New linked di-germanocenes and di-stannocenes

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Abstract

New bridged di-germanocenes and di-stannocenes **2** have been synthesized from a reaction between (pentamethylcyclopentadienyl)metal chloride and the dilithium salts of the corresponding linked cyclopentadienyl ligands (spacer: phenylene, biphenylene, thiophene) in good yields. These di-metallocenes react easily with catechol giving preferentially the substitution reaction. With iodine or with metal 14 dichloride (M = Ge, Sn), the oxidative products are unstable and rapidly loose the linked cyclopentadienyl ligand. Starting from $SnCl_2$, the ionic half-sandwich compound $[Cp*Ge][SnCl_3]$ **8**, so obtained, was characterized by X-ray diffraction analysis which reveals a polymeric form in the solid state. The reaction of the di-germanocenes with *o*-quinone leads to the expected cycloadducts, stable in the case of permethylated compounds. An unusual single electron transfer reaction takes place with $[Cp_2Fe][BF_4]$ and the transient cation radical rapidly gives $[Cp*Ge][BF_4]$. Mass spectra measurements and electrochemistry study confirm the weak stability of this cationic species. © 2002 Published by Elsevier Science B.V.

1. Introduction

Since the discovery of ferrocene in 1951 and the description of a new type of bonding in this complex [1], the metallocene chemistry has been widely developed. Some years after, the first Group 14 sandwich compound $[Cp_2Pb]$ [2] was synthesized forming the starting point of a large study upon Group 14 metallocenes [3]. In contrast, bridged di-germanocenes are still unknown. Recently, we described the preparation of the first *p*-phenylene and *p*-biphenylene bridged di-germanocenes [4]. We report herein the syntheses of new linked di-germanocenes and di-stannocenes with various bridging groups (thienyl, phenyl...) and some aspects of their reactivity.

2. Results and discussion

The syntheses of **1a**–**c** were previously reported [5]. We prepare two new products **1d,e** with a thienyl group

as spacer with moderate yield using a slightly modified [6] method described by Manriquez [5] (Scheme 1). The procedure consists of two successive additions of methyl-substituted cyclopent-2-en-1-one to the lithiated spacers followed by a deshydratation reaction with *p*-toluenesulfonic acid. When the reaction was performed with 2,5-dilithiothiophene [7], the one-step addition of two equivalents of the conjugated ketone slightly decreases the percentage of product and the usual method of two steps was preferentially used.
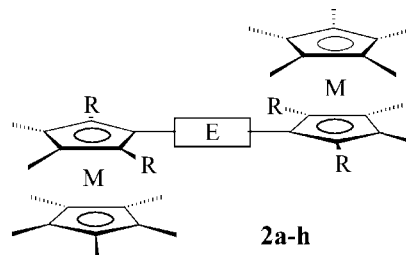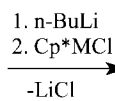

1d: R = H
1e: R = CH₃
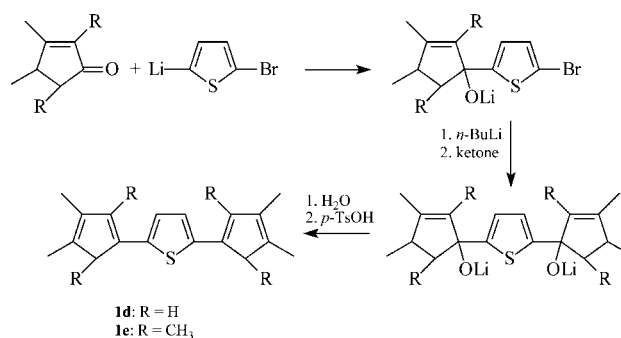
Scheme 1.

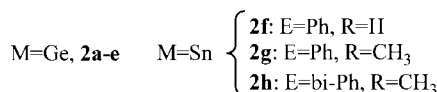* Corresponding author. Tel.: + 33-561-55-8348; fax: + 33-561-55-8204.

The reaction of stoichiometric amounts of the dilithium salts of **1** [5] with [Cp*GeCl] [8] or [Cp*SnCl] [9] at low temperature in THF as solvent affords the corresponding di-germanocenes and di-stannocenes **2** (1).

1a-e
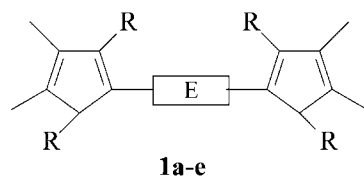
1a: E=Ph, R=H
1b: E=Ph, R=CH₃
1c: E=bi-Ph, R=CH₃
1d: E=Th, R=H
1e: E=Th, R=CH₃

M=Ge, **2a-e**   M=Sn { **2f**: E=Ph, R=H
                          2g: E=Ph, R=CH₃
                          2h: E=bi-Ph, R=CH₃

(1)

These compounds are isolated as pale yellow or red powders in good yields (60–95%). They are very air-sensitive and must be stored at low temperature. In solution, a redistribution reaction takes place with formation of the symmetrical species [Cp*₂M] (M = Ge, Sn) [10]. In all cases, the permethylated compounds are the most stable within the series. They were perfectly characterized by physical and chemical measurements. The ^{1}H-NMR spectra show equivalent methyl groups for the C_5Me_5 ligands in accord with rapidly rotating pentamethylcyclopentadienyl rings [3b,11]. For the same reason, two signals corresponding to the non-equivalent pairs of methyl groups of the C_5Me_4 ligands are observed. In the ^{13}C-NMR spectra, chemical shifts of the ring carbon atoms of the cyclopentadienyl groups are near to those of the spacers (phenyl, thienyl) but they were unambiguously assigned by HMBC (^{1}H/^{13}C–^{3}J) and HSQC (^{1}H/^{13}C–^{1}J) experiments. This ^{13}C-NMR study confirms the equivalence of the methyl groups and ring carbon atoms. ^{119}Sn-NMR data for di-stannocenes reveal high-field chemical shifts (**2f**, − 2110 ppm; **2g**, − 2128 ppm; **2h**, − 2129 ppm) which correspond to the observed shift for decamethylstannocene [3a] indicating a probable π-linked structure for these compounds. The EI and CI (CH₄) mass spectra show the only presence of the cations [(C_5Me_5)M]$^+$ (M = Ge, m/z: 209; M = Sn, m/z: 255) besides the ligand **1**. This behavior seems characteristic of the metallocene series (M = Si, Ge) where the molecular peak was never observed [3b].

