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Cyclo and Spirozirconation: Synthesis of New Phospholane-Boranes and Polyphosphine-Boranes

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Abstract—The diallylic phosphine-borane $Ph(BH_3)P(allyl)_2$ **6**, reacts with the zirconocene 'Cp_2Zr' and gives the bicyclocomplex intermediate **7**, characterized by ^1H and ^{31}P NMR. The electrophilic addition of H^+, Br_2, $PhPCl_2(BH_3)$, $Ph_2PCl(BH_3)$ leads to the corresponding stabilized phospholanes **8, 9, 11** and bicyclophospholane **10**, whereas $Ph_2P(BH_3)Li$ on **9** gives the boro(phospholane–diphosphine) **12**. Under the same conditions, the tetraallylsilane (or germane) **13a–b** leads to the spirometallacyclopentane **14a–b** intermediates. After reaction with Br_2, $Ph_2PLi(BH_3)$ and $PhPCl_2(BH_3)$, the racemic spirannic tetraphosphines **16a–b** and the protected spirannic diphosphine **17b** are obtained with a remarkable selectivity. Decomplexation reaction by Et_2NH gives corresponding free phosphines **3′–17′**.

Introduction

The cyclozirconation reaction, initiated independently by Nugent[1] and Negishi[2] is one of recent powerful carbometallation methods.[3] Heterodiynes and dienes containing oxygen,[4] boron,[5] nitrogen,[6] silicon[7] have been reacted on a zirconium dicyclopentadienyl dichloride complex in the presence of *n*-butyllithium. We recently published cyclozirconation reactions in heteroelementary series (Si, Ge, P,…).[8] As the cyclozirconation with diallyl phosphine oxide failed, we used diallylphosphine bearing a sterically bulky substituent as the protective group. In order to prevent the phosphorus–zirconium interaction,[9] we present a new approach involving the cyclozirconation of protected allylphosphines by borane (BH_3). Furthermore, with the purpose of obtaining polyphosphines, we will use phosphine-boranes acting as an electrophile on zirconocene complex intermediates.

Results and Discussion

We have already synthesized phosphines **3′a–b** or diphosphines **5a–b** by cyclozirconation of diallyl silanes (or germanes) **1a–b**.[8] The addition of non-protected dichlorophosphine on the intermediates **2a–b** led to the bicyclo derivative **3′a–b** (Scheme 1). The reaction is quantitative, but after the purification of **3′b** by chromatography on silica column, we observed the formation of the corresponding phosphine oxide. In order to avoid this oxidation, we protected the phosphines with BH_3[10] and isolated the diphosphine-boranes **5a–b**.

In these cases, the cyclometallation was highly selective and the addition of various electrophiles on the intermediates **2a–b** led to the *trans* isomer only.

In order to prepare new functional phospholanes,[11] we extended the cyclozirconation reaction to diallyl phosphine-borane **6** (Scheme 2). As for diallyl silane or germane, the reaction was carried out from −78°C to room temperature. The zirconocene adduct intermediate **7** was detected by ^{31}P and ^1H NMR on the crude mixture: three isomers were observed at δ ^{31}P=16 (60%); 24 (25%); 28 (15%). The acidic hydrolysis of **7** gave the corresponding borane complex **8** as a mixture of three isomers (Table 1). The *trans* configuration of the major isomer (85%) and the *cis* configuration of the minor isomers are determined from ^{13}C NMR. The bromination of **7** at low temperature leads to the dibromophospholane **9**. As before, we detected the presence of three isomers in the same proportions (Table 1). Notice that the iodination reaction does not lead to the expected C-diiodo isolog of **9**. Competitive reactions may occur giving iodo-substituted borane-phospholane[12] or iodo phosphonium salts. Such reactions may explain the observed low yields.

The bicyclo-diphospholane **10** was obtained in two steps from **7** under treatment, at room temperature, with $PhPCl_2$ followed by the protecting boration reaction. As shown by

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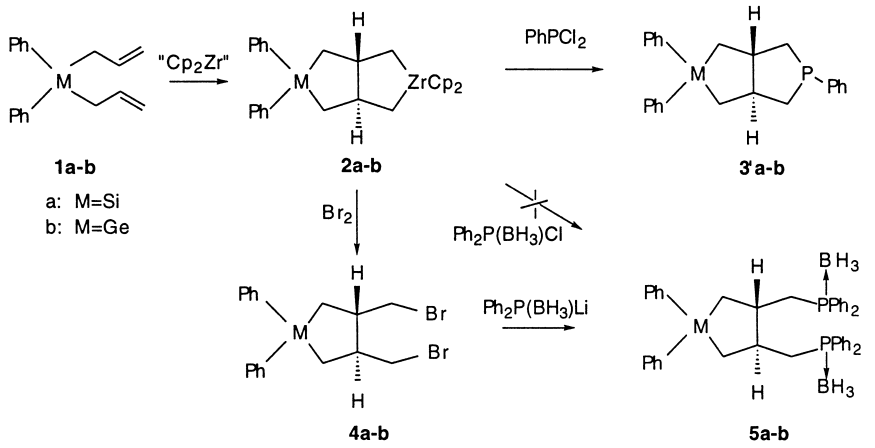


Scheme 1.

^{13}C NMR, three isomers (*trans* and *cis*) were characterized in the isolated product (Table 1).

