Synthesis and Characterization of Novel *p*-Phenylene- and *p*-Biphenylene-Bridged Germanocenes

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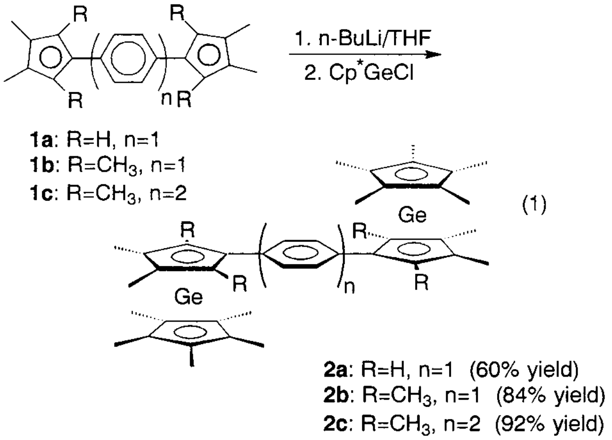
Summary: New p-phenylene- and p-biphenylene-bridged germanocenes have been synthesized and characterized. An X-ray crystal structure reveals a bent-sandwich system. Their reactions with o-quinone and ferrocenium salt are reported.

Group 14 metallocenes, their structures,[1,2] their reactivity, and, more recently, their catalytically active properties[3] have been extensively investigated; linked group 14 metallocenes are unknown. We describe here the preparation of the first *p*-phenylene- and *p*-biphenylene-bridged germanocenes; these can be considered as the germanium analogues of linked ferrocenes, which are well-known for their electrical, magnetic, and optical properties.[4]

Reaction of 2 equiv of Cp*GeCl[5] with the dilithium salts of **1**[6] in THF at −78 °C, followed by warming to room temperature, produced the corresponding complexes **2a**−**c** in good yield (eq 1).



1a: R=H, n=1
1b: R=CH$_3$, n=1
1c: R=CH$_3$, n=2

(1)

2a: R=H, n=1 (60% yield)
2b: R=CH$_3$, n=1 (84% yield)
2c: R=CH$_3$, n=2 (92% yield)

The digermanocene **2a** was isolated as yellow crystals from THF at −30 °C, whereas **2b**,**c** generally were obtained as pale yellow powders. All are very air-sensitive and must be stored at low temperature. In solution, **2a** decomposes rapidly to give the symmetrical species Cp*$_2$Ge.[7] The permethyl compounds **2b**,**c** are the most stable within the series and slowly decompose only after 2 days in CHCl$_3$ solutions.

The ^{1}H and ^{13}C NMR spectra[8] of **2** show equivalent methyl groups and ring carbon atoms for the C$_5$Me$_5$ ligands, in accord with rapidly rotating pentamethylcyclopentadienyl rings.[1b,9] For the same reason, only two signals due to the two nonequivalent pairs of methyl groups are observed for the C$_5$Me$_4$ moiety. In the EI and CI (CH$_4$) mass spectra the molecular ions were not observed. Fragmentate gave the spacer **1** and the [Me$_5$C$_5$Ge]$^+$ fragment. Similar observations were reported previously in the case of decamethylgermanocene,[1b,7] for which the highest mass observed (*m*/*z* 209) corresponded to the [Me$_5$C$_5$Ge]$^+$ cation.

The solid-state structure of **2a** has been investigated by X-ray crystallography[10] (Figure 1). Because of the poor quality of the crystals, the presence of a twinned system, and disorder problems, a detailed discussion of the structure is not possible; however, the atom connectivity is clear. Compound **2a** has a bent structure with an angle between the cyclopentadienyl planes of about 40°. The deviation from a classical metallocene structure of the D_{5d} or D_{5h} type is more similar to that observed in germanocene[11] (angle 50.4°) than in the decamethylgermanocene[12] (angle 22°). The germanium atoms do not reside between the cyclopentadienyl ring centers but are slightly displaced toward the carbon

