Synthesis of Fused 1-Sila-, 1-Germa-, and 1-Selenacyclohepta-2,4,6-trienes

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Received April 7, 2008

A concise route to 1-sila-, 1-germa-, and 1-selenacyclohepta-2,4,6-trienes containing two fused benzo[*b*]thiophene units is described. Metalation of the ethylene acetal of 3-bromobenzo[*b*]thiophene-2-carboxaldehyde and subsequent quenching with Me_2SiCl_2, Me_2GeCl_2, or $(PhSO_2)_2Se$ gave the corresponding bis(benzo[*b*]thiophen-3-yl)silane, -germane, or -selenide, respectively, which were subjected to deprotection, followed by McMurry coupling, eventually affording the target compounds in good overall yields. It was also concluded that application of this approach to synthesis of related benzo-fused metallacyclohepta-2,4,6-trienes is limited to electron-deficient targets, as attempts involving electron-rich substrates failed or gave only low yields at the final McMurry coupling stage.

Introduction

Derivatives of the thiepin ring system (**1**) (Figure 1) have been intensely studied over the years, with particular emphasis on aspects such as pharmacological properties, structure, and aromaticity.[1–3] Likewise, the structurally related 1-metallacycloheptatrienes incorporating the elements silicon, germanium, selenium, or tellurium have also received certain treatment. In particular, the 1-silacyclohepta-2,4,6-triene (silepin) **2** and related structures featuring the 1-silacyclohepta-2,4,6-triene ring system have been subjected to detailed investigations, resulting in several synthetic approaches,[4–16] as well as deeper understanding of their properties,[9,10,13,15,17–20] but only relatively few studies have been devoted to the parent ring system **3**[21,22] and other 1-germacyclohepta-2,4,6-trienes,[11–15,23] or derivatives of 1-selenacyclohepta-2,4,6-triene (**4**).[14,15,24,25] Despite all progress in this area, there is still need for development of new synthetic approaches to these systems, as the existing routes often require time-consuming multistep preparation of rather complex starting materials, giving only low overall yields of the desired products. Therefore, it was envisaged that implementation of a variant of our recently reported approach to dibenzo[*b*,*f*]thiepins[26] would offer a new convenient access to fused derivatives of the 1-metallacyclohepta-2,4,6-trienes **2**−**4** from readily available and inexpensive starting materials.

Results and Discussion

Our synthetic efforts commenced with development of a feasible procedure for preparation of bis(phenylsulfonyl) selenide, a crucial reagent for construction the 1-selenacycloheptatrienes in our planned series of compounds. As the reported procedures involved reaction of selenium oxychloride or selenium tetrachloride with sodium benzenesulfinate in benzene,[27] we sought an alternative method involving a more readily available and inexpensive selenium source. Hence, it was established that generation of selenium dichloride by reaction of elemental selenium with sulfuryl chloride in THF as previously reported,[28] followed by addition of the resulting solution to a suspension of sodium benzenesulfinate in anhy-

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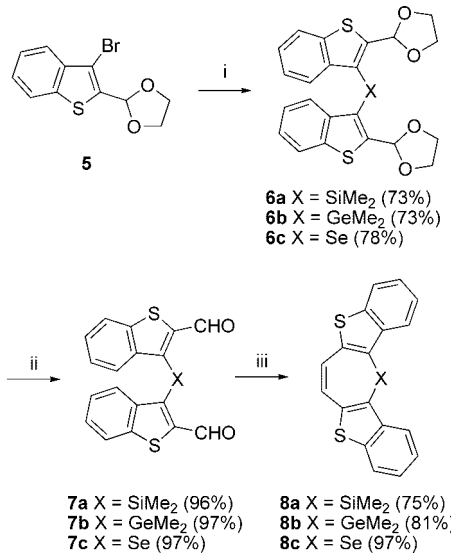
10.1021/om8003114 CCC: $40.75
Publication on Web 07/03/2008

1 X = S
2 X = $SiMe_2$
3 X = $GeMe_2$
4 X = Se

Figure 1

Scheme 1[a]



5

6a X = $SiMe_2$ (73%)
6b X = $GeMe_2$ (73%)
6c X = Se (78%)

7a X = $SiMe_2$ (96%)
7b X = $GeMe_2$ (97%)
7c X = Se (97%)