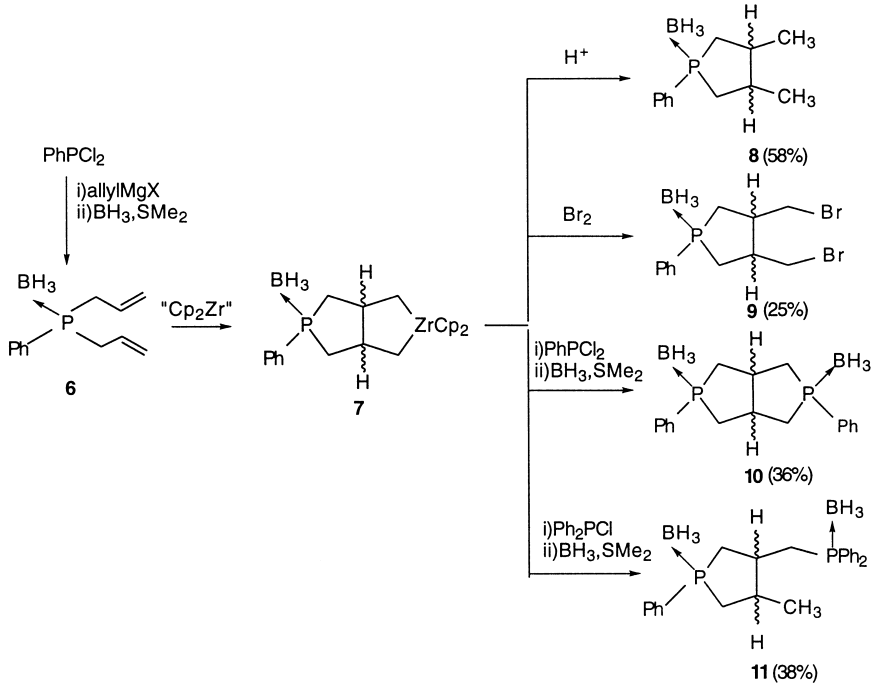
The successive treatment of the intermediate complex **7** by Ph_2PCl and BH_3SMe_2 gave the phosphino-phospholane diborane **11** even if an excess of the chlorophosphine was used. After purification, two isomers were characterized. The diphosphino-phospholane triborane **12** was obtained by addition of lithium phosphide on the dibromo-phospholane **9** (Scheme 3). Three isomers were identified by ^{31}P NMR (Table 1). The major isomer (70%) was in *trans* configuration.

We extended this approach to synthesize new polyphosphines[13] (Scheme 4). The first step was the spirozirconation of tetraallylsilane (**13a**) or germane (**13b**) using the same method as before. The spiro intermediates **14a–b**, stable at room temperature, were characterized by ^{1}H NMR. The bromination at low temperature of the intermediates **14a–b**, gave the tetrabromospirosilane **15a** and germane **15b** after hydrolysis.[14] Such tetrafunctional spiro-compounds, isolated as only one *trans*/*trans* isomer are convenient starting materials to prepare the corresponding protected tetraphosphines **16a–b** (Scheme 4).

Moreover, the electrophilic attack of dichlorophosphine on **14b**, followed by the protection of the two phosphorus atoms by BH_3, led to two isomers of the germaspirane **17b**.

Selectivity and stereochemistry

The stereochemistry and the selectivity of the reactivity of zirconocene towards di- and tetraallylic heteroderivatives are directly dependent on the nature of the substituents linked to the different heteroatoms (P, Si, Ge). Thus, the approach of 'Cp_2Zr' to the unsaturated moities, and consequently the geometry of the intermediates, would be controlled by the

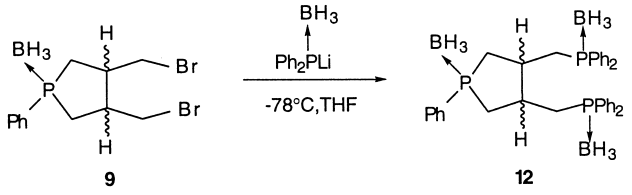


Scheme 2.

Table 1. Selectivity of cyclo and spirozirconation reaction and ^{31}P NMR parameters of phosphine–boranes

Compounds	Diastereoisomers		Configuration.	%	δ ^{31}P PhP–BH_3	δ ^{31}P Ph_2P–BH_3
	Theoretic	Observed				
5a	2	1	*trans*	100		15
5b	2	1	*trans*	100		15
8	3	3	*trans*	85	20	
			cis	10	27	
			cis	5	13	
9	3	3	*trans*	85	5	
			cis	10	−9	
			cis	5	15	
10	5	3	*trans*	43[a]	48	
			cis	36[a]		
			cis	21[a]		
11	4	2	*trans*	70[a]	21	15
			trans	30[a]		
12	3	3	*trans*	70	22	15
			cis	20	25	16
			cis	10	21.9	15
16a	4	1	*trans/trans*	100		15
16b	4	1	*trans/trans*	100		15
17b	4	2	*trans/trans*	50[a]	35	
				50[a]		

[a] % deduced from ^{13}C NMR.



