Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for the Communication

Isolation of a Germanium(II) Cation and a Germylene Iron Carbonyl Complex Utilizing an Imidazolin-2-iminato Ligand

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1.) Experimental Details

General considerations: All experiments and manipulations were conducted under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods. NMR solvents were degassed by multiple freeze-pump-thaw cycles and stored over molecular sieves (3 Å). The starting materials HNIPr (NIPr = bis(2,6-di*iso*propylphenyl)imidazolin-2-imino),[S1] and Ge[N(SiMe$_3$)$_2$]$_2$[S2] were prepared according to the reported procedures. ^{1}H-, ^{11}B-, ^{13}C{^{1}H}-, ^{19}F-, and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker Avance II 200 MHz or 400 MHz spectrometer and referenced to (residual) solvent signals as internal standards (^{1}H and ^{13}C) or an external standard (Et$_2$O•BF$_3$ for ^{11}B, CFCl$_3$ for ^{19}F and Me$_4$Si for ^{29}Si). Values for the chemical shift (δ) are given in parts per million. Abbreviations: s = singlet (NMR) or strong band (IR); d = doublet; t = triplet; sept = septet; m = multiplet; n.a. = not assigned; br = broad; Dip = 2,6-diisopropylphenyl. Elemental analyses and APCI-HRMS {analyte provided in THF (**1**) or CH$_3$CN (**2**$^+$[MeB(C$_6$F$_5$)$_3$]$^-$)} were performed by the microanalytical laboratory and the MS-Service of the Institut für Chemie, Technische Universität Berlin, Germany, respectively.

Experimental Procedure and Analytical Data for Amino(imino)germylene 1

A Schlenk tube equipped with a PTFE-coated magnetic stirring bar was charged with HNIPr (293 mg, 0.727 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (286 mg, 0.727 mmol). Toluene (10 ml) was transferred to the reaction vessel by cannula and the resulting mixture was stirred at 50 ºC for 12 hours. The volatiles were removed under reduced pressure and the oily residue was subjected to prolonged drying in high vacuum (6 h) to afford **1** as a pale red oil (402 mg, 87%).

^{1}H NMR (200.1 MHz, C$_6$D$_6$): δ = 0.17 (s, 18H, Si(C*H*$_3$)$_3$), 1.15 (d, $^3J_{HH}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{HH}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 3.16 (sept, $^3J_{HH}$ = 7 Hz, 4H, C*H*(CH$_3$)$_2$), 6.08 (s, 2H, NC*H*), 7.08-7.26 (m, 6H, Ar-H)^a. **^{13}C{^{1}H} NMR** (50.3 MHz, C$_6$D$_6$): δ = 5.5 (Si(*C*H$_3$)$_3$), 23.3 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 115.4 (N*C*H), 124.2 (Ar-C), 129.9 (Ar-C), 133.9 (Ar-C), 148.0 (Ar-C), 152.8 (N*C*N). **^{29}Si{^{1}H} NMR** (39.8 MHz, C$_6$D$_6$): δ = –0.8. *a*: the signal superimposes with the resonance produced by the NMR solvent. **APCI-HRMS**: *m/z*: 637.3168 (*calc*. 637.3172 for [M+H]$^+$).

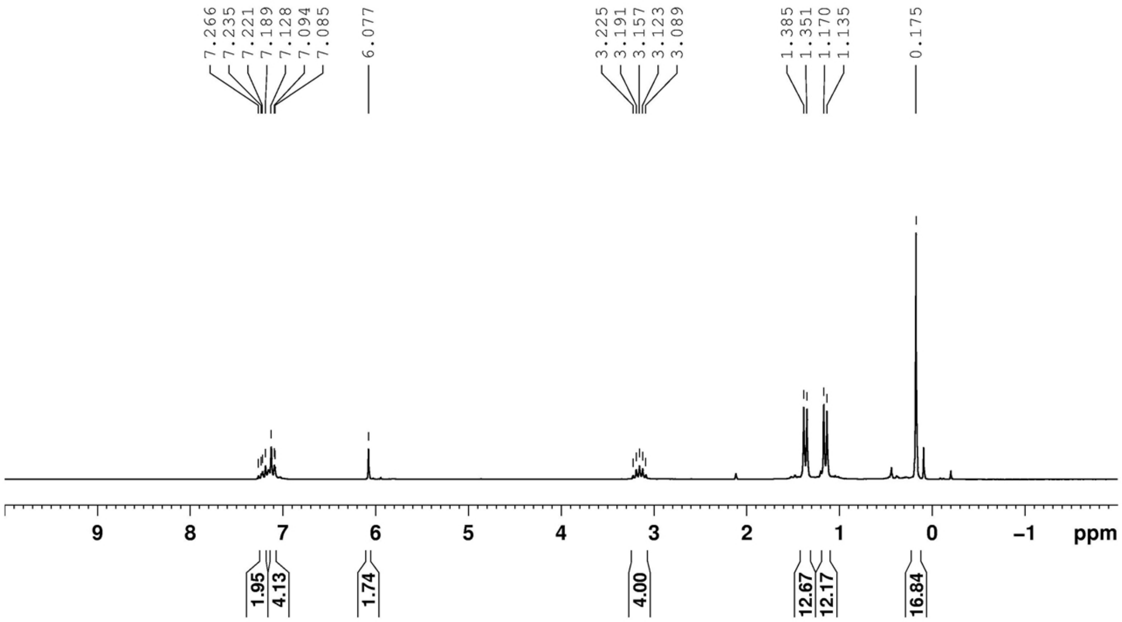


Figure S1. ^{1}H NMR spectrum (200.1 MHz, C_6D_6) of **1**.

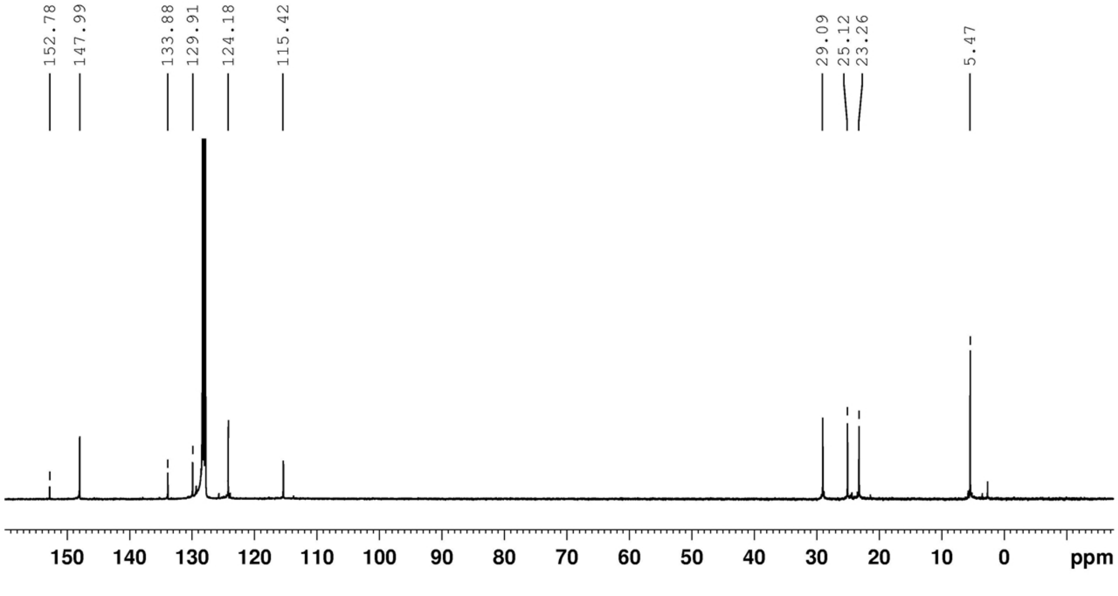


Figure S2. $^{13}C\{^1H\}$ NMR spectrum (50.3 MHz, C_6D_6) of **1**.

