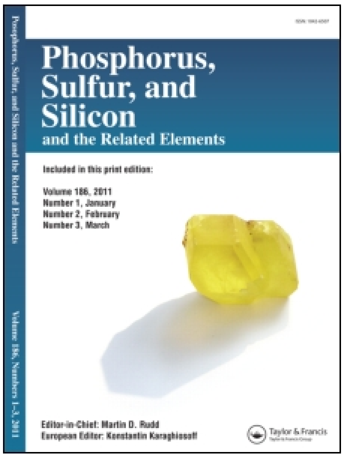


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Reactions Between Phosphorus Halides and (E)-1-Trimethylstannyl-2-Diethylboryl-1-Butene

Bernd Wrackmeyer[a]; Armando Ariza-Castolo[a]
[a] Laboratorium für Anorganische Chemie, Universität Bayreuth, Bayreuth, Germany

To cite this Article Wrackmeyer, Bernd and Ariza-Castolo, Armando(1994) 'Reactions Between Phosphorus Halides and (E)-1-Trimethylstannyl-2-Diethylboryl-1-Butene', Phosphorus, Sulfur, and Silicon and the Related Elements, 90: 1, 121 — 129

To link to this Article: DOI: 10.1080/10426509408016393

URL: http://dx.doi.org/10.1080/10426509408016393

Phosphorus, Sulfur, and Silicon, 1994, Vol. 90, pp. 121–129
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIONS BETWEEN PHOSPHORUS HALIDES AND (E)-1-TRIMETHYLSTANNYL-2-DIETHYLBORYL-1-BUTENE

BERND WRACKMEYER† and ARMANDO ARIZA-CASTOLO‡
Laboratorium für Anorganische Chemie, Universität Bayreuth,
D-95440 Bayreuth, Germany

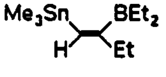
(Received May 17, 1994)

It was found that (E)-1-trimethylstannyl-2-diethylboryl-1-butene (**1**) reacts very slowly, accompanied by extensive decomposition, with phosphorus halides such as PX_3 [X = Cl (**2a**), Br (**2b**)] or $PhPCl_2$ (**3**)]. Only in the presence of a large excess of PBr_3, the expected alkene derivative, (E)-1-dibromophosphinyl-2-diethylboryl-1-butene (**7**), is formed and can be isolated. In contrast, if aminophosphorus halides {$(Me_2N)_2P$—Cl (**4**), $[CH_2(Me)N]_2P$—Cl (**5**), $[OCH_2CH_2(Me)N]P$—Cl (**6**)} are used, the exchange process (Me_3SnCl is eliminated) is much faster and leads quantitatively to the corresponding alkene derivatives **8**–**10** in which a strong coordinative N—B bond is present. Addition of sulfur or selenium to **8**–**10** leads to the adducts **8**(S)–**10**(S) and **8**(Se)–**10**(Se) in which coordinative S—B or Se—B bonds exist. All products were characterized by multinuclear 1D and 2D NMR techniques which also led to the determination of many absolute coupling signs e.g., of $^1J(^{31}P^{13}C)$ and $^2J(^{31}P^1H)$.

Key words: Alkenes; phosphinyl- and boryl-substituted-exchange; Sn—C against P—C bond-coordination; N—B, S—B, Se—B intramolecular-NMR; multinuclear-coupling-sign determination.

INTRODUCTION

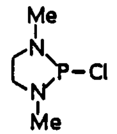
Exchange reactions between phosphorus halides and tetraorganotin compounds can be exploited to form new phosphorus-carbon bonds.[1] In the course of such reactions one expects that the more polar Sn—C= bond in alkenyltrialkyltin compounds is more readily cleaved than the Sn—alkyl bond, and that PX_3 (X = Cl, Br) is more reactive than bis(amino)phosphorus halides or similar compounds. In continuing our studies of the reactivity of organometallic-substituted alkenes, we have investigated the reaction between (E)-1-trimethylstannyl-2-diethylboryl-1-butene[2] (**1**) and various phosphorus halides (**2**–**6**). It was intended to synthesize alkenes with a phosphinyl and a boryl group in cis-position at the C=C double bond in order to study the interaction between these substituents. Only few examples of such compounds have been reported in the literature,[3,4] some of which

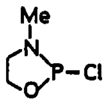

1

PX_3
2a, b
X = Cl, Br

$PhPCl_2$
3

$(Me_2N)_2PCl$
4


5


6

---

†Author to whom correspondence should be addressed.

‡On leave from Centro de Investigacion y de Estudios Avanzados del I.P.N., Departamento de Quimica, A.P. 14-740, 07000 Mexico D.F., Mexico.

