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The First Spirobifluorenes Containing Two Binaphthyl Moieties

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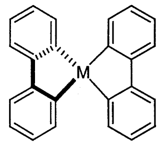
Summary: The first spirobifluorenes comprising two binaphthyl moieties with silicon or germanium at the site of fusion have been synthesized and fully characterized. X-ray crystallographic analysis reveals that both molecules have highly distorted structures, resulting in a low barrier for interconversion between the two atropisomers; the barrier was calculated from the temperature dependency of the NMR spectra.

Introduction

Heterocyclopentadienes incorporating elements other than N, O, or S have been the focus of considerable attention in recent years.[1] In particular, siloles and silole-containing polymers have attracted a great deal of interest due to their potential application as electron-transporting materials in organic electroluminescent devices, a property that results from an unusually low-lying LUMO arising from $\sigma^*-\pi^*$ conjugation.[2] Their spiro-fused analogues, the spirobifluorenes **1**, form an interesting class of compounds, and examples are known with P, As, Sb, Te, and each of the group 14 elements at the site of fusion.[3] Interaction between the orthogonal π-systems through the phenomenon of spiro conjugation[4] has been demonstrated in 9,9′-spirobifluorene and 9,9′-spirobi(9-silafluorene).[5] Despite the synthesis of several binaphthoheteroles[6] incorporating heteroatoms from groups 14, 15, and 16, their spiro-fused analogues **2** are unknown. Indeed, to our knowledge the literature contains only a single example of a spiro-fused molecule incorporating a binaphthyl moiety.[7] We now report the syntheses, X-ray crystal structures, and dynamic NMR studies of the bisbinaphthyl silole **2a** and germole **2b**.



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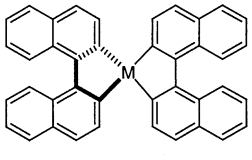
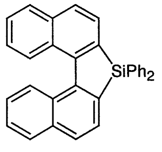


2a (M=Si)
2b (M=Ge)



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Results and Discussion

We adapted the method developed by Gilman[3b] for spirobifluorene synthesis to the preparation of **2a** and **2b**. Lithiation of 2,2′-dibromobinaphthyl (−78 to −30 °C) and subsequent treatment of the dilithio species with 0.5 equiv of silicon tetrachloride or germanium tetrachloride (−78 to 25 °C), followed by chromatography over silica gel, afforded the desired silole **2a** and germole **2b** in yields of 9% and 1.8%, respectively, along with unidentified polymeric material. The yield of the silole was comparable with that of Hoshi and Hagiwara,[8] who obtained a yield of 9.6% for the synthesis of 7-sila-7,7-diphenyl-7*H*-dibenzo[*c*,*g*]fluorene, **3**. Attempts to optimize the yield of the germanium reaction, including syringe-pump addition of germanium tetrachloride, resulted in little improvement. The low yield likely

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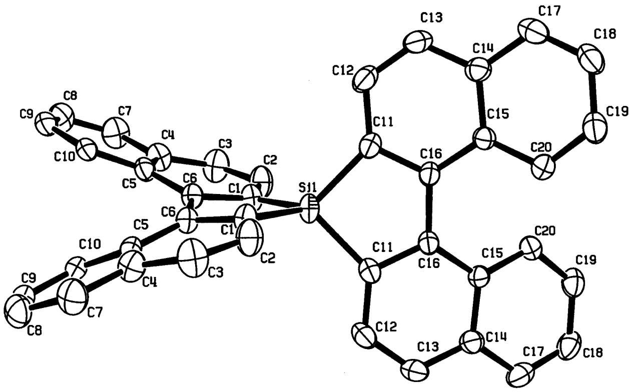

Figure 1. Molecular structure of **2a** in crystals of $\mathbf{2a}\cdot C_7H_8$; ellipsoids drawn at 30% probability level. Hydrogen atoms and toluene have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)−C(1) 1.865(3), Si(1)−C(11) 1.869(3); C(1)−Si(1)−C(1) 91.1(2), C(1)−Si(1)−C(11) 116.6(2), C(1)−Si(1)−C(11) 121.8(2), C(11)−Si(1)−C(11) 91.8(2), C(1)−C(6)−C(6)−C(1) 21.24(1), C(11)−C(16)−C(16)−C(11) 19.11(1), C(5)−C(6)−C(6)−C(5) 32.35(2), C(15)−C(16)−C(16)−C(15) 33.44(2).

