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Inorganica Chimica Acta 291 (1999) 355-364

Inorganica Chimica Acta

# Germanium-containing ferrocenes and ferrocenophanes. Potential precursors for ring-opening polymerizations and 'germaferrocenes'

Stefan Zürcher, Volker Gramlich, Antonio Togni \*

Laboratory of Inorganic Chemistry, ETH Zentrum, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland

Received 8 January 1999; accepted 26 February 1999

#### Abstract

The new germanium-containing ferrocene and ferrocenophane derivatives (2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-germa-[1]ferrocenophane (2), 2-(2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-1,3-dithia-2-germa-[3]ferrocenophane (3), 1,1'-bis(1-tethoxy-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-dienyl)-ferrocene (6), 1,3-bis(2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-1,3-digerma-2-oxo-[3]ferrocenophane (7), 1,1'-bis(1-hydrido-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-dienyl)-ferrocene (8) and 1,2-bis(2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-digerma-[2]ferrocenophane (9) have been prepared starting from the dichlorogermol 1. The synthesis of the known ferrocenophanes dichloro-(ferrocene-1,1'-dithiolato)-germane (10a) and dichloro-(ferrocene-1,1'-dithiolato)-stannane (10b) was improved. X-ray crystal structural studies of 2 (C<sub>18</sub>H<sub>20</sub>FeGe, *a* = 10.907(4), *b* = 11.040(4), *c* = 13.771(5) Å,  $\beta = 110.87^{\circ}$ , monoclinic, *C2/c* (No. 15), *Z* = 4), 3 (C<sub>18</sub>H<sub>20</sub>FeGeS<sub>2</sub>, *a* = 8.104(3), *b* = 8.593(4), *c* = 13.177(6) Å,  $\alpha = 70.79(4)$ ,  $\beta = 77.56(3)$ ,  $\gamma = 85.80(3)$  Å triclinic,  $P\overline{1}$  (No. 2), *Z* = 2), 7 (C<sub>26</sub>H<sub>32</sub>FeGe<sub>2</sub>O, *a* = 18.95(2), *b* = 8.557(6), *c* = 16.69(6) Å,  $\beta = 110.65(6)^{\circ}$ , monoclinic, *C2/c* (No. 15), *Z* = 4), 9 (C<sub>26</sub>H<sub>32</sub>FeGes<sub>2</sub>, *a* = 11.209(6), *b* = 10.839(5), *c* = 19.819(10) Å,  $\beta = 92.89(2)$ ,  $\gamma = 90^{\circ}$ , monoclinic, *C2/c* (No. 14), *Z* = 4), 10a (C<sub>10</sub>H<sub>8</sub>FeGeS<sub>2</sub>, *a* = 10.873(5), *b* = 7.417(4), *c* = 16.415(10) Å, orthorhombic, *Pca*<sub>1</sub> (No. 29), *Z* = 4), 12a (C<sub>20</sub>H<sub>16</sub>Fe<sub>2</sub>GeS<sub>4</sub>, *a* = 7.459(4), *b* = 10.921(5), *c* = 23.552(12) Å, orthorhombic, *Pbcn* (No. 60), *Z* = 4) and cyclovoltammetric characterizations for all ferrocene-containing compounds have been carried out. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ferrocene complexes; Germanium complexes; Ferrocenophane complexes

#### 1. Introduction

Cyclopentadienes, where a heteroatom replaces one of the ring carbons, are an interesting topic from a theoretical point of view, as to the question of aromaticity of such five-membered rings [1-6]. Also, many experimental studies towards the synthesis of such heterocycles and their coordination chemistry have been reported [4,7–20]. With cyclopentadienes containing a Group 15 element (N, P, As, Sb, Bi), ferrocene-like compounds do exist [21–29], implying that these rings display at least some aromaticity. For the elements of Group 14, there exists an extremely large number of complexes containing the cyclopentadienyl anion; however, only very few where one carbon atom is replaced by silicon or germanium [30-33]. In order to obtain new data that would provide insight into the theoretical aspects, and would additionally afford a new class of donor molecules for charge-transfer (CT) complexes, we have investigated the synthesis of ferrocene derivatives containing a germacyclopentadienyl (germol) fragment. We reported previously synthesis and characterizations of CT complexes of ferrocenes bearing sulfur substituents [34–37]. The large germanium atom should enhance intermolecular interactions in CT complexes, thus possibly improving, e.g. magnetic cooperativity effects. Therefore, we were planning not to use very large protecting groups at the Ge atom, such as tris(trimethylsilyl)silyl, introduced and successfully applied by Tilley and co-workers [30,31].

<sup>\*</sup> Corresponding author. Tel.: +41-1-632 22 36; fax: +41-1-632 10 90.

E-mail address: togni@inorg.chem.ethz.ch (A. Togni)

### 2. Experimental

### 2.1. Synthesis. General considerations

General experimental techniques were reported earlier [34]. 1,1-Dichloro-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-diene (1) was prepared as described in Ref. [11].

