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Stepwise synthesis and characterization of germa[4], [5], [8], and [10]pericyclynes†

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The stepwise syntheses of germa[N]pericyclynes, including [5]pericyclynes, and their characterization are

described. The yields of germa[4] and [8]pericyclynes were improved significantly compared to those

obtained in previous studies. The routes reported herein afforded the novel germa[5] and [10]pericyclynes,

which were characterized by X-ray crystallography, UV-Vis spectroscopy, and fluorescence emission spectroscopy. A unique fluorescence emission was observed for the large germa[10]pericyclyne ring.

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Introduction

The acetylene unit, especially as polyynes, has long been focused in materials science, and as building blocks of peculiar structural molecules in synthetic, and physical organic chemistry.^{1,2} In recent decades, cyclic skipped polyyne compounds called [N] pericyclynes,³⁻⁷ which are composed of N-acetylenic units, have received a growing amount of attention. As the reduced bond angles of the vertex sp³ atoms in pericyclynes are considered to reinforce the through-space interaction between skipped alkynes, such characteristics result in unique electronic and optical properties. To develop pericyclyne chemistry facilitating the hyperconjugation of alkynes⁸ and the heavy atom effect of vertexes, we previously reported the synthesis and characterization of germa[N] pericyclynes, novel pericyclynes containing the group 14 element germanium (Fig. 1).9 It was demonstrated that such compounds were efficient building blocks for incorporation into functional materials and polymers. However, our previous one-step synthesis unselectively afforded [4], [6], and [8]pericyclynes in low yields. Moreover, this method was not suitable for the preparation of [5]pericyclynes, containing an odd number of germanium atoms. Since the small [4] and [5]pericyclynes are

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Fig. 1 Germa[N]pericyclynes.

expected to show specific properties due to their reduced vertex angles, their syntheses and characterization are of particular interest. In contrast, germa[8]pericyclynes were revealed to display unique fluorescence emission patterns in fluorescence spectra and we believe that such interesting behaviour was worth investigation through the synthesis of large ring germapericyclynes. We herein report the improved stepwise synthesis of germa[*N*]pericyclynes, including germa[4], [5], [8], and [10]pericyclynes, and their characterization by X-ray crystallography, UV-Vis spectroscopy, and fluorescence spectroscopy.

Results and discussion

We first performed the stepwise synthesis of germapericyclynes from diethynylgermanes **1a–b**.⁹ To monoanions of **1a–b**, generated by the addition of *n*-butyllithium, was added 0.5 eq. of the appropriate germanium dichloride to give trimeric compounds **2a–b** (Scheme 1). Monoacetylidation of **2a–b** with ethyl magnesium bromide followed by coupling with 1 eq. of the germanium dichloride and subsequent ethynylation afforded tetragermanes **3a–b**. With precursors **2** and **3** in hand, we conducted the macrocyclization reaction to give the germapericyclynes. Slow addition of diphenylgermanium dichloride to dilithiated **2a** *via* a syringe pump afforded **4a** and

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Scheme 1 Synthesis of germa[4], [5], [8] and [10]pericyclynes *via* stepwise route.

5a in 12% and 23% yields, respectively. Addition over 5 min via a dropping funnel gave 4a and 5a in only 4% and 17% yields, respectively. The overall yields of both 4a (10%) and 5a (18%) from 1a via the stepwise route were significantly improved in comparison with the previous one-step syntheses (3% and 10% for 4a and 5a, respectively). In addition, the [8] pericyclyne 5b was isolated from 2b in 15% overall yield via the stepwise route, compared to 13% yield in a single step synthesis. The isolation of [4]pericyclyne 4b was not successful via the stepwise approach. For the successful preparation of the germa[5]pericyclynes 6a-b and [10]pericyclynes 7a-b from 3a-b, high-dilution reaction conditions were required. Considering the unsuccessful result to synthesize 4b, the low yield of 6b could be attributed to the presence of the bulky isopropyl groups suppressing the formation of the cyclic species. For comparison, reference compounds 8a-b were also prepared by masking 1a-b with the trimethylgermyl group.

