Heteroatom Chemistry
Volume 4, Number 4, 1993

Benzodiselenagermoles and Spirobisbenzodiselenagermoles

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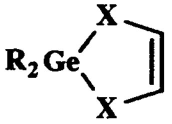
Received 9 April 1992

ABSTRACT

Synthesis of benzodiselenagermoles and bisbenzodiselenagermoles was carried out by transmetallation group 4 → group 14 between diselenophenylenezirconocenes and dialkyl-, diaryl- or alkylaryldichlorogermanes, aryltrichlorogermane or germanium tetrachloride. The new compounds were studied by ^{1}H, ^{77}Se *NMR and mass spectrometry. In the case of compounds with substituted phenyl groups, double irradiation and 2D NMR experiments were performed to determine the chemical shifts of the two selenium atoms. The crystal structure of a spirobisbenzodiselenagermole has been established by X-ray diffraction analysis.*

INTRODUCTION

Although the syntheses and chemistry of compounds containing germanium-oxygen and germanium-sulfur bonds are well documented [1], the first reports on dioxagermoles and dithiagermoles appeared only recently [2,3]



X = O, S

Compounds containing a germanium-selenium bond were described 50 years ago [4], and there has been a renewal of chemical interest in these materials during the last 20 years [5–26]. Particularly, in the metallocenes area, [3]ferrocenophane $[\overline{C_5H_4FeC_5H_4SeGe(Cl_2)Se}]$ has been synthesized and structurally characterized [21]. New six-membered rings incorporating the Se-Ge-Se sequence have also been prepared [26], for which a typical "twisted-boat" conformation has been shown both for the solid state and solution. In addition, some articles deal with the conductive and semiconductive behavior of these compounds. The highly anisotropic electric conduction frequently observed is of great interest in the synthesis of conductive materials [20]. In this field, some valuable results have been obtained from the oxidative addition of germanium-containing diselenides to a macrocyclic square planar complex of rhodium(I) [12]. It is assumed from spectroscopic data and theoretical calculation that conduction might result from introduction of electrons from the electron-rich rhodium atom into the suitable band gap of the germanium-containing chain [27].

Our early work in this area was the synthesis of the first examples of benzodiselenagermoles and

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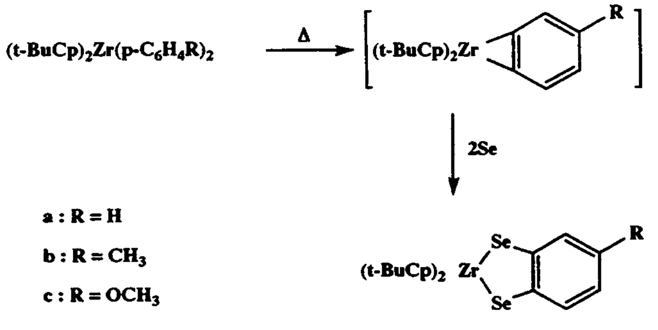
1042-7163/93/$5.00 + .25

spirobisbenzodiselenagermoles published recently as a preliminary report [28]. The present article discusses the synthesis and properties of the large new family of title compounds, either substituted or not in the benzene ring. The recent development of multinuclear NMR spectroscopy makes the observation of the ^{77}Se isotope ($I = 1/2$; 7.5% natural abundance) easy, and we have systematically studied the chemical shifts of the nucleus in the new compounds obtained. Moreover, the structure of the spirobisbenzodiselenagermole had been established by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Our goal was to synthesize a large family of benzodiselenagermoles by diversifying the nature of the substituents either on the germanium or on the benzene ring.

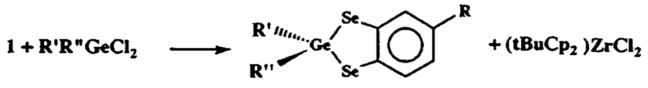
We have previously reported [29] a convenient synthesis of diselenaphenylenezirconocenes (1) starting from substituted diphenylzirconocene.



a : R = H
b : R = CH$_3$
c : R = OCH$_3$

1

Complexes 1 were very easily cleaved by electrophiles, and germanium-containing derivatives were subsequently obtained from reaction with stoichiometric amounts of chlorogermanes. Usually the reaction was carried out at room temperature in tetrahydrofuran solution. The reaction is complete when the deep red color of the starting solution changes to yellow or orange depending on the substituents present. Sometimes the reaction took only a few seconds, but generally it needed some minutes or even some hours. Diselenagermoles, which are fairly more soluble than the side product zirconocene dichloride, were dissolved in pentane or pentane-ether mixture and chromatographed after the solvent was removed. The compounds **2–10** have been synthesized in a 50–70% yield.

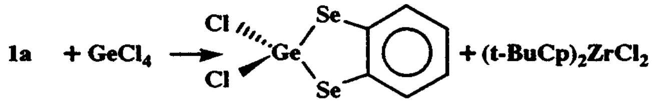


2 : R' = R" = CH$_3$
3 : R' = R" = C$_2$H$_5$
4 : R' = R" = n-C$_3$H$_7$
5 : R' = R" = n-C$_4$H$_9$
6 : R' = R" = i-C$_5$H$_{11}$
7 : R' = R" = Ph
8 : R' = CH$_3$; R" = Ph
9 : R' = CH$_3$; R" = p-H$_3$CPh
10 : R' = Cl ; R" = Ph

a : R = H ; b : R = CH$_3$; c : R = OCH$_3$

Compounds **10** represent interesting intermediates for the preparation of germoles **8** and **9** by reacting with nucleophiles. However, their stability is quite low due to the presence of the germanium-chlorine bond, and they cannot be chromatographed either on silica-gel or on alumina.