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(8) **2a**: yield 60%; mp 215 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.28 (s, 4H, C$_6$H$_4$), 6.06 (s, 4H, C$_5$*H*$_2$Me$_2$), 3.73 (m, 8H, CH$_2$O), 2.04 (s, 12H, C$_5$H$_2$*Me*$_2$), 1.80 (s, 30H, C$_5$*Me*$_5$), 1.75 (m, 8H, *CH*$_2$CH$_2$O); ^{13}C NMR (CDCl$_3$) δ 133.01 (C(quat)), 124.91 (CH) (*C*$_6$H$_4$); 124.41 (C(quat)), 122.28 (C(quat)), 106.48 (CH) (*C*$_5$H$_2$Me$_2$); 118.92 (*C*$_5$Me$_5$); 68.01, 25.65 (*C*$_4$H$_8$O); 12.42, 9.63 (C$_5$*Me*$_5$ and C$_5$H$_2$*Me*$_2$); MS/IE [C$_5$Me$_5$Ge]$^{\bullet+}$ *m*/*z* 209 (100%). Anal. Calcd for C$_{48}$H$_{66}$Ge$_2$O$_2$: C, 70.28; H, 8.11. Found: C, 69.49; H, 7.38. **2b**: yield 84%; mp 235 °C dec; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 7.11 (s, 4H, C$_6$H$_4$), 2.04 and 2.03 (s, 24H, C$_5$*Me*$_4$), 1.95 (s, 30H, C$_5$*Me*$_5$); ^{13}C NMR (CDCl$_3$) δ 133.80 (C(quat)), 129.96 (CH) (*C*$_6$H$_4$); 127.08, 118.67, 118.44, 118.10 (*C*$_5$Me$_4$ and *C*$_5$Me$_5$); 11.01, 10.28, 9.95 (CH$_3$); MS/IE [C$_5$Me$_5$Ge]$^{\bullet+}$ *m*/*z* 209 (100%). **2c**: yield 92%.; mp 300 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.63, 7.26 (syst. AB, $^3J_{\mathrm{HH}} = 8.4$ Hz, 8H, C$_6$H$_4$), 2.04, 2.03 (s, 24H, C$_5$*Me*$_4$), 1.95 (s, 30H, C$_5$*Me*$_5$); ^{13}C NMR (CDCl$_3$) δ 137.94 (C(quat)), 135.80 (C(quat)), 131.07 (CH), 126.15 (CH) (*C*$_6$H$_4$), 126.91, 118.78, 118.58, 118.12 (*C*$_5$Me$_4$ and *C*$_5$Me$_5$), 10.92, 10.27, 9.95 (C$_5$*Me*$_4$ and C$_5$*Me*$_5$); MS/IE [C$_5$Me$_5$Ge]$^{\bullet+}$ *m*/*z* 209 (100%). The compounds **2b**,**c** are not stable in solution and slowly decompose at room temperature. Thus, they did not give reproducible analyses.

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10.1021/om000457h CCC: $19.00
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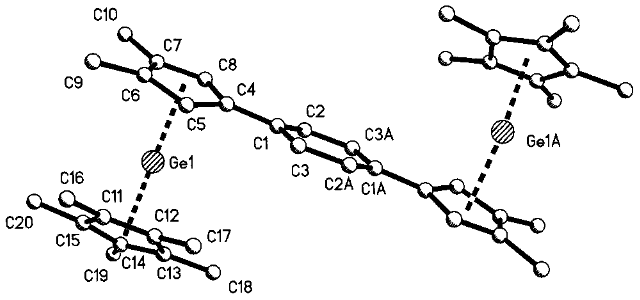


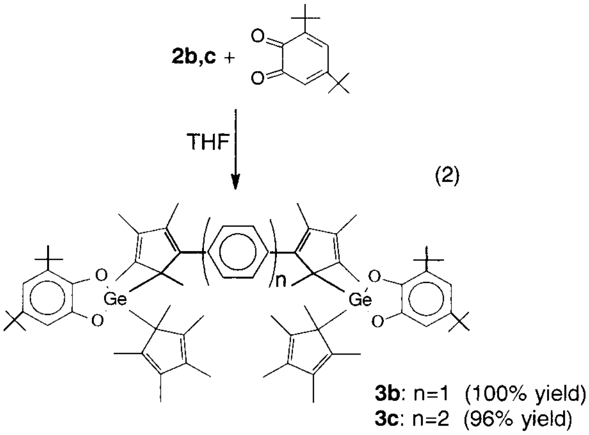
Figure 1. Crystal structure of the digermanocene **2a**.

