Supporting Information

for

**Bis(chlorogermyliumylidene) and its Significant Role in an Elusive Reductive Cyclization**

Moumita Majumdar*, Ravindra K. Raut, Padmini Sahoo and Vikas Kumar

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1. Experimental details

General Remarks. All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk techniques or in a dry box. Tetrahydrofuran was refluxed over sodium/benzophenone. Dichloromethane and acetonitrile were stirred and refluxed over calcium hydride and kept over molecular sieves. All solvents were distilled and stored under argon and degassed prior to use. CD$_3$CN ampoules were purchased from Sigma Aldrich and used as is. All chemicals were used as purchased. Compound 1 and the organosilicon reducing agent 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine were synthesized following the reported literature procedures. $^1$H and $^{13}$C NMR spectra were referenced to external SiMe$_4$ using the residual signals of the deuterated solvent ($^1$H) or the solvent itself ($^{13}$C). $^{19}$F NMR was referenced to external C$_6$H$_5$CF$_3$ (TFT). NMR spectra were recorded on Bruker AVANCE III HD ASCEND 9.4 Tesla/400 MHz and Jeol 9.4 Tesla/400 MHz spectrometer. HRMS spectrum was acquired on Waters Acquity UPLC coupled with SYNAPT G2 mass spectrometer. Solution phase UV/Vis spectra were acquired using a Thermo-Scientific Evolution 300 spectrometer using quartz cells with a path length of 1 cm. Cyclic Voltammetry studies were performed with SP-300 Potentiostat/Galvanostat Biologic Science Instruments. EPR spectra were recorded on X-band Bruker EMX Plus at IIT Bombay and IISER Kolkata. Melting points were determined under argon in closed NMR tubes and are uncorrected. Elemental analyses were performed on Elementar vario EL analyzer. Single crystal data were collected on Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector (Bruker Systems Inc.) with a Cu Kα radiation (1.5418 Å).

Synthesis of 2

Compound 1 (0.5 g, 0.78 mmol) and GeCl$_2$, dioxane (0.18 g, 0.78 mmol) were dissolved in 30 mL of acetonitrile and stirred at room temperature for 12 hours. The solvent was removed completely under vacuum yielding 0.57 g (93%) of 2 (decomp. 153-155°C) as pale yellow solid.

Crystals suitable for X-ray measurement were grown by layering acetonitrile solution of the compound with diethyl ether at room temperature.

$^1$H NMR (400 MHz, CD$_3$CN) δ = 9.18 (d, J = 4.9, 2H, o-Pyr-H); 8.60 (t, J = 7.5, 2H, p-Pyr-H); 8.52 (d, J = 8.2, 2H, m-Pyr-H); 8.16 (t, J = 6.2, 2H, m-Pyr-H); 4.61 (s, 4H, -CH$_2$-CH$_2$-); 2.88 (s, 6H, -CH$_3$) ppm.

$^{13}$C NMR (101 MHz, CD$_3$CN) δ = 178.03 (C-CH$_3$); 148.95 (Pyr-C$_o$); 146.91 (Pyr-C$_o$); 145.11 (Pyr-C$_p$); 130.88 (Pyr-C$_m$); 128.78 (Pyr-C$_m$); 122.45, 119.27 (CF$_3$SO$_3$); 47.71 (-CH$_2$-CH$_2$-); 17.04 (C-CH$_3$).

$^{19}$F NMR (377 MHz, CD$_3$CN) δ = -79.31 (TMSOTf- F) ppm.

UV/Vis (acetonitrile) $\lambda_{\text{max}}$ (ε) 337 nm (4457 M$^{-1}$cm$^{-1}$).

Elemental Analysis: Calcd. for C$_{18}$H$_{18}$Cl$_2$F$_6$Ge$_2$N$_4$O$_3$S$_2$: C, 27.70; H, 2.32; N, 7.18. Found: C, 27.55; H, 2.71; N, 7.28.

