Available online at www.sciencedirect.com

Journal of Organometallic Chemistry 666 (2003) 15–22

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Convenient, zirconocene-coupling routes to germole- and thiophene-containing macrocycles with triangular geometries

Jonathan R. Nitschke, T. Don Tilley *

Department of Chemistry, Center for New Directions in Organic Synthesis, University of California, Berkeley, Berkeley, CA 94720-1460, USA

Received 28 June 2002

Dedicated to Professor Jerry Atwood on the occasion of his 60th birthday

Abstract

Reactions of zirconacyclopentadiene-coupled macrocycles with S_2Cl_2 or $GeCl_4$ gave new macrocycles containing thiophene and dichlorogermole groups, respectively. The germoles, synthesized in high yields, possess labile chloride substituents that are readily displaced via nucleophilic substitution reactions. These germole-containing macrocycles are potentially useful as supramolecular building blocks. A macrocyclic trithiophene compound, with 1,4-phenylene groups that bridge the thiophene rings, was characterized by X-ray crystallography. The X-ray structure of a related trigermole macrocycle, with bridging biphenylene groups, is also presented.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Germole; Macrocyclization; Tecton; Thiophene; Zirconocene

1. Introduction

Macrocycles are important synthons and building blocks in supramolecular chemistry [1]. Macrocyclic compounds that incorporate a number of donor atoms serve as highly selective hosts and receptors [2]. Recently, macrocycles that feature ‘exterior’ functional groups have been shown to serve as building blocks (or tectons) for discrete supramolecular assemblies [3] and designed crystal lattices [4].

The synthesis of macrocyclic tectons for supramolecular chemistry is often a challenging problem. The cyclization reactions employed are often low yielding, requiring high-dilution conditions and lengthy separations to remove oligomeric co-products. We have recently developed a zirconocene-coupling macrocycle synthesis as an alternative to traditional macrocyclization reactions [5–9]. This high-yielding macrocyclization relies on the reversible formation of a zirconacyclopentadiene ring from a zirconocene fragment and two alkyne groups. This reaction therefore allows the self-assembly of complex structures via reactions of a labile C–C bond.

Many of the macrocycles synthesized via zirconocene coupling are rigid and highly symmetrical. The number of monomeric diyne units incorporated into each macrocycle is a function of the geometry and flexibility of the diyne unit [6–8], and the reaction allows the incorporation of functional groups of proven use in supramolecular chemistry, such as perfluorophenylene [7] and bipyridyl [9]. Treatment of the zirconocene-containing macrocycles with acid allows the high-yielding syntheses of air-stable cyclophanes that contain bis(trimethylsilyl)butadiene groups.

Here we report the incorporation of germole and thiophene functionalities into the ‘corners’ of triangular macrocycles obtained by zirconocene coupling. The germole-producing reactions, in particular, are remarkable for the high yields observed and the ease of subsequent nucleophilic displacement of the chlorine

---

* Corresponding author. Fax: +1-510-6428940

E-mail address: tdtilley@socrates.berkeley.edu (T. Don Tilley).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.

PII: S0022-328X(02)02028-4

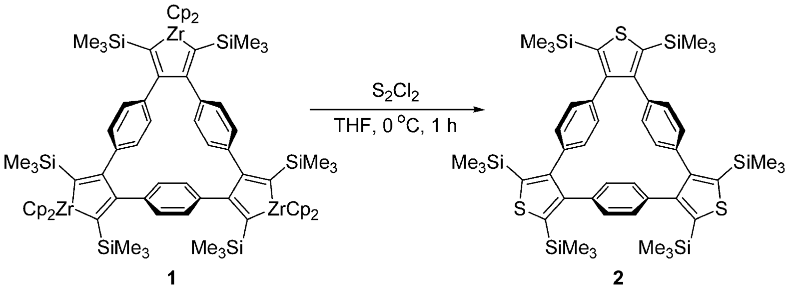
atoms bound to germanium. The symmetrical arrangement of these groups around the periphery of these rigid macrocycles is expected to allow their use as tectons for supramolecular networks and discrete assemblies.

2. Results and discussion

The presence of a trimethylsilyl substituent α to zirconium on a zirconacyclopentadiene ring presents a formidable steric barrier to substitution at zirconium. This results in limitations to the functionalization of macrocycles via reactions at zirconacyclopentadiene rings, especially since the $SiMe_3$ substituent appears to be necessary for the formation of macrocycles via zirconocene coupling [6]. Thus, reported methods of carrying out electrophilic substitutions on zirconacyclopentadienes [10,11] have generally not worked with macrocyclic substrates. However, reactions of zirconocene-containing macrocycles with S_2Cl_2 and $GeCl_4$ have yielded new cyclic products, as detailed below.

