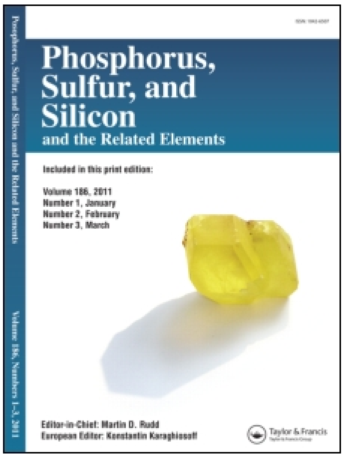

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PENTAALKYL-6-DIPHENYLPHOSPHINO-2,3,4,5-TETRACARBA-*NIDO*-HEXABORANES(6)

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To cite this Article Wrackmeyer, Bernd , Glöckle, Alexandra and Kehr, Gerald(1997) 'PENTAALKYL-6-DIPHENYLPHOSPHINO-2,3,4,5-TETRACARBA-*NIDO*-HEXABORANES(6)', Phosphorus, Sulfur, and Silicon and the Related Elements, 131: 1, 25 — 35

To link to this Article: DOI: 10.1080/10426509708031593

URL: http://dx.doi.org/10.1080/10426509708031593

Phosphorus, Sulfur, and Silicon, 1997, Vol. 131, pp. 25–35
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PENTAALKYL-6-DIPHENYLPHOSPHINO-2,3,4,5-TETRACARBA-*NIDO*-HEXABORANES(6)

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(Received 14 May 1997)

Pentaalkyl-6-bromo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) (**3**-carb-Br and **4**-carb-Br) react with lithium-diphenylphosphide to give the 6-diphenylphosphino substituted carboranes **3**-carb-PPh_2 and **4**-carb-PPh_2. **3**-carb-PPh_2 can be oxidized to give the respective oxide, sulfide and selenide. Treatment of **4**-carb-PPh_2 with an excess of methyl iodide cleaves the P-B bond and **4**-carb-I is formed together with $[Me_2Ph_2P]^+I$. **4**-carb-PPh_2 reacts with borane in tetrahydrofuran (BH_3-THF/THF) or $W(CO)_5$-THF/THF to give the BH_3 and $W(CO)_5$ complexes. All products were characterized by ^1H, ^{11}B, ^{13}C and ^{31}P NMR spectroscopy.

Keywords: Boron; Phosphorus; Carborane; NMR

INTRODUCTION

Peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6) **1** and **2** have been known since the mid-sixties[1] and were found to be exceptionally stable compounds, in contrast to the parent derivative $C_4B_2H_6$[2]. In order to study the chemistry of the carboranes **1** and **2**, functional groups other than alkyl at one or both boron atoms are needed. Recently, we have reported on the synthesis of tetraalkyl-1,6-dibromo-[3] and pentaalkyl-6-bromo-derivatives **3**-carb-Br and **4**-carb-Br[4], and the basic structure of such alkylated carboranes has been determined by an X-ray diffraction analysis of the pentamethyl derivative with an N-bonded $Fe_2(CO)_6$-μ-SN fragment in 6-position[5]. The 6-bromo-derivatives **3** and **4** have already served for the synthesis of novel tin-boron compounds such as carb-$SnPh_3$ and carb-$SnCl_3$[6]. Here we report that the pentaalkylcarboranyl moiety

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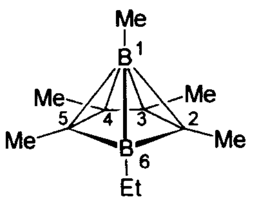
*Corresponding author.



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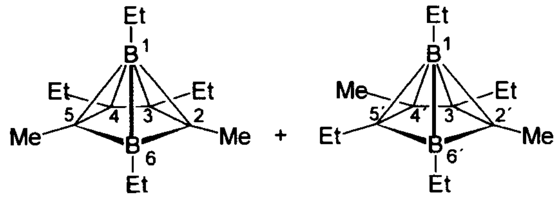

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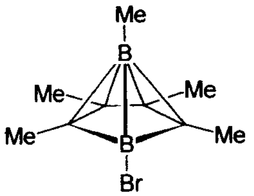
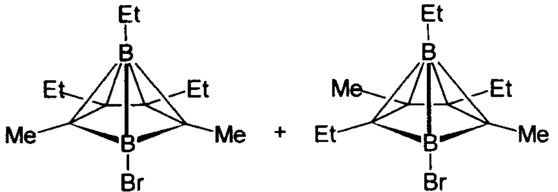