The reactions between germanium tetrachloride and complexes **1** have been especially investigated, and two types of germanium-containing compounds were obtained depending on the stoichiometry used. When a solution of complex **1a** was added dropwise to an equimolar solution of GeCl$_4$, **11** was formed. Owing to its hydrolytic instability, it could not be chromatographed and was isolated as a mixture with small amounts of *t*-butylzirconocene dichloride and spiro-derivative **12a** (see later). When **11** was heated in THF (reflux) for 20 hours, an equilibrium was observed between **11** and the spiro-compound **12a** (34/66%). Similar transformation had been precedently observed [30].

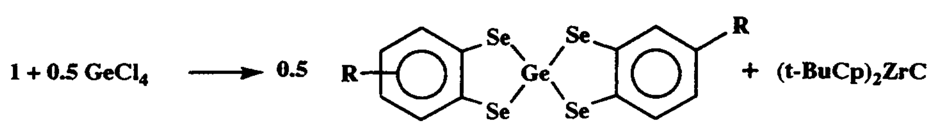


11

In another experiment, the order of the introduction of reagents was inverted and a stoichiometry of half a mole of germanium tetrachloride per mole of the zirconium complex was used. From these new experimental conditions, spirobisbenzodiselenagermoles **12** were obtained in a pure state and in a good yield.

Note that when R is not a hydrogen atom, chiral compounds **12(b,c)** are formed and isolated as racemic mixtures.

The synthesis of a spirobenzodithiadiselenagermole has been attempted from a dichlorogermole. The dichlorogermole **11** represents a convenient precursor for dissymmetric spiro-



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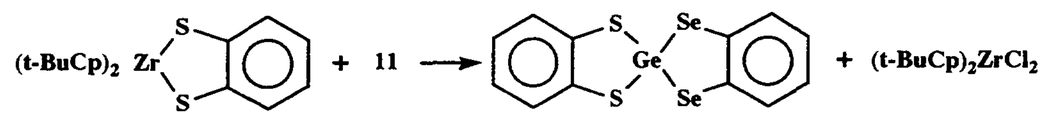
a : R = H ; b : R = CH$_3$; c : R = OCH$_3$



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compounds, and we have examined its reaction with dithiaphenylenezirconocene which we have previously described [31].

The substitution is effective, as shown by the ^{1}H NMR spectrum of the reaction mixture. It exhibits signals from the *t*-butylzirconocene dichloride and from aromatic protons of **13** more or less superposed on those of the spirobisbenzodiselenagermole **12a** which is present as an impurity in the starting reagent **11**. The mass spectrum also exhibits typical fragmentations and isotopic patterns related to the spiro **13** among other peaks. The *t*-butylzirconocene dichloride was easily removed, but even very careful chromatography was inefficient in achieving the separation of the spirocompounds mixture.

The spectroscopic data of the compounds synthesized are given in Table 1. All the mass spectra exhibit the molecular pic; the fragmentation consists firstly of the cleavage of germanium-carbon or germanium-halogen bonds followed by the loss of the germanium atom and the subsequent cleavage of the selenium-containing ring.

The ^{1}H NMR spectra are strongly dependent on the substitution of the benzene ring. For the unsubstituted compounds **2a–7a**, the resonance of the aromatic protons appears as two double doublets (AA'XX" system of spins). The value in chemical shift as the nature of the alkyl groups bonded to the germanium atom is changed is remarkably constant. On the contrary, a slight deshielding (0.05 ppm) is observed when the substituents are two phenyl groups, and the effect is more pronounced (0.1 to 0.2 ppm) for the dichloride **11** (see experimental). The ^{1}H NMR spectra of compounds containing methyl-substituted benzene rings **2b–7b** are very similar to those of **2a–7a**, but the resolution of the spectra, in particular for proton H^6, is bad. On the contrary, the spectra of methoxy-substituted compounds **2c–7c** are very clear for the aromatic protons. As could be predicted, two doublets (J = 8.6 Hz) and a double of doublets (J = 2.7 Hz) related respectively to ortho and meta aromatic protons are observed. The protons H^4 are shifted compared to those of the methyl-substituted compounds, whereas the protons H^5 and H^7 under the direct influence of the methoxy group are highly shifted by about 0.2 ppm.

These comments are also valid for the products with two different substituents bonded to the germanium atom. A final remark is concerned with the ^{1}H NMR signals for bisbenzodiselenagermoles which are only very slightly deshielded (0.05 to 0.10 ppm) with respect to those of the corresponding diselenagermoles.

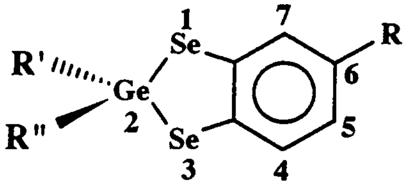
Some interesting features can be deduced from the ^{77}Se NMR spectra. As it has already been mentioned for other organic compounds [32–43] and organometallics [43], the chemical shifts are very dependent on the nature of the substituents present either on the germanium atom or on the benzenic rings. Thus, a methyl group attached to the aromatic ring induces a shift of 5–8 ppm between the signals of the two selenium atoms, whereas the more electron-donating methoxy group increases this value to 35 ppm.

Two methods were used to assign the two signals observed for the heterotopic selenium atoms. The first method was that employing a double irradiation analysis (^{77}Se NMR). Each selenium signal shows a small splitting due to the nearest-neighbor proton (9 Hz for Se^3-H^4 and 6 Hz for Se^1-H^7), and irradiation of the appropriate ^{1}H frequency leads to the collapse of one or the other doublet.

The second method used was a proton-selenium chemical shift correlation. Before performing the experiments and to avoid any inconveniences, we have measured the relaxation time of the selenium atoms and the coupling constant $^3J_{\mathrm{Se\text{-}H}}$. The values of 1.3 sec and ^3J = 9.6 Hz for Se^1 and 0.9 sec and ^3J = 6.4 Hz for Se^3 were found for the reference compound $(i\mathrm{Pr})_2\mathrm{GeSe_2PhOCH_3}$. From the spectrum obtained for **6c** it is clear that the protons H^3 and H^6 are correlated with Se^3 and Se^1, respectively, confirming at the same time our attribution. Similar results were obtained from other representatives of the same family.

