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Stereoselective synthesis of new hetero(P, Si, Ge, Sn)cyclic derivatives from zirconium diyne and diene complexes

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Abstract

The dipropargylic derivatives of Si, Ge, P, **1a–c,** react with the zirconocene entity 'Cp$_2$Zr' and give the intermediate bicyclocomplexes **2a–c** characterized by ^{1}H and ^{31}P-NMR. The electrophilic addition of H$^+$, Br$_2$ leads to the corresponding *exo* dienic metallacyclopentanes **3**,**4**. The cyclozirconation reaction with hetero-diallylic compounds **5a–d** gives the metallacyclopentanes **7–15**, after reaction with different electrophiles such as H$^+$, PCl$_3$, PhPCl$_2$, Ph$_2$PCl or Ph$_2$PCl(BH$_3$), Br$_2$. The cyclozirconation reaction of diynes is stereoselective and leads to the *E*,*E*-exocyclic dienes whereas the selectivity of cyclozirconation of dienes depends on the substituents on the heteroatom. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconocene; Zirconacomplexes; Cyclozirconation; Hetero(Si, Ge, P)cyclopentanes; Bis methylene hetero(Si, Ge, P)cyclopentanes; Phosphines; Diphosphines; Selectivity

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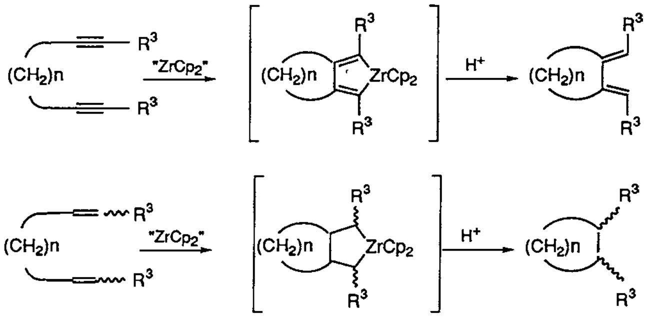
1. Introduction

This study is a part of a larger project developed in our laboratory related to the synthesis and the use of heterocyclic molecules to prepare new compounds such as organometallic polymers, precursors to drugs, chiral molecules and π metalled species [1].

Examination of the literature shows that several series of transition metal complexes such as metallocenes permit the synthesis of cyclic derivatives from polyunsaturated heterocycles. The cyclozirconation reaction, discovered independently by Nugent [2] and Negishi [3], is one of the most powerful carbometallation [4] methods Scheme 1).

Heterodiynes and dienes containing oxygen [5], boron [6], nitrogen ([3]b) [7] and silicon [8] have been reacted with zirconium dicyclopentadienyl dichloride in the presence of n-butyllithium. Such reactions have been studied by Buchwald [9], Negishi [10] and Waymouth [11]. We will consider the simplified Scheme 2 in which the reactive species 'Cp$_2$Zr' is generated by alkylation of Cp$_2$ZrCl$_2$ with n-butyllithium, followed by the elimination of 1-butene. Both σ and π bonded structures are intermediates in this process [12].

In this paper, we will present our results [13] concerning reactions of the in situ generated 'Cp$_2$Zr' species with dipropargylic **1a–d** and diallylic **5a–d** derivatives of silicon, germanium, tin and phosphorus. We will



Scheme 1.

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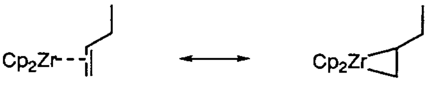


Scheme 2.

discuss the reactivity of these intermediates with different electrophiles and we will present the stereochemical properties of the hetero (Si, Ge, P) cyclopentanes.

2. Results and discussion

2.1. Heterodiynes cyclozirconation

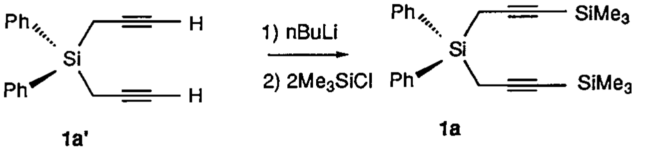
Heterodiynes **1a–d** were synthesized according to literature methods from dichloro-derivatives of Si, Ge, Sn, P and the corresponding propargyl Grignard reagents. For unsubstituted propargylic derivatives as **1a′** ($R^3 = H$), a competitive reaction leads, even at 0°C, to a mixture of dipropargylic, allenic propargylic and diallenic silicon derivatives. These propargylic/allenic rearrangements become the major process with dichlorotin derivatives.

With dichlorophosphines, the reaction of the unsubstituted propargylic Grignard leads to polymeric materials.

To prevent such undesired reactions, we have prepared trimethylsilyl substituted propargylic derivatives ($R^3 = SiMe_3$) of Si, Ge, Sn, P (Scheme 3). This has been achieved by the propargylic substitution of **1a′** according to a two step reaction. Compound **1a** was thus obtained in an 84% yield.

Alternatively, compounds **1a–d** can be prepared from propargylic alcohol as acetylenic starting material [14]. The synthetic Scheme 4 summarizes the four step reactions process. Note that, a bulky substituent is necessary to prevent oxidation of the trivalent phosphorus atom in **1c** [15].

The cyclozirconation reaction was achieved by two methods: the first method A consists of adding an hexane solution of *n*-butyllithium to the (diyne **1a–d**, dichlorozirconocene) solution at −78°C. The zircona complexes **2a–d** were directly characterized by NMR at room temperature (r.t.) (Table 1). In the second method B, *n*-butyllithium solution was added at −78°C to the dichlorozirconocene. The heterodiyne **1a–d** was then added at low temperature. These complexes **2a–d** were treated by electrophiles in order to cleave the zirconium–carbon bonds and to generate corresponding heterocyclopentanes (Scheme 5).



Scheme 3.

In the case of diphenyl dipropargyl silane **1a′**, methods A and B give 1,1-diphenyl 3,4-bis-methylene 1-silacyclopentane **3a′** in low yield by treatment of complex **2a′** with diluted hydrochloric acid. Compound **3a′** has been previously prepared by C. Laurent [16] using a different method.

For bis *α*,*ω*-(trimethylsilyl) dipropargylsilane compound **1a**, prepared according to method B, the cyclozirconation followed by protonation gives the silacyclopentane **3a** in a 72% yield. For **1b**, (M = Ge) and **1c** (M = P), yields are lower than 50%. The later result is probably the consequence of the presence of the bulky group required to prevent phosphorus oxidation and zirconium–phosphorus interaction [17]. In the case of **1d** (M = Sn), the cyclozirconation reaction was unsuccessful.

