

Complete multinuclear magnetic resonance analysis of heterophospholanes and their sulfur, selenium and borane adducts

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¹H, ¹¹B, ¹³C, ¹⁵N, ³¹P and ⁷⁷Se NMR spectra were obtained for 1,3-(dioxa, oxaza or diaza)-2-phospholanes and their sulfur, selenium and borane adducts. The relative sign of the ${}^{3}I({}^{1}H, {}^{31}P)/{}^{2}I({}^{13}C, {}^{31}P)$ coupling constants was found to be positive in the sulfur and selenium adducts for the methylene and methyl groups. Conversely, for the compound with a phosphorus lone pair and in the borane adducts this sign changes for the methylene groups. It was shown that the ³¹P NMR spectra recorded by the CPMG or INEPT-HEED pulse sequences can be used for observation of the ¹⁵N-³¹P coupling constants. In all the investigated compounds the spin-lattice relaxation of ³¹P is controlled by the spin-rotation mechanism. The dipole-dipole ³¹P-¹¹B interactions can provide less than 20% of the relaxation rate in compounds containing the BH₃ group. The transverse ³¹P relaxation is dominated by the scalar contribution. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ¹H NMR; ¹¹B NMR; ¹³C NMR; ¹⁵N NMR; ³¹P NMR; ⁷⁷Se NMR; relaxation time; spin-rotation; scalar coupling; spin-echo; phospholanes

INTRODUCTION

The derivatives of 1,3-diheterodimethylaminephospholanes 1-12 (Scheme 1), as representatives of organophosphorus compounds, attract the attention of chemists owing to their structure¹ and chemical reactivity.² In addition to ³¹P, compounds 1–12 contain other magnetically active nuclei and therefore they are interesting from the NMR spectroscopic point of view. A systematic study of these compounds will be useful for the creation of convenient NMR tests^{1b,3} sensitive to their structure. It is obvious that such a task requires detailed measurements of chemical shifts, coupling constants and relaxation times and rationalization of their dependences on structural and electronic factors. One of these factors is the presence of the free electron pair at the phosphorus atom in 1, 5 and 9 (and also its occupation in 2-4, 6-8 and 10-12), acting as an efficient transmitter of the C-P spin-spin coupling.^{1c,d,4} It should be noted that in spite of the numerous J(P,C) measurements, ^{4a,b} there have been few reports on the absolute or relative signs⁵ of these constants.

The T_1/T_2^{31} P relaxation times and their variations play a very important role in the quantitative analysis of ³¹P NMR data.6 In spite of this circumstance, these NMR parameters remain less popular³ than chemical shifts and coupling constants. It has been found that the spin-lattice relaxation times of ³¹P can vary over a wide range and the dipole-dipole,7 spin-rotation,7e,g,h,8 or chemical shift anisotropy mechanisms7d,9 dictate their values. The transverse relaxation time is usually dominated by scalar relaxation of the second kind via scalar coupling.¹⁰ In this paper we report on T_1 , T_2 relaxation studies of 1–12 and show that the ³¹P spin-lattice relaxation is governed by the spin-rotation mechanism. In addition, we demonstrate that CPMG and INEPT-HEED pulse experiments can be used to determine the ¹⁵N-³¹P coupling constants.

RESULTS AND DISCUSSION

The NMR parameters obtained for 1-12 are collected in Tables 1–5. Note that the spectral and physical properties of $\mathbf{1}_{\prime}^{2a,b,4b,11}$ $\mathbf{2}_{\prime}^{11h,12}$ $\mathbf{5}_{\prime}^{1a,c,e,3c,11e}$ $\mathbf{6}^{12}$ and $\mathbf{9}_{\prime}^{4b,13}$ are in good agreement with previous studies.

The ¹³C NMR data in Table 1 show a remarkable influence of the heterocycle atoms on the chemical shifts of the exocyclic $N(CH_3)_2$ groups in 1, 5 and 9. It is seen that the $N(CH_3)_2$ resonance in the non-symmetrical oxazaphospholane 9 is shifted to a low frequency. It is interesting that when the phosphorus atom changes oxidation state, the chemical shifts of the N(CH₃)₂ groups undergo fairly weak changes, the direction of which depends of the nature of the heterocycle. However, among compounds 2-4, 6-8 and 10-12 with the occupied electron pair one can see the pronounced highfield influence of the BH₃ group. An opposite BH₃ effect is observed for endocyclic carbons C-2 while the C-3 resonance

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Scheme 1

in non-symmetric compounds 10-12 is again shifted towards high field by the BH₃ group.

