Synthesis and Properties of Me_2Ge-Bridged Arenes

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Linear and cyclic oligomers of Me_2Ge-bridged π-systems have been obtained by the reaction of carbo- and heterocyclic anions and dianions with Me_2GeCl_2. The spectroscopic properties of the new compounds are compared with analogous carbon- and Me_2Si-bridged π-systems.

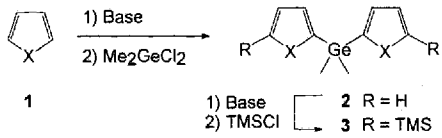
The clean reaction of carbanions with Me_2SiCl_2 has been used by us[1] and other groups[2] for the synthesis of dimeric and oligomeric π-systems bridged by Me_2Si units. We report here the extension of the synthetic route to Me_2Ge-bridged π-systems and compare their synthesis and properties with Me_2Si- and carbon-bridged compounds.

The reaction of lithiated heterocycles, such as furan, thiophene or *N*-methylpyrrole with Me_2GeCl_2 gave Me_2Ge-bridged dimers **2**[3] in good yield. Deprotonation of the heterocycles with *n*BuLi/TMEDA/KO*t*Bu led to the formation of 2,5-dianions, which in turn were allowed to react with Me_2GeCl_2 to yield a mixture of linear oligomers[4]. Macrocyclic products, as formed in the reaction with Me_2SiCl_2[1] were not detected, although the fast reaction of the slowly added Me_2GeCl_2 with carbanions and the limited solubility of the heterocyclic dianions in hexane solution should favour their formation[5].

An alternative route for the synthesis of cyclic oligomers uses **2a–c**. These are cleanly deprotonated at the 5- and 5′-positions upon treatment with BuLi/TMEDA. The resulting dianions were trapped with TMSCl, and NMR spectra of the crude reaction mixtures confirmed the complete formation of dianions. Here again, the reaction of stoichiometric amounts Me_2GeCl_2 with the dianions of **2a** and **b** resulted in the formation of a mixture of linear oligomers as the major product. In the case of **2c**, however, the macrocyclic tetramer **4** was isolated in small amounts. The simple ^1H and ^{13}C-NMR spectra of **4** indicate the unrestricted mobility of the pyrrole rings in solution on the NMR time scale. The incorporation of four germanium atoms is confirmed by the complex isotope pattern of the molecular ion in the mass spectra.

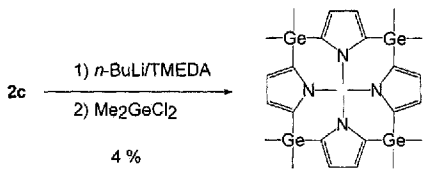
Methoxy-directed *ortho*-lithiation[4] of **5** or **8** and subsequent reaction with Me_2GeCl_2 yielded compounds **6** and **9** in good yield. Both compounds were cleanly lithiated to dianions with BuLi/TMEDA, as confirmed by trapping with TMSCl. The reaction of the dianion of **9** with Me_2GeCl_2 gave linear oligomers exclusively, whereas the reaction of **6** and Me_2GeCl_2 yielded heterocalix[4]arene **11** in small amounts. Again, the mobility of the arene moieties is not restricted on the NMR time scale, as shown by the simple NMR spectra.