Concerning the variation of the ^{77}Se chemical shift (δ) with the length of the aliphatic chains bonded to the germanium atom, it is evident that δ is practically constant beyond three carbon at-

TABLE 1 ^{1}H NMR ($CDCl_3$, TMS), ^{77}Se NMR (C_6D_6, Me_2Se), and Mass Data for Compounds **2–10** and **12**



	δ¹H						*δ⁷⁷Se*		
				C₆H₃					
Product	*R*	*R'*	*R"*	*H⁴*	*H⁵*	*H⁷*	*Se³*	*Se¹*	*Main Fragments (M, %)*
2b	2.22 (s/3)	1.21 (s/6)		7.35 (d/1, *J* = 8.1)	6.77 (d/1, *J* = 8.1 and 1.7	7.31 (broad s/1)	191.7	199.6	354 ($M^{+\cdot}$, 52); 339 (M-CH_3, 75); 324 (M-2CH_3, 38); 170 ($H_3CC_6H_3Se$, 48)
3b	2.21 (s/3)	1.21 (m/6, CH_3) 1.48 (m/4, CH_2)		7.34 (d/1, *J* = 8.0)	6.74 (dd/1, *J* = 8, and 1.5	7.31 (broad s/1)	123.0	131.05	382 ($M^{+\cdot}$, 40); 353 (M-C_2H_5, 76); 324 (M-2C_2H_5, 24); 170 ($H_3CC_6H_3Se$, 39)
4b	2.20 (s/3)	1.01 (m/6, CH_3) 1.56 (m/8, CH_2)		7.34 (d/1, *J* = 8.0)	6.74 (dd/1 *J* = 8.1 and 1.8)	7.30 (broad s/1)	141.9	150.0	410 ($M^{+\cdot}$, 32); 367 (M-C_3H_7, 74); 324 (M-2C_3H_7, 22); 170 ($H_3CC_6H_3Se$, 33)
5b	2.21 (s/3)	0.91 (m/6, CH_3) 1.20–1.55 (m/12, CH_2)		7.34 (d/1 *J* = 8.1)	6.74 (dd/1 *J* = 8.1 and 1.8)	7.30 (broad s/1)	140.8	148.9	438 ($M^{+\cdot}$, 19); 381 (M-C_4H_9, 50); 324 (M-2C_4H_9, 13); 170 ($H_3CC_6H_3Se$, 21)
6b	2.21 (s/3)	0.90 (d/6, CH_3) 1.10–1.50 (m/16, CH + CH_2)		7.34 (d/1 *J* = 7.9)	6.75 (dd/1 *J* = 7.9 and 1.6)	7.30 (broad s/1)	138.0	146.1	446 ($M^{+\cdot}$, 21); 395 (M-C_5H_{11}, 48); 324 (M-2C_5H_{11}, 10); 170 ($H_3CC_6H_3Se$, 14)
7b	2.23 (s/3)	7.35 (m/8 with H^3, H^6 7.73 (m/4)		7.35 (m/8 with Ph and H^6)	6.80 (dd/1 *J* = 8.1 and 1.9)	7.35 (m/8 with Ph and H_3)	167.8	176.2	478 ($M^{+\cdot}$, 66); 401 (M-Ph, 75); 324 (M-2Ph, 9); 244 (M-2Ph-Se, 27); 170 ($H_3CC_6H_3Se$, 30)
2c	3.74 (s/3)	1.22 (s/6)		7.34 (d/1, *J* = 8.7)	6.56 (dd/1 *J* = 8.7 and 2.7)	7.06 (d/1, *J* = 2.7)	180.8	215.1	370 ($M^{+\cdot}$, 33); 355 (M-CH_3, 52); 340 (M-2CH_3, 33); 186 ($H_3COC_6H_3Se$, 6)
3c	3.73 (s/3)	1.22 (s/6, CH_3) 1.50 (m/4, CH_2)		7.34 (d/1, *J* = 8.6)	6.54 (dd/1 *J* = 8.6 and 2.7)	7.06 (d/1, *J* = 2.7)	111.6	146.9	398 ($M^{+\cdot}$, 48); 369 (M-C_2H_5, 71); 340 (M-2C_2H_5, 30)
4c	3.73 (s/3)	1.01 (m/6, CH_3) 1.58 (m/8, CH_2)		7.34 (d/1 *J* = 8.6)	6.54 (dd/1 *J* = 8.6 and 2.7)	7.05 (d/1, *J* = 2.7)	130.3	165.3	426 ($M^{+\cdot}$, 24); 383 (M-C_3H_7, 49); 340 (M-2C_3H_7, 13); 43 (C_3H_7, 100)
5c	3.73 (s/3)	0.91 (d/6, CH_3) 1.20–1.56 (m/12, CH_2)		7.34 (d/1 *J* = 8.6)	6.54 (dd/1 *J* = 8.6 and 2.7)	7.05 (d/1, *J* = 2.7)	129.5	164.6	454 ($M^{+\cdot}$, 30); 397 (M-C_4H_9, 67); 340 (M-2C_4H_9, 14); 186 ($H_3COC_6H_3Se$, 7)
6c	3.73 (s/3)	0.90 (m/6, CH_3) 1.10–1.51 (m/16, CH + CH_2)		7.34 (d/1 *J* = 8.6)	6.54 (dd/1 *J* = 8.6 and 2.8)	7.05 (d/1, *J* = 2.8)	126.8	161.8	482 ($M^{+\cdot}$, 7); 411 (M-C_5H_{11}, 17); 340 (M-2C_5H_{11}, 4)
7c	3.74 (s/3)	7.43 (m/6) 7.75 (m/4)		7.35 (d/1 *J* = 8.7)	6.58 (dd/1 *J* = 8.7 and 2.7)	7.09 (d/1, *J* = 2.7)	156.2	191.9	494 ($M^{+\cdot}$, 17); 401 (M-CH_3, 6); 417 (M-Ph, 14); 402 (M-Ph-CH_3, 8)
8b	2.24 (s/3)	1.45 (s/3)	7.39 (m) 7.74 (m/2)	7.39 (m)	6.80 (dd/1 *J* = 8.0 and 1.6)	7.39 (m)	184.0	192.5	416 ($M^{+\cdot}$, 44); 401 (M-CH_3, 75); 339 (M-Ph, 7); 324 (M-Ph-CH_3, 22); 244 (M-Ph-CH_3-Se, 22); 70 ($H_3CC_6H_3Se$, 52)
9b	2.23 (s/3)	1.43 (s/3)	2.36 (s/3) 7.19–7.41 (m) 7.62 (d/2, *J* = 8.1)	7.19–7.41 (m)	6.79 (dd/1 *J* = 8.0 and 1.5)	7.19–7.41 (m)	184.8	193.3	430 ($M^{+\cdot}$, 36); 415 (M-CH_3, 75); 339 (M-CH_3Ph, 6); 324 (M-CH_3Ph-CH_3, 11); 244 (M-CH_3Ph-CH_3-Se, 26)
10b	2.30 (s/3)		7.54 (m/3) 7.92 (m/2)	7.47 (d/1, *J* = 8.0)	6.92 (dd/1 *J* = 8.0 and 2.0)	7.45 (broad s/1)	284.9	292.4	436 $M^{+\cdot}$, 84); 401 (M-Cl, 12); 359 (M-Ph, 7); 250 ($H_3CC_6H_3Se_2$, 61) 170 ($H_3CC_6H_3Se$, 22); 109 (GeCl, 59)
8c	3.75 (s/3)	1.46 (s/3)	7.43 (m/3) 7.74 (m/2)	7.35 (d/1, *J* = 8.7)	6.58 (dd/1 *J* = 8.7 and 2.7)	7.08 (d/1, *J* = 2.7)	172.8	208.5	432 ($M^{+\cdot}$, 53); 417 (M-CH_3, 68); 340 (M-CH_3-Ph, 18)
9c	3.74 (s/3)	1.44 (s/3)	2.37 (s/3) 7.22 (d/2, *J* = 8.1) 7.63 (d/2 *J* = 8.1)	7.36 (d/1, *J* = 8.6)	6.58 (dd/1 *J* = 8.6 and 2.7)	7.07 (d/1, *J* = 2.7)	173.4	209.1	446 ($M^{+\cdot}$, 50); 431 (M-CH_3, 67); 340 (M-CH_3-PhCH_3, 14)
10c	3.78 (s/3)		7.54 (m/3) 7.92 (m/2)	7.48 (d/1, *J* = 8.7)	6.71 (dd/1 *J* = 8.7 and 2.7)	7.17 (d/1, *J* = 2.7)	276.1	308.65	452 ($M^{+\cdot}$, 80); 417 (M-Cl, 57); 340 (M-Ph-Cl, 19); 266 ($H_3COC_6H_3Se2$, 81); 186 ($H_3COC_6H_3Se$, 12); 109 (GeCl, 16)
12b	2.27 (s/6)			7.40 (d/2, *J* = 7.9)	6.84 (dd/2 *J* = 7.9 and 1.5)	7.37 (broad s/2)	330.2	337.4	574 ($M^{+\cdot}$, 20); 324 (M-H_3CPhSe_2, 28); 250 (H_3CPhSe_2, 100) 170 ($H_3CC_6H_3Se$, 58)

