Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Content:

(S1) Syntheses

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glove box, unless otherwise stated. The cyclic alkyl(amino) carbene (cAAC)[S1]and LGeCl[S2] (L = (tBuN)$_2$C(Ph)) were synthesized according to the literature. Solvents were purified with the M-Braun solvent drying system. Elemental analyses were performed by the Analytisches Labor des InstitutsfürAnorganischeChemie der UniversitätGöttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

(cAAC)Ge(GeL)$_2$ (1): To a mixture of LGeCl(0.34 g, 1mmol), cAAC (0.14 g, 0.5mmol) and KC_8 (0.16 g, 1.2mmol) was added THF (30 mL) at -78 ^{o}C. The mixture was stirred at the same temperature for 1 h to obtain a brown-red suspension. All the volatiles were removed in vacuum and the brown residue was extracted with *n*-hexane (30 mL). Dark red crystals were obtained from the concentrated *n*-hexane solution of **1**under -4 ^{o}C in refrigerator. Yield: 0.11 g (35 %, based on Ge). Melting point: 183^{o}C (dec.). UV-visible absorption bands at 292, 490 (s) nm.^{1}H NMR (C_6D_6, 298 K, 500 MHz, δ ppm): 8.15–6.77 (m, 13 H, Ar-*H*), 3.41 (sept, 2 H, C*H*Me$_2$, $^3J_{HH}$ = 7 Hz), 1.92 (s, 6 H, NC*Me*$_2$), 1.85 (d, 6 H, CH*Me*$_2$, J_{HH} = 7 Hz), 1.42 (s, 2 H, C*H*$_2$), 1.37 (s, 6 H, C*Me*$_2$), 1.34 (s, 18 H, *t*Bu-*H*), 1.32 (s, 18 H, *t*Bu-*H*), 1.30 (d, 6 H, CH*Me*$_2$, J_{HH} = 7 Hz). ^{13}C NMR (C_6D_6, 298 K, 125 MHz, δ ppm) 219.4 ($C_{carbene}$), 159.7, 158.1, (N*C*N) 148.6, 141.3, 138.9, 137.9, 131.2, 130.9, 129.5, 129.2, 128.8, 127.4, 127.0, 126.6, 115.6, 115.4, 68.7, 57.4, 54.2, 53.8, 50.6, 36.4, 33.0, 32.7, 29.0, 28.9, 27.2, 27.0.Anal(%). calcd for $C_{50}H_{77}Ge_3N_5$ (966.10): C, 62.16; H, 8.03; N, 7.25. Found: C, 62.09; H, 7.98; N, 7.06. EI-MS: *m/z*(%) 305.2, 100% (LGe^+); 286.4, 34% ($cAAC^+$).

(cAAC)$_2$Ge (2):To a mixture of LGeCl(0.34 g, 1mmol), cAAC (0.14 g, 0.5mmol) and KC_8 (0.16 g, 1.2mmol) was added THF (30 mL) at -78 ^{o}C. The mixture was allowed to warm to room temperature and stirred for additional 12 h. The color of the suspension turned gradually from brown-red to brownish green. All the volatiles were removed in vacuum and the residue was extracted with *n*-hexane (30 mL). Dark green crystals of **2** were obtained, yielding 0.09 g. A small amount of red crystals **1**and colorless crystals (cAACH)$_2$O[S2]were also grown at the bottom of the flask. Corresponding characterizations of **2** were reported in the previous paper.[S3]

(S2) UV-visible spectroscopy

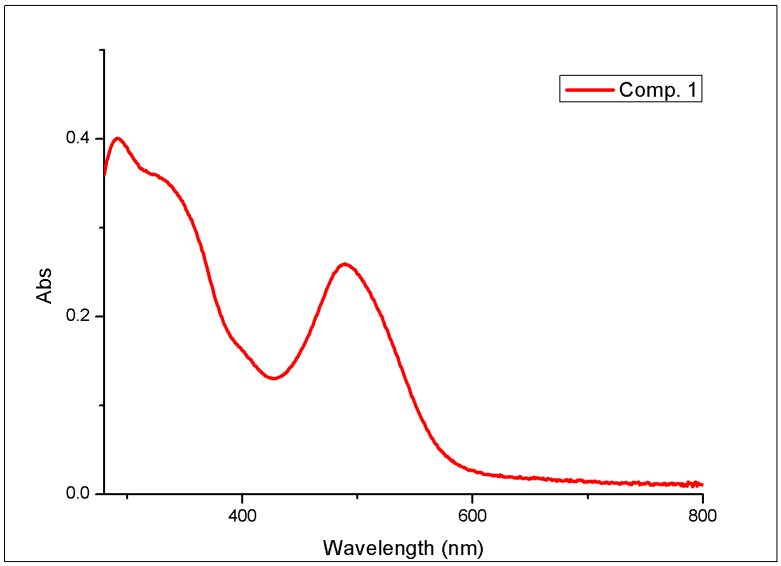

Figure S1 UV-visible spectrum of compound **1**in C_6D_6.

(S3) Crystal structure determination

Suitable single crystals for X-ray structural analysis of **1** were mounted at room temperature in Paratone N inert oil under nitrogen atmosphere. Single-crystal diffraction data were collected at the DESY/PETRA III facility, beamline P11 with a piezo-motor driven goniometer. The Pilatus 6M fast detector was used with standard measurement procedures established at the beamline. An empirical absorption correction with SADABS[S4] was applied after integration with the XDS software[S5] and conversion of the output file with the utility program xds2sad from G. M. Sheldrick. All structures were solved by direct methods. Structure refinement was done with shelxl[S6] and shelxle[S7].

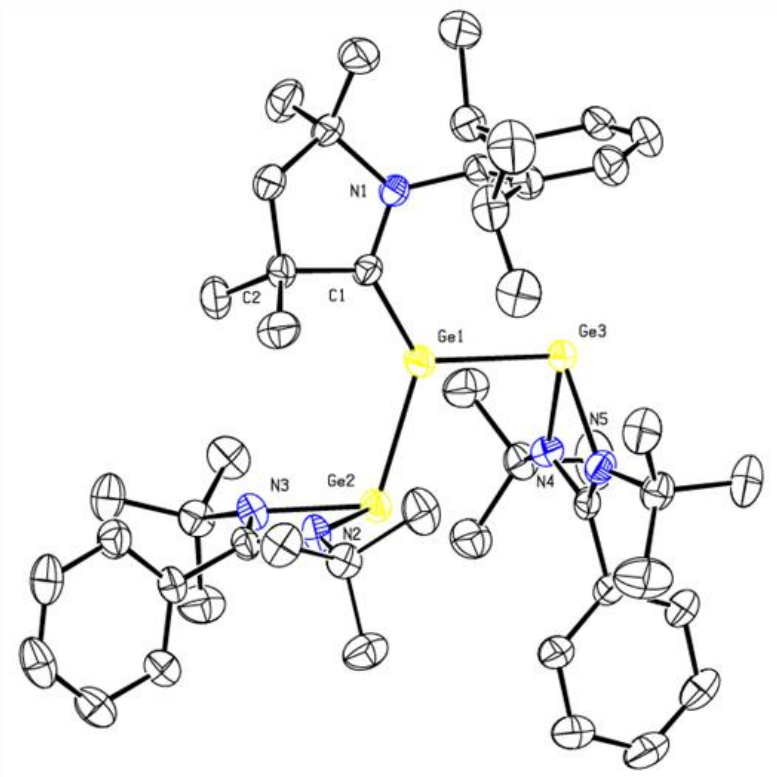

Figure S2 Molecule structure of compound **1**.

Table S1 Crystal data and structure refinement for **1**.