Scheme 1

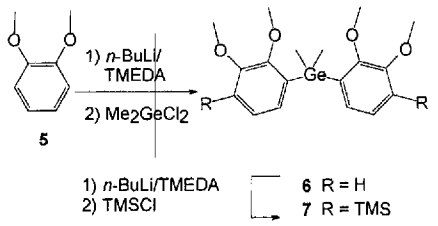


	a	b	c
X =	O	S	NMe
yield **2** (%)	77	64	83
yield **3** (%)	67	87	98

Scheme 2



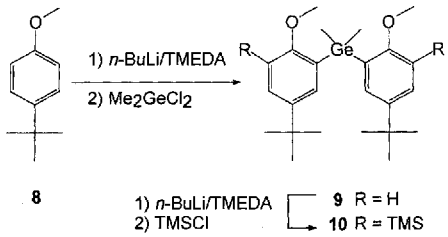
Scheme 3



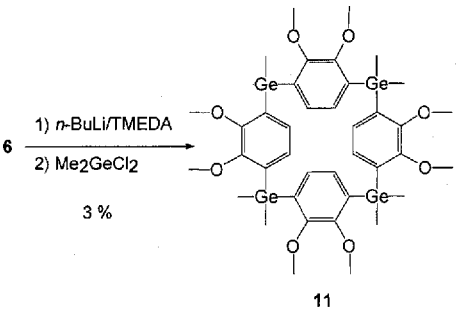
The size and distribution of the obtained oligomers was investigated by gel permeation chromatography[6]. The monomodal distribution for all cases indicates a regular,

  0009–2940/97/0303–0421 $ 15.00+.25/0

Scheme 4



Scheme 5



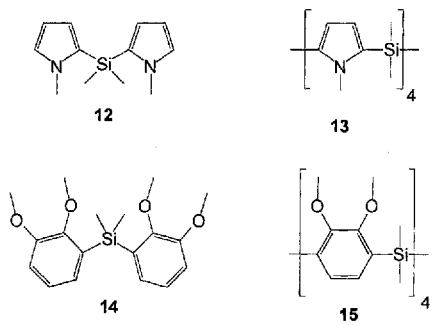
unbranched structure of the oligomers. The average size of the oligomers varies from 4 to 17 repeating units. To investigate the different influence of carbon-, $SiMe_2$- and $GeMe_2$-bridging moieties on the electronic structure, the UV spectra of **2c** and **6**, the cyclic compounds **4** and **11**, and their $SiMe_2$-analogues **12**–**15** were measured. Although the absolute change in λ_{max} is small, a distinct bathochromic shift is observed with increasing size of the molecules[7]. The extent of this shift differs only slightly between $SiMe_2$- and $GeMe_2$-bridged molecules, indicating a similar ability of both elements to electronically link the π-systems via σ-conjugation[8].

Table 1. Change in λ_{max} of Me_2Si- and Me_2Ge-bridged arenes

	1c	**2c/12**	**4/13**
λ_{max} [nm][a]	214	230/232	240/246
	5	**6/14**	**11/15**
λ_{max} [nm]	200	204/204	–[b]/208

[a] All spectra were measured in CH_3CN. – [b] The solubility of the compound in CH_3CN was not sufficient for exact measurements.

Scheme 6



We conclude that, the reaction of carbo- and heterocyclic anions and dianions with Me_2GeCl_2 yields mixtures of linear oligomers. Cyclic tetramers, as produced in the case of $SiMe_2$-bridged arenes, were only obtained in small amounts from **2c** and **6**. The σ-conjugation of $GeMe_2$ and $SiMe_2$ groups results in a small bathochromic shift of the λ_{max} absorption with extension of the oligomer.

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Experimental Section

Melting points were taken on a hot-plate microscope apparatus and are not corrected. – NMR spectra were recorded at 400 MHz (^1H) and 100 MHz (^{13}C) in $CDCl_3$ solution unless otherwise stated. The multiplicity of the ^{13}C signals was determined with the DEPT technique and quoted as: (+) for CH_3 or CH, (–) for CH_2 and (C_{quat}) for quaternary carbons. Column chromatography (CC) was performed on silica gel. PE means petroleum ether with a boiling range of 60–70°C.