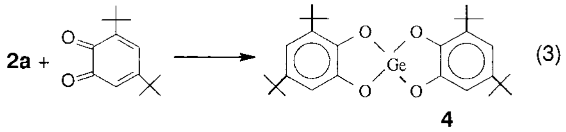
atoms C(5), C(11), and C(12). The Ge−C centroid distances are different according to the cyclopentadienyl plane, about 2.1 Å for C_5Me_5 and about 2.3 Å for $C_5H_2Me_2$, indicating a greater interaction between the germanium atom and the pentamethylcyclopentadienyl ring. The tricyclic bridging system is almost planar. The two Cp*Ge moieties are coordinated to opposite faces of the bridging spacer, as was generally observed in linked metallocenes.[4,6a]

To investigate if these linked germanocenes show the typical reactivity of divalent Ge species, a cycloaddition reaction with quinone was tried.[13] The addition of a stoichiometric quantity of 3,5-di-*tert*-butylorthoquinone to **2b**,**c** at room temperature in THF gave the corresponding cycloadducts **3b**,**c**, which were isolated in good yield[14] (eq 2).

In contrast, only the formation of spiro compound **4**[13] (43% yield) was obtained from the less sterically hindered digermanocene **2a** (eq 3). This probably is a result of a redistribution of the transient cycloadduct, as has been often observed in the case of halogenated germylenes.[13]

The cycloaddition mechanism of such reactions implies a single electron transfer between the germylene and the quinone in the first step.[15] To test the ability of





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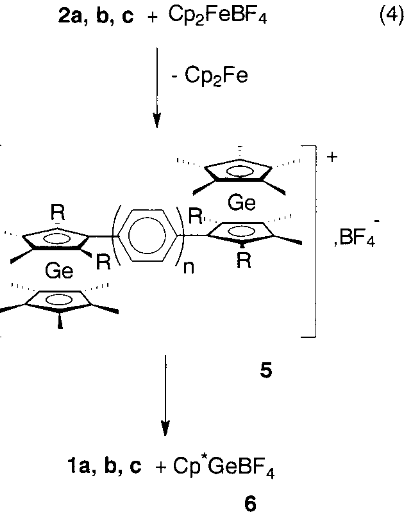
the digermanocenes to undergo single electron transfer, the transfer reaction with a ferrocenium salt was performed. Treatment of **2** with [Cp_2Fe, BF_4] in CH_2Cl_2 at 20 °C gave the well-known ionic species **6**,[16] which was easily isolated by precipitation from diethyl ether (eq 4).



The presence of Cp_2Fe, due to the reduction of the Cp_2Fe^+ species, confirms the electron-donating charac-

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(10) Crystal data for **2a**: $C_{24}H_{33}GeO$, $M_r = 410.09$, monoclinic, $P2_1/c$ (with 2 noncoordinated THF), $a = 8.6005(3)$ Å, $b = 20.9906(8)$ Å, $c = 12.5946(5)$ Å, $\beta = 104.994(1)°$, $V = 2196.3(1)$ Å^3, $Z = 4$, $\rho_c = 1.240$ Mg m^{-3} $F(000) = 868$, $\lambda = 0.710\,73$ Å, $T = 193(2)$ K, μ(Mo Kα) = 1.404 mm^{-1}, crystal size 0.1 × 0.5 × 0.6 mm, $4.23° \leq \theta \leq 21.49°$, 15 990 reflections (6108 independent) were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. At the beginning of the refinement we were blocked at R1 = 0.2, and the difference Fourier gave a high residual electron density peak, which made no chemical sense. By using the program package GEMINI,[17] we found two orientation matrices corresponding a nonmeroheral twin formed by rotation of 180° around the reciprocal vector 010 (for more information about twinned systems, see refs 18 and 19). The reflection intensities for each twin component were integrated. The structure was solved by direct methods (SHELXS-97),[20] and 382 parameters were refined using the least-squares method on F^2.[21] Refinement with the *hkl* file without the partially overlapped reflections gave the best results. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. A disorder of the pentamethylcyclopentadienyl anion was refined in two positions with the occupancies 0.55 and 0.45. The noncoordinated molecule of THF was also refined in two positions (0.72/0.28). We refined the disorders by using 809 distances and ADP restraints. Refinements in noncentrosymmetric space groups gave the same disorders. The BASF was refined to 0.456 15. The refinement as a twinned system is not giving a good *R* value, but the rest of the electron density became much better. The largest electron density residue was 0.754 e Å^{-3}, R1 = 0.1330 (for $F > 2\sigma(F)$) and wR2 = 0.4334 (all data) with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

