New Monomers for Organometallic Poly-*p*-xylylenes: Synthesis of Silyl-, Germyl- and Stannyl[2.2]paracyclophane Derivatives☆

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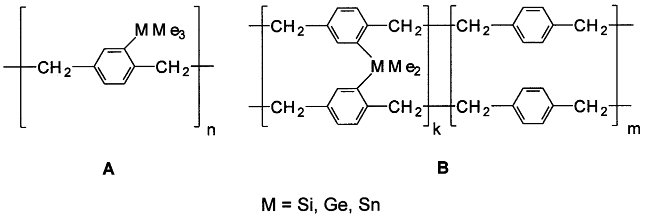
Symmetrically 4,16-disubstituted (**3a–c**) and bridged (**6a**, **b**) organometallic paracyclophane derivatives have been synthesized for use as monomeric precursors of organometallic poly-*p*-xylylenes. Both types of compounds were obtained by lithiation of the appropriately substituted paracyclophane bromides (**1** or **4**) and subsequent quenching of the resulting lithioparacyclophane derivatives with organometallic electrophiles. For the synthesis of 4,16-bis(trimethylsilyl)[2.2]paracyclophane (**3a**) we also examined the Grignard reaction, and as a result the first successful use of a 4,16-bis Grignard reagent is described. According to the spectral data, the bridged compounds **6a, c** are formed as diastereomeric mixtures of a *meso*- and a *d,l* form. The diastereomers were separated by fractional recrystallization and characterized.

Although numerous functional groups have been introduced into the [2.2]paracyclophane nucleus[1], relatively little is known about these bridged aromatic compounds when they bear metal-containing substituents. To date, only mono(trimethylstannyl)-[2], 4,16-bis(triphenylphosphane-gold)-[3], and several trimethylsilyl-substituted paracyclophane derivatives[4] have been synthesized, among them the *meso* and *d,l* diastereomers of dimethylbis([2.2]paracyclophan-4-yl)silane[5].

In principle, these derivatives could find wide application. They are not only of interest because of their stereochemical properties − any monosubstituted [2.2]paracyclophane is chiral, regardless of the position of the substituent in the system − but they could serve as ligands for new metal complexes and be used as monomeric precursors of novel, metal-containing polymers. The parent hydrocarbon is an important monomer in polymer chemistry − the poly-*p*-xylylene (PPX) polymer derived from it is called parylene®. Recently, we succeeded in preparing PPX films containing nanosize metal particles[6][7], which could be used as sensor devices for the detection of gaseous compounds in air[8]. In our methodology, developed for the preparation of polymer−metal nanocomposites, an organometallic PPX film (A or B in Scheme 1) is first produced by pyrolytic polymerization of the corresponding disubstituted or bridged paracyclophane monomers.

Scheme 1. PPX films containing silyl, germyl and stannyl functions



Further annealing of the polymers A and B leads to cleavage of the M−C bonds and the formation of metal nanocrystals in a polymer matrix. In contrast to the previously reported methods[9], we were able to obtain polymer coatings of uniform thickness that contained evenly distributed metal particles. Preliminary investigations on Ge-containing nanocomposites have shown these systems to be very promising sensor materials for air humidity[8].

In this paper we report on the synthesis of new disubstituted (**3a−c**, M = Si, Ge, Sn) and bridged (**6a**, **b**, M = Ge,

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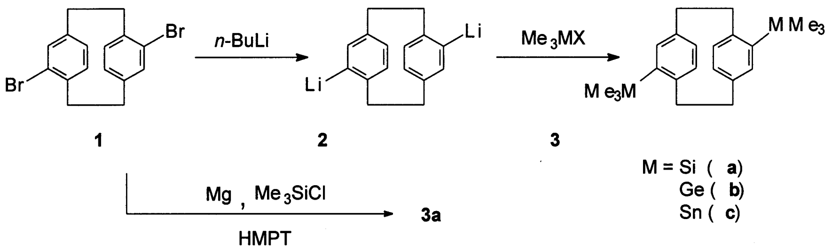
Sn; for Si compound see ref.[5]) paracyclophane monomers, which we plan to employ as monomers for the aforementioned polymer synthesis.