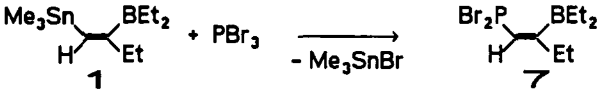
possess a coordinative P—B bond as shown by ^{11}B NMR,[3] ^{31}P NMR[3,4] and X-ray analyses.[3c,4c]

Previously it was found that the reactivity of compounds of type **1** is determined by the combined effects of the stannyl and the boryl group.[5] If the stannyl group can be replaced by a phosphinyl group another interesting class of functionally substituted alkenes[3,4] would become readily available. The major analytical tool used in this work is multinuclear one- and two-dimensional NMR spectroscopy for monitoring reactions, investigating the dynamic behavior and establishing the proposed structure, including also various experiments for the determination of signs of coupling constants $J(^{31}P^{13}C)$ and $J(^{31}P^{1}H)$.[6]

RESULTS AND DISCUSSION

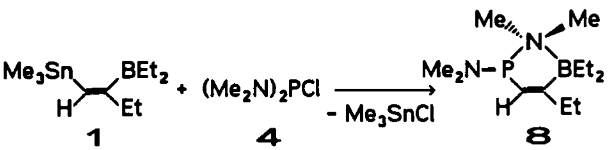
Synthesis

The reaction between **1** and an equimolar amount of **2a,b** or **3** was slow, even at 40–50°C, and after several days trimethyltin chloride and a great number of unidentified decomposition products were formed, as shown when the progress of the reaction was monitored by ^{31}P and ^{119}Sn NMR. If a large excess of PBr_3 (**2b**) was present, a clean reaction with **1** was observed. This afforded the expected alkene derivative **7** [Equation (1)]. The alkene **7** is a yellowish, extremely air- and moisture-sensitive oil and decomposes after a few hours at room temperature.

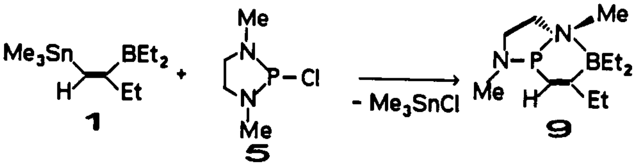


(1)

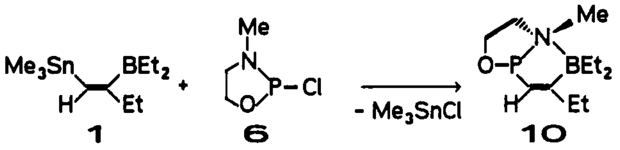
In contrast to the reaction between **1** and **2** or **3**, a smooth and quantitative reaction took place between **1** and **4–6** which started already at low temperature (< – 30°C) and was essentially complete at room temperature or after a few minutes at 40°C. The pure alkene derivatives **8–10** [Equations (2–4)] were isolated as moisture-sensitive, yellowish oily liquids after removing Me_3SnCl in vacuo. According to the NMR data (vide infra) there is a fairly strong coordinative N—B bond in **8–10** which proves that the exchange took place with retention of the configuration at the C═C bond.



(2)

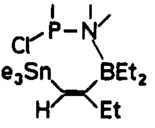


(3)



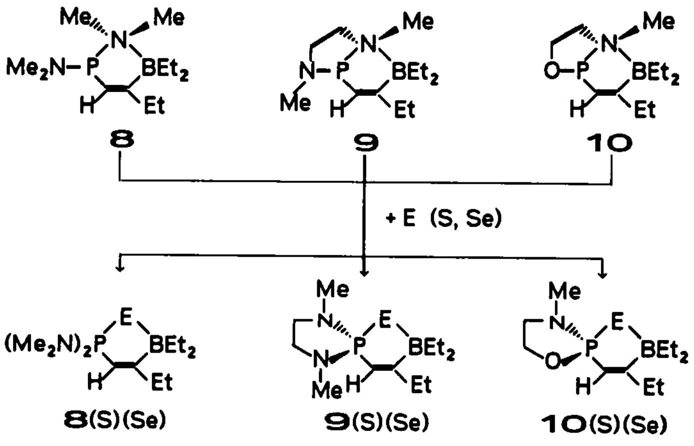
(4)

The surprisingly high reactivity of **1** towards the phosphorus halides **4–6** can be explained by assuming a donor-acceptor interaction between one of the amino-nitrogen atoms and the electrophilic boron atom of the Et_2B group in **1** as shown in **11**. Once the phosphorus halide is anchored, the next step, cleavage of the Sn—C= bond, is an intramolecular reaction which proceeds smoothly. Furthermore, a coordinative N—B bond such as in **11** may enhance the polarity of the P—Cl bond. This mechanistic suggestion is supported by the observation that **1** did not react with phosphorus halides of the type **4–6** if the NMe groups were replaced by more bulky NR′ groups (R′ = ^{t}Bu, ^{i}Pr). Even in the case of $(Et_2N)_2PCl$, the reaction with **1** did not proceed in a rate comparable to that of **4** and **1**. Clearly, one or two sterically more demanding groups attached to the nitrogen atom would significantly weaken or even prevent a coordinative N—B bond. In contrast with **4–6**, donor-acceptor interactions between **2a,b** or **3** and **1** should be very weak and therefore, any exchange processes will depend solely on intermolecular interactions between the organotin fragment and the phosphorus halide.



