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Synthesis of phosphine–borane complexes of P-heterocycles

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Abstract

Dihydro-1H-phosphole–boranes **5** and **10** were prepared from phosphine oxides **1** and **9** respectively. Reaction of borane **5** with dichlorocarbene gave dihydrophosphole–dichloromethylborane **6** and tetrahydro derivative **7a** as the main products, and dichlorocyclopropane **8** as the minor component. Dichlorocarbene addition reaction of boranes **10** did not afford the corresponding phosphabicyclohexanes, but the dichloromethylborane complexes of the dihydro- and tetrahydrophospholes (**11** and **7** respectively). Phosphabicyclohexane–borane **13** was synthesized from P-oxide **12** by change in the functionality. The dihydrophosphinine–boranes (**16**) were prepared by cyclopropane ring opening of phosphabicyclohexane **13**, or by change in the functionality of P-oxide **15**. Reaction of dihydrophosphinine–boranes **17** with dichlorocarbene gave traces of dihydrophosphinine–dichloromethylborane **18** instead of the phosphepine. The phosphepine–borane (**20**) was synthesised from oxide **19**. The preparation of unsaturated phosphine–boranes was complicated by reduction side-reactions. The products were characterized by ^{31}P, ^{11}B, ^{1}H and ^{13}C NMR, as well as MS data.

Keywords: Dihydro-1H-phosphole; Phosphabicyclohexane; Dihydrophosphinine; Phosphepine; Phosphine–borane complex; Dichlorocarbene

1. Introduction

Phosphine–borane complexes prepared readily from phosphines and dimethyl sulfide–borane or tetrahydrofurane–borane reagents [1,2] have been widely used in organic syntheses. The borane moiety was introduced into phosphines to establish a protecting group on the P-atom before dichlorocarbene addition to an unsaturation [3], or before oxidation in the side chain [4]. Phosphines can be protected against oxidation in the phosphine–borane form [5]. Conversion of phosphines to borane complexes may result in activation of the α-carbon atom in alkylation [6]. The protecting or activating borane group can be easily removed by decomplexation with amines [5,7]. Preparation of the phosphine–borane complexes of P-heterocycles has also attracted attention recently. A chiral oxazaphospholidine–borane was utilized in enantioselective borane reduction of ketones [8], while dihydro-1H-phosphole– and phosphole–boranes were described as intermediates in the synthesis of functionalized derivatives [9,10]. An endocyclic phosphine–borane was prepared by intramolecular hydroboration [11]. Dihydro-azaphosphinine–boranes were also synthesized and reacted with dichlorocarbene to give dichloro-cyclopropanation and insertion of dichlorocarbene into the B–H bond [3].

In this paper, phosphine–borane complexes of P-heterocycles, such as dihydro-1H-phospholes, a phosphabicyclo[3.1.0]-hexane, 1,2-dihydrophosphinines and a phosphepine are described. Some of these seemed to be promising intermediates for other P-heterocycles. The change of the phosphine oxide functionality for phosphine–borane moiety has a great impact on the reactivity of the parent compound. We report the limits of the extension of our ring enlargement procedure [12–16] to dihydro-1H-phosphole–boranes and dihydrophosphinine–boranes, and suggest alternative methods for the synthesis of phosphabicyclohexane– and phosphepine–boranes.

2. Results and discussion

Unlike 2,5-dihydro-1H-phosphole 1-oxides [12], the 2,3-dihydro derivatives are not capable of taking part in

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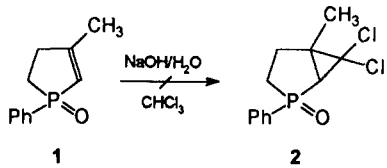
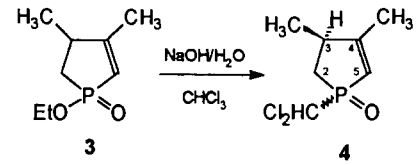


Scheme 1. Ref. [12].