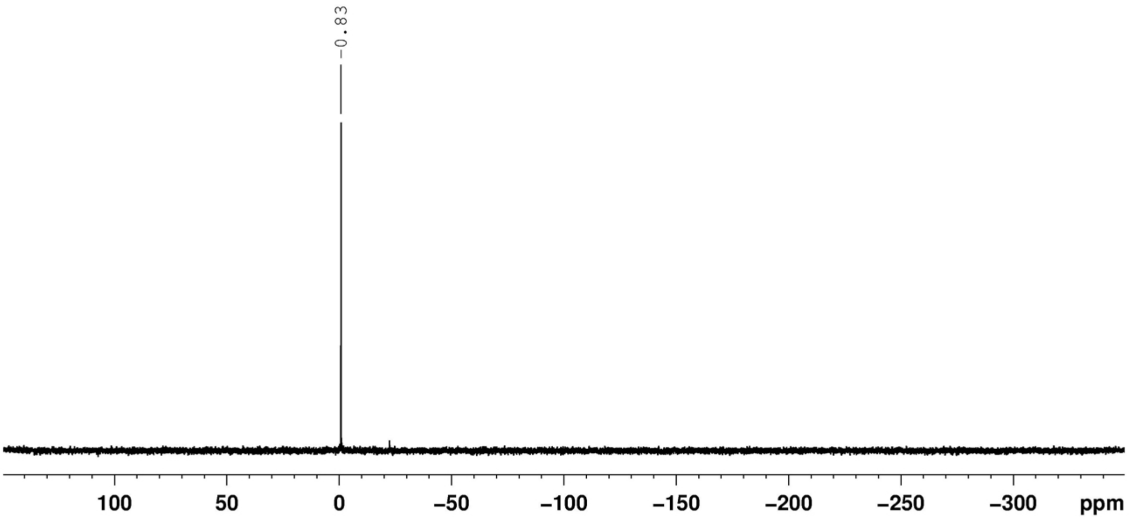


Figure S3. $^{29}Si\{^1H\}$ NMR spectrum (39.8 MHz, C_6D_6) of **1**.

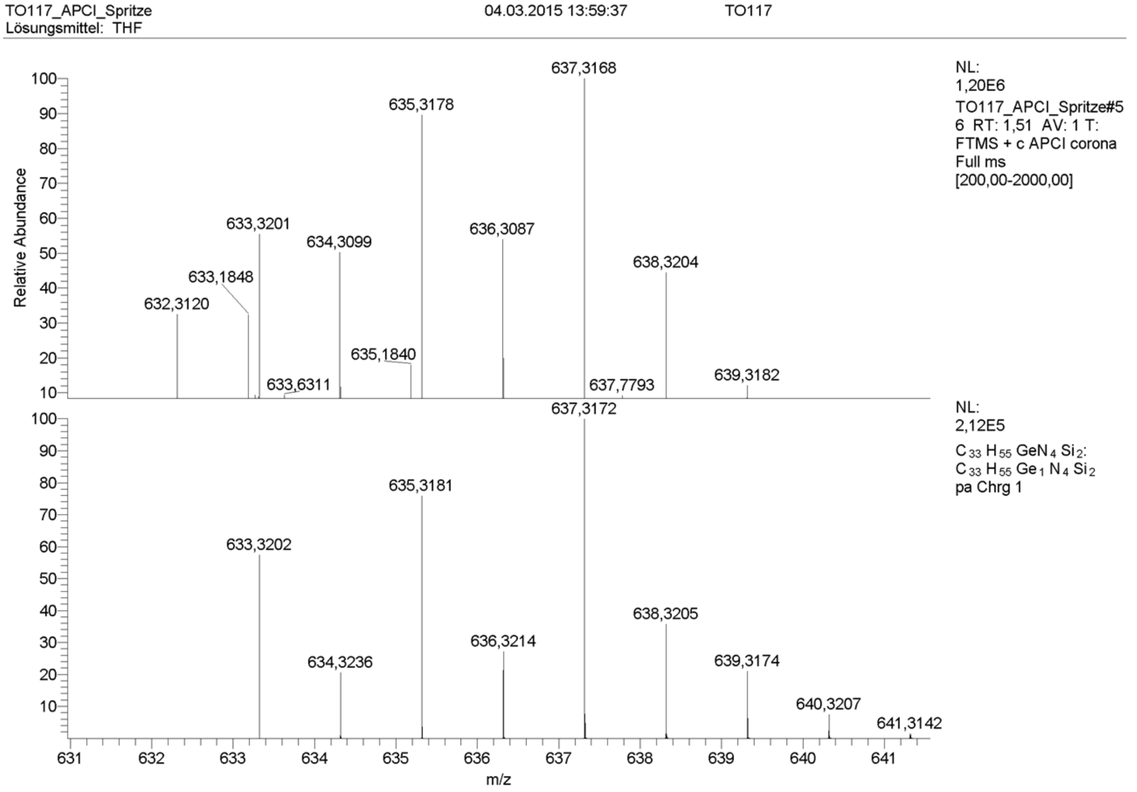


Figure S4. APCI-HRMS analysis of **1**. Observed (top) and calculated (bottom) spectrum for $[M+H]^+$. Note that relative intensity and value of the signal observed at 634.3099 (calculated: 634.3236) significantly deviate from the theoretical amounts due to superimposition with a signal produced by a second species. Presumably, this unassigned species also gives rise to the peaks observed at 632.3120, 633.1848 and 635.1840.

Experimental Procedure and Analytical Data for $2^+[MeB(C_6F_5)_3]^-$

A solution of **1** (597 mg, 0.940 mmol) in hexane (5 mL) was added to a stirring mixture of $B(C_6F_5)_3$ (481 mg, 0.940 mmol) in hexane (5 ml) via syringe. The resulting reaction mixture was stirred for 12 hours at ambient temperature. The solvent was removed under vacuum and toluene was added to the residue. A biphasic liquid formed from which crystals of **2**$^+[MeB(C_6F_5)_3]^-$ separated at –30 °C. The solid fraction contained single crystals suitable for X-ray diffraction analysis. The product was isolated and dried in vacuum (519 mg, 48%). **^{1}H NMR** (200.1 MHz, CD_3CN): $\delta = -0.21$ (s, 6H, $Si(CH_3)_2$), −0.04 (s, 9H, $Si(CH_3)_3$), 0.54 (br, 3H, $MeB(C_6F_5)_3$), 1.21 (d, $^3J_{HH} = 7$ Hz, 12H, $CH(CH_3)_2$), 1.37 (d, $^3J_{HH} = 7$ Hz, 12H, $CH(CH_3)_2$), 2.75 (sept, $^3J_{HH} = 7$ Hz, 4H, $CH(CH_3)_2$), 7.16 (s, 2H, NC*H*), 7.43-7.63 (m, 6H, Ar-H). **^{11}B NMR** (64.2 MHz, CD_3CN): $\delta = -14.9$. **^{13}C{^{1}H} NMR** (100.6 MHz, CD_3CN): $\delta = 2.0$ ($Si(CH_3)_3$), 4.3 ($Si(CH_3)_2$), 23.1 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 29.9 ($CH(CH_3)_2$), 120.5 (N*C*H), 126.8 (Ar-C), 130.6 ($MeB(C_6F_5)_3$), 131.7 (Ar-C), 133.2 (Ar-C), 137.3 ($MeB(C_6F_5)_3$), 138.7 ($MeB(C_6F_5)_3$), 147.9 (Ar-*C*), 148.3 (N*C*N), 150.5 ($MeB(C_6F_5)_3$). **^{19}F NMR** (188.3 MHz, CD_3CN): $\delta = -133.4$ (d, $J = 20$ Hz, 6F), −165.3 (t, $J = 20$ Hz, 3F), −168.2 (m, 6F). **^{29}Si{^{1}H} NMR** (39.8 MHz, CD_3CN): $\delta = 1.3$, 20.1. **APCI-HRMS**: *m/z* (positive ion mode): 621.2849 (*calc*. 621.2859 for $[M–MeB(C_6F_5)_3]^+$). **APCI-HRMS**: *m/z* (negative ion mode): 527.0091 (*calc*. 527.0094 for $[MeB(C_6F_5)_3]^-$). **M.p.** at 130-133 ºC (dec.).