The selective cyclozirconation of **1a** leads to **3a** isomer in the *s-cis* (*EE*) exocyclic configuration. The *s-trans* isomer is quantitatively obtained by heating whereas the photochemical irradiation (300 nm in benzene) gives first the corresponding *s-cis* (*E*,*Z*) and then the *s-cis* (*Z*,*Z*) isomer ([13]a).

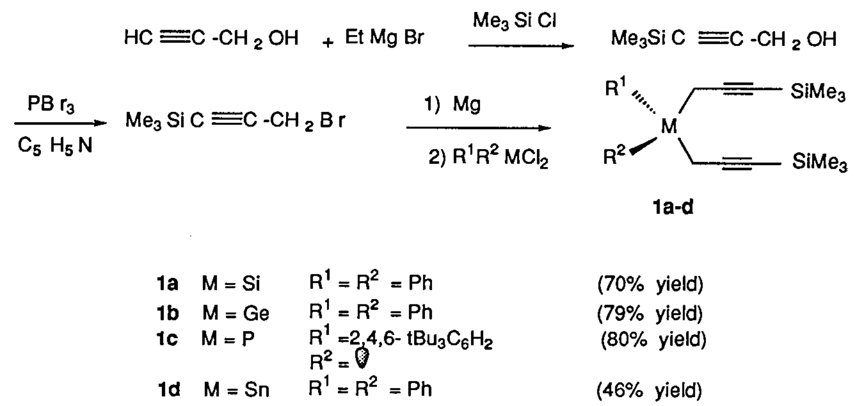
At low temperature, bromine reacts as an electrophile with zirconium-sila (and germa) complexes **2a–b**. The corresponding 3,4-bis(bromo-trimethylsilylmethylene)1-sila (and germa) cyclopentanes **4a–b** were isolated and characterized (Scheme 6):

Comparison of ^1H and ^{13}C-NMR spectra of **3a** and **4a–b** is interesting from a stereochemical point of view. In compounds **4a–b**, the two bulky bromine atoms in the *endo* position induce a noticeable and stable twisting of the silacyclopentane ring. So, the two hydrogen atoms of the methylene group in *α* to silicon are always magnetically equivalent in **3a** whereas they remain an AB system in **4a–b** in the temperature range (−80–+90°C).

2.2. Heterodienes cyclozirconation

Heterodienes **5a–d** were prepared by known methods and then reacted with dichlorozirconocene in the presence of *n*-butyllithium, according to methods A or B. 7-Hetero-3-zirconabicyclo[3.3.0] complexes **6a–b** were characterized in THF solution by ^1H-NMR spectra (see Table 1). Zirconacomplexes **6a–d** were treated with dilute hydrochloric acid and the heterocyclopentanes **7a–c** were isolated and fully characterized (Scheme 7).

It appears that the cyclozirconation reaction is highly dependent on the nature of the heteroatom M and its substituents R^1 and R^2. The best results (82% yield) were obtained with the Ph_2Si group (**7a$_1$**). In the case of Me_2Si (**7a$_2$**), Ph_2Ge (**7b**) and ArP (**7c$_2$**) yields are lower (60, 40 and 33%, respectively). For the other unsaturated phosphorus derivatives **7c$_1$** ($R^1 = Ph$, $R^2 = O$) and



Scheme 4.

n-Bu$_2$Sn groups($\mathbf{7d_2}$), the cyclozirconation reaction does not occur.

Zirconium complexes **6a–d** were also treated with chlorophosphines. With trichlorophosphine, the complex **6a** does not lead to the expected 3-phospha-7-silabicyclo[3.3.0]octane but rather to the mono **8a** and disubstituted dichlorophosphines **9a** (Scheme 8).

With phenyldichlorophosphine, the reaction takes place at r.t. (Scheme 9) and the bicyclo derivatives **10a–b** were isolated and fully characterized.

For **6b**, (M = Ge), the purification leads to the corresponding phosphine oxide **10b′** (δ ^{31}P = 61.6). For M = Sn, the very unstable adduct $\mathbf{10d_1}$ was characterized only by NMR (δ ^{31}P = − 4) and mass spectra (m/z = 465 [MH]$^+$).

The electrophilic reaction of diphenylchlorophosphine on complex **6a** at 20°C leads to a mixture of the mono phosphine **11a** (δ ^{31}P − 18.9), as the major product and **12a** (δ ^{31}P − 19.9) as the minor one (Scheme 10).The by-product Ph$_2$P(O)OBu results from the addition of the phosphine to the mediated zirconocene ring opening of THF.

Similarly, the borane complex [Ph$_2$PCl, BH$_3$] reacts with **6a** and gives the corresponding borane complexed mono and diphosphines **13a** and **14a** in the same ratio as the previous experiment (Scheme 11).

An alternative way to obtain diphosphines **14a** involves reaction of diphosphine **12a**, (Scheme 12) purified by chromatography on silica column, with borane.

2.3. Stereochemical properties of the hetero(Si, Ge, P)cyclopentanes

Results reported in the literature ([2]b) [5]([7]d,g) [18,19] indicate that the stereochemistry of the cyclozirconation depends on several parameters. Among these are the relative position of the two C–C double bonds in the starting diene and the nature of the substituents on the zirconium atom. For carbon chains of suitable length, cyclozirconation is both a regio and stereoselective process if appropriate ligands on zirconium are utilized. This reaction may produce heterocyclopentanes having a well defined stereochemistry. For this reason, we have examined the influence of the different heteroatoms and their substituents on the stereochemistry of the heterocyclopentanes.

2.3.1. Stereochemistry of metallacyclopentanes $\mathit{7a_1}$–$\mathit{7a_2}$

In order to precisely determine the stereochemical properties of **7a**, we prepared the corresponding silacyclopentanes by catalytic hydrogenation of 3,4-dimethyl-1-metallacyclopent-3-enes **16a** (Scheme 13).

It appears that the catalytic hydrogenation method gives a 70/30 ($\mathbf{7a_1}$), 76/24 ($\mathbf{7a_2}$) mixture of *cis*/*trans* isomers whereas the cyclozirconation–protonation reaction is stereoselective and shows the formation of the *trans* isomer only. For the *cis* isomer $\mathbf{7a_2}$, the two methyl groups on the silicon atom are diastereotopic. On the other hand in the *trans* isomer $\mathbf{7a_2}$, the two methyl groups are magnetically equivalent and give only a single signal in either ^{1}H and ^{13}C-NMR.

We observed the same type of magnetic properties for the *ipso* carbons of the two phenyl groups bonded to Si and Ge in the compounds **15a–b** and **12a**.

Based on similar NMR data for compounds **15a–b** and **12a**, we conclude that the cyclozirconation is a *trans* -stereoselective process and that the electrophilic cleavage of the Zr–C bonds, by various electrophiles, proceeds with retention of configuration.