*2.1. Synthesis of trithiophene **2***

The reaction of sulfur monochloride with zirconacycle **1** gave a complex mixture of products, from which trithiophene **2** was isolated in 10% overall yield after two recrystallizations (Eq. (1)). Examination of the ^1H-NMR spectrum of the crude reaction mixture suggested that **2** comprised ca. 20% of the overall soluble product.



(1)

The X-ray crystal structure of **2** was solved from a crystal obtained by vapor diffusion of Et_2O into a toluene solution of the macrocycle. An ORTEP diagram of this structure is shown in Fig. 1, and crystallographic details are given in Table 1. Much of the molecular symmetry of **2** is reflected in this crystal structure; the space group $P6_3/m$ places the macrocycle on a special position of C_{3h} point symmetry that lacks only the vertical mirror planes of the molecule's D_{3h} point group.

The central cavity of **2** could accommodate a sphere of radius 1.06 Å in van der Waals contact with the three phenylene rings. This molecule might therefore host a number of different guest ions, coordinated by the π clouds of the phenylenes, in a fashion similar to that of the 2.2.2-paracyclophane complexes of Schmidbaur [12].

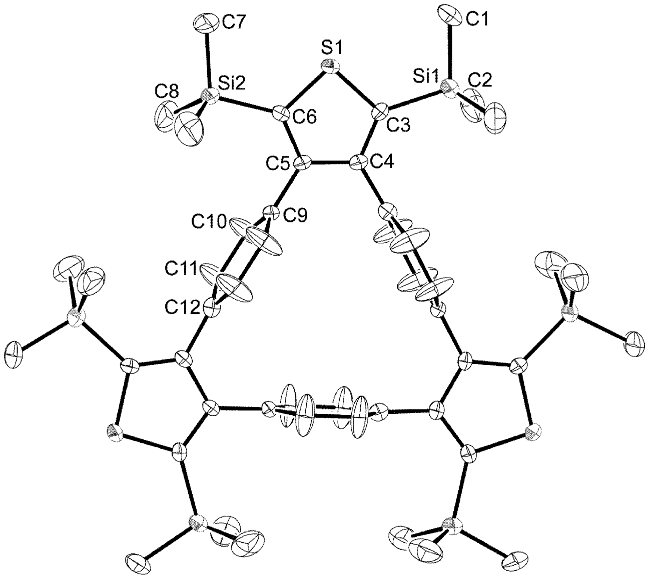


Fig. 1. ORTEP diagram (50% probability ellipsoids) of **2**; atoms of the asymmetric unit are labeled.

*2.2. Syntheses of hexachlorotrigermoles **5**, **6**, and **7***

Reactions of germanium tetrachloride with the trimeric macrocycles **1**, **3**, and **4** provided high yields of trigermoles **5**, **6**, and **7**, as shown in Scheme 1. The high yields observed in this substitution reaction suggest that the three sequential germanium-for-zirconium substitution steps occur in near-quantitative yield. Under identical conditions silicon tetrachloride reacted with **2** to give multiple unidentified products, and tin tetrachloride reacted with **2** to induce a decyclization reaction, with formation of 4,4′-bis(trimethylsilylalkynyl)biphenyl.

Although zirconacyclopentadiene to germole substitution reactions are known [11,13], this transformation

Table 1
Crystallographic data and refinement details for **2** and **6**

	Compound **2**	Compound **6**
Empirical formula	$C_{48}H_{66}Si_6S_3$	$C_{195}H_{228}Cl_{12}Ge_6Si_{12}$
Crystal color, habit	Colorless, Prism	
Temperature (°C)	−102	−105
Reflections used for unit cell determination (2θ range)	5351 (0–45°)	4674 (0–45°)
Space group	$P6_3/m$ (#176)	$P2_1$ (#4)
a (Å)	17.2222(2)	18.8975(3)
b (Å)	17.2222(2)	20.7900(3)
c (Å)	10.5342(1)	24.3797(7)
α (°)	90	90
β (°)	90	90.229(2)
γ (°)	120	90
V (Å^3)	2705.88(5)	9578.2(3)
Z value	2	2
μ(Mo–K$_\alpha$) (cm^{-1})	2.99	12.21
Diffractometer	Siemens SMART	Siemens SMART
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
Monochromator	Graphite	Graphite
Crystal to detector distance (mm)	60 mm	60 mm
Scan type (°)	ω, 0.3	ω, 0.3
Frame collection time (s)	30	30
Crystal dimensions (mm)	0.15 × 0.18 × 0.08	0.05 × 0.08 × 0.15
2θ Range (°)	2–52.3	2–52.2
Reflections measured	12 842	46 536
Unique reflections	1794	31 320
Observations ($I > 3\sigma$)	1066	13 120
Refinement	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Variables	103	977
Reflection/parameter ratio	10.35	13.43
Residuals: R_{int}; R; R_w	0.059; 0.068; 0.069	0.058; 0.069; 0.073
Hydrogen atom treatment	Idealized positions	Idealized positions
Goodness-of-fit indicator	1.90	1.82
Largest difference peak and hole (e$^-$ Å^{-3})	0.47 and −0.47	1.04 and −0.56

