Supporting Information

for

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

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Contents

1.	Experimental details	S2
2.	Plots of NMR spectra	S 6
3.	HRMS	S16
3.	UV-Vis Spectra	S17
4.	Cyclic Voltammogram	S18
5.	EPR Spectra	S20
6.	DFT calculations	S21
7.	X-ray data	S27

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<u>1. Experimental details</u>

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. CD₃CN ampoules were purchased from Sigma Aldrich and used as it is. All chemicals were used as purchased. Compound 1 ^[S1] and the organosilicon reducing agent 1,4-bis(trimethysilyl)-1,4-dihydropyrazine ^[S2] were synthesized following the reported literature procedures. ¹H and ¹³C{¹H} NMR spectra were referenced to external SiMe₄ using the residual signals of the deuterated solvent (¹H) or the solvent itself (¹³C). ¹⁹F NMR was referenced to external C₆H₅CF₃ (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 K α radiation (1.5418 Å).

Synthesis of 2

Compound 1 (0.5 g, 0.78 mmol) and GeCl₂.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.

¹H NMR (400 MHz, CD₃CN) 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, -CH₂-CH₂-); 2.88 (s, 6H, -CH₃) ppm. ¹³C NMR (101 MHz, CD₃CN) δ = 178.03 (*C*-CH₃); 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 (CF₃SO₃); 47.71 (-CH₂-CH₂-); 17.04 (C-CH₃). ¹⁹F NMR (377 MHz, CD₃CN) δ = -79.31 (TMSOTf- *F*) ppm.

UV/Vis (acetonitrile) λ_{max} (ϵ) 337 nm (4457 M⁻¹cm⁻¹).

Elemental Analysis: Calcd. for C₁₈H₁₈Cl₂F₆Ge₂N₄O₆S₂: 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(trimethysilyl)-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).

¹**H** NMR (400 MHz, CD₃CN) $\delta = 8.85$ (d, J = 5.4, 2 H, *o*-Pyr-*H*); 8.30 (td, J = 8.2, 1.4, 2H, *p*-Pyr-*H*); 8.00 (d, J = 8.3, 2H, *m*-Pyr-*H*); 7.79 (t, J = 6.3, 2H, *m*-Pyr-*H*); 5.29 (br., 2H, NH); 3.33 (br., 2H, -CH₂-); 3.13 (br., 2H, -CH₂-); 1.99 (s, 6H, -CH₃).

¹³C NMR (101 MHz, CD₃CN) δ = 157.19 (Pyr-C_o); 146.17 (Pyr-C_o); 145.44 (Pyr-C_p); 126.76 (Pyr-C_m); 126.23 (Pyr-C_m); 122.28, 119.10 (CF₃SO₃); 63.77 (C-CH₃); 38.63 (-CH₂-CH₂-); 21.35 (C-CH₃). ¹⁹F NMR (377 MHz, CD₃CN) δ = -79.46 (TMSOTf- *F*).

Elemental Analysis: Calcd. for $C_{18}H_{20}F_6GeN_4O_6S_2$: C, 33.83; H, 3.15; N, 8.77. Found: C, 33.95; H, 3.42; N, 8.82.

Synthesis of Piperazine 3

1,4-bis(trimethysilyl)-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).

¹**H** NMR (400 MHz, CDCl₃) $\delta = 8.29$ (ddd, 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 (ddd, J = 7.5, 4.8, 1, 2H, m-Pyr-H); 4.50 (br., 2H, NH); 3.10-3.27 (m, 4H, -CH₂-CH₂-); 1.87 (s, 6H, -CH₃).

¹³C NMR (101 MHz, CD₃CN) δ = 162.62 (Pyr-C_o);146.94 (Pyr-C_o); 136.53 (Pyr-C_p); 121.71 (Pyr-C_m), 121.24 (Pyr-C_m), 62.22 (C-CH₃); 40.21 (-CH₂-CH₂-); 23.72 (C-CH₃).

Elemental Analysis: Calcd. For C₁₆H₂₀N₄: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.79; H, 7.71; N, 20.92.

HRMS (ESI-TOF) calculated for $[C_{16}H_{20}N_4 + H]^+$ 269.1758; found 269.1788.