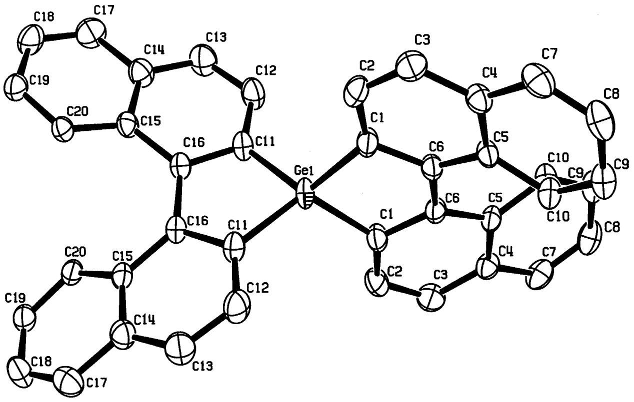

Figure 2. Molecular structure of **2b** in crystals of $\mathbf{2b}\cdot C_7H_8$; ellipsoids drawn at 30% probability level. Hydrogen atoms and toluene have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−C(1) 1.934(4), Ge(1)−C(11) 1.934(4); C(1)−Ge(1)−C(1) 89.6(2), C(1)−Ge(1)−C(11) 117.8(2), C(1)−Ge(1)−C(11) 122.8(2), C(11−Ge(1)−C(11) 89.5(2), C(1)−C(6)−C(6)−C(1) 20.9(4), C(11)−C(16)−C(16)−C(11) 21.1(4), C(5)−C(6)−C(6)−C(5) 33.4(5), C(15)−C(16)−C(16)−C(15) 33.5(5).

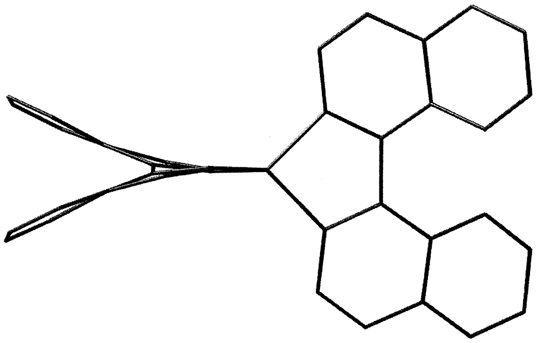

Figure 3. Stick model of **2a**. Hydrogen atoms have been omitted for clarity.

reflects the additional strain in the system that results from accommodating the larger germanium atom; unsurprisingly, we were unable to form the tin analogue via the same route.

Both compounds crystallized from toluene by slow evaporation of the solvent to afford a near quantitative recovery of pale yellow plates, which were suitable for single-crystal X-ray structure determination. Molecules **2a** and **2b** are isostructural with similar unit cell parameters and identical symmetry.[9] In each case examination of several crystals revealed the presence of only one of the two possible diastereomers, the *meso* form. Both molecules exhibit considerable distortion from regular geometry.

Figure 1 shows an ORTEP[10] view of **2a**, illustrating the twist away from planarity of the silole units as a result of the repulsive interactions between the two halves of each binaphthyl moiety, separated by distances of 2.28 Å (H(C10)−H(C10)) and 2.53 Å (H(C20)−H(C20)). Geometrical parameters for the germane **2b** are remarkably similar to those for the silane **2a**, and an ORTEP view of **2b** is shown in Figure 2. The naphthalene rings are significantly twisted away from planarity in both structures, illustrated by the stick representation of **2a** shown in Figure 3. The atoms C1, C2, C3, and C6 are essentially coplanar, but the remaining atoms within the naphthalene ring deviate markedly from this plane, reflecting twisting of the naphthalene in both directions. The distortion is most pronounced for C9, which lies 0.78 Å from the plane. The other half of the molecule exhibits even greater twisting. Once again, C11, C12, C13, and C16 are essentially coplanar, while C19 deviates from this plane by 1.05 Å.