Scheme 2.

dichlorocarbene addition reaction. The double bond gets poor in electrons, due to the electron-withdrawing phosphoryl group, and cannot react with the electrophilic dichlorocarbene. This is demonstrated by the unreactivity of the double bond of dihydrophospholes **1** and **3**. Using the dichlorocarbene in 100-fold excess, starting material **1** could be recovered unchanged (Scheme 1) [12]. Most of ester **3** was also regenerated, a part of it was, however, converted to the diastereoisomeric mixture of dichloromethyl derivative **4** (Scheme 2). The formation of product **4** by the displacement of the ethoxy group by a dichloromethyl group coming from a dichlorocarbene unit is noteworthy. ^{13}C NMR data for the isomers of compound **4** are included in Table 1.

To increase the reactivity of the double bond towards the dichlorocarbene, phosphine oxide **1** was transformed to phosphine–borane **5**. The change of functionality in **1** was accomplished by deoxygenation with trichlorosilane followed by reaction with the dimethyl sulfide–borane reagent. Reaction of complex **5** with dichlorocarbene generated from chloroform under phase transfer catalytic conditions led to the dichloromethylborane complexes of the 2,3-dihydro-1H-phosphole and the tetrahydrophosphole (**6** and **7a** respectively) (Scheme 3). Product **7a** was obtained as a 7:3 mixture of two diastereomers which were formed by reduction. Reductions taking place during the preparation of unsaturated phosphine–boranes are not unusual and involve intermediate hydroboration of the double bond [10]. Moreover, several borane complexes have been described as reducing agents [8]. The reaction of complex **5** with dichlorocarbene generated from sodium trichloroacetate gave rise to dihydrophosphole **6**, together with its adduct with dichlorocarbene (**8**) (Scheme 3). **8** could be isolated in only 5% yield.

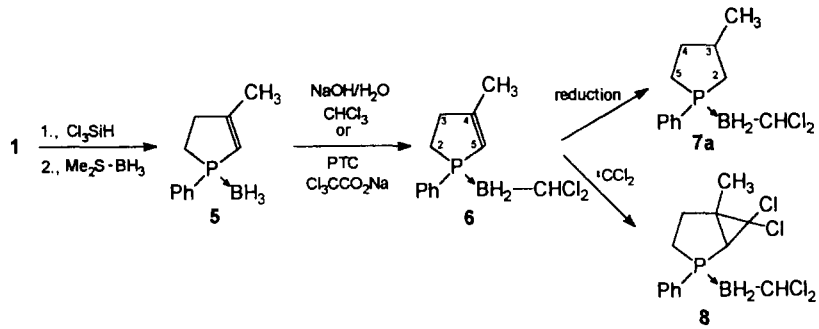
Electron-impact mass spectroscopy was a useful tool in proving the structure of phosphine–boranes **5**, **6**, **7a** and **8**. In the case of complex **5**, intense loss of BH_3 could be seen. Similarly to the observation of others [11], the molecular ions could be detected in their proton lost forms. Interestingly, this was also the case under circumstances of chemical ionization. Owing to the presence of the ^{10}B and ^{11}B isotopes, the molecular ions appeared in doubled forms. The presence of chlorine atoms in the phosphine–borane complexes (**6**, **7a** and **8**) resulted in special distribution patterns for the molecular ion. The isotopic distribution for the molecular ion of **8** is listed in Table 2. Products **6**, **7a** and **8** were characterized by HRMS, and compounds **6** and **7a** also by ^{31}P, ^{11}B, ^{1}H and ^{13}C NMR spectral data. Protons of the borane moiety for these compounds appear as doublets of doublets in the range 5.6–5.8 ppm. The $^{2}J(P,H)$ couplings of 11–18 Hz were confirmed by ^{31}P decoupled ^{1}H NMR spectra. $^{1}J(P,C)$ coupling constants of 36–59 Hz were observed in the ^{13}C NMR spectra (Table 1).