Syntheis of Piperazinium bis(trifluoromethanesulfonate) 4

Method A: 1,4-bis(trimethysilyl)-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).

Method B: Trifluoromethanesulphonic 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.

¹**H** NMR (400 MHz, CD₃CN) δ = 9.07 (br., 4H, N*H*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, CD₃CN) δ = 153.12 (Pyr- *C*_o); 147.81 (Pyr-*C*_o); 138.52 (Pyr-*C*_p); 124.75 (Pyr-*C*_m); 122.55 (Pyr-*C*_m); 122.25, 119.10 (*C*F₃SO₃); 64.26 (*C*-CH₃); 36.71 (-*C*H₂-*C*H₂-); 19.28 (C-*C*H₃). ¹⁹F NMR (377 MHz, CD₃CN) δ = -79.40 (TMSOTf- *F*).

Elemental Analysis: Calcd. For C₁₈H₂₂F₆N₄O₆S₂: 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(trimethysilyl)-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(trimethysilyl)-1,4-dihydropyrazine (0.029 g, 0.13 mmol) taken at room temperature, and shaken well. Subsequently, HCl.Et₂O (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(trimethysilyl)-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 KC8

To a suspension of KC₈ (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 NaHCO₃ (10% w/v, ca. 10 mL) and the aqueous layer was extracted thrice with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄, and evaporated under vacuum to give a viscous liquid.

TR2: Reduction of L with $Zn(0)^{[S3]}$

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 NaHCO₃ was added, and the solution was filtered. The filtrate was extracted with dichloromethane, the organic layer was dried over MgSO₄ and evaporated to give an orange solid.

TR3: Reduction of **L** with $Mn(0)^{[S4]}$

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 (0.023g, 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



Figure S1. ¹H NMR of 2 in CD₃CN (* = acetonitrile solvent peak)



Figure S2. ¹³C NMR of 2 in CD₃CN



Figure S4. ¹H NMR of 2-I in CD₃CN



Figure S6. ¹⁹F NMR of **2-I** in CD₃CN







-60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 ppm

Figure S11. ¹⁹F NMR of 4 in CD₃CN



Figure S12. ¹H NMR of Control Experiment in CD₃CN (the scale 6.8-8.8 ppm has been magnified)





Figure S16. ¹³C NMR of TR2 in CDCl₃



Figure S18. ¹³C NMR of TR3 in CDCl₃



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 ["Bu₄N][PF₆] as the supporting electrolyte in acetonitrile.



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 [$^{n}Bu_{4}N$][PF₆] as the supporting electrolyte.



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 $2\mathbf{r}$ 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 $2\mathbf{r}$).

Note: For a better resolution of the half-field peak of 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 **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.^[S5] Compound **2** was optimized at the stationary point with number of imaginary frequency NIMAG = 0.

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

= 82.153 kcal/mol (optimized structure 2')

Coordinates of Optimized structure 2'

Ge	2.74536900	-1.61447600	-0.47177200
Ge	-1.47961200	0.28233800	-1.28068800
Cl	-0.60461400	1.86673500	0.09768400
Cl	1.58706100	-0.82476100	-2.24431600
Ν	3.51733100	0.22575900	-0.02796600
Ν	-3.38382100	0.68503200	-0.55806300
Ν	1.43461200	-0.93859000	0.99424200
Ν	-1.72079500	-1.16781900	0.21413100
С	2.95284700	0.84887000	1.03726400
С	-5.15424800	-0.06986800	0.85309700
Н	-5.54342900	-0.77303000	1.57895300
С	1.79092400	0.13790200	1.62734200
С	-2.89745500	-1.24969500	0.76068400
С	-3.85711600	-0.19129100	0.36202600
С	-3.35961700	-2.31259300	1.71198800
Н	-2.57170500	-2.99678500	2.01804000
Н	-4.16630000	-2.89863800	1.25652200
Н	-3.76830900	-1.84691900	2.61433500
С	-0.67947500	-2.19895500	0.37470800
Н	-0.21719400	-2.33911900	-0.60612600
Н	-1.12919800	-3.15498800	0.64686000
С	-5.96027500	0.97600700	0.39084100
Н	-6.97288400	1.08732000	0.76400400
С	-4.14788600	1.68466400	-1.01328000
Н	-3.70098300	2.34744500	-1.74787300
С	-5.44962700	1.86817300	-0.54783200
Н	-6.04480800	2.69165400	-0.92542300
С	0.39386900	-1.87717400	1.43793100
Н	-0.07811700	-1.54622300	2.36305000