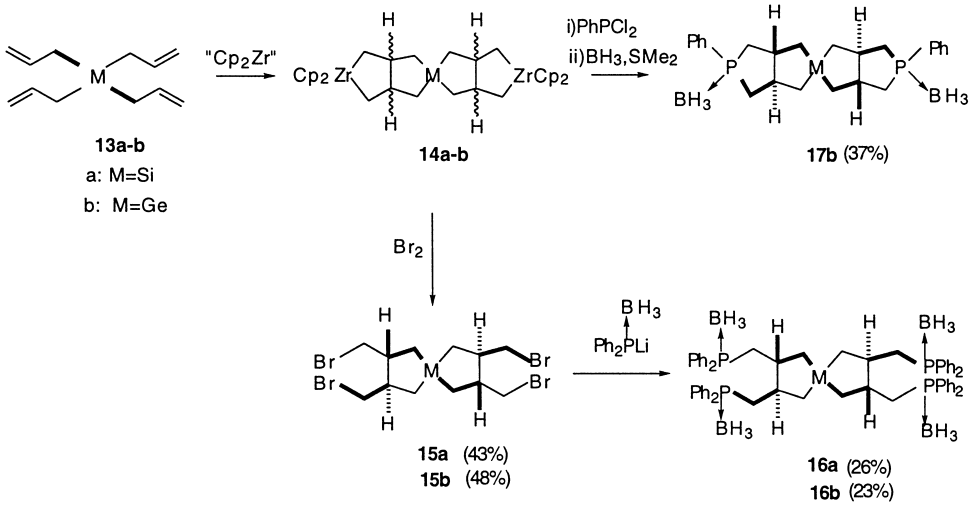
Scheme 3.

symmetry or the dissymmetry of the allylic starting material.

In our studies, all cyclozirconation reactions were carried out on symmetrical derivatives of silicon and germanium **1a–b** and unsymmetrical phosphorus compound **6**. The spirozirconation was performed on symmetrical starting materials **13a–b**.

In the case of diallyldiphenyl silane and germane **1**, it appeared (Table 1) that the cyclozirconation was stereoselective, as only *trans* isomers **3–5** were synthesized, while for the unsymmetrical diallylic phosphine-borane **6**, the cyclozirconation was not selective. The isolated products **8–12** were a mixture of *trans*/*cis* isomers, where the *trans* isomers are predominant.

The spirozirconation[14] involved the symmetrical tetraallylic derivatives **13**. The reactivity of the zirconocene led to a spirannic skeleton bearing four asymmetric carbons (stereogenic centers). In this case, the highly selective synthesis led to only one *trans*/*trans* isomer. We have checked by ^{13}C NMR on the crude product, the absence of any possible other stereoisomers. Moreover, the X-ray structural determination of **15a**[14c] revealed the presence of this *trans/trans* isomer in a racemic form (RRRR/SSSS) and not in a *meso* form (RRSS). Consequently, the spirannic



Scheme 4.

Table 2. Selectivity and ^{31}P NMR parameters of free phosphines **n′** obtained from corresponding phosphine–boranes **n**

Compounds	Diastereoisomers		Configuration	%	δ ^{31}P PhP	δ ^{31}P Ph_2P
	Theoretic	Observed				
3′a	3	1	*trans*	100	−1.0	
3′b	3	1	*trans*	100	−2.6	
5′a	2	1	*trans*	100		−19.2
5′b	2	1	*trans*	100		−19.0
8′	3	3	*trans*	85	−24.0	
			cis	10	−18.4	
			cis	5	−14.0	
10′a	5	3	*trans*	55	21.8	
			cis	25	21.4	
			cis	20	21.1	
12′	3	3	*trans*	70		
			cis	20		
			cis	10		
16′a	1	1	*trans*/*trans*	100		−18.6
16′b	1	1	*trans*/*trans*	100		−18.7
17′b	4	2	*trans*/*trans*	50	−3.0	
				50	−3.1	

tetraphosphine-boranes **16a–b** would be obtained in racemic *trans*/*trans* form.

All the phospholanes and phosphines were isolated in stable borane protected forms. The decomplexation reactions were carried out using an excess of diethylamine[15] (5–10 equiv.) in toluene (or THF) at 34–38°C and monitored by ^{31}P NMR. The half-time reactions varied from 3 h (for **10′** in THF, 38°C, 10 equiv. Et_2NH) to 13 h (for **17′b**, in toluene/THF, 34°C, 10 equiv.): 24 kcal mol^{-1} $<\Delta G^{*}<$25 kcal mol^{-1}. The deboration reactions give free phospholanes and free phosphines with sharpened NMR ^{31}P signals (Table 2).

In the case of the bicyclo-diphospholane **10**, deprotection energies of the two phosphorus were different and allowed observation of the monoborane intermediate leading to three detectable isomers of the free diphospholane **10′** (Scheme 5). In the same experimental conditions, the two steps of the decomplexation of the spirannic diphospholane **17b→17′b** were not observed.

