

## Supporting Information

*for*

### Facile access to a Ge(II) dication stabilized by isocyanides

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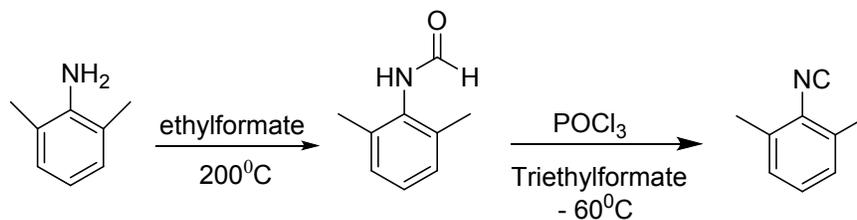
#### Content:

- S1. Synthesis and experimental details of **1**
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- S1. Synthesis and experimental details of 1**

All experiments were carried out under an inert atmosphere of argon applying standard Schlenk techniques or in a glove box. The solvents used were purified by an MBRAUN solvent purification system MB SPS-800. All chemicals purchased from Sigma Aldrich were used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{C}_6\text{D}_6$  and toluene- $d_8$  using a Bruker Avance DPX 200 or a Bruker Avance DRX 400 spectrometer and were referenced to external  $\text{SiMe}_4$ . However, high resolution mass spectra (HRMs) was obtained using a Q Exactive Thermo Scientific. Elemental analysis was performed by CSIR-National Chemical Laboratory, Pune. Melting point was measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus.

### **Preparation of 2, 6–dimethylphenylisonitrile**

The mixture of 2, 6 –dimethylaniline (10 g, 82.5 mmol) and ethylformate (15 mL) was heated under autoclave up to 200 °C overnight. The *n*-formyl derivative of 2, 6-dimethylaniline was obtained and purified in a very good yield (11.07g, 94%). The resultant compound (2.0 g, 13.4 mmol) was dissolved in 60 mL of dry dichloromethane and phosphorousoxychloride (3.61 mL, 39.02 mmol) was added drop by drop to this reaction mixture over a period of five minutes at –60 °C under inert conditions. The reaction mixture was stirred for next 20 minutes and triethylamine (16.2 mL, 117 mmol) was added drop by drop to the reaction mixture over a period of 10 minutes at –60 °C. The reaction was transformed into a orange color when allowed to warm at room temperature for overnight. Finally, the mixture poured on to the 50 mL of cold water and extracted with dichloromethane (2 x 60mL). The organic layer was dried under reduced pressure. The isonitrile was obtained as a white crystalline solid compound through sublimation under vacuum ( $1.5 \times 10^{-2}$  mbar) at 55 °C (1.54g, 87.5 %).  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$  2.06 (s, 6H,  $\text{CH}_3$ ), 6.60 (d, 2H, 7.68 Hz, Ph ), 6.69 (m, 1H, Ph) ppm.



## Preparation of 1

The toluene solution (25 mL) of 2, 6–dimethylphenylisocyanide (0.56 g, 4.31mmol) was added drop by drop to the toluene solution (10 mL) of  $\text{GeCl}_2 \cdot \text{dioxane}$  (1.0 g, 4.31 mmol) at ambient conditions. The resulting reaction mixture was stirred overnight and transformed to a brown red color. The final compound was filtered through celite, solvent was removed under vacuum and the following filtrate was reduced to 5 to 7 mL. Good quality of yellow colored crystal was obtained when crystallization was performed in toluene at  $-30\text{ }^{\circ}\text{C}$  in a freezer. Yield: 220 mg (54 %).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  1.92 (s, 24H,  $\text{CH}_3$ ), 6.4 (d, 8H, 8.03Hz, Ph), 6.65 (m, 4H, Ph) ppm;  $^{13}\text{C}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25\text{ }^{\circ}\text{C}$ )  $\delta$  18.38 ( $\text{CH}_3$ ), 127.18, 130.69, 136.65 (Ph) ppm; Anal. Calcd for  $\text{C}_{36}\text{H}_{36}\text{Cl}_6\text{Ge}_3\text{N}_4$  (955.9): C, 45.19; H, 3.76; N, 5.85. Found : C, 45.2; H, 3.14; N, 5.74.

## S2. Crystal Structure Determination

X-ray intensity data measurements of compound **1** was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized ( $\text{MoK}_{\alpha} = 0.71073\text{ \AA}$ ) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with  $\omega$  scan width of  $0.5^{\circ}$  at different settings of  $\varphi$  and  $2\theta$  keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).<sup>S1</sup> All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and

SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on  $F^2$ .<sup>S2</sup> All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An *ORTEP* III<sup>S3</sup> view of compound **1** was drawn with 50% probability displacement ellipsoids and H atoms omitted for clarity.