2.3.2. Stereochemistry of phosphines *7c* and *10a–b*

A coupling constant between the *ipso* carbon bonded to the phosphorus atom ($^1J_{CP}$ = 23 Hz) is observed in the^{13}C-NMR. Carbon atoms C$_6$ and C$_7$ (Scheme 14) in α position with respect to P are not equivalent ($^1J_{C7P}$ = 39.3 Hz; $^1J_{C6P}$ = 37.4 Hz). Carbon atoms C$_3$ and C$_4$ in β position with respect to P are also magnetically different. A coupling constant with Phosphorus ($^2J_{C6P}$ = 4.3 Hz) is only observed for C$_3$. For carbon

Table 1
NMR parameters of zirconabicycle intermediates

Number of compounds	δ ^{1}H					δ ^{31}P	Solvent
	Cp	H_2CM	H–C	Ph	Me_3Si		
2a	6.0	2.0(s)		7.3–7.7(m)	0.1(s)		$CDCl_3$
2b	5.96(s)	2.2(s)		7.2–7.6(m)	0.2(s)		C_6D_6
	5.95(s)	2.1(s)		7.3–7.6(m)	0.1(s)		$CDCl_3$
2c	6.0–6.05	1.5(m)		7.1	0.1(s)	−19.5(THF)	$CDCl_3$
6a$_1$	5.8–5.9		0.9–1.7	7.2–7.7			C_6D_6
	5.9–6.1		0.5–1.7	7.3–7.6			$CDCl_3$
6b	5.9		0.6–1.7	7.1–7.7			C_6D_6
	5.96–5.99(d)		0.6–1.6	7.2–7.7			$CDCl_3$

atoms C_2 and C_5 in α position with respect to Si, we only observed the coupling between C_5 and the phosphorus atom ($^3J_{C5-P} = 4.4$ Hz).

The ^{1}H-NMR spectra indicates two different $^3J_{HCP}$ coupling constants for the hydrogens bonded to C_3 and C_4: $^3J_{HC3P} = 30$ Hz and $^3J_{HC4P} = 0$. The notable effects observed for the $^3J_{HP}$ values are a consequence of the relative orientation of the phosphorus lone pair towards the plane of the ring atoms. The corresponding coupling constants are enhanced when their respective positions are *syn* to one another [20]. So, we may deduce that the protons directly bonded to C_3 and C_4 are in a *trans* configuration.

The two methyl substituents on the phospholane **7c$_2$** are equivalent ($\delta = 15.9$) by ^{13}C-NMR and have the same coupling constant with the phosphorus atom ($^3J_{CP} = 4.3$ Hz). We may conclude that the two methyl goups are *cis* and probably in a *syn* orientation to the lone pair of phosphorus atoms (Scheme 15).

The difference in stereoselectivity of the zirconacyclisation is a consequence of the nature of the substituents bonded to the heteroatom. When the substituents are identical ($R^1 = R^2$) the products are obtained in *trans* configuration. This configuration induces an intrinsic chirality to the phosphines **10** or to the diphosphines **12** and **14**. When the substituents are different ($R^1 = Ar$, $R^2 =$ lone pair), the preferential configuration is *cis* and the considered molecules as **7c$_2$** are achiral.

3. Conclusion

The heterocyclisation of dipropargyl and diallylic derivatives of silicon, germanium, phosphorus and tin have been carried out. Resulting zirconacomplexes have been reacted with electrophiles as proton, bromine and various chlorophosphines. It appears that the results depend on the nature of the heteroatom and its substituents.

So, the decrease of the Heteroatom–Carbon bond enthalpy (Si > Ge > P > Sn) induces a notable lowering of the stability of the starting material, compared to the unsaturated analogs in the carbon series. For example, the relative weakness of Sn–C bond may explain the lack of cyclozirconation products in the tin series.

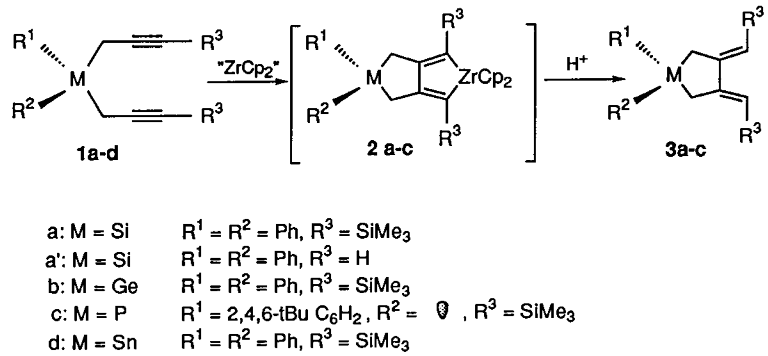
In Si and Ge series, the expected cycloadducts are synthesized with higher yields than the P analogs. Moreover, in the Phosphorus series, the cyclozirconation failed in the case of the phosphine oxide. The oxophilicity of Zirconium or the basicity of the phosphine probably prevents the metallacyclisation. A bulky substituent in phosphine is required in order to decrease its basicity and to allow the cyclozirconation of the heterodiene and heterodiyne.

Finally, the selectivity of such heterocyclisations is closely dependent on the (a)symmetry induced by the steric bulkiness of the heteroatom's substituents. With two identical substituents on the heteroatom (Si, Ge), the resulting cyclopentanes are in *trans* configuration. On the other hand, with two different substituents on the heteroatom (P), the resulting phospholane is substituted in *cis* configuration.

4. Experimental section

4.1. General procedure

All manipulations, except chromatography on silica gel, were carried under an argon atmosphere. THF, diethyl ether and hexane were distilled from solutions of sodium/benzophenone and stored under argon. All NMR spectra were recorded at 25°C on Bruker AC 80 and 250 MHz in deuteriochloroform and deuteriobenzene. The ^{1}H and ^{13}C chemical shifts were referenced relative to TMS while ^{31}P-NMR shifts were 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 serieII gas chromatograph equipped with



Scheme 5.

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 1600Series FTIR.

4.2. Compounds **3a–c**

To a solution of dichlorozirconocene (1.16 g, 4 mmol) in 15 ml of THF at −78°C was added *n*-BuLi 1.6 M (5 ml, 8 mmol). The resulting mixture was stirred for 1 h at −78°C. To this solution was added metalladipropargyles **1a–d** (3.21 mmol) in 5 ml THF at −78°C. The solution was stirred for 2 h at r.t. The reaction was quenched (0°C) with 10% HCl (25 ml), extracted with ether (3 × 50 ml), washed with aqueous sodium bicarbonate and water and dried over $MgSO_4$. Removal of solvent followed by chromatography on silica gel and eluted with hexane/ether: 98/2 ($R_f = 0.71$), hexane/ether: 99/1 ($R_f = 0.71$), hexane/ether: 95/5 ($R_f = 0.81$)] afforded **3a**, 0.94 g as colorless liquid (72%), **3b**, 0.65g as colorless liquid (45%) and **3c**, 0.79g as yellow oil (49%).

