Striking Reactivity of a Ylide-like Germylene toward Terminal Alkynes: [4+2] Cycloaddition versus C-H Bond Activation

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A. Experimental Section

General Considerations.

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material LGe: **2** [A1] {L = CH[(C=CH_2)CMe][N(aryl)]$_2$; aryl = 2,6-*i*$Pr_2C_6H_3$)} was prepared according to literature procedure. ^{1}H, ^{13}C, NMR spectra were recorded on Bruker Spectrometer AV 400. Chemical shifts of the deuterated solvents in ^{1}H NMR data: benzene-d_6: δ(C_6D_5H) = 7.15 ppm. Chemical shifts of the deuterated solvents in ^{13}C NMR data: benzene-d_6: δ = 128.02 ppm.

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of Compounds **3**, **4**, and **5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 [A2] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

*Synthesis of **3**.*

A red-brown solution of **2** (0.33g, 0.67 mmol) in n-hexane (20 mL) was stirred at room temperature. The N_2 atmosphere in the flask was exchanged to carefully dried C_2H_2. After stirring for 8 h, the colour of the solution changed to yellow. The resulting solution was concentrated to 4 mL, and cooled to -20°C for 24 h to isolate yellow crystals of compound **3** (0.28 g, 0.54 mmol, 81 %). M.p. 155 °C (decomp.) ^{1}H NMR (400.13 MHz, C_6D_6, 298K): δ = 0.86 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.05 (d, $^3J_{HH}$ = 6.8

Hz, 3 H, CH*Me*$_2$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.32 (s, 3 H, NC*Me*), 1.35 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.46 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 2.55 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.18 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.29 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.33 (s, 1 H, NC*CH*$_2$), 3.73 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.95 (s, 1 H, NC*CH*$_2$), 4.25 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, γ-C*H*), 6.96 (dd, $^3J_{HH}$ = 10.1 Hz, $^3J_{HH}$ = 6.7 Hz, 1 H, Ge-CH=C*H*), 6.95 - 7.31 (m, br, 6 H, arom. *H*), 7.60 (dd, $^3J_{HH}$ = 10.1 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, Ge-C*H*). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298K): δ = 22.8, 23.8, 24.1, 24.5, 24.6, 25.0, 25.2, 26.1, 27.1, 27.4 (CH*Me*, NC*Me*); 29.0, 29.3 (*C*HMe); 62.3 (γ-*C*); 81.2 (NC*C*H$_2$); 124.6 (Ge-CH=*C*H); 160.8 (Ge-*C*H); 123.8 - 186.8 (N*C*, 2,6-*i*-Pr$_2$*C*$_6$H$_3$). EI-MS: m/z (%): 515.2 (38, [M] $^+$), 500.2 (39, [M-Me]$^+$), 472.2 (32 [M-^{i}Pr]$^+$). Elemental analysis (%): calcd for $C_{31}H_{42}N_2Ge$: C, 72.3; H, 8.2; N, 5.4. Found: C, 72.1; H, 8.1; N, 5.2.

*Synthesis of **4** and **5**.*

Phenyl acetylene (0.16 g, 1.51 mmol) was added to a solution of **2** (0.74 g, 1.51 mmol) in n-hexane (30 ml) at room temperature. After stirring for 8 h, the colour of the solution changed to yellow. Volatiles were removed in vacuo, and the residue was extracted with n-hexane (3 X 15 mL). After concentration of the n-hexane extract to 10 mL, the solution was kept at -20 °C for 12 h, affording rod-like pale yellow crystals of **5** which were isolated by filtration (0.14 g, 0.24 mmol, 16 %). Further concentration of the n-hexane filtrate to about 5 mL, the solution was stored at -20 °C, whereupon block-like yellow crystals of **4** were obtained (0.60 g, 1.0 mmol, 67 %).

