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Inorganica Chimica Acta 305 (2000) 46-52

Inorganica Chimica Acta

Synthesis and characterization of Group 14 elements — dithienylsulfur cycloadducts and oligomers

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Received 20 January 2000; accepted 8 March 2000

Abstract

The reactions of various organometallic dichlorides R_2MCl_2 (R = Bu, Ph; M = Si, Ge, Sn) with 2,2'-dilithio 3,3'-dithienylsulfur were described. They gave simultaneously cycloadducts and oligomers. The X-ray crystal structure of the heterocycle **3b** shows a slightly distorted six-membered ring with the two heteroatoms (sulfur and germanium) in a boat conformation. The molecular weights of the oligomers were determined by size exclusion chromatography. Starting from metal divalent species, insoluble oligomers were obtained. The presence of bivalent metallic sites in these chains was verified by cycloaddition reaction with 3,5-di-*t*-butyl orthoquinone. Electrical studies show that these non-doped oligomers behave as semi-conductors. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Heterocycle; Organometallic polymers; Polygermylenes; Electrical conductivity

1. Introduction

The role of organometallic polymers in material chemistry has recently increased considerably [1]. The presence of a Group 14 metal (M = Si or Ge) in polymeric chains introduces specific physical properties (conductivity [1], electroluminescence [2]). The best known are the polysilanes and polygermanes [3] in which electron delocalization can occur through the σ electrons of metal-metal bonds. On the other hand, for polymers having one or two alternating Group 14 metal atoms and a π -conjugated system (acetylene, phenyl, thiophene, pyrrol, etc.) [1,4], $\sigma - \pi$ delocalization is considered. In this work, we are interested in polycondensed structures having the potential semi-conductors properties. Towards this end, we have used a novel ligand, 3,3'-dithienylsulfur, capable of giving cycloaddition or polymerization reactions.

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2. Experimental

All of the reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques and dry solvents. NMR spectra were recorded on Bruker AC 80 (¹H), AC 200 (¹³C, in the sequence Jmod) and Bruker 300 (13C NMR in the solid state, ENSCM, Montpellier). Mass spectra were measured with a Hewlett-Packard HP 5989 in the electron impact mode (70 eV) or a Rybermag R10-10 spectrometer operating in the electron impact mode or by chemical desorption (DCI, CH₄). IR spectra with a Perkin-Elmer 1600 FT spectrometer. SEC analysis was performed using a Waters apparatus fitted with three Styragel HR[®] columns (10², 10³, and 10⁴ Å) and refractometry detection. Melting points were measured on a Leitz microscope. Elemental analysis were performed by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse.

The 3,3-dithienylsulfur was prepared as described in [5].

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2.1. Reaction of 2 with Bu_2GeCl_2

A solution of Bu₂GeCl₂ (0.39 g, 1.5 mmol) in 3 ml of diethylether was added dropwise to a solution of **2** [5,7] (1.5 mmol) in 3 ml of diethylether at 0°C. After having been stirred at 20°C for 15 h, the mixture was hydrolyzed. After extraction, drying under Na₂SO₄, the solvents were evaporated. The ¹H NMR analysis of the crude mixture shows the formation of **3a** (60%) and **4a** (40%). **4a**: ¹H NMR (CDCl₃): δ 0.70–1.79 (m, 18H, Bu), 6.64–6.94 (m, 2H, H₄), 7.27–7.56 (m, 2H, H₅). The mass spectrum (DCI, CH₄) indicates the presence of **5a**: m/z 767 ([M+1], 2%), 709 ([M-Bu], 2%).

When the same reaction was performed in more dilute solutions (2.8 mmol of Bu_2GeCl_2 in 17 ml of diethylether and **2** (2.8 mmol) in 30 ml of diethylether at $-15^{\circ}C$), the distillation of the residue led to pure **3a**: Eb: 110°C/5.10⁻³ mmHg), 0.21 g (20%). ¹H NMR (CDCl₃): δ 0.70–1.79 (m, 18H, Bu), 7.10 (d, ³*J*=5 Hz, 2H, H₄), 7.63 (d, ³*J*=5 Hz, 2H, H₅). ¹³C{¹H} NMR (CDCl₃): δ 13.70 (CH₃), 16.61, 26.07 and 27.15 (CH₂); 122.75 (C₂), 126.90 (C₅), 130.33 (C₄), 135.63 (C₃) (C₄H₂S). MS: *m*/*z* 384 ([*M*]⁺, 23%), 327 ([*M*-Bu], 100%). *Anal.* Calc. for C₁₆H₂₂GeS₃: C, 50.16; H, 5.79; S, 25.11. Found: C, 50.81; H, 6.09; S, 24.75%.