Following their first successful synthesis, X-ray crystallography of the germa[5] **6a–b** and [10]pericyclynes **7a–b** was carried out (Fig. 2). [5]Pericyclynes **6a–b** displayed envelope conformations, while [4]pericyclyne **4a** was previously found to be planar.⁹ The smallest C–Ge–C angles of **6a–b** were comparable to **4a** (**4a**: 103.66(10)°,⁹ **6a**: 104.1(3)°, **6b**: 103.58(18)°), while the largest C–Ge–C angles were 107.6(3)° for **6a** and 109.01(19)° for **6b**, respectively. The Ge–C≡C angles were found to vary between 170.2(8)° and 178.6(6)° (**6a**), and between 166.0(4)° and 176.8(4)° (**6b**). From these results, it



Fig. 2 ORTEP drawing of germa[5] and [10]pericyclynes; (a) 6a; (b) 7a; (c) 6b; (d) 7b.

could be concluded that **6a–b** exhibited greater strain than methylated sila[5]pericyclynes (average C-X-C and X-C=C angles: 106.0° and 175.1° (**6a**), 106.2° and 172.2° (**6b**), *cf.* 106.1° and 177.2° (Me-sila[5])^{4f}), and were not bent to the extent of **4a** (103.8° and 172.3°). In contrast, [10]pericyclynes **7a–b** were present in zigzag forms,⁹ with **7a** displaying intramolecular π - π interactions between the phenyl rings present in its cavity. From X-ray data, the estimated distance between phenyl rings in the cavity of **7a** was approximately 3.5–3.8 Å with full ring overlap while that of **5a**⁹ was 3.5 Å with only partial overlap.

UV-Vis and fluorescence emission spectra of [5]pericyclynes 6a-b and [10]pericyclynes 7a-b were recorded in dichloromethane and hexane, and were compared to a range of other germapericyclynes.⁹ Both 6a and 7a showed comparable absorption maxima (261 nm, $\varepsilon = 2540$ (6a), 5070 (7a)) to the other phenyl germapericyclynes⁹ (Fig. 3a, see the ESI† for details). In addition, it was observed that the ε values increased with an increase in the number of benzene rings. Although it is expected that 6a and 7a also have absorption bands at short wavelengths, measurement was problematic due to solubility issues. In the UV-Vis spectra of hexanesoluble 6b and 7b (Fig. 3b), shoulders were observed at 205 nm (ε = 14 500 (**6b**), 28 900 (7**b**)) and 213 nm (ε = 10 600 (6b), 23 200 (7b)), as reported for [6]pericyclyne 9b and [8]pericyclyne $5b^9$ (for detailed values, see the ESI^{\dagger}). When compared to compound **8b** (203 nm: ϵ = 4330, 210 nm: ϵ = 2994) and **1b**,⁹ where no such peaks were present, these shoulders could be assigned to the internal germanium-substituted alkynes, as observed for the silapericyclynes.^{4g} It appeared that the ring size did not affect the spectra;¹⁰ however, a small bathochromic shift between compounds 8b and 7b (Fig. 3b) suggested the influence of cyclic structures or ring strain.4f

Strain within the alkyne structure could also be estimated by Raman spectroscopy.¹¹ According to the reported trends, [4]pericyclyne **4a** was found to contain the most-strained alkynes (**4a**: 2107 cm⁻¹) followed by [5]pericyclyne (**6a**: 2110 cm⁻¹) among the phenyl compounds, while the values for [6], [8], and [10]pericyclynes were comparable (**9a**: 2114, **5a**: 2112,⁹ **7a**: 2113 cm⁻¹). However, isopropyl compounds gave opposite results, with the band for [5]pericyclyne (**6b**: 2103 cm⁻¹) found at a higher wavenumber than comparable [6], [8], and [10]pericyclynes (**9b**: 2099, **5b**: 2098, **7b**: 2098 cm⁻¹). The reason is not clear so far because of few referential examples.