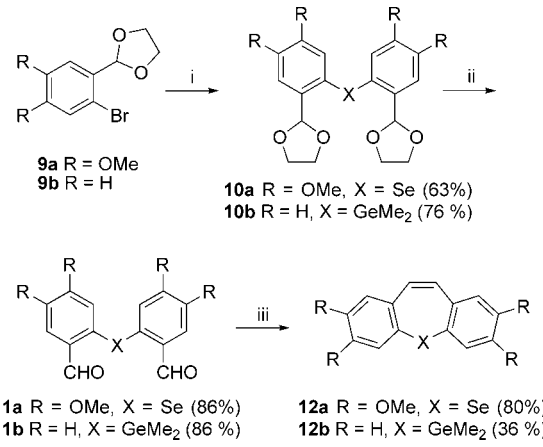
8a X = $SiMe_2$ (75%)
8b X = $GeMe_2$ (81%)
8c X = Se (97%)

[a] Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 0.5 h; then Me_2SiCl_2/Me_2GeCl_2/$(PhSO_2)_2Se$, −78 °C to rt, 16 h; (ii) aq $HClO_4$, 1,4-dioxane, rt, 3−16 h; (iii) $TiCl_4$, Zn, pyridine, THF, reflux, 2.5 h; then **7a**−**c**, rt, 16 h; reflux, 4 h; then aq K_2CO_3, rt, 18 h.

drous benzene, provided practical and convenient access to useful quantities of bis(phenylsulfonyl) selenide. The crude material obtained in this fashion could be conveniently purified by column chromatography or just a simple trituration with diethyl ether and, if necessary, by a subsequent recrystallization from acetonitrile.

With all required reagents in hand, we next embarked upon preparation of a set of extended 1-metallacyclohepta-2,4,6-trienes. The benzo[*b*]thiophene carboxaldehyde acetal **5**,[29] which was readily prepared by protection of 3-bromobenzo[*b*]thiophene-2-carboxaldehyde,[29,30] was selected as the starting material for this purpose. Hence, metalation[31–33] of **5** using *n*-BuLi as described prevously,[26] followed by treatment of the resulting organometallic intermediate with 0.5 equiv of either Me_2SiCl_2, Me_2GeCl_2, or $(PhSO_2)_2Se$, gave the expected products **6a**−**c**, which could thereafter be deprotected, giving the dialdehydes **7a**−**c** by treatment with aqueous perchloric acid (Scheme 1). The intermediates **7a**−**c** were eventually subjected to McMurry coupling,[34,35] producing the novel extended metallacycloheptatrienes **8a**−**c** in good overall yields. It was also noted that the products **8a**,**b** deteriorate slowly when stored at room temperature for prolonged periods of time and should therefore be kept in a freezer.

Scheme 2[a]



9a R = OMe
9b R = H

10a R = OMe, X = Se (63%)
10b R = H, X = $GeMe_2$ (76 %)

11a R = OMe, X = Se (86%)
11b R = H, X = $GeMe_2$ (86 %)

12a R = OMe, X = Se (80%)
12b R = H, X = $GeMe_2$ (36 %)

[a] Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, 0.5 h; then $(PhSO_2)_2Se$ (for **9a**) or Me_2GeCl_2 (for **9b**), −78 °C to rt, 16 h; (ii) aq $HClO_4$, 1,4-dioxane, rt, 3−16 h; (iii) $TiCl_4$, Zn, pyridine, THF, reflux, 2.5 h; then **11a**−**b**, rt, 16 h; reflux, 4 h; then aq K_2CO_3, rt, 18 h.