TABLE 1 Continued

	δ^1H						$\delta^{77}Se$		
				C_6H_3					
Product	R	R′	R″	H^4	H^5	H^7	Se^3	Se^1	Main Fragments (M, %)
12c	3.76 (s/6)			7.41 (d/2, J = 8.7)	6.64 (dd/2 J = 8.7 and 2.7)	7.10 (d/2, J = 2.7)	322.8	356.0	606 ($M^{+\cdot}$, 24); 340 ($H_3COC_6H_3Se_2Ge$, 43); 266 ($H_3COC_6H_3Se_2$, 100); 186 ($H_3COC_6H_3Se$, 7)
8a		1.47 (s/3)	7.43 (m/2) 7.75 (m/2)	H^5, H^6 6.98 (dd/2)	H^4, H^7 7.51 (dd/2)		194.3		402 ($M^{+\cdot}$, 36); 387 (M-CH_3, 73); 325 (M-Ph, 6); 310 (M-Ph-CH_3, 16)
9a		1.45 (s/3)	2.37 (s/3) 7.28 (d/2) 7.64 (d/2)	6.97 (dd/2)	7.50 (dd/2)		194.9		416 ($M^{+\cdot}$, 35); 401 (M-CH_3, 77); 325 (M-H_3CPh, 4); 310 (M-H_3CPh-CH_3, 12); 236 ($C_6H_4Se_2$, 6); 156 (C_6H_4Se, 39)
10a			7.53 (m/3) 7.92 (m/2)	7.11 (dd/2)	7.62 (dd/2)		293.0		422 ($M^{+\cdot}$, 87); 387 (M-Cl, 28); 310 (M-Ph-Cl, 5); 236 (C_6H_4Se, 63) 156 (C_6H_4Se, 45); 109 (GeCl, 44)
2a		1.23 (s/6)		6.95 (dd/2)	7.48 (dd/2)		201.6		340 ($M^{+\cdot}$, 40); 325 (M-CH_3, 75); 310 (M-2CH_3, 34); 236 ($C_6H_4Se_2$, 6); 156 (C_6H_4Se, 58)
3a		1.22 (m/6, CH_3) 1.50 (m/4, CH_2)		6.92 (dd/2)	7.48 (dd/2)		133.5		368 ($M^{+\cdot}$, 12); 339 (M-C_2H_5, 32); 310 (M-2C_2H_5, 22); 236 ($C_6H_4Se_2$, 21) 156 (C_6H_4Se, 54)
4a		1.01 (m/6, CH_3) 1.57 (m/8, CH_2)		6.92 (dd/2)	7.47 (dd/2)		151.9		396 ($M^{+\cdot}$, 12); 353 (M-C_3H_7, 28); 310 (M-2C_3H_7, 8); 156 (C_6H_4Se, 23)
5a		0.91 (m/6, CH_3) 1.22–1.55 (m/12, CH_2)		6.93 (dd/2)	7.48 (dd/2)		150.1		424 ($M^{+\cdot}$, 10); 367 (M-C_4H_9, 27); 310 (M-2C_4H_9, 17); 236 ($C_6H_4Se_2$, 12) 156 (C_6H_4Se, 35)
6a		0.90 (d/6, CH_3) 1.10–1.57 (m/16, CH + CH_2)		6.92 (dd/2)	7.47 (dd/2)		148.1		452 ($M^{+\cdot}$, 10); 381 (M-C_5H_{11}, 29); 310 (M-2C_5H_{11}, 8); 156 ($C_6H_4Se_2$, 20)
7a		7.43 (m/6) 7.77 (m/4)		6.98 (dd/2)	7.52 (dd/2)		177.8		464 ($M^{+\cdot}$, 64); 387 (M-Ph, 73); 310 (M-2Ph, 8)
12a				7.03 (dd/4)	7.54 (dd/4)		336.7		546 ($M^{+\cdot}$, 18); 310 ($C_6H_4Se_2Ge$, 26); 236 ($C_6H_4Se_2$, 100) 156 (C_6H_4Se, 92)