The ^{1}H and ^{13}C NMR spectra for **2a** were fully assigned using a combination of COSY, HSQC, HMBC, and 1D-GOESY.[11] The ^{1}H and ^{13}C NMR spectra ($CDCl_3$, 400 and 100 MHz, respectively) at 27 °C clearly showed the presence of two species in roughly equal proportions, suggesting that both of the expected diastereomers of **2a** were present in solution. In the ^{1}H NMR spectrum there were clearly two sets of signals from H-3 and H-4 (doublets at δ 7.48 and 7.35 for H-3, and δ 7.78 and 7.74 for H-4). The signals from H-5 (at δ 7.92) showed slight overlap, while those from H-6, H-7, and H-8 were coincident. The data are illustrated in Figure 4.

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[9] Crystal data for **2a**. PhMe: $C_{40}H_{24}Si$. C_7H_8, $M_r = 624.82$, monoclinic, space group *C*2/*c* (no. 15), $a = 16.653(2)$ Å, $b = 12.987(2)$ Å, $c = 16.165(2)$ Å, $\beta = 96.666(4)°$, $V = 3472.2(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.195$ g cm^{-3}, $\mu = 0.100$ mm^{-1}, approximate crystal dimensions 0.40 × 0.30 × 0.20 mm, radiation Mo Kα ($\lambda = 0.71069$ Å), $T = 296$ K, 3024 independent reflections ($I > 2\sigma(I) = 2071$), R1 = 0.072, wR2 = 0.189. Crystal data for **2b**. PhMe: $C_{40}H_{24}Ge\cdot C_7H_8$, $M_r = 669.32$, monoclinic, space group *C*2/*c* (no. 15), $a = 16.4570(2)$ Å, $b = 13.0298(2)$ Å, $c = 16.1438(3)$ Å, $\beta = 96.5880(10)°$, $V = 3438.88(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.293$ g cm^{-3}, $\mu = 1.447$ mm^{-1}, approximate crystal dimensions 0.12 × 0.12 × 0.12 mm, radiation Cu Kα ($\lambda = 1.54178$ Å), $T = 296$ K, 3137 independent reflections ($I > 2\sigma(I) = 2683$), R1 = 0.066, wR2 = 0.198. Single-crystal data for **2a** were recorded on a Rigaku R-axis IIc diffractometer equipped with an image plate detector system and a rotating anode generator using graphite-monochromated molybdenum radiation. Data for **2b** were recorded on a Bruker Smart 6000 diffractometer equipped with a CCD detector system and a sealed copper tube. Both structures were solved by direct methods using SHELXS86 and refined using SHELXL93.[15,16] The crystal structures contain toluene solvent, which is disordered. Hydrogen atom positions were calculated and were riding in subsequent refinements.

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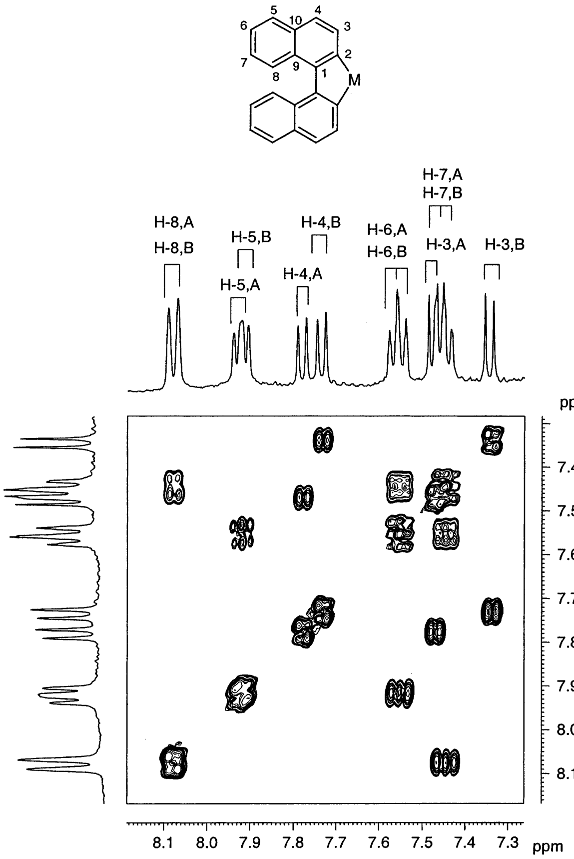

Figure 4. Gradient COSY90 NMR data of **2a** ($CDCl_3$, 400 MHz, 27 °C), showing the numbering system used for NMR assignments. The two diastereomers are denoted A and B.

