Supporting Information

Chlorine-Substituted Germabenzene: Generation and Application as a Precursor for Aryl-Substituted Germabenzenes

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> > (submitted to Organometallics)

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1. Experimental Procedures

General methods

All manipulations of air- and/or moisture-sensitive compounds were performed in a MIWA-MFG glove box under argon atmosphere. Anhydrous hexane, toluene, Et_2O , THF, and CH_2Cl_2 were dried by passage through a GrassContour solvent purification system. Deuterated chloroform (CDCl₃) was distilled from CaH₂ prior to use. Deuterated benzene (C₆D₆) was distilled from sodium/benzophenone prior to use. Aluminacyclohexadiene **1**,^{S1} MesLi (2,4,6-trimethylphenyl),^{S2} and Mes*Li (2,4,6-tri(tert-butyl)phenyllithium)^{S3} were prepared according to the literature procedures. Other chemicals were used as received.

The nuclear magnetic resonance (NMR) measurements were measured on a JEOL ECS-400 spectrometer (399 MHz for ¹H and 101 MHz for ¹³C). Chemical shifts (δ) are given by definition as dimensionless numbers and relative to ¹H or ¹³C NMR chemical shifts of the residual CDCl₃ for ¹H (δ = 7.26), CDCl₃ itself for ¹³C (δ = 77.0), or the residual C₆D₅H for ¹H (δ = 7.16), C₆D₆ itself for ¹³C (δ = 128.0). The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). High-resolution mass spectra were measured on a Bruker micrOTOF II mass spectrometer with an atmospheric pressure chemical ionization (APCI) probe. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Melting points (m.p.) were determined with a MPA100 OptiMelt (Tokyo Instruments, Inc.) and are uncorrected.

Synthesis of germacyclohexadiene 5

To a toluene suspension (5.0 mL) of GeCl₂-dioxane (1.190 g, 5.15 mmol), toluene solution (30.0 mL) of **2** (1.226 g, 2.06 mmol) was added under argon atmosphere. After stirring for 24 h at 100 °C, a reaction mixture was concentrated under vacuum and exposed to air, then quenched with hexane/deionized water. The organic layer was separated, washed with brine, dried over Na₂SO₄, then filtered. The resulting solution was concentrated and recrystallized from hexane to give **5** as colorless crystals (494.5 mg, 0.947 mmol, 46%).: mp (in a sealed tube) 110-113 °C (dec.); ¹H NMR (C₆D₆, 399 MHz) & 1.18 (d, J = 7 Hz, 38H), 1.36-1.47 (m, 6H), 2.62 (t, J = 4 Hz, 2H), 6.78 (t, J = 4 Hz, 2H); ¹³C NMR (C₆D₆, 100 MHz) & 11.9 (CH), 19.1 (CH₃), 34.7 (CH₂), 137.7 (4°), 157.7 (CH, vinyl); HRMS (APCI, positive) Calc. for C₂₃H₄₆ClGeSi₂ [M⁺-Cl]: 487.2033. Found: 487.2048. Purity of **5** was confirmed by ¹H NMR spectrum shown in Figure S1.

Generation of chlorogermabenzene 3 using Mes*Li

To a benzene solution (0.3 mL) of **5** (10.0 mg, 19.1 µmol), benzene suspension (0.3 mL) of Mes*Li^{S3} (6.3 mg, 25 µmol) was added under argon atmosphere. The generation of **3** was confirmed by ¹H NMR spectroscopy (yield was determined to be 83%), and further reaction was performed without any purification: ¹H NMR (C₆D₆, 399 MHz) δ : 1.13 (d, *J* = 8 Hz), 1.45-1.56 (m), 6.60 (t, *J* = 8 Hz), 8.14 (d, *J* = 8 Hz); HRMS (APCI, positive) Calc. for C₂₃H₄₆ClGeSi₂ [M⁺]: 487.2038. Found: 487.2040.

Generation of chlorogermabenzene 3 using KHMDS

To a benzene solution (0.3 mL) of **5** (10.0 mg, 19.1 μ mol), benzene solution (0.3 mL) of KHMDS (3.8 mg, 19 μ mol) was added under argon atmosphere. The generation of **3** was confirmed by ¹H NMR spectroscopy in comparison with **3** generated in the reaction using Mes*Li (yield was determined to be 75%), and further reaction was performed without any purification.