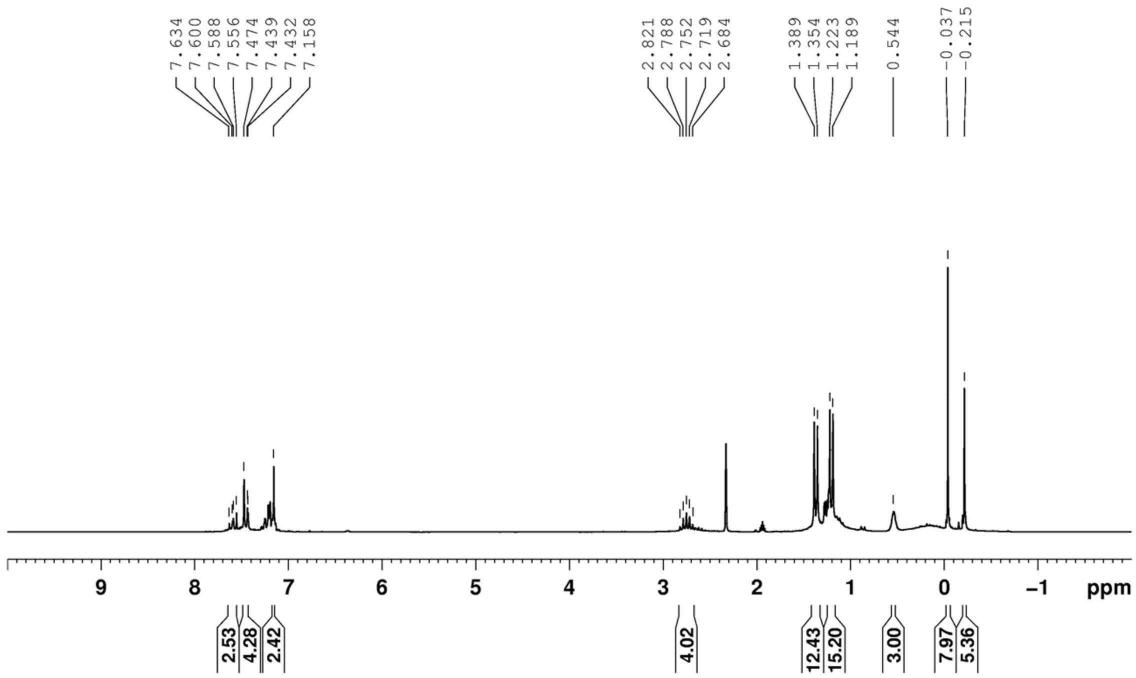


Figure S5. ^{1}H NMR spectrum (200.1 MHz, CD_3CN) of **2**$^+$[$MeB(C_6F_5)_3$]$^-$. Mind the presence of stoichiometric amounts of toluene.

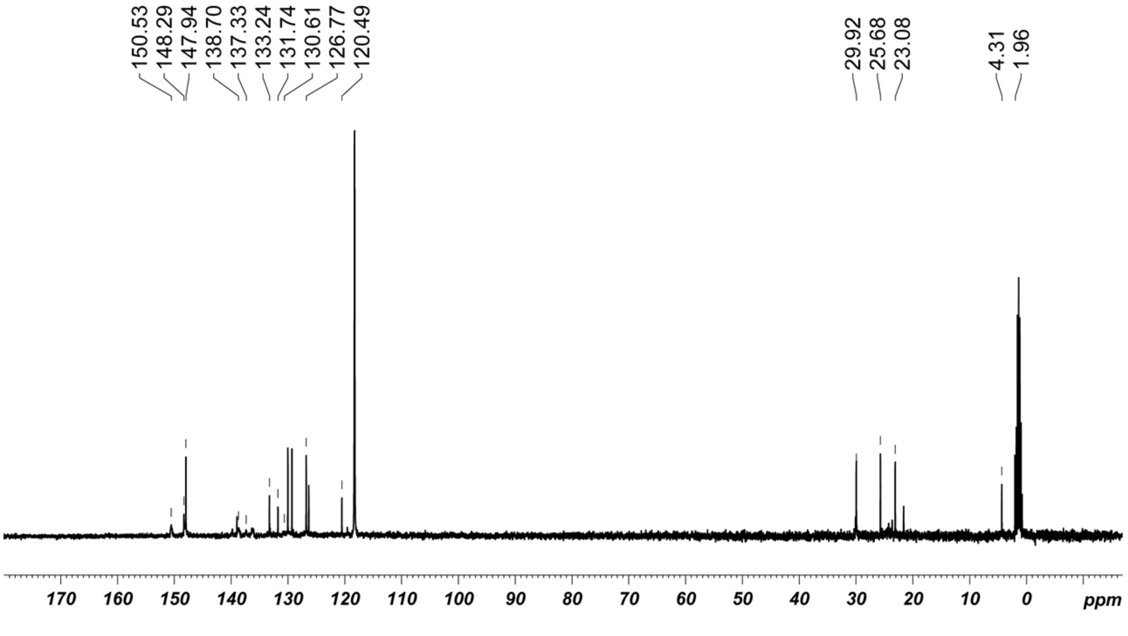


Figure S6. $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, CD_3CN) of **2**$^+$[$MeB(C_6F_5)_3$]$^-$. Mind the presence of toluene.

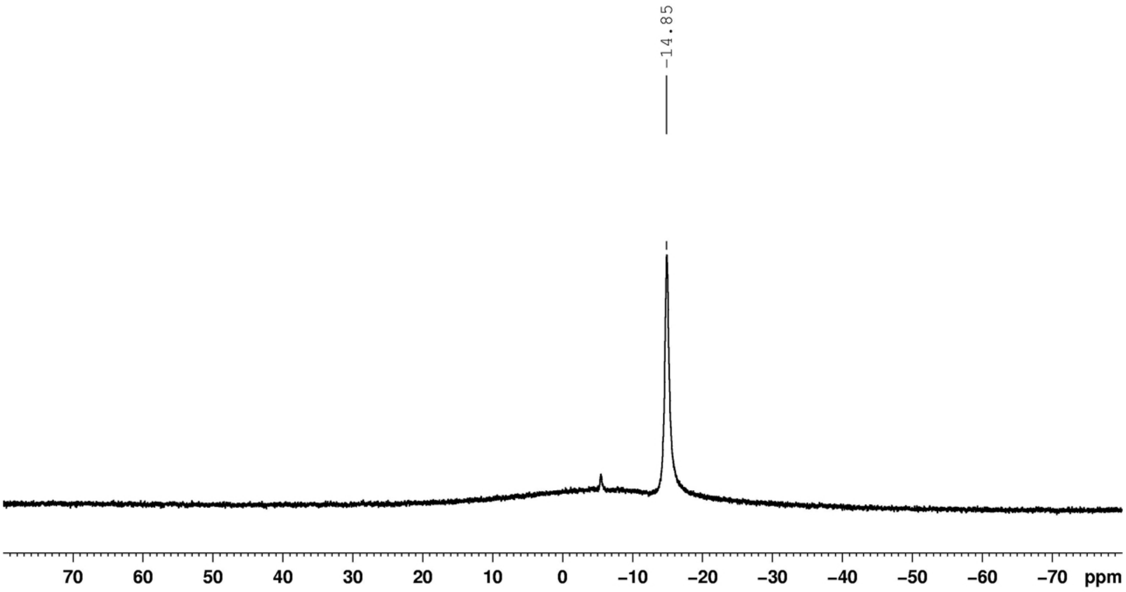


Figure S7. ^{11}B NMR spectrum (64.2 MHz, CD_3CN) of **2**$^+$[$MeB(C_6F_5)_3$]$^-$.