2.2. Reaction of 2 with Ph_2GeCl_2

To a solution of **2** (2 mmol) in 3.5 ml of diethylether was added (0.60 g, 2 mmol) of Ph₂GeCl₂ at 0°C. The mixture was stirred for 12 h at 20°C. After hydrolysis, extraction with a THF/Et₂O mixture, concentration of the solvents, the residue was extracted with 13 ml of methanol leading to the formation of a white powder which was isolated after decantation and drying: **4b**, 0.77 g (90%); m.p. 96–100°C (dec.). ¹H NMR (CDCl₃): δ 7.14–7.65 (m, 14H, C₆H₅, C₄H₂S). ¹³C{¹H} NMR (CDCl₃): δ 128.58 (C₈), 129.68 (C₉), 134.55 (C₇) (C₆H₅); 127.03 (C₅), 131.46 (C₄) (C₄H₂S). *Anal.* Calc. for C₂₀H₁₄GeS₃: C, 56.77; H, 3.33. Found: C, 56.20; H, 3.87%. The mass spectrum (DCI, CH₄) shows the presence of **5b**: *m*/*z* 846 ([*M*]⁺, 3%), 769 ([*M*-Ph], 5%).

Selected bond lengths (Å) and bond angles (°) for 3b

Table 1

Ge(1)–C(1)	1.915(2)	S(1)–C(6)	1.766(3)	
Ge(1)–C(5)	1.926(3)	S(2)–C(4)	1.704(3)	
Ge(1)–C(15)	1.933(2)	S(2)–C(1)	1.719(2)	
Ge(1)–C(9)	1.939(2)	C(1)–C(2)	1.370(3)	
S(1)–C(2)	1.755(2)	C(3)–C(4)	1.351(4)	
C(1)-Ge(1)-C(5) C(1)-Ge(1)-C(15) C(5)-Ge(1)-C(15) C(1)-Ge(1)-C(9) C(5)-Ge(1)-C(9) C(15)-Ge(1)-C(9)	99.60(11) 112.41(10) 114.75(11) 110.33(11) 108.55(11) 110.67(10)	$\begin{array}{c} C(2) - S(1) - C(6) \\ C(4) - S(2) - C(1) \\ C(2) - C(1) - Ge(1) \\ C(1) - C(2) - S(1) \\ C(6) - C(5) - Ge(1) \\ C(5) - C(6) - S(1) \end{array}$	105.77(12) 92.83(12) 125.97(18) 127.2(2) 125.0(2) 127.9(2)	

When more dilute solutions (2.29 mmol of **2** in 15 ml of diethylether and Ph₂GeCl₂ (0.68 g, 2.29 mmol) in 25 ml of diethylether at -15° C) were used, small quantities of monomeric heterocycle 3b can be isolated from the methanolic filtrate using the procedures described: after concentration of MeOH, the extraction of the residue using hot hexane gave a white powder 0.39 g (40%) which was recrystallized from CHCl₃. 3b: m.p. 112–116°C. ¹H NMR (CDCl₃): δ 7.22 (d, ³J=5 Hz, 2H, H₄), 7.72 (d, ${}^{3}J = 5$ Hz, 2H, H₅), 7.01-7.90 (m, 10H, C_6H_5). ¹³C{¹H} NMR (CDCl₃): δ 128.70 (C₈), 130.00 (C₉), 134.65 (C₇), 136.97 (C₆) (C₆H₅); 120.78 (C₂), 127.11 (C₅), 131.61 (C₄), 135.22 (C₃) (C₄H₂S). MS: m/z 424 ([M]⁺, 78%), 347 ([M-Ph], 100%). Anal. Calc. for C₂₀H₁₄GeS₃: C, 56.77; H, 3.33. Found: C, 56.12; H, 3.29%.