Results and Discussion

Dibromide **1** was obtained according to ref.[10] and lithiated with excess *n*-butyllithium in diethyl ether[11]. The resulting intermediate dilithio derivative **2** was then treated with trimethylsilyl chloride, trimethylgermanium bromide or trimethyltin chloride to yield the derivatives **3a−c** (Scheme 2).

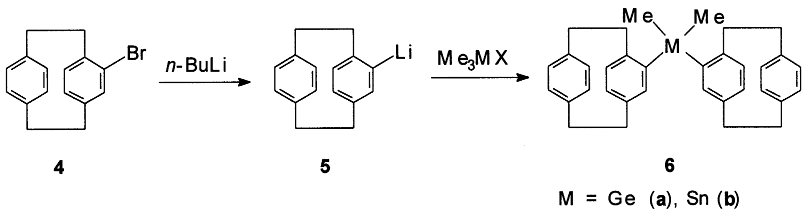
Scheme 2. The preparation of dimetallated [2.2]paracyclophanes



It is known that aromatic silylation can also be performed via organomagnesium reagents[12]. In the paracyclophane series, the mono Grignard reagent has been prepared and used for the synthesis of [2.2]paracyclophane-4-carboxylic acid[13]. Also, the coupling reaction of 4-bromo-[2.2]paracyclophane has been carried out via an organomagnesium intermediate[14]. To study the applicability of the organomagnesium route for the preparation of **3a**, we used the Barbier procedure[15], which has been applied previously for the synthesis of polysilylated benzenes[16]. In this approach, the aryl halide, magnesium and trimethylsilyl chloride are refluxed together in hexamethyl phosphoric triamide (HMPT) in a one-pot reaction. Compared with the lithation of **1**, this required more severe conditions (HMPT, heating, longer reaction time) and produced **3a** in substantially lower yield. Nevertheless, this metallation/quenching is the first example of the successful application of a disubstituted organomagnesium paracyclophane derivative in synthesis.

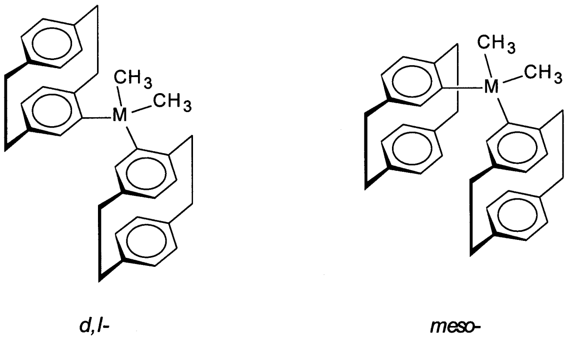
The bridged paracyclophane derivatives **6a**, **b** were synthesized from the monobromide **4**[17] via the monolithiated cyclophane **5**[18] (Scheme 3).

Scheme 3. The preparation of metal-bridged [2.2]paracyclophanes



One of the most striking properties of [2.2]paracyclophanes is their planar chirality, which appears as soon as one hydrogen atom of the parent molecule is replaced by another substituent, with the substituents being introduced into the aromatic nuclei in most cases. Since compounds **6a**, **b** are constructed from two chiral elements, they could in principle be obtained as a mixture of diastereomers, a chiral *d,l* enantiomeric pair and an achiral *meso* form (Scheme 4).