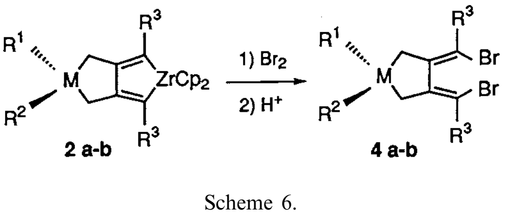
3a': ^{1}H-NMR ($CDCl_3$): δ 2.21 (m, 4H, CH_2Si), 4.71–4.92 (m, 2H, CH_2Si), 5.23–5.36 (m, 2H, $=CH_2$), 7.24–7.61 (m, 10H, Ph). Ms: *m*/*z* 262 $[M]^{+\cdot}$, 184 $[MH-Ph]^{+\cdot}$, 105 $(MH-Ph-C_6H_8]^+$.

3a *S-cis*:^{1}H-NMR ($CDCl_3$): δ 0.13 (s, 18H, Me_3Si), 2.18 (d, $^4J_{HH} = 1.7$ Hz, 4H, CH_2Si), 5.96 (t, $^4J_{HH} = 1.7$ Hz, 2H, CH), 7.24–7.49 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$) '*J*-mod' δ 0.24 (s, $\underline{C}H_3$ Si), 20.71 (s, $\underline{C}H_2$ Si), 122.71 (s, =CH), 127.91, 129.81 and 134.83 (CH arom.), 134.70 (C_{ipso} PhSi), 159.56 (s, =C<). Ms: *m*/*z* 406 $[M]^{+\cdot}$, 332 $[M-H-Me_3Si]^+$. Anal. Calc. for $C_{24}H_{34}Si_3$: C, 70.86; H, 8.42. Found: C, 70.77; H, 8.74%.

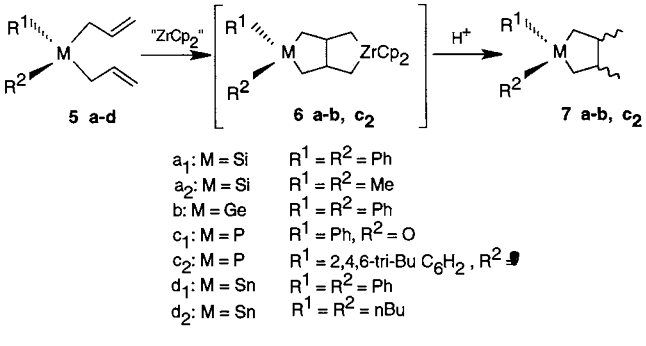
3a *S-trans*: ^{1}H-NMR ($CDCl_3$): δ 0.03 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 2.09 (s, 2H, $\underline{CH_2}SiMe_3$), 2.26 (d,$^4J_{HH} = 1.7$Hz, 2H, $\underline{CH_2}SiPh_2$), 5.88 (t,$^4J_{HH} = 1.5$Hz, 1H, $=\underline{CH}SiMe_3$), 6.06(s, 1H, $=\underline{CH}SiMe3$), 7.15–7.67 (m, 10H, Ph).

3b: ^{1}H-NMR ($CDCl_3$): δ 0.18 (s, 18H, Me), 2.30 (d, $^4J_{HH} = 1.75$, 4H, CH_2Ge), 5.91 (t, $^4J_{HH} = 1.77$, 2H, =CH), 7.34–7.49 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ 0.16 (s, $\underline{C}H_3Si$), 21.09 (s, $\underline{C}H_2Si$), 123.45 (s, =CH), 128.34, 129.21 and 134.19 (CH arom.), 134.04 (C_{ipso}), 162.82 (s, >C=). MS: *m*/*z* 452 $[M]^+$, 378 $[M-Me_3Si]^+$, 363 $[M-Me_3SiH-Me]^+$, 227 $[Ph_2Ge]^+$. Anal. Calc. for $C_{24}H_{34}Si_2Ge$: C, 63.87; H, 7.59. Found: C, 62.98; H, 7.86%.

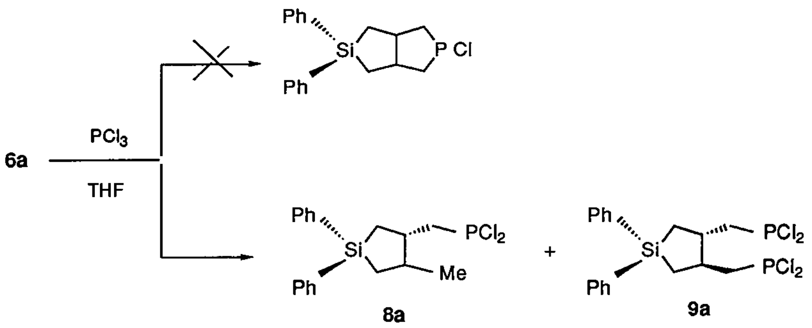
3c: ^{31}P-NMR ($CDCl_3$): δ −11.13. ^{1}H-NMR ($CDCl_3$): δ 0.14 (s, 18H, Me_3Si), 1.26, 1.32 and 1.53 (3s, 27H, CH_3), 3.21–3.31 (m, 4H, CH_2), 5.96 (d, 2H, CH), 7.12 (s, 2H, Ar). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ −0.33 (s, $\underline{C}H_3Si$), 21.71 (s, $CH_3-\underline{C}$ (1'''')), 31.3 (s, $\underline{C}H_3$ (2'''')), 33.33 and 33.58 (2s, $\underline{C}H_3$ (2'' and 2''')), 39.0 (2s, $CH_3-\underline{C}$ (1'' and 1''')), 41.74 (d, $^1J_{PC} = 14.0$ Hz, CH_2P (C_2 and C_5)), 120.3 (d, $^3J_{PC} = 4,3$ Hz, =CH (C_6 and C_7)), 122.47 (s, CH ($C_{3'}$ and $C_{5'}$)), 146.76 (s, C_{ipso} 2', 6' and 4'), 153.85 (d, $J_{CP} = 20,2$ Hz C_{ipso} (1')), 154.25 (s, >C=(C_3, C_4)). MS: *m*/*z* 501 $[MH]^+$ (100%), 485 $[MH-16]^+$, 429 $[MH-72]^+$.