Conclusion

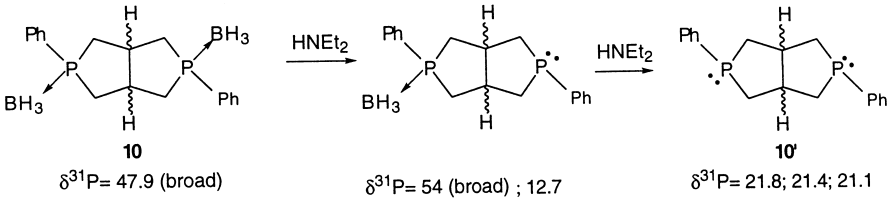
The cyclozirconation of diallyl phosphine-borane constitutes a new way to synthesize functionalized phospholanes, phosphino-phospholanes and bicyclo-diphospholanes. Moreover, the remarkable selectivity of the spirocyclization of tetraallylsilane (or germane) leading to a functionalized spirannic skeleton allows synthesis of chiral (racemic) di- and tetraphosphines. Our results indicate that the selectivity of the cyclo and spirozirconations depend more on the relative size of the substituents than on the nature of the heteroelement.

So, it appears that the protection of unsaturated phosphines by BH_3 which permitted the cyclozirconation reactions, could be extended, in the near future, to other cyclometallation reactions with various transition metals.

Experimental

General procedure

All manipulations, except chromatography on silica gel, were carried out under an argon atmosphere. Tetrahydrofuran, diethylether and hexane were distilled from sodium/benzophenone solution and stored under argon. All NMR spectra were recorded at 25°C on Bruker AC 80 and 250 MHz in $CDCl_3$. The ^{1}H and ^{13}C chemical shifts are referenced relative to TMS while ^{31}P NMR shifts are referenced to H_3PO_4 (85%). Coupling constants are given in Hertz. Mass spectra were obtained on a Ribermag R1010 under electron impact (EI) or chemical ionization (DCI conditions) with CH_4 or NH_3. Low-resolution mass spectra were determined by GC/MS using Hewlett–Packard 5890 series II gas chromatograph equipped with a HP/MS 5989A mass selective detector. Melting points were determined in evacuated capillaries with a Buchi–Tottoli apparatus. IR spectra were recorded on Perkin Elmer 1600 Series FTIR.



10 $\delta^{31}P$= 47.9 (broad)

$\delta^{31}P$= 54 (broad) ; 12.7

10′ $\delta^{31}P$= 21.8; 21.4; 21.1

Scheme 5.

Compound 7

To a solution of dichlorozirconocene (Cp_2ZrCl_2) (0.63 g, 2.2 mmol) in 10 mL of THF at −78°C was added *n*-BuLi 1.6 M (2.8 mL, 4.4 mmol). After stirring (1 h), the diallyl phosphine-borane **6** (0.4 g, 2.0 mmol) in 5 mL THF was added at −78°C. The solution was stirred for 12 h at room temperature. The intermediate **7** was detected by ^{31}P and ^{1}H NMR: three isomers were observed at δ ^{31}P=16 (60%); 24 (25%) and 28 (15%).^{1}H NMR (80 MHz, $CDCl_3$) δ=0.5–2.3 (13H, CH_2P, CH, CH_2Zr, BH_3), 5.9 (s, 10H, Cp), 7.5–7.9 (5H, H arom.)

Compound 8

The solution of **7** (2 mmol) was quenched (room temperature) by HCl (0.1 M) (0.2 mL) in 20 mL of water. After stirring (15 min), the product was extracted with ether (3×15 mL) and dried ($MgSO_4$). Removal of solvents followed by purification with Chromatotron (hexane/CH_2Cl_2:80/20) gave **8** (58%) as yellow liquid. ^{31}P NMR (81 MHz, $CDCl_3$) δ=+13 (5%), +20 (85%), +27 (10%). ^{1}H NMR (80 MHz, $CDCl_3$) δ=1–2.7 (m, 15H, CH_2P, CH, CH_3, BH_3), 7.2–7.9 (m, 5H, Ph). ^{13}C NMR (62, 89 MHz, $CDCl_3$). Isomer **I** (*trans*): δ=18.84 (d, $^{3}J_{C-P}$=24 Hz, *C*H_3), 18.85 (s. *C*H_3), 35.1 (d, *C*H_2P, $^{1}J_{C-P}$=37.4 Hz), 35.6 (d, $^{1}J_{C-P}$=36.5 Hz, *C*H_2P), 41.9 (d, $^{2}J_{C-P}$=2.8 Hz, *C*H), 43.1 (s, *C*H). Isomer **II** (*cis*): δ=16.1 (s, *C*H_3), 32.7 (s, $^{1}J_{C-P}$=36.3 Hz, *C*H_2P), 39.6 (s, *C*H). Isomer **III** (*cis*): δ=16.0 (s, *C*H_3), 33.9 (d, $^{1}J_{C-P}$=35.8 Hz, *C*H_2P), 38.3 (d, $^{2}J_{C-P}$=2.3 Hz, *C*H). MS (EI): *m*/*z*=192 (M−BH^3)$^+$ (100%). Anal. Calc. for $C_{12}H_{20}PB$: C, 69.97, H, 9.70; found: C, 69.92; H, 9.49 %.