The ³¹C-³¹P coupling constants through two chemical bonds in 1, 5 and 9 were found to be in good agreement with previous reports.1a,5c,d The HETCOR experiments, carried out for all the compounds, allowed the determination of the relative signs of the ²J(PN,C) and ³J(PN,CH) constants (see the Experimental section). It is well known that values and signs of the ${}^{2}J(PN,C)$ coupling constants are dictated mainly by an orientation of the lone pair which acts as a transmitter of the coupling.^{1a,4a} Table 1 shows clearly that all the ${}^{2}J(PN,C)$ values in 1 decrease significantly when the phosphorus electron pair is occupied by S, Se and B atoms. More complicated tendencies are observed for 5, 9 and their S, Se and BH₃ adducts. Here the ${}^{2}J(PN,C)$ constants for atoms C-1 and C-4 decrease whereas those for C-2 and C-3 can change sign or even increase depending on the nature of the ring.

The ¹H NMR spectra (Table 2) exhibit AA'BB'X and ABCDX patterns (X = ³¹P) of the methylene protons in the symmetric and non-symmetric compounds, respectively. Borane adducts **4**, **8** and **12** show (at 30 °C) four typical BH₃ resonances with ¹*J*(¹H, ¹¹B) values of 97.2, 96.0 and 96.3 Hz, respectively. Each component of the signals is additionally splitting into a doublet by the ³¹P–B–¹H

Table 2. ¹H chemical shifts, T_1 and correlation times (τ_c) at 308 K

Compound		$\delta^1 H$	<i>T</i> ₁ (s)	$r_{\rm H-H}$ (A) ^a	$\tau_{\rm c}~(10^{-11}~{\rm s})$
1	CH ₂	3.79	3.55 ± 0.05	1.782	1.05
	CH ₂	4.08	3.88 ± 0.21	1.782	0.97
	CH ₃	2.84	2.31 ± 0.21	1.788	1.65
5	CH ₂	2.88	2.79 ± 0.21	1.772	1.30
	CH ₂	3.17	3.08 ± 0.16	1.772	1.18
	CH ₃ (exo)	2.54	2.48 ± 0.11	1.783	0.76
	CH_3 (endo)	2.56	2.51 ± 0.09	1.779	0.74
9	NCH ₂	2.83	2.55 ± 0.03	1.772	1.42
	NCH ₂	3.12	2.81 ± 0.02	1.772	1.29
	OCH ₂	3.95	3.80 ± 0.06	1.784	0.99
	OCH ₂	4.14	3.98 ± 0.02	1.784	0.95
	CH ₃ (exo)	2.44	2.45 ± 0.07	1.779	0.76
	CH_3 (endo)	2.46	2.45 ± 0.04	1.785	0.77
7	CH ₂	2.94	1.39 ± 0.26	1.772	2.60
	CH ₂	3.15	1.39 ± 0.26	1.772	2.60
	CH ₃ (exo)	2.38	2.26 ± 0.24	1.783	0.83
	CH_3 (endo)	2.67	2.40 ± 0.02	1.779	0.77
4	CH ₂	4.26	4.16 ± 0.07	1.823	1.03
	CH ₃	2.37	3.84 ± 0.25	1.835	0.58
	BH ₃	1.12	1.40 ± 0.13	1.963	2.39
8	CH ₂	2.99	4.61 ± 0.02	1.798	0.86
	CH ₂	3.15	4.61 ± 0.02	1.798	0.86
	CH ₃ (exo)	2.45	5.87 ± 0.01	1.833	0.38
	CH ₃ (endo)	2.55	6.36 ± 0.03	1.812	0.33
	BH_3	1.13	1.48 ± 0.02	1.891	3.61
12	NCH ₂	3.09	4.25 ± 0.08	1.794	0.92
	NCH ₂	3.22	4.25 ± 0.08	1.794	0.92
	OCH ₂	4.11	5.12 ± 0.02	1.822	0.84
	OCH ₂	4.17	5.12 ± 0.02	1.822	0.84
	CH ₃ (exo)	2.43	5.77 ± 0.02	1.835	0.37
	CH ₃ (endo)	2.39	6.02 ± 0.05	1.835	0.39
	BH ₃	1.14	1.20 ± 0.29	1.891	2.23

^a Estimated by PM3 for 1, 5, 7 and 9 and by AM1 for 4, 8 and 12.