The solid state structure of **2a** has been investigated by X-ray crystallography [4]. The most important information, which have been revealed are the following ones. First, the two Cp*Ge moieties coordinate to the opposite faces of the bridging spacer. Then, the germanium atoms do not reside over the cyclopentadienyl

ring centers but are slightly displaced. Moreover, the Ge–C centroid distances are different according to the cyclopentadienyl planes indicating a higher interaction between the germanium atom and the C_5Me_5 ring. This

is in agreement with the easy cleavage of the metal–bridging ligand bond in the cationic form of these di-germanocenes during mass measurements.

Cyclic voltammetry (in CH₂Cl₂ with Bu₄NBF₄ as supporting electrolyte) of **2c** reveals one irreversible oxidation peak at + 0.4 V (vs. SCE) similar to those obtained for decamethyl Group 14 metallocenes (Si, Ge, Sn) with the same experimental conditions [11]. As previously observed in mass spectrometry, the radical cation of **2c** is unstable and probably looses the diradical of the bridging ligand with formation of [(C_5Me_5)Ge]$^+$. Further irreversible oxidation peaks are present in the region 0.9–1.5 V corresponding to the area of the oxidation peaks of the starting product **1c** (1.1, 1.3 and 1.6 V) but the evolution of the fragments of the **2c** cation is uncertain and unambiguous attributions cannot be made for these secondary oxidation peaks.

These di-germanocenes and di-stannocenes, as most of the known Group 14 metallocenes, can act as divalent species leading to oxidative-addition reactions with halogen or o-quinone. Due to the weakness of the germanium–(cyclopentadienyl) π-bond, they can also undergo bond cleavage with electrophiles.

Differences in the reactivity of di-germanocenes and di-stannocenes appear from the reaction with two equivalents (one equivalent per metal atom) of 3,5-di-*tert*-butylcatechol. Within the tin series, a substitution process [12] takes place leading to the cyclic divalent species **3** (2) which was prepared separately by the dehydrochlorination reaction of catechol with tin dichloride in presence of triethylamine.

2f-h $\xrightarrow[- Cp*H]{- 1a-c}$ **3**

(2)
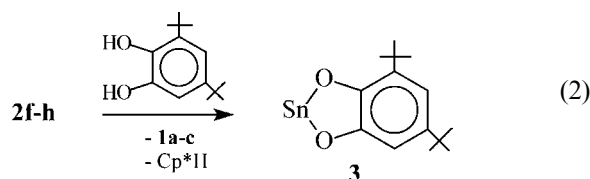
The di-germanocenes give both the cyclic germylene **4** [13] and the spiro-compound **5** (3) [13] in various amounts (Section 3).

$$\text{(3)}$$
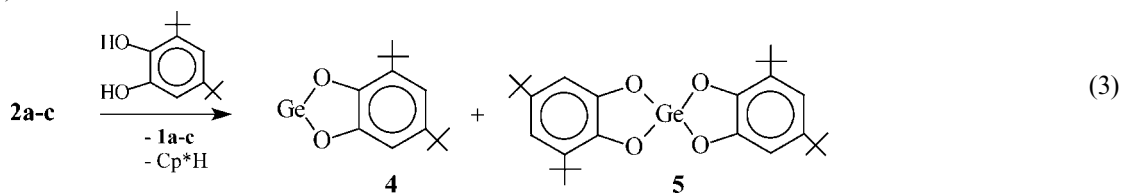
The formation of this by-product **5** can be explained by a similar process of oxidative addition and subsequent H_2-elimination (4) as previously described with silicocene and leading in this case to the di(pentamethylcyclopentadienyl)siladioxolane [3c,12].


$$\text{(4)}$$
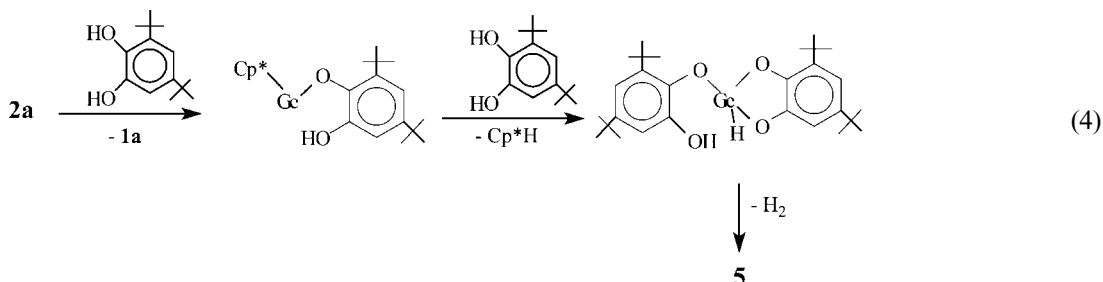
Interestingly, the expected germadioxolane **9a** has not been observed. This is presumably due to the weakness of the germanium–bridging ligand π-bond, revealed by the X-ray and electrochemical analyses. The high reactivity of this bond with protic compounds results in the exclusive formation of **4** and **5**, the bridging-ligand acting as the leaving group in the first step.

In the case of I_2, the products expected from the oxidative addition of the divalent germanium centre were not obtained. The formation of $Cp*GeI_3$ [14] and **1**, resulting from the cleavage of the linked cyclopentadienyl ligand, was observed by ^{1}H-NMR. Furthermore with compound **2d**, a side reaction between iodine and the thienyl group takes place leading to the degradation of the thiophene spacer.