2.3. Crystal and experimental data for 3b

 $[C_{20}H_{14}GeS_3], M_r = 423.08$, orthorhombic, *Pbca*, *a* = 13.544(2), b = 15.115(2), c = 17.544(2) Å, V = 3591.6(8)Å³, Z = 8, $D_{calc} = 1.565$ Mg m⁻³, F(000) = 1712, $\lambda =$ 0.71073 Å, T = 173(2) K, μ (Mo K α) = 2.053 mm⁻¹, crystal size $0.6 \times 0.4 \times 0.3$ mm, $2.33^{\circ} < \theta < 22.59^{\circ}$, 29369 reflections (2363 independent) collected on a STOE-IPDS diffractometer. A semi-empirical absorption correction was performed $(T_{\text{max}} = 0.7337 \text{ and}$ $T_{\rm min} = 0.5094$). The structure was solved by direct method using SHELXS-97 [8] and refined using the leastsquares method on F^2 [9]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were refined with a riding model. Maximum residual electron density 0.239 e Å⁻³, R_1 [I>2 σ (I)] = 0.0202 and wR_2 (all data) = 0.0436 with $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_o|$ and $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$. Selected bond lengths and angles are displayed in Table 1.

2.4. Reaction of 2 with Bu_2SnCl_2

Using the same procedure as described above, 1.49 mmol of 2 in 3.5 ml of diethylether and Bu₂SnCl₂ (0.45 g, 1.49 mmol) gave after concentration, a viscous oil. The ¹H NMR analysis of the crude mixture shows the presence of 3c (39%) and 4c (37%). Treatment by a Et₂O/pentane mixture (1:4), and further decantation gave a yellow oil containing principally the oligomer **4c**, while the pentanic solution indicates the major formation of **3c**. ¹H NMR (CDCl₃): δ 0.70–1.85 (m, 18H, Bu), 7.20 (d, ${}^{3}J = 5$ Hz, 2H, H₄), 7.66 (d, ${}^{3}J = 5$ Hz, 2H, H₅). ¹³C{¹H} NMR (CDCl₃): δ 13.71 (CH₃); 13.55, 27.19 and 28.46 (CH₂); 125.31 (C₂), 127.88 (C₅), 131.32 (C₄), 137.53 (C₃) (C₄H₂S). MS: m/z 430 ([M]⁺, 21%), 373 ([M-Bu], 93%). 4c: ¹H NMR (CDCl₂): δ 0.70-1.85 (m, 18H, Bu), 6.87 (d, ${}^{3}J = 5$ Hz, 2H, H₄), 7.50 (d, ${}^{3}J = 5$ Hz, 2H, H₅). The mass spectrum indicates the presence of 5c. m/z 859 ([M+1], 100%), 801 ([M-Bu], 91%).

2.5. Reaction of 2 with Ph_2SiCl_2

A solution of 2 (1.5 mmol) in 3.5 ml of diethylether was added to a solution of Ph₂SiCl₂ (0.38 g, 1.5 mmol) in 3 ml of diethylether at -15° C. The mixture was stirred for 12 h at 20°C, then refluxed for 1 h. After hydrolysis, extraction with a mixture Et₂O/THF, drying on Na₂SO₄ and concentration of the solvents, a brown oil was obtained. This oil was dissolved in 1 ml of diethylether and added to 15 ml of MeOH. After decantation, a new brown oil was dried under vacuo and identified to be oligomeric form 4d: ¹H NMR (CDCl₃): δ 7.19 (d, ${}^{3}J = 5$ Hz, 2H, H₄), 7.36-7.45 (m, 5H, C_6H_5), 7.64–7.76 (m, 7H, C_6H_5 , H₅). The filtrate was concentrated, the residue extracted with hot hexane. After cooling at -30° C for 12 h, a white powder was isolated after decantation and drying: 3d: 0.16 g (33%). ¹H NMR (CDCl₃): δ 7.20 (d, ³J=5 Hz, 2H, H_4), 7.74 (d, ${}^{3}J = 5$ Hz, 2H, H_5), 7.37-7.78 (m, 10H, C₆H₅). ¹³C{¹H} NMR (CDCl₃): δ 128.36 (C₈), 130.52 (C_9) , 135.82 (C_7) , 139.73 (C_6) (C_6H_5) ; 120.20 (C_2) , 127.14 (C₅), 133.95 (C₃), 135.05 (C₄) (C₄H₂S). MS: m/z378 ($[M]^+$, 78%), 301 ([M-Ph], 100%). We could also detect traces of oxidized compound: m/z 576 ([M]⁺, 30%), 499 ([M-Ph], 25%).