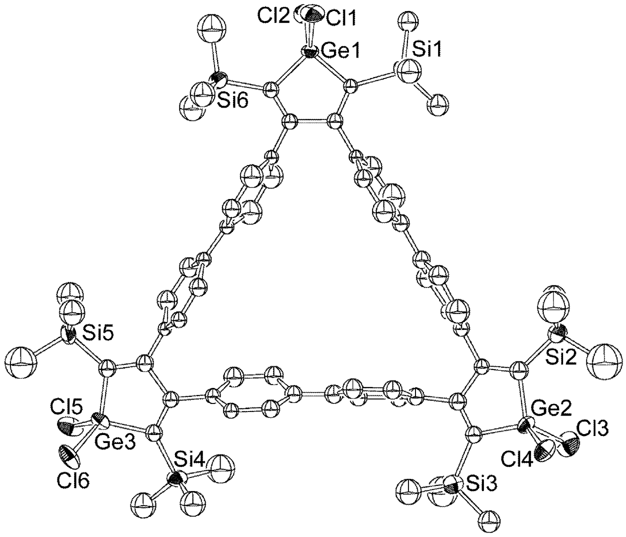
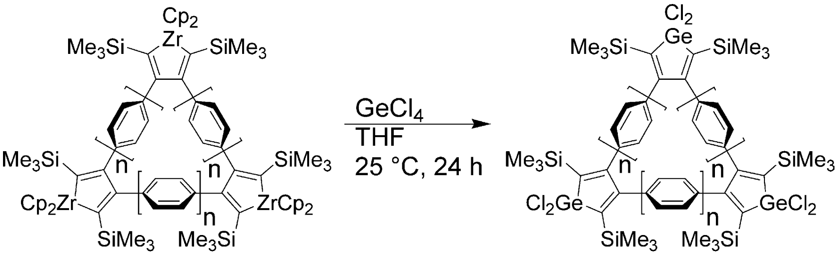


Fig. 2. ORTEP diagram (50% probability ellipsoids) of one of the two independent molecules of **6** present in the asymmetric unit; heteroatoms are labeled.

has rarely been reported for cases involving α-trimethylsilyl substituents on the metallacyclic ring [14]. Furthermore, to our knowledge none of these substitutions have involved zirconacyclopentadienyl rings in which anything bulker than a methyl group occupies the β-position. The rigid geometry imposed by the macrocyclic framework may thus be an important factor in the success of this reaction.

Macrocycle **5** is less soluble than its precursor **1** [6], rendering characterization by NMR spectroscopy infeasible. Its hexabutyl derivative (vide infra), however, is readily soluble in hydrocarbon solvents. Macrocycle **6** has similar solubility properties to the Cp_2ZrCl_2 by-product, necessitating removal of the latter by sublimation. The syntheses of trigermoles **5**–**7** may be carried out in the same reaction flask used for the macrocyclization, which improves the overall isolated yields.



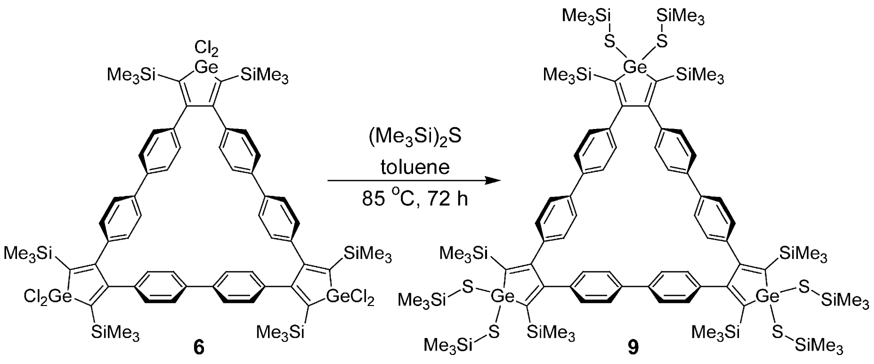
1 (n = 1)
3 (n = 2)
4 (n = 3)

5 (n = 1) (93%)
6 (n = 2) (92%)
7 (n = 3) (89%)

Scheme 1. Syntheses of trigermole macrocycles from the corresponding zirconacycles.

