacuo*, the greyish residue was then dissolved in hot hexane and filtered. **6** was obtained on cooling the hexane solution to −5 °C, yield 0.6 g (67%). M.p. 229–232 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 8.15 (m, Ph), 6.93 (m, Ph), 3.5–1.9 ppm (br, m, B—H); ^{31}P (161.9 MHz, C_6D_6, 25 °C): δ 75.1 ppm; ^{11}B (128.4 MHz, C_6D_6, 25 °C): $\delta -2.7$ (J_{BH} 167 Hz), -4.2 (J_{BH} 166 Hz), -10.3 ppm; ^{13}C (100.6 MHz, C_6D_6, 25 °C): δ 134.3, 133.8, 130.1, 128.9 (Ph), 85.4 (m, $C_2B_{10}H_{10}$). IR (KBr) cm^{-1}: 3059 (C—H); 2664, 2651, 2615, 2583, 2571, 2554 (B—H); 1815 (Ph); 1580; 1480; 1437; 1311; 1187; 1161; 1092; 1078; 1027; 997; 903; 848; 799; 735; 722; 687; 671 ($\nu_s P_2S_2$); 625; 614; 560; 535; 475; 430; 417. Vibrations for P—S—P and $\nu_{as}P_2S_2$ are expected in the range 450–600 cm^{-1} [28]; however, they cannot be unambiguously assigned. Found: C, 37.04; H, 4.89; S, 20.92; P, 13.23. Calc.: for $C_{14}H_{20}B_{10}P_2S_3$: C, 37.00; H, 4.40; S, 21.04; P, 13.59%.

Without solvent. A racemic mixture of **2a, b** (1.0 g, 2.7 mmol) and sulfur (0.35 g, 10.9 mmol) were heated at 105–110 °C for 6 h. After 10 min, 1, 2, 5 and 6 h the reaction mixture was cooled to room temperature and samples were taken for ^{31}P NMR spectroscopic studies. After completion of the reaction, the white mixture was dissolved in hot hexane and worked up as described above giving 0.53 g (44%) of **6**.

Data collection and structural refinement of **2a** *and* **6**

Crystal data for **2a**. $C_{14}H_{22}B_{10}P_2$, $M = 360.36$, white crystals, $0.4 \times 0.3 \times 0.2$ mm, monoclinic, space group $C2/c$ (no. 15), $T = 293(2)$ K, $a = 20.2581(13)$, $b = 8.8653(6)$, $c = 11.8046(9)$ Å, $\beta = 112.374(1)°$, $V = 1960.4(2)$ Å^3, $Z = 4$, $D_c = 1.221$ g cm^{-3}, $F(000) = 744$, μ(Mo-K_α) = 0.216 mm^{-1}, 7114 reflections collected with $2 < \Theta < 26°$; of these 1826 were independent; 162 parameters, refinements converge to $R_1 = 0.0317$, $wR_2 = 0.0816$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0359$, $wR_2 = 0.0837$ (all data).

Crystal data for **6**. $C_{14}H_{20}B_{10}P_2S_3$, $M = 454.52$,

white crystals, $0.3 \times 0.2 \times 0.2$ mm, monoclinic, space group $P2_1/n$ (no. 14), $T = 223(2)$ K, $a = 13.5378(9)$, $b = 11.0197(7)$, $c = 15.6155(10)$ Å, $\beta = 104.996(1)^\circ$, $V = 2250.2(3)$ Å^3, $Z = 4$, $D_c = 1.342$ g cm^{-3}, $F(000) = 928$, $\mu(\text{Mo-}K_\alpha) = 0.472$ mm^{-1}, 9685 reflections collected with $1.8 < \theta < 26^\circ$; of these 4015 were independent; 342 parameters, refinements converge to $R_1 = 0.0413$, $wR_2 = 0.0893$ (for reflections with $I > 2\sigma(I)$), $R_1 = 0.0564$, $wR_2 = 0.0975$ (all data).

Data (Mo-K_α, $\lambda = 0.71073$ Å) were collected with a Siemens CCD (SMART). All observed reflections (2θ range: 4–52°) were used for determination of the unit cell parameters. The structures were solved by direct methods (SHELXTL PLUS [26]) and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL PLUS [26]). Restrictions for **2a**: P, B, and C atoms anisotropic, H atoms located and refined isotropically. Restrictions for **6**: S, P, B, and C atoms anisotropic, H atoms located and refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Fachinformationszentrum [27].