Scheme 6.



Scheme 7.



Scheme 8.

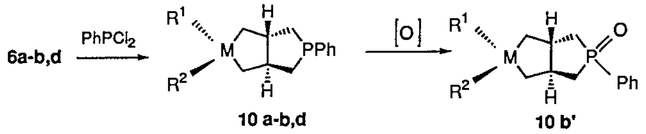
4.3. Compounds ***4a–b***

4.3.1. Compound ***4a***

To a solution of dichlorozirconocene (Cp_2ZrCl_2) (0.72 g, 2.47 mmol) in 15 ml of THF at −78°C was added *n*-BuLi 1.6 M (3 ml, 4.95 mmol). The resulting mixture was stirred for 1 h at −78°C. To this solution was added metalladipropargyle **1a** (1 g, 2.47 mmol) in 5 ml THF at −78°C. The solution was stirred for 2 h at r.t. The mixture was cooled to −78°C and a solution of bromine (1.04 g, 5.8 mmol) in carbon tetrachloride (8ml) was added. The reaction was quenched at r.t. with 10% H_2SO_4 (50 ml), extracted with ether (3 × 50 ml), washed with aqueous sodium bicarbonate and water, and dried ($MgSO_4$). After filtration, the solvent was removed by evaporation under reduced pressure. The residue was purified by chromatography on silica gel and eluted with hexane ($R_f = 0.06$). A white powder (0.50 g), m.p. = 56–58°C was obtained in 35% yield. ^1H-NMR ($CDCl_3$): δ 0.21 (s, 18H, $SiMe_3$), 2.01, 2.39 (AB system, 4H, $J_{AB} = 14.4$ Hz, CH_2), 7.39–7.47 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ 0.59 (s, $\underline{C}H_3Si$), 22.05 (s, $\underline{C}H_2Si$), 120.37 (s, $=\underline{C}-Br$), 128.17, 130.23 and 134.76 (3 s, CH arom.), 133.59 (s, C_{ipso}), 153.90 (s, $>\underline{C}=$). MS: *m*/*z* 582 $[MH+17]^+$, 565 $[MH]^+$. Anal. Calc. for $C_{24}H_{32}Si_3Br_2$: C, 51.05; H, 5.71. Found: C, 51.11; H, 5.73%.

4.3.2. Compound ***4b***

In the same conditions, 1.04g (2.35 equivalent) of bromine in CCl_4 (4 ml) was introduced at −78°C on the intermediate **2b**. We thus obtained, after purification on the Chromatotron apparatus (hexane/CH_2Cl_2: 98/2) 0.78 g of white crystals (52% yield): m.p. 126–127°C. ^1H-NMR ($CDCl_3$): δ 0.28 (s, 18H, $SiMe_3$), 2.09, 2.55 (AB system, 4H, $J_{AB} = 12.5$ Hz, CH_2), 7.4–7.6 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ 0.69 (s, $\underline{C}H_3Si$), 22.32 (s, $\underline{C}H_2Ge$), 120.1 (s, $=\underline{C}-Br$), 128.54, 129.69 and 134.1 (3 s, CH arom.), 135.69 (s, C_{ipso}), 155.11 (s, $>\underline{C}=$). MS: DCI (CH_4) *m*/*z* 608 $[MH]^+$, 595 $[MH-CH3]^+$. Anal. Calc. for $C_{24}H_{32}Si_2GeBr_2$: C, 47.32; H, 5.26. Found: C, 48.12; H, 5.44%.



Scheme 9.

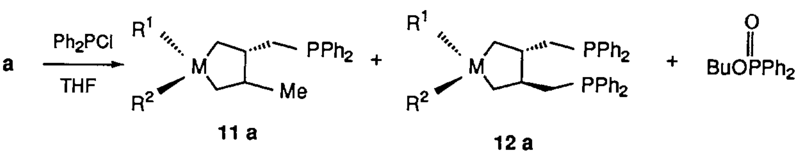
4.4. Compounds ***7a–c***

4.4.1. Cyclozirconation

To a solution of dichlorozirconocene (Cp_2ZrCl_2) (1.16 g, 4 mmol) in 15 ml of THF at −78°C was added *n*-BuLi 1.6 M (5 ml, 8 mmol). The resulting mixture was stirred for 1 h at −78°C. To this new solution was added metalladienes **5a–d** (4 mmol) in 5 ml THF at −78°C. The solution was stirred for 2 h at r.t. The reaction was quenched (0°C) with 10% HCl (50 ml), extracted with ether (or CH_2Cl_2 for **5c$_2$**) (3 × 50 ml).The organic layer was washed with aqueous potassium carbonate and aqueous sodium chloride and dried over anhydrous sodium sulphate. Removal of solvent followed by chromatography on silica gel eluted with hexane (**7a$_1$**); pentane/ether: 98/2 ($R_f = 0.8$) (**7a$_2$**); hexane (**7b**); hexane/ether: 90/10 (**7c$_2$**); afforded **7a$_1$** 0.88 g of white solid (82%), **7a$_2$** 0.35 g of colorless liquid (61%), **7b** 0.50 g of colorless liquid (40%), and **7c$_2$** 0.48 g of yellow oil (33%).

7a$_1$ *Trans*: m.p. = 28–29°C. ^1H-NMR ($CDCl_3$): δ 0.6–1.7 (m, 12H, CH_2, CH and CH_3), 7.3–7.7 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ 21.95 (s, CH_3), 22.68 (s, $SiCH_2$), 42.47 (s, CH), 127.88, 129.21 and 134.7 (CH arom.), 137.18 (C_{ipso}). MS (*m*/*z*) 266 $[M]^+$. Anal. Calc. for $C_{18}H_{22}Si$: C, 81.44; H, 8.31. Found: C, 81.15; H, 8.46%. IR ($CDCl_3$) ν cm^{-1} 3053 (CH arom), 2954 (CH_2).

7a$_2$ *Trans*: ^1H-NMR ($CDCl_3$): δ 0.07 (s, 6H, CH_3Si), 0.16–1.8 (m, 12H, CH_2, CH, CH_3). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ −1.10 (s, CH_3Si), 21.9 (s, CH_3), 23.7 (s, $SiCH_2$), 41.8 (s, CH).



Scheme 10.

7b *Trans*: ^{1}H-NMR (CDCl$_3$): δ 0.9–1.8 (m, 12H, CH$_2$, CH, CH$_3$), 7.34–7.55 (m, 10H, Ph). ^{13}C-NMR (CDCl$_3$): '*J*-mod' δ 21.89 (s, CH$_3$), 23.26 (s, GeCH$_2$), 42.82 (s, CH), 128.19, 128.71 and 134.29 (s, CH arom.), 139.06 (C$_{ipso}$). MS (*m*/*z*) 312 [M]$^+$. Anal. Calc. for $C_{18}H_{22}Ge$: C, 69.52; H, 7.13. Found: C, 70.11; H, 7.28%. IR ν 3049 cm^{-1} (CH arom.).