To verify the identity of trigermole **6**, its X-ray crystal structure was determined. An ORTEP diagram is shown in Fig. 2, and crystallographic details are given in Table 1. Unlike **2**, none of the molecular symmetry of **6** was reflected in this structure; in fact, two symmetry-independent chemically identical macrocycles constitute the asymmetric unit. However, the NMR spectra reflect D_{3h} molecular symmetry.

The reaction of **6** with a slight excess (6.6 equivalents) of hexamethyldisilathiane in toluene gave the macrocyclic hexakis(trimethylsilylsulfido)trigermole **9** in 87% yield (Eq. 3). The trimethylsilylsulfido groups desilylate very readily in the presence of protic media, as evidenced by the FAB mass spectrum of **9** in a matrix of 3-nitrobenzyl alcohol. No peak higher in mass than completely proteodesilylated **9** was present.



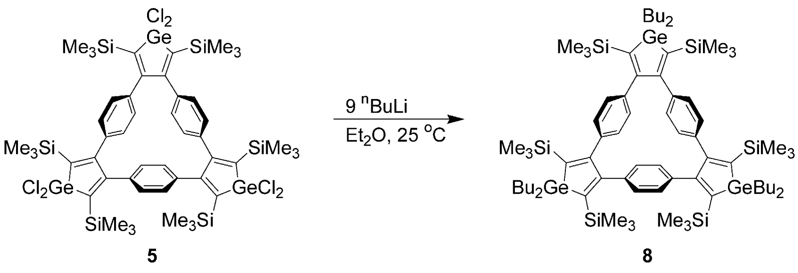
(3)

2.3. Reactions of hexachlorotrigermoles with nucleophiles

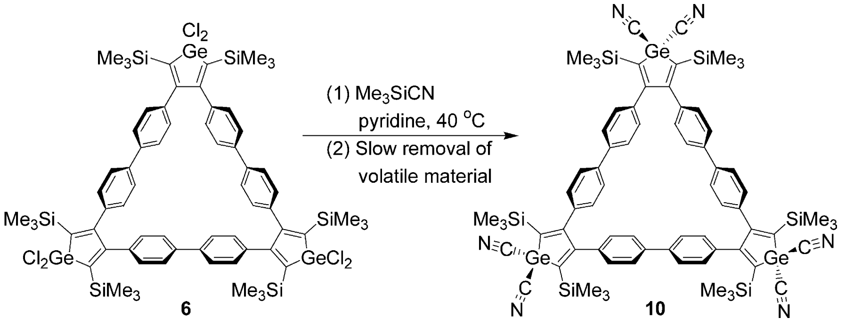
The presence of six symmetry-equivalent, readily displaced [15] chlorine atoms of **5**, **6**, and **7** suggested that derivatives of these molecules might be linked together into coordination networks. In order to investigate this possibility, and to explore the substitution chemistry of these germoles, reactions with nucleophilic reagents were investigated.

The reaction of **5** with excess *n*-BuLi (nine equivalents) gave hexabutyl trigermole **8** in 61% yield (Eq. 2). In contrast to **5**, macrocycle **8** is highly soluble in hydrocarbon solvents, allowing its characterization by NMR spectroscopy.

Initial attempts to synthesize hexacyano trigermole **10** mimicked the synthesis of **9**, using Me_3SiCN in place of $(Me_3Si)_2S$. However, these toluene reaction solutions darkened in color and became viscous above 60 °C, suggesting that **10** may have limited thermal stability. Acetonitrile was then used as the reaction solvent, based on the idea that a more polar solvent might facilitate the desired nucleophilic displacement reaction at lower temperatures. Complex mixtures of products were obtained from this solvent, possibly resulting from the extremely low solubility of **6** in acetonitrile. The reaction of **6** with Me_3SiCN in pyridine finally yielded the desired product **10** in 75% isolated yield (Eq. 4).



(2)



(4)

The slow removal of volatile material over 12 h as the reaction mixture refluxed at 40 °C was crucial to the success of this reaction. Rapid evaporation of the reaction mixture to dryness gave a mixture of products, as evidenced by broad features in the proton NMR spectrum. The substantial difference in the boiling points of Me_3SiCl (57 °C) and Me_3SiCN (118 °C) appears to lead to the preferential evacuation of Me_3SiCl from the reaction mixture, forcing the reaction of Eq. 4 to completion. The Ge–CN bonds are quite moisture sensitive, as the molecule evolves HCN gas in contact with moist air.