With germanium or tin dichloride which can act as Lewis acid, an electrophilic attack at the π-system of the bridging cyclopentadienyl ligands [14] occurs with formation of the ionic complexes **7** [14] and **8**. The recovery of a stoichiometric amount of [Cp*GeCl] by treatment of the reaction mixture by hexane, confirms the cleavage of the metal–ligand bond in the first step of the reaction. The transient chlorodigermanocenes, so formed, seem too unstable to be isolated. The complexes **7** and **8** were identified by comparison with a sample prepared directly by reaction of [Cp*GeCl] with the metal dichloride (5).

$$[Cp*GeCl] + MCl_2 \longrightarrow [Cp*Ge][Cl_3M]$$

M = Ge: **7** [14]
M = Sn: **8**

$$\text{(5)}$$
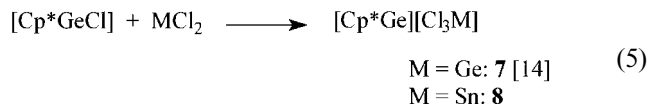
Such ionic half sandwich compounds $[(C_5Me_5)Ge][X]$ ($X = GeCl_3$, $AlCl_4$, $C_5(CO_2Me)_5$, BF_4) [3a,14–16]] have been previously described but only one of them have been structurally characterized to our knowledge. With trichloride metal 14 as counter ion, only the structure of the complex $[(Me_4C_5H)Me_2Si(Me_4C_5)Ge][Cl_3Ge]$ in which the central germanium is η^5-bonded to one of the cyclopentadienyl ring and furthermore weakly η^2-bonded to one of the double bonds of the second cyclopentadienyl ligand has been reported [17]. The crystal structure of compound **8** (Fig. 1 and Table 1)
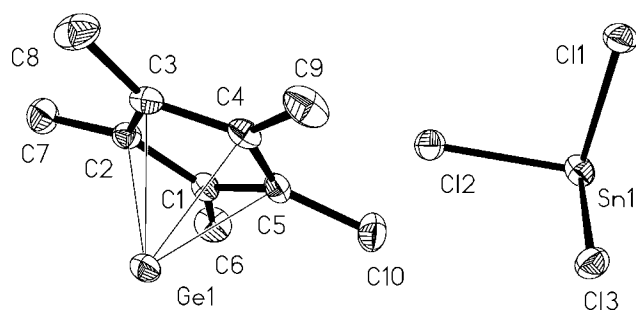
Fig. 1. Crystal structure of the complex **8**.

Table 1
Selected bond lengths (Å) and bond angles (°) for **8**

Bond lengths

Sn(1)–Cl(1)	2.511(8)	Ge(1)–C(4)	2.308(6)
Sn(1)–Cl(2)	2.495(16)	Ge(1)–C(5)	2.281(7)
Sn(1)–Cl(3)	2.478(7)	C(1)–C(2)	1.449(6)
Ge(1)–C(1)	2.258(7)	C(2)–C(3)	1.438(4)
Ge(1)–C(2)	2.279(6)	C(3)–C(4)	1.450(10)
Ge(1)–C(3)	2.302(7)	C(1)–C(5)	1.447(8)

Bond angles

Cl(2)–Sn(1)–Cl(1)	92.7(2)	C(1)–Ge(1)–C(4)	61.25(9)
Cl(3)–Sn(1)–Cl(1)	92.42(8)	C(3)–C(2)–C(1)	107.4(4)
Cl(3)–Sn(1)–Cl(2)	94.10(18)	C(5)–C(1)–C(2)	108.5(4)
C(1)–Ge(1)–C(2)	37.24(16)		

shows the half-sandwich cation $[(C_5Me_5)Ge]^+$ and the trigonal pyramidal anion $[Cl_3Sn]^-$. The Cp* group is pentahapto coordinated to the germanium atom as
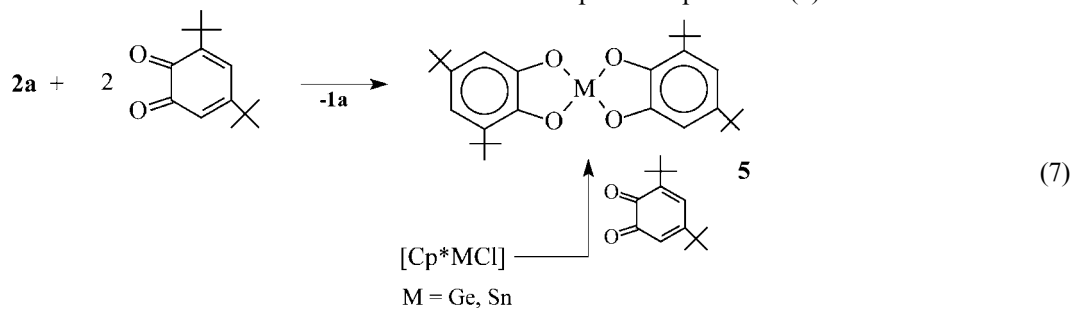
shown by the Ge–C ring bond lengths which range from 2.258(7) to 2.308(6) Å. Comparable values were obtained from the complex [Cp*Ge][BF$_4$] [16]. The Cp* ring is planar and the methyl groups are bent out of the ring plane away from the germanium atom. Two counter ions [Cl$_3$Sn]$^-$ units are associated by two weak Sn–Cl interactions (3.38 Å). Such interactions have been previously observed in [Cp*SnCl] which has two weak Sn–Cl interactions (3.086(1) and 3.444(3) Å) [9]. These dimeric structures are then linked through germanium atoms (four weak interactions, Ge1–Cl1A: 3.31 Å, Ge1–Cl2B: 3.34 Å, Ge1–Cl3D: 3.37 Å, Ge1–Cl3A: 3.45 Å) leading to a polymeric form as shown in Fig. 2.

To verify the presence of bivalent metallic sites in these complexes, we tried oxidative cycloaddition reaction with 3,5-di-*tert*-butyl-*ortho*-quinone; quinones being excellent reagents in the characterization of such divalent species [13,18]. The addition of stoichiometric quantity of *ortho*-quinone to **2b,c** at room temperature gave the corresponding cycloadducts **9b,c**, which were isolated in good yields (6).