Scheme 4. The *d,l* and *meso* form of a metal-bridged [2.2]paracyclophane

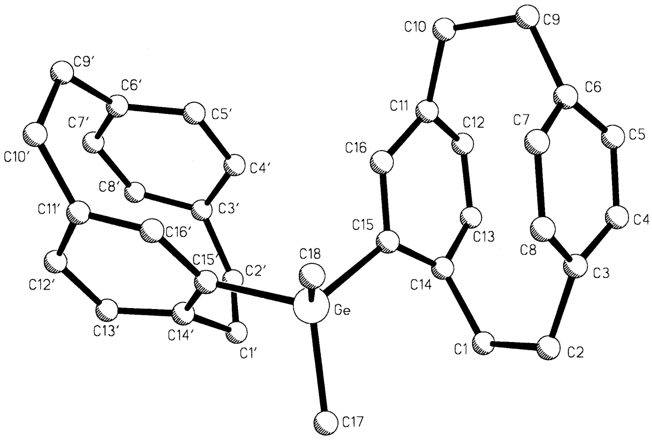


In both cases, the reaction mixtures were analyzed by HPLC (RP-18, methanol or methanol/water) and ^{1}H-NMR spectroscopy. The title compounds were indeed shown to have been formed as a diastereomeric mixture. According to their ^{1}H-NMR data, the diastereomers **6a**, **b** are formed in a *d,l/meso* ratio of about 2:1. The diastereomers could be separated by fractional recrystallization, with the *meso* form usually precipitating from the mixture. The separation of **6b** from the reaction mixture is difficult, since this compound is not stable on silica gel. Fractional recrystallization of the reaction mixture in this case only leads to the *meso* diastereomer in pure form. Full spectral characterization of the diastereomers obtained was performed (see Experimental Section).

The chiral enantiomeric and the *meso* stereoisomers of both compounds **6a**, **b** could also be distinguished directly. Thus, the protons of CH_3 groups in the chiral isomer are related by a C_2 axis, so that they are homotopic and give rise to a single singlet. The corresponding protons in the *meso* form are surrounded by different chiral paracyclophane moieties and are therefore diastereotopic. The signals of these groups are detected as two singlets with a shift difference of 0.2 ppm. It is noteworthy that although the *meso* forms of **6a**, **b** can be unambiguously characterized by ^{1}H-NMR spectroscopy, in the ^{13}C-NMR spectra of these compounds the signals of the methyl C atoms are not resolved.

Furthermore, crystals suitable for an X-ray structural determination could be obtained in the case of *d,l*-**6a**′′. According to X-ray data, the [2.2]paracyclophanyl units of this derivative are very similar to one another and display the typical [2.2]paracyclophane geometry (Figure 1).

Figure 1. The structure of *d,l*-**6a**′′ in the crystal; radii are arbitrary



The aromatic rings are puckered into a boat form, with the bridgehead carbon atoms displaced out of the plane formed by the remaining four carbon atoms of the rings by 0.153−0.163 Å for the unsubstituted, and by 0.168−0.175 Å for the substituted rings. The C(sp^3)−C(sp^3) bond lengths of the ethano bridges range from 1.554 to 1.568 Å, i.e. they are slightly shorter than that in the parent [2.2]-paracyclophane molecule[5]. The lengths of the germanium−carbon bonds (such as Ge−C15) to the paracyclophanyl groups range from 1.955 to 1.962 Å, consistent with what is normally observed for Ge−Ar bonds[19].

The use of these new [2.2]paracyclophanes as monomers for novel metal-containing polymers is under active investigation, and we hope to report on these studies shortly.

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Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AM-400 (400.13 and 100.6 MHz, for ^{1}H and ^{13}C, respectively), $CDCl_3$ as solvent, TMS as internal standard. − MS: Varian CH5, EI (70 eV). − IR: Nicolet 320 FT-IR spectrometer. − UV/Vis: Hewlett-Packard 8452A. − Column chromatography: Kieselgel 60, 70−230 mesh (Merck, Darmstadt). − Diastereomer compositions were determined by analytical HPLC (Milton-Roy HPLC system, methanol/water, 19:1, reversed-phase (S_5 octadecylsilane, SiC_{18} Spherisorb). − Et_2O was distilled from benzophenone ketyl under argon immediately prior to use. Dichloromethane was distilled from P_2O_5. Hexamethylphosphortriamide (HMPT) was distilled from CaH_2 in vacuo and stored under nitrogen. $(CH_3)_3SiCl$, $(CH_3)_3GeBr$, $(CH_3)_2GeCl_2$ were distilled from CaH_2. Other reagents were purchased from Aldrich and were used without purification.