Compound	**1**
Empirical formula	$C_{50}H_{77}Ge_3N_5$
CCDC no.	967854
Molecular weight	966.00
Crystal size [mm]	0.19 x 0.11 x 0.09
Wavelength [pm]	61.99
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a [pm]	1332.0(3)
b [pm]	1751.0(4)
c [pm]	2195.0(4)
α [°]	90.0
β [°]	90.0
γ [°]	90.0
V [nm ^{3}]	5119.5(18)
Z	4
Temperature [K]	120(2)
ρ [Mgm^{-3}]	1.2533(5)
μ [mm^{-1}]	1.237

F (000)	2032.0
θ-area [°]	1.297 to 24.430
Total number of reflect.	72068
Unique reflections	12507
Reflections with $I > 2\sigma(I)$	12205
R_{int}	0.0749
Number of restraints	160
Parameters	583
$R1$ [$I>2\sigma(I)$]	0.0406
$wR2$[$I>2\sigma(I)$]	0.1079
$R1$ [all data]	0.0412
$wR2$ [all data]	0.1084
GooF	1.054
Extinction coefficient	-
Largest diff. peak / hole max. / min. [$10^3 \cdot e \cdot nm^{-3}$]	+1.983 and -0.505

(S4) Theoretical calculation.

Computational Methodology All the geometries were optimized at the gradient-corrected BP86[S8] density functional with the basis set def2-SVP[S9]. The calculations were performed using Gaussian 09 package.[S10] Meta-GGA exchange correlation functional M06[S11] with def2-TZVPP basis set was used for the single point calculation on geometries optimized at the BP86/def2-SVP level of theory. The energies at M06/def2-TZVPP level were corrected by adding the zero point energies from the BP86/def2-TZVPP level of theory. Natural bond order (NBO)[S12] calculations were computed at the same level of theory.

The nature of Ge1–C1 bond was investigated by EDA-NOCV analysis at the BP86/TZ2P[S13] level of theory using ADF 2013.01 program.[S14] Energy Decomposition Analysis (EDA)[S15]gives the instantaneous interaction energy (ΔE_{int}) between two fragments in the frozen geometry of the compound. The interaction energy can be divided into three parts:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

ΔE_{elstat}gives the electrostatic interaction energy between the frozen charge densities of the two fragments. ΔE_{Pauli}gives the repulsive interaction between two fragments, which are caused by the electrons of same spin. $\Delta E_{orb}$is the lowering in energy due to the overlap of orbitals of the two fragments. This can be further divided into contributions by the orbitals belonging to different irreducible representations. Sum of $\Delta E_{int}$and ΔE_{prep}(energy necessary to promote the fragments from their ground state geometry to the geometry in the compound) gives $-D_e$ (dissociation energy)

$$-D_e = \Delta E_{int} + \Delta E_{prep}$$

EDA-NOCV analysis is an extension of EDA analysis in which ΔE_{orb}term is decomposed into the contributions from different natural orbitals of chemical valence (NOCV).[S16] The EDA-NOCV scheme gives insight to the orbital interactions by providing the energy contributions for each specific orbital interaction between fragments to the total bond energy. The deformation density, $\Delta\rho$, which is incorporated with bond formation is partitioned into the different components (σ, π and δ) of the chemical bond.

NOCV scheme has been derived from Nalewajski-Mrozek valence theory as eigenvectors that diagonalize the deformation density matrix. The NOCV pairs (Ψ_{-k},Ψ_k) decompose the differential density $\Delta\rho$ into NOCV contributions ($\Delta\rho_k$)

$$\Delta\rho(r) = \sum_{k=1}^{M/2} \nu_k \left[-\Psi^2_{-k}(r) + \Psi^2_k(r) \right] = \sum_{k=1}^{M/2} \Delta\rho_k(r)$$

whereν_k and M stand for the NOCV eigenvalues and the numberof basis functions, respectively. Visual inspection of deformation density plots ($\Delta\rho_k$) helps to determine the symmetry and the direction of flow of charge. These density plots also provide the energetic estimations, ΔE^k_{orb}, for each $\Delta\rho_k$within EDA-NOCV scheme. In EDA-NOCVmethod, orbital interaction energy (ΔE_{orb}) is expressed in terms of NOCV eigen values (ν_k) as

$$\Delta E_{orb} = \sum_k \Delta E^k_{orb} = \sum_{k=1}^{M/2} \nu_k \left[-F^{TS}_{-k,-k} + F^{TS}_{k,k} \right]$$

where $F^{TS}_{i,i}$ are diagonal Kohn-Sham matrix elements defined over NOCV with respect to the transition state (TS) density (at the midpoint between density of the molecule and the sum offragment densities). The above components ΔE^k_{orb} provide energetic estimation of $\Delta\rho_k$that may be related to the importanceof a particular electron flow channel for the bonding between considered molecular fragments.

We have used the following convention for assigning the oxidation number, valency and coordination number. The oxidation number of an atom is the formal charge when all the atoms or groups attached to it are removed along with the electrons that were used for chemical bonding with that particular atom. The valency of an atom is the number of its electrons used for chemical bonding with

atoms or groups attached to it. The coordination number of an atom is the number of atoms or groups directly linked to it.

Table S2 Selected Wiberg bond orders and bond occupancies given by the Natural Population Analysis for Ge_3 complex in singlet state (**3**) and cyclic alkyl amino carbene (**5**) at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

3			**5**		
	Wiberg bond index	Bond occupancy		Wiberg bond index	Bond occupancy
Ge1-Ge3	0.933	1.888	N1–C1	1.503	1.981(σ) 1.949(π)
Ge1-Ge2	0.965	1.887	C1–C2	0.989	1.953
Ge1-C1	1.351	1.957	LP C1	-	1.874
Ge3-N4	0.417	1.927	-	-	-
Ge3-N5	0.420	1.928	-	-	-
Ge2-N3	0.419	1.928	-	-	-
Ge2-N2	0.421	1.928	-	-	-
C1-N1	1.117	1.978(σ) 1.933(π)	-	-	-
LP Ge1	-	1.019	-	-	-
LP Ge2	-	1.925	-	-	-
LP Ge3	-	1.940	-	-	-
LP N5	-	1.567	-	-	-
LP N3	-	1.564	-	-	-

LP: Lone Pair

Table S3 Optimized Cartesian coordinates and total energies (in a.u.) including zero point energy correction of all the calculated molecules at the BP86/def2-SVP level of theory (E_1)and total energy at M06/def2-TZVPP level of theory including zero point energy correction from the BP86/def2-SVP level of theory (E_2)using G09 program package. Symmetry of the structures is mentioned in the parenthesis. The number of imaginary frequencies is abbreviated as Nimag.

3(C_1)

E_1 = -8453.737035 a.u.
E_2 = -8454.366405 a.u.
Nimag = nil
7 -2.091531000 -2.991918000 -0.396027000
32 -0.476946000 -0.481833000 -0.185547000

7	3.125625000	-0.358348000	1.064792000
32	1.750167000	0.737373000	-0.046922000
7	3.217559000	-0.285773000	-1.131460000
32	-2.395374000	1.164218000	-0.064044000
7	-1.439080000	2.706553000	-1.097112000
7	-1.487453000	2.636030000	1.097466000
6	-0.854668000	-2.351326000	-0.344920000
6	0.255920000	-3.421046000	-0.516389000
6	-0.540720000	-4.756810000	-0.510382000
1	-0.090543000	-5.522440000	-1.175250000
1	-0.547142000	-5.179190000	0.517351000
6	-1.990101000	-4.412344000	-0.917721000
6	1.246053000	-3.393571000	0.670620000
1	0.718764000	-3.527987000	1.637359000
1	1.788941000	-2.428099000	0.712238000
1	1.988979000	-4.216702000	0.571081000
6	1.067459000	-3.223366000	-1.818301000
1	1.791451000	-4.057226000	-1.953603000
1	1.635594000	-2.273203000	-1.760020000
1	0.422187000	-3.180040000	-2.717828000
6	-2.147514000	-4.481964000	-2.456833000
1	-3.196840000	-4.339537000	-2.772736000
1	-1.826675000	-5.481695000	-2.817789000
1	-1.525295000	-3.720241000	-2.965226000
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1	-2.903379000	-5.380375000	0.835033000
1	-2.875337000	-6.377022000	-0.654439000
6	-3.284654000	-2.459087000	0.219419000
6	-4.362918000	-1.935295000	-0.559156000
6	-5.498628000	-1.425545000	0.107710000
1	-6.328866000	-1.015493000	-0.488791000
6	-5.584529000	-1.407272000	1.502177000
1	-6.474346000	-0.989819000	1.999996000
6	-4.530853000	-1.934451000	2.260360000
1	-4.607800000	-1.941594000	3.359733000
6	-3.382909000	-2.478141000	1.651391000
6	-4.368321000	-1.914826000	-2.088210000
1	-3.344165000	-2.177404000	-2.421591000
6	-5.360192000	-2.958064000	-2.653351000
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1	-5.301668000	-3.002658000	-3.762039000
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6	-4.704570000	-0.525145000	-2.668315000
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1	-4.092780000	0.268267000	-2.192556000
1	-5.771166000	-0.258533000	-2.509473000
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1	-3.642687000	-3.855195000	4.169421000

