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Preparation of Axially Chiral (Racemic) Spirosilanes and Spirogermanes by Selective Spirozirconation

Valérie Déjean, Heinz Gornitzka, Gabriel Oba, Max Koenig,* and
Georges Manuel*

*Laboratoire d'Hétérochimie Fondamentale et Appliquée, UPRESA du CNRS 5069,
Université Paul-Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 04, France*

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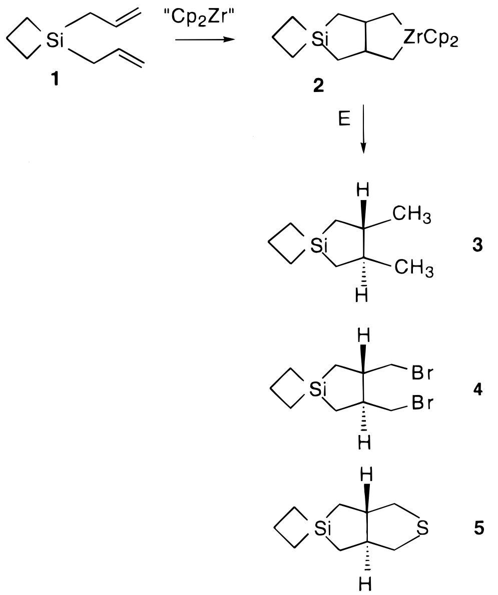
Summary: Chiral (racemic) functional spirosilanes or -germanes, containing two (or four) stereogenic centers, were synthesized by selective cyclozirconation (or spirozirconation) of di- and tetraallylsilanes and di- and tetraallylgermanes.

Spiro functional derivatives containing silicon or germanium as the central atom surrounded by four carbon atoms are useful building units for the preparation of macromolecules and polymers,[1] but few axially chiral heterospiranes have been reported.[2] Recently, the first catalytic asymmetric synthesis of an axially chiral spirosilane of C_2 symmetry via an Rh(I) complex was related.[3]

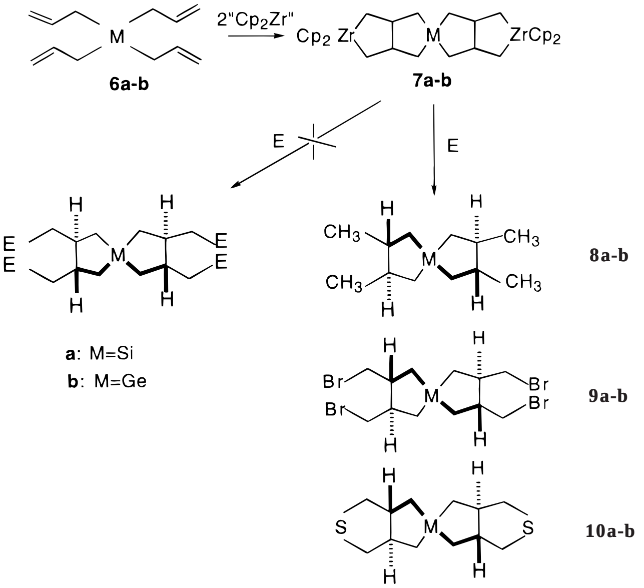
We have used a different strategy to prepare axially chiral (racemic) polyfunctional spirosilanes, taking into account the well-known cyclozirconation reactions.[4−6] We have extended this method to synthesize heterospiranes from allylsilanes and -germanes. Both stoichiometric[4,5] and catalytic methods[6] were used to realize the zirconium-mediated spiro construction from diallylsilacyclobutane (**1**) (Scheme 1) and tetraallylsilane and -germane (**6a**,**b**) (Scheme 2).

After reaction of the precursors of zirconocene Cp_2Zr with **1** or **6a**,**b**, the electrophiles H^+, Br_2, and S_2Cl_2 were added to the corresponding intermediates **2** and **7a**,**b**. All spiranes **3**−**5** and **8**−**10** were isolated in the form of one isomer only. The absence of other stereoisomers in the crude products was shown by NMR spectroscopy.