oms. However, it is worth noting that δ is shifted to a higher field (20 ppm) when R is an ethyl group but surprisingly, deshielded by about 50 ppm when R is methyl. It is not easy to rationalize this behavior.

The large family of compounds synthesized can be used as a support to check the additivity rules concerned with ^{77}Se and ^{125}Te NMR [32,38–41] as the nature of the substituent directly bonded to the chalcogen is modified. In our case, a chemical shift increment (−7.3 ppm) is calculated when a methyl substituent (**2a**) is replaced by a phenyl group (**8a**), but this value is not doubled as two methyl groups are replaced (compounds **2a** and **7a**, −23.8 ppm). Further, the effects of changes in the substituents on the germanium atom on the ^{77}Se chemical shifts are practically independent of the nature of the aromatic group.

The compound **12a** crystallizes in a monoclinic centrosymmetric space group C2/c with four molecules in the conventional cell. The germanium atoms occupy special positions on a twofold axis, so the molecular symmetry is 2 and the molecule has typical spirane-type geometry (Figure 1). The coordination of germanium is tetrahedral with Ge–Se bond lengths equal to 2.323(1) and 2.326(1) Å (Table 2). These bond lengths correspond very well to the values observed in the range of 2.29–2.37 Å in other Ge–Se bonded compounds [24,25, and references therein]: 2.347(1) and 2.344(1) Å for $Ge(SePh)_4$; 2.353(1) and 2.356(1) Å for $EtGe(SePh)_3$ [25]; 2.360 and 2.365 Å for 1,1-diphenylseleno-1-germanocyclopentane [24]. The Se–C bonds are normal and compare well with the values reported in the literature [24,25,44].

The $GeSe_2C_6$ part of the molecule is planar with the highest deviations from the least-squares plane of 0.02 Å observed for Se atoms. Such a geometry is quite different from that found in the complexes of d° zirconocenes with o-Z_1-Z_2-C_6H_4 ligands (Z_1 = Se, (Te, S); Z_2 = Se, (S, Te)) [30,45], where the dihedral angles between the Z_1Z_2 and Z_2C_6 planes are 54–56°. It is worth noting that, in the ditelluraphenylene complex of platinum, $Pt(Te_2C_6H_4)(PPh_3)_2$, the $PtTe_2$ and Te_2C_6 moieties are essentially coplanar [46]. At this time, we do not have a clear explanation for the structural differences observed for these M-o-$Z_2C_6H_4$ complexes; why the formally d^{10} and d^8 (Ge, Pt) ones are planar, while the d^0 (Zr) ones are canted?

Another interesting feature of the crystal structure of **12a** is the presence of the chains running in the lattice direction [101]. There are formally two chains per cell, each one containing two mol-

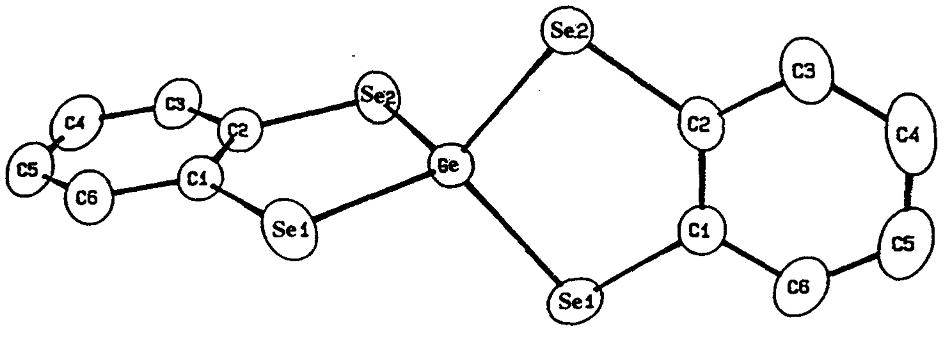


FIGURE 1 Molecular structure of Ge[$Se_2(o\text{-}C_6H_4)]_2$ (the numeration is specific to the X-ray part).