1	-2.098240000	-4.741151000	4.006694000
1	-3.422088000	-5.010089000	2.823865000
6	-1.629566000	-2.052790000	3.455005000
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6	6.714129000	-3.188981000	-0.028088000
1	6.822054000	-4.282450000	-0.108059000
6	7.853238000	-2.376719000	0.119866000
1	8.856293000	-2.830571000	0.155941000
6	7.704965000	-0.982594000	0.221070000
1	8.592019000	-0.339370000	0.335623000
6	6.425029000	-0.401879000	0.176755000
1	6.317250000	0.691051000	0.255956000
6	3.704733000	-0.090164000	-2.515576000
6	4.407542000	-1.344431000	-3.086827000
1	3.756169000	-2.237446000	-2.998840000
1	5.365491000	-1.559905000	-2.575928000
1	4.629011000	-1.187473000	-4.163346000
6	2.457257000	0.210572000	-3.373102000
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1	2.746693000	0.413243000	-4.424560000
1	1.925436000	1.104569000	-2.985609000
6	4.660102000	1.127338000	-2.586884000
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1	5.597251000	0.937752000	-2.026559000
1	4.170429000	2.026497000	-2.158626000
6	3.433869000	-0.375976000	2.510153000
6	-1.194542000	3.401852000	0.027410000
6	-0.643189000	4.798520000	0.089287000
6	-1.479091000	5.935386000	0.027519000
1	-2.568559000	5.807031000	-0.069473000
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1	-1.592091000	8.106768000	0.043505000
6	0.460896000	7.399427000	0.214621000
1	0.890781000	8.412663000	0.263105000
6	1.299895000	6.271333000	0.275226000
1	2.390243000	6.398877000	0.369956000
6	0.753739000	4.979269000	0.214579000
1	1.405485000	4.090662000	0.256408000
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1	0.498119000	3.109766000	2.898334000
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1	-0.683892000	1.082080000	-3.086517000
1	-1.431828000	2.030227000	-4.428999000
6	-2.505502000	4.056234000	-2.892332000
1	-3.483217000	3.597979000	-2.636668000
1	-2.497748000	4.272535000	-3.981824000
1	-2.420336000	5.022208000	-2.355667000
6	0.012666000	3.755220000	-2.862392000
1	0.107822000	3.861717000	-3.963345000
1	0.850457000	3.124734000	-2.499493000
1	0.121528000	4.762204000	-2.416828000
6	2.084613000	-0.213326000	3.241203000
1	1.413615000	-1.069340000	3.032692000
1	1.567319000	0.711546000	2.908068000
1	2.241407000	-0.143750000	4.337105000
6	4.088174000	-1.699196000	2.971673000
1	4.164422000	-1.707618000	4.079236000
1	5.109215000	-1.828847000	2.564805000
1	3.475595000	-2.571022000	2.664768000
6	4.347568000	0.819944000	2.878324000
1	3.889791000	1.773368000	2.542684000
1	5.344828000	0.724383000	2.404597000
1	4.498576000	0.873651000	3.977289000

4(C_1)

E_1 = -8453.692895 a.u.
E_2 = -8454.327252 a.u.
Nimag = nil

7	-2.056329000	-3.008512000	-0.443340000
32	-0.442980000	-0.449121000	-0.001707000
7	3.135384000	-0.283006000	1.063631000
32	1.777972000	0.832789000	-0.073195000
7	3.252390000	-0.209394000	-1.132059000
32	-2.432663000	1.161346000	-0.148550000
7	-1.437715000	2.704052000	-1.130818000
7	-1.602475000	2.634077000	1.056180000
6	-0.807134000	-2.434067000	-0.171143000
6	0.308162000	-3.459204000	-0.401139000
6	-0.491274000	-4.787136000	-0.504371000
1	-0.004722000	-5.530008000	-1.169914000

1	-0.561919000	-5.249201000	0.503767000
6	-1.919015000	-4.422069000	-0.989655000
6	1.294479000	-3.496246000	0.790173000
1	0.771548000	-3.716279000	1.743769000
1	1.809273000	-2.518172000	0.897437000
1	2.070355000	-4.279773000	0.638241000
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1	1.888162000	-3.970549000	-1.850782000
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1	0.498739000	-3.105526000	-2.588105000
6	-2.002592000	-4.462379000	-2.534746000
1	-3.038745000	-4.324149000	-2.894817000
1	-1.653499000	-5.450397000	-2.902348000
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1	-4.002768000	-5.075670000	-0.684423000
1	-2.921268000	-5.410448000	0.703425000
1	-2.797854000	-6.398707000	-0.787974000
6	-3.258658000	-2.531039000	0.197574000
6	-4.359949000	-2.038658000	-0.575785000
6	-5.499921000	-1.550196000	0.096359000
1	-6.344629000	-1.164827000	-0.496662000
6	-5.571252000	-1.511623000	1.492685000
1	-6.463863000	-1.105975000	1.994930000
6	-4.494184000	-2.000706000	2.244818000
1	-4.559624000	-1.996747000	3.345080000
6	-3.345289000	-2.537695000	1.630532000
6	-4.361569000	-2.006044000	-2.105387000
1	-3.328186000	-2.240408000	-2.432078000
6	-5.321389000	-3.065380000	-2.693422000
1	-5.103470000	-4.088100000	-2.323965000
1	-5.262579000	-3.082492000	-3.803010000
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6	-2.286345000	-3.177322000	2.534733000
1	-1.530570000	-3.649523000	1.877270000
6	-2.890427000	-4.289432000	3.422320000
1	-3.596708000	-3.880996000	4.175992000
1	-2.087570000	-4.819125000	3.978362000
1	-3.445609000	-5.041739000	2.824362000
6	-1.542927000	-2.141030000	3.399597000
1	-2.239412000	-1.597719000	4.073147000
1	-1.028306000	-1.390354000	2.763995000
1	-0.779039000	-2.636294000	4.036424000
6	3.908740000	-0.557869000	-0.005319000
6	5.277559000	-1.171069000	0.046653000
6	5.414563000	-2.577308000	-0.041599000
1	4.512548000	-3.199254000	-0.148390000