Application of this strategy for synthesis of benzo-fused metallacyclohepta-2,4,6-trienes proved to be more problematic, particularly in cases involving electron-rich substrates. The starting 2-bromobenzaldehyde acetal **9a**[36] was lithiated and treated with $(PhSO_2)_2Se$, giving the bis(aryl) selenide **10a** (Scheme 2). As anticipated, deacetalization of **10a** afforded the dialdehyde **11a**, which could eventually be annulated to the desired 1-selenacyclohepta-2,4,6-triene **12a**. However, a similar series of reactions starting from **9a** involving Me_2SiCl_2 or Me_2GeCl_2 as the electrophiles proceeded as expected only until the final McMurry coupling, which failed to produce the desired compounds, presumably due to decomposition of the products or the starting materials during the reaction. On the other hand, a similar sequence involving initial metalation and reaction of the less electron-rich acetal **9b**[37,38] with Me_2GeCl_2 afforded the intermediate **10b**, which could next be deprotected, giving **11b**, a substrate for a final annulation to the known product **12b**[23] under McMurry conditions. The modest yield (36%) of the final step in this series of reactions could also in this case be attributed to partial decomposition of the formed electron-rich 1-germacyclohepta-2,4,6-triene or its precursor. Although there are examples of some relatively stable fused 1-germacyclohepta-2,4,6-trienes,[15] it has for instance recently been demonstrated that the parent molecule **3** undergoes complete thermolysis at 80 °C in toluene-d_8 within 30 min, giving benzene and dimethylgermylene, which can be trapped by reaction with 2,3-dimethyl-1,3-butadiene.[22] It is also noteworthy that attempted preparation of the known compound 5,5-dimethyl-5*H*-5-sila-[2,3:6,7]dibenzocyclohepta-2,4,6-triene[5–7] from **9b** using our route resulted in isolation of only small amounts of impure product. This outcome, combined with fact that this molecule is rather stable and has previously been purified by distillation,[5] illustrates one of the limitations of our approach. However, the stability of condensed 1-sila- or 1-germacyclohepta-2,4,6-trienes appears to improve upon fusion to more electron-deficient aromatics or heteroaromatics, rendering such targets compatible with the McMurry conditions, as illustrated by the successful preparation of the extended systems **8a**,**b** described above.

In conclusion, efficient syntheses of several fused 1-metallacyclohepta-2,4,6-trienes have been achieved from simple

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masked aromatic or heteroaromatic aldehydes, giving access to hitherto unknown ring systems. The findings suggest that the strategy used in this work may be implemented for preparation of further related systems containing other elements, except in cases involving electron-rich substrates.

Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 instrument operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C, respectively, using the residual solvent resonances as reference. The IR spectra were performed on an Avatar 330 FT-IR spectrometer (Thermo Nicolet). Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The melting points were measured in open capillary tubes using a Büchi B-545 melting point apparatus. All chemicals originated from commercial sources and were used as received, except THF, which was distilled from sodium and benzophenone, and benzene, which was stored over sodium wire. Chromatography was performed using silica gel (particle size 40−63 μm).

Bis(phenylsulfonyl) selenide [$(PhSO_2)_2Se$]. $SeCl_2$ [generated by reaction of selenium powder (2.0 g, 25.3 mmol) and sulfuryl chloride (3.4 g, 25.3 mmol) in anhydrous THF (60 mL)][28] was added dropwise to a suspension of sodium benzenesulfinate (8.3 g, 50.6 mmol) in anhydrous benzene (100 mL) at room temperature under nitrogen atmosphere. The resulting mixture was stirred at room temperature for 19 h and was thereafter passed through a pad of Celite. The solvents were evaporated in vacuo, and the residue was subjected to column chromatography using *n*-heptane/EtOAc (4:1 → 2:1) to give bis(phenylsulfonyl) selenide[27] (4.9 g, 54%) as a yellow crystalline solid, which decomposes slowly if exposed to ambient temperature and light. If necessary, this material can be recrystallized from acetonitrile, giving a final yield of ∼30%. Alternatively, material of good quality could also be obtained by initial trituration of the crude product with Et_2O, followed by crystallization from acetonitrile. IR (neat): 1447, 1341, 1324, 1306, 1146, 1066, 746, 708, 676 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.03−7.99 (m, 4 H), 7.74−7.68 (m, 2 H), 7.62−7.56 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 146.9 (C), 135.0 (CH), 129.6 (CH), 127.8 (CH). HRMS (FAB): *m*/*z* 362.9267 $[M + H]^+$, $C_{12}H_{10}O_4S_2Se$ + H requires 362.9264.