3-carb-Br



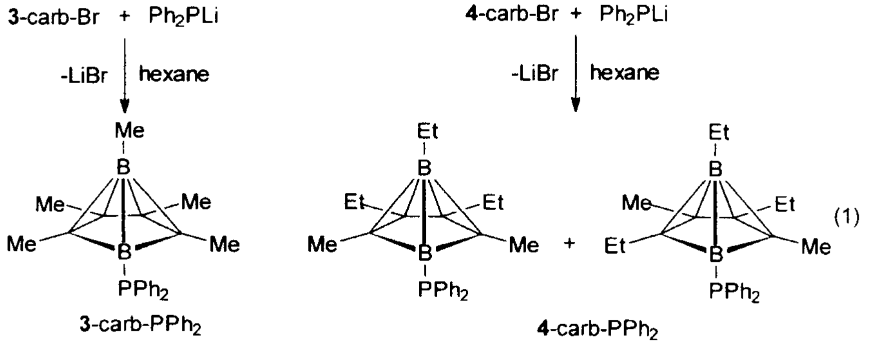
4-carb-Br

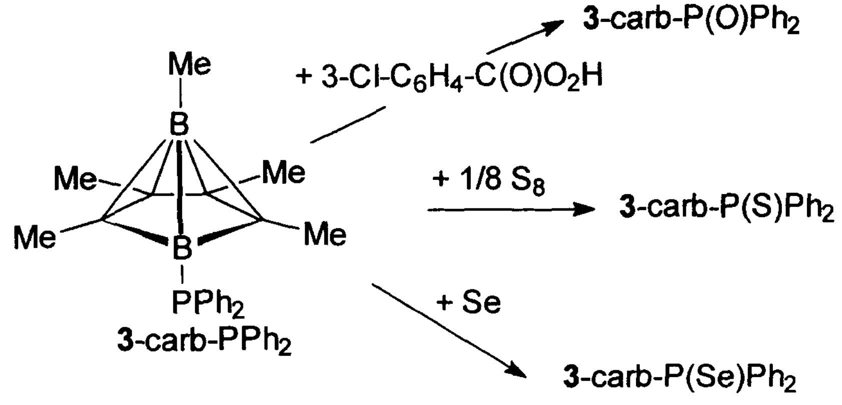
can be linked to phosphorus as shown for the Ph_2P derivatives **3**-carb-PPh_2 and **4**-carb-PPh_2. A few reactions typical of phosphanes are studied.

RESULTS AND DISCUSSION

Synthesis

The reaction of **3**-carb-Br and the isomers **4**-carb-Br with Ph_2PLi proceeds readily to give the new phosphines **3**-carb-PPh_2 and **4**-carb-PPh_2 in high yield (Scheme 1). There was no indication of cluster degradation or of any rearrangement of the 6-substituted isomers to the 1-substituted isomers. This is in agree-





ment with previous findings for the reaction of carb-Br with organo-[7] or stannyl lithium compounds[6].

The new phosphane 3-carb-PPh$_2$ shows the expected typical behavior in the reactions summarized in Scheme 2. Further reactions were carried out with 4-carb-PPh$_2$ on a small scale in NMR tubes in order to explore the reactivity towards methyl iodide, BH$_3$-THF/THF and W(CO)$_5$-THF/THF (Scheme 3). In the case of the latter two reactions, the carboranyl group does not exert any particular effect. However, in the reaction with methyl iodide, the P-B bond is cleaved giving rise to the formation of the 6-iodo derivatives 4-carb-I and [Me$_2$Ph$_2$]$^+$I. This indicates that a systematic study is necessary in order to com-