6	6.682612000	-3.176260000	0.013223000
1	6.771431000	-4.272396000	-0.053890000
6	7.836589000	-2.382752000	0.156072000
1	8.831308000	-2.853730000	0.199891000
6	7.711594000	-0.984398000	0.241712000
1	8.609435000	-0.355270000	0.351075000
6	6.442940000	-0.381842000	0.187147000
1	6.354611000	0.713867000	0.252240000
6	3.735361000	-0.073519000	-2.523468000
6	4.403325000	-1.361462000	-3.060355000
1	3.731319000	-2.235630000	-2.943511000
1	5.358037000	-1.584938000	-2.547252000
1	4.623038000	-1.241445000	-4.142001000
6	2.489071000	0.229485000	-3.382788000
1	1.745312000	-0.588962000	-3.307245000
1	2.770498000	0.355436000	-4.448358000
1	2.000499000	1.166600000	-3.044951000
6	4.721559000	1.115692000	-2.638722000
1	4.997768000	1.295657000	-3.699342000
1	5.655600000	0.918496000	-2.075531000
1	4.258907000	2.041204000	-2.237491000
6	3.452249000	-0.267206000	2.508232000
6	-1.255004000	3.402892000	0.003223000
6	-0.711907000	4.799934000	0.090939000
6	-1.547886000	5.934540000	-0.011210000
1	-2.631124000	5.803135000	-0.160502000
6	-1.005157000	7.228615000	0.079309000
1	-1.667922000	8.105207000	0.000534000
6	0.376935000	7.404030000	0.269220000
1	0.800879000	8.418437000	0.339540000
6	1.215650000	6.278110000	0.368940000
1	2.299822000	6.408804000	0.515704000
6	0.677360000	4.984527000	0.283126000
1	1.329011000	4.097601000	0.357090000
6	-1.870824000	2.996528000	2.463110000
6	-2.080972000	1.666961000	3.217284000
1	-2.373014000	1.858487000	4.270341000
1	-1.152614000	1.061722000	3.214242000
1	-2.883963000	1.064339000	2.741031000
6	-0.692063000	3.751793000	3.120302000
1	-0.573897000	4.777231000	2.721603000
1	0.259210000	3.203985000	2.961206000
1	-0.866328000	3.833355000	4.213827000
6	-3.163958000	3.843484000	2.563874000
1	-4.017025000	3.306096000	2.100208000
1	-3.043089000	4.818617000	2.050407000
1	-3.418061000	4.049824000	3.625279000
6	-1.276357000	3.083532000	-2.547933000
6	-1.386466000	1.777972000	-3.365538000
1	-2.362353000	1.280282000	-3.187084000
1	-0.584409000	1.066201000	-3.083654000

1	-1.306715000	1.992493000	-4.451174000
6	-2.412703000	4.041608000	-2.986111000
1	-3.405022000	3.589261000	-2.781516000
1	-2.346164000	4.253623000	-4.074371000
1	-2.350892000	5.009265000	-2.449356000
6	0.098958000	3.730345000	-2.831847000
1	0.251959000	3.823700000	-3.927382000
1	0.913849000	3.102691000	-2.415466000
1	0.185224000	4.742056000	-2.391734000
6	2.107784000	-0.100540000	3.247534000
1	1.434185000	-0.956779000	3.045841000
1	1.589532000	0.824063000	2.916358000
1	2.272725000	-0.030568000	4.342365000
6	4.122200000	-1.573246000	2.995101000
1	4.201008000	-1.557001000	4.102434000
1	5.143324000	-1.700090000	2.588091000
1	3.519136000	-2.458629000	2.708732000
6	4.357117000	0.944901000	2.843990000
1	3.889641000	1.885725000	2.486636000
1	5.353122000	0.845669000	2.368347000
1	4.512348000	1.026749000	3.940734000

5(C_1)

E_1 =-834.417070a.u.
E_2 = -834.695637 a.u.
Nimag = nil

7	-0.608604000	-0.055571000	0.063928000
6	-1.341266000	-0.084414000	-1.033220000
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6	-2.760222000	-0.483915000	0.953709000
1	-3.541263000	0.068886000	1.515332000
1	-2.941021000	-1.565087000	1.130246000
6	-1.340233000	-0.110879000	1.440678000
6	-3.503668000	-1.316000000	-1.369760000
1	-3.004935000	-2.294334000	-1.206070000
1	-3.481134000	-1.106770000	-2.458528000
1	-4.564480000	-1.414196000	-1.051396000
6	-3.489273000	1.159960000	-0.912319000
1	-4.566512000	1.117022000	-0.642464000
1	-3.407990000	1.386708000	-1.994717000
1	-3.033551000	2.006901000	-0.358710000
6	-1.283571000	1.261864000	2.136760000
1	-0.236868000	1.572522000	2.332511000
1	-1.802369000	1.200726000	3.116238000
1	-1.780747000	2.053618000	1.542744000
6	-0.724639000	-1.161527000	2.377019000
1	0.336538000	-0.933132000	2.606391000
1	-0.780449000	-2.182790000	1.952701000

1	-1.281419000	-1.167928000	3.337377000
6	0.841699000	0.039083000	0.001289000
6	1.465194000	1.317505000	-0.053887000
6	2.875306000	1.366908000	-0.026780000
1	3.380174000	2.344951000	-0.060885000
6	3.645215000	0.197486000	0.018724000
1	4.744784000	0.260000000	0.049851000
6	3.012507000	-1.052426000	-0.018926000
1	3.624258000	-1.967403000	-0.046406000
6	1.606614000	-1.161514000	-0.044163000
6	0.669984000	2.601304000	-0.298984000
1	-0.379019000	2.410788000	-0.003070000
6	1.168482000	3.811316000	0.512265000
1	1.210904000	3.593148000	1.599893000
1	0.490978000	4.678343000	0.364710000
1	2.181544000	4.139140000	0.196457000
6	0.647576000	2.902262000	-1.816025000
1	0.040589000	3.808768000	-2.027062000
1	0.206154000	2.048955000	-2.370780000
1	1.673657000	3.079628000	-2.203402000
6	0.957533000	-2.528418000	-0.272103000
1	-0.101694000	-2.456502000	0.044639000
6	1.606698000	-3.671262000	0.529476000
1	2.646112000	-3.877289000	0.196803000
1	1.033641000	-4.611895000	0.390374000
1	1.639605000	-3.448323000	1.616308000
6	0.938742000	-2.834789000	-1.788136000
1	1.970755000	-2.893859000	-2.195324000
1	0.392184000	-2.039908000	-2.336314000
1	0.436598000	-3.806090000	-1.985929000

6(C_1)

E_1 =-8454.160808 a.u.
E_2 = -8454.792793 a.u.
Nimag = nil

7	-2.118583000	-3.004193000	-0.340046000
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7	3.178717000	-0.413490000	1.105490000
32	1.887770000	0.723593000	-0.006255000
7	3.237301000	-0.376287000	-1.092173000
32	-2.422209000	1.333674000	-0.223205000
7	-1.260581000	2.764777000	-1.139633000
7	-1.555579000	2.699920000	1.034940000
6	-0.936998000	-2.420107000	-0.196798000
6	0.188020000	-3.443467000	-0.377700000
6	-0.571960000	-4.799277000	-0.390454000
1	-0.097117000	-5.543637000	-1.059252000
1	-0.573777000	-5.230522000	0.632644000
6	-2.017679000	-4.489028000	-0.817806000

6	1.155885000	-3.377200000	0.826561000
1	0.620698000	-3.515082000	1.788383000
1	1.699202000	-2.411435000	0.863550000
1	1.900580000	-4.196237000	0.734305000
6	0.988785000	-3.170550000	-1.674240000
1	1.738480000	-3.976417000	-1.816751000
1	1.530456000	-2.206645000	-1.593460000
1	0.349585000	-3.140467000	-2.578625000
6	-2.177696000	-4.588258000	-2.348135000
1	-3.219332000	-4.423403000	-2.673240000
1	-1.897919000	-5.616232000	-2.656111000
1	-1.518999000	-3.884558000	-2.891884000
6	-3.060089000	-5.378566000	-0.138853000
1	-4.094375000	-5.052756000	-0.367923000
1	-2.933521000	-5.409314000	0.958498000
1	-2.942098000	-6.413705000	-0.518900000
6	-3.384031000	-2.414836000	0.112102000
6	-4.325688000	-1.871403000	-0.811053000
6	-5.509640000	-1.308341000	-0.289653000
1	-6.242442000	-0.872769000	-0.985486000
6	-5.771586000	-1.282658000	1.083123000
1	-6.700984000	-0.830457000	1.462713000
6	-4.849630000	-1.849264000	1.969641000
1	-5.069398000	-1.849317000	3.048584000
6	-3.648995000	-2.437426000	1.520562000
6	-4.161645000	-1.881906000	-2.332548000
1	-3.134736000	-2.229623000	-2.562380000
6	-5.172600000	-2.855638000	-2.984113000
1	-5.149201000	-3.866880000	-2.529041000
1	-4.974577000	-2.959936000	-4.071376000
1	-6.210035000	-2.477819000	-2.870379000
6	-4.320116000	-0.483317000	-2.962794000
1	-4.066698000	-0.515618000	-4.042509000
1	-3.665368000	0.261670000	-2.467138000
1	-5.361404000	-0.108630000	-2.880161000
6	-2.760767000	-3.104090000	2.581748000
1	-1.885895000	-3.557818000	2.071816000
6	-3.517443000	-4.234053000	3.321388000
1	-4.331836000	-3.823898000	3.953339000
1	-2.826289000	-4.783140000	3.994012000
1	-3.980015000	-4.966546000	2.630252000
6	-2.213874000	-2.097204000	3.615904000
1	-3.035321000	-1.620024000	4.189775000
1	-1.623570000	-1.295174000	3.131634000
1	-1.558063000	-2.614984000	4.346589000
6	3.921421000	-0.727042000	0.022966000
6	5.278826000	-1.366716000	0.049650000
6	5.382964000	-2.774686000	-0.022440000
1	4.468057000	-3.381662000	-0.101427000
6	6.640885000	-3.397539000	0.010111000
1	6.709112000	-4.495343000	-0.044849000