Table 1. ¹³C chemical shifts and two-bond coupling constants ${}^{2}J({}^{13}C, {}^{31}P)$ (Hz)

	C-1		C-2		C-3		C-4	
Compound	$\delta^{13}C$	$^{2}J(C, P)$	$\delta^{13}C$	$^{2}J(C, P)$	$\delta^{13}C$	$^{2}J(\mathbf{C},\mathbf{P})$	$\delta^{13}C$	$^{2}J(C, P)$
1	35.00	+19.5 ^{a,b}	64.37	-8.6 ^{a,c}	64.37	-8.6 ^{a,c}		
2	37.04	4.9 ^b	65.90	<1.5	65.90	<1.5		
3	37.09	4.9 ^b	65.54	<1.5	65.54	<1.5		
4	34.83	6.9 ^b	67.81	3.6 ^c	67.81	3.6 ^c		
5	37.44	+16.6 ^{b,d}	53.38	-8.9 ^{c,d}	53.38	-8.9 ^{c,d}	34.78	+23.5 ^{b,d}
6	37.22	4.9 ^b	47.99	9.8 ^b	47.99	9.8 ^b	31.82	2.9 ^b
7	37.26	4.9 ^b	47.82	8.8 ^b	47.82	8.8 ^b	32.25	6.8 ^b
8	36.03	3.8 ^b	49.93	1.5 ^c	49.93	1.5	32.08	8.5 ^b
9	35.15	+17.7 ^{a,b}	66.69	-11.5 ^{a,b}	50.08	<1.5	31.54	+23.8 ^{a,b}
10	37.34	3.1 ^b	64.83	2.1 ^b	49.41	13.3 ^b	31.63	5.4 ^b
11	36.89	5.0 ^b	64.49	3.6 ^c	48.91	13.8 ^b	32.08	6.2 ^b
12	35.51	4.9 ^b	65.81	7.2 ^c	48.85	8.6 ^b	31.7	9.6 ^b

^a Coupling constant absolute sign was reported previously. ^{4b}

 ${}^{b}{}^{3}J({}^{31}P, {}^{1}H)/{}^{2}J({}^{31}P, {}^{13}C) > 0$ (positive tilt in ${}^{13}C/{}^{1}H$ HETCOR).

 ${}^{c}{}^{3}J({}^{31}P, {}^{1}H)/{}^{2}J({}^{31}P, {}^{13}C) < 0$ (negative tilt in ${}^{13}C/{}^{1}H$ HETCOR).

^d Coupling constant absolute sign was reported previously.^{1a}



Compound	δ^{77} Se	${}^{1}J({}^{31}\mathrm{P},{}^{11}\mathrm{Se})$	Compound	$\delta^{11} B$	${}^{1}J({}^{31}\mathrm{P},{}^{11}\mathrm{B})$	T_1^{11} B (ms)
3	-317.15	953.9	4	-41.8	93.3	20.6 ± 0.1
7	-325.56	824.7	8	-41.7	95.8	28.3 ± 0.1
11	-313.68	959.2	12	-42.4	95.7	23.6 ± 0.1

Table 3. ⁷⁷Se and ¹¹B chemical shifts and ³¹P coupling constants

Table 4. ³¹P NMR data at 308 K

Compound	$\delta^{31} P$	<i>T</i> ₁ (s)	<i>T</i> ₂ (s)	$T_2^{\rm SC}$ (s)	$T_1^{\rm DD}({}^1{\rm H})$ (s)
1	141.88 ^a	10.2 ± 0.1	0.043 ± 0.002	0.043 ± 0.002	1792 ± 100
		$6.8\pm0.3^{\mathrm{b}}$			
2	89.74 ^c	13.3 ± 0.3	0.47 ± 0.08	0.48 ± 0.08	233 ± 11
3	91.11	$10.5\pm0.2^{\rm d}$	$5.69\pm0.3^{\rm d}$	12.4 ± 1^{d}	99 ± 5
		$7.0\pm0.05^{\rm e}$	$4.88\pm0.2^{\rm e}$	16.1 ± 2^{e}	
4	133.50	$9.6\pm0.2^{\rm f}$	$0.042\pm0.002^{\rm f}$	$0.042\pm0.002^{\rm f}$	47 ± 3
	$^{1}\Delta^{10/11}B = -9.2$	$6.3\pm0.2^{\rm b}$			
	ppb	$11.8\pm0.4^{\rm g}$	$0.075\pm0.002^{\rm g}$	$0.075 \pm 0.002^{\rm g}$	
5	115.26 ^h	11.8 ± 0.1	0.01 ± 0.0005	0.01 ± 0.0005	242 ± 12
		$10.5\pm0.1^{\rm b}$			
6	80.69	13.5 ± 0.5	0.57 ± 0.03	0.59 ± 0.03	207 ± 16
7	79.58	$9.5\pm0.3^{ m d}$	$4.35\pm0.2^{\rm d}$	$8.0\pm0.6^{\rm d}$	73 ± 4
		$9.3\pm0.2^{\rm e}$	$4.35\pm0.2^{\rm e}$	$8.1\pm0.6^{\mathrm{e}}$	
8	104.76	$11.5\pm0.3^{\rm f}$	$0.063\pm0.003^{\rm f}$	$0.063\pm0.003^{\rm f}$	471 ± 28
	$^{1}\Delta^{10/11}B = -9.8$	$8.6\pm0.3^{\mathrm{b}}$			
	ppb	$12.4\pm0.4^{\rm g}$	$0.101 \pm 0.005^{\rm g}$	$0.102\pm0.005^{\rm g}$	
9	133.69 ⁱ	10.7 ± 0.03	0.01 ± 0.0005	0.010 ± 0.0005	62.6 ± 4
		$8.3\pm0.2^{\rm b}$			
10	88.59	12.7 ± 0.6	0.84 ± 0.001	0.899 ± 0.002	142 ± 18
11	89.13	$11.4\pm0.2^{\rm d}$	2.75 ± 0.1^{d}	3.62 ± 0.2^{d}	140 ± 7
		$11.7\pm0.3^{\mathrm{e}}$	$2.69 \pm 0.1^{\mathrm{e}}$	$3.49\pm0.2^{\mathrm{e}}$	
12	118.9	$11.06\pm0.04^{\rm f}$	$0.038\pm0.001^{\rm f}$	$0.038\pm0.001^{\rm f}$	45.3 ± 4
	$^{1}\Delta^{10/11}B = -10.7$	$7.7\pm0.2^{\mathrm{b}}$			
	ppb	$11.3\pm0.3^{\rm g}$	$0.055\pm0.002^{\rm g}$	$0.055\pm0.002^{\rm g}$	