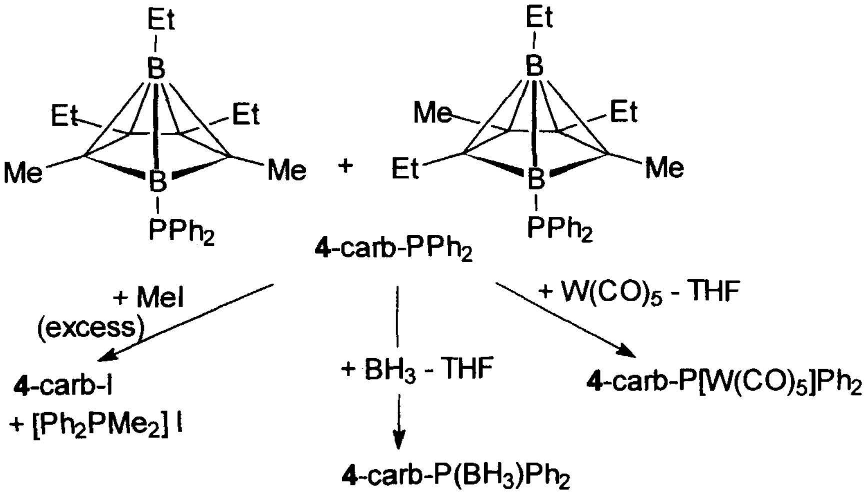


TABLE I ^{11}B, ^{13}C and ^{31}P NMR data[a] of 6-diphenylphosphino- and 6-diphenyl-phosphoryl-pentamethyl-2,3,4,5-tetracarba-*nido*-hexaboranes **3**-carb-PPh$_2$, and **3**-carb-P(O)Ph$_2$, **3**-carb-P(S)Ph$_2$, **3**-carb-P(Se)Ph$_2$,[b]

		3-carb-PPh$_2$	*3-carb-P(O)Ph$_2$*	*3-carb-P(S)Ph$_2$*	*3-carb-P(Se)Ph$_2$*
δ^{11}B	B(1)	−43.7	−42.9	−42.6	−42.4
	B(6)	14.0	8.9	11.1	10.9
δ^{31}P	[^{1}J(^{31}P^{11}B)]	−59.9[80]	34.8[215]	14.4[200]	−4.5[190]
δ^{13}C	B(1)-Me	−17.3 (80)	−17.5 (80)	−17.7 (80)	−17.8 (80)
	C(2/5)	100.0[br][11.0[c]]	100.3[br]	100.5[br][15.0[c]]	100.2[br]
	C(3/4)	110.2[4.4]	111.9[13.0]	110.6[12.5]	110.6[12.0]
	C(2/5)-Me	11.0[4.9]	10.9[< 1]	10.8[< 1]	10.8[< 1]
	C(3/4)-Me	9.4[< 1]	9.0[< 1]	9.1[< 1]	9.0[< 1]
	PPh$_2$; C$_i$	140.2[10.4]	138.7[97.3]	137.4[64.0]	135.0[58.0]
	C$_o$	134.8[17.4]	131.6[10.2]	131.8 [10.0]	132.5 [10.9]
	C$_m$	128.5 [7.1]	128.6 [13.4]	128.4 [11.2]	128.4 [10.9]
	C$_p$	128.3 [< 1]	130.4 [< 1]	130.2 [3.0]	130.2 [2.7]

[a] In C_6D_6 at 25 ± 1 °C; coupling constants ^{1}J(^{31}P,^{11}B) (±10 Hz) and J(^{31}P,^{13}C) (±0.8 Hz) are given in square brackets, ^{1}J(^{13}C,^{11}B) (±5 Hz) in parentheses; [br] indicates the broad signal of a boron-bonded carbon atom owing to unresolved scalar ^{13}C-^{11}B coupling

[b] ^{77}Se NMR: δ^{77}Se = −334.0; ^{1}J(^{77}Se,^{31}P) = 667.0 ± 3 Hz

[c] From heteronuclear ^{13}C{^{1}H,^{11}B} triple resonance experiments.

pare the behavior of **3**-carb-PPh$_2$ or **4**-carb-PPh$_2$ with Ph$_3$P or Ph$_2$(R)P in general.

NMR Spectroscopic Results

^{11}B, ^{13}C, ^{31}P and ^{77}Se NMR data of the carborane derivatives are given in Table I and Table II (see Experimental for ^{1}H NMR data). The NMR data are fully consistent with the proposed structures. The relatively sharp ^{11}B NMR signals at ca. δ −42 ± 1 are typical of an apical B(1)-alkyl group[8]. The δ^{11}B(6) values change slightly for different substituents, and the ^{11}B nuclei become more deshielded by the phosphino than by the various phosphoryl substituents. This is the same trend as for the ^{13}C$_i$ resonance signals. ^{11}B- and ^{31}P NMR spectra serve as excellent tools for monitoring the progress of the reaction and determining the product distribution. As an example, Figure 2 shows that the formation of **4**-carb-P(BH$_3$)Ph$_2$ is readily evident from the ^{11}B NMR spectra, and that both P-B bonds in this borane adduct are kinetically stable in the presence of a large excess of BH$_3$-THF. In the ^{31}P NMR spectra the formation of the P-B bond is indicated either by a broad singulet (**3**-carb-PPh$_2$ and **4**-carb-PPh$_2$) or a partially relaxed quartet [^{1}J(^{31}P,^{11}B) is given by the difference between the frequencies of the inner lines] owing to scalar relaxation of the second kind[9].