The fluorescence emission maxima of the germa[5]pericyclyne **6a** were found to be similar to the [4] and [6]pericyclynes (**4a** and **9a**) (λ = 282, 288 nm) (Fig. 3c).⁹ However, unlike [4], [5], and [6]pericyclynes (**4a**, **6a**, and **9a**), [10]pericyclynes **7a** also displayed emission at 318 nm as well as [8]pericyclynes **5a**. This difference was displayed clearly in the normalized differential spectra (Fig. 3d). Changing the excitation wavelength from 260 to 273.5 nm increased the emission intensities of **5a** and **7a** at approximately 320 nm, whereas no significant changes were observed for **4a**, **6a**, or **9a**. Because the characteristic emissions could be assigned to absorption around 265 nm (Fig. 3e), the emissions were likely derived from



Fig. 3 UV-visible spectra, (a) 0.1 mM in CH₂Cl₂, (b) 0.1 mM in hexane; and fluorescence emission spectra, (c) 0.1 mM in CH₂Cl₂. $\lambda_{ex} = 260$ nm (solid lines), $\lambda_{ex} = 273.5$ nm (dashed lines), (d) normalized differential spectra based on **1a**, $\lambda_{ex} = 260$ nm, (e) excitation spectra, **5a**: $\lambda_{ex} = 321.5$ nm, **7a**: $\lambda_{ex} = 320$ nm.

the excimer, by intramolecular π - π stacking of the benzene rings, as indicated in Fig. 2b. It is expected that the larger ring size of **7a** compared to **5a** allows stronger π - π interactions. Fluorescence emission quantum yields were not recorded because the emissions were observed at only short wavelengths.

From cyclic voltammetry and differential pulse voltammetry (DPV) (Fig. 4), oxidation potentials ($E_{OX}^{DPV} = 1.38$ V (**6a**, Ph-[5]), 1.36 V (**7a**, Ph-[10]), 1.27 V (**6b**, ⁱPr-[5]), and 1.26 V (**7b**, ⁱPr-[10])) were found to be comparable to those previously reported for the germa[4], [6], and [8]pericyclynes.⁹ In addition, the oxidation potentials of isopropyl compounds **6b** and **7b** were found to be smaller than those of the corresponding phenyl compounds **6a** and **7a**.



Fig. 4 Cyclic and differential pulse voltammograms of germa[5] and [10]pericyclynes **6a–b** and **7a–b** (1.0 mM in 0.1 M n-Bu₄NPF₆-CH₂Cl₂ solution; scan rate = 0.1 V s⁻¹).

DFT calculations for germa[5]pericyclynes **6a-b** (Fig. 5) show the through-space interactions between alkynes in the LUMO of **6b**. Delocalized orbitals between the alkyne moieties



6a (Ph) germa[5]pericyclynes 6b (ⁱPr)

Fig. 5 Molecular orbitals for the germa[5]pericyclynes **6a** and **6b** obtained by DFT calculations (Gaussian 09 B3LYP/6-31G(d,p)).

and the phenyl groups through the germanium atoms are also shown for **6a**. As was the case for the [6]pericyclynes,⁹ out-ofplane HOMOs are found in **6b**, while the [4]pericyclynes⁹ display in-plane orbitals. In contrast, the orbitals of **6a** are located close to the benzene rings.

Conclusions

Germa[4], [5], [8], and [10]pericyclynes were synthesized *via* a stepwise route, giving an improvement in yield over our previously reported one-step synthetic route. Novel germa[5] and [10]pericyclynes were characterized by X-ray crystallography, cyclic voltammetry, UV-Vis spectroscopy, and fluorescence emission spectroscopy. The unique fluorescence behaviour of phenylgerma[10]pericyclyne is reported, and the frontier orbitals of [5]pericyclynes were estimated by DFT calculations. Our improved synthesis and optical investigation of cyclic skipped oligo-alkyne compounds may open the door to further studies into the chemistry and design of functional organic–inorganic hybrid materials.