#### 2.2. Synthesis of

# (2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-germa-[1] ferrocenophane (2)

A total of 1.18 g (3.798 mmol) of the 1,1'-dilithiumferrocene-TMEDA complex [38], suspended in 20 ml of hexane and 956 mg (3.798 mmol) of 1,1'-dichloro-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-diene (1) dissolved in 5 ml of hexane were cooled separately to  $-20^{\circ}$ C. The latter solution was then added slowly to the suspension of the dilithiated ferrocene. The reaction mixture was stirred for 6 h at room temperature and filtered. The solvent was removed under reduced pressure until crystallization started. Yield after one night at  $-20^{\circ}$ C: 518 mg (37%) dark red crystals. M.p.: 170°C. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>): δ 1.93 (s, 6H, CH<sub>3</sub>), 2.19 (s, 6H, CH<sub>3</sub>), 4.38 (t, *J* = 1.6, 4H, CH Cp), 4.48 (t, J = 1.6, 4H, CH Cp). <sup>13</sup>C NMR (62.895 MHz, CDCl<sub>3</sub>): 14.14 (CH<sub>3</sub>), 16.32 (CH<sub>3</sub>), 27.08 (C<sup>ipso</sup> Cp), 75.69 (CH Cp), 76.54 (CH Cp), 128.994 (C-Me), 147.07 (C-Me). MS: m/z 366 (M<sup>+</sup>, 80), 351, 292, 277, 259, 245 (100), 229, 203, 193, 139. Anal. Calc. for C<sub>18</sub>H<sub>20</sub>FeGe: C, 59.26; H, 5.53. Found: C, 59.26; H, 5.73% IR (KBr): 3086, 3085, 3069, 2939, 2901, 2846, 1559, 1437, 1372, 1362, 1288, 1213, 1175, 1111, 1058, 1017, 902, 877, 857, 845, 806, 763, 677, 651, 591, 528, 507, 478, 406.

2.3. Synthesis of 2-(2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-1,3-dithia-2-germa-[3]ferrocenophane (**3**)

1.5 g (31 mmol) of sodium hydride dispersion in oil (~50%) were washed three times with hexane and suspended in 30 ml of THF. 948 mg (3.79 mmol) of 1,1'-ferrocenedithiol [38] were added and the reaction mixture was stirred until evolution of hydrogen ceased. A solution of 955 mg (3.79 mmol) of 1,1-dichloro-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-dien (1) in 10 ml of hexane was added dropwise. The resulting yellow solution containing a white solid was filtered and evaporated to dryness. Yield: 1.12 g (69%) of a yellow microcrystalline powder. M.p.: 238–240°C. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  1.88 (d, J = 0.75, 6H, CH<sub>3</sub>), 2.07 (d, J = 0.75, 6H, CH<sub>3</sub>), 4.11 (t, J = 1.9, 4H, CH Cp), 4.26 (t, J = 1.9, 4H, CH Cp). <sup>13</sup>C NMR

(62.895 MHz, CDCl<sub>3</sub>): 13.85 (CH<sub>3</sub>), 14.83 (CH<sub>3</sub>), 69.44 (CH Cp), 75.20 (CH Cp), 84.45 (C<sup>*ipso*</sup> Cp), 117.63 (C–Me), 145.56 (C–Me). MS: m/z 430 ( $M^+$ , 100), 334, 322, 290, 226, 184, 108, 84, 56. *Anal.* Calc. for C<sub>18</sub>H<sub>20</sub>FeGeS<sub>2</sub>: C, 50.40; H, 4.70; S, 14.95. Found: C, 50.24; H, 4.65; S, 14.86% IR (KBr): 3086, 2904, 2846, 1553, 1401, 1386, 1364, 1161, 1056, 1020, 892, 817, 800, 760, 525, 504.

#### 2.4. Synthesis of 1-chloro-1-ethoxy-2,3,4,5tetramethyl-1-germacyclopenta-2,4-diene (4)

To 0.53 ml (9.1 mmol) of ethanol in 20 ml of THF were added 5.7 ml (9.1 mmol; 1.6 M in hexane) of methyllithium. The resulting solution was transferred to 2.3 g (9.1 mmol) of 1,1-dichloro-2,3,4,5-tetramethyl-1germacyclopenta-2,4-diene (1) and stirred for 30 min. The solvent was distilled off and the oily residue was distilled by a bulb-to-bulb distillation (100°C,  $10^{-1}$ mbar). Yield: 1.91 g (80%) of a colourless liquid. In solution, the product is in equilibrium with the corresponding 1,1-dichloro- and 1,1-diethoxy-derivatives, as shown by NMR spectroscopy. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  1.2–2.2 (m complex, ca. 15H), 3.85–4.15 (m complex, 2H). <sup>13</sup>C NMR (62.895 MHz, C<sub>6</sub>D<sub>6</sub>) 12.24, 13.04, 13.32, 13.48, 13.51, 13.97, 14.31, 19.06, 19.46, 59.98, 60.31, 61.25, 121.71, 122.84, 124.26, 145.24, 145.61, 146.28, 146.40, 147.23. GC-MS: m/z 262 ( $M^{+}$ , 43), 227, 218, 181, 163, 123, 109 (100), 93, 77, 67 59. Anal. Calc. for C<sub>10</sub>H<sub>17</sub>OClGe: C, 45.97; H, 6.56. Found: C, 46.24; H, 6.72%.