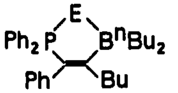
11

The alkenes **8–10** were treated with sulfur and selenium to give the corresponding adducts **8**(S)–**10**(S) and **8**(Se)–**10**(Se) [Equation (5)]. These reaction were carried out in a small scale for NMR studies. From the NMR data (vide infra) it turned out that there is no N—B coordination but the sulfur- or selenium atom bridges the phosphorus- and boron atoms in **8**(S)–**10**(S) and **8**(Se)–**10**(Se), respectively.



(5)

Such a bridging function has been observed previously in **12**, and was established by ^{31}P NMR and, in the case of E = S, by an X-ray analysis.[4c] Similar to **8**(S)(Se)–**10**(S)(Se), the compound **12** is formed by treatment of the corresponding alkene with sulfur or selenium at room temperature.[4c]



12(S)(Se)

NMR Spectroscopic Results

^{11}B-, ^{13}C- and ^{31}P NMR data of the alkene derivatives **7–10** are given in Table I, and the experimental part contains the ^{1}H NMR data. The proposed structures of the alkenes **7–10** are supported by the consistent NMR data sets.

It appears that there is no coordinative P—B interaction in **7**, as indicated by δ^{11}B = +86.2, typical[7] of a trigonal planar surrounding of a boron atom which is linked to three carbon atoms with negligible (pp)π CB bonding. The latter is also apparent from the fairly shielded ^{13}C(P—C=) nucleus in β-position with respect to the boron atom.[8] The absence of even weak P—B bonding is further confirmed by comparing the δ^{31}P value of **7** (δ = +149.8) with that of $Br_2P—CH=CH_2$ (δ^{31}P = +148.6).[9] There is no appreciable change in the δ^{11}B or δ^{31}P values at lower temperature in solution. The negative sign of $^{1}J(^{31}P^{13}C)$ and the positive sign of $^{2}J(^{31}P^{1}H)$ is also typical of a phosphorus atom with such substituents.[6]

The δ^{11}B values of the alkenes **8–10** lie in the characteristic range[7] observed for tetracoordinate boron atoms with a coordinative N—B bond in addition to three organyl groups. The bridging function of an amino group between the phosphorus and boron atom causes significant deshielding of the ^{31}P nucleus (compare e.g. $Ph—P(NMe_2)_2$, δ^{31}P = +102,[10] and $Ph—P[N(Me)CH_2CH_2O]$, δ^{31}P = 141.8).[11] The pattern of ^{1}H- and ^{13}C NMR signals of the NMe groups (Figure 1) and of the NCH_2- and OCH_2 groups are in complete agreement with the proposed structure of **8–10**. This pattern proves that opening of the N—B bond must be slow as compared to the NMR time scale. The well known dependence[12] of magnitude and sign of $^{2}J(^{31}PN^{13}C)$ and $^{3}J(^{31}PNC^{1}H)$ on the mutual orientation of the P—C bond and the lone pair of electrons at the phosphorus atom is observed. Interestingly, the sign and magnitude of $^{1}J(^{31}P^{13}C)$ changes from +4.9 Hz in **8** to −9.5 Hz and −23.6 Hz in **9** and **10**, respectively, whereas the sign of $^{2}J(^{31}P^{1}H)$ remains constant.

The absence of the influence of the lone pair of electrons at the phosphorus atoms in the sulfur-(**8**(S)–**10**(S)) and selenium adducts (**8**(Se)–**10**(Se)) causes the expected changes in many NMR parameters. Most notably are the large and positive coupling constants $^{1}J(^{31}P^{13}C)$. The δ^{11}B values are temperature dependent (see Table I) and better ^{11}B nuclear shielding is observed at lower temperature. The ^{31}P nuclear shielding changes very little under these conditions. Temperature dependent ^{1}H- and ^{13}C NMR spectra also do not change significantly in order to make an unambiguous decision for N—B or E—B (E = S, Se) coordination. In the case of E = Se, ^{77}Se NMR parameters should give a reliable answer. The magnitude of the coupling constants $|^{1}J(^{77}Se^{31}P)|$ in **8**(Se)–**10**(Se) is smaller than in

TABLE I

^{11}B-, ^{13}C-, ^{31}P- and ^{77}Se NMR data[a] of the alkene derivatives **7** to **10**