Synthesis of Mes-substituted germabenzene 4-Mes

To a toluene solution (3.0 mL) of **5** (200.5 mg, 0.383 mmol), toluene suspension (3.0 mL) of KHMDS (76.4 mg, 0.383 mmol) was added under argon atmosphere to generate **3**. After stirred for 5 min, a toluene suspension (6.0 mL) of MesLi^{S2} (50.0 mg, 0.396 mmol) was add to the reaction mixture. The suspension was stirred for 11 h. After removal of volatiles, the residue was filtered through a pad of Celite[®] with hexane. The resulting solution was concentrated and recrystallized from hexane to give pure **4-Mes** as colorless crystals (26.2 mg, 0.100 mmol, 26%): mp (in a sealed tube) 128-130 °C (dec); ¹H NMR (C₆D₆, 399 MHz) δ : 1.09 (d, *J* = 7 Hz, 37H), 1.19-1.28 (m, 6H), 2.03 (s, 3H), 2.48 (s, 6H), 6.72 (s, 2H), 6.95 (t, *J* = 9 Hz, 1H), 8.33 (d, *J* = 9 Hz, 2H); ¹³C NMR (C₆D₆, 100 MHz) δ : 12.8 (CH), 19.4 (CH₃), 21.2 (CH₃, Mes-4-C), 27.5 (CH₃, Mes-2-C), 115.0 (CH,

3-C of germabenzene ring), 128.0 (CH-Mes) 138.0 (4°, Mes), 138.2 (4°, 2-C of germabenzene ring), 140.2 (4°, Mes), 142.4 (4°, Mes), 148.0 (CH, 4-C of germabenzene ring); HRMS (APCI, positive) Calc. for $C_{32}H_{56}GeSi_2$ [M⁺]: 570.3133. Found: 570.3152. Purity of **4-Mes** was confirmed by ¹H NMR spectrum shown in Figure S3.

Estimation of the yield of 4-Mes using KHMDS by ¹H NMR spectroscopy

To a toluene solution (0.5 mL) of **5** (20.0 mg, 38.3 μ mol), toluene solution (0.5 mL) of KHMDS (7.6 mg, 38 μ mol) was added under argon atmosphere to generate **3**. After stirred for 5 min, a toluene suspension (1.0 mL) of MesLi (4.8 mg, 38 μ mol) was add to the reaction mixture. The suspension was stirred for 6 h. After removal of volatiles, phananthrene (6.8 mg, 38 μ mol) as an internal standard was added. The residue was filtered through a pad of Celite[®] with hexane. The yield of **4-Mes** was estimated by ¹H NMR spectroscopy (72%).

Synthesis of acridyl-substituted germabenzene 4-Acr using Mes*Li

To a diethyl ether solution (2.2 mL) of **5** (100 mg, 0.191 mmol), Mes*Li (53.0 mg, 0.210 mmol) was added under argon atmosphere to generate **3**. To a mixture, diethylether solution of acridyllithium prepared from 9-bromoacridine (49.3 mg, 0.191 mmol) and "BuLi/hexane (74.0 μ L, 2.76 M, 0.191 mmol) in Et₂O (2.2 mL) was added at –35 °C. The reaction mixture was stirred for 10 h at –35 °C, then removal of volatiles, the residue was filtered through a pad of Celite[®] with hexane. The resulting solution was concentrated and recrystallized from hexane to give pure **4-Acr** as greenish yellow crystals (34.9 mg, 55.6 μ mol, 29%): mp (in a sealed tube) 168-170 °C (dec); ¹H NMR (C₆D₆, 399 MHz) & 0.50-0.91 (m, 42H), 7.02-7.07 (m, 3H), 7.24 (ddd, *J* = 1, 7, 9 Hz, 2H), 8.26 (d, *J* = 8 Hz, 2H), 8.39 (d, *J* = 9 Hz, 4H); ¹³C NMR (C₆D₆, 100 MHz) & 12.5 (CH), 19.1 (CH₃), 115.8 (CH, 4-C of germabenzene), 126.0 (CH, Acr-H), 130.2 (CH, Acr-H), 131.3 (CH, Acr-H), 132.0 (CH, Acr-H), 142.1 (4°, 2-C of germabenzene ring), 148.4 (CH, 3-C of germabenzene ring), 149.1 (4°, Acr) 151.5 (4°, Acr) ; HRMS (APCI, positive) Calc. for C₃₆H₅₃GeNSi₂ [M + H]⁺: 630.3009, Found: 630.2993. Purity of **4-Acr** was confirmed by ¹H NMR spectrum shown in Figure S4.