The ^{13}C NMR spectra show all the required signals, together with the typical pattern of the *nido*-C$_4$B$_2$ cage[8]: broad (partially relaxed scalar ^{13}C-^{11}B coup-

TABLE II ^{11}B, ^{13}C, and ^{31}P NMR-data[a] of **4**-carb-PPh_2 and complexes with BH_3 and $W(CO)_5$

		4-carb-PPh_2	*4-carb-$P[W(CO)_5]Ph_2$*	*4-carb-$P(BH_3)Ph_2$*
$\delta^{11}B$	B(1)	−44.0	−43.6	−43.9
	B(6)	14.3	14.7	10.7[b]
$\delta^{31}P$		−59.6	−40.7/−42.7 (ratio 2:1[d])	−24.2 [180]
$\delta^{13}C$	B(1)-Et	−4.4 [br] (86); 11.7	−3.9 [br]; 10.1	−4.8[br]; 10.2
	C(2/2′)	99.7[br][10.9[c]]; 99.4 [br][10.9[c]]	97.9 [br]; 97.9 [br]	100.7 [br]; 100.7 [br]
	C(5/5′)	99.4[br][10.9[c]]; 106.3 [br] [10.9[c]]	97.9 [br]; 103.7 [br]	100.7 [br]; 104.3 [br]
	C(3/3′)	114.9 [3.8]; 114.9 [3.8]	116.2 [8.0]; 116.2 [8.0]	116.3 [9.0]; 116.3 [8.7]
	C(4/4′)	114.4[3.8]; 109.2 [3.8]	115.3 [8.0]; 109.8 [8.0]	115.6 [8.7]; 110.5 [8.7]
	C(2)-Me	11.8 [3.8]	11.5	10.8
	C(2′)-Me	11.8 [3.8]	11.5	10.8
	C(3)-Et	19.3 [4.9]; 15.1	18.7 [8.8]; 14.2	19.0[14.2
	C(3′-Et	17.8 [6.0]; 13.7	17.7; 13.6	17.7 [8.5]; 13.8
	C(4)-Et	19.3 [4.9]; 15.1	18.7 [8.8]; 14.2	19.0; 14.7
	C(4′)-Me	9.0	9.3	9.1
	C(5)-Me	11.8 [3.8]	11.5	10.8
	C(5′)-Et	17.8 [6.0]; 12.9	17.7; 12.8	17.7 [8.5]; 12.9
	PPh_2 C_i	139.9[9.8]; 139.8[9.8];	137.2[37.5];137.1[37.5];137.0[36.9]	133.3[47.3];133.3[47.2];133.5[47.6]
	C_o	135.5[16.3]; 135.2[16.3];134.9[17.4];	134.8[11.2];134.2[11.0];134.1[11.2]	134.1[8.7];133.9[8.2];133.8[8.7]
	C_m	128.5[9.0];127.3[9.3];127.1[10.3];	128.6[9.7];128.5[9.7];128.4[9.7]	128.5[9.8];128.4[9.3]
	C_p	128.4 [2.2–3.2]	129.3[2.1];129.2[2.1];129.1[2.1]	129.9[3];129.8[3]

[a] In C_6D_6 at 25 ± 1 °C; coupling constants $^1J(^{31}P,^{11}B)$ (± 10 Hz) and $J(^{31}P,^{13}C)$ (± 0.8 Hz) are given in square brackets, $^1J(^{13}C,^{11}B)$ (± 5 Hz) in parentheses; [br] indicates the broad signal of a boron-bonded carbon atom owing to unresolved scalar ^{13}C-^{11}B coupling; n.m. means not measured owing to insufficient signal-to-noise ratio.

[b]: $\delta^{11}B$ (carb-P-BH_3) −39.9, broad, $^1J(^{31}P,^{11}B)$ and $^1J(^{11}B,^1H)$ are not resolved.

[c] From selective heteronuclear $^{13}C\{^1H,^{11}B\}$ triple resonance experiments.