General Procedure for Synthesis of Diacetals 6a−c and 10a,b. A solution of *n*-BuLi (1.6 M in hexanes, 3.0 mL, 4.8 mmol) was added dropwise to a solution of the acetal **5**,[29] **9a**,[36] or **9b**[37,38] (4.0 mmol) in anhydrous THF (30 mL) at −78 °C under nitrogen atmosphere. The mixture was stirred for 30 min at −78 °C, followed by addition of a solution of Me_2SiCl_2, Me_2GeCl_2, or $(PhSO_2)_2Se$ (2.0 mmol) in THF (10 mL) during 10 min at −78 °C. The resulting mixture was allowed to warm to room temperature over 16−18 h, thereafter treated with saturated aqueous NH_4Cl (30 mL), and extracted with Et_2O (2 × 30 mL). The combined organic extracts were washed with water (2 × 30 mL) and brine (30 mL) and dried over Na_2SO_4. Evaporation of the solvents in vacuo gave a residue, which was subjected to column chromatography as indicated for each specific example, giving the diacetals **6a−c** or **10a**,**b**.

Bis(2-[1,3]dioxolan-2-yl-benzo[*b*]thiophen-3-yl)dimethylsilane (6a). Column chromatography using *n*-heptane/EtOAc (5:1 → 3:1) gave **6a** (0.68 g, 73%) as white solid; mp 153−156 °C. IR (neat): 2888, 1514, 1506, 1365, 1345, 1251, 1191, 1179, 1157, 1138, 1093, 1076, 1055, 1024, 994, 957, 931, 829, 787, 756, 732 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.93 (br d, J = 8.0 Hz, 2 H), 7.66 (br d, J = 8.1 Hz, 2 H), 7.28−7.22 (m, 2 H), 7.16−7.10 (m, 2 H), 4.18−3.94 (m, 8 H), 0.83 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 151.0 (C), 143.8 (C), 139.1 (C), 132.2 (C), 124.4 (CH), 124.3 (CH), 124.1 (CH), 122.4 (CH), 99.0 (CH), 65.2 (CH_2), 1.1 (CH_3). Anal. Calcd for $C_{24}H_{24}O_4S_2Si$: C, 61.51; H, 5.16. Found: C, 61.65; H, 5.12.

Bis(2-[1,3]dioxolan-2-yl-benzo[*b*]thiophen-3-yl)-dimethylgermane (6b). Purification by column chromatography using *n*-heptane/EtOAc (6:1 → 3:1) gave **6b** (0.75 g, 73%) as a white solid; mp 149−151.5 °C. IR (neat): 2884, 1349, 1182, 1153, 1085, 1061, 1023, 955, 940, 914, 836, 813, 754, 730 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.95 (d, J = 7.9 Hz, 2 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.29−7.24 (m, 2 H), 7.18−7.13 (m, 2 H), 4.15−3.90 (m, 8 H), 0.97 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 148.5 (C), 143.4 (C), 139.1 (C), 133.1 (C), 124.5 (CH), 124.2 (CH), 124.2 (CH), 122.6 (CH), 99.1 (CH), 65.2 (CH_2), 1.5 (CH_3). Anal. Calcd for $C_{24}H_{24}GeO_4S_2$: C, 56.17; H, 4.71. Found: C, 56.22; H, 4.67.

Bis(2-[1,3]dioxolan-2-yl-benzo[*b*]thiophen-3-yl) selenide (6c). Purification by column chromatography using *n*-heptane/EtOAc (5:1 → 2:1) gave **6c** (0.76 g, 78%) as a yellow solid; mp 174−177.5 °C. IR (neat): 2885, 1363, 1194, 1076, 1055, 1017, 992, 941, 755, 727 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.98−7.95 (m, 2 H), 7.70−7.68 (m, 2 H), 7.37−7.26 (m, 4 H), 4.19−4.00 (m, 8 H). ^{13}C NMR (DMSO-d_6): δ 144.4 (C), 140.2 (C), 137.9 (C), 125.7 (CH), 125.0 (CH), 123.2 (CH), 123.2 (CH), 117.8 (C), 99.3 (CH), 65.4 (CH_2). Anal. Calcd for $C_{22}H_{18}O_4S_2Se$: C, 53.98; H, 3.71. Found: C, 54.02; H, 3.75.