^a In agreement with Refs 11b–e.

^b At 338 K.

^c In agreement with previous report.¹²

^d Main signal.

^{e 31}P-⁷⁷Se satellite.

 ${}^{f 31}P - {}^{11}B.$

 $^{g 31}P - ^{10}B.$

^h In agreement with Refs 3c, 11e.

ⁱ In agreement with Ref. 11e.

coupling with ${}^{2}J({}^{1}\text{H}, {}^{31}\text{P}) = 17.8$, 16.7 and 19.1 Hz for **4**, **8** and **12**, respectively.¹⁴ The appearance of these well resolved resonances is explained by the fairly long T_{1} relaxation times of ${}^{11}\text{B}$ (Table 3).

In accord with Letcher and van Wazer's¹⁵ explanation, the ³¹P resonance of dioxaphospholane is considerably shifted with respect to oxazaphospholane and diazaphospholane (Table 4). Although the S and Se adducts show similar chemical shifts, their ³¹P lines are shifted to low frequency by 49, 44 and 34 ppm with respect to **1**, **5** and **9**. The effect of the BH₃ group is significantly less and lies between 6.8 and 14.8 ppm.

As can be seen from Table 3, the chemical shifts of the 77 Se and 11 B nuclei in adducts 3, 4, 7, 8, 11 and

12 are characteristic, demonstrating the relatively weak dependence of the nature of the heterocycle. The ${}^{1}J({}^{77}Se, {}^{31}P)$ constants >820 Hz correspond to the P=Se double bond. Identically, the ${}^{1}J({}^{11}B, {}^{31}P)$ constants >90 Hz indicate well the presence of a strong coordination bond.^{14a} Finally, the modification of the parameters of ${}^{15}N$ NMR on going from **1** and **5** to their S, Se and BH₃ adducts can be found in Table 5. Here the results of measurements of the ${}^{1}J({}^{31}P, {}^{15}N)$ coupling constants are of the greatest interest. The comparison of adducts **2** and **4** or **6** and **7** shows that the ${}^{1}J({}^{31}P, {}^{15}N)$ value in the exocyclic fragments depends reasonably on the nature of the atom bonding with phosphorus. However, the similarity of these exocyclic constants in **5** and **6** seems surprising. Actually, this result demonstrates that the phosphorus lone

Table 5. ¹⁵N chemical shifts and one-bond coupling constants ${}^{1}J({}^{15}N, {}^{31}P)$ (Hz)

Compound	$\delta^{15} \mathrm{N}$ (endocyclic)	¹ <i>J</i> (¹⁵ N, ³¹ P)	δ^{15} N (exocyclic)	${}^{1}J({}^{15}N, {}^{31}P)$
1			-339.61	90
2			-301.56	70
4			-297.26	98
5 ^a	-343.90	52	-334.75	90
6	-327.27	51	-323.80	89
7	n.c	o. ^c	-340.30	71
9 ^b	-334.00	51	-324.10	89

^a In agreement with Ref. 3c.

^b In agreement with Ref. 4b.