Experimental

General procedures

¹H and ¹³C NMR spectra were recorded using a JEOL JNM-ECP500 spectrometer (500 MHz for ¹H NMR and 126 MHz for ¹³C NMR). Chemical shifts are reported as δ values in ppm and calibrated with respect to the residual solvent peak (CDCl₃, δ 7.26 for ¹H NMR and δ 77.00 for ¹³C NMR) or tetramethylsilane (δ 0 for ¹H NMR). The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad peak), and m (complex multiplet). Melting points were measured using a Yanaco Micro melting point apparatus. Infrared spectra were measured using a JASCO FT-IR-4200 spectrometer. Mass spectra were recorded using a JEOL JMS-700 MStation [EI (70 eV), CI, FAB, and ESI]. X-ray crystal analyses were performed using a Rigaku R-AXIS RAPID/S imaging plate diffractometer. Raman spectra were obtained using a JASCO laser Raman spectrophotometer, NRS-2100. The cyclic voltammetry measurements of the compounds were performed using a BAS electrochemical analyser ALS612D in dichloromethane containing n-Bu₄NPF₆ as the supporting electrolyte at 298 K (100 mV s⁻¹). The glassy carbon working electrode was polished using the BAS polishing alumina suspension and rinsed with water before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to Ag/AgNO₃ and normalized with respect to Fc/Fc^+ . Flash column chromatography was performed using Merck Silica gel 60. The progress of the reactions was monitored by silica gel thin layer chromatography (TLC) (Merck TLC Silica gel 60 F_{254}) with an iodine/silica gel stain. The purification of the mixture of germapericyclynes was performed using a LC-908 recycling preparative high-performance liquid chromatography (HPLC)

equipped with a JAIGEL 2H-40 column (chloroform elution) made by Japan Analytical Industry Co., Ltd. Anhydrous tetrahydrofuran (THF) was purchased from Kanto Chemical, which was further dehydrated over activated molecular sieves 4A. Density functional theory (DFT) calculations were performed using the Gaussian09, and the geometries of the molecules were optimized by employing the B3LYP density functionals and the 6-31G(d,p) basis set in this series of calculations.

Bis((ethynyldiphenylgermyl)ethynyl)diphenylgermane (2a). n-Butyllithium (1.63 M in hexane, 3.21 mL, 5.24 mmol) was added dropwise to a stirred solution of diethynyldiphenylgermane 1a⁹ (1.45 g, 5.24 mmol) in THF (52 mL) at -78 °C under a nitrogen atmosphere. After 2 h, dichlorodiphenylgermane (744 mg, 2.50 mmol) was added at the same temperature. Then the reaction mixture was warmed up to ambient temperature and stirred for 13 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic laver was dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/dichloromethane = 10/1to 3/1) to afford 2a (1.57 g, 80%). White solid; $R_{\rm f}$ value 0.3 (hexane/dichloromethane = 3/1); m.p. 123.7-124.6 °C; IR (KBr, disc) v_{max} 3273, 3070, 3028, 2035, 1485, 1433, 1095, 736 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.73-7.70 (m, 12H), 7.44-7.37 (m, 18H), 2.60 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 133.8, 133.7, 133.3, 133.2, 130.1, 130.1, 128.6, 128.5, 107.8, 107.4, 95.3, 82.6; LRMS (ESI, M = $C_{44}H_{32}Ge_3$) m/z = 801 $[M + Na]^+$; Anal. Calcd for C₄₄H₃₂Ge₃: C, 67.87; H, 4.14. Found: C, 67.69, H, 3.97.

Bis((ethynyldiisopropylgermyl)ethynyl)diisopropylgermane (2b). n-Butyllithium (1.63 M in hexane, 9.04 mL, 14.73 mmol) was added dropwise to a stirred solution of diethynyldiisopropylgermane $\mathbf{1b}^9$ (3.07 g, 14.73 mmol) in THF (150 mL) at -78 °C under a nitrogen atmosphere. After 2 h, dichlorodiisopropylgermane⁵ (1.61 g, 7.02 mmol) was added at the same temperature. Then the reaction mixture was warmed up to ambient temperature and stirred for 16 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting residue was purified by silica gel column chromatography (hexane to hexane/dichloromethane = 5/1) to afford 2b (2.81 g, 70%). Colorless oil; $R_{\rm f}$ value 0.16 (hexane); IR (NaCl, neat) $\nu_{\rm max}$ 3292, 2944, 2865, 2032, 1463, 1005, 878, 668 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.32 (s, 2H), 1.48-1.37 (m, 6H), 1.20-1.17 (m, 36H); 13 C NMR (126 MHz, CDCl₃) δ 107.8, 106.3, 93.9, 83.5, 18.8, 18.74, 18.70, 16.7, 16.6; LRMS (ESI, M = C₂₆H₄₄Ge₃) $m/z = 597 [M + Na]^+$.