Data for **4** are as follows. M.p. 117 °C (decomp.) ^{1}H NMR (400.13 MHz, C_6D_6, 298K): δ = 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 1.45 (s, 3 H, NC*Me*), 1.46 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me*$_2$), 2.70 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.25 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.31 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 3.42 (s, 1 H, NC*CH*$_2$), 3.77 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*Me$_2$), 4.08 (s, 1 H, NC*CH*$_2$), 5.05 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, γ-C*H*), 7.67 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, Ge-C*H*), 6.95 - 7.58 (m, br, 11 H, arom. *H*).$^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298K): δ = 23.1, 23.8, 24.1 , 24.5, 24.6, 24.7, 25.1, 26.1, 26.8, 27.6, 27.7 (CH*Me*, NC*Me*); 29.1, 29.4 (*C*HMe); 66.7 (γ-*C*); 81.8 (NC*C*H$_2$); 156.6 (Ge-*C*H); 123.8 - 187.3 (N*C*, Ge-CH=*C*Ph, and arom. *C*).EI-MS: m/z (%): 591.3 (100, [M] $^+$), 576.2 (79, [M-Me]$^+$), 474.2 (94, [M-PhCCH-Me]$^+$). Elemental analysis (%): calcd for $C_{37}H_{46}N_2Ge$: C, 75.1; H, 7.8; N, 4.7. Found: C, 74.5; H, 7.8; N, 4.5.

Data for **5** are as follows. M.p. 184 °C (decomp.) ^{1}H NMR (400.13 MHz, C_6D_6, 298K): δ = 1.13 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.27 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.45 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.61 (s, 6 H, NC*Me*), 3.46 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2 H, C*H*Me$_2$), 4.11 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2 H, C*H*Me$_2$), 5.10 (s, 1 H, γ-C*H*), 6.93 - 7.54 (m, br, 11 H, arom. *H*).^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298K): δ = 23.5 (NC*Me*); 24.1, 24.7 , 24.8, 28.1 (CH*Me*$_2$); 28.6, 29.2 (*C*HMe$_2$); 100.1 (γ-*C*); 103.3, 113.0 (Ph*CC*Ge); 124.2 - 166.2 (N*C*, arom. *C*).EI-MS: m/z (%): 591.3 (76, [M]$^{+}$), 576.2 (58, [M-Me]$^{+}$), 475.1 (100, [M-PhCC-Me]$^{+}$). Elemental analysis (%): calcd for $C_{37}H_{46}N_2Ge$: C, 75.1; H, 7.8; N, 4.7. Found: C, 74.7; H, 7.6; N, 4.6.

*Crystal data and structure refinement for **3**.*

Empirical formula	C31 H42 Ge N2	
Formula weight	515.26	
Temperature	150(2) K	
Wavelength	71.073 pm	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 1053.67(4) pm	α= 90°.
	b = 1248.40(5) pm	β= 90°.
	c = 4266.2(2) pm	γ = 90°.
Volume	5.6118(4) nm^3	
Z	8	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	1.112 mm^{-1}	
F(000)	2192	
Crystal size	0.32 x 0.19 x 0.14 mm^3	
Theta range for data collection	2.91 to 25.00°.	
Index ranges	-12<=h<=12, -14<=k<=14, -50<=l<=49	
Reflections collected	33432	
Independent reflections	4942 [R(int) = 0.1403]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85057	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4942 / 0 / 316	
Goodness-of-fit on F^2	0.721	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0584	
R indices (all data)	R1 = 0.1361, wR2 = 0.0705	

Largest diff. peak and hole	0.541 and -0.413 e.Å^{-3}

*Crystal data and structure refinement for **4**.*

Empirical formula	C37 H46 Ge N2	
Formula weight	591.35	
Temperature	150(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 877.80(3) pm	α= 83.171(3)°.
	b = 1038.84(3) pm	β= 88.937(2)°.
	c = 1808.41(6) pm	γ = 88.879(3)°.
Volume	1.63685(9) nm^3	
Z	2	
Density (calculated)	1.200 Mg/m^3	
Absorption coefficient	0.962 mm^{-1}	
F(000)	628	
Crystal size	0.28 x 0.22 x 0.19 mm^3	
Theta range for data collection	3.02 to 25.00°.	
Index ranges	-9<=h<=10, -12<=k<=12, -21<=l<=21	
Reflections collected	15397	
Independent reflections	5751 [R(int) = 0.0254]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5751 / 0 / 370	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR2 = 0.0587	
R indices (all data)	R1 = 0.0372, wR2 = 0.0607	
Largest diff. peak and hole	0.306 and -0.300 e.Å^{-3}	

*Crystal data and structure refinement for**5**.*

Empirical formula	C37 H46 Ge N2
Formula weight	591.35
Temperature	150(2) K
Wavelength	71.073 pm

Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 1414.20(3) pm	α= 90°.
	b = 2059.33(6) pm	β= 90°.
	c = 1119.05(3) pm	γ = 90°.
Volume	3.25901(15) nm^3	
Z	4	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.966 mm^{-1}	
F(000)	1256	
Crystal size	0.39 x 0.18 x 0.17 mm^3	
Theta range for data collection	3.05 to 25.00°.	
Index ranges	-16<=h<=16, -24<=k<=24, -13<=l<=13	
Reflections collected	23042	
Independent reflections	2959 [R(int) = 0.0630]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.94891	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2959 / 0 / 195	
Goodness-of-fit on F^2	0.913	
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0734	
R indices (all data)	R1 = 0.0588, wR2 = 0.0793	
Largest diff. peak and hole	0.479 and -0.214 e.$Å^{-3}$	

B.1. Computational Details and Results

Density functional calculations have been carried out for analogs (**2A, 3A**) of compounds **2** and **3** in which the 2,6-$^{i}Pr_2C_6H_3$ ligands at the nitrogen atoms of the β-diketimitate ligand have been replaced by phenyl (C_6H_5) groups. Furthermore, the 1,4-adduct of ethyne to **2A** has been calculated (compound **5A**, a structural analog to **5** which is the 1,4-addut of phenyl-ethyne to **2**) as well as the 1,1-adduct of ethyne to **2A** (compound **6A**), for which no structural analog has been found experimentally. However, such adducts are known for the silicon homologue (see Scheme **2**, rightmost structure). We also investigated reaction pathways leading from **2A** + ethyne to **3A** (via a concerted 4+2 cycloaddition), to **5A** (via proton abstraction from ethyne by the basic exocyclic CH_2 group and simultaneous transfer of the resulting acetylide to germanium), and to **6A** (insertion of Ge into the C-H bond of ethyne).

Finally, a germacyclopropene structure **7A** (a structural analogue of the leftmost structure in Scheme **2**) has also been calculated. Such a structure has been experimentally found starting from **1**, but not for the germanium analogue.

The calculations were done using a gradient-corrected exchange-correlation functional ("bp86") [B1, B2] with the TURBOMOLE [B3, B4, B5] program package. A density fitting technique (also known as "RI method") [B6] was used to evaluate the matrix elements of the electrostatic Coulomb potential, because this speeds up the calculation considerably. Split-valence polarized basis sets of *triple zeta* quality (TZVP, Ref. [B7]) were used for all atoms.

While TURBOMOLE was used to evaluate the energy as well as its first and second derivatives with respect to nuclear coordinates, we used the Berny algorithm [B8] as implemented in the Gaussian program [B9] to locate local minima (molecular structures) and first-order saddle points (transition structures) on the potential energy surface. The nature of the transition structures has been verified by a frequency calculation (one negative eigenvalue of the molecular Hessian).

Convergence problems were encountered locating the transition state of the direct insertion of the Ge atom into a C-H bond of ethyne (**TS-6A**) such that this structure is not fully converged. In the case of the silicon homologue, where the 1,1-Adduct was indeed experimentally observed, such a transition structure could be found and was so high in energy that this reaction pathway was excluded [B10]. In the present investigation it is even higher in energy so it is not of much interest. The transition structures for two reaction pathways which are energetically accessible have been fully optimized, namely **TS-3A** for the concerted 4+2 cycloaddition and **TS-5A** for the 1,4-addition. Their relative energy (without zero point vibrational energy) are (cartesian coordinates and calculated total energies are given in the next section):

Table. Relative energies (DFT calculations, bp86 functional)

2A + Ethyne	0.0 kJ/mol
3A	–126.4 kJ/mol
5A	–98.7 kJ/mol
6A	–3.8 kJ/mol
7A	+53.5 kJ/mol
TS-3A	+33.5 kJ/mol
TS-5A	+87.7 kJ/mol
TS-6A	> 200.0 kJ/mol

It can be seen that the both the 1,1-adduct **3A** and the cyclopropene analogue **7A** are not thermodynamically favoured. Such structures have been experimentally found for the silicon analogue [B10]. In this work only compounds structurally equivalent to **3A** and **5A** have been observed. These structures have lower coordination at Ge and are, according to the density functional calculations, the most stable isomers. Note that **5A** and **6A** are tautomers, and the different relative stability in the Si and Ge case can be explained with the different basicity of the Si/Ge center [A1].

B.2. Optimized geometries and transition structures

Total energies are given in atomic units (Hartree units). Cartesian coordinates are given in Angstrom.