[d] $\delta^{13}C(CO_{cis})$ = 198.8 [6.3] $\{^1J^{183}W, {}^{13}C) = 126$ Hz}; 198.9 [6.1] {126} (ratio 2:1); $\delta^{13}C(CO_{trans})$ = 200.3[16.9]{n.m.};200.4[16.9]{n.m.}. (ratio 2:1).

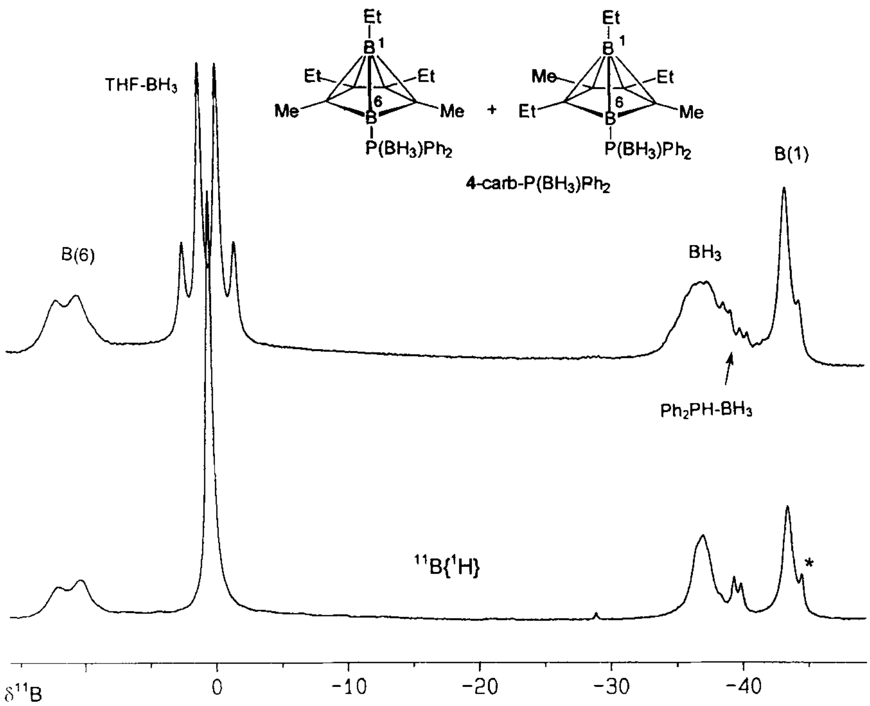


FIGURE 1 80.3 MHz ^{11}B NMR spectra (with and without ^{1}H decoupling) of the reaction solution containing **4**-carb-P(BH$_3$)Ph$_2$ in the presence of a large excess of THF-BH$_3$. The sample also contains a small amount of Ph$_2$PH-BH$_3$ which arises from traces of Ph$_2$PH present in **4**-carb-PPh$_2$.

ling[8,10] ^{13}C NMR signals for the C(2,5)- and sharp signals for the C(3,4) atoms as doublets owing to $^{3}J(^{31}P,^{13}C(3,4))$. By selective heteronuclear $^{13}C\{^{1}H, ^{11}B\}$ triple resonance experiments, the broad ^{13}C(2,5) NMR signals become sharp doublets owing to $^{2}J(^{31}P, ^{13}C(2,5))$ (Figure 2).

The comparison of $^{1}J(^{31}P, ^{13}C)$ and $^{1}J(^{31}P, ^{11}B)$ values for Ph$_3$P and derivatives with those for **3**-carb-PPh$_2$ and derivatives (Table III) suggests that rehybridization[11] at the phosphorus atom in the P(V) compounds is induced by the 6-carboranyl group. The large magnitude of the coupling constants $^{1}J(^{31}P, ^{11}B)$ indicates increased s character of the P-B hybrid orbital, whereas the smaller magnitude of $^{1}J(^{31}P, ^{13}C)$ in **3**-carb-P(E)Ph$_2$ (E = O, S, Se) as compared with P(E)Ph$_3$ indicates reduced s character in the P-C hybrid orbitals. The δ^{31}P values in Table III also show the markedly different substituent effects exerted by the 6-carboranyl and phenyl groups.