Synthesis of 2-I

1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.087 g, 0.38 mmol) was dissolved in 10 mL of acetonitrile and was added dropwise to a 20 mL acetonitrile solution of compound 2 (0.3 g, 0.38 mmol) maintaining temperature at 0°C. The resultant intense green-blue solution was stirred for 10 minutes before adding trifluoroacetic acid (0.059 mL, 0.77 mmol). The volatile by-products were removed completely under vacuum. The solid was then redissolved in 8-10 mL of acetonitrile from which colourless single crystals of 2-I appeared (crystallization yield = 0.036 g (15%)), (decomp. 164-166°C).
**Synthesis of Piperazine 3**

1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.058 g, 0.26 mmol) was dissolved in 10 mL of acetonitrile and was added dropwise to a 15 mL acetonitrile solution of compound 2 (0.2 g, 0.26 mmol) maintaining temperature at 0°C. The resultant intense blue-green solution was stirred for 10 minutes before quenching with trifluoroacetic acid (0.08 mL, 1.02 mmol). The volatile by-products were removed completely under vacuum. The solid residue was then washed with NaHCO₃ (10% w/v, ca. 10 mL) and the aqueous layer was extracted twice with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and concentrated giving yellow viscous oil. The viscous oil was dissolved in ~2 mL of dichloromethane and added dropwise to 20 mL of n-pentane giving a white precipitate. The white precipitate was dried under vacuum yielding 0.048 g (70%) of 3 (melting point 118 °C).

**1H NMR (400 MHz, CD₃CN) δ = 8.29 (dd, J = 4.8, 1.9, 1, 2H, o-Pyr-H); 7.47 (td, J = 8.2, 2, 2H, p-Pyr-H); 7.26 (dt, J = 8.2, 1, 2H, m-Pyr-H); 6.97 (dd, J = 7.5, 4.8, 1, 2H, m-Pyr-H); 4.50 (br., 2H, NH); 3.10-3.27 (m, 4H, -CH₂₂-CH₂₂-); 1.87 (s, 6H, -CH₃).

**13C NMR (101 MHz, CD₃CN) δ = 162.62 (Pyr-C₀); 146.94 (Pyr-C₀); 136.53 (Pyr-Cₚ); 121.71 (Pyr-Cₘ), 121.24 (Pyr-Cₘ), 62.22 (C-CH₃); 40.21 (-CH₂₂-CH₂₂-); 23.72 (C-CH₃).

**Elemental Analysis:** Calcd. For C₁₈H₂₀N₄O₆S₂: C, 33.83; H, 3.15; N, 8.77. Found: C, 33.95; H, 3.42; N, 8.82.

**Synthesis of Piperazinium bis(trifluoromethanesulfonate) 4**

**Method A:** 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.072 g, 0.32 mmol) was dissolved in 10 mL of acetonitrile and was added dropwise to a 20 mL acetonitrile solution of compound 2 (0.25 g, 0.32 mmol) maintaining temperature at 0°C. The resultant intense green-blue solution was stirred for 10 minutes before quenching with trifluoroacetic acid (0.1 mL, 1.28 mmol). The volatile by-products were removed completely under vacuum. The solid residue was then dissolved in 10 mL of tetrahydrofuran and filtered. The filtrate was concentrated and layered with diethyl ether to get colorless crystals of 4 (crystallization yield = 0.124 g (68%); decomp. 173-175 °C).

**1H NMR (400 MHz, CDCl₃) δ = 7.47 (td, J = 8.2, 2, 2H, p-Pyr-H); 7.26 (dt, J = 8.2, 1, 2H, m-Pyr-H); 6.97 (dd, J = 7.5, 4.8, 1, 2H, m-Pyr-H); 4.50 (br., 2H, NH); 3.10-3.27 (m, 4H, -CH₂₂-CH₂₂-); 1.87 (s, 6H, -CH₃).

**13C NMR (101 MHz, CDCl₃) δ = 162.62 (Pyr-C₀); 146.94 (Pyr-C₀); 136.53 (Pyr-Cₚ); 121.71 (Pyr-Cₘ), 121.24 (Pyr-Cₘ), 62.22 (C-CH₃); 40.21 (-CH₂₂-CH₂₂-); 23.72 (C-CH₃).