Ethyne (HCCH): Total energy = -77.358577005

C	0.000000	0.000000	0.604175
H	0.000000	0.000000	1.674701
C	0.000000	0.000000	-0.604175
H	0.000000	0.000000	-1.674701

Compound **2A**: Total energy = -2844.51352180

C	-1.241401	1.818613	-0.135075
C	1.308151	1.858542	0.059203
C	-0.025343	2.429636	-0.066383
H	-0.035637	3.518462	-0.121828
C	-2.484021	2.656796	-0.320895
H	-3.065778	2.311112	-1.189420
H	-3.156921	2.609715	0.547610
H	-2.207157	3.705359	-0.481726
C	2.396481	2.665711	0.207547
H	3.406977	2.277000	0.298270
H	2.261519	3.745263	0.240821
N	1.412524	0.444206	0.009026
N	-1.397917	0.422515	-0.109421
Ge	0.036732	-0.841747	-0.078038
C	2.731025	-0.130816	0.043339
C	3.499091	-0.206285	-1.128901
C	3.237218	-0.663427	1.236792
C	4.754985	-0.816542	-1.105645
H	3.097863	0.215505	-2.051709
C	4.494086	-1.278446	1.254988
H	2.639020	-0.587009	2.146257
C	5.255413	-1.354848	0.085889
H	5.341866	-0.880059	-2.023682
H	4.876491	-1.698583	2.186888
H	6.234398	-1.836667	0.100106
C	-2.700214	-0.165943	-0.030884
C	-3.159899	-0.987923	-1.073584

C	-3.504051	-0.003329	1.112548
C	-4.399859	-1.627865	-0.978142
H	-2.541551	-1.106618	-1.965166
C	-4.747745	-0.631131	1.196157
H	-3.132633	0.599857	1.942670
C	-5.201168	-1.446413	0.152037
H	-4.742109	-2.263716	-1.796512
H	-5.359746	-0.497373	2.090003
H	-6.170747	-1.941359	0.223436

Compound **3A**: Total energy = -2921.92024513

Ge	0.107949	-0.179537	1.350068
N	1.388822	0.376126	-0.096863
C	1.939864	2.035025	-1.837485
H	2.814180	1.514784	-2.223654
H	1.660036	2.974067	-2.310909
N	-1.466539	0.433997	-0.000187
C	1.214382	1.551470	-0.794382
C	-0.033411	2.347436	-0.346616
H	-0.068830	3.260459	-0.950937
C	-1.254901	1.511670	-0.686971
C	-2.096176	1.972763	-1.838322
H	-2.877038	1.255131	-2.111538
H	-1.436814	2.150560	-2.702089
H	-2.565576	2.939725	-1.594906
C	2.570596	-0.397043	-0.214992
C	2.479615	-1.796500	-0.345257
C	3.629874	-2.588179	-0.391605
H	3.531678	-3.671061	-0.491818
C	4.896946	-2.002398	-0.324836
H	5.795084	-2.620226	-0.368689
C	4.997986	-0.611571	-0.197975
H	5.980887	-0.139846	-0.132021
C	3.853345	0.183476	-0.137978
C	-2.618312	-0.393728	-0.157368
C	-2.463060	-1.721534	-0.581090
C	-3.581514	-2.551306	-0.682934
H	-3.457311	-3.580452	-1.023426
C	-4.851513	-2.073118	-0.343099
H	-5.720812	-2.728105	-0.415159
C	-5.000267	-0.755465	0.100137
H	-5.985257	-0.379107	0.380997
C	-3.888698	0.085554	0.196436
C	0.052290	1.729139	2.055404
H	0.124844	1.969530	3.120584
C	0.027271	2.697168	1.134297
H	0.077250	3.768006	1.364730
H	-3.993831	1.107336	0.564325
H	-1.468552	-2.088910	-0.835542
H	1.492905	-2.258734	-0.404959
H	3.940904	1.264011	-0.020005