3. Conclusions

In conclusion, electrophilic substitution at zirconium has been employed to synthesize thiophene and germole-containing macrocycles, the latter in high yields. Nucleophilic substitution of the chloride ligands bonded to germanium provides a means to introduce exocyclic binding sites into these macrocycles, making them potential tectons for supramolecular self-assembly. The use of these molecules as ‘preformed macropores’ to construct supramolecular assemblies and networks is a focus of current investigations.

4. Experimental

4.1. General

All reactions involving air-sensitive compounds were carried out under nitrogen or argon using standard Schlenk techniques and dry, oxygen-free solvents. Pentane, Et_2O, C_6H_6, and tetrahydrofuran were distilled under nitrogen from sodium benzophenone ketyl. Toluene, $C_6H_5CH_3$-d_8, and C_6H_6-d_6 were distilled under nitrogen from Na/K. Methylene chloride-d_2 was distilled under vacuum from CaH_2. *n*-BuLi was used as a 1.6 M solution in hexanes. Zirconium-containing macrocycles **1** [6], **3** [5d], and **4** [6] were synthesized as previously described.

All NMR spectra were recorded at room temperature. Chemical shifts are referenced to the residual proton or carbon resonance of the deuterated solvent. In some cases, DEPT [16] was used to assign carbon resonances. Mass spectra and combustion analyses were provided by the Micro-Mass Facility of the University of California, Berkeley.

4.2. Trithiophene **2**

Macrocycle **1** (1.00 g, 0.678 mmol) was loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. On a Schlenk line, dry THF (75 ml) was added. This mixture was stirred rapidly for 1 h, giving a finely divided suspension. This suspension was chilled to − 5 °C in an ice/brine bath, and S_2Cl_2 (2 ml of 1 M CH_2Cl_2 solution, 2 mmol) was added dropwise via syringe with rapid stirring. The precipitate slowly dissolved over 30 min, as the color of the reaction mixture deepened from yellow to orange. The cold bath was then removed, and stirring was continued for 30 min. The volatile material was then removed under dynamic vacuum (30 μmHg over 12 h) and the solid residue was suspended in C_5H_{12} (100 ml). The C_5H_{12} suspension was sonicated for 10 min and then filtered through a plug of celite (10 ml), and the volatile components of the filtrate were removed under dynamic vacuum. The product was recrystallized twice from $C_6H_5CH_3$–C_5H_{12}. The yield of white crystals was 0.061 g, 10%. ^{1}H-NMR (500 MHz, C_6H_6-d_6) δ 0.26 (s, 18H, $Si(CH_3)_3$), 7.02 (s, 4H, phenylene). $^{13}C\{^1H\}$-NMR (125 MHz, C_6H_6-d_6) δ 1.1 ($Si(CH_3)_3$), 130.2 (phenylene), 138.0, 140.9, 153.4. EI MS *m*/*z* 906 [M^+], 891 [$M^+ - CH_3$]. Anal. Calc. for $C_{48}H_{66}S_3Si_6$: C, 63.51; H, 7.33. Found: C, 63.60; H, 7.22%. X-ray quality crystals of **2** were obtained through vapor diffusion of Et_2O into a $C_6H_5CH_3$ solution. Details of the crystal structure are given in Table 1.

4.3. *Trigermole* **5**

Macrocycle **1** (1.00 g, 0.678 mmol) was loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. On a Schlenk line, dry THF (75 ml) was added. This mixture was stirred rapidly for 1 h, giving a finely divided suspension. Germanium tetrachloride (0.116 ml, 1.02 mmol) was added at room temperature (r.t.) dropwise via syringe with rapid stirring. The reaction mixture bleached to an ivory color over 12 h at r.t. The finely divided product was allowed to stand for 12 h, and then the supernatant was removed by cannula filtration. The product was washed with dry THF (2 × 100 ml) and dried under dynamic vacuum. The yield of off-white powder was 0.862 g; 93% as a THF solvate. Extremely poor solubility precluded NMR characterization. THF was noted in the ^{1}H spectrum of a suspension of the dried product, however, EI-MS *m/z* 1242 ([M^+], this peak matches an isotopic simulation well), 1227 [$M^+ - CH_3$]. Anal. Calc. for $C_{48}H_{66}Cl_6Ge_3Si_6 \cdot C_4H_8O$: C, 47.52; H, 5.68. Found: C, 47.63; H, 5.64%.