2.6. Reaction of 2 with MesGeCl₃

To a solution of **2** (2 mmol) in 3.5 ml of diethylether was added (0.60 g, 2 mmol) of MesGeCl₃ in 3 ml of diethylether at -10° C. The mixture was stirred at 20°C for 3 h. After hydrolysis (3 N HCl), extraction and drying, the solution was concentrated. The ¹H NMR analysis shows the formation of **3e** (20%) and polygermylenes (MesClGe)_{*n*}. **3e**: ¹H NMR (CDCl₃): δ 2.26 (s, 6H, *o*-CH₃), 2.43 (s, 3H, *p*-CH₃), 6.86 (sl, 2H, C₆H₂), 7.12 (d, ³J = 5 Hz, 2H, H₄), 7.72 (d, ³J = 5 Hz, 2H, H₅). MS: *m*/*z* 424 ([*M*]⁺, 17%), 389 ([*M*-Cl], 4%), 305 ([*M*-Mes], 23%).

2.7. Reaction of 2 with Mes_2GeCl_2

Using the same procedure as described above, **2** (0.9 mmol) in 2 ml of diethylether and Mes_2GeCl_2 (0.35 g, 0.9 mmol) in 1.5 ml of diethylether at 0°C gave an orange solid. The ¹H NMR analysis shows the major formation of $(Mes_2Ge)_n$: 2.25 (sl, 18H, *o*-CH₃ and *p*-CH₃), 6.79 (sl, 4H, C₆H₂). The mass spectrum indicates the formation of **3f**: m/z 508 ([*M*]⁺, 3%), 389 ([*M*-Mes], 19%).

2.8. Reaction of 2 with Cl_2M

A 1.49 mmol sample of **2** in 15 ml of Et₂O was added to a suspension of Cl₂M (Cl₂Ge, dioxane or Cl₂Sn) (1.50 mmol) in 8 ml of diethylether at -15° C. The mixture was stirred for 12 h at 20°C, yielding a precipitate. After decantation and drying, yellow powder very sensitive to hydrolysis was obtained. **7a**: m.p. > 300°C. ¹H NMR (CDCl₃, DMSO-d₆): δ 6.50–7.40 (m, 4H, C₄H₂S). IR (Nujol): δ (CH): 720 and 865 cm⁻¹, we also observed the presence of H₂O: ν (OH): 3391 cm⁻¹ and δ (HOH): 1633 cm⁻¹. **7b**: m.p. > 300°C. ¹H NMR (CDCl₃, DMSO-d₆): δ 6.50–7.20 (m, 4H, C₄H₂S). IR (Nujol) δ (CH): 716 and 865 cm⁻¹, ν (OH): 3391 and δ (HOH): 1633 cm⁻¹.

2.9. Preparation of 9

To a solution of 2,5-dilithiothiophene [10] (1.0 mmol) in 2 ml of THF was added Cl_2Ge -dioxane (0.21 g, 0.9 mmol) at -40° C. The mixture was stirred for 3 h at this temperature and then slowly warmed to room temperature (r.t.). After decantation and washing with THF, a yellow powder was obtained. ¹³C NMR (solid state): δ 125–140 (large signal, C_4H_2 S). IR (Nujol): δ (CH): 808 cm⁻¹.