Within the thiophene series, a mixture of the cycloadduct **9e** and the spiro-compound **5** was obtained. The less hindered di-germanocene **2a** gives only the formation of the spiro-compound **5** (7).

This probably results from a redistribution reaction of the transient cycloadduct **9a** as previously observed in the case of the halogenated germylenes [13]. The same redistribution reaction has been obtained starting from [Cp*MCl] (M = Ge, Sn) confirming the weakness of the metal–cyclopentadienyl bonds.

Recently, we have shown a single electron transfer mechanism as the first step of the reaction between the germylene and the quinone [18]. In order to test the ability of the di-germanocene to undergo single electron transfer, the reaction with a ferrocenium salt was performed. Treatment of these di-metallocenes with [Cp$_2$Fe][BF$_4$] in CH$_2$Cl$_2$ gave the reduced product [Cp$_2$Fe] and confirms their reducing character. Depending on the nature of the used metallocenes various results were observed. The di-germanocenes **2a–c** led to the well known species [Cp*Ge][BF$_4$] [14,16] (8) whereas in the case of tin analogues, the insolubility of the products prevented their identification.
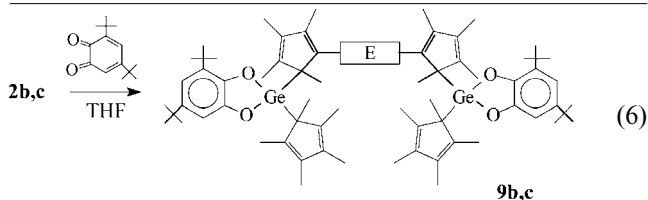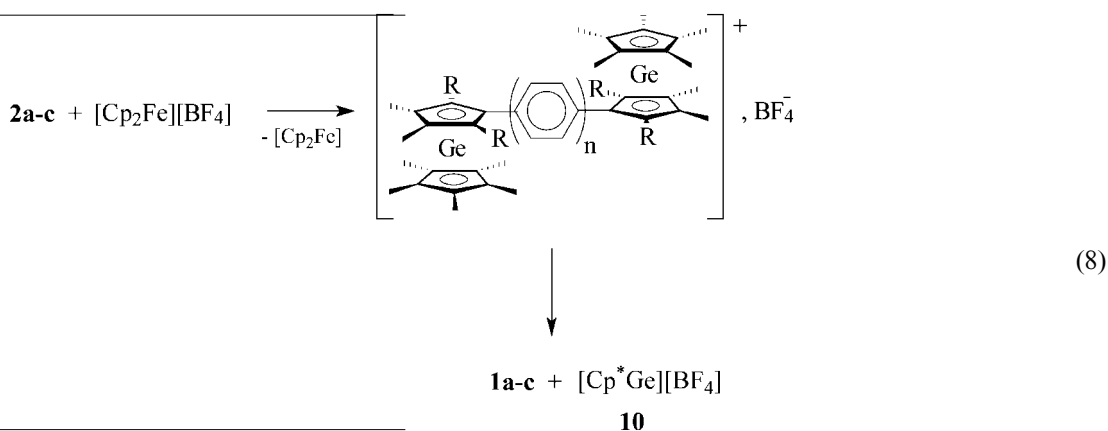
The transient radical ion is unstable, as previously observed in mass spectrometry and electrochemistry and it looses the diradical bridging ligand, giving **10** and, **1** by abstraction of hydrogen atoms from the solvent.
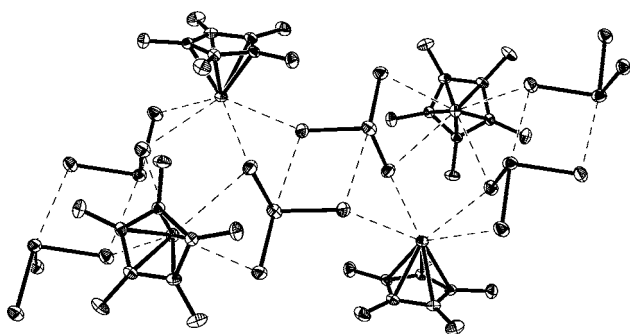
Fig. 2. Polymeric organization of **8** in the solid state.

3. Experimental

All the reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques and dry solvents. NMR spectra were recorded on Brucker AC 80 (80.13 MHz) and ARX 400 (400.13 MHz) (^{1}H), AC 200 (50.32 MHz) and ARX 400 (100.62 MHz) (^{13}C), ARX 400 (111.93 MHz) (^{119}Sn). Mass spectra were measured with a Hewlett–Packard HP 5989A in the electron impact mode (70 eV) or a Rybermag R10-10 spectrometer operating in the electron impact mode or by chemical desorption (DCI, CH_4). Electrochemical measurements were performed under argon with a Electro-kemat potentiostate using a platinum electrode (diameter 1 mm) and Bu_4NBF_4 as supporting electrolyte. Potentials reported are versus Ag/AgCl/KCl(sat). M.p. were measured on a Leitz microscope or Electrothermal apparatus (capillary). Elemental analysis were performed by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse. The compounds **1a**–**c** [5], [Cp*GeCl] [8] and [Cp*SnCl] [9] were prepared according to the literature procedures.

3.1. Preparation of 1d,e

To a solution of 2,5-dibromothiophene 6.17 g (25.51 mmol) in 50 ml of diethyl ether was added dropwise 35.23 mmol of *n*-BuLi in hexane (1.6 M). After the solution was stirred for 20 min, the 3,4-dimethylcyclopent-2-en-1-one 3.37 g (30.61 mmol) was added. The mixture was then refluxed for 1 h. After cooling at room temperature (r.t.), 35.23 mmol of *n*-BuLi were added. The white precipitate was stirred for 1 h, and 3.37 g (30.61 mmol) of the 3,4-dimethylcyclopent-2-en-1-one was then added dropwise. The mixture was stirred at r.t. for 30 min and then refluxed for 1 h. The solution was quenched with aqueous (aq.) saturated ammonium chloride, the layers were separated, and the aq. phase extracted twice with diethyl ether. After drying on Na_2SO_4, the solution was concentrated to 30 ml and 1.1 g of *p*-toluene sulfonic acid was added under nitrogen. After 2 h of stirring, the precipitate was

filtered, washed with successively water and methanol and dried under vacuum.