Bis(2-[1,3]dioxolan-2-yl-4,5-dimethoxyphenyl) selenide (10a). Purification by column chromatography using *n*-heptane/EtOAc (4:1 → 1:1) gave **10a** (0.63 g, 63%) as a white solid; mp 116−118 °C. IR (neat): 2960, 2865, 1596, 1505, 1398, 1378, 1263, 1251, 1198, 1163, 1079, 1027, 983, 961, 938, 865, 840, 766 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.08 (s, 2 H), 6.87 (s, 2 H), 6.00 (s, 2 H), 4.13−4.04 (m, 4 H), 4.00−3.93 (m, 4 H), 3.76 (s, 6 H), 3.60 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 149.5 (C), 148.6 (C), 131.1 (C), 121.4 (C), 117.2 (CH), 110.1 (CH), 102.4 (CH), 64.9 (CH_2), 55.5 (CH_3), 55.5 (CH_3). Anal. Calcd for $C_{22}H_{26}O_8Se$: C, 53.12; H, 5.27. Found: C, 53.07; H, 5.24.

Bis(2-[1,3]dioxolan-2-yl-phenyl)dimethylgermane (10b). Purification by column chromatography using *n*-heptane/EtOAc (6:1 → 4:1) gave **10b** (0.61 g, 76%) as a white solid; mp 81−84.5 °C. IR (neat): 2895, 1398, 1215, 1121, 1079, 1049, 1018, 985, 968, 940, 803, 763, 731 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.55−7.52 (m, 2 H), 7.44−7.33 (m, 6 H), 5.56 (s, 2 H), 3.98−3.86 (m, 4 H), 3.80−3.68 (m, 4 H), 0.70 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 142.4 (C), 139.3 (C), 133.7 (CH), 128.7 (CH), 128.5 (CH), 126.1 (CH), 102.2 (CH), 64.5 (CH_2), 0.7 (CH_3). Anal. Calcd for $C_{20}H_{24}GeO_4$: C, 59.90; H, 6.03. Found: C 59.93; H, 5.96.

General Procedure for Synthesis of Dialdehydes 7a−c and 11a,b. A solution of aqueous $HClO_4$ (70%, 0.24 mL) in water (1 mL) was added to a solution of the diacetals **6a−c** or **10a**,**b** (0.85 mmol) in acetone (15−20 mL) at room temperature. The reaction mixture was stirred at room temperature for 16 h (3 h for **11b**), and was thereafter treated with saturated aqueous $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc/CH_2Cl_2 (30 mL), washed with water (2 × 30 mL) and brine (30 mL), and dried over Na_2SO_4. Evaporation of the solvents in vacuo gave a residue, which was either triturated with Et_2O or subjected to column chromatography as indicated below, to afford the desired products **7a−c** or **11a**,**b**.

Bis(2-formylbenzo[*b*]thiophen-3-yl)dimethylsilane (7a). The crude product was triturated with Et_2O to give compound **7a** (0.31 g, 96%) as a white solid; mp 158−161.5 °C. IR (neat): 1652, 1476, 1426, 1244, 1184, 1152, 930, 836, 786, 777, 758, 748, 725 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 10.09 (s, 2 H), 8.15−8.12 (m, 2 H), 7.87−7.84 (m, 2 H), 7.53−7.47 (m, 2 H), 7.37−7.31 (m, 2 H), 1.09 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 186.3 (CH), 150.3 (C), 144.8 (C), 143.4 (C), 141.7 (C), 127.8 (CH), 126.9 (CH), 125.4 (CH), 123.6 (CH), 2.4 (CH_3). Anal. Calcd for $C_{20}H_{16}O_2S_2Si$: C, 63.12; H, 4.24. Found: C, 63.11; H, 4.21.

Bis(2-formylbenzo[*b*]thiophen-3-yl)dimethylgermane (7b). The crude product was triturated with Et_2O to give compound **7b** (0.35 g, 97%) as a white solid; mp 155−157 °C. IR (neat): 1656, 1487,

1475, 1246, 1182, 1159, 1110, 914, 824, 756, 732, 712 cm^{-1}; ^1H NMR (DMSO-d_6): δ 10.01 (s, 2 H), 8.16−8.13 (m, 2 H), 7.86−7.83 (m, 2 H), 7.55−7.49 (m, 2 H), 7.39−7.33 (m, 2 H), 1.21 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 186.1 (CH), 148.3 (C), 147.0 (C), 142.9 (C), 141.6 (C), 128.0 (CH), 126.8 (CH), 125.5 (CH), 123.7 (CH), 3.1 (CH_3). Anal. Calcd for $C_{20}H_{16}GeO_2S_2$: C, 56.51; H, 3.79. Found: C, 56.44; H, 3.84.