3,3,6,6,9,9,12,12-Octaphenyl-3,6,9,12-tetragermatetra-deca-1,4,7,10,13-pentayne (3a). Ethylmagnesium bromide (0.97 M in THF, 1.58 mL, 1.53 mmol) was added dropwise to a stirred solution of 2a (1.19 g, 1.53 mmol) in THF (15 mL) at -78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 1 h at the same temperature, and then the reaction mixture was warmed up to ambient temperature and stirred for 2 h. The reaction mixture was cooled down to -78 °C and dichlorodiphenylgermane (414 mg, 1.39 mmol) was added. The reaction mixture was warmed up to ambient temperature and stirred for 17 h. The reaction mixture was cooled down to 0 °C and ethynylmagnesium bromide (0.5 M in THF, 3.48 mL, 1.74 mmol) was added. After that, the reaction mixture was warmed up to ambient temperature and stirred for 9 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The mixture was extracted with dichloromethane and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 4/1 to 3/1) to afford **3a** (233 mg, 16%). White solid; $R_{\rm f}$ value 0.26 (hexane/dichloromethane = 2/1); m.p. 132.6-134.9 °C; IR (KBr, disc) $\nu_{\rm max}$ 3275, 3069, 3045, 2035, 1484, 1432, 1095 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.73–7.69 (m, 16H), 7.43-7.35 (m, 24H), 2.586 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 133.8, 133.7, 133.4, 133.1, 130.1, 130.0, 128.6, 128.5, 107.9, 107.7, 107.4, 95.2, 82.6; LRMS (ESI, $M = C_{58}H_{42}Ge_4$) m/z = 1053 $[M + Na]^+$. Anal. Calcd for $C_{58}H_{42}Ge_4$: C, 67.67; H, 4.11. Found: C, 67.58; H, 4.18.

3,3,6,6,9,9,12,12-Octaisopropyl-3,6,9,12-tetragermatetra-deca-1,4,7,10,13-pentayne (3b). Ethylmagnesium bromide (0.97 M in THF, 12.76 mL, 12.38 mmol) was added dropwise to a stirred solution of 2b (7.11 g, 12.38 mmol) in THF (123 mL) at -78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 1 h at the same temperature, then the reaction mixture was warmed up to ambient temperature and stirred for 2 h. The reaction mixture was cooled down to -78 °C and dichlorodiisopropylgermane⁹ (2.58 g, 11.23 mmol) was added. The reaction mixture was again warmed up to ambient temperature. After 14 h, the reaction mixture was cooled down to 0 °C. Ethynylmagnesium bromide (0.5 M in THF, 28.13 mL, 14.07 mmol) was added to the mixture, and was stirred for 1 h at the same temperature. Then the mixture was warmed up to ambient temperature and stirred for 7 h. The reaction mixture was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 20/1 to 10/1) to afford **3b** (2.30 g, 27%). Colorless oil; $R_{\rm f}$ value 0.11 (hexane/dichloromethane = 10/1); IR (NaCl, neat) $\nu_{\rm max}$ 3292, 2944, 2864, 2032, 1463, 1004, 878, 668 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.32 (s, 2H), 1.47-1.36 (m, 8H), 1.20-1.17 (m, 48H); ¹³C NMR (126 MHz, CDCl₃) δ 108.0, 107.2, 106.2, 93.9, 83.5, 18.8, 18.8, 18.7, 18.7, 16.7, 16.6; LRMS (ESI, $M = C_{34}H_{58}Ge_4$) $m/z = 779 [M + Na]^+$.

Synthesis of octaphenylgerma[4]pericyclyne (4a) and hexadecaphenylgerma[8]pericyclyne (5a) from 2a. To a stirred solution of 2a (450 mg, 0.58 mmol) in THF (36 mL) was added

Paper

n-butyllithium (1.60 M in hexane, 0.72 mL, 1.16 mmol) dropwise at -78 °C under a nitrogen atmosphere. After 1.5 h, dichlorodiphenylgermane (0.12 mL, 0.58 mmol) was added dropwise over 1 h with a syringe pump at the same temperature, and the mixture was stirred at room temperature for 16 h. The reaction was quenched with ammonium chloride saturated aqueous solution at 0 °C. The mixture was extracted with dichloromethane and was washed with brine. The combined organic layer was dried over magnesium sulfate, and was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/dichloromethane = 4/1) and recycling preparative HPLC to afford germa[4]pericyclyne **4a** (70 mg, 12%) as a white powder and germa[8]pericyclyne **5a** (130 mg, 23%) as a white powder.⁹