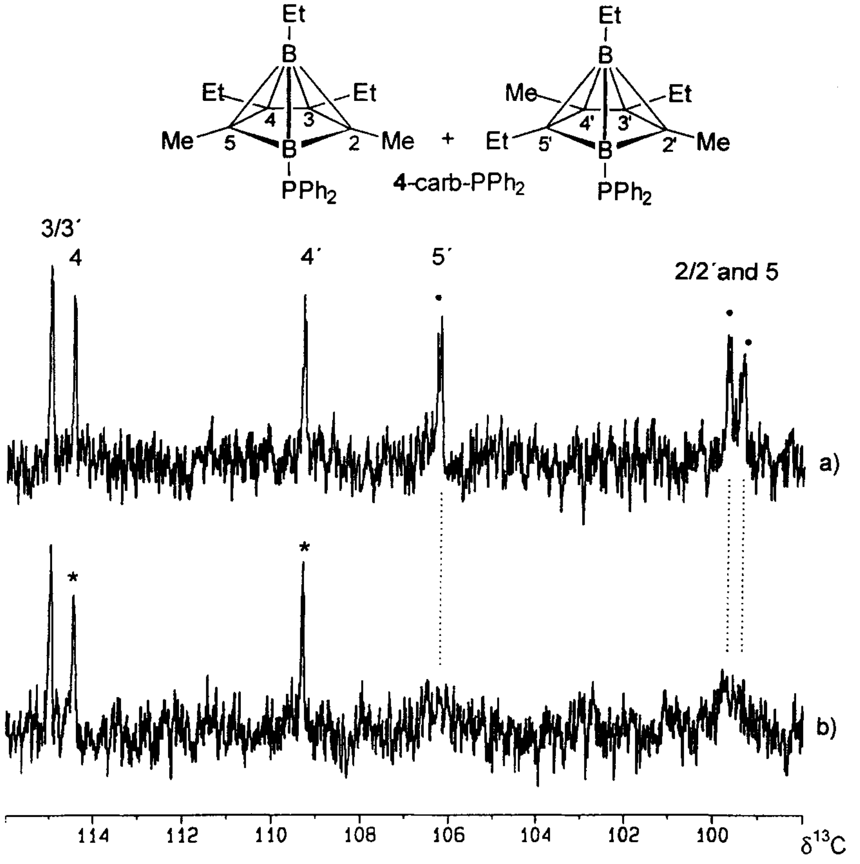


FIGURE 2 125.75 MHz ^{13}C NMR spectra of the isomers 4-carb-PPh_2 showing the carboranecage ^{13}C resonances a) Heteronuclear $^{13}C\{^1H,^{11}B(6)\}$ triple resonance experiment showing C(2/2′ to 5/5′), with resolved splitting owing to $^2J(^{31}P,^{13}C)$ and $^3J(^{31}P,^{13}C)$ as marked (*). $^{13}C(2/2')$ and $^{13}C(5/5')$ resonances are broad due to partially relaxed scalar ^{13}C-^{11}B coupling. b) Normal $^{13}C\{^1H\}$ NMR spectrum showing the same region as in a). The $^{13}C(2/2')$ and $^{13}C(5/5')$ resonances are now typically broad due to partially relaxed scalar ^{13}C-^{11}B coupling.

CONCLUSIONS

The first 2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives with a phosphino group in 6-position were prepared, and characterized by multinuclear magnetic resonance. Oxidation of these compounds leads to the first boron compounds in which boron is linked to phosphorus in the formal +5 oxidation state. Although the P-B bond is cleaved by the attempt to prepare a methyl phosphonium iodide, the P-B bond is stable in the presence of an excess of borane, and therefore, the new phosphanes may become interesting ligands in coordination chemistry.

TABLE III Comparison of $\delta^{31}P$ values and coupling constants $^1J(^{31}P,^{13}C)$ and $^1J(^{31}P,^{11}B)$ (proposed signs are given in parentheses) for Ph_3P and **3**-carb-PPh_2 derivatives

	$\delta^{31}P$	$^1J(^{31}P,^{13}C_i)$	$^1J(^{31}P,^{13}C_i)$	$^1J(^{31}P,^{11}B)$	$\delta^{31}P$	
PPh_3	−6.0	−12.5[a]	(−)10.0	(+)80	−59.9	**3**-carb-PPh_2
$P(O)Ph_3$	+29.3	+104.4[b]	(+)94.3	(+)215	+34.8	**3**-carb-$P(O)Ph_2$
$P(S)Ph_3$	+43.2	(+)88.5[c]	(+)67.0	(+)200	+14.4	**3**-carb-$P(S)Ph_2$
$P(Se)Ph_3$	+34.1	(+)75.8[d]	(+)58.0	(+)190	−4.5	**3**-carb-$P(Se)PPh_2$

[a] H. J. Jakobsen, T. Lund, and S. Sorensen, *J. Magn. Reson.* **33**, 477 (1977).