**Elemental Analysis:** Calcd. For C₁₆H₂₉N₄O₆S₂⁺: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.79; H, 7.71; N, 20.92.

**HRMS (ESI-TOF) calculated for [C₁₆H₂₀N₄ + H]⁺ 269.1758; found 269.1788.**

**Method B:** Trifluoromethanesulfonic acid (0.034 mL, 0.39 mmol) was added to 5 mL dichloromethane solution of piperazine 3 (0.05 g, 0.19 mmol). The solution was stirred for 1 hour and then added to 20 mL of hexane resulting in white precipitate. The white precipitate was filtered, dried under vacuum yielding 0.09 g (86%) of 4 as white solid.
1H NMR (400 MHz, CD$_3$CN) δ = 9.07 (br., 4H, NH$_2$); 8.44 (ddd, $J = 4.8$, 1.8, 1, 2H, o-Pyr-H); 7.77 (td, $J = 7.8$, 1.4, 2H, p-Pyr-H); 7.42 (d, $J = 8.2$, 2H, m-Pyr-H); 7.34 (dd, $J = 7.6$, 4.9, 2H, m-Pyr-H); 4.11 (m, 2H, -CH$_2$-); 3.72 (m, 2H, -CH$_2$-); 2.17 (s, 6H, -CH$_3$).

13C NMR (101 MHz, CD$_3$CN) δ = 153.12 (Pyr-C$_a$); 147.81 (Pyr-C$_o$); 138.52 (Pyr-C$_p$); 124.75 (Pyr-C$_m$); 122.55 (Pyr-C$_e$); 122.25, 119.10 (CF$_3$SO$_3$); 64.26 (C-CH$_3$); 36.71 (-CH$_2$-CH$_2$-); 19.28 (C-CH$_3$).

19F NMR (377 MHz, CD$_3$CN) δ = -79.40 (TMSOTf- F).

**Elemental Analysis:** Calcd. For C$_{18}$H$_{22}$F$_6$N$_4$O$_6$S$_2$: C, 38.03; H, 3.90; N, 9.86. Found: C, 38.15; H, 4.01; N, 10.05.

**Synthesis of Lr**
Freshly cut potassium (0.063 g, 1.61 mmol) was added to a 15 mL tetrahydrofuran solution of ligand L (0.2 g, 0.75 mmol) at room temperature. The intense red-green reaction mixture was stirred for 24 hours and then filtered. Subsequently 18-crown-6 (0.4 g, 1.50 mmol) was added to the filtrate and stirred. The solvent was removed under vacuum. The residue was washed with hexane and dried to obtain a green solid of Lr (yield = 0.53 g (81%)).

Crystals suitable for X-ray measurement were grown from the saturated solution of THF at -40 °C.

**Control NMR Experiments**
A: In a NMR tube, 0.6 mL of acetonitrile-$d_3$ was added to a mixture of ligand L (0.03 g, 0.11 mmol) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.025 g, 0.11 mmol) taken at room temperature, and shaken well. The NMR spectra was recorded after 12 hours.

B: In a NMR tube, 0.6 mL of acetonitrile-$d_3$ was added to a mixture of ligand L (0.035 g, 0.13 mmol) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.029 g, 0.13 mmol) taken at room temperature, and shaken well. Subsequently, HCl.Et$_2$O (0.26 mL 0.52 mmol) was added to the mixture. The NMR spectra was recorded after 6 hours.

C: In a NMR tube, 0.6 mL of acetonitrile-$d_3$ was added to a mixture of ligand L (0.032 g, 0.12 mmol) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.027 g, 0.12 mmol) taken at room temperature, and shaken well. Subsequently, trifluoroacetic acid (0.037 mL, 0.48 mmol) was added to the mixture. The NMR spectra was recorded after 6 hours.