Н	0.90427700	-2.82320600	1.65326200
С	3.46370200	2.05849600	1.49691400
Н	3.02592800	2.55756800	2.35226400
С	1.18449200	0.67942800	2.88378600
Н	0.27835200	0.15955800	3.18351100
Н	0.93112700	1.73316800	2.74353400
Н	1.91032300	0.61197700	3.70272400
С	4.56990000	0.75788200	-0.66300300
Н	4.96589000	0.20111300	-1.50648200
С	4.55724000	2.62947400	0.83737700
Н	4.96483500	3.57462700	1.18023800
С	5.11234700	1.97642800	-0.25982900
Н	5.95733000	2.39219600	-0.79641000

Contour plots of 2' at 0.03 isovalue





Coordinates of Optimized structure L'

N	-1.85871200	-0.03980400	-0.00019600
Ν	-5.27676400	-1.06631000	0.00039200
N	1.85870900	0.03977300	0.00003200
N	5.27674900	1.06632500	0.00020100
С	-4.22477400	-0.23096500	-0.00002700
С	4.22477100	0.23096600	0.00004000
С	2.85535700	0.84503300	0.00018200
С	5.65737300	-1.70146100	-0.00039200
Η	5.80306800	-2.77796900	-0.00062600
С	-4.37605600	1.16551800	-0.00051700
Η	-3.48799000	1.78544400	-0.00085300
С	-2.85536700	-0.84505500	0.00003100
С	-0.50656100	-0.57238900	-0.00017800
Н	-0.32612400	-1.21040400	-0.87872200
Η	-0.32621600	-1.21087900	0.87803700
С	-6.75289700	0.83519300	-0.00010400
Н	-7.77159400	1.20958900	-0.00010900
С	4.37608100	-1.16551900	-0.00024200
Η	3.48802600	-1.78546100	-0.00033100
С	6.50484700	0.53610100	0.00006000
Η	7.33081500	1.24521700	0.00020000
С	0.50655600	0.57235100	0.00016400
Н	0.32615200	1.21085500	-0.87802800
Н	0.32616200	1.21033900	0.87873300
С	-5.65734200	1.70148400	-0.00055200
Н	-5.80301700	2.77799400	-0.00092500

С	-6.50485100	-0.53606300	0.00035000
Η	-7.33083300	-1.24516400	0.00070100
С	6.75291600	-0.83514900	-0.00024400
Η	7.77161900	-1.20953000	-0.00036700
С	-2.74970000	-2.35280500	0.00031600
Η	-2.19119700	-2.69356600	-0.87939600
Η	-3.73596300	-2.81274700	0.00049200
Η	-2.19103000	-2.69323600	0.88005300
С	2.74967100	2.35278400	0.00050800
Η	2.19105200	2.69356600	-0.87912500
Η	3.73593100	2.81273200	0.00057200
Η	2.19112100	2.69318500	0.88033100

DFT calculations were performed on the dicationic part of the triplet diradical proposed structure $2\mathbf{r}$ at the B3LYP level of theory (6-31G(d,p) basis set for Ge, C, N, H) using *Gaussian 09* suite of programs.^[S5] Compound $2\mathbf{r}$ was optimized at the stationary point with number of imaginary frequency NIMAG = 0.