Dimethylbis(1-methyl-2-pyrrolyl)germane (**2c**): *n*-BuLi (3.7 ml, 37.0 mmol, 10 M in hexane) was added to a solution of *N*-methylpyrrole (2.7 g, 34 mmol) and TMEDA (4.3 g, 37.0 mmol) in 100 ml hexane. The mixture was stirred for 2 h at room temp. and dichlorodimethylgermane (2.9 g, 17 mmol) was added. The reaction mixture was hydrolyzed with 100 ml water, and the aqueous phase was extracted with diethyl ether (2 × 50 ml). The combined organic phases were washed with sat. aqueous NH_4Cl and water until the washings were pH neutral, dried with $MgSO_4$ and the solvent was removed in vacuo. Recrystallization from *n*-heptane yielded 3.7 g (83%) of **2c** as a white solid, m.p. 76°C. – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 1291. – UV (CH_3CN): λ_{max} (lg ε) = 192 nm (4.39), 230 (4.25). – ^1H NMR: δ = 0.68 (s, 6H), 3.49 (s, 6H), 6.18 (m, 2H), 6.33 (m, 2H), 6.78 (m, 2H). – ^{13}C NMR: δ = –1.6 (+), 36.4 (+), 108.0 (+), 117.6 (+), 126.3 (+), 130.9 (C_{quat}). – MS (70 eV); *m/z* (%): 264 (43) [M^+], 249 (100). – $C_{12}H_{18}GeN_2$ (262.9): calcd. C 54.82, H 6.90, N 10.65; found C 54.84, H 6.89, N 10.65. – Mol. mass 264 (MS).

Bis(2,3-dimethoxyphenyl)dimethylgermane (**6**): A mixture of 1,2-dimethoxybenzene (**5**) (4.0 g, 29 mmol), TMEDA (3.7 g, 32 mmol) and *n*-BuLi (3.2 ml, 32 mmol, 10 M in hexane) in 250 ml hexane was stirred at room temp. for 12 h. Dichlorodimethylgermane (1.67 ml, 14.5 mmol) was then added, the mixture was stirred for 2 h, and then hydrolyzed with 100 ml water. The reaction mixture was worked-up as described for **2c**. CC (PE/Et_2O, 19:1) yielded 3.9 g (71%) **6** as a colourless oil. – IR (film): $\tilde{\nu}$ = 2939 cm^{-1}, 1463, 1261. – UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.86), 278 (3.57). – ^1H NMR: δ = 0.69 (s, 6H), 3.60 (s, 6H), 3.84 (s, 6H), 6.9 (m, 4H), 7.03 (m, 2H). – ^{13}C NMR: δ = –1.3 (+), 55.6 (+), 60.5 (+), 113.3 (+), 124.0 (+), 126.3 (+), 134.4 (C_{quat}), 152.0 (C_{quat}), 152.7 (C_{quat}). – MS (70 eV); *m/z* (%): 373 (15) [M^+], 363 (100). – $C_{18}H_{24}GeO_4$ (377.0): calcd. C 57.35, H 6.42; found C 57.38, H 6.40.

Bis(5-tert-butyl-2-methoxyphenyl)dimethylgermane (**9**): 1.5 g (9.14 mmol) of 4-*tert*-butylmethoxybenzene, *n*-BuLi/TMEDA (1.1 equiv., 10 mmol) and dichlorodimethylgermane (790 mg, 4.5 mmol) were allowed to react as described for **6**. CC (PE, R_f = 0.23) gave 1.530 g (79%) of **9** as a white solid, m.p. 97°C. – IR (KBr): $\tilde{\nu}$ = 2999 cm^{-1}, 1485, 1241. – UV (CH_3CN): λ_{max} (lg ε) = 202 nm (4.89), 280 (3.75). – ^1H NMR: δ = 0.67 (s, 6H), 1.24 (s, 18H), 3.72 (s, 6H), 6.77 (d, ^3J = 8.4 Hz, 2H), 7.3 (m, 4H). – ^{13}C NMR: δ = –1.6 (+), 31.5 (+), 34.0 (C_{quat}), 55.1 (+), 108.9 (+), 126.5

(+), 127.7 (C_{quat}), 132.3 (+), 142.6 (C_{quat}), 161.2 (C_{quat}). – MS (70 eV); *m/z* (%): 430 (13) [M^+], 415 (100). – $C_{24}H_{36}GeO_2$ (429.2): calcd. C 67.17, H 8.45; found C 67.36, H 8.54. – Mol mass 430 (MS).