TABLE 2 Bond Distances (Å) and Angles (°) for Ge[$Se_2(o)C_6H_4)]_2$ (**12a**)

Ge		Se1	2.3232(9)	C1		C6	1.388(9)
Ge		Se2	2.3258(9)	C2		C3	1.40(2)
Se1		C1	1.917(8)	C3		C4	1.38(1)
Se2		C2	1.910(6)	C4		C5	1.38(1)
C1		C2	1.373(9)	C5		C6	1.37(1)
Se1	Ge	Se1′	110.60(5)	C2	C1	C5	120.2(7)
Se1	Ge	Se2	99.31(3)	Se2	C2	C1	124.8(5)
Se1	Ge	Se2′	119.04(3)	Se2	C2	C3	115.4(5)
Se2	Ge	Se2′	110.73(5)	C1	C2	C3	119.7(6)
Ge	Se1	C1	95.9(2)	C2	C3	C4	119.1(7)
Ge	Se2	C2	95.7(3)	C3	C4	C5	121.0(8)
Se1	C1	C2	124.2(5)	C4	C5	C6	119.6(8)
Se1	C1	C6	115.7(5)	C1	C6	C5	120.3(7)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Primed atoms are related to the nonprimed ones by rotation 1-*x*, *y*, 1/2-*z*.

ecules from the four building it. Inside one chain (e.g., A in Figure 2), the molecules are reproduced by symmetry centers and the two neighbor molecules in a chain have parallel phenyl rings. The distances between the phenyl planes of the neighboring molecules are equal to 3.62 Å. The Ge . . . Ge distances inside a chain are equal to 8.136 Å. To each molecule in a chain corresponds one closest molecule from the neighboring chain, e.g., B_1 to A_1 and C_1 to A_0 (Figure 2). This gives the pseudodimers in which the phenyl rings are mutually perpendicular with Ge . . . Ge distances of 5.370 Å and the shortest phenyl plane-selenium contacts of 3.59 Å.

The phenyl rings of adjacent molecules in a chain are slightly slipped in the direction of the chain from an ideal face-to-face superposition. According to Hunter and Sanders [47], such a slipping results from electrostatic π-π repulsions. The phenyl ring of one molecule (e.g., A_0, Figure 2) is in the proximity of the $GeSe_2$ unit of the neighbor (e.g., A_1 and A_2). This indicates that the selenium lone pairs do not apparently contribute to the repulsion system and that the germanium center behaves as an electrophilic site. Because, despite the repulsive π-π interactions between the phenyl groups, their rings remain parallel, and the Van der Waals intermolecular interactions should be strong. The presence of the pseudo-dimers, joining the chains with mutually perpendicular phenyl rings, suggests that the π-σ attractions, which dominate in an edge-on geometry, supply supplementary attractive energy to the overall stabilization of the structure.

EXPERIMENTAL

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded in $CDCl_3$ with a JEOL FX100 (100 MHz) spectrometer using tetramethylsilane as the internal standard. Selenium nuclear magnetic resonance (^{77}Se NMR) spectra were determined in C_6D_6 with a BRUKER WR300 or WR200 spectrometer operating at 57.240 and 39.168 MHz, respectively, using dimethyl selenide as the external standard.

Mass spectra were recorded at the "Service Central de Spectrométrie de Masse du CNRS" by electron ionization of the samples (70 eV). Chromatography was carried out on Silicagel Merck 9385 according to Still *et al.* [48]. All reactions were carried out under argon. The solvents were distilled from sodium-benzophenone ketyl complex prior to use. Diselenophenylenezirconocenes were obtained according to Ref. [29] and [31].

Germanium tetrachloride was purchased from Merck. Dialkyl and diaryldichlorogermanes have been synthesized according to the literature methods: Ph_2GeCl_2 [49]; $(n\text{Pr})_2GeCl_2$ [50]; Et_2GeCl_2 [51]; Me_2GeCl_2 [52]; $(n\text{-Bu})_2GeCl_2$ [49b, 53]; Ph(Cl)$GeCl_2$ [49b, 53b, 54]; Ph(Me)$GeCl_2$ [55]; $(iC_5H_{11})_2GeCl_2$; and Me(*p*-tolyl)$GeCl_2$ [56].

Specific conditions of syntheses and physical and analytical data of compounds **2–10** and **12** are reported in Table 3.

Compounds with Ge–C Bonds **2–10**

The general procedure is described for **7a**. Under argon, a solution of diphenyldichlorogermane (0.39

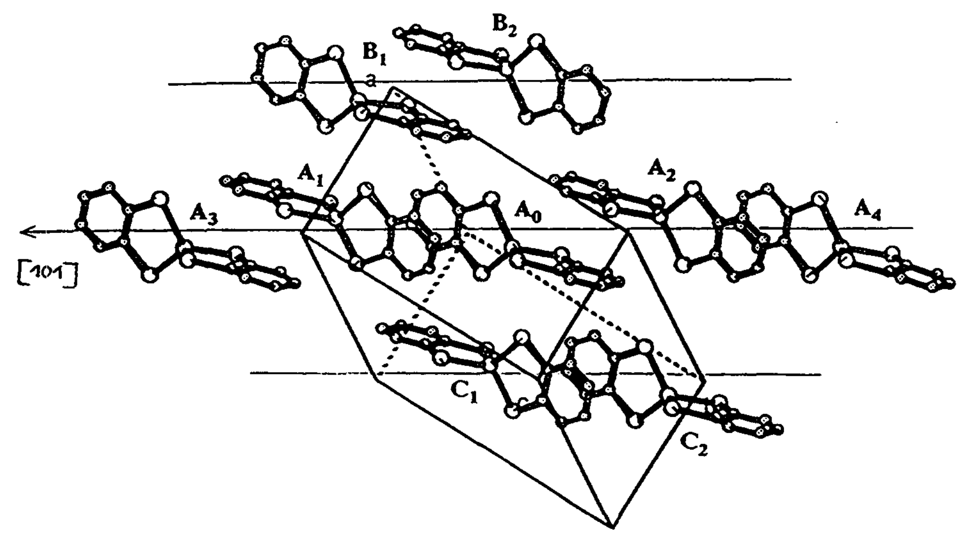


FIGURE 2 Structural arrangement of molecules from chain (A) with molecules of next chains (B and C) in structure of compound **12a**.