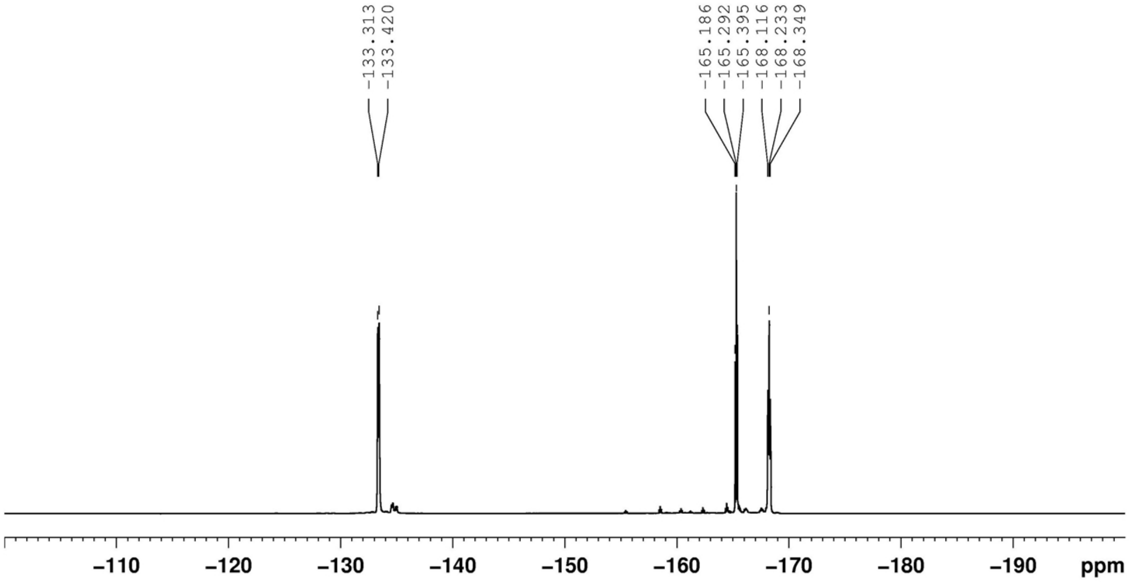


Figure S8. ^{19}F NMR spectrum (188.3 MHz, CD_3CN) of **2**$^+$[$MeB(C_6F_5)_3$]$^-$.

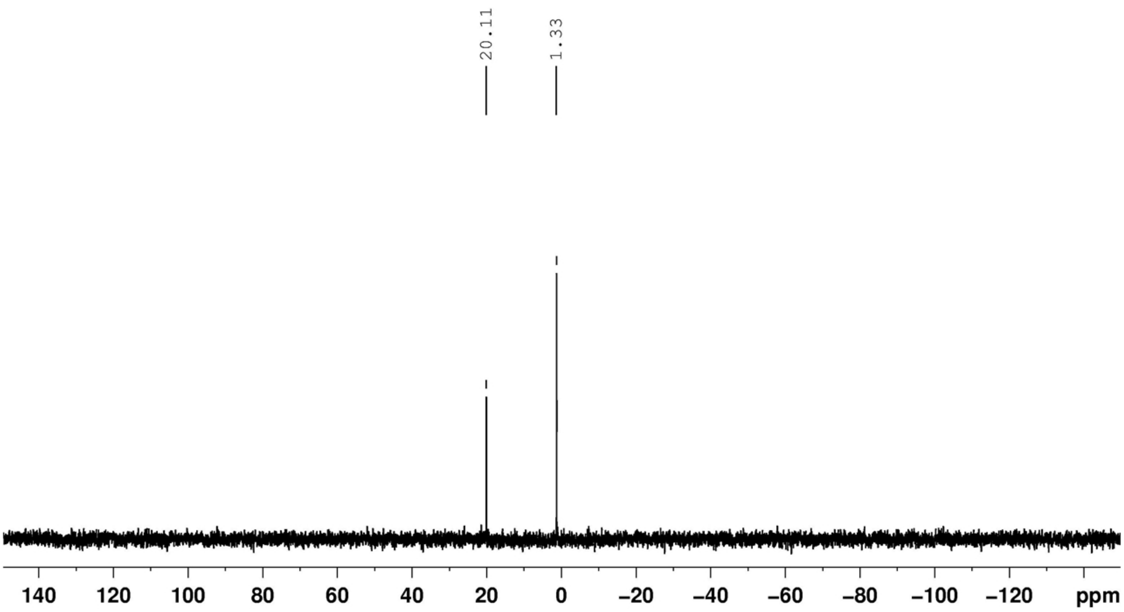


Figure S9. $^{29}Si\{^1H\}$ NMR spectrum (39.8 MHz, CD_3CN) of **2**$^+[MeB(C_6F_5)_3]^-$.

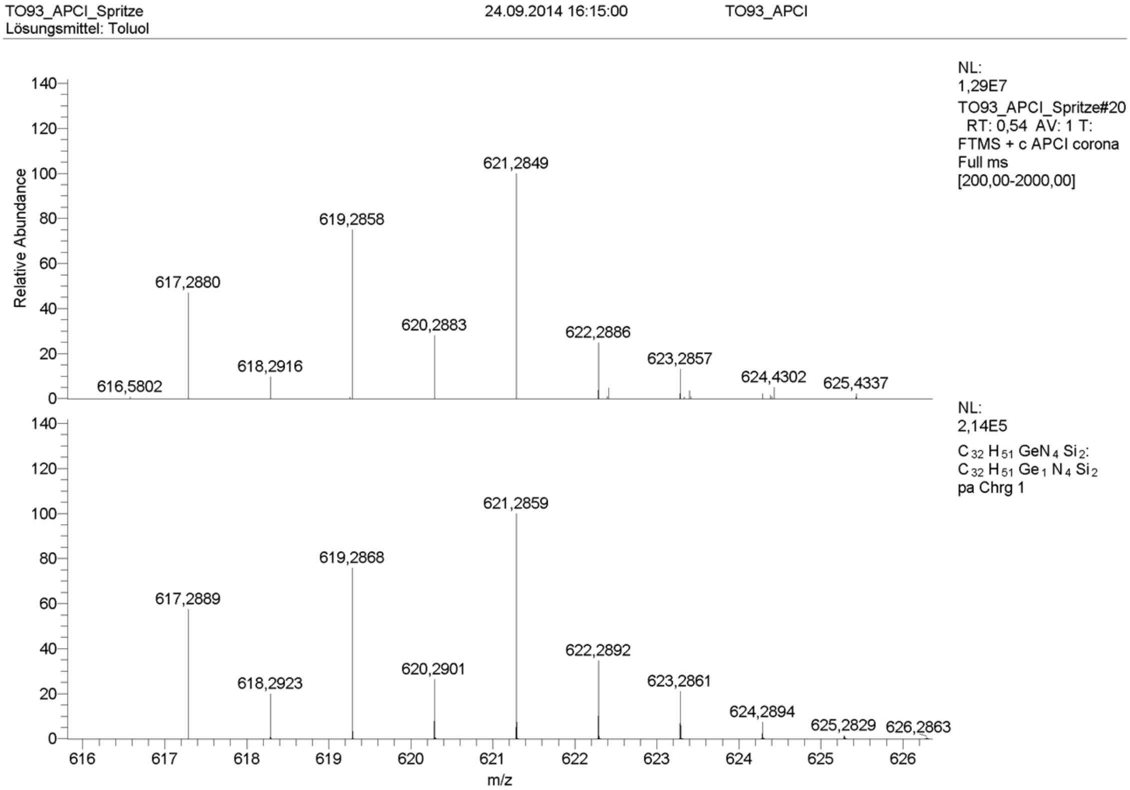


Figure S10. APCI-HRMS analysis (positive mode) of **2**$^+[MeB(C_6F_5)_3]^-$. Observed (top) and calculated (bottom) spectrum for $[M–MeB(C_6F_5)_2]^+$.