^c Not observed.

pair in 5 does not play a significant role in the one-bond P–N coupling, which is rather dictated by geometric factors.^{1a,4b} In addition, the ${}^{1}J({}^{31}P, {}^{15}N)$ constants in the rings of both compounds are also identical.

Table 4 lists the ³¹P spin–lattice and spin–spin relaxation data collected for the investigated compounds. It can be seen that the room temperature T_1 values remain within a fairly narrow range between 9.3 and 13.5 s whereas the T_2 times change significantly from 0.01 s in **5** and **9** to 5.7 s in **3**.

The small variation in T_1 is dictated by similar moments of inertia of the molecules and reflects the same relaxation mechanism for all the compounds. It is well known that the ³¹P T_1 relaxation rate can be governed by dipole–dipole,⁷ spin-rotation⁸ and chemical shift anisotropy contributions.⁹ The last contribution, being proportional to the square of the magnetic field used, can be ruled out because the T_1 measurements at 6.3 and 9.3 T gave almost identical results. The ³¹P NMR spectra, recorded in the presence and absence of {¹H} irradiation, showed negligibly small NOE values and thus the ³¹P relaxation due to phosphorus–proton dipole–dipole interactions can be also ruled out. It is obvious that the dipole–dipole ³¹P–¹⁴N contribution¹⁶

$$\frac{1}{T_1({}^{31}\mathrm{P}^{-14}\mathrm{N})} = \frac{0.019 \times 10^{11}\tau_{\rm c}}{r(\mathrm{P}^{-1}\mathrm{N})^6} \tag{1}$$

where *r* is in Å is not effective because of the small value of the magnetogyric ratio of ¹⁴N. Actually, for example, the $T_1({}^{31}P_-{}^{14}N)$ value in **1** is calculated as ~1600 s if the *r*(P–N) value is taken as 1.78 Å from a PM3 calculation.¹⁷ Note that the τ_c value of 10^{-11} s can be determined from the ¹H T_1 relaxation measurement (see below). Theoretically, a remarkable contribution to the total ³¹P relaxation rate could be expected only for **4**, **8** and **12** owing to ³¹P–¹¹B dipole–dipole interactions. The corresponding contribution¹⁶ is expressed by

$$\frac{1}{T_1({}^{31}\mathrm{P}^{-11}\mathrm{B})} = \frac{0.48 \times 10^{11} \tau_{\rm c}}{r(\mathrm{P}^{-}\mathrm{B})^6}$$
(2)

The correlation times τ_c for molecular motions of **1**, **4**, **5**, **7**, **8**, **9** and **12** are easily estimated from the ¹H T_1 relaxation measurements on the basis of the equation

$$\frac{1}{T_1(\mathrm{H-H})} = \frac{8.55 \times 10^{11} \tau_{\rm c}}{r(\mathrm{H-H})^6}$$
(3)

where $1/T_1$ (H–H) (s) is the relaxation rate for the methylene protons and r(H-H) (Å) is the distance between them. The H-H distances can be found by PM317 or AM118 calculations and the τ_c values determined by this approach are presented in Table 2. It should be noted that the correlation times for the different methylene protons differ insignificantly, showing a practically isotropic character of molecular motions. However, the T_1 data of the methyl protons give the reduced τ_c times due to the well known internal fast rotation of the CH₃ group.¹⁹ For 4, containing the BH₃ group, the relaxation measurements provided an average τ_c value of 1.03×10^{-11} s. On the basis of this value and r(P-B) = 1.7 Å (AM1 calculation), Eqn (2) leads to a $1/T_1({}^{31}P-{}^{11}B)$ relaxation rate of 0.0205 s⁻¹. In turn, this value corresponds well to the difference in the ³¹P relaxation rates, measured for the ¹¹B and ¹⁰B satellites (Table 4). It should be noted that in the last case the ³¹P-¹⁰B interactions are negligible because of the lower magnetogyric ratio of ¹⁰B. Thus even in the compounds containing the BH₃ group, the dipole-dipole mechanism can provide less than 20% of the relaxation rate of ³¹P.

A significant scalar contribution to the ³¹P T_1 time has been reported for the phosphorus ligands binding to Re.²⁰ This mechanism was operating effectively due to the exceptionally large ¹*J*(P,Re) values and the very short T_1 times of rhenium quadrupolar isotopes. It is obvious that this scalar mechanism cannot operate in the case quadrupole nuclei such as ¹⁴N and ^{11,10}B. Note that the ¹¹B nuclei in **4**, **8** and **12** showed moderately short T_1 times between 0.021 and 0.028 s. Taking into account all the data, one can suggest that the spin–lattice relaxation rate of ³¹P in all the investigated compounds is controlled by the spin-rotation mechanism.^{16c,19,21} In full accord with this proposition, the relaxation rate increases significantly with temperature (Table 4).