Bis(2-formylbenzo[*b*]thiophen-3-yl) selenide (7c). The crude product was triturated with Et_2O to give compound **7c** (0.33 g, 97%) as a light yellow solid; mp 211−214 °C. IR (neat): 1661, 1587, 1492, 1425, 1288, 1244, 1191, 1165, 1129, 907, 752, 726, 712 cm^{-1}. ^1H NMR (DMSO-d_6): δ 10.56 (s, 2 H), 8.12 (ddd, J = 8.2, 1.1, 0.7 Hz, 2 H), 7.79 (ddd, J = 8.2, 1.2, 0.7 Hz, 2 H), 7.5 (ddd, J = 8.2, 7.1, 1.2 Hz, 2 H), 7.40 (ddd, J = 8.2, 7.1, 1.1 Hz, 2 H). ^{13}C NMR (DMSO-d_6): δ 186.0 (CH), 142.2 (C), 140.2 (C), 140.1 (C), 130.3 (C), 128.9 (CH), 126.2 (CH), 124.9 (CH), 124.1 (CH). Anal. Calcd for $C_{18}H_{10}O_2S_2Se$: C, 53.86; H, 2.51. Found: C, 53.76; H, 2.42.

Bis(2-formyl-4,5-dimethoxyphenyl) selenide (11a). The crude product was triturated with Et_2O to give compound **11a** (0.30 g, 86%) as an off-white solid; mp 160−163.5 °C. IR (neat): 1668, 1579, 1549, 1501, 1458, 1436, 1362, 1336, 1260, 1227, 1215, 1189, 1155, 1040, 1021, 870, 807, 788, 738 cm^{-1}. ^1H NMR (DMSO-d_6): δ 10.07 (s, 2 H), 7.59 (s, 2 H), 6.79 (s, 2 H), 3.85 (s, 6 H), 3.65 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 191.9 (CH), 153.9 (C), 148.6 (C), 128.5 (C), 128.1 (C), 116.0 (CH), 113.9 (CH), 55.8 (CH_3), 55.8 (CH_3). Anal. Calcd for $C_{18}H_{18}O_6Se$: C, 52.82; H, 4.43. Found: C, 52.78; H, 4.47.

Bis(2-formylphenyl)dimethylgermane (11b). Purification by column chromatography using *n*-heptane/EtOAc (7:1 → 4:1) gave **11b** (0.23 g, 86%) as a white solid; mp 95−99 °C. IR (neat): 1693, 1676, 1559, 1292, 1194, 1117, 1065, 839, 816, 750 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.94 (s, 2 H), 7.99−7.97 (m, 2 H), 7.67−7.58 (m, 6 H), 0.68 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 193.6 (CH), 142.6 (C), 139.7 (C), 135.2 (CH), 133.4 (CH), 133.2 (CH), 129.2 (CH), −0.1 (CH_3). The molecular ion peak was not detected in the FAB mass spectrum of **11b**, which displayed a fragment ion (base peak) with m/z 299.0127, resulting from loss of a CH_3 group.

General Procedure for Synthesis of Metallacycloheptatrienes 8a−c and 12a,b. $TiCl_4$ (2.7 mL, 25 mmol) was added dropwise during 10 min to anhydrous THF (100 mL) at −78 °C under argon atmosphere, and the resulting solution was stirred for 5 min. The yellow slurry was allowed to warm to room temperature, followed by addition of zinc powder (3.3 g, 50 mmol) and pyridine (0.5 mL). This suspension was heated at reflux for 2.5 h and was then allowed to cool to room temperature. The appropriate dialdehyde (**7a−c** or **11a**,**b**) (0.50 mmol) was added slowly as a dilute solution in anhydrous THF (100 mL) over 4 h at room temperature. After complete addition, the reaction mixture was allowed to stir at room temperature for 16 h and was thereafter heated at reflux for an additional period of 4 h. After cooling to room temperature, a 50% aqueous solution of K_2CO_3 (50 mL) was added. The resulting mixture was stirred vigorously for 18 h and thereafter passed through a pad of Celite, which was washed with EtOAc (40 mL). The layers were separated and the aqueous phase was extracted with EtOAc (50 mL). The combined organic layers were washed with water (2 × 50 mL) and brine (50 mL) and dried (Na_2SO_4). Evaporation of the solvents in vacuo, followed by purification of the crude product as indicated for each specific example, yielded the metallacycloheptatrienes **8a−c** and **12a**,**b**.