6	7.810305000	-2.622807000	0.113513000
1	8.796524000	-3.111924000	0.139220000
6	7.716166000	-1.222205000	0.183692000
1	8.628169000	-0.610238000	0.263729000
6	6.458097000	-0.595351000	0.152435000
1	6.393506000	0.502241000	0.207603000
6	3.712752000	-0.214367000	-2.492086000
6	4.352153000	-1.505415000	-3.051577000
1	3.664086000	-2.369422000	-2.953933000
1	5.302370000	-1.757096000	-2.544216000
1	4.574302000	-1.368151000	-4.129765000
6	2.463609000	0.128535000	-3.328016000
1	1.713459000	-0.686523000	-3.286389000
1	2.736987000	0.293621000	-4.389357000
1	1.988863000	1.061083000	-2.956877000
6	4.716139000	0.959867000	-2.591408000
1	4.978443000	1.157571000	-3.651394000
1	5.656263000	0.735062000	-2.050608000
1	4.277947000	1.886670000	-2.166036000
6	3.518088000	-0.398988000	2.551927000
6	-1.107025000	3.455244000	0.005850000
6	-0.510181000	4.826702000	0.125239000
6	-1.285382000	5.992042000	-0.066499000
1	-2.359304000	5.906434000	-0.293772000
6	-0.692776000	7.262605000	0.037663000
1	-1.306783000	8.164633000	-0.111059000
6	0.676859000	7.381821000	0.330868000
1	1.139517000	8.378040000	0.410139000
6	1.453986000	6.225186000	0.523623000
1	2.527618000	6.313767000	0.752972000
6	0.865509000	4.954067000	0.424439000
1	1.472101000	4.045184000	0.567590000
6	-1.879033000	3.083344000	2.432831000
6	-2.369133000	1.797421000	3.127760000
1	-2.672821000	2.013760000	4.171636000
1	-1.569700000	1.030293000	3.149753000
1	-3.249393000	1.368908000	2.601398000
6	-0.637122000	3.607941000	3.188503000
1	-0.284433000	4.578699000	2.791922000
1	0.197444000	2.879646000	3.125369000
1	-0.885383000	3.752667000	4.260231000
6	-3.012876000	4.135681000	2.469305000
1	-3.904956000	3.770859000	1.918896000
1	-2.690610000	5.096068000	2.021355000
1	-3.316457000	4.340069000	3.517099000
6	-1.038517000	3.151866000	-2.551994000
6	-1.113045000	1.845954000	-3.370048000
1	-2.102411000	1.358953000	-3.250699000
1	-0.332682000	1.129042000	-3.045753000
1	-0.970190000	2.052066000	-4.449991000
6	-2.155174000	4.109189000	-3.034889000

1	-3.157142000	3.662770000	-2.868101000
1	-2.046308000	4.316295000	-4.119849000
1	-2.110082000	5.079238000	-2.501981000
6	0.346516000	3.800525000	-2.772359000
1	0.539325000	3.902560000	-3.860006000
1	1.150713000	3.174310000	-2.333444000
1	0.413176000	4.809276000	-2.323810000
6	2.193356000	-0.156251000	3.303511000
1	1.478489000	-0.987095000	3.139491000
1	1.711551000	0.785509000	2.963061000
1	2.378570000	-0.064127000	4.392398000
6	4.125709000	-1.736604000	3.031058000
1	4.225318000	-1.719459000	4.135857000
1	5.131856000	-1.917078000	2.608235000
1	3.473243000	-2.591940000	2.761946000
6	4.490578000	0.764729000	2.860806000
1	4.068659000	1.731872000	2.517325000
1	5.469849000	0.612643000	2.366113000
1	4.673378000	0.837346000	3.952908000
1	-0.512753000	-0.543014000	1.689516000

7(C_1)

E_1 =-8454.162333 a.u.
E_2 = -8454.788325 a.u.
Nimag = nil

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32	1.659753000	-0.012178000	-0.042302000
7	3.306816000	-0.547923000	-1.091221000
32	-2.201727000	1.453756000	-0.242348000
7	-0.936880000	2.812303000	-1.127858000
7	-1.316266000	2.791961000	1.034583000
6	-1.140987000	-2.349508000	-0.392913000
6	-0.137742000	-3.470182000	-0.749346000
6	-1.029823000	-4.744228000	-0.711076000
1	-0.699728000	-5.511155000	-1.439636000
1	-0.965290000	-5.201915000	0.298542000
6	-2.478948000	-4.289262000	-0.967889000
6	0.988455000	-3.617119000	0.297989000
1	0.578586000	-3.736765000	1.321489000
1	1.673421000	-2.746463000	0.305107000
1	1.593576000	-4.518821000	0.062455000
6	0.506809000	-3.227247000	-2.135072000
1	1.131831000	-4.098744000	-2.422542000
1	1.160251000	-2.333805000	-2.095803000
1	-0.240088000	-3.061773000	-2.935150000
6	-2.807601000	-4.337968000	-2.477503000

1	-3.862737000	-4.087005000	-2.682636000
1	-2.640406000	-5.373172000	-2.838901000
1	-2.162761000	-3.665060000	-3.074265000
6	-3.512661000	-5.129186000	-0.210103000
1	-4.535480000	-4.714675000	-0.316632000
1	-3.276359000	-5.210117000	0.866649000
1	-3.521446000	-6.154929000	-0.631348000
6	-3.538817000	-2.150614000	0.153903000
6	-4.485889000	-1.453298000	-0.657106000
6	-5.534956000	-0.763841000	-0.011926000
1	-6.272441000	-0.222173000	-0.623825000
6	-5.660606000	-0.750727000	1.380556000
1	-6.486324000	-0.200196000	1.858028000
6	-4.740754000	-1.459629000	2.161713000
1	-4.859391000	-1.471364000	3.256620000
6	-3.675725000	-2.180465000	1.582574000
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1	-3.519155000	-1.909230000	-2.514604000
6	-5.647825000	-2.294233000	-2.737740000
1	-5.690099000	-3.309050000	-2.292094000
1	-5.574215000	-2.403004000	-3.840183000
1	-6.619601000	-1.805430000	-2.515845000
6	-4.528784000	-0.037423000	-2.802006000
1	-4.416557000	-0.094804000	-3.904635000
1	-3.725389000	0.612785000	-2.400763000
1	-5.494784000	0.469231000	-2.596705000
6	-2.784345000	-2.997474000	2.528380000
1	-2.029160000	-3.528730000	1.913012000
6	-3.607898000	-4.057794000	3.298515000
1	-4.297537000	-3.579341000	4.024184000
1	-2.934678000	-4.724544000	3.876866000
1	-4.224984000	-4.688150000	2.627848000
6	-2.017004000	-2.114297000	3.535203000
1	-2.711617000	-1.572632000	4.211122000
1	-1.386482000	-1.366249000	3.012602000
1	-1.357284000	-2.739906000	4.172404000
6	3.974841000	-0.875474000	0.035812000
6	5.388791000	-1.372159000	0.090026000
6	5.648842000	-2.754568000	-0.049837000
1	4.811792000	-3.454289000	-0.196855000
6	6.967464000	-3.235627000	0.002521000
1	7.158971000	-4.314598000	-0.105559000
6	8.038025000	-2.343877000	0.192521000
1	9.071216000	-2.722344000	0.232993000
6	7.785939000	-0.967759000	0.330295000
1	8.620705000	-0.265031000	0.477895000
6	6.468483000	-0.481070000	0.280199000
1	6.278210000	0.597819000	0.386594000
6	3.769489000	-0.384879000	-2.496097000
6	4.292283000	-1.717213000	-3.079214000
1	3.525906000	-2.514549000	-2.999213000