The presence of both expected species in solution, but only one in the solid, suggests the occurrence of crystallization-induced asymmetric transformation.[12] Redissolving the *meso* crystals of **2a** and acquiring the ^1H NMR spectrum again showed both species in equal amounts, indicating that the two forms equilibrate in solution with a relatively low barrier to interconversion. To calculate the barrier, a variable-temperature NMR study was performed.

The temperature dependence of the ^1H NMR spectra is shown in Figure 5. The coalescence temperatures for the two sets of signals from H-4 and H-5 were measured at 67 and 52 °C, respectively. The energy barrier to exchange between the two diastereomers was calculated from the Eyring equation;[13] both data treatments yielded an energy barrier between the two diastereomers of 73 ± 1 kJ mol^{-1}. Doubling was also evident in the ^{29}Si spectrum ($CDCl_2CDCl_2$, 99 MHz, 27 °C), which exhibited two signals at δ -2.6 and -3.6. These were similarly shown to be in exchange, coalescing to a single broad resonance at 100 °C.

Germole **2b** exhibited very similar spectral features. Again the ^1H and ^{13}C NMR spectra showed the presence of both diastereomers in roughly equal proportions at 27 °C, with the ^1H NMR signals from H-3 and H-4 clearly distinguishable in both diastereomers (doublets at δ 7.53 and 7.41 for H-3, and δ 7.80 and 7.76 for H-4). Some doubling of H-5 (δ 7.92) was evident, while the signals from H-6, H-7, and H-8 were coincident. The NMR spectral data for the germole **2b** showed a temperature dependence similar to those for the silole **2a**, confirming that the two diastereomers of **2b** were in chemical exchange. The coalescence temperatures for the two sets of signals from H-4 and H-5 were measured at 88 and 56 °C, respectively, both data treatments yielding an energy barrier between the two diastereomers of 77 ± 1 kJ mol^{-1}.

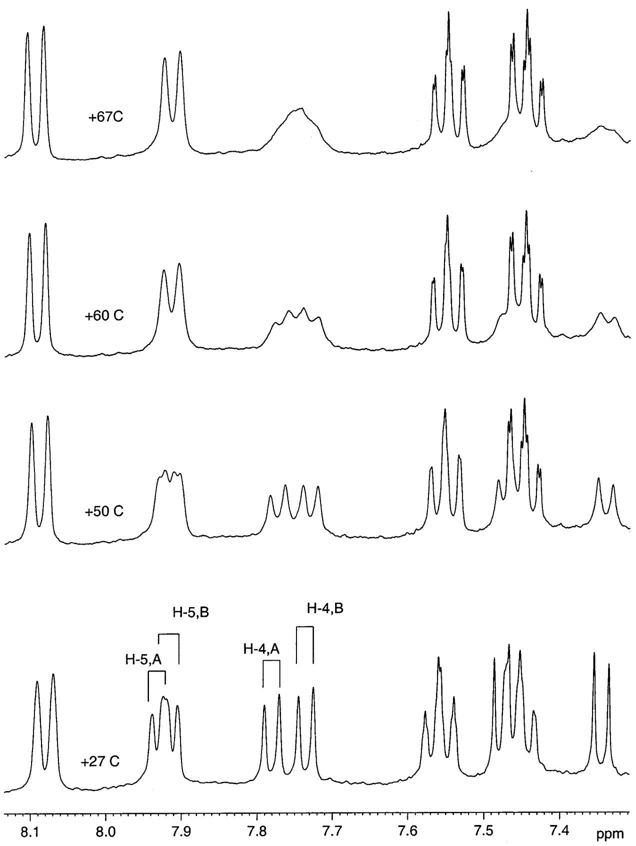

Figure 5. Temperature dependence of ^1H NMR data of **2a** ($CDCl_3$, 400 MHz).

The ^{73}Ge NMR spectrum was extremely broad at 25 °C, suggesting that this temperature was close to the coalescence point for the two germanium resonances. Reacquiring the data at -10 °C afforded a spectrum with a single resonance at 2.19 ppm (referenced to $Ph_4Ge = 0$ ppm), suggesting that the ^{73}Ge resonances from the two diastereomers were coincident or unresolved. The possibility of the two signals being unresolved is perhaps unsurprising given the large quadrupolar moment of ^{73}Ge (spin 9/2), which results in line-broadening, leading to a half-height line width of 15 Hz in this case.