Comp.	$\delta^{13}C$						$\delta^{31}P$	$\delta^{11}B$
No.	B-C=	P-C=	$=C-CH_2-CH_3$	$B-CH_2-CH_3$	$N-CH_3$	$N/O-CH_2$		
7	175.4 (br) [50.0]	126.8 [-43.3]	27.7, 9.1 [22.6] [3.9]	21.7, 11.2 (br)	--	--	+149.8	+86.2
8	185.8 (br)	115.4[b] [+4.9]	28.8, 11.7 [8.9][4.9]	13.5, 12.7 (br) 11.7, 10.6 (br)	43.8[c], 41.1[d] [+41.7][<1.0] 43.5[e], 38.9[e] [+27.6][12.8[f]]	--	+159.2	+3.1
8(S)	201.4 (br)	108.8 [+129.9]	27.5, 12.6 [29.5[h]][< 1.0]	18.4, 12.2 (br)	36.8 [-3.0]	--	+97.6	+16.3[g]
8(Se)[i]	200.4 (br) [37.4]	111.6 [+118.1]	27.4, 13.0 [30.5][<1.0]	18.7, 12.6 (br)	37.3 [-3.0]	--	+96.5 (606.8)	+19.9[g]
9	181.4 (br)	121.6[j] [-9.5]	28.1, 11.5 [7.9[k]][4.9]	14.4, 12.4 (br) 12.8, 10.9 (br)	39.8, 41.2[e] [+31.5][+9.7]	57.8, 54.4[e] [4.9][7.9]	+174.3	+4.6
9(S)	207.8 (br)	110.7 [+130.9]	27.7, 12.6 [32.5[h]][2.0]	18.2, 12.3 (br)	31.7 [-6.9]	48.5 [5.9[l]]	+95.5	+12.7[g]
9(Se)[m]	207.7 (br)	114.3 [+118.0]	27.6, 12.9 [33.5[h]][< 1.0]	18.9, 12.9 (br)	32.1 [6.9[l]]	48.7 [4.9]	+94.8[n] (603.0)	+18.4[o]
10	188.1 (br)	121.3[p] [-23.6]	28.0, 11.4 [5.9[k]][6.9]	14.6, 12.1 (br) 13.6, 10.6 (br)	42.0 [+20.7]	55.6, 69.2 [2.0][10.8]	+201.4[q]	+5.6
10(S)	nm	110.7 [+138.8]	27.7, 12.2 [34.5[h]][2.0]	17.6, 12.0 (br) 17.6, 11.5 (br)	31.4 [-6.9]	49.3, 65.8 [9.9][4.9]	+112.4	+16.3[g]
10(Se)[r]	208.2 (br) [53.2]	114.7 [+125.0]	27.7, 12.2 [33.4[h]][< 3.0]	18.1, 12.6 (br)	32.0 [<3.0]	49.7, 66.4 [7.9][5.9]	+114.2 (667.3)	+20.9[g]

[a] Measured in C_6D_6 at 298 K if not mentioned otherwise; coupling constants $J(^{31}P^{13}C)$ in Hz are given in square brackets; coupling constants $^1J(^{77}Se^{31}P)$ in Hz are given in curved brackets; (br) denotes the broadened ^{13}C NMR signal of a boron-bonded ^{13}C nucleus; nm = not measured, the signal was too broad.

[b] $^1J(^{13}C=^{13}C)$ 54.7 Hz

[c] NMe Group in *syn*-position with respect to the orientation of the lone pair of electrons at the phosphorus.atom.

[d] NMe Group in *anti*-position with respect to the orientation of the lone pair of electrons at the phosphorus atom.

[e] Linked to three-coordinate nitrogen.

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

[g] $\delta^{11}B$ at 300 K; $\delta^{11}B = 0$ (± 2) at 233 K.

[h] $^4J(^{31}P^1H)/^3J(^{31}P^{13}C) < 0$ (negative tilt in $^{13}C/^1H$ HETCOR).

[i] $\delta^{77}Se$ (300 K) = -243.9 (606.8); (233 K) -258.3 (588.8)

[j] $^1J(^{13}C=^{13}C)$ 52.0 Hz

[k] $^4J(^{31}P^1H)/^3J(^{31}P^{13}C) > 0$ (positive tilt in $^{13}C/^1H$ HETCOR).

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

[m] $\delta^{77}Se$ (300 K) -172.4.

[n] $^1J(^{77}Se^{31}P)$ (270 K) 598.0 Hz.

[o] $\delta^{11}B$ at 300 K; $\delta^{11}B = 2.6$ (± 1) at 233 K.

[p] $^1J(^{13}C=^{13}C)$ 51.2 Hz.

[q] INEPT-HEED: $^1J(^{31}P^{15}N)$ 43.5 Hz; isotope induced shift $^1\Delta^{15/14}N(^{31}P) = -23$ (±1) ppb.

[r] $\delta^{77}Se$ (300 K) = -145.5 (667.3); (233 K) -152.3 (651.8).