2.5. Synthesis of

1,1'-bis(1-ethoxy-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-dienyl)-ferrocene (**6**)

A total of 732 mg (2.8 mmol) of 1-chloro-1-ethoxy-2.3.4.5-tetramethyl-1-germacyclopenta-2,4-diene (4) were dissolved in 2 ml of THF and cooled to  $-78^{\circ}$ C. 440 mg (1.4 mmol) of 1,1'-dilithioferrocene TMEDA complex [38] were dissolved in 10 ml of THF and added slowly to the germacyclopentadiene solution dropwise. After slowly warming up the solution to room temperature, the solvent was evaporated under reduced pressure. The product was extracted with 20 ml of dry hexane, filtered over celite. After partial evaporation to a volume of about 5 ml, the product crystallized overnight at  $-20^{\circ}$ C. Yield: 347 mg (39%) of a yellow product. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  1.14 (t,  $J = 6.9, 6H, CH_3$ , 1.92 (s, 12H, CH<sub>3</sub>), 2.03 (s, 12H,  $CH_3$ ), 3.59 (q, J = 6.9, 4H,  $CH_2$ ), 4.16 (t, 4H, CH Cp), 4.23 (t, 4H). <sup>13</sup>C NMR (62.895 MHz, CDCl<sub>3</sub>) 14.07 (CH<sub>3</sub>), 15.26 (CH<sub>3</sub>), 19.30 (CH<sub>3</sub>), 60.60 (CH<sub>2</sub>), 65.92 (Cipso Cp), 71.72 (CH Cp), 73.36 (CH Cp), 125.97 (C-Me), 147.32 (C-Me). MS: m/z 636 ( $M^{+1}$ , 100),

562, 544, 365, 299, 180. *Anal.* Calc. for  $C_{30}H_{42}O_2FeGe_2$ : C, 56.68; H, 6.66. Found: C, 56.71; H. 6.73% IR (KBr): 3080, 2968, 2919, 2853, 1560, 1478, 1438, 1383, 1214, 1159, 1099, 1061, 1033, 908, 829, 762, 663, 613, 482, 372, 285, 226, 210.

2.6. Synthesis of 1,3-bis(2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-1,3-digerma-2-oxa-[3]ferrocenophane (7)

A total of 105 mg (0.165 mmol) 1,1'-bis(1-ethoxy-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-dienyl)-ferrocene (**6**) were dissolved in 10 ml of hexane, 4 drops of a 2N HCl solution were added and the solution was stirred overnight. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. Yield: 40 mg (43%) of a yellow, crystalline product. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  1.80 (s, 12H, CH<sub>3</sub>), 2.02 (s, 12H, CH<sub>3</sub>), 4.30–4.35 (t, J = 1.6, 4H, CH Cp), 4.40–4.43 (t, J = 1.6, 4H, CH Cp). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>) 13.6 (CH<sub>3</sub>), 14.7 (CH<sub>3</sub>), 68.6 (C<sup>ipso</sup> Cp), 71.2 (CH Cp), 72.4 (CH Cp), 126.7 (C–Me), 146.2 (C–Me). MS: m/z562 ( $M^{++}$ , 100), 459, 365, 302, 292, 245, 194, 107, 91, 77. Anal. Calc. for C<sub>26</sub>H<sub>32</sub>OFeGe<sub>2</sub>: C, 55.61; H, 5.74. Found: C, 55.81; H, 5.71.

2.7. Synthesis of 1,1'-bis(1-hydrido-2,3,4,5-tetramethyl-1germacyclopenta-2,4-dienyl)-ferrocene (8)

A total of 173.4 mg (0.27 mmol) of 1,1'-bis(1-ethoxy-2,3,4,5-tetramethyl-1-germacyclopenta-2,4-dienyl)-ferrocene (6) were dissolved in 15 ml of THF and cooled to 0°C. 0.27 ml (0.27 mmol, 1 M in THF) of LiAlH<sub>4</sub> solution were added. The reaction mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure, the product dissolved in hexane and filtered twice over celite. Yield: 111 mg (75%) of an orange oil. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  1.85 (s, 12H, CH<sub>3</sub>), 2.16 (s, 12H, CH<sub>3</sub>), 4.27-4.30 (t, 4H, CH Cp), 4.30–4.40 (t, 4H, CH Cp), 5.54 (s, 2H, Ge-H). <sup>13</sup>C NMR (62.895 MHz, CDCl<sub>3</sub>) 14.10 (CH<sub>3</sub>), 15.95 (CH<sub>3</sub>), 67.21 (Cipso Cp), 71.30 (CH Cp), 73.62 (CH Cp), 129.24 (C-Me), 146.97 (CMe). MS: m/z 548 ( $M^{+1}$ , 100), 438, 367, 330, 2912, 259, 245, 186, 139. Anal. Calc. for C<sub>26</sub>H<sub>34</sub>FeGe<sub>2</sub>: C, 57.03; H, 6.26. Found: C, 57.22; H, 6.28.