4,16-Bis(trimethylsilyl)[2.2]paracyclophane (**3a**) *via Organolithium Compound* **2**: To a stirred suspension of 1.0 g (2.73 mmol) of **1** in 60 ml of dry diethyl ether under nitrogen, was added 9.76 ml of a 1.64 M *n*BuLi solution in hexane (16 mmol). The reaction mixture was stirred for 3 h, and then 2.03 ml (16 mmol) of $(CH_3)_3SiCl$ was added by means of a syringe over a period of 15 min. The reaction mixture was stirred overnight, heated for an additional 1 h, and then quenched with saturated NH_4Cl solution. The organic layer was washed several times with water, and dried with Na_2SO_4. The solvent was evaporated under reduced pressure. Column chromatography of the residue (pentane/dichloromethane, 8:1) gave 0.64 g (67%) of **3a**, m.p. 156°C. − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (m), 2880 (w), 1240 (s), 1105 (m), 905 (m), 860 (s), 842 (s), 832 (s), 755 (m), 720 (m). − UV/Vis (CH_3CN): λ_{max} (lg ε) = 230 nm (3.95), 255 (3.27), 266 (3.06). − ^{1}H NMR ($CDCl_3$): δ = 0.4 (s, 18 H, CH_3), 2.96−3.35 (m, 8 H, CH_2CH_2), 6.29 (d, *J* = 7.8 Hz, 2 H, 8-, 12-H), 6.37 (dd, *J* = 7.8, *J* = 1.9 Hz, 2 H, 7-, 13-H), 6.82 (d, *J* = 1.9 Hz, 2 H, 5-, 15-H). − ^{13}C NMR ($CDCl_3$): δ = 1.00 (s, CH_3), 35.67, 35.82 (s, C-1, -2, -9, -10), 133.47, 134.37, 137.15, 137.9, 138.76, 146.2 (s, all C-Ar). − MS (70 eV); *m/z* (%): 352 (10) [M$^+$], 337 (13), 176 (100), 160 (85), 145 (15). − $C_{22}H_{32}Si_2$ (352.67): calcd. C 74.93, H 9.15; found C 74.80, H 8.74.

4,16-Bis(trimethylsilyl)[2.2]paracyclophane (**3a**) *via an Organomagnesium Derivative:* Under nitrogen, 0.36 g (14.9 mmol) of magnesium and 2.0 g (5.46 mmol) of **1** in dry HMPT (8 ml) were placed in a two-necked round-bottomed flask equipped with a dropping funnel and a condenser, and the mixture was stirred for 10 min. Then, 2.52 ml (19.86 mmol) of $(CH_3)_3SiCl$ was added, the mixture was heated to 50°C, and reaction was initiated by adding a few drops of 1,2-dibromomethane (frothing and temperature increase). The reaction mixture was refluxed at 60°C for 40 h and, after cooling to room temp., was hydrolyzed by pouring it into a 0.5% sodium hydrogen carbonate solution, while the neutrality of the solution was tested at regular intervals. The resulting mixture was extracted with hexane, and the organic phase was washed several times with water and dried with Na_2SO_4. The solvent was evaporated under reduced pressure, and column chromatography of the residue on silica gel (pentane/dichloromethane, 8:1) gave 0.8 g (42%) of **3a**.

