Supplementary Information for

Reversible Addition of Terminal Alkenes to Digermynes

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All manipulations were carried out under an argon atmosphere, using either Schlenk line or glove box techniques. All solvents were purified by standard methods and/or the Ultimate Solvent System, Glass Contour Company.\(^{S1}\) Remaining trace amounts of water and oxygen in the solvents were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. \(^1\)H and \(^{13}\)C NMR spectra were measured on a JEOL JNM-ECA600 (\(^1\)H: 600 MHz, \(^{13}\)C: 151 MHz) in the Joint Usage/Research Center (JURC, Institute for Chemical Research, Kyoto University) or on a JEOL AL-300 spectrometer (\(^1\)H: 300 MHz, \(^{13}\)C: 75 MHz). Signals arising from residual C\(_6\)D\(_6\) (7.15 ppm) in the C\(_6\)D\(_6\) or C\(_6\)D\(_3\)CD\(_2\)H (2.08 ppm, –CD\(_2\)H) in toluene-\(d_8\) were used as internal standards for the \(^1\)H NMR spectra, whereas the signals of C\(_6\)D\(_6\) (128.0 ppm) and toluene-\(d_8\) (137.48 ppm, –C–CD\(_3\)) were used to reference the \(^{13}\)C NMR spectra. High-resolution mass spectra (HRMS) were obtained from a Bruker micrOTOF focus-Kci mass spectrometer (DART). All melting points were determined on a Büchi Melting Point apparatus M-565 and are uncorrected. Digermynes BbtGe=GeBbt and TbbGe=GeTbb (Bbt: 2,6-[CH(SiMe\(_3\))\(_2\)]\(_2\)-4-[C(SiMe\(_3\))\(_3\)]-C\(_6\)H\(_2\); Tbb: 4-tBu-2,6-[CH(SiMe\(_3\))\(_2\)]\(_2\)-C\(_6\)H\(_2\)) were prepared according to literature procedures.\(^{S2,S3}\)

2. Experimental Details.

**Synthesis of 1,2-Bbt\(_2\)-1,2-digermacyclobutene (10a):** A hexane solution (0.2 mL) of digermyne 5a (24.0 mg, 17.2 \(\mu\)mol) was treated with styrene (2.5 mg, 24.0 \(\mu\)mol, 1.4 equiv.) for 10 min at room temperature. After the solvent and residual styrene were removed under reduced pressure, 1,2-digermacyclobutene 10a was obtained as a purple solid (24.5 mg, 16.6 \(\mu\)mol, 97%). 10a: purple solid, mp 90.5-91.5 °C (dec); \(^1\)H NMR (600 MHz, toluene-\(d_8\), 253 K): \(\delta\) 0.35 (s, 36H), 0.36 (s, 36H), 0.40 (s, 54H), 2.54 (bs, 2H), 2.83 (bs, 2H), 3.19 (dd, \(J = 13.8, 4.8\) Hz, 1H), 3.26 (dd, \(J = 13.8, 7.8\) Hz, 1H), 4.88 (dd, \(J = 7.8, 4.8\) Hz, 1H), 6.96–7.01 (m, 5H), 7.19–7.22 (m, 2H), 7.58 (d, \(J = 7.2\) Hz, 2H); \(^{13}\)C NMR (151 MHz, toluene-\(d_8\), 253 K): \(\delta\) 2.08 (q), 5.63 (q), 5.64 (q), 34.98 (d), 35.03 (s), 45.41 (t), 55.39 (d), 125.26 (d), 126.57 (d), 126.83 (d), 127.61 (d), 129.15 (d), 137.40 (s), 142.46 (s), 146.09 (s), 146.27 (s), 146.89 (s), 147.56 (s), 150.45 (s), 150.98 (s); UV/vis [0.334 mM, n-hexane]: \(\lambda_{\text{max}}\) (nm, \(\varepsilon\)) = 459 (5,600); MS (DART-TOF, positive mode): \(m/z\) calcd for C\(_{68}\)H\(_{144}\)Ge\(_2\)Si\(_{14}\) 1499.6383 ([M+H]\(^+\)), found 1499.6438 ([M+H]\(^+\)).
Synthesis of 1,2-Bbt₂-1,2-digermacyclobutene (11): A hexane solution (0.3 mL) of digermyne 5a (22.5 mg, 16.1 µmol) was treated with 1-hexene (5.1 mg, 60.6 µmol, 3.8 equiv.) for 10 min at room temperature. After the solvent and residual 1-hexene were removed under reduced pressure, 1,2-digermacyclobutene 11 was obtained as a purple solid (22.7 mg, 15.4 µmol, 96%). 11: purple solid, mp 52.4-53.4 °C (dec); ¹H NMR (600 MHz, C₆D₆, 273 K): δ 0.28 (s, 36H), 0.36 (s, 36H), 0.36 (s, 54H), 0.98 (t,  J = 7.4 Hz, 3H), 1.36–1.49 (m, 2H), 1.59–1.79 (m, 2H), 2.18 (dd,  J = 13.5, 1.8 Hz, 1H), 2.48–2.53 (m, 1H), 2.56 (bs, 2H), 2.65 (bs, 2H), 3.53 (ddd,  J = 13.5, 6.6, 1.8 Hz, 1H), 6.91 (bs, 2H), 6.93 (bs, 2H); ¹³C NMR (151 MHz, C₆D₆, 273 K): δ 1.88 (q), 5.62 (q), 5.68 (q), 14.65 (q), 23.53 (t), 34.55 (t), 34.66 (s), 34.76 (d), 39.69 (t), 45.71 (t), 52.79 (d), 126.76 (d), 126.85 (d), 145.53 (s), 145.65 (s), 146.95 (s), 149.33 (s), 150.04 (s), 150.93 (s); UV/vis [2.48 mM, n-hexane]: λ_max (nm, ε) = 473 (2,000); MS (DART-TOF, positive mode): m/z calcd for C_{66}H_{147}Ge₂Si_{14} 1478.6618 ([M]+), found 1478.6669 ([M]+).