**Trials to synthesize piperazine 3 using conventional methods**

**TR1:** Reduction of 2 with KC$_8$
To a suspension of KC$_8$ (0.042 g, 0.31 mmol) in 10 mL of tetrahydrofuran kept at -78 °C, was added compound 2 (0.123 g, 0.16 mmol) suspended in 10 mL of tetrahydrofuran. The suspension was slowly warmed to room temperature and the yellow solution was stirred for a period of 4 hours. Subsequently, the reaction mixture was filtered and the filtrate was quenched with trifluoroacetic acid (0.048 mL, 0.63 mmol). The colourless solution was evaporated completely. The solid residue was then washed with NaHCO$_3$ (10% w/v, ca. 10 mL) and the aqueous layer was extracted thrice with ethyl acetate. The organic layer was dried over anhydrous Na$_2$SO$_4$, and evaporated under vacuum to give a viscous liquid.

**TR2:** Reduction of L with Zn(0)$^{[3]}$
To a solution of ligand L (0.266 g, 1.0 mmol) in 20 mL of tetrahydrofuran, were added Zinc powder (0.654 g, 10.0 mmol) and methanesulfonic acid (MsOH) (0.65 mL, 10 mmol) maintaining temperature at 0°C. The suspension was stirred for 12 hours at this temperature. Subsequently, 20 mL of saturated aqueous solution of NaHCO$_3$ was added, and the solution was filtered. The filtrate was extracted with dichloromethane, the organic layer was dried over MgSO$_4$ and evaporated to give an orange solid.
TR3: Reduction of L with Mn(0)[54]
Mn(0) (0.093 g, 1.69 mmol) was suspended in 5 mL of acetonitrile. The ligand L (0.3 g, 1.12 mmol) dissolved in 20 mL of toluene was added to the Mn(0) suspension at room temperature. Trifluoroacetic acid (0.26 mL, 3.38 mmol) was then added to this stirring suspension, and the mixture was stirred at room temperature for 6 hours. The organic solvent mixture was evaporated and the residue was washed with saturated aqueous solution of Na2CO3. The aqueous layer was extracted with chloroform, and dried over anhydrous Na2SO4. The volatiles were evaporated to get a viscous yellow liquid.

TR4: Reduction of L with Na
Freshly cut sodium (0.023 g, 1.0 mmol) was added to 20 mL tetrahydrofuran solution of ligand L (0.115 g, 0.43 mmol). The intense red-brown reaction mixture was stirred at room temperature for 24 hours and then filtered. Trifluoroacetic acid (0.13 mL, 1.72 mmol) was then added to the filtrate. The solvent was removed under vacuum and the residue was washed with saturated aqueous solution of Na2CO3. The aqueous layer was extracted twice with chloroform. The organic layer was dried over anhydrous Na2SO4 and evaporated under vacuum to get a brown solid.

Routes leading to L stabilized mono(chlorogermyliumylidene)

Scheme S1. Synthesis of chlorogermyliumylidene by (a) auto-ionization of GeCl2; (b) chloride abstraction
2. Plots of NMR spectra

**Figure S1.** $^1$H NMR of 2 in CD$_3$CN (* = acetonitrile solvent peak)

**Figure S2.** $^{13}$C NMR of 2 in CD$_3$CN
Figure S3. $^{19}$F NMR of 2 in CD$_3$CN

Figure S4. $^1$H NMR of 2-I in CD$_3$CN
Figure S5. $^{13}$C NMR of 2-I in CD$_3$CN

Figure S6. $^{19}$F NMR of 2-I in CD$_3$CN
Figure S7. $^1$H NMR of Piperazine 3 in CDCl$_3$ (* = impurity)

Figure S8. $^{13}$C NMR of Piperazine 3 in CDCl$_3$
Figure S9. $^1$H NMR of 4 in CD$_3$CN

Figure S10. $^{13}$C NMR of 4 in CD$_3$CN
Figure S11. $^{19}$F NMR of 4 in CD$_3$CN