4,16-Bis(trimethylgermanyl)[2.2]paracyclophane (**3b**): 4,16-Dilithio[2.2]paracyclophane (**2**) was obtained as described above from 1.0 g (2.73 mmol) of **1** and 9.76 ml (16 mmol) of *n*BuLi (1.64 M solution in hexane). Subsequent reaction of **2** with 2.05 ml (16 mmol) of $(CH_3)_3GeBr$ and work-up of the reaction mixture were performed as in the case of **3a**. Column chromatography on silica gel of the resulting solid (heptane/benzene, 6:1) afforded 0.39 g (32%) of **3b**, m.p. 158−159°C. − IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (m), 2900 (w), 1225 (m), 1105 (w), 905 (m), 855 (s), 840 (s), 822 (s), 750 (w), 720 (m). − UV/Vis (CH_3CN): λ_{max} (lg ε) = 230 nm (4.03), 255 (3.30), 266 (3.10). − ^1H NMR ($CDCl_3$): δ = 0.48 (s, 18 H, CH_3), 2.94−3.33 (m, 8 H, CH_2CH_2), 6.30 (br. s, 4 H, 7-, 8-, 12-, 13-H), 6.72 (br. s, 2 H, 5-, 15-H). − ^{13}C NMR ($CDCl_3$): δ = 1.14 (s, CH_3), 34.22, 34.38 (s, C-1, -2, -9, -10), 131.92, 132.38, 134.85, 136.70, 140.32, 143.70 (s, all C-Ar). − MS (70 eV); *m/z* (%): 444 (29) [M^+], 429 (25), 310 (24), 222 (100), 207 (78), 177 (30), 118 (46). − $C_{22}H_{32}Ge_2$ (441.72): calcd. C 59.83, H 7.30, Ge 32.87; found C 59.73, H 7.24.

4,16-Bis(trimethylstannyl)[2.2]paracyclophane (**3c**): 10 ml of a 3.0 N *n*BuLi solution in hexane (30 mmol) was added to a stirred suspension of 0.50 g (1.37 mmol) of **1** in 50 ml of dry diethyl ether under argon. The reaction mixture was stirred for 5 h, and then a solution of 5.98 g (30 mmol) of $(CH_3)_3SnCl$ in dry diethyl ether was added dropwise over a period of 30 min. The reaction mixture was left overnight, and was then quenched with saturated NH_4Cl solution. The organic layer was washed several times with water and dried with Na_2SO_4. The solvent was evaporated under reduced pressure to give 0.45 g (62%) of **3c**, m.p. 162−164°C. − IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1} (m), 2886 (w), 1170 (s), 1100 (s), 1050 (s), 920 (w), 868 (s), 860 (s), 845 (s), 762 (s), 722 (w). − UV/Vis (CH_3CN): λ_{max} (lg ε) = 230 nm (4.20), 2.55 (3.39), 266 (3.18). − ^1H NMR ($CDCl_3$): δ = 0.35 [dt, 18 H, $J(^{117}Sn\text{-}H)$ = 51.6 Hz, $J(^{119}Sn\text{-}H)$ = 53.6 Hz, CH_3], 2.94−3.16 (m, 4 H, CH_2CH_2), 3.24−3.34 (m, 4 H, CH_2CH_2), 6.26 (dd, J_1 = 7.8, J_2 = 1.9 Hz, 2 H, 7-, 13-H), 6.37 (d, *J* = 7.8 Hz, 2 H, 8-, 12-H), 6.71 (d, *J* = 1.9 Hz, 2 H, 5-, 15-H). − ^{13}C NMR ($CDCl_3$): δ = −9.36 (s, CH_3), 34.36, 36.48 (s, C-1, -2, -9, -10), 131.13, 132.67, 136.61, 137.31, 142.85, 145.34 (s, all C-Ar). − MS (70 eV); *m/z* (%): 534 (2.5) [M^+], 519 (10) [$M^+ - CH_3$], 253 (100), 223 (34), 185 (64), 165 (62), 104 (84). − $C_{22}H_{32}Sn_2$ (533.88): calcd. C 49.50, H 6.04, Sn 44.46; found C 49.87, H 5.91, Sn 44.20.