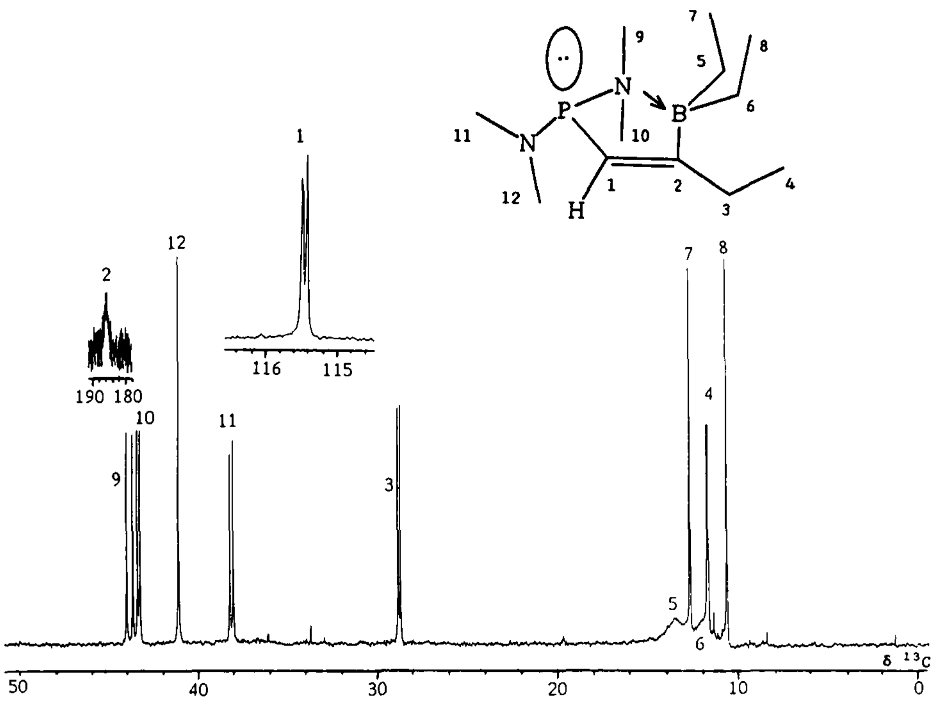


FIGURE 1 67.95 MHz $^{13}C\{^1H\}$ NMR spectrum of compound **8** at 25 ± 1°C. Note the four different signals (9, 10, 11, 12) of the PNMe groups which prove (i) that the coordinative N—B bond is kinetically stable with respect to the NMR time scale and (ii) that there is restricted rotation about the exocyclic P—N bond. There are also two sets of ^{13}C NMR signals for the BEt_2 group.

other comparable selenium adducts.[13] This is in accord with the known trend for $|^1J(^{77}Se^{31}P)|$ in complexes of R_3PSe.[14] Furthermore, smaller values $|^1J(^{77}Se^{31}P)|$ in **8**(Se)–**10**(Se) are observed at lower temperatures. The ^{77}Se nuclear shielding increases slightly with decreasing temperatures. Together with the known molecular structure of **12**(S),[4c] all evidence points towards the preference for a chalkogenide bridge in all of the alkenes **8**(S)(Se)–**10**(S)(Se).

EXPERIMENTAL

The synthetic work and the handling of the NMR samples was carried out in an inert atmosphere (N_2 or Ar). Hexane was distilled from Na/K alloy prior to use. The alkenyltin compound **1**[2] and the phosphorus halides **4**[15], **5**[16] and **6**[17] were prepared following the literature procedures. In the case of **1**, it is essential to purify the compound immediately after its synthesis by distillation in order to avoid the formation of a mixture of isomers.

(E)-1-Dibromophosphinyl-2-diethylboryl-1-butene (**7**). After addition of 16.2 g (60 mmol) of PBr_3 (**2b**) to 0.287 g (1 mmol) of **1**, the mixture was stirred at 40°C for 1 h. An extremely air- and moisture-sensitive, yellow oil was left when all volatile material had been removed in vacuo. The yellow oil was identified by NMR as pure (>95%) **7**.

^{1}H NMR (C_6D_6): $\delta^1H\ [J(^{31}P^1H)] = 6.67\ [+12.0]$ d,t ($^4J(^1H^1H) = 1.7$ Hz) 1H, =CH; 1.88 d,q ($^4J(^1H^1H) = 1.7$ Hz, $^3J(^1H^1H) = 7.3$ Hz) 2H, 0.73 [0.9] d,t ($^3J(^1H^1H) = 7.3$ Hz) 3H, =CEt; 1.12–1.15 m, 4H, 0.87 t ($^3J(^1H^1H) = 7.3$ Hz) 6H, BEt_2.