The fluxional behavior of strained binaphthyl heteroles of groups 15 and 16 has previously been reported, and the barriers to exchange are relatively low.[6b,d,14−16] Recently Kurita and co-workers have shown that the

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[12] We are grateful to one of the reviewers for helpful comments. For leading references see: (a) Harris, M. M. *Prog. Stereochem.* **1958**, *2*, 157−195. For a previous example of crystallization-induced asymmetric transformation of a silicon compound see: (b) Klebe, J. F.; Finkbeiner, H. *J. Am. Chem. Soc.* **1968**, *90*, 7255−7261.

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corresponding siloles and germoles exhibit similar fluxional properties, and they calculated barriers to exchange of 77 and 80 kJ mol^{-1}, respectively.[6c]

In common with **3**, the electronic properties of **2a** are typical of a silole. The UV absorbance of **3**, reported by Hoshi and Hagiwara, was markedly red-shifted from that for the analogous acyclic systems, reflecting the lowered LUMO resulting from the $\sigma^*-\pi^*$ conjugation, achieved despite a twist from planarity in the silole unit of 22°. Interestingly, the UV absorption maximum for **2a** is even more red-shifted than that for **3** (373 nm for **2a**, 367 nm for **3**), possibly reflecting the slightly flatter nature of the silole units in **2a** compared with **3**. The fluorescence maximum of 441 nm for **2a** was likewise red-shifted compared with the value of 430 nm for **3**. The germole **2b** exhibited a UV absorption maximum of 365 nm and a fluorescence maximum at 428 nm, suggesting that it also exhibits a degree of $\sigma^*-\pi^*$ conjugation.

In conclusion, we have synthesized and fully characterized the spiro-fused bisbinaphthyl silole **2a** and germole **2b**. Study of the temperature dependency of the NMR spectra demonstrated that **2a** and **2b** were fluxional, with a low barrier to interconversion between the diastereoisomers. The X-ray data indicated that both molecules were extremely distorted, with the naphthalene rings being considerably bent out of planarity.

Experimental Section

Silane 2a. 2,2′-Dibromo-1,1′-binaphthyl (0.5 g, 1.2 mmol) was dissolved in dry THF (80 mL) under an argon atmosphere. The solution was cooled to −78 °C, and a 2.4 M solution of *n*-butyllithium in hexanes (1.1 mL, 2.6 mmol) was added over 1 min. The resulting solution was stirred for 2 h while being allowed to warm to −30 °C. The solution was then cooled to −78 °C before silicon tetrachloride (70 μL, 0.6 mmol) was added via syringe. The dry ice/acetone bath was then allowed to warm to room temperature. After stirring overnight at room temperature the THF was removed in vacuo. Water (50 mL) and diethyl ether (200 mL) were added. The aqueous phase was then further extracted with diethyl ether (2 × 100 mL), and the combined organic extracts were dried over $MgSO_4$. Solvent was removed in vacuo and the crude product purified by column chromatography (9:1, petroleum ether−dichloromethane, $R_f = 0.26$) to yield a yellow powder (28 mg, 9%). Crystallization by slow evaporation of a toluene solution gave pale yellow plates. (In the following NMR assignments the two diastereoisomers are denoted [a] and [b].)