Compound 9

To a solution of **7** (2 mmol) in 10 mL of THF, was added a solution of bromine (0.75 g, 4.7 mmol) in carbon tetrachloride (15 mL) at −78°C. The reaction was quenched (room temperature) with saturated aqueous NH_4Cl (20 mL), extracted with ether (3×15 mL) and dried ($MgSO_4$). Removal of solvents followed by chromatography (hexane/CH_2Cl_2:95/5) afforded **9** (25%) as white powder. m.p: 108–110°C ^{31}P NMR (81 MHz, $CDCl_3$) δ=−9 (m), +5 (m), +15.4 (m) (three isomers). ^{1}H NMR (80 MHz, $CDCl_3$) δ=0.8–3.41 (m, 9H, CH_2P, CH, BH_3), 3.42–3.68 (m, 4H, CH_2Br), 7.5–7.9 (m, 5H, Ph). ^{13}C NMR (62.89 MHz, $CDCl_3$). Isomer **I** (*trans*): δ=26.7 (d, $^{1}J_{C-P}$=41.4 Hz, *C*H_2P), 26.3 (d, $^{1}J_{C-P}$=42.1 Hz, *C*H_2P), 34.3 (d, $^{3}J_{C-P}$=12.4 Hz, *C*H_2Br), 35.2 (d, $^{3}J_{C-P}$=12.2 Hz, *C*H_2Br), 43.6 (s, *C*H), 43.8 (d, $^{2}J_{C-P}$=1.7 Hz, *C*H). Isomer **II** (*cis*): δ=26.1 (d, *C*H_2P, $^{1}J_{C-P}$=33.6 Hz), 34.9 (d, *C*H_2Br, $^{3}J_{C-P}$=12.5 Hz), 43.3 (d, $^{2}J_{C-P}$=3 Hz, *C*H). Isomer **III** (*cis*): δ=25.4 (d, *C*H_2P, $^{1}J_{C-P}$=33.9 Hz), 34.9 (d, *C*H_2Br, $^{3}J_{C-P}$=11.2 Hz), 43.9 (s, *C*H) MS (DCI/NH_3): *m*/*z*=351 (M−BH_3)$^+$, 271(M−BH_3−Br).

Compound 10

To a solution of **7** (2 mmol) in 10 mL of THF, was added $PhPCl_2$ (0.43 g, 0.33 mL) at room temperature. The mixture was stirred for 4 h 30 min, then $BH_3.SMe_2$ was added (0.2 mol, 0.25 mL) at room temperature. After 12 h, the solvent was removed in vacuo and the product was extracted from the residue with CH_2Cl_2. Removal of solvent followed by chromatography on silica gel (hexane/CH_2Cl_2:30/70) afforded **10** (36%) as white powder. m.p.: 182–185°C ^{31}P NMR (81 MHz, $CDCl_3$) δ=47.9 (m). ^{1}H NMR (250 MHz, $CDCl_3$) δ=0.5–2.5 (m, 16H, CH_2P, CH, BH_3), 7.5–7.8 (m, 10H, Ph), ^{13}C NMR (62.89 MHz, $CDCl_3$). Isomer **I** (*trans*): δ=30.75 (dd, $^{1}J_{C-P}$=34.5 Hz, $^{3}J_{C-P}$=11 Hz, *C*H_2P), 50.82 (d, $^{2}J_{C-P}$=3.2 Hz, *C*H). Isomer **II** (*cis*): δ=31.22 (dd, $^{2}J_{C-P}$=36 Hz, $^{3}J_{C-P}$=9 Hz, *C*H_2P), 52.6 (s, *C*H). Isomer **III** (*cis*): 30.11 (dd, $^{1}J_{C-P}$=36 Hz, $^{3}J_{C-P}$=12 Hz, *C*H_2P), 49.08 (s, *C*H). MS (DCI/NH_3): *m*/*z*=344 (M, NH_4)$^+$ (100%), 313 (MH−BH_3)$^+$, 299 (M−2BH_3)$^{+\cdot}$ Anal. Calc. for $C_{18}H_{26}P_2B_2$: C, 66.33; H, 8.00; found: C, 65.48; H, 8.2%.

Compound 11

To a solution of **7** (2 mmol) in 10 mL of THF, was added Ph_2PCl (0.53 g, 2.42 mmol) at room temperature. The mixture was stirred for 1 h 30 min, then $BH_3.SMe_2$ was added (2.42 mmol, 0.18 mL) at room temperature. After 12 h, the mixture was hydrolysed with 0.33 mL of HCl (0.1 M) in 20 mL of water. The product was extracted with ether and dried with $MgSO_4$.

Removal of solvent followed by chromatography on silica gel (hexane/CH_3Cl:70/30) afforded **11** (38%) as white powder. m.p: 50–52°C ^{31}P NMR (81 MHz, $CDCl_3$) δ=21.4 (m, *P*–Ph), 14.7 (m, *P*-Ph_2). ^{1}H NMR (80 MHz, $CDCl_3$) δ=1.01–2.8 (m, 17H, CH_2P, CH, BH_3), 7.2–7.5 (m, 15H, Ph). ^{13}C NMR (50.3 MHz, $CDCl_3$). Isomer **I**: δ=18.6 (d, $^{3}J_{C-P}$=13 Hz, *C*H_3,), 30.3 (dd, $^{1}J_{C-P}$=36 Hz, $^{3}J_{C-P}$=10.5 Hz, *C*H_2PPh_2), 33.6 (d, $^{1}J_{C-P}$=36 Hz, *C*H_2PPh), 35.2 (d, $^{1}J_{C-P}$=36 Hz, *C*H_2PPh), 41.9 (dd, $^{2}J_{C-P}$=2 Hz, $^{2}J_{C-P}$=13 Hz, *C*H), 43.9 (s,*C*H). Isomer **II**: δ=15.4 (s, *C*H_3), 30.2 ($^{1}J_{C-P}$=36 Hz, *C*H_2PPh_2), 33.4 (d, $^{1}J_{C-P}$=36 Hz, *C*H_2PPh), 34.9 (d, $^{1}J_{C-P}$=36 Hz, *C*H_2PPh), 40.1 (d, $^{2}J_{C-P}$=11 Hz, *C*H), 40.7 (s, *C*H) MS (EI): *m*/*z*=389 (M−CH_3)$^+$ (100%), 299 (M−Ph−2BH_3)$^+$.