It follows from the data in Table 4 that the transverse relaxation time, being significantly shorter than T_1 , changes strongly on going from one compound to another. This feature can be attributed to the mechanism of scalar relaxation of the second kind (T_2^{SC}) .¹⁰ According to Mlynárik,^{10b} the scalar contribution to T_2 is given by

$$\frac{1}{T_2^{\rm SC}} = \frac{1}{T_2} - \frac{1}{T_1} \tag{4}$$

It should be noted that a reason for the operation of this mechanism for all the compounds could be the presence of the ¹⁴N quadrupole nuclei. In such a case the largest scalar contribution should be expected for **5** and **9**, containing more than one nitrogen atom. Indeed, these compounds show the shortest T_2^{SC} times (see Table 4). It is interesting that the scalar contribution to the T_2 relaxation rate decreases in the S and Se derivatives and increases again in the boron adducts. These results can be explained in terms of the variation in the T_1 times of the ¹⁴N nuclei because the $J(^{31}P, ^{14}N)$ coupling constants change insignificantly (see Table 5).

Finally, we found that the ¹⁵N-³¹P coupling constants can be observed directly in the ³¹P NMR spectra of the compounds, containing one nitrogen atom, using for the first time the CPMG or in agreement with Kupče and





Figure 1. (a) T_2 measurement of compound **1**. The delays are 10–120 ms and $\tau = 1$ ms. In the inset, the broad residual signal of the ³¹P(¹⁴N) isotopomer and the sharp doublet of the ³¹P(¹⁵N) isotopomer are already clearly visible. (b) Top, ³¹P INEPT-HEED (Hahn-echo delay, 50 ms; recycle delay, 4 s; acquisition time, 1 s; total detection time, 5 min); bottom, ³¹P{¹H} NMR spectrum.

Wrackmeyer²² the INEPT-HEED pulse sequences (Fig. 1) under the conditions $T_2 \ll T_1$.

EXPERIMENTAL

Spectra

The electron ionization (EI) mass spectra (70 eV) were recorded using a Hewlett-Packard HP-5998A spectrometer.

The ¹H, ¹³C{¹H}, ¹¹B{¹H}, ⁷⁷Se{¹H}, ³¹P{¹H} and ¹⁵N{¹H} NMR spectra were recorded with a JEOL DELTA-GSX-270 spectrometer equipped with a 5 mm multinuclear probe, using O₂-free²³ benzene-*d*₆ solutions (0.2 mmol of the compound per 0.4 ml of C₆D₆). The chemical shifts are referenced to internal (CH₃)₄Si(δ^{1} H = 0, δ^{13} C = 0), neat CH₃NO₂(δ^{15} N for Ξ^{15} N = 10.136767 MHz), (C₂H₅)₂O · BF₃(δ^{11} B, Ξ^{11} B = 32.083 972 MHz), 85% H₃PO₄(δ^{31} P, Ξ^{31} P = 40.480 747 MHz), neat (CH₃)₂Se (δ^{77} Se, Ξ^{77} Se = 19.071 252 3 MHz). ¹H NMR spectra were recorded at 270.05 MHz (spectral width 2700 Hz, acquisition time 1.516 s, pulse width 45°, 32 scans, recycle delay 2 s). ¹¹B NMR spectra were recorded at

86.55 MHz (spectral width 17241.4 Hz, acquisition time 0.475 s, pulse width 75°, 64 scans, recycle delay 0.5 s. $^{13}C{^1H}$ NMR spectra were recorded at 67.80 MHz (spectral width 12224.9 Hz, acquisition time 1.34 s, pulse width 30°, 128 scans, recycle delay 0.8 s). The $^{15}N{^1H}$ NMR spectra were obtained by the INEPT method, 24 using a $^2J(^{15}N, ^{1}H)$ value of 2.5 Hz (spectral width 16393 Hz, recycle delay 4 s, acquisition time 0.999 s). $^{31}P{^1H}$ NMR spectra were obtained at 109.37 MHz (spectral width 21881.8 Hz, acquisition time 1.4981 s, pulse width 60°, recycle delay 0.4 s, 64 scans). $^{77}Se{^1H}$ NMR spectra were recorded at 51.50 MHz (spectral width 40 000.0 Hz, acquisition time 0.41 s, pulse width 30°, recycle delay 0.1 s, 256 scans).