Compound **5A**: Total energy = -2921.90969476

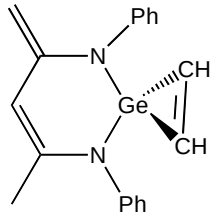
C	-1.265867	1.756760	0.399366
C	1.261235	1.758101	0.394444
C	-0.001712	2.317709	0.658477
H	-0.001997	3.352926	0.993415
C	-2.466372	2.673091	0.506677
H	-2.807378	3.005139	-0.484736
H	-3.312594	2.162133	0.985107
H	-2.207620	3.565797	1.088728
C	2.464195	2.670865	0.503484
H	3.280989	2.178143	1.048985
H	2.191041	3.596818	1.023288
N	1.437321	0.472798	0.062092
N	-1.441735	0.472499	0.065691
Ge	0.000029	-0.980385	0.262607
C	2.706017	-0.023675	-0.365972
C	3.253215	0.352962	-1.603367
C	3.375697	-0.973622	0.422817
C	4.465985	-0.192013	-2.030544
H	2.708583	1.056031	-2.235713
C	4.587420	-1.517701	-0.012455
H	2.945232	-1.266334	1.382331
C	5.138694	-1.127173	-1.236425
H	4.880133	0.105392	-2.995704
H	5.101891	-2.251572	0.610383
H	6.083246	-1.555481	-1.575164
C	-2.710181	-0.025072	-0.361115
C	-3.260173	0.354169	-1.596325
C	-3.376676	-0.978379	0.426468
C	-4.472477	-0.192312	-2.023063
H	-2.718762	1.061427	-2.226704
C	-4.588115	-1.523431	-0.008150
H	-2.944364	-1.272343	1.384754
C	-5.141870	-1.131042	-1.230463
H	-4.889203	0.107383	-2.986394
H	-5.100524	-2.259412	0.613902
H	-6.086093	-1.560327	-1.568880
C	0.002727	-0.900817	2.274801
C	0.029059	-1.120332	3.479956
H	0.046793	-1.281926	4.539831
H	2.855804	2.942911	-0.487030

Compound **6A**: Total energy = -2921.87356426

C	1.327471	1.807228	-0.514342
C	-1.236200	1.806277	-0.729531
C	0.112569	2.369824	-0.782273
H	0.131898	3.417436	-1.082206
C	2.590369	2.623582	-0.659973
H	3.105701	2.701059	0.310540
H	3.305157	2.176068	-1.364134
H	2.350676	3.633498	-1.013344
C	-2.291450	2.542637	-1.173299
H	-3.314844	2.177989	-1.128038
H	-2.117823	3.522316	-1.613458
N	-1.388936	0.499194	-0.210193
N	1.474043	0.521295	0.042889
Ge	-0.043095	-0.158946	0.897816
C	-0.149690	0.564402	2.667493
C	-0.242850	0.985190	3.806545

H	-0.048450	-1.690875	0.910832
H	-0.320272	1.363375	4.806639
C	-2.586127	-0.252483	-0.372517
C	-3.247872	-0.783423	0.747475
C	-3.086304	-0.537738	-1.657242
C	-4.371127	-1.602796	0.587399
H	-2.890782	-0.533360	1.749296
C	-4.218777	-1.336241	-1.808330
H	-2.573875	-0.129330	-2.528843
C	-4.864610	-1.878862	-0.688820
H	-4.868550	-2.011333	1.468976
H	-4.592205	-1.552400	-2.811150
H	-5.745178	-2.510542	-0.814752
C	2.582018	-0.318837	-0.233805
C	3.148615	-1.093371	0.795379
C	3.104581	-0.435995	-1.536659
C	4.207911	-1.963313	0.527215
H	2.768197	-0.989109	1.814147
C	4.180298	-1.287888	-1.790722
H	2.641529	0.125693	-2.349514
C	4.736843	-2.059048	-0.763612
H	4.634212	-2.554951	1.339329
H	4.572355	-1.367133	-2.806543
H	5.571529	-2.730408	-0.969032

Compound **7A**: Total energy = -2921.85170545



C	-1.271528	1.969244	-0.262602
C	1.289678	2.029998	-0.025428
C	-0.052748	2.577335	-0.189317
H	-0.066222	3.663427	-0.275328
C	-2.511877	2.808092	-0.459249
H	-3.089075	2.456101	-1.328411
H	-3.188301	2.770591	0.406640
H	-2.229761	3.854106	-0.625853
C	2.354781	2.870996	0.097204
H	3.373166	2.512009	0.219921
H	2.190414	3.946237	0.079724
N	1.446233	0.624850	0.002822
N	-1.463617	0.575195	-0.258497
Ge	0.034951	-0.541300	-0.264264
C	0.022993	-2.378264	0.232844
C	0.151546	-2.248940	-1.112473
H	-0.014598	-3.236731	0.912587
H	0.258103	-2.966125	-1.934750
C	2.754321	0.051239	0.134542
C	3.548119	-0.170035	-1.000198
C	3.234160	-0.316697	1.399196
C	4.809095	-0.758225	-0.869207
H	3.166348	0.125310	-1.978728
C	4.495841	-0.905023	1.526899
H	2.608937	-0.134334	2.274584
C	5.284427	-1.127742	0.393565