Compound 12

To a solution of Ph_3P (1.15 g, 4.4 mmol) in 20 mL of THF, was added $BH_3.SMe_2$ (2.2 mL, 4.4 mmol) and stirred 12 h at room temperature. Then, lithium (0.3 g, 44 mmol) was added in the reactor. After stirring (1 h 30 min), excess lithium was removed, and *t*-BuCl (0.48 mL, 4.4 mmol) was introduced. After cooling at −78°C, **9** (0.53 g, 1.46 mmol) in 4 mL of THF was added. The mixture was stirred for 15 h. Removal of solvent followed by chromatography on silica gel (hexane/CH_2Cl_2:40/60) afforded **12** (30%) as colorless oil. ^{31}P NMR (81 MHz, $CDCl_3$) δ=(three isomers) 21.9, 22.0, 25 (m, *P*–Ph), 14.9 (m, *P*–Ph_2). ^{1}H NMR (80 MHz, $CDCl_3$) δ=0.5–2.8 (m, 19H, CH, CH_2P, BH_3), 7.2–7.8 (m, 25H, CH arom.). ^{13}C NMR (62.89 MHz, $CDCl_3$), *trans* isomer: δ=30.7 (dd, $^{1}J_{C-P}$=35 Hz, $^{3}J_{C-P}$=12 Hz, *C*H_2PPh_2), 30.8 (dd, $^{1}J_{C-P}$=35 Hz, $^{1}J_{C-P}$=17 Hz, *C*H_2PPh_2), 33.6 (d, $^{1}J_{C-P}$=37 Hz, *C*H_2PPh), 33.7 (d, $^{1}J_{C-P}$=37 Hz, *C*H_2PPh), 42.3 (d, $^{2}J_{C-P}$=3 Hz, *C*H). 43.1 (d, $^{2}J_{C-P}$=10 Hz, *C*H), 128.4–132.8 (CH arom.). MS (EI): *m*/*z*=511 (M−Ph−BH_3)$^+$, 389 (M-PPh_2−2BH_3)$^+$.

Compound 14a

To a solution of dichlorozirconocene (Cp_2ZrCl_2) (2.6 g, 8.76 mmol) in 30 mL of THF at −78°C was added *n*-BuLi 1.6 M (10.9 mL, 17.52 mmol). The resulting mixture was stirred for 1 h at −78°C. To this new solution was added the tetraallyl silane **13a** (4.17 mmol) in 5 mL THF at −78°C. The solution was stirred for 12 h at room temperature. The intermediate **14a** was identified by ^{1}H NMR. ^{1}H NMR (80 MHz, $CDCl_3$) δ=0.6–2.3 (m, 20H, CH_2Si,CH, CH_2Zr), 6.1 (s, 20H, Cp).

Compound 14b

To a solution of dichlorozirconocene (Cp_2ZrCl_2) (2.7 g, 9.3 mmol) in 30 mL of THF at −78°C was added *n*-BuLi 1.6 (11.6 mL, 18.6 mmol). The resulting mixture was stirred for 1 h at −78°C. To this new solution was added the tetraallyl silane germane **13b** (4.17 mmol) in 5 mL THF at −78°C. The solution was stirred for 12 h at room temperature. The intermediate **14b** was detected by ^{1}H NMR. ^{1}H NMR (80 MHz, $CDCl_3$) δ=0.6–2.3 (m, 20H, CH_2Ge, CH, CH_2Zr), 6.1 (s, 20H, Cp).

Compounds 15a–b[14]

To a solution of **14a–b** (4.2 mmol) in 25 mL of THF, was added a solution of bromine (2.82 g, 20.85 mmol) for **15a** or (3.4 g, 21.2 mmol) for **15b** in CCl_4 (20 mL) at −78°C. The reaction was quenched (room temperature) with H_2SO_4 10% (30 mL), extracted with ether (3×20 mL) and dried ($MgSO_4$). Removal of solvent followed by precipitation in pentane and ether afforded **15a** (43%, m.p.: 146°C) and **15b** (48%, m.p.: 150°C) as white powder. ^{1}H NMR (80 MHz, $CDCl_3$) δ=0.5–2.2 (m, 12H, CH_2M, CH), 3.4–3.6 (m, 8H, CH).