2.10. Reaction of **7a** and **9** with 3,5-di-t-butyl ortho-quinone

A mixture of polymer **7a** or **9** (0.67 mmol) and (0.11 g, 0.50 mmol) of quinone in 2 ml of THF was heated in a sealed tube at 100°C for 2 days. After concentration, the residue was extracted with a mixture of 2 ml of Et_2O and 3 ml of pentane giving a white powder, identified to be the spirocompound **8** [11] (20–30%).

2.11. Preparation of 10

Triethylamine (0.16 g, 1.55 mmol) was added dropwise to a solution of catechol (0.18 g, 0.79 mmol) and dithienyldichlorogermane (0.23 g, 0.75 mmol) in 2 ml of benzene. The mixture was refluxed for 4 h. Benzene (9 ml) was then added and the mixture filtered (elimination of Et₃N·HCl). The filtrate was concentrated and the residue extracted with 5 ml of pentane. The white solid, obtained after decantation and drying, was recrystallized from 2 ml of toluene. **10**: m = 0.20 g (59%); m.p. 175°C. ¹H NMR (CDCl₃): δ 1.30 (s, 9H, t-Bu), 1.40 (s, 9H, t-Bu), 7.36 (dd, $J_{3-4} = 3.5$, $J_{4-5} = 4.8$ Hz, 2H, H₄), 7.71 (d, $J_{3-4} = 3.5$ Hz, 2H, H₃), 7.87 (d, $J_{4-5} = 4.8$ Hz, 2H, H₅), 6.86 (d, J = 2.2 Hz, 1H, H₅'), 6.99 (d, J = 2.2 Hz, 1H, H₃'). ¹³C{¹H} NMR (CDCl₃): δ 29.58 and 31.78 (CH₃); 34.90 (C_{quat}, t-Bu); 109.38 (C₃), 114.62 (C₅'), 134.56 (C₄', C₆'), 142.43 (C₁'); 148.88 (C₂') (C₆H₂); 127.31 (C₂), 128.68 (C₄), 134.56 (C₅),



Fig. 1. Molecular structure of 3b in the solid state.

138.46 (C₃) (C₄H₂S). MS: m/z 460 ([M]⁺, 51%), 445 ([M-CH₃], 66%). *Anal.* Calc. for C₂₂H₂₆GeO₂S₂: C, 57.55; H, 5.70. Found: C, 57.80; H, 5.88%.

A solution of **10** (0.05 g, 0.11 mmol) in 1 ml of benzene was heated to 100°C for 12 h. The decomposition was followed by ¹H NMR spectroscopy showing the formation of **8** (90%) and the presence of **10** (10%) unchanged.

3. Results and discussion

The ligand 3,3'-dithienylsulfur was prepared in 35% yield by the reaction of 3-thienyllithium with di(phenyl-sulfonyl)sulfur (Eq. (1)) [5]. This low yield can be explained by the low thermal stability of 3-thienyl-lithium, which decomposes at -70° C [6] to give the dithiophene. By contrast, 3,3'-dithienylsulfur is very stable and was isolated in pure form after distillation.



Interest in this species rests in achieving selective metallation reactions at positions 2 and 2' [5,7]. The dilithio reagent, 2,2'-dilithio 3,3'-dithienylsulfur **2**, obtained by the reaction of **1** with "BuLi at 0°C, reacts easily with organometallic dichlorides to give heterocycles **3** and oligomers **4** simultaneously, which are very difficult to separate (Eq. (2)).