1d: (dark orange powder): 2.2 g, (32%). Melting point (m.p): 150–153 °C. ^{1}H-NMR (CDCl$_3$) δ 1.85 and 1.93 (sl, 12H, $C_5H_3Me_2$), 3.23 (sl, 4H, CH_2), 6.41 (s, 2H, CH), 6.75 (s, 2H, C_4H_2S). ^{13}C-NMR (CDCl$_3$) δ 12.58 and 13.44 ($C_5Me_2H_3$); 46.02 (CH_2); 131.07 (CH); 122.38 (CH) and 138.29 (Cquat.) (C_4H_2S); 134.77, 135.61, 136.99 (Cquat.) ($C_5Me_2H_3$). MS/IE: m/z 268 ([M]$^+$, 100%), 253 ([M]$^+$–Me, 50%). Anal. Calc. for $C_{18}H_{20}S$: C, 80.55; H, 7.51. Found: C, 79.67; H, 7.34%.

1e: The same procedure was used starting from 6.17 g (25.51 mmol) of 2,5-dibromothiophene, 28.06 mmol of *n*-BuLi, 3.52 g (25.51 mmol) of 2,3,4,5-tetramethyl-cyclopent-2-en-1-one) except that after *p*-toluene sulfonic acid treatment the mixture was washed twice with water and dried on Na_2SO_4. After evaporation of the solvent, the residue was washed with ethanol, dried under vacuum and recrystallized in pentane giving **1e**: (brown powder): 0.62 g (8%). m.p.: 131–135 °C. ^{1}H-NMR (CDCl$_3$) δ 1.16 (d, $^3J = 7.6$ Hz, 6H, CHMe), 1.84, 1.91, 2.13 and 2.15 (s, 18H, C_5Me_3); 3.08 (q, $^3J = 7.6$ Hz, 2H, CHMe); 6.81 (s, 2H, C_4H_2S). ^{13}C-NMR (CDCl$_3$) δ 11.25, 12.16, 13.42, 16.66 (C_5Me_4); 50.50 (CHMe); 123.74 (CH) and 141.02 (Cquat.) (C_4H_2S); 135.33, 136.64, 137.14, 137.81 (Cquat.) (C_5Me_4). MS/IE: m/z 324 ([M]$^+$, 100%), 309 ([M]$^+$ –Me, 61%). Anal. Calc. for $C_{22}H_{28}S$: C, 81.42; H, 8.69. Found: C, 80.81; H, 8.11%.

3.2. General procedure for the preparation of 2a–h

(1.9 mmol) of *n*-BuLi (1.6 M) in hexane were added dropwise to a solution of (0.9 mmol) of **1** in 8 ml of THF at −78 °C. The suspension was warmed to r.t. and stirred over a period of 30 min. Then the mixture was cooled to −78 °C and (1.8 mmol) of [Cp*MCl] (M = Ge, Sn) in 5 ml of THF were slowly added. The mixture was allowed to warm slowly to r.t. and stirred for 2 h (for **2f**–**h**, only 1 h). The solution was evaporated in vacuo and the residue was extracted with 25 ml of toluene and filtered. After removing the solvent in vacuo, the residue was:

– recrystallized from THF giving pale yellow crystals for **2a**.
– only dried for **2b**–**h**. These compounds are unstable in solution and cannot be recrystallized.

2a: Yield: 60%. m.p. (dec.): 215 °C. ^{1}H-NMR (CDCl$_3$) δ 1.75 (m, 8H, CH_2CH_2O); 1.80 (s, 30H, C_5Me_5); 2.04 (s, 12H, $C_5H_2Me_2$); 3.73 (m, 8H, CH_2O); 6.06 (s, 4H, $C_5H_2Me_2$); 7.28 (s, 4H, C_6H_4). ^{13}C-NMR (CDCl$_3$) δ 9.63, 12.42 (C_5Me_5 and $C_5H_2Me_2$); 25.65, 68.01 (C_4H_8O); 106.48 (CH), 122.28, 124.41 (Cquat.) ($C_5H_2Me_2$); 118.92 (C_5Me_5); 124.91 (CH), 133.01 (Cquat.) (C_6H_4). MS/IE: m/z 209 ([(C$_5$Me$_5$)Ge]$^+$, 100%); 262 ([**1a**]$^+$, 64%). Anal. Calc. for $C_{48}H_{66}Ge_2O_2$: C, 70.28; H, 8.11. Found: C, 69.49; H, 7.38%.

2b: Yield: 84%. m.p. (dec.): 235 °C. ^{1}H-NMR (CDCl$_3$, 250 MHz) δ 1.95 (s, 30H, C$_5Me_5$); 2.03 and 2.04 (s, 24H, C$_5Me_4$); 7.11 (s, 4H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 9.95, 10.28, 11.01 (C$_5Me_5$ and C$_5Me_4$); 118.10, 118.44, 118.67, 127.08 (*C*$_5$Me$_5$ and *C*$_5$Me$_4$); 129.96 (CH); 133.80 (Cquat.) (*C*$_6$H$_4$). MS/IE: *m/z* 209 ([(C$_5$Me$_5$)Ge]$^+$, 100%); 318 ([**1b**]$^+$, 4%).

2c: Yield: 92%. m.p. (dec.): 300 °C. ^{1}H-NMR (CDCl$_3$) δ 1.95 (s, 30H, C$_5Me_5$); 2.03 and 2.04 (s, 24H, C$_5Me_4$); 7.26 and 7.63 (syst. AB, $^3J_{HH} = 8.4$ Hz, 8H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 9.95, 10.27, 10.92 (C$_5Me_5$ and C$_5Me_4$); 118.12, 118.58, 118.78, 126.91 (*C*$_5$Me$_5$ and *C*$_5$Me$_4$); 126.15, 131.07 (CH), 135.80, 137.94 (Cquat.) (*C*$_6$H$_4$). MS/IE: *m/z* 209 ([(C$_5$Me$_5$)Ge]$^+$, 100%); 394 ([**1c**]$^+$, 24%).