Compound 8a. Purification by column chromatography using *n*-heptane gave **8a** (0.13 g, 75%) as a yellow solid; mp 149−151 °C. IR (neat): 2921, 1505, 1425, 1311, 1298, 1270, 1248, 1126, 1091, 1048, 943, 843, 803, 768, 749, 725 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.11−8.04 (m, 4 H), 7.52−7.41 (m, 4 H), 6.89 (s, 2 H), 0.85 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 146.3 (C), 144.9 (C), 141.0 (C), 130.5 (C), 125.1 (CH), 124.9 (CH), 124.8 (CH), 123.3 (CH), 122.3 (CH), 0.6 (CH_3). HRMS (FAB): m/z 348.0456 [M^+], $C_{20}H_{16}S_2Si$ requires 348.0463.

Compound 8b. Purification by column chromatography using *n*-heptane gave **8b** (0.16 g, 81%) as a yellow solid; mp 168−170 °C. IR (neat): 2921, 1426, 1308, 1048, 1043, 939, 798, 773, 750, 723 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.08−7.97 (m, 4 H), 7.52−7.41 (m, 4 H), 6.79 (s, 2 H), 0.93 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 144.5 (C), 144.4 (C), 140.8 (C), 131.1 (C), 125.1 (CH), 124.9 (CH), 124.5 (CH), 122.9 (CH), 122.4 (CH), 0.7 (CH_3). HRMS (FAB): m/z 393.9912 [M^+], $C_{20}H_{16}GeS_2$ requires 393.9905.

Compound 8c. Purification by column chromatography using *n*-heptane/EtOAc (9:1 → 7:1) gave **8c** (0.18 g, 97%) as a yellow solid; mp 187.5−188.5 °C. IR (neat): 1431, 1251, 1085, 891, 857, 810, 759, 744, 724 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.01−7.95 (m, 4 H), 7.53−7.40 (m, 4 H), 7.26 (s, 2 H). ^{13}C NMR (DMSO-d_6): δ 141.2 (C), 140.4 (C), 139.1 (C), 127.8 (CH), 125.7 (CH), 125.3 (CH), 123.1 (CH), 122.9 (CH), 117.5 (C). Anal. Calcd for $C_{18}H_{10}S_2Se$: C, 58.53; H, 2.73. Found: C, 58.46; H, 2.85.

2,3,7,8-Tetramethoxy-5*H*-5-selena[2,3:6,7]dibenzocyclohepta-2,4,6-triene (12a). Purification by column chromatography using *n*-heptane/EtOAc (4:1 → 2:1) gave **12a** (0.15 g, 80%) as a white solid; mp 199−201.5 °C. IR (neat): 1587, 1496, 1464, 1346, 1331, 1237, 1197, 1147, 1037, 871, 859, 792 cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.05 (s, 2 H), 6.92 (s, 2 H), 6.87 (s, 2 H), 3.76 (s, 6 H), 3.73 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 149.5 (C), 148.7 (C), 133.2 (C), 132.8 (CH), 119.8 (C), 116.2 (CH), 112.5 (CH), 55.6 (CH_3), 55.6 (CH_3). Anal. Calcd for $C_{18}H_{18}O_4Se$: C, 57.30; H, 4.81. Found: C, 57.19; H, 4.87.

5,5-Dimethyl-5*H*-5-germa[2,3:6,7]dibenzocyclohepta-2,4,6-triene (12b). Purification by column chromatography using *n*-heptane gave **12b** (0.05 g, 36%) as a colorless viscous oil. IR (neat): 2921, 2852, 829, 798, 769, 733 cm^1. ^1H NMR (DMSO-d_6): δ 7.49−7.46 (m, 2 H), 7.42−7.31 (m, 6 H), 6.94 (s, 2 H), 0.56 (s, 6 H). ^{13}C NMR (DMSO-d_6): δ 140.7 (C), 138.9 (C), 133.0 (CH), 131.9 (CH), 129.3 (CH), 128.6 (CH), 127.6 (CH), −5.4 (CH_3). HRMS (FAB) m/z 283.0535 [M + H]$^+$, $C_{16}H_{16}Ge$ + H requires 283.0542.

Acknowledgment. The Magnus Bergvall Foundation is gratefully acknowledged for financial support.

Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **8a**, **8b**, **11b**, and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8003114