Regardless of the experimental conditions used (reaction temperature, mode of addition of reagents, dilution, etc.) it was not possible to favor monomeric heterocycles. All these heterocycles are sensitive to hydrolysis and oxidation. They decomposed rapidly during attempts at recrystallization or during separation of the reaction mixture. Nevertheless, they were perfectly characterized by physical and chemical measurements (¹H and ¹³C NMR and mass spectrometry). Compounds 3a and 3b could be isolated in pure form after distillation or recrystallization. An X-ray crystal-structure study of compound **3b** confirmed its monomeric form as shown in Fig. 1. It also shows a slightly distorted six-membered ring with the two heteroatoms (sulfur and germanium) in a boat conformation. The Ge(1) and S(1) atoms are 0.37 and 0.33 Å out of the best plane formed by C(1), C(2)-C(5) and C(6). The bond distances C(1)-C(2), 1.370(3) Å and C(5)-C(6), 1.368(4) Å are very close to that of the standard double bond indicating that they are localized double bonds. The corresponding angles C(1)-C(2)-S(1), $127.2(2)^{\circ}$, C(2)-C(1)-Ge(1),125.97(18)°, C(5)-C(6)-S(1), 127.9(2)° and C(6)–C(5)–Ge(1), 125.0(2) deviate slightly from the values expected for an sp²-hybridized C atom, as it was often observed in heterocyclic structure containing a germanium element [12,13]. The thiophene rings are almost planar, with maximum deviation from the mean plane of the thiophene ring of 0.009 Å for C(1). The thiophene planes formed an angle of 155.5° preventing any planarity of the tricyclic system in contrast to the structure of dithienosilole [14]. The germanium atom retains its tetrahedral geometry though it is slightly deformed. The C(1)-Ge(1)-C(5) angle is decreased to 99.60(11)°, whereas the C(1)–Ge(1)–C(15)and C(5)-Ge(1)-C(15) are increased to 112.41(10) and 114.75(11), respectively, probably due to the six-membered ring strain [13]. The Ge-C distances are consistent with literature data [13].

Molecular weights of the oligomers **4** were determined by SEC (size exclusion chromatography), by comparison with polystyrene references using THF as the eluent. Due to this determination, only the comparison between the masses of the different samples from one series is significant. This method cannot give exact molecular weights. To test its range of validity, we analyzed reaction mixtures containing mixtures of monomers **3a** (M_w 384), **3b** (424), and **3c** (430). The molecular weights obtained were 450, 470, and 490, respectively. Agreement with exact values is not very high. We conclude that the derivatives in Table 2 are oligomers having four to eight units.

In the polymeric portion, we were also able to detect cyclic dimers of calixarene type [15,16] (Eq. (3)), which could be identified only by mass spectrometry.



By contrast, when steric hindrance of the organometallic group increases ($R_2M = MesClGe$, Mes_2Ge), the nucleophilic substitution reaction becomes more difficult and heterocycle **3** could be detected only in low yield ($R_2M = MesClGe$ **3e**, 25%; $R_2M = Mes_2Ge$ **3f**, traces in mass spectra).

In the case of MesGeCl₃, a competitive halogen/ lithium exchange reaction occurred because we were able to identify 3,3'-dithienylsulfur monochloride $[M^+]$ 232 and dichloride ($[M^+]$ 266) (Eq. (4)) by mass spectrometry.



The weakly stable organochlorogermyllithium **6** decomposes to give mesitylchlorogermylene, which polymerizes rapidly.

The reaction of 2,2'-dilithio 3,3'-dithienylsulfur with dichlorogermylene and stannylene results in oligomers **7** (Eq. (5)).



Table 2 Molecular weights of oligomers **4**

M_n	$M_{ m w}$	Ι
2330	3280	1.4
1910	3500	1.8
1440	1740	1.2
1010	1100	1.1
	M _n 2330 1910 1440 1010	M _n M _w 2330 3280 1910 3500 1440 1740 1010 1100

These compounds do not melt and are practically insoluble in common organic solvents (ethers, chlorinated solvents, DMSO, DMF). They could be characterized by their IR spectra. The bands observed at 720 and 820 cm⁻¹ seem to correspond to deformation vibrations δ (CH) out of the plane of the 2,3-disubstituted species. Indeed, all of the δ (CH) bands of the diand tri-substituted thiophenes are found in this region [17]: 788 cm⁻¹ corresponding to 2,5-disubstituted, 730 and 820 cm⁻¹ for the 2,4-disubstituted, and 810 cm⁻¹ for the 2,3,5-trisubstituted. These oligomers readily react water as evident from IR bands at 3400 cm⁻¹ ν (OH) and 1636 cm⁻¹ δ (OH) which are observed regardless of the method used (KBr disk or Nujol mull under nitrogen).

To verify the presence of bivalent metallic sites in these chains, we tried cycloaddition reactions with 3,5-di-*tert*-butyl orthoquinone; quinones being excellent reagents in the characterization of bivalent species [11]. The reaction of oligomers with 3,5-di-*tert*-butyl orthoquinone, when carried out in sealed tubes at 100°C, gave mainly the spiro compound **8** (Eq. (6)).