# 2.8. Synthesis of 1,2-bis(2,3,4,5-tetramethylbuta-1,3-dien-1,4-diyl)-digerma-[2] ferrocenophane (9)

(a) 111 mg (0.203 mmol) of 1,1'-bis(1-hydrido-2,3,4, 5-tetramethyl-1-germacyclopenta-2,4-dienyl)-ferrocene (8) were dissolved in 10 ml of THF and cooled to  $-78^{\circ}$ C. 0.25 ml (0.23 mmol, 1.6 M in hexane) of

n-BuLi were added. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The mixture was then cooled to  $-78^{\circ}$ C, 30 mg (0.23 mmol) of anhydrous iron(II) chloride were added in one portion and the mixture was warmed up slowly to room temperature. At  $-20^{\circ}$ C, the solution darkened and became a black suspension at room temperature (probably because of the formation of elemental iron). The solvent was evaporated under reduced pressure and the product extracted with hexane. Yield after crystallization at  $-20^{\circ}$ C: 6 mg (5%) of orange crystals. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  1.80 (s, 12H, CH<sub>3</sub>), 2.24 (s, 12H, CH<sub>3</sub>), 4.20-4.30 (q, 4H, CH Cp), 4.70–4.75 (q, 4H, CH Cp). <sup>1</sup>H NMR (300.13) MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.70 (s, 12H), 2.39 (s, 12H), 4.25-4.31 (q, 4HCp), 4.80–4.90 (q, 4H-Cp). <sup>13</sup>C NMR (75.47 MHz, C<sub>6</sub>D<sub>6</sub>) 13.7 (CH<sub>3</sub>), 16.5 (CH<sub>3</sub>), 69.6 (CH Cp), 74.0 (CH Cp), 77.4 (C<sup>ipso</sup> Cp), 130.5 (C-Me), 145.1 (C-Me). MS: m/z 446 ( $M^{+}$ , 100), 438, 365, 292, 245. Anal. Calc. for C<sub>26</sub>H<sub>32</sub>FeGe<sub>2</sub>: C, 57.24; H, 5.91. Found: C, 56.98; H, 5.93.

(b) 100 mg (0.157 mmol) of 1,1'-bis(1-ethoxy-2,3,4,5tetramethyl-1-germacyclopenta2,4-dienyl)-ferrocene (6) and 3.6 mg (0.52 mmol) of lithium in 5 ml of THF were refluxed for 2 h. The solvent was removed under reduced pressure and the residue recrystallized from hexane. Yield: 12 mg (14%) of orange crystals with the same analytical data as the product obtained under a). A second but less clean crop of product (28 mg (32%)) was obtained by flash chromatography on silica with dichloromethane as eluent.

# 2.9. Synthesis of dichloro-(ferrocene-1,1'-dithiolato)-germane [39] (10a)

A total of 2.32 g (9.25 mmol) of ferrocene-1,1'-dithiol [38] and 1.6 ml (13.9 mmol) of germanium tetrachloride were refluxed for 2 h in benzene until no evolution of HCl gas could be detected. The resulting orange solution was evaporated to dryness and the product dried under high vacuum. Yield: 3.31 g (90%). <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$  4.18–4.23 (m, 4H, CH Cp), 4.43–4.45 (m, 4H, CH Cp). <sup>13</sup>C NMR (62.895 MHz, CDCl<sub>3</sub>): 71.29 (CH Cp). 75.01 (CH Cp), 76.00 (C<sup>ipso</sup> Cp). MS: m/z 392 ( $M^+$ , 100), 357, 261, 248, 214, 170, 152, 126, 64, 56, 40. *Anal.* Calc. for C<sub>10</sub>H<sub>8</sub>FeGeS<sub>2</sub>Cl<sub>2</sub>: C, 30.67; H, 2.06; S, 16.37. Found: C, 30.85; H, 1.98; S, 16.43. IR (KBr): 3099, 1654, 1636, 1407, 1389, 1163, 1056, 1028, 1020, 890, 858, 825, 523, 497, 441, 412.

# 2.10. Synthesis of dichloro-(ferrocene-1,1'dithiolato)-stannane [39] (10b)

A total of 525 mg (2.1 mmol) ferrocen-1,1'-dithiol [38] were dissolved in 50 ml of benzene and 0.37 ml

(3.15 mmol) of tin tetrachloride were added. The resulting dark violet solution was refluxed for 1 h and evaporated to dryness. Yield: 772 mg (84%). A very clean fraction for elemental analysis could be obtained by sublimation. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>):  $\delta$ 3.60-3.76 (m, 4H, CH Cp), 3.85-3.40 (m, 4H, CH Cp). <sup>13</sup>C NMR (62.895 MHz. CDCl<sub>3</sub>): 71.17 (CH Cp), 75.33 (CH Cp). MS: m/z 435 (M<sup>++</sup>, 100), 402, 341, 306, 259, 248, 223, 152, 120, 56. Anal. Calc. for C<sub>10</sub>H<sub>8</sub>FeSnS<sub>2</sub>Cl<sub>2</sub>: C, 27.44; H, 1.84; S, 14.65. Found: C, 27.58; H, 2.08; S, 14.68. IR (KBr): 3099, 1654, 1407, 1388, 1362, 1162, 1052, 1028, 887, 849, 823, 517, 496, 415, 390, 360, 343, 321.