Experimental Procedure and Analytical Data for 3

A solution of **1** (486 mg, 0.765 mmol) in toluene (5 mL) was added to a stirring suspension of $Fe_2(CO)_9$ (306 mg, 0.841 mmol) and toluene (5 ml) via syringe. The resulting reaction mixture was stirred for 12 hours at ambient temperature. The solvent was removed under vacuum and the residue was recrystallized from hexane at –30 ºC to yield **3** in the form of yellow crystals (381 mg, 62%). The solid fraction contained X-ray quality single crystals. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 0.12 (s, 18H, Si(C*H*$_3$)$_3$), 1.05 (d, $^3J_{HH}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.46 (d, $^3J_{HH}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 3.18 (br, 4H, *CH*(CH$_3$)$_2$), 6.11 (s, 2H, NC*H*), 7.12-7.21 (m, 6H, Ar-H)[a]. **^{13}C{^{1}H} NMR** (50.3 MHz, C_6D_6): δ = 4.22 (Si(*C*H$_3$)$_3$), 23.1 (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 116.7 (N*C*H), 124.8 (Ar-C), 130.3 (Ar-C), 133.1 (Ar-C), 147.3 (Ar-C), 151.3 (N*C*N), 214.6 (*C*O). **^{29}Si{^{1}H} NMR** (39.8 MHz, C_6D_6): δ =0.8. *a*: the signal superimposes with the resonance produced by the NMR solvent. **Elemental analysis** calcd (%) for $C_{37}H_{54}FeGeN_4O_4Si_2$: C 55.31, H 6.77, N 6.97; found: C 55.18, H 6.77, N 6.64. IR (KBr, [cm^{-1}]): 2039 (s) (CO), 1965 (s) (CO), 1930 (s) (CO). **M.p.** at 185-187 °C (dec.).

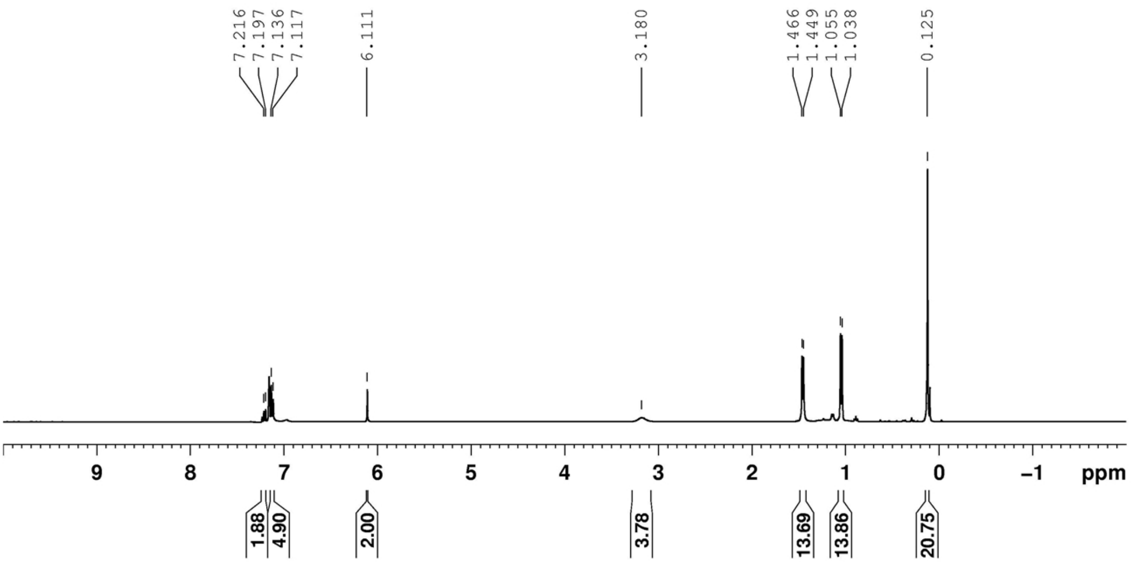


Figure S11. ^{1}H NMR spectrum (200.1 MHz, C_6D_6) of **3**.

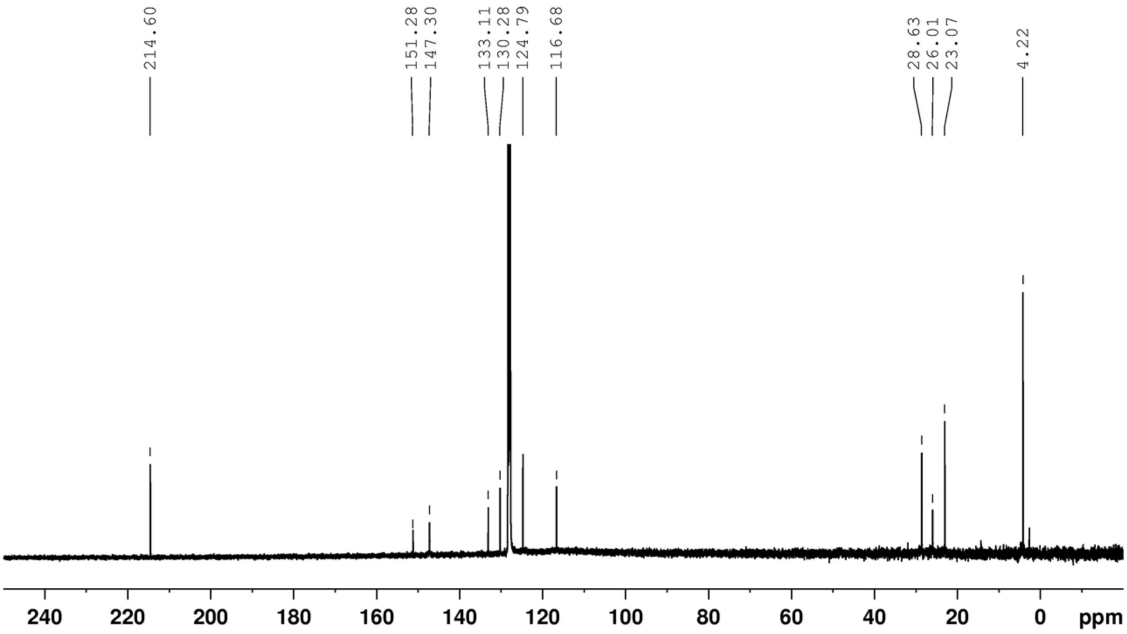


Figure S12. $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6) of **3**.

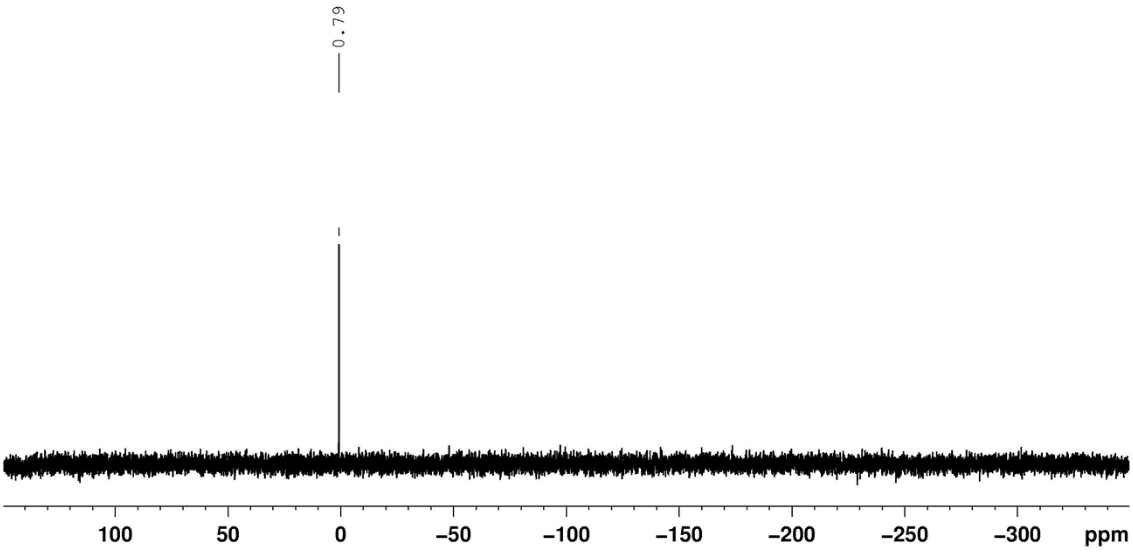


Figure S13. $^{29}Si\{^1H\}$ NMR spectrum (39.8 MHz, C_6D_6) of **3**.