Compound **8** probably resulted by thermal redistribution of the intermediate cycloadduct. We tried to confirm the intermediate beginning with a simpler species: a thiophene. The 2,5-dilithiothiophene was prepared by the reaction of the ⁿBuLi with the dibromo derivative [10] (Eq. (7)). Its reaction with dichlorogermylene gave oligomer **9** which, as before, does not melt and is only slightly soluble in common organic solvents. It was characterized by IR and ¹³C NMR measurements in the solid state. We observed a large signal (125–140 ppm) which corresponds to carbon atoms of the cyclic thiophene. The strong widening of this signal is due in part to the presence of reticular polymers.



The reaction with 3,5-di-*tert*-butyl orthoquinone causes a change in colour of the reaction mixture, an indication of a monoelectronic transfer [18], and therefore the presence of germylenes. After heating the mixture at 100°C in a sealed tube, ¹H NMR measurements showed the spiroderivative as the main product, proba-

Table 3Characteristic UV band of some compounds

Compound	λ (nm) (THF)	
1	268	
4 a	289	
4b	292	
4c	283	
7a	290 ª	
7b	286 ^a	

^a Wide band.

Table 4 Conductivity data

Compound	Conductivity (S cm ⁻¹)	
4b	<10 ⁻¹⁴	
7a	3×10^{-7}	
7b	10^{-7}	
9	10^{-6}	

bly by decomposition of the germadioxolane. In order to test this proposal, we prepared dithienylgermadioxolane by a dehydrohalogenation reaction in the presence of an excess of an amine (Eq. (8)).



Compound **10** is stable at r.t. and it can be isolated in good yield. However, it decomposes rapidly upon heating (100°C) with formation of the spiro derivative **8** (90%). The same type of redistribution was observed in the halogenated series [11].

Knowing that the bivalent germanium centers of oligomers 7 and 9 react with the quinone at 100°C, the formation of the spiro 8 in the two case can be explained by the low stability of germadioxolane intermediates having the thiophenic substituents. Moreover, we had confirmed that the starting dichlorogermylene had reacted completely. In addition, treatment of the reaction mixture with THF at 50°C caused complete removal of residual dichlorogermylene.

The results of UV spectroscopic measurements of compounds $4\mathbf{a}-\mathbf{c}$ and $7\mathbf{a}-\mathbf{b}$ in THF are given in Table 3.

The wavelengths of the oligomers exhibit a weak bathochromic effect ($\Delta \lambda \sim 20$ nm) by comparison with the starting reagent [19] confirming also an increase in

the conjugation of the thiophenic cycles. Since this effect has already been observed in the literature [20], the nature of the substituent on the germanium atom (butyl or phenyl) or the nature of the Group 14 metal (Ge or Sn) have little effect on the wavelengths. However, note the large band-widening when the Group 14 metal is in the bivalent form (**7a** and **7b**).

Electrical conductivities for compounds **4b**, **7a**, **7b**, and **9** have also been examined. Measurements were made with the aid of an ohm meter on disks of press powder (10 min under 10 ton cm^{-2}) (Table 4).

Oligomer **4b**, which contains only tetravalent germanium atoms does not show any conductivity. This agrees with results known up to the present time [1] which show that polymers having alternatively organometallic and π -conjugated units are insulators in a non-doped state. On the other hand, polymeric chains having divalent metals, **7a**, **7b**, and **9** have a surface conductivity which is not negligible $(10^{-7}-10^{-6} \text{ S} \text{ cm}^{-1})$ due probably to electronic mobility arising from the electron gaps introduced by the divalent metal. A measure of the volume conductivity¹ gave a value of $2.10^{-4} \text{ S cm}^{-1}$ for compound **9**, confirming the semiconductor character of this undoped oligomer.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publication No. 138867. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033: e-mail: deposit@ccdc. cam.ac.uk).

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¹ The volume conductivity measures were performed by the Laboratoire de Génie Electrique de l'Université Paul Sabatier, Toulouse, France.

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