TABLE 3 Experimental Conditions and Analytical Results for Compounds **2–10** and **12**

Compound	Reaction Time (hour)	Solvent for Extraction	Eluent	Crystallization	Yield (%)	MP (°C)	Formula	C		H	
								Calc	Found	Calc	Found
2a	2	A	C	F	30	114	$C_8H_{10}GeSe_2$	28.54	28.46	2.99	2.92
3a	4	A	C	oil	92		$C_{10}H_{14}GeSe_2$				
4a	4	A	C	oil	89		$C_{12}H_{18}GeSe_2$				
5a	3	A	C	oil	75		$C_{14}H_{22}GeSe_2$				
6a	2	A	C	oil	30		$C_{16}H_{26}GeSe_2$				
7a	1	A	C	E	55	114	$C_{18}H_{14}GeSe_2$	46.91	47.16	3.06	3.09
8a	15	A	C	F	57	70	$C_{13}H_{12}GeSe_2$	39.15	39.12	3.03	2.81
9a	3	B	C	F	67	98	$C_{14}H_{14}GeSe_2$	40.74	40.93	3.42	3.49
10a	1	A		F	53	90	$C_{12}H_9ClGeSe_2$	34.38	35.15	2.16	2.15
12a	1	B	D	E	40	216	$C_{12}H_8GeSe_4$	25.64	26.53	1.48	1.94
2b	2	A	C	oil	63		$C_9H_{12}GeSe_2$				
3b	3	A	C	oil	90		$C_{11}H_{16}GeSe_2$				
4b	4	A	C	oil	85		$C_{13}H_{20}GeSe_2$				
5b	3	A	C	oil	87		$C_{15}H_{24}GeSe_2$				
6b	4	A	C	oil	90		$C_{17}H_{18}GeSe_2$				
7b	3	B	D	E	77	147	$C_{19}H_{16}GeSe_2$	48.06	48.29	3.39	3.62
8b	15	A	C	A	39	49	$C_{14}H_{14}GeSe_2$	40.74	41.22	3.42	3.61
9b	3	A	C	F	52	70	$C_{15}H_{16}GeSe_2$	42.21	42.36	3.78	3.85
10b	1	A		F	25	50	$C_{13}H_{11}ClGeSe_2$	36.04	36.29	2.56	2.79
12b	1	B	D	E	76	178	$C_{14}H_{12}GeSe_4$	29.57	30.12	2.13	2.26
2c	5	B	C	F	58	106	$C_9H_{12}OGeSe_2$	29.48	30.89	3.3	2.47
3c	6	A	C	oil	73		$C_{11}H_{16}OGeSe_2$				
4c	6	A	C	oil	95		$C_{13}H_{20}OGeSe_2$				
5c	5	A	C	oil	72		$C_{15}H_{24}OGeSe_2$				
6c	15	A	C	oil	82		$C_{17}H_{28}OGeSe_2$				
7c	5	B	D	E	40	133	$C_{19}H_{16}OGeSe_2$	46.49	46.35	3.28	3.10
8c	6	B	D	F	54	104	$C_{14}H_{14}OGeSe_2$	39.21	39.09	3.29	3.01
9c	4	B	D	F	66	74	$C_{15}H_{16}OGeSe_2$	40.69	40.80	3.64	3.69
10c	1	A		F	51	72	$C_{13}H_{11}ClOGeSe_2$	34.76	35.13	2.47	2.48
12c	1	B	D	E	50	197	$C_{14}H_{12}GeO_2Se_4$	27.99	27.67	2.01	1.98

A: pentane, B: pentane + ether, C: pentane-ether 9/1, D: pentane-ether 8/2, E: CH_2Cl_2-hexane I/I, and F: hexane.

TABLE 4 Crystallographic Data for Ge[Se_2(*o*-C_6H_4)]$_2$ (**12a**)

Molecular formula	$C_{12}H_8GeSe_4$
Formula weight, g	540.63
Crystal system	monoclinic
Space group	C2/c (No. 15)
Cell dimension:	
a, Å	15.200(2)
b, Å	11.310(1)
c, Å	8.383(2)
β, deg	103.08(1)
V, $Å^3$	1403.7
z	4
ρcalc, g · cm^{-3}	2.558
Linear abs, μ, cm^{-1}	123.99
F(000)	992
Radiation, Å	$\lambda(MoK_\alpha)$ 0.71073
Scan type	ω-2θ
Scan speed, deg · min^{-1}	1.3–4.1
Scan width, deg	$\Delta\omega - 1.0 + 0.347 \tan\theta$
Reflections measured	*h*, *k*, ±1
θ range, deg	2–30
Number of reflections measured	4448
Temperature, K	296(1)
Decay, %	−1.2, corrected
Cut off for observed data	$I \geq 4\sigma(I)$
Number of unique observed data (NO)	1064
Number of variables (NV)	91
Empirical absorption corrections	
(psi-can, EAC), $transm_{min-max}$	44.547–99.534
(DIFABS), $transm_{min-max}$	0.6831–1.4879
R(F)	0.033
Isotropic extinction parameter	1.4772 * 10^{-6}
GOF	3.053

TABLE 5 Positional and Thermal Parameters for Ge[Se_2(*o*-C_6H_4)]$_2$ (**12a**)