[b] B. E. Mann and B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds*, Academic Press, New York 1981.

[c] S. D. Postle, *Phosphorus, Sulfur*, **3**, 269 (1977).

[d] This work.

EXPERIMENTAL

All reactions were carried out in an inert atmosphere of Ar or N_2, using carefully dried solvents, oven-dried glassware, and generally observing all necessary precautions to exclude moisture and oxygen. 6-Ethyl-pentamethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**1**) and a 2:1 mixture of the isomers 2,4-dimethyl-1,3,5-triethyl- and 2,5-dimethyl-1,3,4-triethyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) (**2**)[1] served as starting materials. These were converted into the bromides **3**-carb-Br and **4**-carb-Br[4]. Suspensions of $LiPPh_2$ in hexane were prepared in the usual way from diphenylphosphane and ^nBuLi (1.6 M in hexane).

^1H, ^{11}B, ^{13}C, ^{31}P, ^{77}Se NMR spectra were recorded by using Bruker AC 300, ARX 250, and DRX 500 instruments equipped with multinuclear probe heads (ca. 10–20% in C_6D_6 at 25 ± 1°C in 5mm o.d. tubes, if not mentioned otherwise). Heteronuclear $^{13}C\{^1H, ^{11}B\}$ triple resonance experiments were carried out using the Bruker DRX 500 spectrometer equipped with three independent frequency channels. Chemical shifts are given with respect to Me_4Si) [δ^1H 7.15 (C_6D_5H); 7.24 ($CHCl_3/CDCl_3$), $\delta^{13}C$ 128.0 (C_6D_6); 77.0 ($CDCl_3$)], external Et_2O-BF_3 [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz], external H_3PO_4 (85%, aq.) [$\delta^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz], and external neat Me_2Se [$\delta^{77}Se = 0$ for $\Xi(^{77}Se) = 19.071523$ MHz].-IR spectra were recorded by using a Perkin-Elmer 983G spectrometer.

6-Diphenylphosphino-1,2,3,4,5-pentamethyl-2,3,4,5-tetracarba-nido-hexaborane(6) 3-carb-PPh$_2$

3-carb-Br (1.3 g; 0.94 ml; 5.8 mmol) was added to a suspension of $LiPPh_2$ (5.8 mmol) in 50ml of hexane. The reaction mixture was heated for 12 h at 60°C. Then insoluble material was filtered off and the solvent was removed in vacuo.

Fractional distillation gave a 1.88 g of **3**-carb-PPh$_2$ as a colorless oil (b.p. 50°C/ 10^{-4} Torr; yield 87%). ^{1}H-NMR: δ^1H −0.64 br (s, 3H, B(1)-Me); 1.38 (s, 6H, C(2/5)-Me); 1.42 (s, 6H, C(3/4)-Me), 7.0 to 7.8 (m, 10H, -PPh$_2$).

6-Diphenylphosphinyl-2,4-dimethyl-1,3,5-triethyl- und 2,5-dimethyl-1,3,4-triethyl-2,3,4,5-tetracarba-nido-hexaborane(6) 4-carb-PPh$_2$

The mixture of isomers **4**-carb-Br (0.91ml; 4.4 mmol) was added to a suspension of LiPPh$_2$ (4.4 mmol) in 30 ml of hexane at −78°C. After 15 minutes the reaction mixture was allowed to warm to room temperature and was heated for 5 h at 60°C. Insoluble material was filtered off, and the solvent was removed in vacuo. Distillation of the yellow residue gave 1.39 g of **4**-carb-PPh$_2$ as a colorless oil (b.p. 55°C/10^{-4} Torr; yield 85%).-^{1}H-NMR: δ^1H 0.19 br (q), 0.72 br (t) (15H, B(1)-Et); 1.50 (s, 12H, C(2/2′/5)-Me); 1.97 bis 2.16 (m), 0.94 (t), (10H, C(3/4)-Et); 1.90 bis 1.99 (m), 0.91 (t), (10H, C(3′)-Et); 1.90 bis 2.00 (m), 0.89 (t), (10H, C(5′)-Et); 1.56 (s, 6H, C(4′)-Me); 6.9 bis 8.05 (m, 30H, -PPh$_2$).