### 2.11. Synthesis of bis(ferrocene-1,1'-dithiolato)germane [39] (12a)

To 50.6 mg (0.32 mmol) of toluene-3,4-dithiol dissolved in 4 ml of THF were added 0.4 ml (0.64 mmol) of n-BuLi (1.6 M in hexane). The resulting solution was transferred at 0°C to a solution containing 1,1'-(1,3dithia-2,2-dichlorogermyl)-[3]ferrocenophane (10a) in 20 ml of THF, stirred for 5 min at 0°C and for an additional hour at room temperature. Subsequently, the

Table 1a Experimental data for the X-ray diffraction studies of 2, 3, 7 and 9

solution was evaporated to dryness. A mass spectrum of the residue showed it to be a mixture of at least three products (bis(ferrocene-1,1'-dithiolato)germanium (12a), bis(tolyl-3,4-dithiolato)germanium (13a) and (ferrocene - 1,1' - dithiolato - tolyl - 3,4 - dithiolato)germanium (11a)). The residue was extracted with dichloromethane and recrystallized from 1,2-dichloroethane. 62 mg (68%) of 12a were obtained as yellow crystals, which could be used directly for X-ray analysis. <sup>1</sup>H NMR (250.13 MHz, CDCl<sub>3</sub>): δ 4.3-4.7 (m, 8H, CH Cp), 4.2-4.7 (m, 8H, CH Cp). <sup>13</sup>C NMR (62.895 MHz, CDCl<sub>3</sub>): 70.11 (CH Cp), 74.83 (CH Cp). MS: m/z 569  $(M^+, 100)$ , 377, 322, 304, 272. Anal. Calc. for C<sub>20</sub>H<sub>16</sub>Fe<sub>2</sub>S<sub>4</sub>Ge: C, 42.22; H, 2.83; S, 22.55. Found: C, 41.98; H, 2.71; S, 22.65. IR (KBr): 3098, 3087, 1407, 1385, 1360, 1162, 1052, 1024, 890, 848, 830.

# 2.12. Synthesis of

bis(ferrocene-1,1'-dithiolato)-stannane [39,40] (12b)

A similar procedure as for the synthesis of 12a was followed. Recrystallization from chloroform yielded a few red platelets.

	2	3	7	9
Empirical formula	C <sub>18</sub> H <sub>20</sub> FeGe	C <sub>18</sub> H <sub>20</sub> FeGeS <sub>2</sub>	C <sub>26</sub> H <sub>32</sub> FeGe <sub>2</sub> O	C <sub>26</sub> H <sub>32</sub> FeGe <sub>2</sub>
Formula weight	364.8	428.9	561.5	545.5
Crystal dimensions (mm)	$0.3 \times 0.1 \times 0.1$	$0.8 \times 0.7 \times 0.2$	$0.5 \times 0.2 \times 0.2$	$0.22 \times 0.20 \times 0.16$
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group (No.)	C2/c (15)	$P\overline{1}(2)$	C2/c (15)	$P2_1/n$ (14)
a (Å)	10.907(4)	8.104(3)	18.95(2)	11.209(6)
b (Å)	11.040(4)	8.953(4)	8.557(6)	10.839(5)
c (Å)	13.771(5)	13.177(6)	16.69(6)	19.819(10)
α (°)	90	70.79(4)	90	90
$\beta$ (°)	110.87(3)	77.56(3)	110.65(6)	92.89(2)
γ (°)	90	85.80(3)	90	90
$V(Å^3)$	1549.4(10)	881.6(7)	2533(5)	2405(2)
Z	4	2	4	4
$\rho$ (calc) <sub>r</sub> (g cm <sup>-3</sup> )	1.564	1.616	1.472	1.507
$\mu ({\rm mm^{-1}})$	2.863	2.757	7.429	7.774
F(000)	744	436	1144	1112
Diffractometer	Syntex P21	Syntex P21	Picker STOE	Picker STOE
Wavelength $\lambda$ (Å)	Mo Kα, $\lambda = 0.71073$	Mo K $\alpha$ , $\lambda = 0.71073$	Cu K $\alpha$ , $\lambda = 1.54178$	Cu K $\alpha$ , $\lambda = 1.54178$
$\theta$ Range (°)	2.72-20.04	1.67-20.03	4.99-49.93	4.4-50.00
Measured reflections	787	1803	1428	2474
Reflections observed $(n)^{a}$	737	1645	1314	2474
Parameters refined ( <i>p</i> )	109	232	138	271
$wR_2 [1 > 2\sigma(I)]^{b}$	0.0639	0.091	0.0889	0.0882
$R_1 \left[1 > 2\sigma(I)\right]^c$	0.0236	0.030	0.0347	0.0324
GOF on $F^{2d}$	0.573	1.095	1.106	0.991

<sup>a</sup>  $(|F_0^2| = 4.0 \ \sigma(|F|^2)).$ 

 $\begin{aligned} & (\Gamma_{o}) = 4.0 \text{ o} (\Gamma | r)). \\ & b \ wR_2 = [\sigma(w(F_{o}^2 - F_{c}^2)^2)]/\sigma[w(F_{o}^2)^2]^{1/2}. \\ & c \ R_1 = \sigma ||F_o| - |F_c||/\sigma|F_o|. \\ & d \ \text{GOF} = S = [\sigma(w(F_{o}^2 - F_{c}^2)^2]/(n-p)]^{1/2}. \end{aligned}$ 

Table 1b												
Experimental	data	for	the	X-rav	diffraction	studies	of 1	10a.	12a	and	12b	