Synthesis of 1,2-Bbt₂-1,2-digermacyclobutene (10b): A hexane solution (0.5 mL) of digermyne 5b (28.4 mg, 27.2 µmol) was treated with styrene (3.0 mg, 28.8 µmol, 1.1 equiv.) for 10 min at room temperature. After the solvent and residual styrene were removed under reduced pressure, the residue was recrystallized from hexane to afford 1,2-digermacyclobutene 10b as stable orange crystals in quantitative yield (31.4 mg, 27.2 µmol, quant). 10b: orange crystals, mp 135.7-136.7 °C (dec); ¹H NMR (300 MHz, C₆D₆, 298 K): δ 0.18 (s, 36H), 0.25 (s, 36H), 1.30 (s, 18H), 2.86 (s, 4H), 2.93 (dd,  J = 14.1, 8.1 Hz, 1H), 3.47 (dd,  J = 14.1, 5.1 Hz, 1H), 5.13 (dd,  J = 8.1, 5.1 Hz, 1H), 6.93–6.99 (m, 5H), 7.18 (t,  J = 7.7 Hz, 2H), 7.55 (d,  J = 7.7 Hz, 2H); ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 1.04 (q), 1.24 (q), 31.25 (q), 33.87 (d), 34.49 (s), 46.42 (t), 54.55 (d), 121.66 (d), 125.23 (d), 126.93 (d), 129.08 (d), 147.32 (s), 147.51 (s), 148.11 (s), 151.33 (s); UV/vis [0.383 mM, n-hexane] λ_max (nm, ε) = 462 (5,700); MS (DART-TOF, positive mode): m/z calcd for C_{64}H_{111}Ge₂Si_{14} 1151.4950 ([M+H]⁺), found 1151.4889 ([M+H]⁺).
Figure S1. $^1$H NMR spectrum of 10a in toluene-$d_8$.

Figure S2. $^{13}$C NMR spectrum of 10a in toluene-$d_8$. 

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**Figure S3.** $^1$H NMR spectrum of 11 in toluene-$d_8$.

**Figure S4.** $^{13}$C NMR spectrum of 11 in toluene-$d_8$. 
Figure S5. $^1$H NMR spectrum of 10b in C$_6$D$_6$.

Figure S6. $^{13}$C NMR spectrum of 10b in C$_6$D$_6$. 
Regeneration of 1,2-Bbt₂-1,2-digermyne (5a) from 1,2-Bbt₂-1,2-digermacyclobutenes 10a/11: Solutions of 10a or 11 (10a: 7.2 µmol, 11: 4.2 µmol) in toluene-\textsubscript{d₈} (10a: 0.38 mL, 11: 0.40 mL) were heated for 1 h under reduced pressure (10a: 80 °C, 11: 60 °C). Judging from the \textsuperscript{1}H NMR spectra, 5a was regenerated in high NMR yield (10a: 81%, 11: 97%).

Figure S7. Regeneration of 1,2-Bbt₂-1,2-digermyne (5a) from 10a or 11.