Acknowledgements—We gratefully acknowledge support from the Fonds der Chemischen Industrie. Chemetall has provided a generous donation of lithium alkyls.

REFERENCES

1. Hart, F. A. and Owen, D. W., *Inorg. Chim. Acta*, 1985, **103,** L1.
2. Longato, B. and Bresadola, S., *Inorg. Chem.*, 1982, **21,** 168.
3. Bakun, A. V., Dokuchaev, Yu. P., Lapidis, I. I., Moskovskii, Yu. V., Skvortsov, I. M. and Antokin, B. G., *USSR Pat.*, 402241.
4. Hsu, M. T. S., Chen, T. S. and Riccitiello, S. R., *J. Appl. Polym. Sci.*, 1991, **42,** 851.
5. Hawthorne, M. F., *Angew. Chem.*, 1993, **105,** 997.
6. Gelen, M., Bouhdid, A., Willem, R., Bregadze, V. I., Ermanson, L. V. and Tiekink, E. R. T., *J. Organomet. Chem.*, 1995, **501,** 277.
7. Godovikov, N. N., Balema, V. P., Rys, E. G., Zhukovskiy, Yu. G., Sotchilina, E. E. and Moralev, S. N., *Bioorganicheskja khimija* (*Bioorganic Chemistry Russ.*), 1993, **19,** 1077.
8. *Metal Complexes in Cancer Chemotherapy*, ed. B. K. Keppler, VCH, Weinheim, New York, 1993.
9. Alexander, R. P. and Schroeder, H., *Inorg. Chem.*, 1963, **2,** 1107.
10. Bregadze, V. J., *Chem. Rev.*, 1992, **92,** 209.
11. Kasantsev, A. V., Zhubekova, M. N. and Zakharkin, L. I., *Zh. Obshch. Khim.*, 1971, **41,** 2027.
12. VARIAN VNMR SOFTWARE, Version 4.1 Revision C, SunOS™ 4.1.2.
13. Hitchcock, P. B., Lappert, M. F., Leung, W.-P. and Yin, P., *J. Chem. Soc., Dalton Trans.*, 1995, 3925.
14. Kimpton, B. R., McFarlane, W., Muir, A. S., Patel, P. G. and Bookham, J. L., *Polyhedron*, 1993, **12,** 2525.
15. Nifant'ev, E. E., *Spektroskopie* ^{31}P; MGPI, Moskau 1986, p. 149.
16. Kivekäs, R., Teixidor, F., Viñas, C. and Nuñez, R., *Acta Cryst.*, 1995, **C51,** 1868.
17. Hill, W. E., Rackley, B. G. and Silva-Trivino, L. M., *Inorg. Chim. Acta*, 1983, **75,** 51.
18. Issleib, K. and Döll, G., *Z. anorg. allg. Chem.*, 1963, **324,** 259.
19. Grossmann, G., Walther, B. and Gastrock-May, U., *Phosphorus and Sulfur*, 1981, **11,** 259.
20. Corbridge, D. E. C., *Phosphorus. An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam–New York, 1980.
21. Teixidor, F., Viñas, C., Benakki, R., Kivekäs, R. and Sillanpää, R., *Inorg. Chem.*, 1997, **36,** 1719.
22. Kivekäs, R., Sillanpää, R., Teixidor, F., Viñas, C. and Nuñez, R., *Acta Cryst.*, 1994, **C50,** 2027.
23. Kivekäs, R., Sillanpää, R., Teixidor, F., Viñas, C., Nuñez, R. and Abad, M., *Acta Cryst.*, 1995, **C51,** 1864.
24. Wunderlich, H. and Wussow, H.-G., *Z. Naturforsch.*, 1984, **39b,** 1581.
25. Foreman, M. R. St. J., Slawin, A. M. Z. and Woollins, J. D., *J. Chem. Soc., Chem. Commun.*, 1995, 2217.
26. SHELXTL PLUS, Siemens Analyt. X-ray Inst. Inc., 1990, XS: *Program for Crystal Structure Solution*, XL: *Program for Crystal Structure Determination*, XP: *Interactiv Molecular Graphics*.
27. Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, giving reference to the depository number CSD 407662 (for **2a**) and CSD 408309 (for **6**), and citing the authors and this paper.
28. Weidlein, J., Müller, U. and Dehnicke, K., *Schwingungsfrequenzen I*, G. Thieme Verlag, Stuttgart–New York, 1981.