**Crystal Data for compound 1.** C<sub>36</sub> H<sub>36</sub> Cl<sub>6</sub> Ge<sub>3</sub> N<sub>4</sub>, M =956.16, yellow color, 0.34 x 0.22 x 0.17 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$ ,  $a = 9.4793(10)$  Å,  $b = 16.9178(19)$  Å,  $c = 25.305(3)$  Å,  $\beta = 92.288(3)$  °,  $V = 4054.9(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150(2)$  K,  $2\theta_{\max} = 50.498^\circ$ ,  $D_{\text{calc}}$  (g cm<sup>-3</sup>) = 1.566,  $F(000) = 1916$ ,  $\mu$  (mm<sup>-1</sup>) = 2.636, 158406 reflections collected, 7348 unique reflections ( $R_{\text{int}} = 0.0621$ ), 5586 observed ( $I > 2\sigma(I)$ ) reflections, multi-scan absorption correction,  $T_{\text{min}} = 0.776$ ,  $T_{\text{max}} = 0.768$ , 450 refined parameters,  $S = 1.041$ ,  $R1 = 0.0612$ ,  $wR2 = 0.1731$  (all data  $R = 0.0877$ ,  $wR2 = 0.1965$ ), maximum and minimum residual electron densities;  $\Delta\rho_{\text{max}} = 4.907$ ,  $\Delta\rho_{\text{min}} = -0.621$  (eÅ<sup>-3</sup>).

### S3. DFT Computations of **1**

#### Computational Details

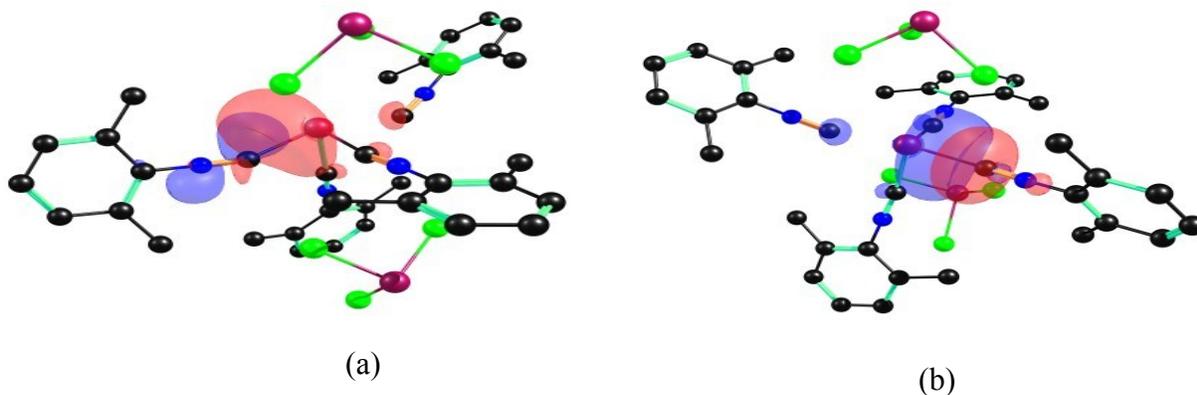
All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 6.4 suite of programs,<sup>S4</sup> employing the PBE functional<sup>S5</sup> and the TZVP<sup>3</sup> basis set. The resolution of identity (RI),<sup>S6</sup> along with the multipole accelerated resolution of identity (marij)<sup>S7</sup> approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model,<sup>S8</sup> with toluene ( $\epsilon = 2.38$ ) as the solvent. Full frequency calculations on the optimized minima and also normal mode analysis was performed for compound **1** using the same level of theory. Consequently, all reported energy values represent gas phase data at 298.15 K temperature.

The nature of germanium-carbon interaction in compound **1** was investigated with the natural bond orbitals (NBO) analysis procedures as implemented in the Gaussian 09 program. The analyses was performed at the PBEPBE/TZVP optimized geometry using the PBEPBE density functional together with the all electron TZVP basis set.