VT \textsuperscript{1}H NMR spectra of 1,2-Bbt₂-1,2-digermacyclobutenes 10a or 11 in toluene-\textsubscript{d₈}: Solutions of 10a or 11 (10a: 8.1 mg, 5.4 µmol, 11: 22.5 mg, 15.4 µmol) in toluene-\textsubscript{d₈} (10a: 0.45 mL, 11: 0.50 mL) were monitored by \textsuperscript{1}H NMR spectroscopy at various temperatures. A van’t Hoff analysis established sufficiently small values for the Gibbs free energy values of the equilibrium reactions between 10a or 11 and alkenes 8 and 9 (10a: \(\Delta H = -20.4 \text{ kcal/mol}, \Delta S = -58.2 \text{ cal/mol} \cdot \text{K}, \Delta G_{298K} = -3.1 \text{ kcal/mol}, 11: \Delta H = -21.0 \text{ kcal/mol}, \Delta S = -55.0 \text{ cal/mol}, \Delta G_{298K} = -4.5 \text{ kcal/mol})$, respectively.
Figure S8. VT $^1$H NMR spectra of 5a + 8 $\rightleftharpoons$ 10a in toluene-$d_8$ (left: 4.7–5.9 ppm; right: 2.5–3.3 ppm).

Table S1. VT $^1$H NMR and temperature data for the reaction 5a + 8 $\rightleftharpoons$ 10a.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>5a</th>
<th>8</th>
<th>10a</th>
<th>K</th>
<th>ln(K)</th>
<th>1/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>0.002692</td>
<td>0.002790</td>
<td>0.009245</td>
<td>1231</td>
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<td>293</td>
<td>0.004671</td>
<td>0.004964</td>
<td>0.007266</td>
<td>313.4</td>
<td>5.749</td>
<td>0.003413</td>
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<tr>
<td>303</td>
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<td>0.004965</td>
<td>98.13</td>
<td>4.587</td>
<td>0.003300</td>
</tr>
<tr>
<td>313</td>
<td>0.009086</td>
<td>0.009354</td>
<td>0.002851</td>
<td>33.54</td>
<td>3.513</td>
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<tr>
<td>323</td>
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<td>0.001542</td>
<td>13.83</td>
<td>2.626</td>
<td>0.003096</td>
</tr>
</tbody>
</table>

[a] The uncertainty for the integrations was estimated to be typically 5%, while that of the temperatures was 1 °C (determined by monitoring the VT NMR).
Figure S9. Plot of ln(K) as a function of T$^{-1}$ for 5a + 8 ⇄ 10a [$\Delta H = -20.4(\pm 1.1)$ kcal/mol, $\Delta S = -58.2(\pm 3.8)$ cal/mol·K, $\Delta G_{298K} = -3.1(\pm 0.2)$ kcal/mol].

$y = 10326x - 29.418$  
$R^2 = 0.999$

Figure S10. VT$^1$H NMR spectra for 5a + 9 ⇄ 11 in toluene-$d_8$ (2.8–5.1 ppm).
Table S2. VT $^1$H NMR and temperature data for $5a + 9 \rightleftharpoons 11$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$5a$</th>
<th>9</th>
<th>11</th>
<th>K</th>
<th>ln(K)</th>
<th>1/T</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>0.003095</td>
</tr>
</tbody>
</table>

Figure S11. Plot of ln(K) as a function of $T^{-1}$ for $5a + 9 \rightleftharpoons 11$ [$\Delta H = -21.0(\pm 2.4)$ kcal/mol, $\Delta S = -55.0(\pm 7.9)$ cal/mol·K, $\Delta G_{298K} = -4.5(\pm 0.3)$ kcal/mol].

**Reaction of 1,2-Bbt$_2$-1,2-digermacyclobutene 10a with an excess of ethylene in C$_6$D$_6$:** In a J-Young Schlenk tube, a solution of 10a (12.2 mg, 8.8 µmol) in C$_6$D$_6$ (0.5 mL) was degassed by several freeze-pump-thaw cycles. Subsequently, the degassed solution was exposed to an excess of ethylene (~1 atm) at room temperature for 20 min, before all volatiles were removed *in vacuo* at room temperature to afford 1,2-Bbt$_2$-1,2-digermacyclobutene 6 in quantitative yield (12.3 mg, 8.8 µmol).
3. X-Ray Crystallographic Analysis.

Single crystals of [10a·C₆H₆], 11, and 10b were obtained from recrystallization of the respective target compounds in benzene (10a) or n-hexane (11, 10b) at room temperature (10a) or –20 °C (11, 10b) in an argon-filled glove box. Intensity data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo optics using MoKα radiation (10a: λ = 0.71069 Å, 11: λ = 0.71075 Å, 10b: λ = 0.71073 Å). The crystal data are shown in reference 20 of the main manuscript. All structures were solved by direct methods (SIR2004) and refined by a full-matrix least square method on F² for all reflections (SHELXL-97). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC; reference numbers: CCDC-1583291 for [10a·C₆H₆], CCDC-1583292 for 11, and CCDC-1583293 for 10b), and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

4. Theoretical calculations.

The level of theory and the basis sets used for the structural optimization are contained within the main text. Frequency calculations confirmed minimum energies for all optimized structures. All calculations were carried out on the Gaussian 09 (Revision D.01) program package. Computational time was generously provided by the Supercomputer Laboratory in the Institute for Chemical Research (Kyoto University).

5. References

S6) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.