Atom	*x*	*y*	*z*	*B*($Å^2$)
Ge	0.500	0.35159(9)	0.250	2.35(2)
Se1	0.60541(5)	0.46853(7)	0.42459(9)	3.53(1)
Se2	0.59761(5)	0.23472(7)	0.14042(8)	3.06(1)
C1	0.7096(4)	0.3962(6)	0.3729(8)	2.7(1)
C2	0.7060(4)	0.3073(6)	0.2601(8)	2.6(1)
C3	0.7864(5)	0.2615(7)	0.2299(9)	3.7(2)
C4	0.8681(5)	0.3079(8)	−0.314(1)	4.6(2)
C5	0.8712(5)	0.3974(8)	0.425(1)	4.6(2)
C6	0.7923(5)	0.4399(7)	0.458(1)	4.0(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as follows:
(4/3) * [a2 * B(1,1) + b2 * B(2,2) + c2 * B(3,3) + ab(cos gamma) * B(1,2) + ac(cos beta) * B(1,3) + bc(cos alpha) * B(2,3)].

g, 1.30 mmol) in THF (16 mL) was added dropwise at room temperature to a stirred deep red solution of diselenophenylenezirconocene **1a** (0.74 g, 1.34 mmol) in THF (24 mL). The red color of the reaction mixture was discharged after 1 hour stirring. The reaction glass was opened to air and the solvent evaporated in vacuum. The crude product was extracted from the residue with pentane (40 mL); the insoluble was identified to be *tert*-butylzirconocene dichloride. The yellow solid from the pentane was chromatographed (silicagel, pentane-ether 9/1), and the first yellow fraction collected afforded yellow crystals from a mixture of dichloromethane-hexane 1/1 (10 mL). There was obtained 0.33 g (0.72 mmol), 55% yield, mp 114°C.

Monochlorides **10**

They have been obtained under the same experimental conditions which are described for **10c**: a deep red solution of **1c** (0.7 g, 1.17 mmol) in THF (28 mL) was slowly added at room temperature under argon and with stirring to a colorless solution of phenyltrichlorogermane (0.3 g, 1.17 mmol) in THF (14 mL). The color readily turned yellow during the addition. Stirring was maintained for 1 hour, the reaction mixture was opened to air and the solvent was evaporated. The crude material was extracted with pentane, and the product was crystallized from hexane (16 mL) after having been allowed to stay at −20°C for 3 days. Pale yellow crystals (0.27 g, 0.6 mmol), 51% yield, mp 72°C, were obtained.

Spirobisbenzodiselenagermoles **12**

Under argon and with stirring, a colorless solution of $GeCl_4$ (1 mole) in THF was slowly added at room temperature to a deep red solution of **1** (2 moles) in the same solvent. The reaction proceeded for a few seconds, and just after the end of the addition, the solvent was removed at reduced pressure. The residue was extracted with a pentane-diethyl ether 3/1 mixture, and the crude solid from extracts was chromatographed on silicagel with pentane-diethyl ether 8/2 as eluent. The yellow solid obtained from elution was crystallized from a cold dichloromethane-hexane 1/1 solution.

Dichloride **11**

The reagents were mixed in the inverse order to that reported previously for **12**. At room temperature, a THF solution (25 mL) of **1** (0.84 g, 1.48 mmol) was added dropwise to a stirred solution of $GeCl_4$ (0.17g, 1.48 mmol) in THF (16 mL). The red color was immediately discharged, and the solvent was evaporated as the reaction mixture was air protected. The residue was extracted with ether, and the solid obtained after evaporation of the ether was washed three times with pentane and then dried. ^1H NMR ($CDCl_3$) δ 7.11 (dd, 2H); 7.58 (dd, 2H). ^{77}Se δ 378.25. MS (*m/z*, %) 380 (M, 18); 345 (M-Cl, 3); 310 (M-2Cl, 9); 236 ($C_6H_4Se_2$, 100); 156 (C_6H_4Se, 38); 109 (GeCl, 21).

Spirodithiadiselenagermole **13**

To a light red solution of dithiophenylenetert-butylzirconocene (0.14 g, 0.29 mmol) in THF (16 mL), a pale yellow solution of **20** (0.11 g, 0.29 mmol) in THF (10 mL) was slowly added at room temperature and under argon. After 5 hours of stirring, the orange solution was evaporated and the residue was chromatographed (pentane-diethyl ether 9/1). The yellow fraction afforded 55 mg (0.12 mmol) of yellow crystals (42% yield), which were 80% pure by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6) δ 6.56 (m, 4H); 7.06 (m, 4H). Mass spectrum m/z (relative intensity %) 450 (M, 100), 310 (M-$Se_2C_6H_4$, 20), 236 ($C_6H_4Se_2$, 92), 214 (C_6H_4SeGe, 56), 156 (C_6H_4Se, 25), 140 ($C_6H_4S_2$, 10), 108 (C_6H_4S, 10).

From the spectroscopic results, it is clear that **13** contains a small amount of **12a** present in the reagent **11** used in the synthesis.

Crystal Structure Analysis of $Ge[Se_2(o\text{-}C_6H_4)]_2$

A yellow crystal (0.45 × 0.35 × 0.25 mm) suitable for X-ray analysis was grown from CH_2Cl_2/hexane 1/1 solution and mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined from 25 randomly selected reflections (CAD4 routines) and reduced cell calculations revealed the monoclinic space group C2/c. Crystallographic data are summarized in Table 4. The intensities were measured in an ω-2θ scan (λ(Mo-K_α) radiation, graphite monochromator) and corrected for L_P and absorption effects (psi-scan). All calculations were carried out using the Enraf-Nonius SDP library [57]. Neutral atom scattering factors and anomalous dispersion corrections were those given by Cromer and Waber [58]. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. An absorption correction (DIFABS [59]) was applied after isotropic refinement of all atoms. All nonhydrogen atoms were further refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions (HYDRO program of SDP), riding on the carbon atoms bearing them, and included in final calculations with B_{iso} fixed at 5.0 Å^2. The final refinement with unit weights and an isotropic extinction parameter gave $R = 0.033$ and GOF = 3.053. The atomic coordinates of nonhydrogen atoms are given in Table 5.

Tables of anisotropic temperature factors, hydrogen atom positions, least-squares planes, and listing structure factors are available from the authors.

We are currently investigating other molecules containing several metal (main group)-chalcogen bonds starting from zirconium complexes.

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