Relative signs of the coupling constants $[{}^{3}J({}^{31}P, {}^{1}H)/{}^{2}J({}^{31}P, {}^{13}C)]$ were determined via 2D ${}^{13}C/{}^{1}H$ heteronuclear shift correlations (HETCOR), observing the positive (alike signs) or negative tilt (opposite signs) of the cross peaks in the contour plot. 25 The ${}^{1}H$, ${}^{11}B$ and ${}^{31}P$ spin–lattice relaxation times were measured by the inversion–recovery method with continuous proton decoupling at 308 K (for the **1**, **4**, **5**, **8**, **9** and **12** we recorded the T_1 of ${}^{31}P$ also at 338 K), using recycle delays greater than five times T_1 and at least 10 variable delays, eight scans (spectral width 2000 Hz, 1024 data points for ${}^{31}P$ and spectral width 4053 Hz, 8192 data points for ${}^{1}H$).

Transverse relaxation times (T_2) were measured by the Carr–Purcell–Meiboom–Gill sequence²⁶ with continuous proton decoupling at 308 K, using recycle delays greater than five times T_1 and at least 10 variable delays, eight scans, spectral width 2000 Hz, 1024 data points and two different values of τ (τ = 2.5 and 1 ms for **1**, **2**, **4**, **5**, **6**, **8**, **9**, **10** and **12** and τ = 0.1 and 0.05 s for **3**, **7** and **11**). The T_1 and T_2 values were calculated by a non-linear fitting procedure using the peak intensities (errors <5%). All the ¹H, ¹¹B and ³¹P pulses were calibrated prior to acquisition.

NOEs were obtained from the increase in the signal intensity when proton broadband decoupling was used compared with when it was absent. A recycle delay of 10 times T_1 was used to ensure complete relaxation of the ³¹P magnetization. The accuracy of the NOE was better than 10%.

The ³¹P INEPT-HEED spectra were collected using Hahn-echo extended pulse sequence²² with the parameters presented in Fig. 1.

The 31 P NMR spectra at 9.4 T were recorded on a JEOL Eclipse +400 spectrometer,

Compounds

The synthetic work and the handling of NMR samples were carried out in an inert atmosphere $(N_2).\ BH_3\cdot THF$ was prepared as reported. 27

Compounds 1, 5 and 9 were prepared by a standard method.²⁸ The phospholanes were formed on reaction of $[(CH_3)_2N]_3P$ with the appropriate diol, diamine or amino alcohol derivatives under reflux for 2 h, using tetrahydrofuran as the solvent.

1

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.84 d [+8.3] 6H, 3.79 m [+8.6] 2H, 4.08 m [+4.4] 2H, [²*J*(H,H) = -8.6, ³*J*(H,H) = +7.0 *cis*,



 ${}^{3}J(H,H) = +6.3 trans]$. El-MS, m/z (%) 135 (71) [M⁺], 91 (100), 75 (26), 43 (68), 45 (60).

5

¹H NMR, $\delta^{1}H[{}^{3}J({}^{1}H, {}^{31}P)]$: 2.54 d [+7.2] 6H, 2.56 d [7.2] 6H, 2.88 m [+8] 2H, 3.17 m [+4.5] 2H [${}^{2}J(H,H) = -8.4, {}^{3}J(H,H) = +6.9 \text{ cis}, 3J(H,H) = +5.7 \text{ trans}]$. El-MS, m/z (%) 161 (32) [M⁺], 117 (100), 74 (14), 60 (15), 42 (4).

9

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.44d [+8.7] 6H, 2.46d [+12.3] 3H, 2.83 m [+7.5] 1H, 3.12 m [+4.3] 1H, 3.95 m [+4.3] 1H, 4.14 m 1H [²*J*(H,H) = -6.9 NCH₂, ²*J*(H,H) = -7.76 OCH₂, ³*J*(H,H) = +7.7 *cis*, ³*J*(H,H) = +7.4 *trans*]. El-MS, *m/z* (%) 148 (5) [M⁺], 117 (100), 106 (9), 74 (14.8), 60 (35), 44 (66.9).

Sulfur and selenium adducts 2, 3, 6, 7, 10 and 11

Solutions of 3.1 mmol of the phospholane in 0.5 ml of tetrahydrofuran were treated with 3.1 mmol of sulfur or selenium. The mixture was stirred at room temperature for 5 min and after the solvent had evaporated under vacuum, pure (>95%) adducts were obtained.

2

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.54d [3.9] 6H, 3.43 m [14.2] 2H, 3.70 m [8.5] 2H, [²*J*(H,H) = -8.8, ³*J*(H,H) = +7.3 *cis*, ³*J*(H,H) = +6.3 *trans*]. El-MS, *m/z* (%) 167 (70) [M⁺], 134 (68), 91 (100).