Then, we wished to prepare several 2,5-dihydro-1H-phosphole–boranes to utilize them in dichlorocarbene addition reactions. The complexes (**10a,b**) were prepared from the oxides (**9a,b**), as shown above for the **1** → **5** transformation; the reducing agent was, however, phenylsilane in these cases. The reaction of complexes **10a,b** with dichlorocarbene was accompanied by intensive decomposition and led to a complex mixture. Purification by column chromatography afforded the 2,5-dihydrophosphole– and the tetrahydrophosphole–di-

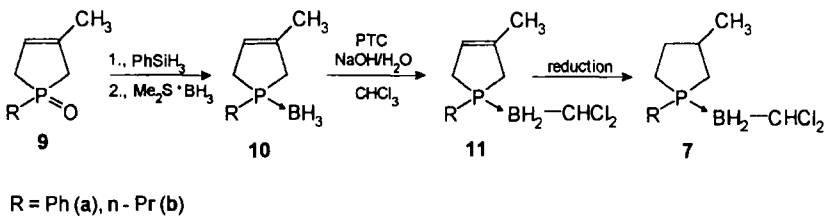
Table 1
^{13}C NMR data for phosphole derivatives **4**, **6** and **7a** in $CDCl_3$ solutions

Compound	^{13}C, $\delta(J_{PC})$						
	C_2	C_3	C_4	C_5	C_3–CH_3	C_4–CH_3	$CHCl_2$
4/major	29.4	40.2	172.5	114.7	18.9 [a]	20.4 [a]	64.6
	(69.7)	(9.5)	(25.7)	(103.3)	(16.1)	—	(65.2)
4/minor	28.8	39.4	172.6	115.1	[b]	[b]	64.2
	(70.4)	(9.6)	(26.4)	(103.3)			(64.4)
6	23.4	37.3	165.1	112.1		20.6	71.2 [c]
	(38.4)	—	(6.3)	(59.2)		(13.8)	
7a/major	31.9	36.0	34.8	24.9	20.2 [d]		71.4 [c]
	(35.5)	—	—	(35.7)	(10.9)		

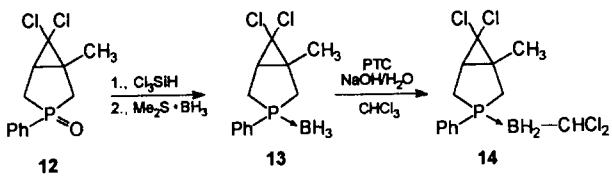
[a] May be reversed. [b] Not resolved. [c] Broad signal.
[d] For the minor isomer 20.6 ($^{3}J(P,C) = 13.6$, Me).



Scheme 3.



Scheme 4.

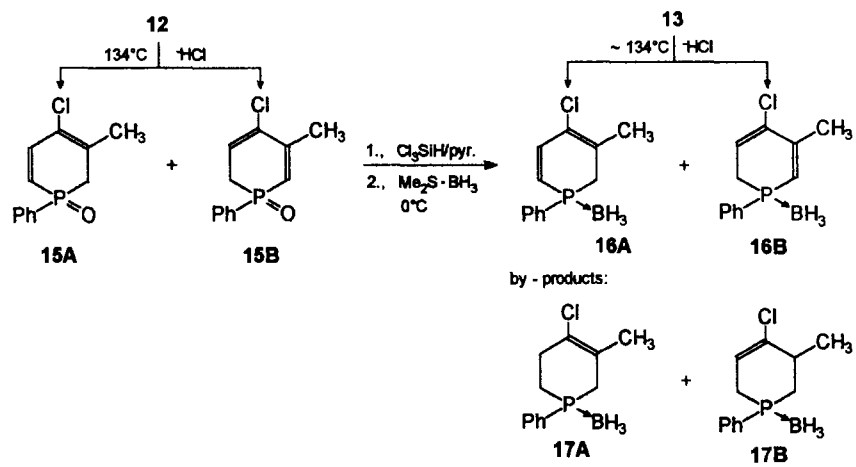


Scheme 5.

chloromethylboranes (**11** and **7**) (Scheme 4). The total yield of products **11** and **7** was only 11%. Among the decomposition products, we could identify the corresponding tetrahydrophosphole oxides (for the P-phenyl derivative, see Ref. [17]). The structure of products **11a,b** and **7a,b** was confirmed by ^{31}P and ^{11}B NMR, as well as mass spectral data. **7a** was identical to that isolated from the dichlorocarbene addition reaction of complex **5** (for ^{13}C NMR data, see Table 1).