Dimethylbis([2.2]paracyclophane-4-yl)germane (**6a**): To a stirred solution of 1.0 g (3.49 mmol) of **4** in dry diethyl ether (80 ml) under dry nitrogen, was added 2.5 ml of a 1.64 M *n*BuLi solution in hexane (4.1 mmol). After 3 h, 0.2 ml (1.75 mmol) of $Ge(CH_3)_2Cl_2$ was slowly added by means of a syringe, the reaction mixture was stirred for 2 h, and left to stand overnight. Saturated aqueous NH_4Cl solution was then added, the organic layer was washed twice with water, and dried with Na_2SO_4. The solvent was removed in vacuo, and the residue was separated by column chromatography on silica gel using CCl_4 as eluent, to afford a diastereomeric mixture of **6a** (1.28 g, 71%). − MS (70 eV); *m/z* (%): 518 (68) [M^+], 503 (95), 414 (36), 399 (56), 309 (42), 205 (100), 191 (78), 104 (36). − $C_{34}H_{36}Ge$ (517.25): calcd. C 78.95, H 7.02, Ge 14.03; found C 78.98, H 7.08. − The diastereomeric mixture was recrystallized from 2-propanol/dichloromethane (5:1, v/v). The precipitated solid was removed by filtration: 0.71 g (40%) of dimethyl-*meso*-bis([2.2]paracyclophane-4-yl)germane (**6a′**): M.p. 244°C. − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1} (s), 2891 (m), 2850 (m), 1410 (w), 1237 (w), 902 (m), 833 (m), 798 (s), 720 (s), 576 (m). − UV/Vis (CH_3CN): λ_{max} (lg ε) = 228 nm (4.54), 256 (3.86), 266 (3.64). − ^1H NMR ($CDCl_3$): δ = 0.72 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 2.67−3.27 (m, 16 H, CH_2CH_2), 6.20 (dd, J_1 = 7.8, J_2 = 1.3 Hz, 2 H), 6.30 (dd, J_1 = 7.8, J_2 = 1.3 Hz, 2 H), 6.38 (d, *J* = 7.8 Hz, 2 H, 8-, 8′-H), 6.44 (dd, J_1 = 7.8, J_2 = 1.6 Hz, 2 H, 7-, 7′-H), 6.55 (m, 4 H), 6.73 (d, *J* = 1.6 Hz, 2 H, 5-, 5′-H). − ^{13}C NMR ($CDCl_3$): δ = 35.65 (s, 6 C), 36.35 (s, 2 C) (C-1, -1′, -2, -2′, -9, -9′, -10, -10′), 132.51, 132.56, 132.94, 133.40, 134.16, 134.29, 137.00, 138.77, 139.41, 139.78, 140.40, 145.65 (s, all C-Ar). − The filtrate, after concentration and recrystallization of the residue from hexane, yielded 0.18 g (10%) of dimethyl-*d,l*-bis([2.2]paracyclophane-4-yl)germane (**6a′′**): M.p. 163°C. − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1} (s), 2891 (m), 2850 (m), 1410 (m), 1237 (m), 902 (m), 833 (m), 805 (s), 718 (s), 580 (w). − UV/Vis (CH_3CN): λ_{max} (lg ε) = 228 nm (4.28), 256 (3.76), 266 (3.60). − ^1H NMR ($CDCl_3$): δ = 0.89 (s, 3 H, CH_3), 2.80−3.27 (m, 16 H, CH_2CH_2), 6.07 (dd, J_1 = 7.9, J_2 = 1.7 Hz, 2 H), 6.33 (dd, J_1 = 7.9, J_2 = 1.7 Hz, 2 H), 6.37−6.49 (m, 4 H), 6.51−6.62 (m, 4 H), 6.76 (d, *J* = 1.9 Hz, 2 H). − ^{13}C NMR ($CDCl_3$): δ = −0.67 (s, CH_3), 34.15, 34.21, 34.36, 34.68 (C-1, -1′,-2, -2′, -9, -9′, -10, -10′), 131.10 (2 C), 131.41, 131.78, 131.71 (2 C), 135.49, 136.96, 137.98, 138.24, 139.34, 143.85 (s, all C-Ar).