H	5.420326	-0.932354	-1.756610
H	4.862246	-1.192258	2.514078
H	6.267781	-1.590462	0.493520
C	-2.736725	-0.014570	0.012694
C	-3.314975	-0.890223	-0.920214
C	-3.405747	0.234679	1.223959
C	-4.543814	-1.497876	-0.650030
H	-2.796234	-1.078959	-1.861433
C	-4.642579	-0.359441	1.480035
H	-2.939272	0.884669	1.966381
C	-5.215773	-1.229595	0.545996
H	-4.982627	-2.175691	-1.384426
H	-5.154205	-0.155141	2.422548
H	-6.178927	-1.698820	0.752434

Compound **TS-3A**: Total energy = -2921.85933120

Ge	0.074962	-0.611322	0.685258
N	1.415032	0.292591	-0.367594
C	2.324044	2.382000	-1.274076
H	3.329058	1.990508	-1.405546
H	2.124633	3.392305	-1.626752
N	-1.418019	0.333960	-0.167731
C	1.302200	1.629045	-0.768533
C	-0.030227	2.232402	-0.662576
H	-0.050014	3.286550	-0.943090
C	-1.275457	1.619912	-0.596307
C	-2.513616	2.440713	-0.873424
H	-3.006220	2.126132	-1.805346
H	-2.251754	3.500784	-0.974953
H	-3.254306	2.330122	-0.067734
C	2.690019	-0.348934	-0.326012
C	2.860238	-1.570977	-0.997214
C	4.067296	-2.272194	-0.903669
H	4.181036	-3.221810	-1.429792
C	5.123588	-1.756675	-0.149396
H	6.067189	-2.300322	-0.080059
C	4.961396	-0.536910	0.520760
H	5.778039	-0.132513	1.122273
C	3.756079	0.160701	0.439222
C	-2.686739	-0.321954	-0.165061
C	-3.313603	-0.668689	-1.374389
C	-4.526915	-1.359148	-1.366307
H	-5.002764	-1.622323	-2.312788
C	-5.121463	-1.730952	-0.155300
H	-6.065867	-2.277184	-0.152064
C	-4.493633	-1.402677	1.049557
H	-4.948596	-1.688519	1.999612
C	-3.285966	-0.698746	1.048207
C	0.067938	1.158829	2.318986
H	0.101178	0.603114	3.244975
C	0.144855	2.299969	1.833288
H	0.294366	3.339506	1.621651
H	-2.805086	-0.420819	1.987402
H	-2.829416	-0.409318	-2.317298
H	2.036359	-1.957777	-1.599256
H	3.624106	1.103736	0.971243

Compound **TS-5A**: Total energy = -2921.83870019

C	-1.251965	1.634746	-0.375572
C	1.211665	1.588320	-0.912199
C	-0.025386	2.205504	-0.856817
H	-0.070821	3.256638	-1.141305
C	-2.118728	2.411395	0.430502
H	-3.123503	2.055854	0.660468
H	-1.244544	1.767896	1.547249
H	-1.968002	3.491862	0.462319
N	1.440370	0.387090	-0.305958
N	-1.402854	0.261728	-0.370559
Ge	0.027175	-0.607917	0.695324
C	-0.409761	1.003602	2.218974
C	0.077066	1.026040	3.358100
H	0.502841	1.030412	4.344070
C	2.714557	-0.254326	-0.331611
C	2.871512	-1.475040	-1.010514
C	3.803153	0.266682	0.391362
C	4.095669	-2.149709	-0.982404
H	2.026518	-1.881101	-1.569024
C	5.027700	-0.404304	0.405709
H	3.671842	1.189016	0.959218
C	5.179547	-1.614429	-0.280745
H	4.201702	-3.095970	-1.515879
H	5.864095	0.012500	0.970019
H	6.135475	-2.140070	-0.261745
C	-2.710638	-0.292379	-0.372311
C	-3.627392	0.113740	-1.363799
C	-3.102147	-1.297248	0.531092
C	-4.895346	-0.461059	-1.437979
H	-3.322481	0.874869	-2.083384
C	-4.369312	-1.879239	0.440717
H	-2.417739	-1.618361	1.318688
C	-5.275351	-1.464430	-0.539030
H	-5.588288	-0.131150	-2.214433
H	-4.651579	-2.655530	1.154344
H	-6.264898	-1.918899	-0.603929
C	2.340361	2.269078	-1.648038
H	3.161909	2.555336	-0.976088
H	1.973708	3.167076	-2.158245
H	2.770329	1.589590	-2.399725

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