Table 2
Isotopic distribution for the molecular ion of complexes **8** and **14**

	Relative intensity (%)							
	M–H		Isotope$_1$	Isotope$_2$	Isotope$_3$	Isotope$_4$	Isotope$_5$	Isotope$_6$
	^{10}B	^{11}B						
Theoretical	19	77	25	100	14	48	7	12
For **8**	22	79	30	100	21	50	9	13
For **14**	18	80	31	100	22	52	11	15

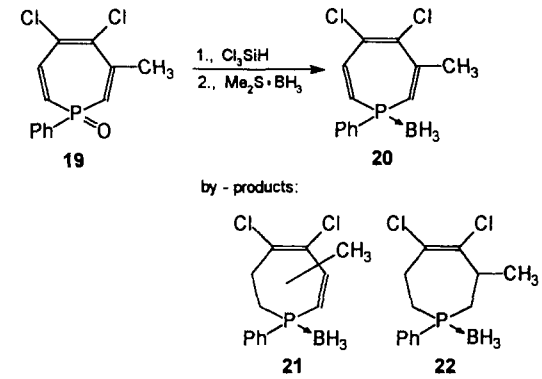


Scheme 6.

It can be concluded that the reaction of 2,5-dihydrophosphole–boranes **10** with dichlorocarbene does not give the expected phosphabicyclohexanes. For this, we tried to make advantage of another strategy: to prepare the desired phosphine–boranes by change in the functionality. Phosphabicyclohexane oxide **12** was deoxygenated and the phosphine so obtained reacted with the dimethyl sulfide–borane reagent to give complex **13** in quantitative yield (Scheme 5). To prepare a more stable derivative, we wanted to insert a dichlorocarbene unit into the B–H bond of **13**. Reaction of complex **13** with dichlorocarbene resulted in dichloromethylborane derivative **14** (Scheme 5). Contrary to phosphine–borane **13**, dichloromethylborane **14** could be purified by column chromatography. Both products (**13** and **14**) were fully characterized by ^{31}P, ^{11}B, ^{1}H, ^{13}C NMR and mass spectral data. The ^{13}C NMR data of **13** and **14** are listed in Table 3, while the isotopic distribution for the molecular ion of **14** can be found in Table 2. IR spectra of the complexes (**13** and **14**) revealed absorption at ca. 2370 cm^{-1} due to the B–H stretching vibration.

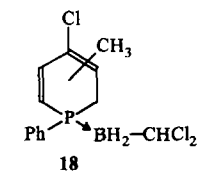
Then, we wanted to prepare the 1,2-dihydrophosphinine–boranes. Two methods were tried out: preparation by the opening of the cyclopropane ring of phosphabicyclohexane **13**, or synthesis by change in the functionality of the dihydrophosphinine oxides (**15A** and **15B**). Both approaches gave the dihydrophosphinine–boranes (**16A** and **16B**), but the first was accompanied by considerable decomposition of the starting material (**13**) and the products (**16A** and **16B**), while the second was complicated by formation of tetrahydrophosphinines **17A** and **17B** (Scheme 6). It was mentioned earlier that the preparation of unsaturated phosphine–boranes is usually accompanied by reduction side-reactions. The formulae of product **16** and by-product **17** were confirmed by ^{31}P NMR and mass spectroscopy (including HRMS).

We have described recently [14] how the dichlorocarbene addition reaction of certain dihydrophosphinine oxides resulted in the formation of phosphepine oxides. The ring expanded products could only be obtained in poor yields. We thought that the dihydrophosphinine–boranes might be better starting materials for the phosphepines. Unfortunately, this was not the case, as dihydrophosphinines **16A** and **16B** suffered almost



Scheme 7.

complete decomposition under the circumstances of the dichlorocarbene addition reaction, and only traces of the dichloromethylborane complexes of the dihydrophosphinines (**18**) could be detected [18].