4.4. *Trigermole* **6**

Macrocycle **3** (0.568 g, 0.333 mmol) was loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. On a Schlenk line, dry THF (50 ml) was added. This mixture was stirred for 5 min, giving an orange solution. Germanium tetrachloride (0.116 ml, 1.02 mmol) was added at r.t. dropwise via syringe with rapid stirring. The reaction solution became colorless over 20 min at r.t. After stirring for 1 h, the volatile material was removed under dynamic vacuum. Dry C_6H_6 (50 ml) was added to the reaction flask, and the resulting solution was then sonicated until a finely divided suspension was obtained (20 min). The product suspension was then transferred via cannula to a N_2-purged sublimator, and the reaction flask was rinsed with an additional portion of dry C_6H_6 (25 ml), which was also transferred to the sublimator. The product suspension was flash-frozen with liquid N_2, and the benzene was lyophylized under dynamic vacuum (6 h). The byproduct Cp_2ZrCl_2 was then sublimed away from the desired product (12 h, 75 °C) under dynamic vacuum. The product was washed with dry Et_2O (25 ml) and dried under dynamic vacuum. The yield of white microcrystalline powder was 0.450 g, 92%. ^{1}H-NMR (500 MHz, C_6H_6-d_6) δ 0.10 (s, 18H, $Si(CH_3)_3$), 6.59 (d, $J = 8.5$ Hz, 4H, phenylene), 6.88 (d, $J = 8.5$ Hz, 4H, phenylene). $^{13}C\{^1H\}$-NMR (125 MHz, C_6H_6-d_6) δ 0.74 ($Si(CH_3)_3$), 126.0 (phenylene), 129.6 (phenylene), 138.0, 138.3, 139.2, 164.2. EI-MS *m/z* 1470 [M^+], 1326 [$M^+ - GeCl_2$]. Anal. Calc. for $C_{66}H_{78}Cl_6Ge_3Si_6$: C, 53.91; H, 5.35. Found: C, 53.65; H, 5.24%. X-ray quality crystals of **6** were obtained through vapor diffusion of hexamethyldisiloxane into a toluene solution. Details are given in Table 1.

4.5. *Trigermole* **7**

Macrocycle **4** (2.54 g, 3.84 mmol) was loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. On a Schlenk line, dry THF (75 ml) was added. This mixture was stirred rapidly for 1 h, giving a finely divided suspension. Germanium tetrachloride (0.656 ml, 5.76 mmol) was added at r.t. dropwise via syringe with rapid stirring. The reaction mixture bleached to an ivory color over 6 h at r.t., as much of the solid dissolved. The volatile material was removed under dynamic vacuum, and the ivory-colored residue was washed with dry $C_6H_5CH_3$ (2 × 100 ml) and dried under dynamic vacuum. The yield of white microcrystals was 2.10 g; 89% as a bis(THF) solvate. ^{1}H NMR (500 MHz, C_6H_6-d_6) δ 0.20 (s, 18H, $Si(CH_3)_3$), 6.93 (d, $J = 8.5$ Hz, 4H, phenylene), 7.20 (d, $J = 8.5$ Hz, 4H, phenylene), 7.27 (s, 4H, central phenylene). FAB-MS *m/z* 1698 [M^+], 1555 [$M^+ - GeCl_2$]. Anal. Calc. for $C_{84}H_{90}Cl_6Ge_3Si_6 \cdot 2\ C_4H_8O$: C, 59.96; H, 5.80. Found: C, 60.14; H, 5.53%.

4.6. *Tetrabutyl trigermole* **8**

Macrocycle **5** (0.371 g, 0.894 mmol) was loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. On a Schlenk line, dry Et_2O (70 ml) was added. This mixture was stirred rapidly for 1 h, giving a finely divided suspension. Using a syringe, *n*-BuLi in hexanes (1.1 ml, 2.7 mmol) was added at r.t. dropwise with rapid stirring. The solid present in the reaction mixture dissolved over 5 min, giving a reddish solution. This solution was filtered through a plug of silica (10 ml) under aerobic conditions. The volatile material was removed under dynamic vacuum, and the product was recrystallized from C_5H_{12} (50 ml) at −80 °C. The yield of white microcrystals was 0.250 g, 61%. ^{1}H-NMR (500 MHz, C_6H_6-d_6) δ 0.14 (s, 18H, $Si(CH_3)_3$), 0.98 (t, $J = 7.5$ Hz, 3H, $GeCH_2CH_2CH_2CH_3$), 1.32 (t, $J = 7.5$ Hz, 2H, $GeCH_2CH_2CH_2CH_3$), 1.42 (m, $J = 7.5$ Hz, 2H, $GeCH_2CH_2CH_2CH_3$), 1.61 (m, 2H, $GeCH_2CH_2$-CH_2CH_3), 6.71 (s, 4H, phenylene). $^{13}C\{^1H\}$-NMR (125 MHz, C_6H_6-d_6) δ 2.0 ($Si(CH_3)_3$), 14.5 (butyl), 16.8 (butyl), 26.6 (butyl), 28.9 (butyl), 128.7 (phenylene), 141.6, 146.2, 168.6. High Resolution ES-MS *m/z* 1395.564 [$M - Na^+$], calculated 1395.559; the calculated isotope pattern was in good agreement with experiment.