3

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.46 d [12.3] 6H, 3.40 m [14.1] 2H, 3.67 m [8.5] 2H, [²*J*(H,H) = -8.8, ³*J*(H,H) = +7.3 *cis*, ³*J*(H,H) = +6.3 *trans*]. El-MS, *m/z* (%) 218 (1), 217 (7), 216 (5), 215 (40), 213 (19), 212 (7), 211 (7), 209 (1), 134 (47), 91 (100).

6

¹H NMR, δ^1 H[³*J*(¹H, ³¹P)]: 2.33 d [11.7] 6H, 2.59 d [11.0] 6H, 2.65 m [8.4] 2H, 2.85 m [12.4] 2H [²*J*(H,H) = -8.4, ³*J*(H,H) = +6.9 *cis*, ³*J*(H,H) = +5.7 *trans*]. El-MS, *m/z* (%) 193 (77) [M⁺], 149 (77), 117 (100), 44 (15).

7

¹H NMR, δ^{1} H[³J(¹H, ³¹P)]: 2.38 d [12.4] 6H, 2.67 d [11.5] 6H, 2.94 m [7.1] 2H, 3.15 m [11.2] 2H, [²J(H,H) = -8.4, ³J(H,H) = +6.9 *cis*, ³J(H,H) = +5.7 *trans*]. El-MS, *m/z* (%) 243 (5), 242 (3), 241 (29), 239 (14), 238 (5), 237 (5), 193 (77), 149 (47), 117 (100).

10

¹H NMR, δ^1 H[³*J*(¹H, ³¹P)]: 2.42 d [11.1] 6H, 2.53 d [11.6] 3H, 2.83 m [3.9] 1H, 2.95 m [18.5] 1H, 3.81 m [3.0] 1H, 3.83 m [7.1] 1H [²*J*(H,H) = -8.0 NCH₂, ²*J*(H,H) = 7.6 OCH₂, ³*J*(H,H) = +8.1 *cis*, ³*J*(H,H) = +7.8 *trans*]. El-MS, *m/z* (%) 180 (18) [M⁺], 151 (25), 136 (46), 119 (6), 104 (60), 44 (100).

11

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.50 d [11.5] 6H, 2.63 d [12.1] 3H, 3.15 m [3.8] 1H, 3.19 m [24.8] 1H, 4.16 m 1H, 4.21 m [12.8] 1H,

 $[{}^{2}J(H,H) = -8.1 \text{ NCH}_{2}, {}^{2}J(H,H) = -9.1 \text{ OCH}_{2}, {}^{3}J(H,H) = +8.9 \text{ cis}, {}^{3}J(H,H) = +7.4 \text{ trans}].$ El-MS, m/z (%) 231 (0.4), 230 (5.2), 229 (2.5), 228 (28), 226 (14), 225 (5.2), 224 (5.5), 222 (0.5), 184 (2.4), 148 (34), 104 (100), 56 (30), 42 (28).

Borane adducts 4, 8 and 12

The borane adducts were prepared from the reaction of borane–tetrahydrofuran and the phospholane in equimolar proportions at 0° C. The solvent was evaporated under vacuum 5 min after the borane addition. The reactions gave quantitative yields.

4

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.37 d [9.8] 6H, 4.26 m [9.5] 2H, 4.39 m [4.8] 2H, [²*J*(H,H) = -8.0, ³*J*(H,H) = +9.0 *cis*, ³*J*(H,H) = +6.6 *trans*]. El-MS, *m/z* (%) 149 (22), 109 (100), 91 (57), 78 (11.7), 41 (36.6).

8

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.45 d [12.0] 6H, 2.55 d [11.7] 6H, 2.99 m [9.3] 2H, 3.15 m [6.1] 2H [²*J*(H,H) = -8.4, ³*J*(H,H) = +6.9 *cis*, ³*J*(H,H) = +5.7 *trans*]. El-MS, *m/z* (%) 175 (2), 174 (3), 157 (9.1), 131 (23.3), 117 (34.3), 101 (25), 57 (100).

12

¹H NMR, δ^{1} H[³*J*(¹H, ³¹P)]: 2.43 d [9.7] 6H, 2.39 d [9.9] 3H, 3.09 m [5.5] 1H, 3.22 m [4.1] 1H, 4.11 m [8.2] 1H, 4.17 m [7.1] 1H, [²*J*(H,H) = -8.6 NCH₂, ²*J*(H,H) = -9.2 OCH₂, ³*J*(H,H) = +8.6 *cis*, ³*J*(H,H) = +5.9 *trans*]. El-MS, *m/z* (%) 162 (11), 161 (4), 148 (53.8), 104 (100), 60 (44), 42 (33).

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