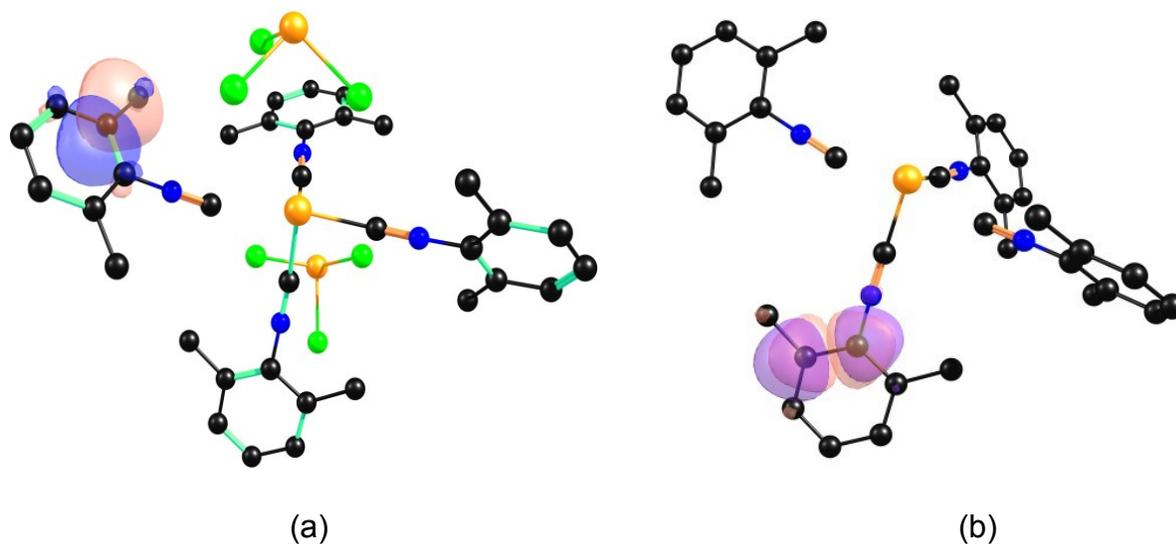
In order to gain insight into the interaction of the isocyanide ligands with the central germanium atom, the intermolecular charge transfer in the complex has been analysed with the natural bond orbital (NBO) analysis. The energetic estimate of donor (i) – acceptor (j) orbital interactions can be obtained by the second order perturbation theory analysis of the Fock matrix in the NBO basis. The donor–acceptor interaction energy  $E(2)$  is given by

$$E(2) = \Delta E(i,j) = q(i,j)F(i,j)^2 / \{\varepsilon(i) - \varepsilon(j)\}$$

where  $q(i)$  is the donor orbital occupancy,  $\varepsilon(i)$  and  $\varepsilon(j)$  are the diagonal elements (orbital energies), and  $F(i,j)$  is the off-diagonal NBO Fock matrix element. In the present investigation, the important interactions between the central germanium and the isocyanide ligands have been analyzed.

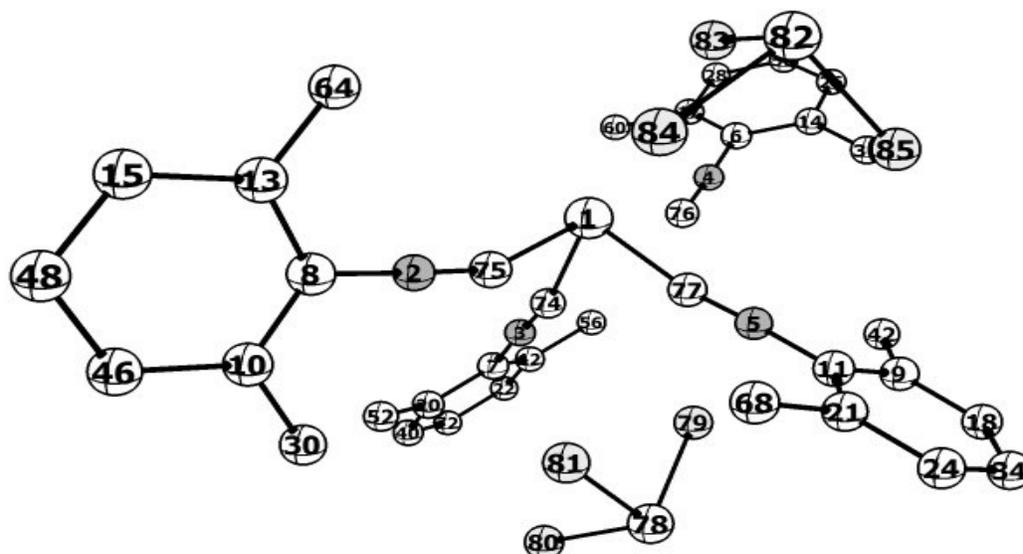


**Figure S1** (a) Strong  $\sigma$  (LP (C $\equiv$ N) $\rightarrow$ LP (Ge)) interactions and (b) weak  $\pi$ (LP(Ge) $\rightarrow \pi^*$ (C $\equiv$ N)) interaction



**Figure S2:** (a) LUMO of **1** and (b) LUMO of **1**<sup>2+</sup> (contour value  $\pm 0.03$ ). Hydrogen atoms have been omitted for clarity.