Figure S12. $^1$H NMR of Control Experiment in CD$_3$CN (the scale 6.8-8.8 ppm has been magnified)
Figure S13. $^1$H NMR of TR1 in CDCl$_3$

Figure S14. $^{13}$C NMR of TR1 in CDCl$_3$
Figure S15. $^1$H NMR of TR2 in CDCl$_3$

Figure S16. $^{13}$C NMR of TR2 in CDCl$_3$
Figure S17. $^1$H NMR of TR3 in CDCl$_3$

Figure S18. $^{13}$C NMR of TR3 in CDCl$_3$
Figure S19. $^1$H NMR of TR4 in CDCl$_3$

Figure S20. $^{13}$C NMR of TR4 in CDCl$_3$
3. HRMS of Piperazine 3

Figure S21. HRMS of 3.
3. UV/Vis spectra

**Figure S22.** UV-Vis Spectra of 2 in acetonitrile.

**Figure S23.** Linear Fit for UV-Vis data of 2
4. Cyclic Voltammetry

Cyclic voltammogram of the organosilicon reducing agent was recorded in Argon atmosphere at room temperature using three electrode cell (Glassy Carbon working electrode, Pt wire counter electrode and Ag wire reference electrode) and 0.1 M \([\text{N}^+\text{Bu}_4\text{N}]\text{[PF}_6\text{]}\) as the supporting electrolyte in acetonitrile.

![Cyclic Voltammogram of the organosilicon reducing agent in acetonitrile (Scan rate = 100 mV/s)](image)

**Figure S24.** Cyclic Voltammogram of the organosilicon reducing agent in acetonitrile (Scan rate = 100 mV/s)

Cyclic voltammograms of \(L\) and \(2\) were recorded in Argon atmosphere at room temperature using three electrode cell (Pt working electrode, Pt wire counter electrode and non-aqueous Ag/Ag\(^+\) reference electrode) and 0.1 M \([\text{N}^+\text{Bu}_4\text{N}]\text{[PF}_6\text{]}\) as the supporting electrolyte.

![Cyclic Voltammogram of \(L\) in tetrahydrofuran (Scan rate = 100 mV/s)](image)

**Figure S25.** Cyclic Voltammogram of \(L\) in tetrahydrofuran (Scan rate = 100 mV/s)
Figure S26. Cyclic Voltammogram of 2 in acetonitrile (Scan rate = 100 mV/s)
3. EPR spectra

**Figure S27.** EPR Spectrum (second derivative) of $\text{2r}$ recorded in acetonitrile at 100 K. Conditions: frequency = 9.4 GHz, modulation amplitude = 1 G, microwave power = 0.3170 mW. (Inset: Green-blue solution of $\text{2r}$).

Note: For a better resolution of the half-field peak of $\text{2r}$ at 1687 G (Figure 3 bottom left in maintext), EPR was recorded in acetonitrile at 100 K under the following conditions: frequency = 9.4 GHz, modulation amplitude = 11 G, microwave power = 11.5 mW.

**Figure S28.** EPR Spectrum (first derivative) of $\text{Lr}$ ($g_{iso} = 2.004$) recorded in toluene at 298 K. Conditions: frequency = 9.4 GHz, modulation amplitude = 2 G, microwave power = 1.12 mW.
4. DFT calculations

DFT calculations were performed on the dicationic part of the experimental structure 2 at the B3LYP level of theory (6-31G(d,p) basis set for Ge, Cl, C, N, H) using Gaussian 09 suite of programs.[55] Compound 2 was optimized at the stationary point with number of imaginary frequency NIMAG = 0.