7c$_2$ *Cis*: ^{31}P-NMR (CDCl$_3$): δ 7.65. ^{1}H-NMR (CDCl$_3$): δ 0.7–1.8 (m, 39H, CH$_2$, CH, CH$_3$ and *t*Bu), 7.1 (2s, 2H, Ar). ^{13}C-NMR (CDCl$_3$): '*J*-mod' δ 15.93 (d, $^3J_{CP} = 4.3$ Hz, $\underline{CH_3}$CH), 30.49 (s, $\underline{C}$–CH$_3$ (*p*)), 31.38, 33.54 and 33.96(3s, CH$_3$ (*p* and *o*)), 38.87 (s, C$_3$ and C$_4$), 39.37 (s, $\underline{C}$–CH$_3$ (*o*)), 41.91 (d, $^1J_{CP} = 13.6$ Hz, PCH$_2$), 121.55 (s, CH, Ar), 145.83 (C$_{ipso}$ Ar (*p*)), 149.90 (C$_{ipso}$ Ar (*o*)), 153.95 (d, $^1J_{CP} = 3.45$ Hz, C–P). MS (*m*/*z*) 360 [M–H]$^+$, 317 [M–H–C$_3$H$_6$]$^+$. IR ν 3049 cm^{-1} (CH arom.).

4.4.2. (b) Hydrogenation

7a$_1$ *Cis*/*trans*: A solution of silacyclopentene **16a$_1$** (2 g, 7.57 mmol) in 60 ml of hexane and 200 mg (1.42 mmol) of palladium on carbon 10% in a autoclave filled with hydrogen at a pressure of 100 bar was maintained at 100°C. After 1 h, the mixture was filtered. Distillation afforded 0.70 g of **7a$_1$** (*cis*/*trans*:70/30) in 35% yield.

^{1}H-NMR (CDCl$_3$): δ 0.70–2.21 (m, 12H, CH$_2$, CH, CH$_3$), 7.3–7.8 (m, 10H, Ph). ^{13}C-NMR (C$_6$D$_6$) 'J mod' δ 19.38 (s, CH$_3$ (*cis*)), 22.03 (s, CH$_3$ (*trans*)), 22.75 (s, SiCH$_2$ (*trans*)), 23.85 (s, SiCH$_2$ (*cis*)), 38.90 (s, CH (*cis*)), 42.55 (s, CH (*trans*)), 130.82 and 136.48 (2s, C$_{ipso}$ (*cis*)), 137.23 (s, C$_{ipso}$ (*trans*)), 127.96, 127.98, 129.28, 129.48, 134.71 and 134.84 (CH arom. (*cis* and *trans*)).

7a$_2$ *Cis*/*trans*: A solution of silacyclopentene **16a$_2$** (2 g, 14 mmol) in 60 ml of hexane and 152 mg (1.42 mmol) of palladium on carbon 10% in a autoclave filled with hydrogen at a pressure of 100 bar, was maintained at 100°C. After 1 h, the mixture was filtered. Distillation of the solution afforded 0.81 g of **7a$_2$** (*cis*/*trans*:76/24) in 41% yield.

Retention time(s): 210 (*trans*); 243 (*cis*). ^{1}H-NMR (CDCl$_3$): δ 0.06 (s, 3 H, CH$_3$Si (*cis*)), 0.07 (s, 6H, CH$_3$Si (*trans*)), 0.15 (s, 3H, CH$_3$Si (*cis*)), 0.16–2.10 (m, 12H, CH$_2$Si, CH, CH$_3$). ^{13}C-NMR (C$_6$D$_6$) '*J*-mod' δ − 1.10 (s, CH$_3$Si (*trans*)), − 0.87 (s,CH$_3$ (*cis*)), 0.19 (s, CH$_3$Si (*cis*)), 17.69 (s, CH$_3$ (*cis*)), 21.02 (s,CH$_2$Si (*cis*)), 22.48 (s, CH$_3$ (*trans*)), 23.76 (s, CH$_2$Si (*trans*)), 38.36 (s, CH (*cis*)), 41.91 (s, CH (*trans*)).

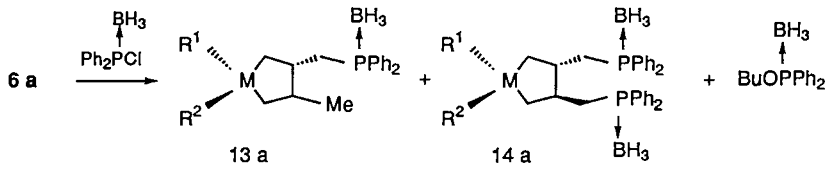
4.5. Compounds **10a–b′**

4.5.1. Compounds **10a$_1$**

To a solution of **6a$_1$** (one equivalent) in 15 ml of THF, PhPCl$_2$ (0.61 g, 3.41 mmol) was added at r.t. The mixture was stirred for 30 min and the solvent was removed in vacuo. The product was extracted from the residue with hexane. The fractions containing product were combined. Removal of solvent followed by chromatography (silica gel eluted with hexane/ether: 97/3) afforded **10a$_1$** as white powder (0.58 g, 46%). M.p. = 108–111°C. ^{31}P-NMR (CDCl$_3$): δ − 1.15.^{1}H-NMR (CDCl$_3$): δ 0.97 (m, 2H, CH$_2$Si), 1.61–1.87 (m, 4 H, CH$_2$Si and CH$_2$P), 2.12 (m, 2 H, CH$_2$P), 2.33 (dd, 1H, CH), 2.59–2.77 (m, 1H, CH, $^3J_{PH} = 30$ Hz), 7.34–7.68 (m, 15H, Ph). ^{13}C-NMR (CDCl$_3$): '*J*-mod' δ 18.28 (s, SiCH$_2$), 18.63 (d, SiCH$_2$, $^3J_{PC} = 4.4$ Hz), 33.47 (d, PCH$_2$(C6), $^1J_{CP} = 37.4$ Hz), 33.67 (d, PCH$_2$(C$_7$), $^1J_{CP} = 39.3$ Hz), 51.47 (d, CH(C$_3$), $^2J_{CP} = 4.2$ Hz), 52.45 (s, CH(C$_4$)), 127.41 (s, C$_p$ (PhP)), 128.49 (d, C$_m$ (PhP), $^3J_{CP} = 5.0$ Hz), 130.32 (d, $^2J_{CP} = 15.8$ Hz, C$_o$ (PhP)), 128.16, 128.33, 129.63, 134.67 and 134.70 (CH arom.), 136.61 (C$_{ipso}$), 136.81(C$_{ipso}$), 143.35 (d, $^1J_{CP} = 23.1$, C$_{ipso}$ of PhP). MS (*m*/*z*) 372 [M]$^+$. Anal. Calc. for $C_{24}H_{25}$ SiP: C, 77.38; H, 6.76. Found: C, 74.06; H, 6.59%.