Estimation of the yield of 4-Acr using Mes*Li by ¹H NMR spectroscopy

To a diethyl ether solution (0.5 mL) of **5** (20.0 mg, 38.3 μ mol), Mes*Li (10.6 mg, 42.1 μ mol) was added under argon atmosphere to generate **3**. To a mixture, diethyl ether solution of acridyllithium prepared from 9-bromoacridine (9.9 mg, 38.3 μ mol) and ^{*n*}BuLi/hexane (14.0 μ L, 2.76 M, 38.3 μ mol) in Et₂O (0.5 mL) was added at –35 °C. The reaction mixture was stirred for 6 h at –35 °C, then removal of volatiles, adamantane (2.4 mg, 19 μ mol) as an internal standard was added. The residue was filtered through a pad of Celite[®] with hexane. The yield of **4-Acr** was estimated by ¹H NMR spectroscopy (73%).

Synthesis of acridyl-substituted germabenzene 4-Acr using KHMDS

To a diethyl ether solution (3.0 mL) of **5** (200 mg, 0.382 mmol), diethyl ether solution (3.0 mL) of KHMDS (76.4 mg, 0.382 mmol) was added under argon atmosphere to generate **3**. To a mixture, diethylether solution of acridyllithium prepared from 9-bromoacridine (98.8 mg, 0.382 mmol) and ^{*n*}BuLi/hexane (140 μ L, 2.76 M, 0.382 mmol) in Et₂O (6.0 mL) was added at –35 °C. The reaction mixture was stirred for 10 h at –35 °C, then removal of volatiles, the residue was filtered through a pad of Celite[®] with hexane. The resulting solution was concentrated and recrystallized from hexane to give pure **4-Acr** as greenish yellow crystals (34.6 mg, 55.0 μ mol, 14%).

Synthesis of Mes-substituted germabenzene 4-Mes by using 2 equiv. of MesLi

To a toluene solution (0.5 mL) of **5** (20.0 mg, 38.3 μ mol) and MesLi (10.1 mg, 80.4 μ mol) was added under argon atmosphere. After stirring for 11 h, a reaction mixture was concentrated under vacuum and phananthrene (6.8 mg, 38 μ mol) as an internal standard was added. The residue was filtered through a pad of Celite[®] with hexane. The yield of **4-Mes** was estimated by ¹H NMR spectroscopy (81%).



Figure S1. ¹H (top) and ¹³C (bottom) NMR spectra of 5 in C_6D_6 . •:residual solvent signal.



Figure S2. ¹H NMR spectrum of in-situ generated **3** in C_6D_6 using Mes*Li (top) and KHMDS (bottom). •:residual solvent signal, *: tri(tert-butyl)benzene, °: hexamethyldisilazane, x: phenanthrene as an internal standard.



Figure S3. ¹H (top) and ¹³C (bottom) NMR spectra of **4-Mes** inC₆D₆). •:residual solvent signal.



Figure S4. ¹H (top) and ¹³C (bottom) NMR spectra of **4-Acr** in C_6D_6 . •:residual solvent signal.

2. X-ray Crystallographic Analysis

Crystallographic data for **2**, **4-Mes**, and **4-Acr** are summarized in table S1. The crystals were coated with immersion oil and put on a MicroMountTM (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Rigaku Saturn CCD or a Bruker Photon detectors using MoK α radiation. The Bragg spots were integrated using CrysAlis^{Pro} program package.^{S4} Absorption corrections were applied. All the following procedure for analysis, Yadokari-XG 2009 was used as a graphical interface.^{S5} The structure was solved by a direct method with programs of SIR2014^{S6} or SHELEXT^{S7} and refined by a full-matrix least squares method with the program of SHELXL-2014 or SHELXL-2018.^{S7} Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions, and refined applying riding models. The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 1886739 (**2**), CCDC 1886740 (**4-Mes**), and CCDC 1886741 (**4-Acr**). A copy of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request.