4.7. *Hexakis(trimethylsilylsulfido) trigermole* **9**

Macrocycle **6** (0.490 g, 1 mmol) and hexamethyldisilathiane (0.464 ml, 2.2 mmol) were loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. On a

Schlenk line, dry $C_6H_5CH_3$ (10 ml) was added. This mixture was heated to 85 °C with stirring, giving a colorless solution. The reaction mixture was kept at 85 °C for 72 h, and then the volatile components were removed under dynamic vacuum over 12 h. Dry C_5H_{12} (100 ml) was added to the crude product, and this suspension was sonicated for 30 min and allowed to stand for 6 h. The supernatant was removed by cannula filtration, and the product was dried under dynamic vacuum. The yield of white microcrystals was 0.548 g, 87%. ^{1}H-NMR (500 MHz, C_6H_6-d_6) δ 0.24 (s, 18H, Si(CH_3)$_3$ α to germanium), 0.49 (s, 18H, S–Si(CH_3)$_3$), 6.95 (d, $J = 8.5$ Hz, 4H, phenylene), 7.11 (d, $J = 8.5$ Hz, 4H, phenylene). ^{13}C{^{1}H}-NMR (125 MHz, C_6H_6-d_6, not all resonances observed) δ 2.0 (Si(CH_3)$_3$), 4.7 (Si(CH_3)$_3$), 126.0 (phenylene), 129.7 (phenylene). FAB-MS, 3-nitrobenzyl alcohol matrix m/z 1456 (proteodesilylated **9**$^+$, calculated isotope pattern in good agreement with experiment), 1423 (proteodesilylated **9**$^+$ − SH). Anal. Calc. for $C_{84}H_{132}Ge_3S_6Si_{12}$: C, 53.40; H, 7.04; S, 10.18. Found: C, 53.37; H, 6.78; S, 10.02%.

4.8. *Hexacyano trigermole* ***10***

Macrocycle **6** (0.100 g, 0.204 mmol), trimethylsilylcyanide (0.544 ml, 4.08 mmol), and dry pyridine (20 ml) were loaded into a 100 ml Teflon-stoppered Schlenk flask in a glovebox. The clear, slightly yellow reaction mixture was stirred for 20 min at r.t., then placed in a 40 °C oil bath such that the bottom of the reaction flask was just touching the oil. The Teflon stopcock was cracked open very slightly, such that reflux occurred on the walls of the reaction flask within several minutes. The volatile material was removed through the slightly open stopcock over 12 h, and then the tan solid product was washed with dry Et_2O (70 ml). The yield of white microcrystalline product was 0.072 g, 75%. ^{1}H-NMR (500 MHz, C_6H_6-d_6) δ −0.01 (s, 18H, Si(CH_3)$_3$), 6.50 (d, $J = 8.5$ Hz, 4H, phenylene), 6.87 (d, $J = 8.5$ Hz, 4H, phenylene). ^{13}C{^{1}H}-NMR (125 MHz, C_6H_6-d_6) δ 0.8 (Si(CH_3)$_3$), 118.2 (cyano), 126.1 (phenylene), 129.4 (phenylene), 134.8, 138.5, 139.3, 171.0. Anal. Calc. for $C_{72}H_{78}Ge_3N_6Si_6$: C, 61.17; H, 5.56; N, 5.94. Found: C, 61.21; H, 5.27; N, 5.58%.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 186845 and 186846 for compounds **2** and **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the National Science Foundation for their generous support of this work. The Center for New Directions in Organic Synthesis is supported by Bristol-Myers Squibb as Sponsoring Member. We thank Frederick Hollander of the U.C. Berkeley College of Chemistry X-ray Crystallographic Facility for help with solving the crystal structures.