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(14) **3b**: yield 100%; mp 104−106 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (s, 4H, C_6H_4), 6.94 (d, $^4J_{HH} = 2.2$ Hz, 2H, C_6H_2), 6.72 (d, $^4J_{HH} = 2.2$ Hz, 2H, C_6H_2), 1.86, 1.82, 1.81, 1.72, 1.68 (s, 54H, $C_5\mathit{Me}_4$ and $C_5\mathit{Me}_5$), 1.46 and 1.31, 1.30 (s, 36H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 151.39, 147.07, 141.09 (C(quat), C_6H_2 and C_6H_4), 113.22, 108.93 (C_6H_2), 133.90, 133.79 (C_5Me_4 and C_5Me_5), 128.89 (C_6H_4), 34.72, 34.57 ($\mathit{C}(CH_3)_3$), 31.93, 29.77 ($C(\mathit{C}H_3)_3$), 13.50, 13.31, 12.42, 12.24 ($C_5\mathit{Me}_4$ and $C_5\mathit{Me}_5$); DCI/NH_4 $M^{\bullet+}$ *m*/*z* 1172 (11%), [M − CH_3] 1157 (2%). Anal. Calcd for $C_{72}H_{98}Ge_2O_4$: C, 73.74; H, 8.42. Found: C, 73.19; H, 8.38. **3c**: yield 96%; mp 130−133 °C; ^{1}H NMR ($CDCl_3$) δ 7.61, 7.30 (syst. AB, $^3J_{HH} = 8.0$ Hz, 8H, C_6H_4), 6.93, 6.72 (d, $^4J_{HH} = 2.1$ Hz, 4H, C_6H_2), 1.85, 1.81, 1.77, 1.73, 1.69 (s, 54H, $C_5\mathit{Me}_4$ and $C_5\mathit{Me}_5$), 1.48 and 1.32, 1.31 (s, 36H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 151.42, 147.12, 142.15, 141.33, 141.17, 138.51, 135.27, 133.87 (C(quat) C_6H_2, C_6H_4, C_5Me_4 and C_5Me_5), 113.32, 109.01 (C_6H_2); 130.06, 126.33 (C_6H_4), 34.79, 34.61 ($\mathit{C}(CH_3)_3$), 32.01, 29.85 (CH_3, $C(\mathit{C}H_3)_3$), 13.42, 13.26, 12.52, 12.29 ($C_5\mathit{Me}_4$ and $C_5\mathit{Me}_5$); DCI/CH_4: $[M + H]^{\bullet+}$ *m*/*z* 1249 (3%). Anal. Calcd for $C_{78}H_{102}Ge_2O_4$: C, 75.02; H, 8.23. Found: C, 74.44; H, 8.15.

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ter of such digermanocenes. The transient radical ion **5** is unstable and probably loses the diradical spacer, giving the ligand **1** by abstraction of a hydrogen atom from the solvent. These results complement those obtained by mass spectrometry and confirm the poor stability of the cationic species **5**. Moreover, the observed Ge−C bond cleavage between the spacer and the metal and the formation of Cp*GeBF$_4$ is in agreement with the greater interaction between the germanium atom and the pentamethylcyclopentadienyl ring, as revealed by the X-ray study.

Further studies are in progress on the preparation of analogous tin species as well as on their reactivity and application.

Supporting Information Available: Text giving experimental details on the preparation of **2a**−**c** and their reactions with 3,5-di-*tert*-butyl-*o*-quinone and the ferrocenium salt and tables and figures giving details of the X-ray structure determination, atomic coordinates, and bond distances and angles for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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