Scheme 1. Cyclozirconation of 1,1-Diallyl-1-silacyclobutane and Addition of Electrophiles E (H^+, Br_2, S_2Cl_2)



Scheme 2. Spirozirconation of Tetraallylsilane and Germane and Addition of Electrophiles E (H^+, Br_2, S_2Cl_2)



The cyclozirconation reaction creates two chiral carbons in spiranes **3**−**5**, and the spirozirconation generates four chiral carbon atoms in spiranes **8**−**10**. As shown by ^{13}C NMR, all the carbon atoms in α- and β-positions with respect to the central heteroatom are equivalent, respectively. Such results rule out the existence of the *cis* isomer for **3**−**5** and both *cis/cis* and *cis/trans* isomers for **8**−**10**. Consequently, spiranes **3**−**5** are in a *trans* configuration and **8**−**10** in a *trans/trans* configuration. The *trans* configuration of **3**−**5** implies that spiranic skeletons are chiral (racemic). The *trans/*

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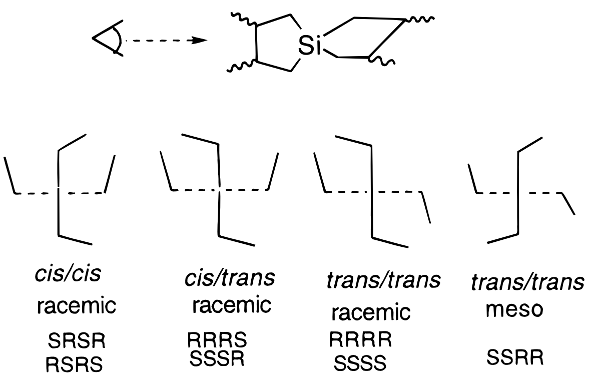
Chart 1. Four Possible Silaspiranic Diastereoisomers



trans configuration of **8**−**10** may correspond to meso (S_4) or racemic (D_2) diastereoisomers[7] (Chart 1). We were unable to discriminate between meso and racemic isomers by NMR spectroscopy, but the X-ray structural determination of **9a** (Figure 1) indicated the axial chirality of the spiro building units induced by the same configuration of the four chiral carbon atoms. This structural study confirmed the *trans/trans* racemic (*RRRR*/*SSSS*) isomer in an quasi orthogonal arrangement of two planes ($\theta = 94°$).

In the literature, zirconocene-promoted stereoselective cyclization of 1,6-dienes led to *cis,trans* disubstituted cyclopentanes with a predominant *trans* isomer.[5] Our recent results confirmed that the selectivity depends on the size of the substituents and on symmetry of the precursors.[8,9] Therefore, a *cis* phospholane was obtained from 2,4,6 tri-*tert*-butylphenyldiallylphosphine[9] but a *cis/trans* phospholane mixture was formed from dissymmetrical phenyldiallylphosphine−borane.[10] Note that dissymmetrical methylphenyldiallylsilane afforded the corresponding *cis*-3,4-dimethylsilacyclopentane by cyclozirconation−protonation,[11] while the symmetrical (C_{2v}) diallylsilanes and -germanes led to *trans* heterocyclopentanes only.[9] By a similar process, the formation of a *trans/trans* isomer was induced in the spirozirconation of symmetrical tetraallylsilane and -germane (T_d). Moreover, a remarkable selectivity was demonstrated for **9a**. This tetrafunctional, racemic synthon constitutes a new example of the very few known axially chiral heterospiranes.[2,3,7]

Experimental Section

Materials. Allylic derivatives of Si and Ge were prepared by the standard Grignard method from the corresponding chloro derivatives.[12] Cp_2ZrCl_2, *n*-BuLi (1.6 M, hexane), and *n*-BuMgCl (2 M, Et_2O) were commercially available from Aldrich. Solvents were purified by conventional methods and distilled immediately before use.