1	5.211704000	-2.058957000	-2.566794000
1	4.536107000	-1.584310000	-4.153125000
6	2.540487000	0.072754000	-3.305322000
1	1.723143000	-0.675107000	-3.261865000
1	2.813669000	0.216775000	-4.369564000
1	2.152018000	1.040230000	-2.925727000
6	4.859013000	0.708843000	-2.593303000
1	5.099756000	0.908659000	-3.657685000
1	5.796450000	0.399953000	-2.092156000
1	4.508348000	1.657796000	-2.137742000
6	3.399826000	-0.854238000	2.560498000
6	-0.817063000	3.521957000	0.016201000
6	-0.230161000	4.899479000	0.129496000
6	-1.034346000	6.054176000	-0.001033000
1	-2.115063000	5.952191000	-0.184583000
6	-0.462448000	7.334103000	0.103617000
1	-1.100078000	8.225952000	-0.000091000
6	0.915709000	7.475905000	0.340588000
1	1.361720000	8.479379000	0.422703000
6	1.722667000	6.331660000	0.473275000
1	2.802941000	6.436845000	0.660158000
6	1.154817000	5.051500000	0.368843000
1	1.787422000	4.156133000	0.473030000
6	-1.581382000	3.147768000	2.450224000
6	-2.077715000	1.857493000	3.134184000
1	-2.345119000	2.060633000	4.190765000
1	-1.297548000	1.069890000	3.117023000
1	-2.983033000	1.458342000	2.627634000
6	-0.299624000	3.627070000	3.168288000
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1	-0.502795000	3.752191000	4.251818000
6	-2.688520000	4.224180000	2.551758000
1	-3.606633000	3.892113000	2.024124000
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6	-0.923757000	1.924118000	-3.374082000
1	-1.938321000	1.492728000	-3.245677000
1	-0.186001000	1.158128000	-3.063487000
1	-0.784357000	2.134059000	-4.453650000
6	-1.854972000	4.223604000	-2.974792000
1	-2.867406000	3.816395000	-2.773242000
1	-1.780340000	4.433624000	-4.062083000
1	-1.750017000	5.187777000	-2.439861000
6	0.639004000	3.810469000	-2.804012000
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1	0.769707000	4.798165000	-2.322920000
6	2.050877000	-0.580019000	3.254653000
1	1.271910000	-1.299511000	2.931462000

1	1.685480000	0.444701000	3.031857000
1	2.167847000	-0.663950000	4.353575000
6	3.870910000	-2.280438000	2.923484000
1	3.952080000	-2.376451000	4.025603000
1	4.864221000	-2.511588000	2.493714000
1	3.145536000	-3.040314000	2.568011000
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8(C_1)

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7	3.289489000	0.709833000	-1.085129000
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7	-2.197536000	2.117526000	1.101789000
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6	1.243626000	-3.403642000	-0.527410000
6	0.806497000	-4.892107000	-0.393435000
1	1.398030000	-5.562163000	-1.048377000
1	0.967287000	-5.232956000	0.650984000
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1	2.517597000	-1.970660000	0.575517000
1	3.103972000	-3.675039000	0.589607000
6	1.959374000	-3.106265000	-1.867420000
1	2.871110000	-3.734151000	-1.954782000
1	2.273011000	-2.042884000	-1.910225000
1	1.316783000	-3.306304000	-2.747039000
6	-0.910364000	-5.192429000	-2.236637000
1	-1.978060000	-5.304817000	-2.496221000
1	-0.403065000	-6.137258000	-2.520061000
1	-0.480473000	-4.380154000	-2.854568000
6	-1.451614000	-6.025019000	0.066201000
1	-2.543488000	-5.980553000	-0.120645000
1	-1.279165000	-5.944792000	1.155668000
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6	-2.430775000	-3.216567000	0.217532000
6	-3.546084000	-2.954316000	-0.632270000
6	-4.786451000	-2.653309000	-0.027061000

1	-5.658921000	-2.453101000	-0.668636000
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1	-5.911331000	-2.362742000	1.809074000
6	-3.833847000	-2.885027000	2.184890000
1	-3.961691000	-2.876788000	3.278788000
6	-2.574423000	-3.213548000	1.643409000
6	-3.489964000	-3.017939000	-2.159761000
1	-2.428324000	-3.147189000	-2.449692000
6	-4.302816000	-4.223051000	-2.688806000
1	-4.022134000	-5.174873000	-2.193782000
1	-4.157663000	-4.347088000	-3.782327000
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1	-3.862516000	-1.792686000	-3.936321000
1	-3.422246000	-0.840146000	-2.484852000
1	-5.064169000	-1.538526000	-2.637434000
6	-1.445131000	-3.594635000	2.607809000
1	-0.606058000	-3.988498000	1.999923000
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1	-2.635348000	-4.354858000	4.310580000
1	-0.998392000	-5.053467000	4.181337000
1	-2.297021000	-5.590095000	3.064098000
6	-0.902847000	-2.379209000	3.384809000
1	-1.685370000	-1.933669000	4.034184000
1	-0.537098000	-1.592509000	2.695485000
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6	7.473045000	-1.097690000	0.045610000
1	7.909057000	-2.104730000	-0.046902000
6	8.308982000	0.019562000	0.221975000
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1	1.710034000	1.810432000	-2.929150000
6	4.360729000	2.446897000	-2.518662000
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1	3.681494000	3.206262000	-2.078240000

6	3.438095000	0.476737000	2.552713000
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6	-2.507176000	4.445415000	0.173899000
6	-3.790595000	5.021049000	0.041644000
1	-4.665370000	4.378299000	-0.141604000
6	-3.955126000	6.412636000	0.153550000
1	-4.959650000	6.852198000	0.052797000
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6	-1.563676000	6.669866000	0.525488000
1	-0.689913000	7.313577000	0.712039000
6	-1.393590000	5.280166000	0.422181000
1	-0.391445000	4.835917000	0.523518000
6	-2.536426000	2.284353000	2.539886000
6	-2.222155000	0.931425000	3.204192000
1	-2.483256000	0.961099000	4.280947000
1	-1.144662000	0.687939000	3.117119000
1	-2.807776000	0.109529000	2.739399000
6	-1.674321000	3.379031000	3.207507000
1	-1.925176000	4.391512000	2.838775000
1	-0.595638000	3.195211000	3.025703000
1	-1.845948000	3.369036000	4.303441000
6	-4.040783000	2.599215000	2.710711000
1	-4.665553000	1.819550000	2.227987000
1	-4.302045000	3.582613000	2.272955000
1	-4.304628000	2.631348000	3.787893000
6	-2.200907000	2.720061000	-2.511320000
6	-1.670042000	1.549449000	-3.360111000
1	-2.295794000	0.642181000	-3.239311000
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1	-1.684548000	1.826048000	-4.433386000
6	-3.645520000	3.050947000	-2.954164000
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1	-3.666010000	3.301480000	-4.034711000
1	-4.049178000	3.920861000	-2.400243000
6	-1.275795000	3.938148000	-2.731249000
1	-1.187630000	4.138142000	-3.818605000
1	-0.259127000	3.735711000	-2.335841000
1	-1.662418000	4.857686000	-2.253845000
6	2.064779000	0.305498000	3.233015000
1	1.594669000	-0.653235000	2.938069000
1	1.378587000	1.132654000	2.948659000
1	2.170778000	0.321247000	4.336205000
6	4.362984000	-0.680001000	2.994642000
1	4.436915000	-0.692858000	4.101517000
1	5.388027000	-0.571844000	2.592292000
1	3.959256000	-1.659527000	2.668036000
6	4.044713000	1.834408000	2.982198000
1	3.397391000	2.676079000	2.658870000
1	5.054537000	1.982142000	2.551885000
1	4.141995000	1.881442000	4.086808000