	10a	12a	12b
Empirical formula	$C_{10}H_8FeGeS_2$	C <sub>20</sub> H <sub>16</sub> FeGeS <sub>4</sub>	$C_{20}H_{16}Fe_2SnS_4$
Molecular weight	391.6	568.9	615.0
Crystal dimensions (mm)	$0.2 \times 0.2 \times 0.14$	$0.6 \times 0.5 \times 0.1$	$0.3 \times 0.3 \times 0.06$
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group (No.)	$Pca2_{1}$ (29)	<i>Pbcn</i> (60)	<i>Pbcn</i> (60)
a (Å)	10.873(5)	7.459(4)	7.484(4)
b (Å)	7.417(4)	10.921(5)	10.953(6)
c (Å)	16.415(10)	23.552(12)	23.917(12)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
$V(Å^3)$	1323.8(12)	1918.5(17)	1961(2)
Z	4	4	4
$\rho$ (calc) <sub>r</sub> (g cm <sup>-3</sup> )	1.965	1.969	2.083
$\mu  ({\rm mm}^{-1})$	4.052	17.905	25.766
F(000)	768	1136	1208
Diffractometer	Syntex P21	Picker STOE	Picker STOE
Wavelength $\lambda$ (Å)	Mo K $\alpha$ , $\lambda = 0.71073$	Cu K $\alpha$ , $\lambda = 1.54178$	Cu K $\alpha$ , $\lambda = 1.54178$
$\theta$ Range (°)	2.48-20.0	3.75-49.99	3.70-49.98
Measured reflections	650	1196	1006
Reflections observed $(n)^{a}$	650	989	1006
Parameters refined (p)	144	124	124
$wR_2 [1 > 2 \sigma(I)]^{b}$	0.1192	0.0795	0.1142
$R_1 [1 > 2 \sigma(I)]^{\circ}$	0.0522	0.0294	0.0493
GOF on $F^{2 d}$	1.222	1.117	1.044

<sup>a</sup> ( $|F_o^2| > 4.0 \sigma(|F|^2)$ ).

 $\begin{aligned} & (1 \circ | f \circ$ 

# 2.13. X-ray crystallographic studies of 2, 3, 7, 9, 10a, 12a and 12b

Suitable crystals for an X-ray analysis of all these compounds were obtained by cooling hot saturated hexane solutions to  $-20^{\circ}$ C. Selected crystallographic and relevant data collection parameters are listed in Tables 1a and 1b. Data were measured at room temperature (293(2) K) with variable scan speed to ensure constant statistical precision on the collected intensities. One standard reflection was measured every 120 reflections and no significant variation was detected. The structures were solved by Direct or Patterson Methods and refined by full-matrix least squares using anisotropic displacement parameters for all non hydrogen atoms. The contribution of the hydrogen atoms in their idealized position (Riding model with fixed isotropic  $U = 0.080 \text{ Å}^2$ ) was taken into account but not refined. All calculations were carried out by using the Siemens SHELX93 (VMS) system.

#### 3. Results and discussion

#### 3.1. Synthesis

The starting idea was to introduce two germol fragments onto ferrocene, and to use them subsequently as ligands for the construction of a second metallocene, thus leading to a biferrocene-like structure.

For all germacyclopentadiene-containing ferrocenes reported here, 1,1-dichloro-1-germa-2,3,4,5-tetramethylcyclopentadiene (1) (dichlorogermol) (see Scheme 1) was used as starting material as obtained following a reported procedure [11]. By the direct reaction of dichlorogermol 1 with the dilithiated ferrocene-TMEDA complex [38,41,42] [1]ferrocenophane 2 was obtained as main product (40% yield) together with oligomeric by-products that were not further characterized. Compound 2 should be a useful precursor for ring opening polymerizations (ROP) [43]. Even if an excess of 1 was used, no disubstituted ferrocene could be



Scheme 1. Synthesis of germacyclopentadiene-containing ferrocenes, starting from 1,1-dichloro-2,3,4,5-tetramethyl-1-germacyclopentadiene (1).

obtained. Similarly, the [3]ferrocenophane **3** was obtained in good yields (70%) by deprotonation of ferrocene-1,1'-dithiol with NaH and reaction with dichlorogermol 1.

Since the desired disubstituted ferrocene was not accessible by the above route, one chloride of the dichlorogermol was replaced by an ethoxy group, in order to ensure different reactivity of the two leaving groups, favouring a disubstitution reaction of fer-



Scheme 2. Attempted synthesis of germanium and tin complexes with two different chelating sulfur ligands.

rocene. A 2D <sup>1</sup>H NMR experiment (proton-proton correlation) of the observed intermediate formed by the addition of 1 equiv. of LiOEt to 1 showed that an equilibrium mixture of the desired 1-chloro-1-ethoxygermol 4, the dichlorogermol 1 and the diethoxygermol 5 is formed. By reacting this mixture with the dilithiated ferrocene-TMEDA complex, the disubstituted compound 6 could be isolated in 39% yield together with oligomers and the [1]ferrocenophane 2. By an attempt to recrystallize 6 from chloroform, a small amount of yellow crystals were obtained. This compound turned out to be the oxygen bridged [3] ferrocenophane 7. The same compound was obtained in moderate yield by the reaction of 6 with 2N aq HCl in hexane. The reduction of the diethoxy compound 6with  $LiAlH_4$  produced 8 in good yield (75%) as an orange oil. When 8 was reacted with n-BuLi and iron(II) chloride, the expected diferrocene-like compound could not be isolated but the [2]ferrocenophane **9** was isolated in a very low yield of 5%. This was accompanied by a significant amount of a black residue (probably elemental iron). A better yield of 46% could be obtained by the direct reduction of the diethoxy compound 6 with lithium in THF. The formation of 9 from either 6 or 8 is at first sight quite surprising. However, it is known that germanides, here both formed from 6 and 8, respectively, as intermediates, readily couple affording digermanes [1a].