Dimethylbis([2.2]paracyclophane-4-yl)stannane (**6b**): Monolithio[2.2]paracyclophane **5** was obtained as described above from 1.0 g (3.49 mmol) of **4** and 2.5 ml (4.1 mmol) of *n*BuLi (1.64 M solution in hexane). Subsequent reaction of **4** with 0.387 g (1.75 mmol) of $(CH_3)_2SnCl_2$ and work-up of the reaction mixture were performed as in the case of **6a**. Since this compound is not stable on silica gel, the mixture of diastereomers could not be separated by column chromatography. Recrystallization (three times) from 2-propanol/dichloromethane (4:1, v/v) yielded 0.85 g (43%) of dimethyl-*meso*-bis([2.2]paracyclophane-4-yl)stannane (**6b′**): M.p. 208°C. − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2890 (m), 2851 (s), 1410 (w), 1181 (w), 1092 (m), 898 (w), 742 (m), 720 (s), 520 (m), 510 (m). − UV/Vis (CH_3CN): λ_{max} (lg ε) = 228 nm (4.51), 256 (3.85), 266 (3.62). − ^1H NMR ($CDCl_3$): δ = 0.61 [dt, 3 H, $J(^{117}Sn\text{-}H)$ = 51.6 Hz, $J(^{119}Sn\text{-}H)$ = 53.6 Hz, CH_3], 0.77 [dt, 3 H, $J(^{117}Sn\text{-}H)$ = 51.6 Hz, $J(^{119}Sn\text{-}H)$ = 53.6 Hz, CH_3], 2.71−3.29 (m, 16 H, CH_2CH_2), 6.21 (br d, 2 H), 6.36 (br d, 2 H), 6.40−6.59 (m, 8 H), 6.76 (br s, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 35.73, 35.75, 35.80, 38.16 (s, C-1, -2, -9, -10), 132.72, 132.87, 133.05, 133.20, 133.61, 134.21, 138.84, 139.25, 139.34, 139.90, 143.81, 146.90 (s, all C-Ar). − MS (70 eV); *m/z* (%): 564 (100) [M^+], 549 (98), 445 (74), 413 (16), 309 (32), 205 (84), 191 (58), 135 (18), 104 (36). − $C_{34}H_{36}Sn$ (563.35): calcd. C 72.49, H 6.44; found C 71.95, H 6.07.

*X-ray Crystallographic Study of Dimethyl-d,l-bis([2.2]paracyclophan-4-yl)germane (d,l-***6a′′**): Crystal data: $C_{34}H_{36}Ge$, 517.25 g mol^{-1}, *a* = 14.001(3), *b* = 17.814(4), *c* = 10.554(2) Å, β = 93.09 (3)°, *V* = 2628.5 (10) $Å^3$, *Z* = 4, *d* = 1.307 mg/m^3, monoclinic crystals, space group *P*2(1)/*c*. Data collection: A colorless prism of dimensions 0.45 × 0.30 × 0.28 mm was mounted in inert oil. Data were collected to $2\theta_{max}$ = 50° [$I > 2\sigma(I)$] with an Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), β-filter monochromator. Of 1965 measured data, 1844 were unique (R_{int} = 0.0155). μ = 1.186 mm^{-1}, *T* = 20°C. The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, Univ. Göttingen). Hydrogen atoms were refined in isotropic approximation. The final $wR^2(F^2)$ was 0.0553 for 461 parameters. Conventional *R*(*F*) = 0.022, *S* = 1.086; max Δ/σ < 0.001; max Δρ 0.332 e$Å^{-3}$. Crystallographic data (excluding structure factors) for the structure *d,l*-**6a′′** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101369. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int. code) + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk; World Wide Web: http://www.ccdc.cam.ac.uk].

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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