(E)-1-Bis(dimethylamino)phosphinyl-2-diethylboryl-1-butene (**8**). To a solution of 0.861 g (3 mmol) of **1** in 5 ml of hexane 0.465 g (3 mmol) of bis(dimethylamino)phosphorus chloride (**4**) was added in one portion at room temperature. The reaction was complete after stirring and warming the mixture up to 40°C for 2.5 h. All volatile material was removed in vacuo and a yellowish oil was left, identified as pure (>95%) **8**.

^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.35 [+39.5] d, 1H, =CH; 2.22 [5.5] d,q ($^{3}J(^{1}H^{1}H)$ = 7.5 Hz) 2H, 0.89 t ($^{3}J(^{1}H^{1}H)$ = 7.5 Hz) 3H, =CEt; 0.5–0.6 m, 4H, 1.03 t, 0.96 t, ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 6H, BEt_2; 2.55 [+12.4] d, 3H, syn-PN(B)Me; 1.83 [1.4] d, 3H, anti-PN(B)Me; 2.28 [+14.9] d, 3H, syn-PNMe; 2.34 [3.7] d, 3H, anti-PNMe. —$C_{12}H_{28}BN_2P$ (242.15): Calcd. C 59.52, H 11.65, N 11.57; Found C 59.38, H 11.42, N 11.50%.

The synthesis of **9** and **10** was carried out in the same way as described for **8** except that the formation of **9** was complete already after mixing at room temperature and, in the case of **10**, stirring at room temperature for 2.5 h proved sufficient.

9: ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.46 [46.8] d, 1H, =CH; 2.20 m, 2H, 1.11 t ($^{3}J(^{1}H^{1}H)$ = 7.9 Hz) 3H, =CEt; 0.51–0.76 m, 4H, 1.04 t ($^{3}J(^{1}H^{1}H)$ = 7.7 Hz) 6H, BEt_2; 2.47 [+13.4] d, 3H, PN(B)Me; 2.25 [+14.2] d, 3H, PNMe; 2.20 m, 1H, 3.51 m, 1H, PN(B)CH_2; 2.44 [4.3] m, 1H, 2.93 [2.8] m, 1H, $PNCH_2$.

10: ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.51 [+46.8] d, 1H, =CH; 2.15 m, 2H, 1.02 t ($^{3}J(^{1}H^{1}H)$ = 7.0 Hz) 3H, =CEt; 0.48–0.76 m, 4H, 0.99 t, 1.11 t ($^{3}J(^{1}H^{1}H)$ = 7.5 Hz) 6H, BEt_2; 2.19 [+14.3] d, 3H PN(B)Me; 3.14 [4.3] m, 1H, 1.66 [<1] m, 1H, PN(B)CH_2; 3.60 [1.4] m, 1H, 3.57 [<1.0] m, 1H, $POCH_2$. —$C_{11}H_{23}BNOP$ (227.11): Calcd. C 58.17, H 10.21, N 6.17; Found C 58.03, H 10.12, N 6.05%.

Sulfur and selenium adducts **8***(S)*–**10***(S) and* **8***(Se)*–**10***(Se)*. Solutions of 1 mmol of **8–10** in 0.5 ml of C_6D_6 were treated with an excess of sulfur or selenium and after 24 h insoluble material was separated in a centrifuge, and clear brown solutions were left, containing the pure (>95%) adducts.

8(S): ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.38 [+35.6] d,t ($^{4}J(^{1}H^{1}H)$ = 1.2 Hz) 1H, =CH; 2.26 [2.5] d,d,q ($^{4}J(^{1}H^{1}H)$ = 1.2 Hz, $^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 2H, 1.07 t ($^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 3H, =CEt; 0.87–0.9 m, 4H, 1.15 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 6H, BEt_2; 2.29 [+11.9] d, 12H $P(NMe_2)_2$.

8(Se): ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.47 [+32.3] d,t ($^{4}J(^{1}H^{1}H)$ = 1.6 Hz) 1H, =CH; 2.11 [2.7] d,d,q ($^{4}J(^{1}H^{1}H)$ = 1.6 Hz, $^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 2H, 1.00 t ($^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 3H, =CEt; 0.66–0.68 m, 4H, 1.19 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 6H, BEt_2; 2.36 [+12.5] d, 12H, $P(NMe_2)_2$.

9(S): ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.09 [+37.7] d, 1H, =CH; 2.30 m, 2H, 1.03 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 3H, =CEt; 0.88–0.91 m, 4H, 1.28 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 6H, BEt_2; 2.31 [+12.2] d, 6H, PNMe; 2.55 m, 2.44 m, 4H, $PNCH_2$.

9(Se): ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.17 [+34.2] d, 1H, =CH; 2.26 m, 2H, 1.03 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 3H, =CEt; 0.98–0.99 m, 4H, 1.28 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 6H, BEt_2; 2.28 [+13.0] d, 6H, PNMe; 2.37 m, 4H, $PNCH_2$.