4.6. Compound **10b′**

To a solution of **6b** (one equivalent) in 15 ml of THF, PhPCl$_2$ (0.53 g, 2.96 mmol) was added at r.t. The mixture was stirred for 6 h and solvent was removed in vacuo. The product was extracted from the residue with hexane. The fractions containing the product were combined. Removal of solvent followed by chromatography (silica gel eluted with chloroform/dichloromethane 1/1) afforded **10b'** as white powder (0.58 g, 45%). M.p. = 178–180°C. ^{31}P-NMR (CDCl$_3$): δ 61.64. ^{1}H-NMR (CDCl$_3$): δ 0.98–2.4 (m, 8H, GeCH$_2$, PCH$_2$), 2.5–2.6 (m, 2H, CH), 7.5–7.7 (m, 15H, Ph). ^{13}C-NMR (CDCl$_3$): '*J*-mod' δ 19.8 (d, GeCH$_2$, $^3J_{CP} = 9.9$ Hz), 20.11 (d, GeCH$_2$, $^3J_{CP} = 9.37$ Hz), 37.90 (d, PCH$_2$, $^1J_{CP} = 40.8$ Hz), 38.9 (d, PCH$_2$, $^1J_{CP} = 39.7$ Hz), 48.43 (d, CHC$_3$, $^2J_{CP} = 6.1$ Hz), 49.6 (d, CHC$_4$, $^2J_{CP} = 6.2$ Hz), 128.4–134.6 (CH arom.), 135.5 (s, C$_{ipso}$ PhGe), 139.51 (d, C$_{ipso}$ PPh, $^1J_{CP} = 6.9$ Hz). MS (*m*/*z*) 435 (MH)$^+$, 357 (M–Ph)$^+$ · IR (CDCl$_3$) ν cm^{-1} 3068 (CH), 2962 (CH$_2$), 1212 (P=O).



Scheme 11.

4.7. Compounds *11a–12a*

4.7.1. Compound *11a*

To a solution of **6a** (one equivalent) in 15 ml of THF, Ph_2PCl (1.47 g, 6.68 mmol) was added at r.t. The mixture was stirred for 9 h and solvent was removed in vacuo. The product was extracted from the residue with hexane. The fractions containing product were combined. Removal of solvent followed by chromatography (silica gel eluted with hexane/ether 98/2) afforded **11a** as white crystals (0.90 g, 30%). ^{31}P-NMR ($CDCl_3$): δ -18.6. ^{1}H-NMR ($CDCl_3$): δ 0.9 (m, 2H, CH_2 Si), 1.1 (d, $^3J_{HH} = 7.5$ Hz, 3H, CH_3), 1.2–2.1 (m, 5H, CH_2Si, CH_2 P, $C\underline{H}-CH_3$), 3.6 (m, 1H, $C\underline{H}-CH_2P$), 7.4–7.8 (m, 20H, Ph). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ 20.51 (d, $SiCH_2$, $^3J_{CP} = 8.6$ Hz), 21.74 (s, CH_3), 22.13 (s, $SiCH_2$), 35.97 (d, PCH_2, $^1J_{CP} = 11.6$ Hz), 42.36 (d, $C\underline{H}CH_3$, $^3J_{CP} = 8.8$ Hz), 44.9 (d, $C\underline{H}CH_2P$, $^2J_{CP} = 12.6$ Hz), 127.85–134.75 (CH arom.), 136.70 and 136.75 (2s, C_{ipso} PhSi), 138.48 (d, C_{ipso} PPh, $^1J_{CP} = 13.2$ Hz), 140.4 (d, C_{ipso} PPh, $^1J_{CP} = 13.4$ Hz). MS (*m*/*z*) 451 $[MH]^+$.

4.7.2. Compound *12a*

A sample of Ph_2PLi was prepared from 0.37 g of Ph_3P (two equivalents, 1.41 mmol) in 8 ml of degazed THF and 0.11 g of lithium (20 equivalents, 15.7 mmol) at r.t. To this solution, after removal of lithium, was added 0.17 ml of *t*BuCl (two equivalents, 1.56 mmol). To a solution of Ph_2PLi (1.41 mmol, two equivalents) in 8 ml of THF, was added dibromo silacyclopentane **15a** (0.32 g, 0.75 mmol) in 4 ml of THF at -78°C. The mixture was stirred for 15 h and the precipitate was removed. Removal of solvent followed by chromatography (silica gel eluted with pentane/ether 98/2) afforded **12a** as white powder (0.30 g, 62%). M.p. 118–120°C. ^{31}P-NMR ($CDCl_3$): δ -19.2. ^{1}H-NMR ($CDCl_3$): δ 1.02–1.36 (m, 4H, CH_2 Si), 1.78–1.90 (m, 4H, CH_2 P), 2.57–2.61 (m, 2H, CH), 7.05–7.52 (m, 30H, Ph). ^{13}C-NMR (C_6D_6): '*J*-mod' δ 20.33 (d, $SiCH_2$, $^3J_{CP} = 9.7$ Hz), 36.36 (d, PCH_2, $^1J_{CP} = 12.6$ Hz), 44.02 (dd, $^2J_{CP} = 12.4$ Hz, $^3J_{CP} = 8.4$ Hz, CH), 129.03–135.11 (CH arom.), 136.9 (s, C_{ipso} PhSi), 139.4 (d, $^1J_{CP} = 14.1$ Hz, C_{ipso} PhP), 140.9 (d, $^1J_{CP} = 13.08$ Hz, C_{ipso} PhP). MS (*m*/*z*) 635 $[MH]^+$. Anal. Calc. for $C_{42}H_{40}SiP_2$: C, 79.48; H, 6.34. Found: C, 78.34; H, 6.38%. IR ν cm^{-1} 3063 (CH), 2922 (CH_2), 1110 (PhSi).