The phosphine–borane complex (**20**) was finally prepared by change in the functionality of the phosphepine oxide (**19**) (Scheme 7). This reaction was, however, complicated by reduction of the α,β-double bond(s) to give the dihydro- and tetrahydrophosphepines (**21** and **22** respectively) as by-products. The small-scale experiment made possible only GC-MS (and HRMS) identification of the products (**20–22**).

3. Experimental details

The ^{31}P, ^{11}B and ^{13}C NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 160.4 and 125.7 MHz respectively. ^{1}H NMR spectra were recorded on a Bruker AW-80 instrument. Chemical shifts are downfield relative to 85% H_3PO_4, $F_3B \cdot OEt_2$

Table 3
^{13}C NMR data for phosphabicyclohexane–boranes **13** and **14** in $CDCl_3$ solutions

Compound	^{13}C, δ (J_{PC})									
	C_1	C_2	C_4	C_5	C_6	CH_3	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$
13	39.1	33.8	28.0	39.3	74.0	21.7	127.3	129.0 [a]	131.8 [a]	132.1
	(6.0)	(38.1)	(38.9)	(4.9)	(10.7)	(4.3)	(43.9)	(9.8)	(9.5)	—
14 [b]	40.8	32.1	27.2	41.0	71.4	21.0	126.1	129.0 [a]	131.3 [a]	131.5
	(3.5)	(36.9)	(37.2)	(2.0)	(5.9)	(5.9)	(52.9)	(10.5)	(7.8)	—

[a] May be reversed. [b] $CHCl_2$: 71.0 (bs).

and TMS respectively, and have a positive sign. The coupling constants are given in Hertz. Infrared spectra were recorded on a Perkin-Elmer spectrometer. Mass spectra were obtained on an MS 25-RFA instrument at 70 eV.

The 3-phenyl-3-phosphabicyclohexane 3-oxide (**12**), 1-phenyl-1,2-dihydrophosphinine 1-oxide (**15**) and 1-phenylphosphepine 1-oxide (**19**) were prepared by procedures developed by us [12–14].

3.1. Preparation of the phosphine–borane complexes

3.1.1. 4-Methyl-1-phenyl-2,3-dihydro-1H-phosphole–borane (5)

To 1.5 g (7.81 mmol) of oxide **1** in 25 ml of dichloromethane was added 0.87 ml (8.62 mmol) of trichlorosilane at 0°C under nitrogen (method A). After a 6 h period of stirring, volatile components were removed in vacuo to give 1.37 g of the phosphine (^{31}P NMR ($CDCl_3$): δ +4.0, lit. [19] +4.0 (neat)). The 20 ml dichloromethane solution of the intermediate so obtained was treated with 7.8 ml of 1 M dichloromethane solution of $BH_3 \cdot SMe_2$ at 0°C under nitrogen, and the mixture stirred for 6 h. Filtration and evaporation of the volatile components of the filtrate led to 1.41 g (95%) of **5**. MS, *m/z* (rel. int.) 189 (M^+–H, 6), 176 (M–BH_3, 100), 99 (176-Ph, 39). HRMS, $(M^+-H)_{found}$ = 189.0969, $C_{11}H_{15}BP$ requires 189.1004 for the ^{11}B isotope.

3.1.2. 3-Methyl-1-n-propyl-2,5-dihydro-1H-phosphole–borane (10b)

The solution of 1.5 g (9.49 mmol) of oxide **9b** and 0.47 ml (3.81 mmol) of phenylsilane in 25 ml of dichloromethane was stirred at room temperature for 16 h under nitrogen (method B). Evaporation of the volatile components gave 1.35 g of the phosphine (MS, *m/z* (rel. int.) 142 (M^+, 54), 99 (M–Pr)). The 20 ml dichloromethane solution of the phosphine was reacted with 9.5 ml of 1 M dichloromethane solution of $BH_3 \cdot SMe_2$ at 0°C to afford 1.45 g (98%) of **10b** after concentration in vacuo. ^{31}P NMR (dmso): δ +34.5. MS *m/z* (rel. int.) 155 (M^+–H, 1), 142 (M–BH_3, 56), 99 (142-Pr, 100). IR (KBr disc) 2362 cm^{-1}.