	2	4-Mes	4-Acr
Formula	$C_{23}H_{46}Cl_2GeSi_2$	$C_{32}H_{56}GeSi_2$	C ₃₆ H ₅₃ GeNSi ₂
M	522.27	569.53	628.56
T/\mathbf{K}	93	113	123
color	colorless	colorless	yellow
size / mm	0.30 x 0.14 x 0.10	0.80 x 0.02 x 0.02	0.40 x 0.38 x 0.36
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_{1}/m$	$P2_{1}/n$	$P2_1$
<i>a</i> / Å	7.742(2)	15.4609(14)	9.3730(2)
<i>b</i> / Å	25.402(6)	9.2117(9)	29.3546(9)
<i>c</i> / Å	7.893(2)	23.847(3)	12.7365(3)
lpha / °	90	90	90
eta / °	114.755(3)	100.048(9)	93.073(2)
γ/\circ	90	90	90
$V/\text{\AA}^3$	1409.6(6)	3344.2(6)	3499.29(15)
Ζ	2	4	4
D_x / g cm ⁻³	1.230	1.131	1.193
μ / mm-1	1.369	1.005	0.968
<i>F</i> (000)	556	1232	1344
heta range / °	3.006 to 27.430	2.375 to 25.999	1.745 to 25.000
reflections collected	11373	24280	25635
unique reflections	3259	6402	11482
refined parameters	140	331	745
GOF on F^2	1.181	1.040	1.034
$R1 \left[I > 2\sigma(I)\right]^{a}$	0.0405	0.0597	0.0273
wR2 $[I > 2\sigma(I)]^{b}$	0.1069	0.1223	0.0591
R1 (all data) ^a	0.0467	0.1116	0.0294
wR2 (all data) ^b	0.1096	0.1481	0.0615
$\Delta ho_{ m min}$, $_{ m max}$ / e Å ⁻³	0.684, -0.669	0.802, -0.882	0.545, -0.493

	Table S1.	Crystallog	raphic data	a for 2 ,	4-Mes,	and 4-Ac	r.
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^a $R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|, ^b wR2 = [\Sigma {w(Fo^2 - Fc^2)^2 / \Sigma w(Fo^2)^2}]^{1/2}$



Figure S5. Molecular structure of **2** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **2**: Ge1–C1 = 1.918(3), Ge1–Cl1 = 2.1779(12), Ge1–Cl2 = 2.1580(12), C1–C2 = 1.342(4), C1–Si1 = 1.890(3), C2–C3 = 1.518(4), C1–Ge1–C1* = 109.34(18), Ge1–C1–C2 = 110.0(2), C1–C2–C3 = 128.5(3), C2–C3–C2* = 118.6(4).



Figure S6. A) Molecular structure of **4-Mes** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. **B**) Side view of germabenzene ring. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond distances (Å) and angles (°) for **4-Mes**: Ge1–C1 = 1.867(4), Ge1–C5 = 1.861(4), Ge1–C6 = 1.951(4), C1–C2 = 1.414(5), C1–Si1 = 1.886(4), C2–C3 = 1.395(5), C3–C4 = 1.387(5), C4–C5 = 1.423(5), C5–Si2 = 1.880(4), C1–Ge1–C5 = 111.26(17), Ge1–C1–C2 = 112.4(3), C1–C2–C3 = 128.6(4), C2–C3–C4 = 126.6(4), C3–C4–C5 = 128.8(4), C4–C5–Ge1 = 112.2(3), C1–Ge1–C6 = 123.05(16), C5–Ge1–C6 = 125.54(17).



Figure S7. Molecular structure of **4-Acr** (50% thermal ellipsoid probability). There are two crystallographically independent molecules in asymmetric unit. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **4-Acr**: Ge1–C1 = 1.861(4), Ge1–C5 = 1.854(4), Ge1–C6 = 1.954(3), C1–C2 = 1.406(5), C2–C3 = 1.394(5), C3–C4 = 1.381(6), C4–C5 = 1.405(5), C1–Ge1–C5 = 111.91(16), Ge1–C1–C2 = 111.9(3), C1–C2–C3 = 128.2(4), C2–C3–C4 = 127.3(3), C3–C4–C5 = 128.7(3), C4–C5–Ge1 = 111.9(3), C1–Ge1–C6 = 122.13(16), C5–Ge1–C6 = 125.90(16), Ge2–C37 = 1.857(4), Ge2–C41 = 1.866(4), Ge2–C42 = 1.963(3), C37–C38 = 1.399(5), C38–C39 = 1.397(5), C39–C40 = 1.386(6), C40–C41 = 1.407(5), C37–Ge2–C41 = 111.88(16), Ge2–C37–C38 = 112.2(3), C37–C38–C39 = 128.6(4), C38–C39–C40 = 126.7(3), C39–C40–C41 = 129.3(3), C40–C41–Ge2 = 111.3(3), C37–Ge2–C42 = 120.16(16), C41–Ge2–C42 = 127.74(16).

3. UV-vis Absorption Spectra

UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer using a 10 mm square quartz cell. Dry hexane was used for the sample solution. UV-vis spectra of **4-Mes**, **4-Acr** and acridine are shown in Figure S8-10.