With the aim of preparing Ge (and Sn) spiro compounds, the known dichlorides 10 were needed. Thus, the dichloro [3]ferrocenophane 10a was formed in excellent yield upon reaction of ferrocene dithiol and germanium tetrachloride in boiling benzene. The original synthesis reported by Osborne [39], in which a 10-fold excess of germanium tetrachloride and triethylamine as a base were used (yield 61%), could be improved. The analogous tin derivative 10b was obtained by the same procedure. The reaction of this compound with a second different dithiol ligand, such as toluene-3,4-dithiol, did not allow us to isolate the desired mixed ligand compounds 11a or 11b but the bis(ferrocene-1,1'dithiolato)germanium (12a) and the analogous tin derivative 12b, respectively. Thus, ligand scrambling leading to the homoleptic derivatives is the major pathway under the reported conditions. Therefore, we did not pursue the synthesis of compounds 11 any further (Scheme 2).

# 3.2. Solid-state structure of germanium substituted ferrocenes

For seven of the obtained products, single crystal X-ray studies were carried out. Tables 1a and 1b give the relevant crystal and data collection parameters. Bond distances and angles of each asymmetric unit were found to fall in the expected ranges and will not



Fig. 1. ORTEP plots and atom numbering schemes of the seven compounds 2, 3, 7, 9, 10a, 12a, and 12b. Thermal ellipsoids are drawn at the 30% probability level at 293 K.

be discussed in detail (they are provided as Supplementary Material). ORTEP representations of the seven molecules are depicted in Fig. 1 and relevant structural features are shown in the schematic plot of Fig. 2.

[1]Ferrocenophane 2 crystallizes in the monoclinic space group C2/c, with iron and germanium on the 2-fold axes. The bridging germanium shows a relatively short distance of 2.80 Å to iron. The two different Ge-C distances are in the normal range (1.93 Å for Ge-Cp and 1.97 Å for the germol ring). The coordination sphere at germanium is tetrahedrally distorted with quite small angles of  $92^{\circ}$  for C(1)–Ge–C(1A) and C(6)–Ge–C(6A). The two Cp rings span an angle of 18.9°, which is comparable to angles found in other [1]ferrocenophanes with silicon or germanium bridges [44,45]. The bond Ge–C(1) is bent by 36.7° out of the Cp plane.

The [3]ferrocenophane **3** crystallizes in the triclinic space group  $P\overline{1}$ . The two Cp rings are eclipsed and parallel (interplanar angle: 1°). The geometry of the bridge is comparable to the one found in similar SES-[3]ferrocenophanes (E = C, S, Si, Ge, Sn, and others)

[38,40] where the two sulfur atoms are always eclipsed and the central bridging atom is out of the plane of the four atoms S(1), C(1), C(1'), and S(2). The corresponding interplanar angle is 53.6°. The two sulfur atoms are slightly above the respective Cp planes and the S–S distance is 3.64 Å whereas the distance C(1)-C(1') is only 3.33 Å The two sulfur atoms form an angle with germanium of 109°, corresponding to the angle in a tetrahedron. The distance germanium–iron is quite large (3.85 Å).

The [3]ferrocenophane 7 crystallizes in the monoclinic space group C2/c with oxygen and iron on the 2-fold axes. The two Cp rings are parallel (interplanar angle 0.32°) but rotated against each other by 11.8°. The two germacyclopentadienyl rings span a mutual angle of 74.3 and of 52.8° with the Cp rings, respectively. The germanium atom lies almost perfectly in the plane of the respective Cp ring (distance to this plane is 0.05 Å). Because of the 2-fold axes, the six-membered ring, constituted by iron, the two C<sup>ipso</sup>-carbon atoms, the two germanium atoms and oxygen shows a twist conformation.

The [2]ferrocenophane 9 crystallizes in the monoclinic space group  $P2_1/n$ . The two Cp rings are bent



Fig. 2. Schematic drawings of the seven compounds 2, 3, 7, 9, 10a, 12a, and 12b with the most important angles and bond distances.