Synthesis of hexadecaisopropylgerma[8]pericyclyne (5b) from 2b. To a stirred solution of 2b (2.36 g, 4.11 mmol) in THF (205 mL) was added n-butyllithium (1.63 M in hexane, 5.04 mL, 8.22 mmol) at -78 °C under a nitrogen atmosphere. After 2 h, 1:0.11 inseparable mixture of dichlorodiisopropylgermane⁹ and chlorotriisopropylgermane (1.05 g, of mixture, 4.11 mmol for ${}^{i}Pr_{2}GeCl_{2}$) was added at the same temperature, and the reaction mixture was warmed up to room temperature. After 34 h, the reaction was quenched with saturated ammonium chloride aqueous solution at 0 °C. The mixture was extracted with dichloromethane and was washed with brine. The combined organic layers were dried over magnesium sulfate, and were concentrated in vacuo. The obtained residue was purified by silica gel column chromatography (hexane/dichloromethane = 15/1 to 5/1) and recycling preparative HPLC to afford **5b** (653 mg, 21%) as a white powder.⁹

Synthesis of decaphenylgerma[5]pericyclyne (6a) and icosaphenylgerma[10]pericyclyne (7a). To a stirred solution of 3a (675 mg, 0.66 mmol) in THF (32 mL) was added *n*-butyllithium (1.63 M in hexane, 0.85 mL, 1.38 mmol) dropwise at -78 °C under a nitrogen atmosphere. After 2 h, dichlorodiphenylgermane (215 mg, 0.72 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature. After 46 h, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with dichloromethane and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (dichloromethane/hexane = 1/3 to 1/1.5) and recycling preparative HPLC to afford **6a** (80 mg, 10%) and **7a** (90 mg, 11%).

Decaphenylgerma[5]**pericyclyne (6a, CCDC: 1057090).** Colorless crystal; $R_{\rm f}$ value 0.33 (hexane/dichloromethane = 2/1); m.p. 271.7–273.0 °C; IR (KBr, disc) $\nu_{\rm max}$ 3070, 3049, 1485, 1433, 1095, 735, 695 cm⁻¹; Raman $\nu_{\rm max}$ 2110 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.72–7.68 (m, 20H), 7.43–7.35 (m, 30H); ¹³C NMR (126 MHz, CDCl₃) δ 133.9, 133.3, 129.9, 128.5, 107.1; LRMS (ESI, M = C₇₀H₅₀Ge₅) m/z = 1277 [M + Na]⁺. Recrystallization for X-ray crystallographic analysis was carried out using dichloromethane and hexane.

Icosaphenylgerma[10]pericyclyne (7a, CCDC: 1057091). Colorless crystal; R_f value 0.16 (dichloromethane/hexane = 1/2); m.p. 213.2–215.0 °C; IR (KBr, disc) $\nu_{\rm max}$ 3070, 3049, 1485, 1434, 1095, 736, 694 cm⁻¹; Raman $\nu_{\rm max}$ 2113 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.68–7.66 (m, 40H), 7.34–7.27 (m, 60H); ¹³C NMR (126 MHz, CDCl₃) δ 133.7, 133.4, 129.9, 128.5, 107.8; LRMS (ESI, M = C₁₄₀H₁₀₀Ge₁₀) m/z = 2530 [M + Na]⁺. Recrystallization for X-ray crystallographic analysis was carried out using dichloromethane and hexane.

Synthesis of decaisopropylgerma[5]pericyclyne (6b) and icosaisopropylgerma[10]pericyclyne (7b). To a stirred solution of 3b (1.05 g, 1.38 mmol) in THF (280 mL) was added n-butyllithium (1.60 M in hexane, 1.90 mL, 3.04 mmol) dropwise at -78 °C under a nitrogen atmosphere. After 2 h, dichlorodiisopropylgermane⁵ (381 mg, 1.66 mmol) was added at the same temperature, and the reaction mixture was warmed up gradually to ambient temperature. After 40 h, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with dichloromethane and washed with brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (dichloromethane/hexane = 1/20 to 1/5) and recycling preparative HPLC to afford 6b (31 mg, 2%) and 7b (164 mg, 13%).