Compound 16a

To a solution of Ph_3P (0.53 g, 2.02 mmol) in 10 mL of THF, was added BH_3.SMe_2 (1.02 mL, 2.02 mmol). The mixture was stirred for 12 h at room temperature. Then, lithium (0.14 g, 20.2 mmol) was added in the reactor. After stirring (1 h 30 min), the excess of lithium was removed, and *t*-BuCl (0.22 mL, 2.02 mmol) was introduced. After cooling at −78°C, **15a** (0.24 g, 0.24 mmol) in 4 mL of THF was added. The mixture was stirred for 15h. Removal of solvent followed by chromatography (hexane/CH_2Cl_2:30/70) afforded **16a** (26%) as white powder. m.p: 160–161°C. ^{31}P NMR (81 MHz, $CDCl_3$) δ=14.7 (m). ^{1}H NMR (250 MHz, $CDCl_3$) δ=0–2.4 (m, 32H, CH_2Si, CH, CH_2P, BH_3), 7.2–7.8 (m, 40H, CH arom.). ^{13}C NMR (62.89 MHz, $CDCl_3$) δ=19.9 (s, *C*H_2Si), 32.3 (d, $^1J_{C-P}$=35 Hz, *C*H_2P), 41.9 (d, $^2J_{C-P}$=12 Hz, *C*H). MS (DCI/NH_3): *m*/*z*=1006 (M,NH_4)$^+$, 975 (MH−BH_3). Anal. Calc. for $C_{60}H_{72}SiP_4B_4$: C,72.93; H, 7.29; found: C, 70.93; H, 7.38%.

Compound 16b

A solution of Ph_3P (0.7 g, 2.7 mmol) in 10 mL of THF was treated with BH_3.SMe_2 (1.4 mL, 2.7 mmol) and stirred for 12 h at room temperature. After addition of lithium (0.15 g, 21 mmol), the mixture was stirred for 1 h 30 min, then excess lithium was removed, and *t*-BuCl (0.3 mL, 2.7 mmol) was introduced. After cooling at −78°C, **15b** (0.32 g, 0.75 mmol) in 4 mL of THF was added. The mixture was stirred for 15 h. Removal of solvent followed by chromatography on silica gel (hexane/CH_2Cl_2:40/60) afforded **16b** (23%) as white powder. m.p: 102–105°C. ^{31}P NMR (81 MHz, $CDCl_3$) δ=15 (m). ^{1}H NMR (250 MHz, $CDCl_3$) δ=0.3–2.3 (32H, CH_2Ge, CH_2P, CH, BH_3), 7.2–7.7 (40H, PH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ=19.5 (s, *C*H_2Ge), 32.3 (d, $^1J_{C-P}$=35.3 Hz, *C*H_2P), 42.4 (d, $^2J_{C-P}$=11.5 Hz, *C*H), 128–132 *CH* arom.). MS (DCI/NH_3): *m*/*z*=1051 (M, NH_4)$^+$ (^{72}Ge), 1020(M−BH_3)$^+$ (^{72}Ge).

Compound 17b

To a solution of **14b** (2.1 mmol) in 25 mL of THF, was added $PhPCl_2$ (1.2 mL, 4.2 mmol) at room temperature. The mixture was stirred for 3 h 30 min, then BH_3.SMe_2 was added (8.4 mmol, 4.2 mL) at room temperature. After 12 h, the solvent was removed in vacuo and the product was extracted from the residue with CH_2Cl_2. Removal of solvent followed by chromatography on silica gel (hexane/CH_2Cl_2; 50/50) afforded **17b** (37%) as white powder. m.p.: 218–219°C. ^{31}P NMR (81 MHz, $CDCl_3$) δ=+34.9 (m). ^{1}H NMR (250 MHz, $CDCl_3$) δ=0–2.5 (m, 26H, CH_2Ge, CH_2P, CH, BH_3), 7.3–7.7 (m, 10H, Ph). ^{13}C NMR (62.89 MHz, $CDCl_3$). Isomer **I**: δ=19.8 (d, $^3J_{C-P}$= 10.8 Hz, *C*H_2Ge), 20.0 (d, $^3J_{C-P}$=10.3 Hz, *C*H_2Ge), 32.5 (d, $^1J_{C-P}$=38 Hz, *C*H_2P), 33.3 (d, $^1J_{C-P}$=40 Hz, *C*H_2P), 50.3 (s, *C*H), 51.9 (d, $^2J_{C-P}$=4.3 Hz, *C*H). Isomer **II**: δ=20.1 (d, *C*H_2Ge, $^3J_{C-P}$=8.6 Hz), 20.4 (d, $^3J_{C-P}$=8.8 Hz, *C*H_2Ge), 32.8 (d, $^1J_{C-P}$=34.2 Hz, *C*H_2P), 33.3 (d, $^1J_{C-P}$= 34 Hz, CH_2P), 50.3 (s, *C*H), 51.9 (d, $^2J_{C-P}$=4.3 Hz, *C*H). MS (DCI/NH_3): *m*/*z*=500 (M, NH_4)$^+$, 468 (M-BH_3)$^+$, 454 (M−2BH_3)$^+$. Anal. Calc. for $C_{24}H_{36}B_2GeP_2$: C, 59.97; H, 7.49; found: C, 59.63; H, 7.55%.