References

[1] B. Dietrich, Macrocyclic Chemistry: Aspects of Organic and Inorganic Supramolecular Chemistry, VCH, Weinheim, Germany, 1993.
[2] F. Vogtle, Host Guest Complex Chemistry: Macrocycles: Synthesis, Structures, Applications, Springer, New York, 1985.
[3] (a) P.N.W. Baxter, J.M. Lehn, B.O. Kneisel, G. Baum, D. Fenske, Chem. Eur. J. 5 (1999) 113;
(b) K. Campbell, R. McDonald, R.R. Tykwinski, J. Org. Chem. 67 (2002) 1133;
(c) M.M. Conn, J. Rebek, Jr., Chem. Rev. 97 (1997) 1647;
(d) C.M. Drain, K.C. Russell, J.-M. Lehn, Chem. Commun. (1996) 337;
(e) K. Campbell, R. McDonald, R. Tykwinski, J. Org. Chem. 67 (2002) 1133;
(f) S. Rucareanu, O. Mongin, A. Schuwey, N. Hoyler, A. Gossauer, W. Amrein, H.U. Hediger, J. Org. Chem. 66 (2001) 4973.
[4] (a) F. Hajek, M.W. Hosseini, E. Graf, A. De Cian, J. Fischer, Angew. Chem. Int. Ed. Engl. 36 (1997) 1760;
(b) C. Kleina, E. Graf, M.W. Hosseini, A. De Cian, J. Fischer, Chem. Commun. (2000) 239;
(c) M. Loi, E. Graf, M.W. Hosseini, A. De Cian, J. Fischer, Chem. Commun. (1999) 603;
(d) G. Mislin, E. Graf, M.W. Hosseini, A.D. Cian, N. Kyritsakas, J. Fischer, Chem. Commun. (1998) 2545;
(e) C. Kaes, M.W. Hosseini, C.E.F. Rickard, B.W. Skelton, A.H. White, Angew. Chem. Int. Ed. Engl. 37 (1998) 920;
(f) M.W. Hosseini, A. De Cian, Chem. Commun. (1998) 727.
[5] (a) S.S.H. Mao, T.D. Tilley, J. Am. Chem. Soc. 117 (1995) 5365;
(b) F.-Q. Liu, G. Harder, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 3271;
(c) S.S.H. Mao, F.-Q. Liu, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 1193;
(d) S.S.H. Mao, T.D. Tilley, J. Am. Chem. Soc. 117 (1995) 7031.
[6] L.L. Schafer, J.R. Nitschke, S.S.H. Mao, F.-Q. Liu, G. Harder, M. Haufe, T.D. Tilley, Chem. Eur. J. 8 (2002) 74.
[7] J.R. Nitschke, T.D. Tilley, J. Am. Chem. Soc. 123 (2001) 10183.
[8] J.R. Nitschke, T.D. Tilley, Angew. Chem. Int. Ed. Engl. 40 (2001) 2142.
[9] (a) J.R. Nitschke, S. Zuercher, T.D. Tilley, J. Am. Chem. Soc. 122 (2000) 10345;
(b) J. Nitschke, T.D. Tilley, J. Org. Chem. 63 (1998) 3673.
[10] T. Takahashi, Z. Xi, A. Yamazaki, Y. Liu, K. Nakajima, M. Kotora, J. Am. Chem. Soc. 120 (1998) 1672.
[11] P.J. Fagan, W.A. Nugent, J.C. Calabrese, J. Am. Chem. Soc. 116 (1994) 1880.
[12] (a) T. Probst, O. Steigelmann, J. Riede, H. Schmidbaur, Chem. Ber. 124 (1991) 1089;
(b) T. Probst, O. Steigelmann, J. Riede, H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 29 (1990) 1397.

[13] P. Dufour, M. Dartiguenave, Y. Dartiuenave, J. Dubac, J. Organomet. Chem. 384 (1990) 61.

[14] (a) K.-I. Kanno, M. Kira, Chem. Lett. (1999) 1127;
(b) X. Sava, N. Mezailles, N. Maigrot, F. Nief, L. Ricard, F. Mathey, P. Le Floch, Organometallics 18 (1999) 4205;
(c) M. Westerhausen, M.H. Digeser, C. Gueckel, H. Noeth, J. Knizek, W. Ponikwar, Organometallics 18 (1999) 2491.

[15] S. Patai, The Chemistry of Organic Germanium, Tin, and Lead Compounds, Wiley, New York, 1995.

[16] A.E. Derome, Modern NMR Techniques for Chemistry Research, Pergamon, Oxford, 1987.