6-Diphenylphosphoryl-1,2,3,4,5-pentamethyl-2,3,4,5-tetracarba-nido-hexaborane(6) 3-carb-P(O)Ph$_2$

A solution of 3-chloroperbenzoic acid (0.25g; 0.08 mmol) in 10ml of THF was added to a solution of **3**-carb-PPh$_2$ (0.03g; 0.08 mmol) in 20ml of THF at room temperature. After the reaction mixture was stirred for 3 h, the solvent was removed in vacuo. **3**-carb-P(S)Ph$_2$ was obtained as a white waxy solid (0.03g; 90%; mp. 150–157°C). ^{1}H-NMR: δ^1H −0.50 br (s, 3H, B(1)-Me); 1.21 (s, 6H, C(2/5-Me); 1.49 (s, 6H, C(3/4)-Me), 6.90 to 8.18 (m, 10H, -PPh$_2$).

6-Diphenylthiophosphoryl-1,2,3,4,5-pentamethyl-2,3,4,5-tetracarba-nido-hexaborane (6) 3-carb-P(S)Ph$_2$

Sulfur (0.15 g; 0.6 mmol) dissolved in 5ml of THF was added to a solution of **3**-carb-PPh$_2$ (0.14g; 0.6 mmol) in 20ml of THF. After stirring the reaction mixture for 12 h and removing the solvent in vacuo, 0.23 g of **3**-carb-P(S)Ph$_2$ as a yellowish solid was obtained. (90%; m.p. 162–170° C). ^{1}-NMR: δ^1H −0.36 br (s, 3H, B(1)-Me); 1.32 (s, 6H, C(2/5)-Me); 1.40 (s, 6H, C(3/4-)Me), 7.00 to 8.35 (m, 10H, -PPh$_2$.

6-Diphenylselenophosphoryl-1,2,3,4,5-pentamethyl-2,3,4,5-tetracarba-nidohexaborane(6) 3-carb-P(Se)Ph$_2$

A suspension of an excess of selenium (2.8 g; 0.81 mmol) in 5ml of ThF was added to a solution of **3**-carb-PPh$_2$ (0.11g; 0.285 mmol) in 20ml of THF. The reaction mixture was stirred for 12 h and then the excess of selenium was filtered off. The solvent was removed in vacuo and **3**-carb-P(Se)Ph$_2$ was obtained as a dark solid (0.12g; >90%; m.p. > 100°C, decomp.). ^{1}H-NMR; δ^1H -0.34 br (s, 3H, B(1)-Me); 1.31 (s, 6H, C(2/5)-Me); 1.40 (s, 6H, C(3/4)-Me), 6.95 to 8.45 (m, 10H, -PPh$_2$).

Reaction of 4-carb-PPh$_2$ with methyl iodide

A tenfold excess of methyl iodide was added to a solution of 0.05 g (0.13 mmol) of **4**-carb-PPh$_2$ in 0.5 mL of C_6D_6. The ^{11}B NMR spectrum showed the formation of the isomers **4**-carb-I [δ^{11}B(1) 5.9, δ ^{11}B(6) -42.8[4]].

Reaction of 4-carb-PPh$_2$ with W(CO)$_5$-THF/THF

A THF solution (50 mL) of 0.5 mmol of W(CO)$_5$-THF was prepared in the usual way by UV irradiation of W(CO)$_6$ in THF (1.5 h), and 0.192 G of **4**-carb-PPh$_2$ was added. After stirring for 24 h at room temperature most of the THF was removed in vacuo and the residue was dissolved in 1 mL of C_6D_6 (see Table II for NMR data). IR (C_6D_6): 2065 w; 1932 s; 1922 m, sh

Reaction of 4-carb-PPh$_2$ with BH$_3$-THF/THF

A fivefold excess of BH$_3$-THF/THF was added to a solution of 0.05 g (0.13 mmol) of **4**-carb-PPh$_2$ in 0.5 mL of C_6D_6. The ^{11}B NMR spectra (Figure 1)) showed the formation of the borane adduct **4**-carb-P(BH$_3$)Ph$_2$, together with a small amount of Ph$_2$PH-BH$_3$ [δ ^{11}B = -39.9, ^{1}J(^{11},^{1}H) = 105 Hz; δ^{31}P = 2.5, ^{1}J(^{31}P,^{11}B) = 53 Hz; δ^1H(PH) = 5.75, ^{1}J(^{31}P, ^{1}H) = 376 Hz, ^{3}J(^{1}HPB^{1}H) = 7.3 Hz; the NMR data differ from those given Ref 12] which arises from a small amount of Ph$_2$PH present in the starting material.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.

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