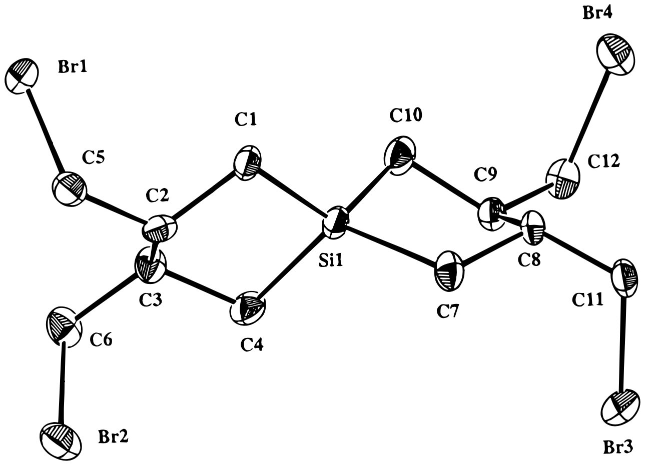


Figure 1. Representation of the crystal structure of **9a**. Anisotropic displacement parameters are depicted at a probability level of 50%. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)−C(1) = 1.877(7), Si(1)−C(4) = 1.870(7), Si(1)−C(7) = 1.880(7), Si(1)−C(10) = 1.887(7), C(5)−Br(1) = 1.953(7), C(6)−Br(2) = 1.961(7); C(4)−Si(1)−C(1) = 94.8(3), Si(1)−C(1)−C(2) = 104.3(4), C(1)−C(2)−C(3) = 106.2(5), C(2)−C(3)−C(4) = 106.6(5), Si(1)−C(4)−C(3) = 103.3(4).

General Data. All manipulations were carried out under an argon atmosphere. All NMR spectra were recorded at 25 °C on a Bruker ARX 400 MHz instrument in $CDCl_3$. The ^1H and ^{13}C chemical shifts are referenced relative to TMS and reported in ppm. Coupling constants are given in Hz. Elemental analyses were performed by the Microanalytical Laboratory of the Ecole Nationale Superieure de Chimie de Toulouse. Melting points were determined on a Buchi-Tottoli apparatus.

Stoichiometric Cyclozirconation and Additions of Electrophiles (H^+, Br_2, S_2Cl_2). To a solution of Cp_2ZrCl_2(1.16 g, 4 mmol) in 15 mL of THF at −78 °C was added *n*-BuLi (1.6 M in hexane; 5 mL, 8 mmol). The resulting mixture was stirred for 1 h at −78 °C. To this solution was added 1,1-diallyl-1-silacyclobutane (**1**; 0.61 g, 4 mmol), tetraallylsilane (**6a**; 0.40 g, 2 mmol), or tetrallylgermane (**6b**; 0.47 g, 2 mmol) in 5 mL of THF at −78 °C. The solution was stirred for 2 h at room temperature. The reaction mixture was quenched at 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 solvents was followed by chromatography on silica gel. Elution with pentane afforded **3** (0.22 g, 35% yield), **8a** (0.31 g, 80% yield), and **8b** (0.35 g, 73% yield) as colorless liquids. To prepare **4**, the solution of complex **2a** (prepared from 4 mmol of **1**) was treated at −78 °C with bromine (0.64 g, 8 mmol) in 20 mL of CCl_4. The reaction mixture was quenched at room temperature with 10% H_2SO_4 (50 mL) extracted with Et_2O (3 × 50 mL), washed with aqueous $NaHCO_3$ and then H_2O, and dried over $MgSO_4$. After filtration, solvents were removed by evaporation under reduced pressure. The residue was purified by chromatography on silica gel and eluted with hexane. Evaporation of solvents gave **4** as a yellow powder (1.01 g, 80% yield), mp: 150 °C. According to this procedure, **9a** and **9b** were isolated as yellow powders from complexes **7a** and **7b**, respectively (prepared from 2 mmol of **6a** and **6b**). **9a**: 0.46 g, 45% yield; mp 146 °C. **9b**: 0.47 g, 42% yield; mp 150 °C.

Compound **5** was prepared from complex **2** (4 mmol) by adding a THF solution of S_2Cl_2 (0.54 g, 4 mmol) in 15 mL of THF at room temperature. The mixture was stirred for 12 h and then hydrolyzed at 0 °C with 10% HCl for 1 h and extracted with Et_2O. The organic phase was treated with $NaHCO_3$, NaCl, and then H_2O and dried over $MgSO_4$. Evaporation of solvents and recrystallization from Et_2O gave color-

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less crystals of **5** (0.51 g, 70% yield). Compounds **10a**,**b** were respectively prepared from complexes **7a**,**b** (2 mmol), using a THF solution of S_2Cl_2 (0.54 g, 4 mmol) in 15 mL of THF at room temperature for 12 h. The mixture was hydrolyzed at 0 °C with 10% HCl for 1 h and extracted with Et_2O. The organic phase was treated with $NaHCO_3$, NaCl, and then H_2O and dried over $MgSO_4$. Evaporation of solvents and recrystallization from Et_2O gave colorless crystals of **10a** (0.24 g, 48% yield; mp 138 °C) and **10b** (0.26 g, 43% yield; mp 141 °C).