Table 2 Formal electrode potentials (vs.  $F_c/F_c^+$ ) for ferrocene derivatives in dichloromethane solution<sup>a</sup>

Compound	$E^{\circ\prime}_{0/+'}$ (V)	$\Delta E_{\mathbf{p}'}$ (mV)	$i_{ m pc}/i_{ m pa}$	$E^{\circ'}_{1+/2+'}$ (V)	$\Delta E_{\mathbf{p}'}$ (mV)	$i_{\rm pc}/i_{\rm pa}$
2	+0.15 <sup>b</sup>	335	1.3			
3	+0.25 <sup>b</sup>	245	1.04			
6	$+0.26^{\circ}$	308	1.49	(+0.77)(+1.23)		
7	$+0.44^{\circ}$	132	1.06			
9	$+0.24^{\circ}$	112	1.11			
10a	$+0.43^{d}$	183	1.24			
12a	$+0.42^{b}$	101	2.70	+0.58	94	1.1
12b	$+0.26^{b}$	482	4.99			

<sup>a</sup> All experiments carried out in dry dichloromethane/0.1 M (NBu<sub>4</sub>)(BF<sub>4</sub>) versus 0.05 M  $F_c/F_c^+$  reference electrode with  $E^{\circ\prime} = +0.042$  V for ferrocene, and a Pt working electrode (all values are corrected for 0 V). Values in brackets are  $E_{pa}$  (anodic peak potential) only assigned to irreversible oxidation steps.  $\Delta E_p$  is the difference between anodic and cathodic peak potential and  $i_{pc}/i_{pa}$  is a measure for the reversibility of the redox process.

<sup>b</sup> Scan rate: 100 mV s<sup>-1</sup>.

<sup>c</sup> Scan rate: 30 mV s<sup>-1</sup>.

<sup>d</sup> Scan rate: 10 mV s<sup>-1</sup>.

slightly by 4.9°. The planes of the two germacyclopentadienyl rings are almost perpendicular to each other (interplanar angle is 85.1°) and the two crystallographically independent angles between the Cp rings and the germacyclopentadienyl rings are 41.0 and 49.0°. The two Cp rings are not staggered perfectly. This is shown by the torsion angle  $-11^{\circ}$  of C(1)–Ge(1)–Ge(2)–C(1') or by the rotation of the two Cp rings against each other by 7.8°, respectively. As in **2**, the two C<sup>*ipso*</sup>–Ge bonds are bent slightly by about 9.5° out of the plane of the Cp ring. The distances of germanium to iron are 3.39 and 3.40 Å, and the Ge–Ge bond distance is 2.43 Å.

The [3]ferrocenophane **10a** crystallizes in the orthorhombic space group  $Pca2_1$ . The two Cp rings are almost parallel with an interplanar angle of 3.4° and the two sulfur atoms lie 0.15(1) Å above the respective Cp rings. The S–S distance is 3.76 Å, whereas the distance between the two C<sup>ipso</sup> carbon atoms is only 3.36 Å The iron–germanium distance is with 3.36 Å a little shorter than the corresponding distance in **3**. The conformation of the bridge is comparable to the one in ferrocenophane **3**. The germanium atom displays an almost perfect tetrahedral coordination sphere. Only the angle S(1)-Ge(1)-S(1') (118.5°) deviates more than by 9° from the expected optimum value for a tetrahedral geometry. The sulfur–germanium distances are 2.19 Å and the chloro–germanium distances 2.14 Å.

The two compounds **12a** and **12b**, the crystal structure of which has not been reported before, are isomorphous and crystallize in the orthorhombic space group *Pbcn* (values for the tin derivative in brackets). The germanium (tin) lies on the 2-fold axes which converts one of the ferrocene ligands into the other. The single molecules are chiral. The two Cp rings are not perfectly parallel (interplanar angle 2.2° (4.5°)) and they are rotated against each other by 5.9° (6.7°). In these two compounds the bridges have a similar conformation as in the other two [3]ferrocenophanes with SES-bridges **3** and **10a**.

#### 3.3. Electrochemical characterization

In order to judge the ability of the new compounds to act as electron donors in CT complexes, their oxidation potentials were determined by means of cyclovoltammetric measurements. The redox potentials are reported in Table 2. All derivatives turn out to be relatively hard to oxidize, as they all display positive  $E^{\circ'}$ -values, as compared to non-substituted ferrocene. Even the strong acceptor TCNQF<sub>4</sub> ( $E^{\circ'}_{1-/0} = +0.14$  V) should not be able to oxidize one of these ferrocenes under the typical conditions used for the formation of CT complexes (e.g. in hot dichloromethane). As it is expected for ferrocene compounds, the derivatives examined all show at least one reversible oxidation wave. The diethoxy compound 8 displays two additional irreversible oxidation waves at higher potential, probably connected with the oxidation of the germacyclopentadienyl rings. The bisferrocene 12a can be reversibly oxidized twice, meaning that the two iron atoms communicate with each other through the sulfur-germanium bridge. The analogous tin derivative, in the contrary, shows only one irreversible oxidation wave.

#### 4. Conclusions

Some ferrocene derivatives containing Ge substituents were prepared. However, the final goal to obtaining a biferrocene-like compound was not achieved. Iron(II) behaves as an oxidating agent for the germacyclopentadienyl anion, thus giving an oxidative coupling of the germanium atoms. Further studies toward a digermabiferrocene will address the possibility of an oxidative addition of the Ge–Ge bond onto a suitable Fe(O) precursor. The electrochemical experiments have shown that the compounds obtained to date are not suitable for the formation of CT complexes with common organic acceptors. We are currently investigating the properties of the strained ferrocenophane 2 towards ring-opening polymerization reactions.

#### 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 112439-CCDC 112445. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk), or may be obtained from the authors upon request.

#### Acknowledgements

S.Z. is grateful to the Swiss National Science Foundation for financial support (Grant 20-41974.94).

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