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9(C_1)

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32	1.633410000	-2.065911000	1.186884000
7	2.298333000	-0.101656000	1.416575000
7	2.753035000	-1.266173000	-0.401970000
6	-3.053485000	0.234126000	-0.448653000
6	-4.432841000	0.378616000	0.123323000
6	-4.630404000	0.290803000	1.521486000
1	-3.759836000	0.118332000	2.173717000
6	-5.913445000	0.444128000	2.072035000
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1	-0.251795000	2.929875000	-0.512085000
1	-1.055523000	4.379253000	-1.211727000
1	-0.756944000	2.937131000	-2.242587000
6	-3.479878000	3.225049000	-1.799281000
1	-3.478772000	4.335443000	-1.810396000
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6	-2.873000000	-2.330473000	-0.587724000
6	2.989598000	-0.115758000	0.215413000
6	3.832944000	1.012183000	-0.293197000
6	5.240328000	0.903234000	-0.385894000
1	5.737501000	-0.018195000	-0.046157000
6	6.008370000	1.965458000	-0.891837000
1	7.103835000	1.865690000	-0.952412000
6	5.383499000	3.151497000	-1.315844000
1	5.985828000	3.981682000	-1.717460000
6	3.985025000	3.271690000	-1.224155000

1	3.486670000	4.195677000	-1.557894000
6	3.215823000	2.213643000	-0.714107000
1	2.120259000	2.300584000	-0.655653000
6	3.121829000	-1.784730000	-1.737956000
6	2.088333000	-2.881759000	-2.072961000
1	2.341487000	-3.376168000	-3.032735000
1	1.073922000	-2.443760000	-2.163209000
1	2.068708000	-3.661612000	-1.281804000
6	3.079831000	-0.709919000	-2.846349000
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1	3.250469000	-1.193447000	-3.830756000
6	4.527759000	-2.428912000	-1.659957000
1	4.567658000	-3.178538000	-0.843208000
1	5.309890000	-1.666560000	-1.473845000
1	4.771559000	-2.939222000	-2.615216000
6	2.726201000	0.581866000	2.678520000
6	1.874249000	-0.007539000	3.822752000
1	2.006793000	-1.109842000	3.885605000
1	0.794977000	0.200465000	3.668327000
1	2.187193000	0.432788000	4.791975000
6	4.213527000	0.279675000	2.974857000
1	4.391690000	-0.816350000	2.974726000
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6	2.481648000	2.105913000	2.616380000
1	2.698251000	2.565474000	3.603472000
1	1.420632000	2.314800000	2.364665000
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6	-1.698189000	-3.224690000	-1.034221000
1	-0.843732000	-3.135143000	-0.331650000
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1	-2.013399000	-4.287398000	-1.069610000
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1	-2.539370000	-2.638193000	1.560126000
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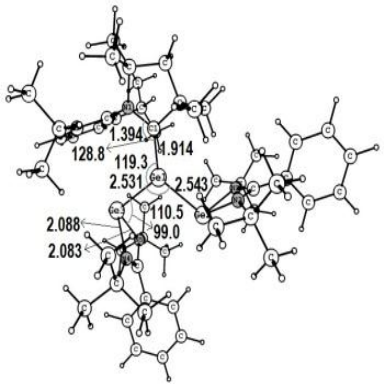

3
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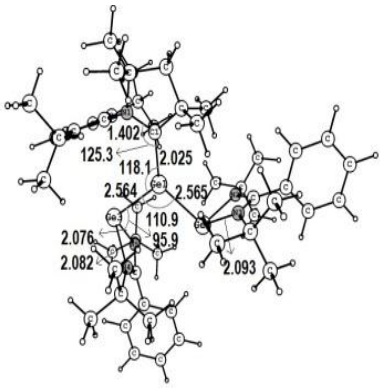
N1-C1-C2-Ge1 = 177.3°



4
(24.6)
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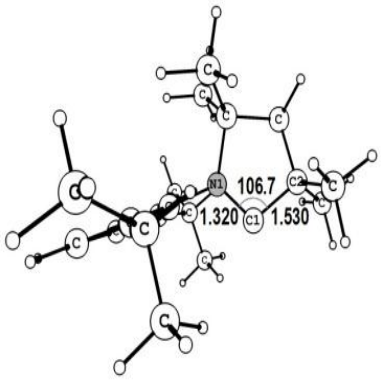
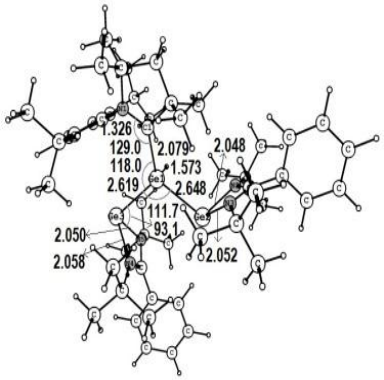
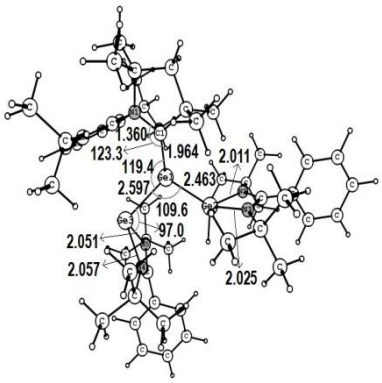
N1-C1-C2-Ge1 = 164.8°



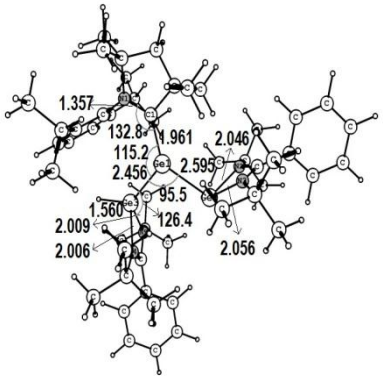
5



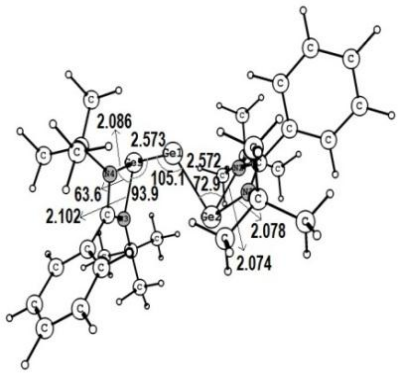
6
Ge3-Ge1-Ge2-C1 = -134.2°
N1-C1-C2-Ge1 = 177.0°



7
Ge3-Ge1-Ge2-C1 = -134.2°
N1-C1-C2-Ge1 = -168.8°



8
Ge3-Ge1-Ge2-C1 = 133.5°
N1-C1-C2-Ge1 = 167.2°



9

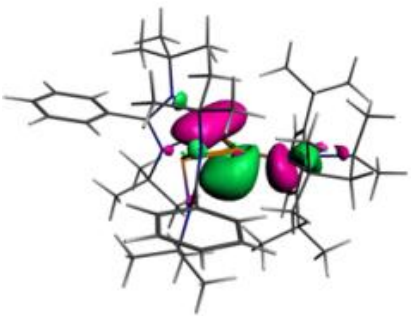
Figure S3 Optimized geometries (M06/def2-TZVPP//BP86/def2-SVP level of theory) and important geometrical parameters of Ge_3 complex in singlet state (**3**), Ge_3 complex in triplet state (**4**), cyclic alkyl amino carbene (**5**),protonated structures of **3** at Ge1 (**6**), at Ge2 (**7**), at Ge3(**8**),and trigermaallene complex (**9**). Distances are given in Å, angles are given in deg. Relative energies in kcal/molare also given in brackets.