The Cartesian coordinates of the optimized singlet geometry of complex **1** [Ge(RNC)<sub>4</sub>]<sup>2+</sup> 2[:GeCl<sub>3</sub>]<sup>-</sup> is given below:



**Figure S3** : Ge(1)–C(74) = 2.10 , Ge(1)–C(75) = 2.22 , Ge(1)–C(76) = 2.50 , Ge(1)–C(77) = 2.05 , C(74)–N(3)=1.167 , C(75)–N(2)=1.173 , C(76)–N(4)=1.175 , C(77)–N(5)=1.163, Ge(1)-C(74)-N(3) = 164.1°; Ge(1)-C(75)-N(2) = 156.3°; Ge(1)-C(76)-N(4) = 142.0°;Ge(1)-C(77)-N(5) = 170.2° ;The isocyanide ligands are almost linear about the nitrogen atoms with the C-N-C angles between 176.7° and 177.7°

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Ge	3.593030	13.076805	9.174184
N	1.473438	13.000861	6.609878
N	6.009829	12.340042	7.132063
N	5.985785	13.301296	11.726511
N	2.992827	10.078158	10.115168
C	6.526969	13.950043	12.818779
C	7.099778	12.196599	6.302307
C	0.526618	13.346690	5.665675
C	3.470250	8.198102	11.518726
C	0.510077	12.646149	4.436727
C	2.635796	8.830054	10.568572
C	8.382054	12.152731	6.896033
C	-0.371965	14.393594	5.985082
C	6.298373	13.410997	14.104591
C	-1.323821	14.724452	5.015070
H	-2.035151	15.524852	5.226803
C	7.262479	15.134835	12.588987
C	3.084740	6.921998	11.938470
H	3.704445	6.397713	12.668177
C	6.869111	12.094230	4.912127
C	1.443155	8.263984	10.059372

C	9.468089	12.003578	6.029992
H	10.474716	11.957574	6.449368
C	1.112577	6.986977	10.521031
H	0.201773	6.513084	10.150655
C	6.843174	14.108992	15.187841
H	6.681555	13.723920	16.196509
C	7.784025	15.787530	13.709739
H	8.354576	16.707566	13.568425
C	1.498860	11.555243	4.148933
H	2.529611	11.940873	4.151702
H	1.306015	11.103199	3.168323
H	1.470327	10.760651	4.909494
C	1.923849	6.322067	11.444196
H	1.644099	5.324159	11.787048
C	5.494392	12.158087	14.283953
H	4.474146	12.278612	13.886620
H	5.421060	11.889431	15.344859
H	5.951608	11.313109	13.745526
C	7.996032	11.951945	4.098832
H	7.858677	11.857738	3.020225
C	4.692662	8.884708	12.048808
H	4.413678	9.831749	12.536865
H	5.394005	9.120664	11.233405
H	5.206665	8.252043	12.782420
C	-0.465425	13.025068	3.508494
H	-0.509935	12.504694	2.550033
C	-1.371825	14.049428	3.792653
H	-2.124271	14.325893	3.051803
C	7.577239	15.281364	14.995595
H	7.989996	15.808998	15.857381
C	5.475181	12.097572	4.359788
H	4.913804	11.232616	4.748808
H	5.491651	12.037617	3.264764
H	4.927175	13.008699	4.649177
C	8.548297	12.238665	8.385095
H	9.609456	12.206916	8.660087
H	8.031371	11.400882	8.879040
H	8.114917	13.169125	8.785110
C	7.452673	15.668219	11.197501
H	6.484469	15.897182	10.725172
H	7.961991	14.934749	10.552272
H	8.052960	16.586037	11.210707
C	-0.295410	15.111539	7.301168
H	-0.393343	14.419026	8.151379
H	-1.086505	15.867584	7.376209
H	0.674641	15.619991	7.421025