2d: Yield: 49%. m.p. (dec.): 243 °C. ^{1}H-NMR (CDCl$_3$) δ 1.87 (s, 30H, C$_5Me_5$); 2.03 (s, 12H, C$_5$H$_2Me_2$); 5.94 (s, 4H, C$_5$*H*$_2$Me$_2$); 6.67 (s, 2H, C$_4$H$_2$S). ^{13}C-NMR (CDCl$_3$) δ 9.65, 12.37 (C$_5Me_5$ and C$_5$H$_2Me_2$); 106.72, 106.95 (CH) (C$_5$*H*$_2$Me$_2$); 117.22, 119.14, 123.82 (Cquat.) (*C*$_5$Me$_5$ and *C*$_5$H$_2$Me$_2$); 120.36 (CH), 136.39 (Cquat) (*C*$_4$H$_2$S). MS/IE: *m/z* 209 ([(C$_5$Me$_5$)Ge]$^+$, 55%); 268 ([**1d**]$^+$, 100%).

2e: Yield: 53%. m.p. (dec.): 290 °C. ^{1}H-NMR (CDCl$_3$) δ 1.97 (s, 30H, C$_5Me_5$), 2.05 and 2.12 (s, 24H, C$_5Me_4$), 6.69 (s, 2H, C$_4$H$_2$S). ^{13}C-NMR (CDCl$_3$) δ 9.86, 10.32, 11.15 (C$_5Me_5$ and C$_5Me_4$); 118.41, 118.82, 118.89, 119.03, (*C*$_5$Me$_5$ and *C*$_5$Me$_4$); 125.62 (CH), 136.72 (Cquat) (*C*$_4$H$_2$S).

2f: Yield: 92%. m.p. (dec.): 240 °C. ^{1}H-NMR (CDCl$_3$) δ 1.90 (s, ^3J(H–$^{117/119}$Sn) = 3.2 Hz, 30H, C$_5Me_5$); 2.10 (s, 12H, C$_5$H$_2Me_2$); 6.16 (s, 4H, C$_5$*H*$_2$Me$_2$); 7.30 (s, 4H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 9.85, 12.51 (C$_5Me_5$ and C$_5$H$_2Me_2$); 105.35 (CH) (C$_5$*H*$_2$Me$_2$); 117.67, 121.31, 123.50 (Cquat.) (*C*$_5$Me$_5$ and *C*$_5$H$_2$Me$_2$); 124.63 (CH), 132.93 (Cquat) (*C*$_6$H$_4$).

2g: Yield: 68%. m.p. (dec.): 188 °C. ^{1}H-NMR (CDCl$_3$) δ 2.03 (s, ^3J(H–$^{117/119}$Sn) = 3.6 Hz, 30H, C$_5Me_5$); 2.11 and 2.13 (s, 24H, C$_5Me_4$); 7.19 (s, 4H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 10.25, 10.55, 11.39 (C$_5Me_5$ and C$_5Me_4$); 117.02, 117.12, 117.54, 125.77 (*C*$_5$Me$_5$ and *C*$_5$Me$_4$); 130.06 (CH), 133.75 (Cquat) (*C*$_6$H$_4$). MS/IE: *m/z* 255 ([(C$_5$Me$_5$)Sn]$^+$, 14%); 318 ([**1b**]$^+$, 100%).

2h: Yield: 58%. m.p. (dec.): 180 °C. ^{1}H-NMR (CDCl$_3$) δ 2.01 (s, ^3J(H–$^{117/119}$Sn) = 3.6 Hz, 30H, C$_5Me_5$); 2.12 and 2.13 (s, 24H, C$_5Me_4$); 7.29, 7.61 (syst. AB, $^3J_{HH} = 7.7$ Hz, 8H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 10.41, 10.51, 10.95 (C$_5Me_5$ and C$_5Me_4$); 117.08, 117.15, 117.62, (*C*$_5$Me$_5$ and *C*$_5$Me$_4$); 126.18, 131.02 (CH), 135.21, 137.81 (Cquat) (*C*$_6$H$_4$).

The compounds **2b–h** are not stable in solution and decompose slowly at r.t. Thus, they did not give reproducible analyses.

3.3. Reaction of 2f–h with 3,5-di-tert-butylcatechol

A solution of 0.17 g (0.78 mmol) of 3,5-di-*tert*-butylcatechol in 4 ml of THF was added to a solution of di-stannocenes **2f**–**h** (0.39 mmol) in 8 ml of THF at r.t. The mixture was stirred for 2 h. After evaporation of the solvent, the residue was washed with Et$_2$O (elimination of the ligands **1a**–c), giving powders. The ^{1}H-NMR analyses of these residues show the formation of:
- **1a** (10%), **3** (90%);
- **1b** (8%), **3** (82%);
- **1c** (17%), **3** (83%).