Calculated $\Delta E_{\text{HOMO-LUMO}} = 117.795$ kcal/mol (optimized free ligand $L'$)

$= 82.153$ kcal/mol (optimized structure $2'$)

**Coordinates of Optimized structure $2'$**

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Contour plots of $2'$ at 0.03 isovalue

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### Coordinates of Optimized structure L'

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<td>1.16551800</td>
<td>-0.00051700</td>
</tr>
<tr>
<td>H</td>
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<td>1.78544400</td>
<td>-0.00085300</td>
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<tr>
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<td>-0.84505500</td>
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<td>-1.21040400</td>
<td>-0.87872200</td>
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<tr>
<td>H</td>
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<tr>
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<td>H</td>
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<td>-0.00010900</td>
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<tr>
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<td>-0.00024200</td>
</tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>H</td>
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<td>1.21085500</td>
<td>-0.87802800</td>
</tr>
<tr>
<td>H</td>
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<td>1.21033900</td>
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</tr>
<tr>
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<td>-5.80301700</td>
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</tbody>
</table>
DFT calculations were performed on the dicationic part of the triplet diradical proposed structure $2r$ at the B3LYP level of theory (6-31G(d,p) basis set for Ge, C, N, H) using Gaussian 09 suite of programs.[55] Compound $2r$ was optimized at the stationary point with number of imaginary frequency NIMAG = 0.

Coordinates of Optimized structure $2r$

<table>
<thead>
<tr>
<th>Element</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
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<td>0.37142800</td>
<td>-1.49498700</td>
</tr>
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<td>Ge</td>
<td>0.89751200</td>
<td>-0.68140600</td>
<td>-0.37144600</td>
</tr>
<tr>
<td>N</td>
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</tr>
<tr>
<td>N</td>
<td>2.74226500</td>
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<tr>
<td>N</td>
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<td>1.36856700</td>
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</tr>
<tr>
<td>N</td>
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<td>1.11233700</td>
<td>-0.31621500</td>
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<tr>
<td>C</td>
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<td>0.83706800</td>
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<td>-0.21130300</td>
<td>0.55555100</td>
</tr>
<tr>
<td>H</td>
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<td>0.63627600</td>
<td>0.65124200</td>
</tr>
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<td>C</td>
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<td>1.06381900</td>
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<tr>
<td>C</td>
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<td>1.23539400</td>
<td>-0.02005400</td>
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<tr>
<td>C</td>
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<tr>
<td>C</td>
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<td>0.02556100</td>
</tr>
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<td>H</td>
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<td>3.24147100</td>
<td>0.73130400</td>
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<tr>
<td>H</td>
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<td>3.03312500</td>
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<td>2.44105700</td>
<td>0.33595200</td>
</tr>
<tr>
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</tr>
<tr>
<td>H</td>
<td>0.43985000</td>
<td>2.19175200</td>
<td>-1.69183800</td>
</tr>
</tbody>
</table>
Optimized Geometry of 2r

Ge1….Ge2 = 2.97 Å

Wiberg Bond Index for Ge1….Ge2 = 0.29
Contour plots of 2r at 0.03 isovalue

Heat of formation of 2r in acetonitrile

The reactants and products have been optimized at the stationary point with number of imaginary frequency NIMAG = 0 at the B3LYP level of theory (6-31G(d,p) basis set for Ge, Cl, Si, C, N, H) using Gaussian 09 suite of programs.\cite{S5} Acetonitrile was chosen as the solvent using CPCM model.

\[
\begin{array}{c}
2' \quad 2^+ \quad \text{+} \quad \text{SiMe}_3 \text{N} \quad \text{SiMe}_3 \quad \text{N} \quad \text{SiMe}_3 \\
\text{products} \quad \text{Reactants} \\
\end{array}
\]

\begin{array}{c|c|c|c}
\hline
\text{Reactants} & \text{Products} \\
\hline
\begin{array}{c}
\begin{array}{c}
\text{SiMe}_3 \\
\text{N} \\
\text{SiMe}_3 \\
\end{array}
\end{array} & \begin{array}{c}
\text{SiMe}_3 \\
\text{N} \\
\text{SiMe}_3 \\
\end{array} & \begin{array}{c}
\text{SiMe}_3 \\
\text{N} \\
\text{SiMe}_3 \\
\end{array} & \begin{array}{c}
\text{SiMe}_3 \\
\text{N} \\
\text{SiMe}_3 \\
\end{array} \\
\hline
\text{E (Hartree)} & -5909.8373187 & -1082.9111661 & -4989.3311522 & -264.3282457 & -869.5407814*2 \\
\hline
\end{array}
\]

\[\Delta E = E_{\text{Products}} - E_{\text{Reactants}} = 0.0075241 \text{ Hartree} = +4.7 \text{ Kcal/mol}\]
### 6. X-ray data