Catalytic Cyclozirconation and Protonation. Cp_2ZrCl_2 (1.16 g, 4 mmol) was added to *n*-BuMgCl (2 M in Et_2O; 6 mL, 12 mmol), with stirring. Allylic derivatives **1** (4 mmol) and **6a**,**b** (2 mmol), respectively, in 10 mL of Et_2O were added dropwise at room temperature. The mixture was refluxed for 48 h and then treated at 0 °C with 10% HCl solution (25 mL). The aforementioned procedure afforded **3** (0.25 g, 40% yield), **8a** (0.35 g, 90% yield), and **8b** (0.41 g, 85% yield).

Compound **3**: ^{1}H NMR δ_H 0.44 (m, 2H, HC−Si), 0.84 (m, 2H, HC−Si), 0.96 (d, 6H, $^3J_{HH}$ = 5.9 Hz, CH_3), 1.09 (m, 4H, HC−Si), 1.23 (m, 2H, HC), 1.82−2.30 (m, 2H, H_2C−CH_2Si); ^{13}C NMR δ_C 15.3 (CH_2−CH_2−Si), 18.6 (CH−CH_2−Si), 22.0 (CH_3), 23.7 (CH_2−CH_2−Si), 41.2 (*C*H). Anal. Calcd for $C_9H_{18}Si$ (M_r = 154.32): C, 70.04; H, 11.76. Found: C, 70.12; H, 11.83.

Compound **4**: ^{1}H NMR δ_H 0.9 (m, 2H, HCSi), 1.17 (m, 2H, HCSi), 1.16 (t, 4H, $^3J_{HH}$ = 8.4 Hz, CH_2Si), 1.91 (m, 2H, HC), 2.05 (m, 2H, H_2C−CH_2−Si), 3.50, 3.54 (part ABX, 4H, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 4.3 Hz, CH_2Br); ^{13}C NMR δ_C 15.3 (CH_2−CH_2−Si), 18.7 (CH−CH_2−Si), 18.7 (CH_2−CH_2−Si), 39.9 (CH_2Br), 42.9 (*C*−H). Anal. Calcd for $C_9H_{16}Br_2Si$ (M_r = 312.0): C, 34.64; H, 5.13. Found: C, 34.58; H, 5.08.

Compound **5**: ^{1}H NMR δ_H 0.38 (m, 2H, HC−Si), 1.01−1.12 (m, 4H, H_2C−Si), 1.13 (m, 2H, HC−Si), 1.72 (m, 2H, HC), 1.91−1.99 (m, 2H, CH_2−CH_2−Si), 2.26 (m, 2H, HC−S), 2.70−2.75 (m, 2H, HC−S); ^{13}C NMR δ_c 16.3 (CH_2−CH_2−Si), 18.0 (CH_2−CH_2−Si), 18.5 (CH−CH_2−Si), 35.8 (CH_2S), 53.0 (*C*−H). Anal. Calcd for C_9H_{16} SSi (M_r = 184.26): C, 58.66; H, 8.70. Found: C, 58.41; H, 8.62.

Compound **8a**: ^{1}H NMR δ_H 0.30 (m, 4H, H_2C−Si), 0.90 (m, 4H, H_2C−Si), 0.93 (m, 12H, CH_3), 1.25 (m, 4H, HC); ^{13}C NMR δ_C 22.1 (CH_2−Si), 22.4 (CH_3), 41.9 (*C*H). Anal. Calcd for $C_{12}H_{24}Si$ (M_r = 196.40): C, 73.38; H, 12.32. Found: C, 73.80; H, 12.58.