Coordinates of Optimized structure 2r

Ge	-1.64891500	0.37142800	-1.49498700
Ge	0.89751200	-0.68140600	-0.37144600
Ν	-2.99389300	-0.53616600	-0.43044400
Ν	2.74226500	-1.11524900	0.10905800
Ν	-1.42885100	1.36856700	0.14923800
Ν	1.60116600	1.11233700	-0.31621500
С	-3.17276600	-0.01693600	0.83706800
С	4.92159200	-0.21130300	0.55555100
Н	5.58820300	0.63627600	0.65124200
С	-2.27835300	1.06381900	1.14813200
С	2.90738100	1.23539400	-0.02005400
С	3.57055300	-0.02127900	0.22704700
С	3.61745800	2.55307500	0.02556100
Н	3.14046300	3.24147100	0.73130400
Н	3.62157700	3.03312500	-0.96001200
Н	4.65431900	2.44105700	0.33595200
С	0.76156100	2.28320900	-0.64781100
Н	0.43985000	2.19175200	-1.69183800

1.35209800	3.19723600	-0.59247100
5.40508100	-1.49805300	0.75550500
6.44873700	-1.65214200	1.00754200
3.21439900	-2.37183100	0.30426700
2.50107600	-3.18172100	0.19131800
4.53767600	-2.59552700	0.62838900
4.89120800	-3.60888500	0.77830200
-0.44369000	2.45583300	0.28432900
-0.09239500	2.51131400	1.31787200
-0.92344700	3.41164900	0.04237200
-4.16396400	-0.56232000	1.66952600
-4.32125200	-0.16399200	2.66394100
-2.28760200	1.79956200	2.45103300
-1.36192700	1.62284600	3.01268200
-3.11702200	1.49121000	3.08499100
-2.37735300	2.87944900	2.29355400
-3.76827000	-1.55859200	-0.88095900
-3.56561100	-1.90958900	-1.88748400
-4.94752200	-1.61088400	1.21082900
-5.71550500	-2.03423900	1.84909700
-4.74326400	-2.12034900	-0.08465900
-5.34456100	-2.93683200	-0.46649500
	1.35209800 5.40508100 6.44873700 3.21439900 2.50107600 4.53767600 4.89120800 -0.44369000 -0.09239500 -0.92344700 -4.16396400 -4.32125200 -2.28760200 -1.36192700 -3.11702200 -3.7735300 -3.76827000 -3.56561100 -4.94752200 -5.71550500 -4.74326400 -5.34456100	1.352098003.197236005.40508100-1.498053006.44873700-1.652142003.21439900-2.371831002.50107600-3.181721004.53767600-2.595527004.89120800-3.60888500-0.443690002.45583300-0.092395002.51131400-0.923447003.41164900-4.16396400-0.56232000-4.32125200-0.16399200-2.287602001.79956200-1.361927001.62284600-3.117022001.49121000-2.377353002.87944900-3.76827000-1.55859200-3.56561100-1.90958900-4.94752200-1.61088400-5.71550500-2.03423900-4.74326400-2.12034900-5.34456100-2.93683200

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.^[S5] Acetonitrile was chosen as the solvent using CPCM model.



	Reacta	ints		Products	
		SiMe ₃	$\begin{bmatrix} \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots &$		2 Me ₃ SiCl
E (Hartree)	-5909.8373187	-1082.9111661	-4989.3311522	-264.3282457	-869.5407814*2

 $\Delta E = E_{Products} - E_{Reactants} = 0.0075241 \text{ Hartree} = + 4.7 \text{ Kcal/mol}$

6. X-ray data

 Table S1. Crystal data and structure refinement for 2.

Empirical formula	C18 H18 Cl2 F6 Ge2 N4	C18 H18 Cl2 F6 Ge2 N4 O6 S2	
Formula weight	780.56		
Temperature	100(2) K		
Wavelength	1.54178 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 8.3092(11) Å	$\alpha = 64.284(4)^{\circ}.$	
	b = 13.8633(19) Å	$\beta = 80.304(4)^{\circ}.$	
	c = 13.8680(19) Å	$\gamma = 73.576(4)^{\circ}$.	
Volume	1378.6(3) Å ³		
Z	2		
Density (calculated)	1.880 Mg/m^3		
Absorption coefficient	6.664 mm ⁻¹		
F(000)	772		
Crystal size	0.32 x 0.20 x 0.10 mm ³		
Theta range for data collection	3.54 to 72.81°.		
Index ranges	-10<=h<=10, -17<=k<=1	17, -16<=l<=17	
Reflections collected	14028		
Independent reflections	5238 [R(int) = 0.0365]		
Completeness to theta = 67.679°	96.4 %		
Absorption correction	multi-scan		
Max. and min. transmission	0.514 and 0.253		
Refinement method	Full-matrix least-squares	on F ²	
Data / restraints / parameters	5238 / 0 / 363		
Goodness-of-fit on F ²	1.081		
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.10)80	
R indices (all data)	R1 = 0.0421, wR2 = 0.12	117	
Largest diff. peak and hole	0.912 and -0.443 e.Å ⁻³		