References

1. Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435.
2. (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (c) Negishi, E.; Zhang, Y.; Cederbaum, F. E.; Webb, M. B. *J. Org. Chem.* **1986**, *51*, 4080. (d) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (e) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (f) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (g) Negishi, E.; Miller, S. R. *J. Org. Chem.* **1989**, *54*, 6014. (h) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Paquette L. A. Eds. Pergamon Press, 1991, vol. 5, 1163.
3. (a) Gordon, G. J.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1997**, 1045. (b) Barluenga, J.; Sanz, R.; Fananas, F. J. *J. Org. Chem.* **1997**, *62*, 5953. (c) Mori, M.; Kuroda, S.; Zhang, C. S.; Sato, Y. *J. Org. Chem.* **1997**, *62*, 3263.
4. (a) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (b) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105. (c) Bird, A. J.; Taylor, R. J. K.; Wei, X. *Synlett.* **1995**, 1237.

5. (a) Metzler, N.; Nöth, H.; Thomann, M. *Organometallics* **1993**, *12*, 2423. (b) Desurmont, G.; Klein, R.; Uhlenbrock, S.; Laloë, E.; Deloux, L.; Giolando, D. M.; Kim, Y. W.; Pereira, S.; Srebnik, M. *Organometallics* **1996**, *15*, 3323.
6. (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1989**, *111*, 4495. (c) Mori, M.; Saitoh, F.; Uesaka, N.; Okamura, K.; Date, T. J. *J. Org. Chem.* **1994**, *59*, 4993. (d) Mori, M.; Uesaka, N.; Saitoh, F.; Shibasaki, M. *J. Org. Chem.* **1994**, 5643. (e) Kemp, M. I.; Whitby, R. J.; Coote, S. J. *Synlett* **1994**, 451. (f) Takahashi, T.; Kondakov, D. Y.; Suzuki, N. *Organometallics* **1994**, *13*, 3411. (g) Negishi, E.; Maye, J. P.; Choueiry, D. *Tetrahedron* **1995**, *51*, 4447. (h) Barluenga, J.; Sanz, R.; Fananas, F. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1009.
7. (a) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623. (b) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662. (c) Horn, T. D.; Baumgarten, M.; Gerghel, L.; Enkelmann, V.; Müllen, K. *Tetrahedron Lett.* **1993**, *34*, 5889.
8. (a) Mirza-Aghayan, M.; Boukherroub, R.; Etemad-Moghadam, G.; Manuel, G.; Koenig, M. *Tetrahedron Lett.* **1996**, *37*, 3109. (b) Mirza-Aghayan, M.; Boukherroub, R.; Oba, G.; Manuel, G.; Koenig, M. *J. Organomet. Chem.* **1998**, *564*, 61.
9. (a) Hey, E.; Lappert, M. F.; Atwood, J. L., Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1987**, 597. (b) Binger, P.; Biedenbach, B.; Krüger, C.; Regitz, M. *Angew. Chem. Int. Ed. Engl.* **1987**, 764. (c) Zablocka, M.; Boutonnet, F.; Igau, A.; Dahan, F.; Majoral, J. P.; Pietrusiewicz, K. M. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1735. (d) Le Floch, P.; Kolb, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2065. (e) Hey-Hawkins, E.; Kurtz, S.; Baum, G. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 239. (f) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914. (g) Zablocka, M.; Miquel, Y.; Igau, A.; Majoral, J. P.; Skowronska, A. *Chem. Commun.* **1998**, 1177.
10. (a) Gourdel, B.; Pelon, P.; Toupet, L.; Le Corre, M. *Tetrahedron Lett.* **1994**, *35*, 1197. (b) Brodie, N.; Jugé, S. *Inorg. Chem.* **1998**, *37*, 2438 and references cited therein. (c) Lipshutz, B. H.; Buzard, D. J.; Yun, C. S. *Tetrahedron Lett.* **1999**, *40*, 201.
11. (a) Fell, B.; Barhmann, H. *Synthesis* **1974**, 119. (b) Morimoto, T.; Ando, N.; Achiwa, K. *Synlett.* **1996**, 1211. (c) Guillen, F.; Moinet, C.; Fiaud, J. C. *Bull. Soc. Chim. Fr.* **1997**, 371. (d) Holz, J.; Quirmbach, M.; Schmidt, U.; Heller, D.; Stürmer, R.; Börner, A. *J. Org. Chem.* **1998**, *63*, 8031.
12. (a) Smith, G. L.; Kelly, H. C. *Inorg. Chem.* **1969**, *8*, 2000. (b) Myers, W. H.; Ryschkewitsch, G. E. *Phosphorus* **1975**, *5*, 97. (c) Imamoto, T.; Hikosaka, T. *J. Org. Chem.* **1994**, *56*, 6753.
13. (a) Ellermann, J.; Dorn, K. *Chem. Ber.* **1966**, 653. (b) Antberg, M.; Pregel, C.; Dahlenburg, L. *Inorg. Chem.* **1984**, *23*, 4170. (c) Schmidbaur, H.; Stützer, A.; Herdtweck, E. *Chem. Ber.* **1991**, *124*, 1095. (d) Seitz, Th.; Huttner, G.; Büchner, M. *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 1813.
14. (a) Déjean, V.; Manuel, G. XIth Symposium International de la Chimie des Organosiliciés, Montpellier, 1996. (b) Oba, G.; Moreira, G.; Déjean, V.; Manuel, G.; Koenig, M. *Société Française de Chimie*, Pau, 1998. (c) Déjean,V.; Gornitzka, H.; Oba, G.; Koenig, K.; Manuel, G., to be submitted.
15. Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993,** *34*, 4523.