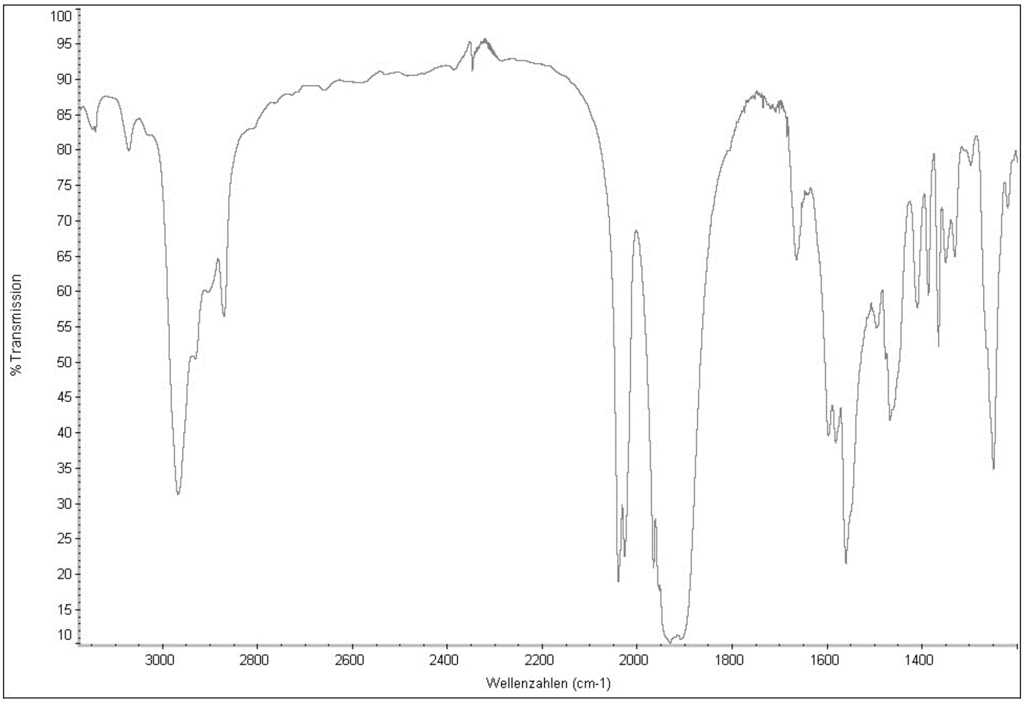


Figure S14. IR Spectrum (KBr) of **3**.

2.) Crystallographic Data for $2^+[MeB(C_6F_5)_3]^-$ and 3

General Considerations: Data for the single crystal structure determinations of **2**$^+[MeB(C_6F_5)_3]^-$ and **3** were collected on an Agilent SuperNova diffractometer, equipped with a CCD area Atlas detector and a mirror monochromator utilizing CuK_α radiation (λ = 1.54184 Å). The crystal structures were solved by Direct Methods and refined on F^2 using full-matrix least squares with SHELXL-97[S3]. The positions of the H atoms at the carbon atoms were calculated by standard methods. CCDC deposition numbers: 1054432 for **2**$^+[MeB(C_6F_5)_3]^-$ and 1054431 for **3**.

Table S1. Crystal data and structure refinement for **2**$^+[MeB(C_6F_5)_3]^-$.

Empirical formula	$C_{51}H_{54}BF_{15}GeN_4Si_2$	
Formula weight	1147.56	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system, space group	Triclinic, *P*-1	
Unit cell dimensions	a = 11.9070(4) Å	alpha = 76.511(2)°
	b = 14.4773(4) Å	beta = 72.772(3)°
	c = 16.6752(5) Å	gamma = 88.005(2)°
Volume	2667.97(14) A^3	
Z, Calculated density	2, 1.428 Mg/m^3	
Absorption coefficient	2.021 mm^{-1}	
F(000)	1176	
Crystal size	0.42 x 0.20 x 0.06 mm	
Theta range for data collection	2.85 to 67.49°	
Limiting indices	-14<=h<=14, -12<=k<=17, -18<=l<=19	
Reflections collected / unique	17356 / 9601 [R(int) = 0.0182]	
Completeness to theta = 67.49	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.64546	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9601 / 0 / 681	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.1191	
R indices (all data)	R1 = 0.0359, wR2 = 0.1284	
Largest diff. peak and hole	0.453 and -0.572 e.A^{-3}	

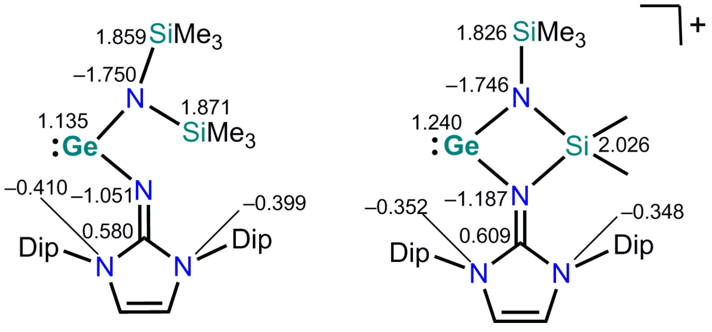
Table S2. Crystal data and structure refinement for **3**.

Empirical formula	$C_{37}H_{54}FeGeN_4O_4Si_2$	
Formula weight	803.46	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 20.6549(2) Å	a= 90°.
	b = 20.42240(10) Å	b= 116.9550(10)°.
	c = 22.6744(2) Å	g = 90°.
Volume	8525.50(12) Å^3	
Z	8	
Density (calculated)	1.252 Mg/m^3	
Absorption coefficient	4.448 mm^{-1}	
F(000)	3376	
Crystal size	0.36 x 0.12 x 0.08 mm^3	
Theta range for data collection	2.40 to 67.50°.	
Index ranges	-24<=h<=24, -24<=k<=21, -27<=l<=24	
Reflections collected	55960	
Independent reflections	15370 [R(int) = 0.0484]	
Completeness to theta = 67.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7174 and 0.2974	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15370 / 0 / 911	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0896	
R indices (all data)	R1 = 0.0545, wR2 = 0.0987	
Largest diff. peak and hole	0.605 and -0.411 e.Å^{-3}	

3.) Details to the DFT Calculations of 1, 2^+ and 3

General Considerations: DFT calculations of model compounds to **1**, $\mathbf{2^+}$ and **3** were carried out by the GAUSSIAN 09 program[S4]. The B3LYP functional[S5], as well as the LanL2DZ basis sets[S6] (for Ge and Fe) or the 6-31G(d) basis sets[S7] (for all other atoms) were adopted. Cartesian coordinates of the optimized structures are shown in Table S3, S4 and S5, respectively. The structures obtained by the X-ray analyses for $\mathbf{2^+}$ and **3** were used as input for these calculations. For **1** a model compound was generated by removing the $Fe(CO)_4$ fragment from **3**. The NBO approach at the B3LYP/Def2-TZVP levels[S8] was used to calculate the Wiberg Bond Indices (WBI).

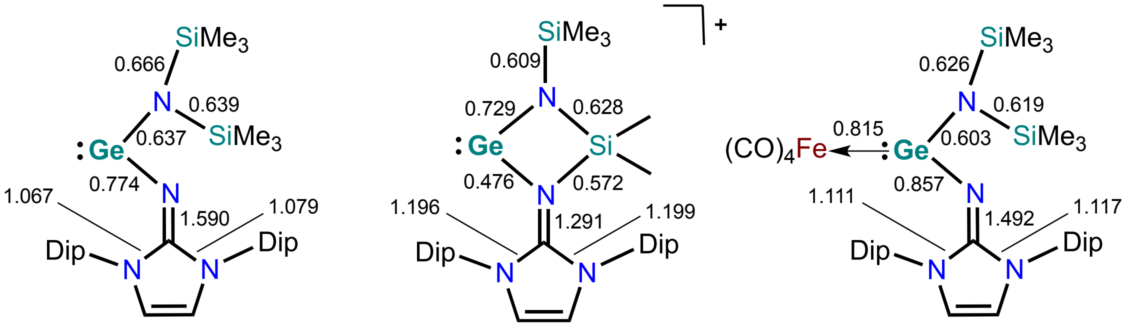
3.1) DFT Calculations: Comparison of the Natural Population Analysis (NPA) Charges of 1 and 2^+



1 $\mathbf{2^+}$

Figure S15. Selected values for the NPA Charges of **1** and $\mathbf{2^+}$.