Empirical formula	C18 H20 F6 Ge N4 O6 S2	
Formula weight	639.09	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 20.604(4) Å	$\alpha = 90.00(3)^{\circ}.$
	b = 13.372(3) Å	$\beta = 118.50(3)^{\circ}$
	c = 20.162(4) Å	$\gamma = 90.00(3)^{\circ}.$
Volume	4882(2) Å ³	
Z	8	
Density (calculated)	1.739 Mg/m ³	
Absorption coefficient	4.140 mm ⁻¹	
F(000)	2576	
Crystal size	0.20 x 0.12 x 0.08 mm ³	
Theta range for data collection	2.440 to 66.798°.	
Index ranges	-24<=h<=24, -15<=k<=15,	-24<=1<=24
Reflections collected	60046	
Independent reflections	8602 [R(int) = 0.0362]	
Completeness to theta = 66.798°	99.4 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.718 and 0.578	
Refinement method	Full-matrix least-squares on	F^2
Data / restraints / parameters	8602 / 0 / 687	
Goodness-of-fit on F ²	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0926	
R indices (all data)	R1 = 0.0400, wR2 = 0.0947	
Largest diff. peak and hole	1.361 and -0.760 e.Å-3	

 Table S2.
 Crystal data and structure refinement for 2-I.

-		
Empirical formula	C18 H22 F6 N4 O6 S2	
Formula weight	568.51	
Temperature	100 (2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.8024(17) Å	$\alpha = 90^{\circ}$.
	b = 17.854(3) Å	$\beta = 113.836(5)^{\circ}.$
	c = 12.5096(19) Å	$\gamma = 90^{\circ}.$
Volume	2411.2(6) Å ³	
Z	4	
Density (calculated)	1.566 Mg/m ³	
Absorption coefficient	2.833 mm ⁻¹	
F(000)	1168	
Crystal size	0.12 x 0.09 x 0.08 mm ³	
Theta range for data collection	4.349 to 66.858°.	
Index ranges	-14<=h<=13, -19<=k<=2	21, -14<=l<=14
Reflections collected	19759	
Independent reflections	4241 [R(int) = 0.0488]	
Completeness to theta = 66.858°	99.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.797 and 0.773	
Refinement method	Full-matrix least-squares	s on F ²
Data / restraints / parameters	4241 / 0 / 327	
Goodness-of-fit on F ²	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.13	318
R indices (all data)	R1 = 0.0554, wR2 = 0.13	350
Largest diff. peak and hole	0.575 and -0.484 e.Å ⁻³	

 Table S3. Crystal data and structure refinement for 4.

Empirical formula	C40 H66 N4 O12 K2	
Formula weight	873.16	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 23.5972(19) Å	<i>α</i> = 90°.
	b = 14.6704(10) Å	$\beta = 104.411(5)^{\circ}.$
	c = 26.824(2) Å	$\gamma = 90^{\circ}.$
Volume	8993.9(12) Å ³	
Z	8	
Density (calculated)	1.290 Mg/m ³	
Absorption coefficient	2.382 mm ⁻¹	
F(000)	3744	
Crystal size	0.9 x 0.75 x 0.58 mm ³	
Theta range for data collection	2.234 to 66.932°.	
Index ranges	-27<=h<=25, -17<=k<=1	16, -31<=l<=29
Reflections collected	59611	
Independent reflections	30226 [R(int) = 0.2375]	
Completeness to theta = 66.932°	99.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.189 and 0.152	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	30226 / 1 / 2097	
Goodness-of-fit on F ²	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.1133, wR2 = 0.133	338
R indices (all data)	R1 = 0.3799, wR2 = 0.19	936
Largest diff. peak and hole	0.352 and -0.408 e.Å ⁻³	

Table S4. Crystal data and structure refinement for Lr.



Figure S29. Structure of **4** in the solid state (thermal ellipsoids at 30%, H atoms except the N_{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.

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