10(S): ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.28 [+38.4] d,d ($^{4}J(^{1}H^{1}H)$ = 1.5 Hz) 1H, =CH; 2.27 [3.0] d,d,t ($^{4}J(^{1}H^{1}H)$ = 1.5 Hz, $^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 2H, 1.00 t ($^{3}J(^{1}H^{1}H)$ = 7.3 Hz) 3H, =CEt; 0.90–0.93 m, 4H, 1.21 t, 1.20 t ($^{3}J(^{1}H^{1}H)$ = 7.0 Hz) 6H, BEt_2; 2.22 [+12.4] d, 3H, PNMe; 2.28 m, 2H, $PNCH_2$; 3.44 m, 2H, $POCH_2$.

10(Se): ^{1}H NMR (C_6D_6): δ^{1}H [$J(^{31}P^{1}H)$] = 5.37 [+35.1] d,t ($^{4}J(^{1}H^{1}H)$ = 1.3 Hz) 1H, =CH; 2.20 [1.5] d,d,t ($^{4}J(^{1}H^{1}H)$ = 1.3 Hz, $^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 2H, 0.98 t ($^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 3H, =CEt; 0.86–0.89 m, 4H, 1.14 t ($^{3}J(^{1}H^{1}H)$ = 7.2 Hz) 6H, BEt_2; 2.22 [+13.2] d, 3H, PNMe; 2.40 m, 2H, $PNCH_2$; 3.57 m, 2H, $POCH_2$.

NMR measurements. NMR spectra were recorded from samples (ca. 10–20% in C_6D_6 at 25°C or at low temperature in [D_8] toluene) in 5 mm tubes by using JEOL EX 270 (^{1}H-, ^{13}C NMR), JEOL FX 90 Q (^{11}B-, ^{31}P NMR) and Bruker AC 300 or AM 500 spectrometers (^{1}H-, ^{11}B-, ^{13}C-, ^{31}P, ^{77}Se- and ^{119}Sn NMR), all equipped with a variable temperature unit. Chemical shifts are given with respect to Me_4Si [$\delta^{1}H(C_6D_5H)$ = 7.15, $(C_6D_5CD_2H)$ = 2.03; $\delta^{13}C(C_6D_6)$ = 128.0, $(C_6D_5CD_3)$ = 20.4]; external Et_2O—BF_3 (δ^{11}B, Ξ (^{11}B) = 32.083972 MHz), external H_3PO_4 (aq. 85%) (δ^{31}P, Ξ (^{31}P) = 40.480747 MHz), external neat Me_2Se (δ^{77}Se, Ξ (^{77}Se) = 19.071523 MHz).

Relative signs of coupling constants $J(^{31}P^{13}C)$ and $J(^{31}P^{1}H)$ 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.[18] Absolute signs of coupling constants were determined by selective 1D $^{1}H\{^{31}P\}$ heteronuclear double resonance experiments,[19] observing differential effects on the ^{13}C satellite signals in the ^{1}H NMR spectra. This allows us to compare the sign of $^{1}J(^{13}C^{1}H)$ (known to be positive[20]) with that of $J(^{31}P^{13}C)$. Together with the HETCOR experiments a number of absolute coupling signs become available.

The ^1H- and ^{13}C NMR signals of the NMe groups in **8** have been assigned by NOE difference spectra[21] and $^{13}C/^1H$ HETCOR experiments.

Coupling constants $^1J(^{13}C{=}^{13}C)$ were measured by using the INADEQUATE pulse sequence.[22] The coupling constant $^1J(^{31}P^{15}N)$ and the isotope effects $^1\Delta^{15/14}N(^{31}P)$ (negative sign indicates shift to lower frequency of the $^{15}N{-}^{31}P$ isotopomer) were measured by using Hahn-echo extended (HEED) pulse sequences.[23]

ACKNOWLEDGEMENTS

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. A.A.-C. thanks the DAAD (Germany) and CONACYT (Mexico) for scholarships.