3.2) DFT Calculations: Comparison of the Wiberg Bond Indices (WBI) of 1, 2^+ and 3



1 $\mathbf{2^+}$ **3**

Figure S16. Selected values for the WBI of **1**, $\mathbf{2^+}$ and **3**.

3.3) DFT Calculations: Supplementary Data to 1

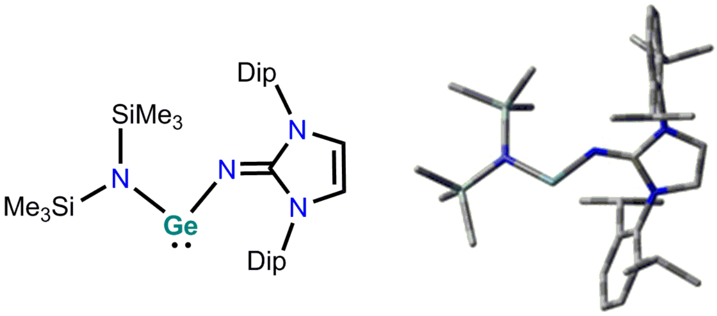


Figure S17. Lewis structure (left) and optimized structure (right) for **1**.

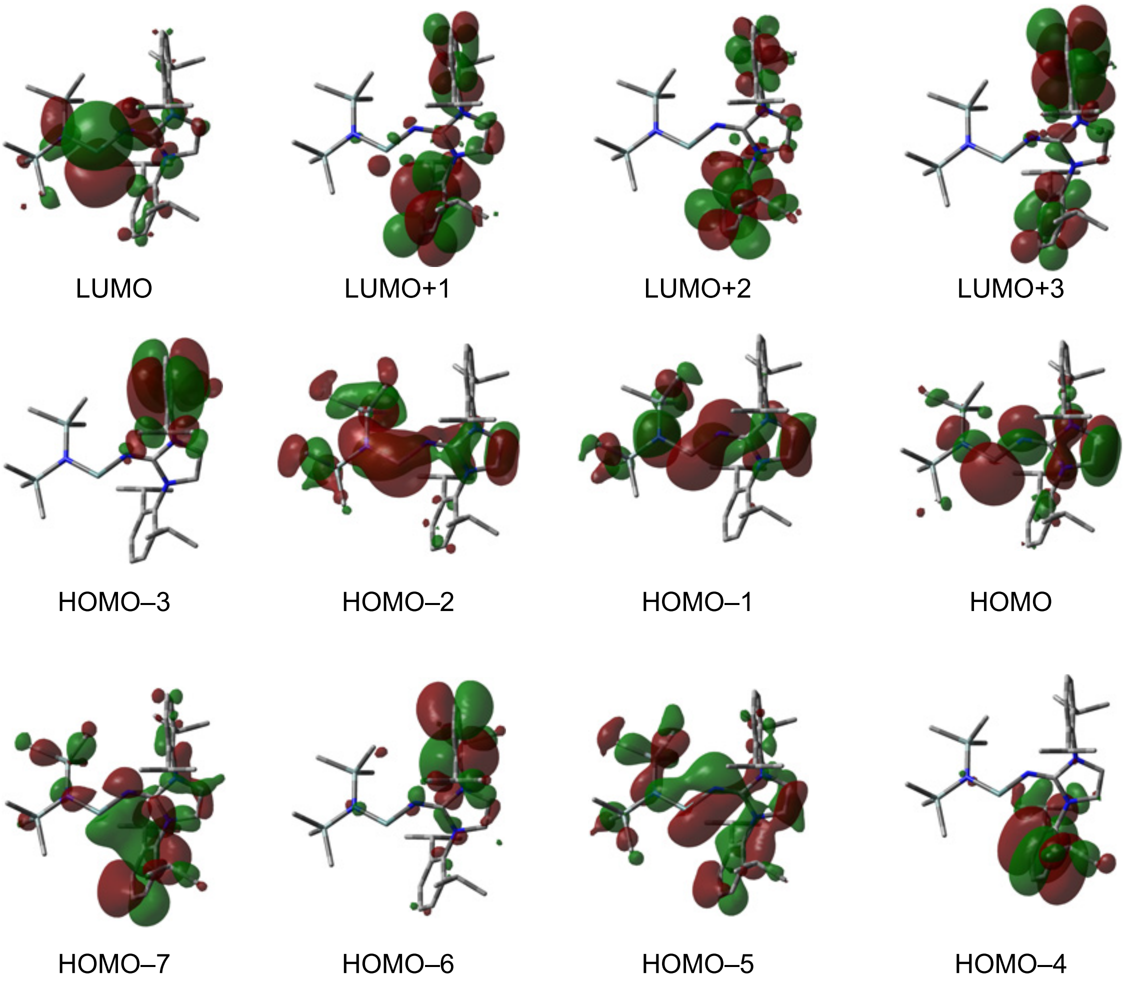
Table S3. Cartesian coordinates (x, y, z) for the optimized structure of **1**.

Ge	-1.363880	-0.214481	-1.120155
Si	-1.387183	-3.077761	0.402011
N	0.168028	-0.195358	-0.105704
C	1.011098	0.742430	0.154212
Si	-3.980044	-1.849709	-0.798622
N	2.408868	0.634256	0.153135
C	2.992536	1.840601	0.547071
N	0.782612	2.071159	0.559437
C	2.000033	2.718600	0.799159
N	-2.240217	-1.789149	-0.476393
C	3.150398	-0.542899	-0.201511
C	3.644983	-1.372233	0.827887
C	4.418603	-2.480074	0.460453
C	4.681109	-2.763590	-0.876804
C	4.175006	-1.937302	-1.875817
C	3.403874	-0.810996	-1.563165
C	3.387691	-1.081817	2.303628
C	4.659088	-0.543320	2.991309
C	2.842421	-2.309694	3.056469
C	2.899083	0.091698	-2.683783
C	2.047809	-0.681627	-3.708102

C	4.067924	0.823225	-3.374185
C	-0.500011	2.709469	0.664937
C	-1.277417	2.497669	1.826802
C	-2.506082	3.161247	1.918305
C	-2.942311	4.013663	0.905885
C	-2.157097	4.214438	-0.224151
C	-0.925166	3.563939	-0.374944
C	-0.778906	1.615679	2.967919
C	0.053346	2.444757	3.969621
C	-1.906281	0.867947	3.699744
C	-0.089215	3.812702	-1.627555
C	0.496073	5.239845	-1.628039
C	-0.881496	3.545708	-2.921601
C	-4.597894	-0.245289	-1.610344
C	-4.964400	-2.006721	0.818297
C	-4.474881	-3.247340	-1.983083
C	-1.073870	-2.578079	2.202050
C	0.240107	-3.521628	-0.454838
C	-2.371953	-4.706984	0.446729
H	4.063500	1.950858	0.606803
H	2.032565	3.745782	1.125415
H	4.818137	-3.131463	1.232260
H	5.280593	-3.630944	-1.140752
H	4.385852	-2.166164	-2.916705
H	2.623664	-0.300632	2.362884
H	5.467734	-1.283460	2.959064
H	4.457849	-0.310325	4.043769
H	5.023945	0.369287	2.506970
H	1.941943	-2.701799	2.575120
H	2.586645	-2.035019	4.086691
H	3.580602	-3.118541	3.107983
H	2.255228	0.855539	-2.238370
H	2.637389	-1.440143	-4.236588