3.4. Preparation of 3

To a solution of 3,5-di-*tert*-butylcatechol 0.35 g (1.58 mmol) and SnCl$_2$ 0.30 g (1.58 mmol) in 6 ml of toluene was added dropwise Et$_3$N 0.32 g (3.16 mmol) at r.t. The mixture was stirred for 10 min then refluxed for 1 h. After filtration (elimination of Et$_3$N,HCl), the filtrate was evaporated and the solid washed by pentane. After drying under vacuo, a white powder of **3** was obtained: 0.48 g (69%). m.p.: 194 °C (dec.). ^{1}H-NMR (CDCl$_3$/ DMSO d_6) δ 1.17, 1.34 (s, 18H, C(C*H*$_3$)$_3$); 1.19 (t, $^3J = 7.7$ Hz, 9H, N(CH$_2$C*H*$_3$)); 2.96 (q, $^3J = 7.7$ Hz, 6H, N(C*H*$_2$CH$_3$)); 6.58, 6.75 (d, $^4J = 1.9$ Hz, 2H, C$_6$H$_2$). ^{13}C-NMR (CDCl$_3$/DMSO d_6) δ 8.88 (N(CH$_2$*C*H$_3$)); 29.79, 31.95 (C(*C*H$_3$)); 34.07, 34.91 (*C*(CH$_3$)); 46.04 (N(*C*H$_2$CH$_3$)); 111.32, 113.25 (CH), 135.83, 138.26, 148.43, 151.08 (C$_6$H$_2$). ^{119}Sn-NMR (DMSO d_6) δ − 63 ppm. MS/EI: *m/z* 340 ([M]$^+$–Et$_3$N, 13%), 325 ([M]$^+$ –Et$_3$N–CH$_3$, 33%). Anal. Calc. for C$_{14}$H$_{20}$SnO$_2$: C, 49.60; H, 5.95. Found: C, 48.96; H, 6.67%.

3.5. Reaction of 2a–c with 3,5-di-tert-butylcatechol

Using the same procedure described for **2f**–**h** excepted the reaction time (20 h), 0.12 g (0.52 mmol) of catechol and (0.26 mmol) of the di-germanocenes **2a**–**c** in 8 ml of THF give white solids after evaporation of the solvents.
- from **2a**: treatment of the residue by little THF (elimination of **1a** in the precipitate), decantation and drying, the ^{1}H-NMR analysis of the white powder shows: **4** (64%), **5** (36%).
- from **2b**: the ^{1}H-NMR spectrum of the crude mixture indicates the presence of **1b** (27%), **4** (42%), **5** (31%).
- from **2c**: after treatment of the residue by a mixture THF–pentane (elimination of **1c** in the precipitate), decantation and drying, the ^{1}H-NMR spectrum indicates the formation of **4** (44%), **5** (56%).

3.6. Reaction of 2a with Cl$_2$Ge.dioxane

To a solution of **2a** 0.26 g (0.38 mmol) in 4 ml of CH$_2$Cl$_2$ was added a solution of 0.18 g (0.77 mmol) of

Cl$_2$Ge·dioxane in 4 ml of CH$_2$Cl$_2$ at -78 °C. The mixture was slowly warmed to r.t. and the solvent evaporated. The ^{1}H-NMR analysis of the crude mixture shows the formation of [Cp*Ge][Cl$_3$Ge] [14] and **1a**. The treatment by CH$_2$Cl$_2$ allowed the extraction of 41% of this complex which was identified by ^{1}H- and ^{13}C-NMR spectroscopies: ^{1}H-NMR (CDCl$_3$) δ 2.13 (s, 15H, C$_5$Me$_5$). ^{13}C-NMR (CDCl$_3$) 9.62 (C$_5$*Me$_5$*); 121.26 (*C$_5$*Me$_5$).

3.7. Reaction of **2a** with SnCl$_2$

A solution of SnCl$_2$ 0.13 g (0.70 mmol) in 4 ml of THF was added to a solution of **2a** 0.53 g (0.78 mmol) in 12 ml of THF at -78 °C. The mixture was stirring at -40 °C for 1 h. After concentration of the solvent under vacuo, the treatment of the residue by 2×7 ml of hexane gave in the filtrate 0.17 g (91%) of [Cp*GeCl] identified by ^{1}H-NMR ($\delta = 2.01$ ppm) and mass spectrometry ([M]$^+$: 244). The precipitate was treated by 8 ml of THF. The filtrate was concentrated and analyzed by ^{1}H-NMR: [Cp*Ge][Cl$_3$Sn] (39%), **1a** (61%).

3.8. Preparation of [Cp*Ge][Cl$_3$Sn] (**8**)

To a solution of [Cp*GeCl] 0.31 g (1.29 mmol) in 7 ml of THF was slowly added a solution of SnCl$_2$ 0.25 g (1.29 mmol) in 7 ml of THF at -78 °C. The mixture was warmed to -40 °C and stirred for 1 h at this temperature. The solvent was reduced to 6 ml. After cooling to -30 °C, colorless crystals appeared and were isolated after decantation and drying: 0.36 g (65%). m.p.: 290 °C (dec.). ^{1}H-NMR (CDCl$_3$) δ 2.14 (s, 15H, C$_5$Me$_5$). ^{13}C-NMR (CDCl$_3$) δ 9.60 (C$_5$*Me$_5$*); 121.23 (*C$_5$*Me$_5$). ^{119}Sn-NMR (THF–ext. ref. D$_2$O) δ -199 ppm. MS/EI: m/z 209 ([(C$_5$Me$_5$)Ge]$^+$, 49%). Anal. Calc. for C$_{10}$H$_{15}$Cl$_3$GeSn: C, 27.74; H, 3.49. Found: C, 27.73; H, 3.52%.

3.8.1. Crystal data for **8**

C$_{10}$H$_{15}$Cl$_3$GeSn, $M = 432.85$, monoclinic, $C2/c$, $a = 10.24(8)$ Å, $b = 7.91(7)$ Å, $c = 16.70(11)$ Å, $\beta = 111.6(2)°$, $V = 2979(23)$ Å^3, $Z = 8$, $\rho_c = 1.930$ Mg m^{-3}, $F(000) = 1664$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, μ(Mo–K$_\alpha$) $= 4.202$ mm^{-1}, crystal size $0.5 \times 0.5 \times 0.6$ mm^3, $1.81° \leq \theta \leq 32.30°$, 17 895 reflections (4982 independent, $R_{int} = 0.0326$), $T_{min} = 0.589313$, T_{max} 1.0, 141 parameters, R_1 [$I > 2s(I)$] $= 0.0265$, wR_2 [all data] $= 0.0710$, largest electron density residue: 0.677 e Å^{-3}. Data were collected at low temperature using oil-coated shock-cooled crystals on a Bruker-AXS CCD 1000 diffractometer. Semi-empirical absorption corrections were employed [19]. The structure was solved by direct methods (SHELXS-97) [20] and refined using the least-squares method on F^2. [21] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$.