Dimethylbis(5-trimethylsilyl-2-furyl)germane (**3a**): To a solution of 1.3 mmol *n*-BuLi in 20 ml hexane/THF (1:1), 120 mg (0.5 mmol) of **2a** was added at 0°C. The mixture was stirred for 2 h and TMSCl (150 mg, 1.4 mmol) was added. The reaction mixture was quenched with 50 ml water and worked-up as described above. CC (PE, R_f = 0.32) yielded 130 mg (67%) of **3a** as a colourless oil. – IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1250, 842. – UV (CH_3CN): λ_{max} (lg ε) = 240 nm (4.47). – ^1H NMR: δ = 0.26 (s, 18H), 0.67 (s, 6H), 6.61 (m, 4H). – ^{13}C NMR: δ = −2.9 (+), −1.6 (+), 118.6 (+), 119.3 (+), 161.8 (C_{quat}), 164.5 (C_{quat}). – MS (70 eV); *m/z* (%): 382 (24) [M^+], 367 (100).

Dimethylbis(5-trimethylsilyl-2-thienyl)germane (**3b**): 134 mg (0.5 mmol) of **3b**, 1.25 mmol of *n*-BuLi and TMSCl (150 mg, 1.4 mmol) were allowed to react and worked-up as described for **3a**. CC (PE, R_f = 0.48) gave 180 mg (87%) of **3b** as a colourless oil, which slowly solidified; m.p. 38°C. – IR (film): $\tilde{\nu}$ = 2857 cm^{-1}, 1250, 1000. – UV (CH_3CN): λ_{max} (lg ε) = 192 nm (4.36), 246 (4.41). – ^1H NMR: δ = 0.32 (s, 18H), 0.77 (s, 6H), 7.32 (m, 4H). – ^{13}C NMR: δ = −0.1 (+), 0.0 (+), 134.8 (+), 134.8 (+), 143.6 (C_{quat}), 145.6 (C_{quat}). – MS (70 eV); *m/z* (%): 414 (13) [M^+], 399 (100).

Bis(2,3-dimethoxy-4-trimethylsilylphenyl)dimethylgermane (**7**): A mixture of 283 mg (0.75 mmol) of **6**, TMEDA (220 mg, 1.9 mmol) and *n*-BuLi (0.2 ml, 2 mmol, 10 M in hexane) in 20 ml hexane was stirred for 12 h at room temp. Then, TMSCl (220 mg, 2.0 mmol) was added, the reaction mixture was stirred for 1 h, quenched with 20 ml water and worked-up as described before. The crude product was purified by CC (PE/Et_2O, 49:1, R_f = 0.42) to yield 370 mg (95%) of **7**, as a slowly solidifying, colourless oil; m.p. 71°C. – IR (film): $\tilde{\nu}$ = 2953 cm^{-1}, 1376. – UV (CH_3CN): λ_{max} (lg ε) = 208 nm (4.90), 284 (3.48). – ^1H NMR: δ = 0.30 (s, 18H), 0.73 (s, 6H), 3.67 (s, 6H), 3.85 (s, 6H), 7.05 (d, ^3J = 7 Hz, 2H), 7.11 (d, ^3J = 7 Hz, 2H). – ^{13}C NMR: δ = −0.9 (+), −0.4 (+), 59.6 (+), 59.6 (+), 129.5 (+), 129.5 (+), 135.2 (C_{quat}), 136.8 (C_{quat}), 155.8 (C_{quat}), 156.9 (C_{quat}). – MS (70 eV); *m/z* (%): 522 (14) [M^+], 507 (100). – $C_{24}H_{40}GeO_4Si_2$ (521.4): calcd. C 55.29, H 7.73; found C 55.04, H 7.76. – Mol. mass 522 (MS).

Bis(5-tert-butyl-2-methoxy-3-trimethylsilylphenyl)-dimethylgermane (**10**): **9** (215 mg, 0.5 mmol), 2.5 equiv. *n*-BuLi/TMEDA (1.3 mmol) and TMSCl (152 mg, 1.4 mmol) were allowed to react and worked-up as described for **7**. CC (PE, R_f = 0.1) gave 200 mg (70%) **10** as a colourless oil. – IR (film): $\tilde{\nu}$ = 2961 cm^{-1}, 1391. – UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.93), 284 (3.56). – ^1H NMR: δ = 0.31 (s, 18H), 0.77 (s, 6H), 1.27 (s, 18H), 3.51 (s, 6H), 7.44 (d, ^4J = 3 Hz, 2H), 7.48 (d, ^4J = 3 Hz, 2H). – ^{13}C NMR: δ = −0.3 (+), 0.3 (+), 31.6 (+), 34.5 (C_{quat}), 63.2 (+), 130.8 (C_{quat}), 132.1 (C_{quat}), 133.4 (+), 134.6 (+), 145.1 (C_{quat}), 168.3 (C_{quat}). – MS (70 eV); *m/z* (%): 574 (11) [M^+], 559 (100).