Table S4 EDA-NOCV results for Ge-C bond at the BP86/TZ2P level of theory. Energies are in kcal/mol.

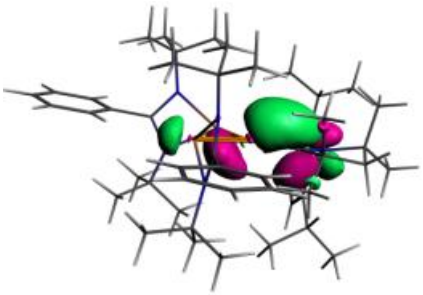
	ΔE_{Int}	ΔE_{Pauli}	ΔE_{Elstat} [a]	ΔE_{orb} [a]	ΔE_1 [b]	ΔE_2 [b]	ΔE_{rest} [b,c]	ΔE_{prep}	$-D_e$
Ge1 ⇌ C1	-74.3	278.4	-190.6 (54.0%)	-162.2 (46.0%)	-62.1 (38.3%)	-77.2 (47.6%)	-22.9 (14.1%)	47.4	-26.9
Ge1 ═ C1	-98.6	231.6	-153.6 (46.5%)	-176.7 (53.5%)				71.7	-26.9

[a]Values in parenthesis give the percentage contribution to the total attractive interactions $\Delta E_{Elstat}+\Delta E_{Orb}$; [b]Values in parenthesis give the percentage contribution to orbital interaction ΔE_{Orb};[c]$\Delta E_{rest} = \Delta E_{Orb} -(\Delta E_1 +\Delta E_2)$.

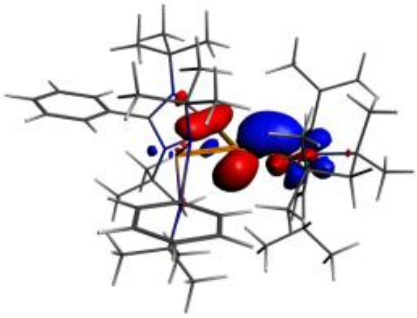
EDA data were calculated for electron sharing interaction (Ge1═C1) of triplet Ge_3L_2 fragment with triplet cAAC. (Table S4) The corresponding ΔE_{orb} is higher (-176.7 kcal/mol) than that of the donor-acceptor interaction (-162.2 kcal/mol).(Table S4)Hence, the donor-acceptor interaction (Ge1 ⇌ C1) between the singlet Ge_3L_2fragment with singlet cAAC can be considered as best bonding representation and in turn taken for further analysis. The lone pairs on Ge2 and Ge3 lie in between the plane of σ- and π-type orbitals on Ge1. Therefore, the linear combination of the lone pairs on Ge2 and Ge3 with σ- and π-type orbitals on Ge1 results orbitals, which are neither σ- nor π-symmetric in the Ge_3L_2 fragment. The electronic state of the Ge_3L_2 fragment considered for bonding study are vacant orbital with maximum σ-contribution on Ge1and filled orbital with maximum π-contribution on Ge1. The high value of the preparation energy corresponds to the promotion of the electrons from the orbital with maximum σ-contribution on Ge1 on Ge_3L_2 fragment to the orbital with maximum π-contribution on Ge1. In addition, the electronic state of cAAC fragment is a singlet with filled σ-lone pair on the carbene carbon atom and the empty C1–N1 π*-MO. Even though, there is no mixing between σ-type and π-type orbital on cAAC fragment. These orbitals mix significantly to undergo effective overlap with the Ge_3L_2 fragment orbitals. This is depicted in the pictorial representation of NOCV pair of orbitals Ψ_{-1}/Ψ_1 and Ψ_{-2}/Ψ_2. (Fig. S4)



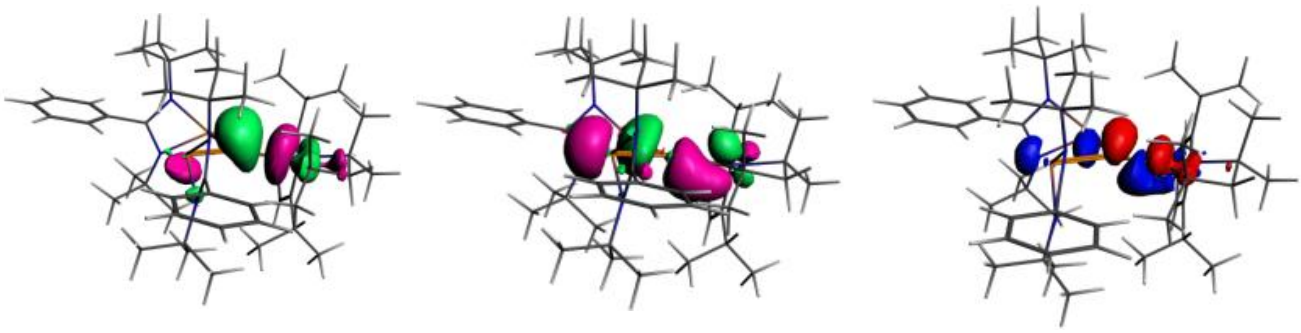
Ψ_{-1}(-1.23)



Ψ_1(1.23)



$\Delta\rho_1$
(ΔE_1 = -62.1 kcal/mol)



Ψ_{-2}(-0.85) Ψ_2(0.85) $\Delta\rho_2$ (ΔE_2 = -77.2 kcal/mol)

Fig.S4 NOCV pair of orbitals Ψ_{-1}/ Ψ_1 and Ψ_{-2}/ Ψ_2 with their eigen values (eV) in parenthesis, the associated deformation density plots $\Delta\rho_1$ and $\Delta\rho_2$ and orbital stabilization energies ΔE for the complex **3** for Ge1-C bond at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plots is from red → blue.

Scheme S1 Reaction energies at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

1. 4 LGeCl + 4 K→ [:Ge:] + 2 [LGe·] + 4 KCl + L_2Ge: ΔE = -1.2 kcal/mol
2. [:Ge:] + 2 [LGe·] + cAAC → (cAAC)Ge($LGe)_2$ ΔE = -143.8 kcal/mol
3. 4 LGeCl+ 4K + cAAC→ (cAAC)Ge($LGe)_2$ + 4 KCl + L_2Ge: ΔE = -145.0 kcal/mol
4. (cAAC)Ge($LGe)_2$ + cAAC→ LGe-GeL + $(cAAC)_2$Ge ΔE = 4.2 kcal/mol
5. (cAAC)Ge($LGe)_2$→LGe-Ge-GeL + cAAC ΔE = 44.6 kcal/mol

The first step of the reaction can be considered as the formation of the intermediates [:Ge:], [LGe·], and L_2Ge: by the reaction of LGeCl with KC_8. The reaction energy is slightly exothermic (ΔE_1 = -1.2 kcal/mol). Although L_2Ge: is not isolated, its presence in the reaction mixture has been detected by NMR study.[17] The transient intermediates [:Ge:] and [LGe·] thus formed undergo fast reaction with cAAC and result in the formation of **1**. The reaction energy for this step is substantially exothermic (ΔE_2 = -143.8 kcal/mol) and hence the overall reaction for the formation of **1** is highly favorable ($\Delta E_1 + \Delta E_2$ = -145.0 kcal/mol). The synthesis of **1** at very low temperature (-78°C) supports the high exothermic reaction energy. The reaction energy for the formation of $(cAAC)_2$Ge(**2**), by the reaction of cAAC with **1** is slightly endothermic (ΔE_3 = 4.2 kcal/mol). The conversion of **1** to **2** is practically slow at room temperature and the yield of **2** (10-20%) is low. Moreover, **1** is very stable toward the decomposition to

LGe-Ge-GeLand cAACby 44.6 kcal/mol. This clearly indicates that cAAC plays a significant role for stabilizing the trigermylene species LGe-Ge-GeL which was not successfully isolated.

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