3.1.3. 3-Methyl-1-phenyl-2,5-dihydro-1H-phosphole–borane (10a)

Prepared by method B. Yield 98%. ^{31}P NMR (dmso): δ +33.3. HRMS, $(M^+-H)_{found}$ = 189.0966, $C_{11}H_{15}BP$ requires 189.1004 for the ^{11}B isotope. IR (KBr disc) 2372 cm^{-1}.

3.1.4. 6,6-Dichloro-1-methyl-3-phenyl-3-phosphabicyclo[3.1.0]-hexane–borane (13)

Prepared by method A. Yield 95% ^{31}P NMR ($CDCl_3$): δ +59.0 (q ^1J(P,B) = 64.7). ^{11}B NMR ($CDCl_3$): δ −38.6. ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 3H, Me), 7.20–8.0 (m, 5H, Ar). ^{13}C NMR, Table 3. MS, *m/z* (rel. int.) 271 (M^+–H, 11), 258 (M^+–BH_3, 100), 223 (258-Cl, 57). HRMS, $(M^+-H)_{found}$ = 271.0348, $C_{12}H_{15}BCl_2P$ requires 271.0382 for the ^{11}B and ^{35}Cl isotopes. IR (KBr, disc) 2371 cm^{-1}.

3.1.5. 3- and 5-Methyl-4-chloro-1-phenyl-1,2- dihydrophosphinine–borane (16)

The trichlorosilane reduction was carried out in boiling benzene, in the presence of 3 equivalents of pyridine. Yield 60%. ^{31}P NMR ($CDCl_3$): δ +1.8 (broad signal). MS, *m/z* (rel. int.) 235 (M^+–H, 11), 222 (M–BH_3, 100). HRMS, $(M^+-H)_{found}$ = 235.0602, $C_{12}H_{14}BClP$ requires 235.0615 for the ^{11}B and ^{35}Cl isotopes. According to GC-MS, the sample of **16** contained ca. 10% of tetrahydrophosphinine **17**. MS, *m/z* (rel. int.) 237 (M^+–H, 6), 224 (M–BH_3, 100). HRMS, $(M^+-H)_{found}$ = 237.0718, $C_{12}H_{16}BClP$ requires 237.0771 for the ^{11}B and ^{35}Cl isotopes.

3.1.6. 4,5-Dichloro-3-methyl-1-phenylphosphepine–borane (20)

Prepared by method A. GC-MS revealed 60% of **20** (M^+–H, 281), 22% of **21** (M^+–H, 283) and 18% of **22** (M^+–H, 285). HRMS (for the ^{11}B and ^{35}Cl isotopes):

Compound	$(M^+-H)_{found}$	Formula	$(M^+-H)_{calc.}$
20	281.0267	$C_{13}H_{13}BCl_2P$	281.0225
21	283.0310	$C_{13}H_{15}BCl_2P$	283.0382
22	285.0481	$C_{13}H_{17}BCl_2P$	285.0538

3.2. Dichlorocarbene addition reaction of the phosphine–boranes

3.2.1. Reaction of complex 5 with dichlorocarbene: 4-Methyl-1-phenyl-2,3-dihydro-1H-phosphole–dichloromethylborane (6), 6,6-Dichloro-1-methyl-4-phenyl-4-phosphabicyclo[3.1.0]hexane–dichloromethylborane (8) and 3-Methyl-1-phenyl-2,3,4,5-tetrahydro-1H-phosphole–dichloromethylborane (7a)

The mixture of 1.4 g (7.37 mmol) of **5**, 20.6 g (0.111 mol) of sodium trichloroacetate, 0.25 g (1.10 mmol) of triethylbenzylammonium chloride (TEBAC) and 50 ml of alcohol-free chloroform was stirred under reflux for 48 h. The contents of the flask was filtrated and the solvent of the filtrate evaporated. The components of the residue so obtained were separated and purified by repeated column chromatography (silica gel, 2% methanol in chloroform) to give 0.66 g (33%) of **6** and 0.08 g (3%) of **8**.