REFERENCES

1. a) A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 3293 (1971); b) W. Siebert, W. E. Davidsohn and M. C. Henry, *J. Organomet. Chem.*, **17**, 65 (1969); c) R. K. Ismagilov, A. I. Razumov and R. L. Yafarova, *Zh. Obshch. Khim.*, **42**, 1248 (1971); d) H. Roland, P. Potin, J.-P. Majoral and G. Bertrand, *Tetrahedron Lett.*, 5095 (1992).
2. G. Menz and B. Wrackmeyer, *Z. Naturforsch., Teil B*, **32**, 1400 (1977).
3. a) P. Binger and R. Köster, *J. Organomet. Chem.*, **73**, 205 (1974); b) R. Köster, *Pure Appl. Chem.*, **49**, 765 (1977); c) L. A. Hagelee and R. Köster, *Synth. React. Inorg. Metallorg. Chem.*, **7**, 53 (1977).
4. a) A. S. Balueva and O. A. Erastov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 163 (1988); b) A. S. Balueva, G. N. Nikonov, B. A. Arbuzov, R. Z. Musin and Yu. Ya. Efremov, *Izv. Akad. Nauk SSSR, Ser Khim.*, 2397 (1991); (c) A. S. Balueva, Yu. Ya. Efremov, V. M. Nekhoroshkov and O. A. Erastov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2793 (1989).
5. a) B. Wrackmeyer and K. Wagner, *Chem. Ber*, **122**, 857 (1989); b) B. Wrackmeyer and K. Wagner, *Chem. Ber.*, **124**, 503 (1991); c) B. Wrackmeyer, K. Wagner and R. Boese, *Chem. Ber.*, **126**, 595 (1993).
6. a) C. J. Jameson, in J. G. Verkade and L. D. Quin (eds.), "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis," VCH, Weinheim, 1987, pp. 205–230; b) W. A. Anderson, R. Freeman and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963); c) R.-M. Lequan and M.-P. Simonnin, *Tetrahedron Lett.*, 145 (1972); d) T. Bundgaard and H. J. Jakobson, *Tetrahedron Lett.*, 3353 (1972); e) H.-O. Berger, H. Nöth and B. Wrackmeyer, *Chem. Ber.*, **112**, 2866 (1979); f) V. Ya. Komarov, V. I. Zakharov, Yu. Y. Belov and B. I. Ionin, *Zh. Obshch. Khim.*, **50**, 1262 (1980); g) E. I. Lazhko, E. V. Luzikova, G. Yu. Mikhailov, M. A. Kazankova and Yu. A. Ustynyuk, *Zh. Obshch. Khim.*, **58**, 1247 (1988); h) D. Hänssgen and E. Odenhausen, *Chem. Ber.*, **112**, 2389 (1979); i) T. N. Mitchell, K. Heesche-Wagner and H.-J. Belt, *Magn. Reson. Chem.*, **29**, 78 (1991).
7. a) H. Nöth and B. Wrackmeyer, in P. Diehl, E. Fluck and R. Kosfeld (eds.), "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds—NMR—Basic Principles and Progress," Vol. 14, Springer-Verlag, Berlin 1978; b) B. Wrackmeyer and R. Köster, in R. Köster (ed.), "Houben-Weyl, Methoden der Organischen Chemie," 4th edition, Vol. XIII/3c, Thieme, Stuttgart, 1984, pp. 377–611; c) B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.*, **20**, 61 (1988).
8. R. Köster, G. Seidel, K. Wagner and B. Wrackmeyer, *Chem. Ber.*, **126**, 305 (1993).
9. W. Althoff, M. Fild, H.-P. Rieck and R. Schmutzler, *Chem. Ber.*, **111**, 1845 (1978).
10. D. Houalla, T. Mouheich, M. Sanchez and R. Wolf, *Phosphorus*, **5**, 229 (1975).
11. J. B. Robert and H. Weichmann, *J. Org. Chem.*, **43**, 3031 (1978).
12. L. D. Quin, in J. G. Verkade and L. D. Quin (eds.), "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis," VCH, Weinheim, 1987, pp. 381–424, and references cited therein.
13. W. McFarlane and D. S. Rycroft, *J. Chem. Soc. Dalton Trans.*, 2162 (1973).
14. J. G. Verkade and J. A. Masbo in J. G. Verkade and L. D. Quin (eds.), "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis," VCH, Weinheim, 1987, pp. 425–463, and references cited therein.
15. H. Nöth and H.-J. Vetter, *Chem. Ber.*, **94**, 1505 (1961).
16. F. Ramirez, A. V. Patwardhan, H. J. Kugler and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 6276 (1967).
17. M. McGuigan and B. Swords, *J. Chem. Soc. Perkin Trans. I*, 783 (1990).
18. A. Bax and R. Freeman, *J. Magn. Reson.*, **45**, 177 (1981).

19. a) W. McFarlane, *Annu. Rep. NMR Spectrosc.*, **1,** 135 (1968); ibid **5A,** 353 (1972); b) W. McFarlane in J. G. Verkade and L. D. Quin (eds.), "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis," VCH, Weinheim, 1987, pp. 115–150.
20. C. S. Jameson, in J. Mason (ed.), "Multinuclear NMR," Plenum Press, New York, 1987, pp. 89–131.
21. K. E. Köver and G. Batta, *Progr. NMR Spectrosc.*, **19,** 223 (1987).
22. A. Bax, R. Freeman and S. P. Kempsell, *J. Am. Chem. Soc.*, **102,** 4849 (1980).
23. E. Kupce and B. Wrackmeyer, *J. Magn. Reson.*, **97,** 568 (1992).