Compound **8b**: ^{1}H NMR δ_H 0.49 (m, 4H, CH_2−Ge), 0.92 (m, 12H, CH_3), 1.25 (m, 4H, CH_2−Ge), 1.37 (m, 4H, HC); ^{13}C NMR δ_C 21.8 (CH_2−Ge), 22.0 (CH), 42.0 (CH_3). Anal. Calcd for $C_{12}H_{24}Ge$ (M_r = 240.90): C, 59.82; H, 10.04. Found: C, 59.77; H, 10.01.

Compound **9a**: ^{1}H NMR δ_H 0.92, 0.96 (part ABX, 8H, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 5.9 Hz, $^3J_{HH}$ = 11.1 Hz, CH_2Si), 1.89 (m, 4H, CH), 3.50, 3.55 (part ABX, 8H, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.7 Hz,$^3J_{HH}$ = 2 Hz, CH_2Br); ^{13}C NMR δ_C 17.0 (CH_2−Si), 39.7 (CH_2-Br), 43.3 (*C*H). Anal. Calcd for $C_{12}H_{20}$ Br_4Si (M_r = 511.98): C, 28.15; H, 3.94. Found: C, 28.48; H, 3.97.

Crystal Data for 9a: recrystallized from chloroform, $C_{12}H_{20}Br_4Si$, M_r = 512.01, triclinic, $P\bar{1}$, a = 7.941(1) Å, b = 8.836(2) Å, c = 12.254(2) Å, α = 85.19(2)°, β = 71.47(2)°, γ = 88.88(2)°, V = 812.4(2) Å^3, Z = 2, ρ_c = 2.093 Mg m^{-3}, $F(000)$ = 492, λ = 0.710 73 Å, T = 173(2) K, μ(Mo Kα) = 9.961 mm^{-1}, crystal size 0.5 × 0.4 × 0.2 mm, 2.31° < θ < 23.25°. A total of 4374 reflections (2210 independent, R_{int} = 0.064) were collected at low temperatures using an oil-coated shock-cooled crystal[13] on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97),[14] and 154 parameters were refined using the least-squares method on F^2.[15] The largest electron density residue was 0.969 e Å^{-3}. R_1 (for $F > 2\sigma(F)$) = 0.048 and $wR2$ (all data) = 0.126 with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

Compound **9b**: ^{1}H NMR δ_H 1.11, 1.16 (part ABX, 8H,$^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 10.2 Hz,$^3J_{HH}$ = 5.9 Hz, CH_2−Ge), 1.94 (m, 4H, CH), 3.50 (part ABX, 8H, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.4 Hz,$^3J_{HH}$ = 2.8 Hz, CH_2Br); ^{13}C NMR δ_C 17.3 (CH_2Ge), 39.6 (CH_2Br), 43.9 (*C*H). Anal. Calcd for $C_{12}H_{20}$ Br_4Ge (M_r = 556.48): C, 25.89; H, 3.62. Found: C, 25.87; H, 3.62.

Compound **10a**: ^{1}H NMR δ_H 0.42−0.52 (m, 4H, HC−Si), 1.10−1.15 (m, 4H, HC−Si) 1.80−1.90 (m, 4H, HC), 2.35−2.47 (m, 4H, HCS), 2.81−2.92 (m, 4H, HCS); ^{13}C NMR δ_C 17.2 (CH_2-Si), 17.4 (CH_2Si), 35.7 (CH_2S), 53.4 (*C*H), 53.5 (*C*H). Anal. Calcd for $C_{12}H_{20}S_2Si$ (M_r = 256.49): C, 56.19; H, 7.86. Found: C, 56.07; H, 7.83.

Compound **10b**: ^{1}H NMR δ_H 0.55−0.66 (m, 4H, HC−Ge), 1.34−1.45 (m, 4H, HC−Ge), 1.79−1.92 (m, 4H, CH), 2.41−2.50 (m, 4H, HC−S), 2.85−2.91 (m, 4H, HC−S); ^{13}C NMR δ_C 16.5 (CH_2Ge), 16.7 (CH_2−Ge), 35.3 (CH_2S), 54.6 (*C*−H), 54.7 (*C*−H). Anal. Calcd for $C_{12}H_{20}S_2Ge$ (M_r = 301.0): C, 47.88; H, 6.69. Found: C, 47.78; H, 6.61.

Supporting Information Available: A labeled ORTEP diagram and tables of X-ray crystal structure data for **9a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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