6. ^{31}P NMR ($CDCl_3$): δ +34.1 (q, ^1J(P,B) = 90.3). ^{11}B NMR ($CDCl_3$): δ −8.5. ^{1}H NMR ($CDCl_3$) [250 MHz]: δ 2.08 (s, 3H, Me), 5.59 (dd, ^2J(P,H) = 12.8, ^4J(H,H) = 5.0, 1H, BH), 5.76 (dd, ^2J(P,H) = 17.9, ^4J(H,H) = 3.7, 1H, BH), 5.86 (d, ^3J(P,H) = 10.6, 1H,

$CHCl_2$), 6.08 (d, ^2J(P,H) = 31.0, 1H, =CH), 7.40–7.82 (m, 5H, Ar). ^{13}C NMR, Table 1. MS, *m/z* (rel. int.) 271 (M^+–H, 14), 176 (M–BH_2CHCl_2, 100). HRMS, $(M^+-H)_{found}$ = 271.0395, $C_{12}H_{15}BCl_2P$ requires 271.0382 for the ^{11}B and ^{35}Cl isotopes.

8. MS, *m/z* (rel. int.) 353 (M^+–H, 24, for the isotopic distribution see Table 2), 319 (M–Cl, 100). HRMS, $(M^+-H)_{found}$ = 352.9716, $C_{13}H_{15}BCl_4P$ requires 352.9759 for the ^{11}B and ^{35}Cl isotopes. IR (neat) 2367 cm^{-1}.

The solution of 1.4 g (7.37 mmol) of **5** and 0.42 g (1.85 mmol) of TEBAC in 30 ml of chloroform was treated with 30 g of 50% aqueous sodium hydroxide under vigorous stirring, whereupon the temperature rose to reflux. After a period of 5 h stirring, the mixture was filtered and the solvent of the filtrate evaporated. Column chromatography (as earlier) afforded 0.14 g (7%) of **6** and 0.56 g (27%) of **7a**. **7a** consisted of a 7:3 mixture of two diastereomers.

7a. ^{31}P NMR ($CDCl_3$): δ +22.4 (q, ^1J(P,B) = 81.8). ^{11}B NMR ($CDCl_3$): δ −10.7. ^{1}H NMR ($CDCl_3$) [500 MHz]: δ 1.15 (d, ^3J(H,H) = 6.6, 2.1H, Me for the major isomer), 1.20 (d, ^3J(H,H) = 6.3, 0.9H, Me for the minor isomer), 5.61 (dd, ^2J(P,H) = 11.2, ^4J(H,H) = 3.9, BH), 5.63 (dd, ^2J(P,H) = 15.2, ^4J(H,H) = 4.0, BH) overlapped, total int. 2H, 5.83 (d, ^3J(P,H) = 10.5, 1H, $CHCl_2$), 7.44–7.87 (m, 5H, Ar). ^{13}C NMR, Table 1. MS, *m/z* (rel. int.) 273 (M^+–H, 32), 178 (M–BH_2CHCl_2, 100). HRMS, $(M^+-H)_{found}$ = 273.0569, $C_{12}H_{17}BCl_2P$ requires 273.0538 for the ^{11}B and ^{35}Cl isotopes.

*3.2.2. Reaction of complex **10b** with dichlorocarbene: 3-Methyl-1-n-propyl-2,5-dihydro-1H-phosphole–dichloromethylborane (**11b**) and 3-Methyl-1-n-propyl-2,3-4,5-tetrahydro-1H-phosphole–dichloromethylborane (**7b**)*

10b was reacted with dichlorocarbene (generated from chloroform) as described above for the reaction of **5**. Separation by column chromatography (silica gel, 3% methanol in chloroform) afforded a mixture of **11b** (35%) and **7b** (65%). Yield 12%.

11b. ^{31}P NMR ($CDCl_3$): δ +25.9. ^{11}B NMR ($CDCl_3$): δ −8.9. GC-MS, *m/z* (rel. int.) 237 (M^+–H, 58), 203 (M–Cl, 20), 142 (M–BH_2CHCl_2, 100), 99 (142-Pr, 99).