C	0.590436	9.008706	9.074883
H	1.147859	9.193659	8.142405
H	0.288615	9.989975	9.474233
H	-0.312999	8.434964	8.834670
C	9.278518	11.906111	4.649039
H	10.142833	11.785090	3.993611
C	5.090458	12.403593	7.848857
C	2.246039	12.718328	7.445629
C	5.481686	12.793864	10.793382
C	3.268360	11.117401	9.671375
Ge	5.127233	7.976295	6.991646
Cl	6.288680	9.163600	8.668964
Cl	6.491409	8.573722	5.206816
Cl	3.441513	9.611450	6.592468
Ge	0.883269	13.321437	12.624641
Cl	2.835915	14.592371	12.404893
Cl	0.589908	12.875361	10.273216
Cl	1.907482	11.295751	13.160094

*The cartesian coordinates of optimized triplet geometry of complex 1 [Ge(RNC)<sub>4</sub>]<sup>2+</sup> 2[:GeCl<sub>3</sub>]<sup>-</sup> is given below*

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Ge	3.697343	14.577448	8.790389
N	1.401317	12.971046	6.421340
N	6.112399	13.151387	7.461996
N	5.460183	14.905401	11.551182
N	4.025799	11.564910	9.701800
C	6.120900	14.935730	12.759063
C	6.657056	11.943875	7.128826
C	0.102239	12.633305	6.089361
C	5.326177	9.966309	10.927413
C	-0.108192	11.522839	5.241435
C	4.534772	10.298838	9.798277
C	7.549664	11.327999	8.048434
C	-0.946215	13.414053	6.626145
C	5.379606	14.651706	13.931915
C	-2.251376	13.039206	6.291801
H	-3.085656	13.617699	6.693586
C	7.505037	15.232088	12.757918
C	5.884091	8.686032	10.956247
H	6.497914	8.399843	11.812985
C	6.300908	11.339437	5.893314
C	4.273642	9.388652	8.741994
C	8.038316	10.062912	7.724087
H	8.705592	9.560888	8.427814
C	4.859191	8.124235	8.829554

H	4.682007	7.409444	8.023449
C	6.088026	14.657155	15.137706
H	5.550978	14.439162	16.062873
C	8.153309	15.227154	13.995647
H	9.221202	15.450938	14.032868
C	1.045452	10.729622	4.699960
H	1.762141	11.368612	4.162008
H	0.701241	9.946638	4.014130
H	1.606513	10.239230	5.509294
C	5.659901	7.773985	9.920004
H	6.108309	6.779999	9.966211
C	3.909401	14.362076	13.868354
H	3.352081	15.196000	13.414956
H	3.504517	14.182875	14.871571
H	3.686668	13.476287	13.254004
C	6.820733	10.070394	5.628232
H	6.533698	9.571996	4.700289
C	5.523719	10.944057	12.050282
H	4.557102	11.217989	12.501390
H	5.991821	11.879647	11.706254
H	6.161855	10.515321	12.832793
C	-1.435034	11.194968	4.942176
H	-1.632635	10.339154	4.293620
C	-2.494876	11.942377	5.461312
H	-3.522286	11.666261	5.216688
C	7.455886	14.940283	15.172810
H	7.984366	14.939312	16.127799
C	5.390791	12.042348	4.929751
H	4.427594	12.301388	5.398812
H	5.189863	11.412543	4.054787
H	5.832673	12.990722	4.584904
C	7.947162	12.031481	9.313347
H	8.514786	11.362483	9.971808
H	7.068862	12.393910	9.867484
H	8.572328	12.912684	9.094508
C	8.228945	15.534750	11.477376
H	7.805900	16.419087	10.975946
H	8.151998	14.698709	10.765088
H	9.292324	15.724750	11.667070
C	-0.656204	14.577589	7.528978
H	-0.144526	14.245680	8.445813
H	-1.583779	15.086456	7.819345
H	0.003672	15.311908	7.041196
C	3.397155	9.784048	7.592449
H	3.761988	10.701196	7.107593
H	2.372390	9.994486	7.938839

H	3.358791	8.987520	6.839809
C	7.675427	9.431227	6.530752
H	8.057119	8.434451	6.304045
C	5.584154	14.149542	7.849527
C	2.503103	13.252849	6.731773
C	4.897162	14.821739	10.523278
C	3.582041	12.657862	9.615636
Ge	2.996046	6.720628	3.533901
Cl	3.942857	8.769179	3.363033
Cl	0.819081	7.136201	3.115424
Cl	3.033066	6.317055	5.759223
Ge	0.088248	12.373514	11.636327
Cl	0.998901	14.456793	11.274911
Cl	0.264608	11.436393	9.565160
Cl	1.788987	11.323280	12.750703

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