Figure S8. UV-vis absorption spectra of **4-Mes** (yellow line) and **4-Acr** (red line) at room temperature in hexane. λ_{max} of **4-Mes** (ε): 346 nm (5500), λ_{max} of **4-Acr** (ε): 386 nm (5700), 364 nm (9900), 346 nm (12000).



Figure S9. Normalized UV-vis absorption spectra of **4-Acr** (red line) and acridine (blue line) at room temperature in hexane. λ_{max} of **4-Acr**: 386 nm, 364 nm, 346 nm; λ_{max} of acridine: 371 nm, 355 nm, 339 nm.



Figure S10. UV-vis absorption spectra of **4-Acr** in hexane (red line) and THF (yellow line) at room temperature in hexane. λ_{max} of **4-Acr** in hexane (ε): 386 nm (5700), 364 nm (9900), 346 nm (12000); λ_{max} of **4-Acr** in THF (ε): 389 nm (5700), 365 nm (9700), 346 nm (12000).

4. Theoretical Calculations

Theoretical calculations were carried out by using Gaussian 16 program package.^{S8} The geometry optimizations of **4-Mes**, and **4-Acr** were performed at the B3LYP/6-31G(d)^{S9-11} level of theory. The optimized structures and selected structural parameters of **4-Mes**, and **4-Acr** are shown in Figures S11 and S12. The HOMO and LUMO of optimized structures of **4-Mes**, and **4-Acr** are shown in Figures S13 and S14. The calculated excitation energies of **4-Acr** at the B3LYP/6-311+G(2d,p) were summarized in Table S2.



Figure S11. Optimized structure of **4-Mes** at the B3LYP/6-31G(d) level of theory. Selected bond distances (Å) and angles (°) for **4-Mes**: Ge1–C1 = 1.853, Ge1–C5 = 1.853, Ge1–C6 = 1.943, C1–C2 = 1.408, C1–Si1 = 1.889, C2–C3 = 1.399, C3–C4 = 1.399, C4–C5 = 1.408, C5–Si2 = 1.889, C1–Ge1–C5 = 110.61, Ge1–C1–C2 = 113.28, C1–C2–C3 = 128.48, C2–C3–C4 = 125.82, C3–C4–C5 = 128.48, C4–C5–Ge1 = 113.28, C1–Ge1–C6 = 124.57, C5–Ge1–C6 = 125.57.



Figure S12. Optimized structure of **4-Acr** at the B3LYP/6-31G(d) level of theory. Selected bond distances (Å) and angles (°) for **4-Acr**: Ge1–C1 = 1.848, Ge1–C4 = 1.957, C1–C2 = 1.406, C1–Si1 = 1.894, C2–C3 = 1.401, C1–Ge1–C1* = 111.84, Ge1–C1–C2 = 112.57, C1–C2–C3 = 128.31, C2–C3–C2* = 126.37, C1–Ge1–C4 = 124.08.



Figure S13. Selected MOs of **4-Mes** calculated at the B3LYP/6-31G(d) level of theory.















Figure S14. Selected MOs of 4-Acr calculated at the B3LYP/6-31G(d) level.

excited state	transition energy / eV	wavelength / nm	oscillator strength	orbital number
1	2.5063	494.69	0.0002	168 -> 169 (0.70612)
2	3.0992	400.05	0.0853	167 -> 169 (0.69988)
3	3.5852	345.82	0.0004	160 -> 169 (0.57316)
				161 -> 169 (-0.25907)
				163 -> 169 (0.26248)
				164 -> 169 (0.15130)
4	3.6539	339.32	0.0035	166 -> 169 (0.69510)
5	3.7823	327.80	0.0019	165 -> 169 (0.68991)
6	3.7884	327.27	0.0380	163 -> 169 (-0.20203)
				164 -> 169 (0.53613)
				167 -> 171 (0.34970)
				167 -> 172 (0.14192)
7	4.0093	309.25	0.0016	160 -> 169 (-0.30640)
				162 -> 169 (-0.16978)
				163 -> 169 (0.52957)
				164 -> 169 (0.26238)
				168 -> 171 (-0.11074)
8	4.0386	307.00	0.0712	163 -> 169 (0.11310)
				166 -> 170 (-0.16832)
				168 -> 171 (0.63838)
				166 -> 170 (-0.18252)
				105 -> 110 (-0.17989)
				106 –> 113 (0.33767)

Table S2. Calculated electronic transitions of **4**-Acr by TD-DFT method (number of states: 8) at the B3LYP/6-311+G(2d,p) level (168th orbital and 169th orbitals are the HOMO and LUMO).

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