#### Table S1. Crystal data and structure refinement for 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C18 H18 Cl2 F6 Ge2 N4 O6 S2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>780.56</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.3092(11) Å, α = 64.284(4)°.</td>
</tr>
<tr>
<td></td>
<td>b = 13.8633(19) Å, β = 80.304(4)°.</td>
</tr>
<tr>
<td></td>
<td>c = 13.8680(19) Å, γ = 73.576(4)°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1378.6(3) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.880 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>6.664 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>772</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.32 x 0.20 x 0.10 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.54 to 72.81°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10 ≤ h ≤ 10, -17 ≤ k ≤ 17, -16 ≤ l ≤ 17</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>14028</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5238 [R(int) = 0.0365]</td>
</tr>
<tr>
<td>Completeness to theta = 67.679°</td>
<td>96.4 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.514 and 0.253</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5238 / 0 / 363</td>
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</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<tr>
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</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.912 and -0.443 e.Å⁻³</td>
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Table S2. Crystal data and structure refinement for 2-I.

<table>
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<th>Property</th>
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<tbody>
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<td>Wavelength</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 20.604(4) Å, α = 90.00(3)°</td>
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<tr>
<td></td>
<td>b = 13.372(3) Å, β = 118.50(3)°</td>
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<tr>
<td></td>
<td>c = 20.162(4) Å, γ = 90.00(3)°</td>
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<td>Volume</td>
<td>4882(2) Å(^3)</td>
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<td>Density (calculated)</td>
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<tr>
<td>F(000)</td>
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<tr>
<td>Crystal size</td>
<td>0.20 x 0.12 x 0.08 mm(^3)</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.440 to 66.798°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-24≤h≤24, -15≤k≤15, -24≤l≤24</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>60046</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8602 [R(int) = 0.0362]</td>
</tr>
<tr>
<td>Completeness to theta = 66.798°</td>
<td>99.4%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.718 and 0.578</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F(^2)</td>
</tr>
<tr>
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<td>8602 / 0 / 687</td>
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Table S3. Crystal data and structure refinement for 4.

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<td>100 (2) K</td>
</tr>
<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>P 21/n</td>
</tr>
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<tr>
<td></td>
<td>b = 17.854(3) Å, β = 113.836(5)°</td>
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<tr>
<td></td>
<td>c = 12.5096(19) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2411.2(6) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.566 Mg/m³</td>
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<tr>
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<tr>
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<tr>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<tr>
<td>Completeness to theta = 66.858°</td>
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<td>Absorption correction</td>
<td>multi-scan</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.797 and 0.773</td>
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<tr>
<td>Property</td>
<td>Value</td>
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<td>----------------------------------------------</td>
<td>--------------------------------</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<tr>
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<td>multi-scan</td>
</tr>
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<td>Max. and min. transmission</td>
<td>0.189 and 0.152</td>
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<tr>
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<td>R indices (all data)</td>
<td>R1 = 0.3799, wR2 = 0.1936</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.352 and -0.408 e.Å⁻³</td>
</tr>
</tbody>
</table>
Figure S29. Structure of 4 in the solid state (thermal ellipsoids at 30%, H atoms except the N\textsubscript{amine}-H, triflate anion omitted for clarity). Selected bond lengths [Å]: C3-C4 = 1.581(3), C1-C2 = 1.506(4), C2-N3 = 1.481(4), N3-C3 = 1.531(3), C1-N2 = 1.498(3), N2-C4 = 1.511(3).

Figure S30. Structure of Lr in the solid state (ball and stick model, H atoms omitted for clarity). Due to poor data quality, anisotropic refinement for some atoms were not possible.

References