Decaisopropylgerma[5]**pericyclyne** (6b, CCDC: 1057092). Colorless crystal; $R_{\rm f}$ value 0.16 (hexane/dichloromethane = 10/1); m.p. 74.4–76.1 °C; IR (KBr, disc) $\nu_{\rm max}$ 2944, 2887, 2863, 1463, 1003, 670 cm⁻¹; Raman $\nu_{\rm max}$ 2103 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.40 (sept, 10H, J = 7.5 Hz), 1.19 (d, 60H, J = 7.5 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 106.8, 19.0, 16.5; LRMS (ESI, M = C₄₀H₇₀Ge₅) m/z = 937 [M + Na]⁺.

Icosaisopropylgerma[10]pericyclyne (7b, CCDC: 1057093). Colorless crystal; $R_{\rm f}$ value 0.11 (hexane/dichloromethane = 10/1); m.p. 49.2–50.5 °C; IR (KBr, disc) $\nu_{\rm max}$ 2945, 2887, 2864, 1463, 1006, 669 cm⁻¹; Raman $\nu_{\rm max}$ 2093 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.39 (sept, 20H, J = 7.5 Hz), 1.17 (d, 120H, J = 7.5 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 107.2, 18.8, 16.7; LRMS (ESI, M = C₈₀H₁₄₀Ge₁₀) m/z = 1851 [M + Na]⁺.

Diphenylbis((trimethylgermyl)ethynyl)germane (8a). n-Butyllithium (1.63 M in hexane, 2.44 mL, 3.97 mmol) was added dropwise to a stirred solution of diethynyldiphenylgermane 1a⁹ (500 mg, 1.81 mmol) in THF (18 mL) at -78 °C under a nitrogen atmosphere. After 2 h, chlorotrimethylgermane (609 mg, 3.97 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature and stirred for 8 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layer was dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting residue was purified by silica gel column chromatography (hexane to hexane/dichloromethane = 10/1) to afford 8a (927 mg, quant.). White solid; $R_{\rm f}$ value 0.13 (hexane/dichloromethane = 20/1); m.p. 86.6-87.3 °C; IR (KBr, disc) ν_{max} 3066, 3051, 2979, 2911, 2102, 1483, 1430, 1240, 1092, 835 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.69–7.67 (m, 4H), 7.40–7.38 (m, 6H), 0.40 (s, 18H); ¹³C NMR

(126 MHz, CDCl₃) δ 134.7, 133.7, 129.6, 128.3, 116.6, 103.2, 0.16; LRMS (ESI, M = C₂₄H₂₈Ge) m/z = 533 [M + Na]⁺; Anal. Calcd for C₂₂H₂₈Ge₃: C, 51.78; H, 5.53. Found: C, 51.61; H, 5.52.

Diisopropylbis((trimethylgermyl)ethynyl)germane (8b). To a stirred solution of 1b⁹ (750 mg, 3.59 mmol) in THF (35 mL) was added n-butyllithium (1.63 M in hexane, 4.85 mL, 7.90 mmol) dropwise at -78 °C under a nitrogen atmosphere. After 2 h, chlorotrimethylgermane (1.21 g, 7.90 mmol) was added at the same temperature, and the reaction mixture was warmed up to ambient temperature. After 2 h, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C. The resulting mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layers were dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting residue was purified by silica gel column chromatography (hexane to dichloromethane/hexane = 1/10) and recycling preparative HPLC to afford **8b** (1.08 g, 68%). Colorless oil; $R_{\rm f}$ value 0.14 (hexane); IR (NaCl, neat) $\nu_{\rm max}$ 2944, 2865, 1464, 1241, 1004, 833, 768, 667 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.38 (sept, 2H, J = 7.5 Hz), 1.16 (d, 12H, J = 7.5 Hz), 0.34 (s, 18H); ¹³C NMR (126 MHz, CDCl₃) δ 115.1, 104.2, 18.9, 16.7, 0.04, 0.02, 0.00; LRMS (ESI, M = $C_{16}H_{32}Ge_3$) $m/z = 465 [M + Na]^+$.

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