Octamethoxy-[1₄]dimethylgerma-1,4-calixarene (**11**): A mixture of **6** (500 mg, 1.3 mmol), TMEDA (385 mg, 3.3 mmol) and *n*-BuLi (0.33 ml, 3.3 mmol, 10 M in hexane) in 200 ml hexane was stirred at room temp. for 12 h. Dichlorodimethylgermane (230 mg, 1.3 mmol) in 50 ml hexane was then added by syringe pump over a period of 6 h. Subsequently, 200 ml of water was added, and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 ml). The combined organic phases were washed with water, dried with $MgSO_4$ and the solvent was removed in vacuo. The solid residue was extracted with PE to yield 20 mg (3%) **11** as a white solid, m.p. 282°C. – IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1}, 1377. – ^1H NMR: δ = 0.74 (s, 24H), 3.63 (s, 24H), 6.53 (s, 8H). – ^{13}C NMR: δ = −1.1 (+), 59.6 (+), 129.6 (+), 136.2 (C_{quat}), 156.1 (C_{quat}). – MS (70 eV); *m/z* (%): 956 (20) [M^+], 941 (100)[9].

[1₄]Dimethylgerma-2,5-(1-methylpyrrolo)calixarene (**4**): **2c** (500 mg, 1.9 mmol), TMEDA (550 mg, 4.8 mmol) and *n*-BuLi (0.48 ml, 4.8 mmol, 10 M in hexane) in 200 ml hexane were stirred for 3 h at room temp. Dimethyldichlorogermane (330 mg, 1.9 mmol) in 50 ml hexane was then added via syringe pump over a period of 10 h. Subsequently, the reaction mixture was quenched with 200 ml water, and the aqueous phase was extracted with 50 ml diethyl ether. The combined organic phases were washed with water, dried with $MgSO_4$ and the solvent was removed in vacuo. The solid residue was extracted with PE to yield 25 mg (4%) **4** as a white solid, m.p. >280°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2911 cm^{-1}, 1284. – UV (CH_3CN): λ_{max} (lg ε) = 192 nm (4.92), 240 (4.73). – ^1H NMR: δ = 0.62 (s, 24H), 3.08 (s, 12H), 6.39 (s, 8H). – ^{13}C NMR: δ = −2.3 (+), 35.5 (+), 116.9 (+), 135.9 (C_{quat}). – MS (70 eV); *m/z* (%): 728 (100) [M^+], 713 (81)[9].

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[6] [6a]H.-G. Elias, *Makromoleküle, Bd. 1*, Hüthig & Wepf, Basel, **1990**, p. 817–820. – [6b]The molecular mass (g/mol) calculated from the retention time vs polystyrene standards is in good agreement with the molecular weight determined by mass spectroscopy for compound **4** (MS: 727; GPC: 737), whereas a larger deviation was found for compound **11** (MS: 955; GPC: 769).

[7] [7a]The λ_{max} absorptions for a similar sequence of carbon-bridged pyrroles do not show any shift: pyrrole, 2,2-dipyrrylpropane and the cyclic tetramer of pyrrole and acetone all show λ_{max} (CH_3CN) = 216 nm. – [7b]W. H. Brown, W. N. French, *Can. J. Chem.* **1958**, *36*, 371–377. – [7c]J. Nagy, P. Hencsei, E. Z. Gergö, *Anorg. Allg. Chem.* **1969**, *367*, 293–302.

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[9] Compounds **4** and **11** were only obtained in small amounts. Therefore no elemental analysis was possible. The purity of the compounds was confirmed by HPLC-analysis. Their identity was unambiguously shown by the molecular ion isotope pattern from mass spectra.

[96241]