3.9. Reaction of **2b,c** with 3,5-di-tert-butyl-ortho-quinone

3,5-di-*tert*-Butyl-*ortho*-quinone (0.80 mmol) in 4 ml of THF was added to a solution of (0.40 mmol) of the di-germanocene **2b** or **2c** dissolved in 6 ml of THF at r.t. The mixture was stirred for 2 h. The solvent was evaporated in vacuo to give white powders identified, respectively, as **9b** and **9c**.

9b: Yield: 63% after recrystallization from hexane. m.p.: 104–106 °C. ^{1}H-NMR (CDCl$_3$) δ 1.30, 1.31 and 1.46 (s, 36H, C(CH$_3$)$_3$); 1.68, 1.72, 1.81, 1.82, 1.86 (s, 54H, C$_5$Me$_4$ and C$_5$Me$_5$); 6.72 and 6.94 (d, $^4J_{HH} = 2.2$ Hz, 4H, C$_6$H$_2$); 7.20 (s, 4H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 12.24, 12.42, 13.31, 13.50 (C$_5$Me$_4$ and C$_5$Me$_5$); 29.77, 31.93 (C(*CH$_3$*)$_3$); 34.57, 34.72, (*C*(CH$_3$)$_3$); 108.93, 113.22 (CH) (C$_6$H$_2$); 128.89 (CH) (C$_6$H$_4$); 133.79, 133.90 (C$_5$Me$_4$ and C$_5$Me$_5$); 141.09, 147.07, 151.39 (Cquat., C$_6$H$_2$ and C$_6$H$_4$). MS/DCI,NH$_4$: m/z 1172 ([M$^+$, 11%), 1157 ([M–CH$_3$], 2%). Anal. Calc. for C$_{72}$H$_{98}$Ge$_2$O$_4$: C, 73.74; H, 8.42. Found: C, 73.19; H, 8.38%.

9c: Yield: 96%. m.p.: 130–133 °C. ^{1}H-NMR (CDCl$_3$) δ 1.31, 1.32 and 1.48 (s, 36H, C(CH$_3$)$_3$); 1.69, 1.73, 1.77, 1.81, 1.85 (s, 54H, C$_5$Me$_4$ and C$_5$Me$_5$); 6.72 and 6.93 (d, $^4J_{HH} = 2.1$ Hz, 4H, C$_6$H$_2$); 7.30, 7.61 (syst. AB, $^3J_{HH} = 8.0$ Hz, 8H, C$_6$H$_4$). ^{13}C-NMR (CDCl$_3$) δ 12.29, 12.52, 13.26, 13.42 (C$_5$Me$_4$ and C$_5$Me$_5$); 29.85, 32.01 (C(*CH$_3$*)$_3$); 34.61, 34.79 (*C*(CH$_3$)$_3$); 109.01, 113.32 (CH) (C$_6$H$_2$); 126.33, 130.06 (CH) (C$_6$H$_4$); 133.87, 135.27, 138.51, 141.17, 141.33, 142.15, 147.12, 151.42 (Cquat., C$_6$H$_2$, C$_6$H$_4$, C$_5$Me$_4$ and C$_5$Me$_5$). MS/DCI,CH$_4$: m/z 1249 ([M + H]$^+$, 3%). Anal. Calc. for C$_{78}$H$_{102}$Ge$_2$O$_4$: C, 75.02; H, 8.23. Found: C, 74.44; H, 8.15%.

3.10. Reaction of **2e** with 3,5-di-tert-butyl-ortho-quinone

Following the same procedure, a mixture of **1e** (27%), **9e** (41%), and **5** (32%) (relative% calculated from the NMR spectrum) was obtained. The compound **9e** could not be extracted in a pure form from this residue whatever the techniques of separation (crystallization, chromatotron...) may be used.

9e: ^{1}H-NMR (CDCl$_3$) δ 1.32, 1.33 and 1.50, 1.52 (s, 36H, C(*CH$_3$*)$_3$). 1.61, 1.63, 1.65, 1.68, 1.86 (s, 54H, C$_5$Me$_4$ and C$_5$Me$_5$), 6.73, 6.96 (d, $^4J_{HH} = 2.1$ Hz, 4H, C$_6$H$_2$), 7.33 (s, 2H, C$_4$H$_2$S). MS/DCI,NH$_3$: m/z 1196 ([M + NH$_4$]$^+$, 12%), 1179 ([M + H]$^+$, 3%).

3.11. Reaction of **2a** with 3,5-di-tert-butyl-ortho-quinone

The same procedure was followed, except **5** was isolated from a mixture THF–pentane and identified by ^{1}H-NMR [13] (61% yield). ^{1}H-NMR (CDCl$_3$) δ 1.24 and 1.36 (s, 36H, CH$_3$), 1.75 (m, 8H, CH$_2$, THF), 3.83 (m, 8H, OCH$_2$, THF), 6.75 (d, $J = 2$ Hz, 2H, C$_6$H$_2$), 6.98 (d, $J = 2$ Hz, 2H, C$_6$H$_2$).

*3.12. Reaction of **2a**–**c** with [Cp$_2$Fe][BF$_4$]*

A solution of (0.63 mmol) of **2** in 10 ml of CH$_2$Cl$_2$ was treated with (0.44 mmol) of [Cp$_2$Fe][BF$_4$] in 6 ml of CH$_2$Cl$_2$ at r.t. Stirring was continued for 1 h 30 min before the solvent was removed in vacuo. The residue was washed with ether. In any case, the ^{1}H-NMR analysis of the filtrate shows the formation of [Cp$_2$Fe] (4.16 ppm). Various products could be identified from the precipitate.

– **10** (28%) and **1a** (72%) for **2a**.
– **10** (63%) and **1b** (34%) for **2b**.
– **10** (78%) and **1c** (22%) for **2c**.

4. Supplementary material

Crystallography data have been deposited with the Cambridge Crystallography Data Centre as supplementary publications CCDC no. 176098 for **8**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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