4.8. Compounds *13a–14a*

4.8.1. Compound *13a*

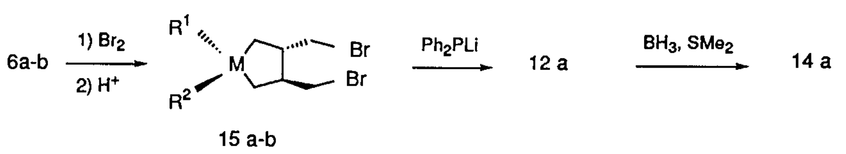
To a solution of Ph_2PCl (1.50 g, 6.8 mmol) in 3 ml of THF [BH_3, SMe_2] (3.4 ml, 6.8 mmol, 2 M in toluene) was added at 25°C. The mixture was stirred for 15 h. The resulting solution was added to **6a** at r.t. After 2 h the solvent was removed in vacuo. The product was extracted from the residue with hexane. The fractions containing the product were combined. Removal of solvent followed by chromatography (silica gel eluted with hexane/dichloromethane 1/1) afforded 1.26 g of **13a** as colorless liquid (40%). ^{31}P-NMR (C_6D_6): δ 14.16. ^{1}H-NMR (C_6D_6): δ 0.82–2.40 (m, 11H, CH_2 Si, BH_3, CH and CH_2P), 0.99 (d, $^3J_{HH} = 7.5$ Hz, 3H, CH_3), 7.11–7.71 (m, 20H, H arom.). MS (*m*/*z*) 482 $[MH+NH_3]^+$(100%), 451 $[MH-BH_3]^+$. IR ($CHCl_3$) ν cm^{-1} 2956 (CH), 2870 (CH_2), 759 (Ph–Si).

4.8.2. Compound *14a*

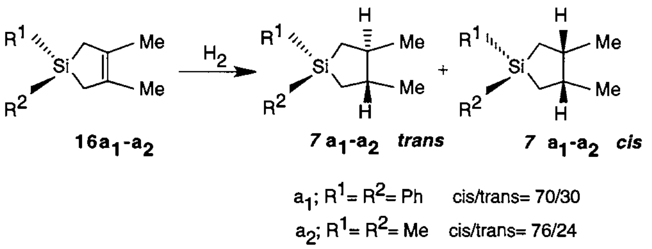
To a solution of diphosphine **12a** (0.1 g, 0.16 mmol) in 4 ml of THF [BH_3, SMe_2] (0.16 ml, 0.32 mmol, 2 M in toluene) was added at 25°C. After 15 h we observed the formation of a precipitate. The supernatant was separated, concentrated and purified by preparative thin layer chromatography (hexane/ether 60/40).This afforded afforded 0.07 g of **14a** as white crystals (67%). ^{31}P-NMR (C_6D_6): δ 14.23. ^{1}H-NMR (C_6D_6): δ 0.50–2.66 (m, 16H, CH_2Si, CH, CH_2P and BH_3), 6.94–7.73 (m, 30H, Ph). ^{13}C-NMR (C_6D_6): '*J*-mod' δ 21.68 (s, CH_2Si), 32,52 (d, CH_2P, $^1J_{CP} = 35$ Hz), 43.27 (d, CH, $^2J_{CP} = 12$ Hz), 129.04–135.07 (CH arom.), 132.13 (s, C_{ipso} PhSi), 132.6 (s, C_{ipso} PhP), 135.9 (s, C_{ipso} PhP). ^{11}B-NMR (C_6D_6): δ -38.6. MS (*m*/*z*) 680 $[MH+NH_3]^+$ (100%), 649 $[MH-BH_3]^{+\cdot}$ IR (C_6D_6) ν cm^{-1} 3050 (CH), 2923 (CH_2), 1108 (Ph–Si). Anal. Calc. for $C_{42}H_{46}B_2P_2Si$: C, 76.15; H, 7.00. Found: C, 74.04; H, 7.20%.

4.9. Compounds *15a–b*

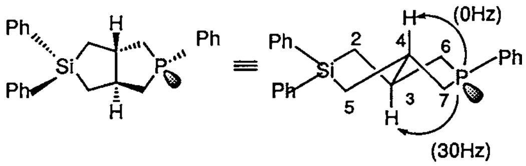
To a solution of **6a–b** (3 mmol) in 15 ml of THF, a solution of bromine (2.35 equivalents) was added in carbon tetrachloride (10 ml) at -78°C. The reaction was quenched (r.t.) with 10% H_2SO_4 (50 ml), extracted with ether (3 × 50 ml), washed with aqueous sodium bicarbonate and water, and dried on anhydrous $MgSO_4$. Removal of solvent followed by chromatogra-



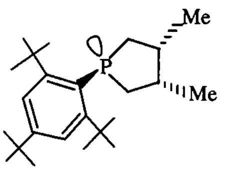
Scheme 12.



Scheme 13.



Scheme 14.



Scheme 15.

phy (silica gel eluted with hexane/ether 97/3 and hexane/ether 90/10) afforded 0.58 g of **15a** (46%) and 0.65 g of **15b** (46%) as white crystals.

15a: M.p. 73–75°C. ^{1}H-NMR ($CDCl_3$): δ 1.43–1.53 (m, 4H, CH_2Si), 2.05–2.26 (m, 2H, 2 CH), 3.59–3.72 (m, 4H, CH_2 Br), 7.37–7.59 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): '*J*-mod' δ 17.07 (s, CH_2Si), 39.76 (s, CH_2Br), 43.48 (s, CH), 128.11, 129.7 and 137.76 (CH arom.), 137.39 (C_{ipso}). MS (*m*/*z*) 424 $[M]^+$ 345 $[M-Br]^+$, 263 $[M-Br-Ph]^+$. Anal. Calc. for $C_{18}H_{20}SiBr_2$: C, 50.96; H, 4.75%. Found: C, 50.72; H, 4.73%. IR (KBr) ν cm^{-1} 3090(CH), 2950 (CH_2), 1421 (C=C), 1400 (C–C), 1169 and 1106 (Ph_2Si).

15b: M.p. 87–89°C. ^{1}H-NMR ($CDCl_3$): δ 1.49–1.63 (m, 4H, CH_2Ge), 2.02–2.25 (m, 2H, 2 CH), 3.50–3.75 (m, 4H, CH_2–Br), 7.41–7.60 (m, 10H, Ph). ^{13}C-NMR ($CDCl_3$): 'J mod' δ 17.82 (s, CH_2Ge), 39.74 (s, CH_2Br), 44.13 (s, CH (C_3 and C_4)), 128.47, 129.24 and 134.22 (CH arom.), 137.34 (C_{ipso}). MS (*m*/*z*) 389 $[MH-Br]^+$, 307 $[MH-2Br]^+$ (100%). Anal. Calc. for $C_{18}H_{20}GeBr_2$: C, 46.11; H, 4.30. Found: C, 45.89; H, 4.25%. IR ($CHCl_3$) ν cm^{-1} 3068 (CH), 2962 (CH_2).

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