7b. ^{31}P NMR ($CDCl_3$): δ +22.5. ^{11}B NMR ($CDCl_3$): δ −11.6. ^{1}H NMR ($CDCl_3$): δ 1.23 (d, ^3J(H,H) = 7, C_3–Me for the major isomer). GC-MS, *m/z* (rel. int.) 239 (M^+–H, 100), 205 (M–Cl, 33), 144 (M–BH_2CHCl_2, 93), 101 (144-Pr, 65).

*3.2.3. Reaction of complex **10a** with dichlorocarbene: 3-Methyl-1-phenyl-2,5-dihydro-1H-phosphole–dichloromethylborane (**11a**)*

10a was reacted with dichlorocarbene as described above for the reaction of **5**. Repeated column chromatography led to the mixture of **11a** (40%) and **7a** (60%). Yield 11%.

11a. ^{31}P NMR ($CDCl_3$): δ +26.0. ^{11}B NMR ($CDCl_3$): δ −8.4. GC-MS, *m/z* (rel. int.) 271 (M^+–H, 38), 176 (M–BH_2CHCl_2, 100). HRMS, $(M^+-H)_{found}$ = 271.0361, $C_{12}H_{15}BCl_2P$ requires 271.0382 for the ^{11}B and ^{35}Cl isotopes.

*3.2.4. Reaction of complex **13** with dichlorocarbene*

The mixture of 0.94 g (3.46 mmol) of **13**, 19.3 g (0.104 mol) of sodium trichloroacetate, 0.24 g (1.05 mmol) of TEBAC and 40 ml of chloroform was stirred under reflux for 4 days. Purification of the concentrated organic phase by column chromatography (silica gel, 2% methanol in chloroform) gave 0.6 g (49%) of **14**. ^{31}P NMR ($CDCl_3$): δ +53.4. ^{11}B NMR ($CDCl_3$): δ −10.9. ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 3H, Me), 5.38–5.90 (m, 3H, BH_2CHCl_2), 7.33–7.94 (m, 5H, Ar). ^{13}C NMR, Table 3. MS, *m/z* (rel. int.) 353 (M^+–H, 6), 258 (M–BH_2BHCl_2, 100), 223 (258-Cl, 79), 83 ($CHCl_2$, 85). HRMS, $(M^+-H)_{found}$ = 352.9685, $C_{13}H_{15}BCl_4P$ requires 352.9758 for the ^{11}B and ^{35}Cl isotopes. IR (KBr, disc) 2363 cm^{-1}.

*3.3. Dichlorocarbene addition reaction of 2,5-dihydro-1H-phosphole 3: 1-Dichloromethyl-3,4-dimethyl-2,3-dihydro-1H-phosphole 1-oxide (**4**)*

46.0 g of sodium hydroxide in 46 ml of water was added dropwise to a mixture of 2.0 g (11.5 mmol) of **3**, 0.13 g (0.571 mmol) of TEBAC and 100 ml of alcohol-free chloroform with stirring, whereupon the temperature of the mixture rose to reflux. The contents of the flask were stirred at ca. 50°C for 4 h, then the mixture was filtered and the solvent of the filtrate evaporated. Repeated column chromatography (silica gel, 3% methanol in chloroform) gave 1.16 g (58%) of starting material **3** and 0.15 g (6%) of product **4** as a 68–32% mixture of two diastereomers. ^{1}H NMR ($CDCl_3$): δ 1.2 (d, 3H, C_3–Me), 2.06 (d, 3H, C_4–Me), 5.37 (d, ^2J(P,H) = 24, 1H, =CH). ^{13}C NMR, Table 1. HRMS, M^+_{found} = 211.9959, $C_7H_{11}Cl_2OP$ requires 211.9925 for the ^{35}Cl isotope. IR (neat) 1250 ($\nu_{P=O}$), 760 (ν_{C-Cl}) cm^{-1}.

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[17] 3-Methyl-1-phenyl-2,3,4,5-tetrahydro-1H-phosphole 1-oxide: 194 (M^+, 88), 179 (23), 125 (100), 77 (64). IR (neat) 1179 cm^{-1}.
[18] $[M^+-H]_{found}$ = 316.9969, $C_{13}H_{14}BCl_3P$ requires 316.9992 for the ^{11}B and ^{35}Cl isotopes.
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