Mp: 320 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ 7.35 (d, ^3J(H−H) = 7.8 Hz, 1H; H-3[b]), 7.44−7.49 (m, 2H; H-7[a+b]), 7.49 (d, ^3J(H−H) = 7.7 Hz, 1H; H-3[a]), 7.54−7.59 (m, 2H; H-6[a+b]), 7.75 (d, ^3J(H−H) = 7.8 Hz, 1H; H-4[b], 7.79 (d, ^3J(H−H) = 7.7 Hz, 1H; H-4[a]), 7.92 (d, ^3J(H−H) = 7.4 Hz, 1H; H-5[a]), 7.94 (d, ^3J(H−H) = 7.6 Hz, 1H; H-5[b]), 8.09 ppm (d, ^3J(H−H) = 8.6 Hz, 2H; H-8[a+b]). ^{13}C NMR (100.6 MHz, $CDCl_3$, 27 °C, TMS): δ 124.6 (C-7[a+b]), 126.4 (C-6[a+b]), 127.0 (C-8[a+b]), 128.29 (C-4[b]), 128.35 (C-4[a]), 128.5 (C-5[a+b]), 129.4 (C-3[a]), 129.7 (C-3[b]), 129.8 (C-10[a+b]), 133.4 (C-2[a]), 134.2 (C-2[b]), 136.48 and 136.55 (C-9[a] and C-9[b]), 150.5 and 150.6 ppm (C-1[a] and C-1[b]). ^{29}Si NMR (99.35 MHz, $CDCl_3$, 27 °C, TMS): δ −2.50, −3.49 ppm. IR (solid): ν 648, 741, 810, 880, 949, 1026, 1157, 1250, 1319, 1443, 1504, 1612, 1697, 1906, 2854, 2924, 3040 cm^{-1}. UV/vis (hexane, 8.72×10^{-5} M): λ_{max} (ϵ) 347 (8654), 373 nm (8847). MS (EI, 70 eV): *m/z* (%) 532 (100) [M$^+$], 279 (24), 264 (17), 252 (17). HRMS (EI, 70 eV): calcd for $C_{40}H_{24}Si$ 532.1647, found 532.1661. Anal. Calcd for $C_{40}H_{24}Si$: C, 90.19; H, 4.54. Found: C, 82.24; H, 4.92. [Note: the low carbon analysis is indicative of incomplete combustion and silicon carbide formation.]

Germole 2b. This compound was prepared by an analogous method using 2,2′-dibromo-1,1′-binaphthyl (0.5 g, 1.2 mmol) and germanium tetrachloride (69 μL, 0.6 mmol). Column chromatography (9:1, petroleum ether−dichloromethane, $R_f = 0.26$) yielded a pale yellow solid (6.3 mg, 1.8%). Crystallization by slow evaporation of a toluene solution gave yellow plates.

Mp: 305 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): δ 7.40−7.45 (m, 2H; H-7[a+b]), 7.41 (d, ^3J(H−H) = 7.9 Hz, 1H; H-3[b]), 7.51−7.56 (m, 3H; H-6[a+b] and H-3[a]), 7.75 (d, ^3J(H−H) = 7.9 Hz, 1H; H-4[b], 7.80 (d, ^3J(H−H) = 7.8 Hz, 1H; H-4[a]), 7.91 (d, ^3J(H−H) = 8.8 Hz, 1H; H-5[a]), 7.92 (d, ^3J(H−H) = 7.2 Hz, 1H; H-5[b]), 8.02 ppm (d, ^3J(H−H) = 8.6 Hz, 2H; H-8[a+b]). ^{13}C NMR (100.6 MHz, $CDCl_3$, 27 °C, TMS): δ 126.3 (C-7[a+b]), 127.8 (C-6[a+b]), 129.6 (C-8[a+b]), 130.1 (C-5[a+b]), 130.2 (C-4[a+b]), 131.2 (C-3[a]), 131.4 (C-3[b]), 131.9 (C-10[a+b]), 137.3 and 137.4 (C-9[a] and C-9[b]), 137.7 (C-2[a]), 138.8 (C-2[b]), 148.9 ppm (C-1[a+b]). ^{73}Ge NMR (17.4 MHz, CD_2Cl_2, −10 °C, Ph_4Ge): δ 2.19 ppm. IR (solid): ν 529, 590, 625, 644, 671, 694, 745, 772, 814, 864, 964, 1022, 1261, 1331, 1447, 1504, 2847, 2916, 3044 cm^{-1}. UV/vis (hexane, 4.15×10^{-5} M): λ_{max} (ϵ) 344 (7207), 365 nm (7701). MS (EI, 70 eV): *m/z* (%) 578 (100) [M$^+$], 500 (15), 377 (36), 324 (10), 287 (6), 252 (60), 207 (9). HRMS (EI, 70 eV): calcd for $C_{40}H_{24}Ge$ 578.1090, found 578.1078.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure of compounds **2a** and **2b**, as well as ^{1}H NMR spectra and analytical HPLC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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