H	1.642052	0.005269	-4.460203
H	1.208528	-1.186046	-3.219179
H	4.650623	1.411050	-2.655836
H	3.691565	1.505763	-4.145587
H	4.751440	0.115642	-3.858658
H	-3.129247	3.014922	2.794342
H	-3.898241	4.522255	1.000282
H	-2.507743	4.879908	-1.007686
H	-0.121659	0.855921	2.533964
H	0.912280	2.920988	3.485294
H	0.432573	1.804226	4.775073
H	-0.558651	3.233257	4.424316
H	-2.541505	1.546054	4.282152
H	-1.475996	0.145097	4.401336
H	-2.542933	0.317042	2.999812
H	0.753038	3.114051	-1.613676
H	-0.299481	5.994409	-1.643088
H	1.123309	5.396351	-2.513679
H	1.111776	5.423947	-0.740418
H	-1.289294	2.529667	-2.931863
H	-0.226014	3.663452	-3.792839
H	-1.714698	4.247955	-3.041633
H	-4.405637	0.648584	-1.005505
H	-5.686712	-0.328445	-1.733491
H	-4.168082	-0.070535	-2.602576
H	-4.735713	-2.916738	1.382746
H	-6.042495	-2.010706	0.610263
H	-4.757638	-1.151282	1.473810
H	-3.900258	-3.184794	-2.915532
H	-5.537826	-3.159420	-2.243927
H	-4.320074	-4.245453	-1.562571
H	-0.460767	-1.672444	2.241335
H	-0.553490	-3.372476	2.752952

H	-2.016210	-2.374190	2.724846
H	0.057582	-3.853179	-1.485238
H	0.735792	-4.347907	0.071731
H	0.924960	-2.671145	-0.482548
H	-3.369625	-4.624434	0.889982
H	-1.806397	-5.424580	1.056563
H	-2.479690	-5.147522	-0.550761



LUMO LUMO+1 LUMO+2 LUMO+3

HOMO–3 HOMO–2 HOMO–1 HOMO

HOMO–7 HOMO–6 HOMO–5 HOMO–4

Figure S18. Kohn-Sham depictions of selected molecular orbitals of **1**.

3.4) DFT Calculations: Supplementary Data to 2^+

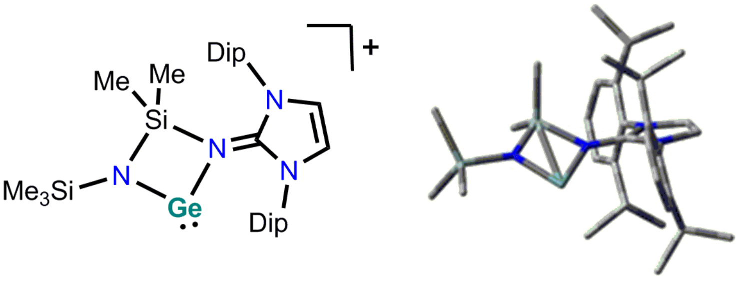
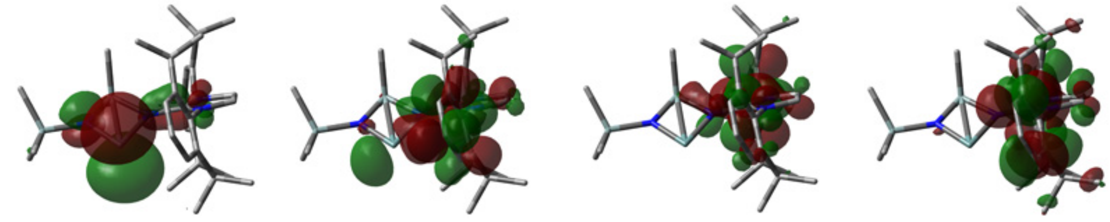
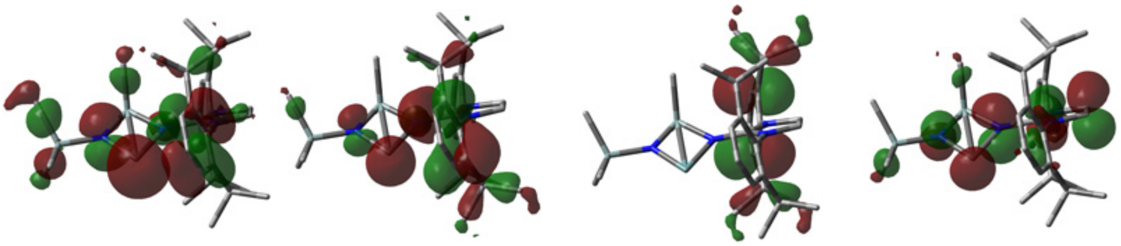


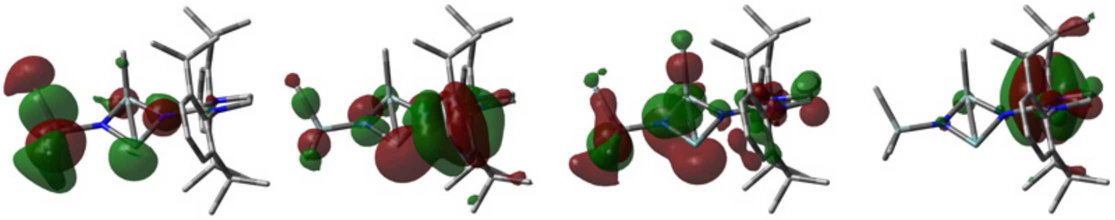
Figure S19. Lewis structure (left) and optimized structure (right) for $\mathbf{2}^+$.



LUMO LUMO+1 LUMO+2 LUMO+3



HOMO–3 HOMO–2 HOMO–1 HOMO



HOMO–7 HOMO–6 HOMO–5 HOMO–4

Figure S20. Kohn-Sham depictions of selected molecular orbitals of $\mathbf{2}^+$.

Table S4. Cartesian coordinates (x, y, z) for the optimized structure of **2^+**.

Ge	-1.862352	0.789781	-0.847911
Si	0.205112	2.018583	0.489382
C	0.483310	-0.876964	0.162929
Si	-2.206434	4.006792	-0.386675
C	1.948823	-2.576840	0.413647
C	0.708965	-3.093460	0.545304
C	2.940976	-0.367976	-0.187540
N	-0.073962	0.319983	-0.051523
C	3.172006	-0.122431	-1.558748
C	4.298963	0.638290	-1.893281
C	5.168858	1.109117	-0.914278
C	4.933893	0.821596	0.427790
C	3.817680	0.074774	0.827704
C	2.301948	-0.701356	-2.671753
C	3.068310	-1.797004	-3.442606
N	1.815836	-1.206812	0.177021
C	1.775312	0.379259	-3.634886
C	3.630410	-0.273698	2.303282
C	4.550612	-1.445189	2.712577
N	-1.345986	2.454494	-0.215983
C	3.875801	0.926161	3.239348
N	-0.199376	-2.046925	0.392416
C	-1.636299	-2.224105	0.426432
C	-2.329629	-1.930420	1.622832
C	-3.713679	-2.141782	1.626394
C	-4.370545	-2.645178	0.505433
C	-3.656052	-2.954208	-0.647622
C	-2.272101	-2.750535	-0.720071
C	-1.614648	-1.475235	2.892476
C	-2.410942	-0.432829	3.697617
C	-1.272144	-2.692307	3.779788
C	-1.517637	-3.135098	-1.991328

C	-2.138000	-2.518733	-3.260183
C	-1.425396	-4.670104	-2.125227
C	1.638406	2.941977	-0.284328
C	0.243898	2.123723	2.362696
C	-4.017668	3.613839	-0.744862
C	-2.046085	4.981479	1.221026
C	-1.461501	4.986639	-1.817161
H	2.919758	-3.041849	0.451645
H	0.372974	-4.100708	0.729899
H	4.507909	0.848400	-2.937699
H	6.041238	1.690443	-1.198572
H	5.633309	1.177143	1.177233
H	1.429125	-1.180184	-2.216951
H	2.423442	-2.246328	-4.206149
H	3.410759	-2.594119	-2.773722
H	3.948424	-1.385218	-3.948639
H	1.205916	1.148840	-3.102554
H	1.117729	-0.074149	-4.384974
H	2.589025	0.876966	-4.173309
H	2.593685	-0.600860	2.447087
H	4.368611	-2.344682	2.115471
H	4.392726	-1.703350	3.765581
H	5.604418	-1.172706	2.586590
H	4.934364	1.204998	3.271896
H	3.581121	0.666866	4.261961
H	3.308993	1.811462	2.934314
H	-4.284626	-1.926560	2.523142
H	-5.444058	-2.807686	0.536584
H	-4.180319	-3.360514	-1.506726
H	-0.668662	-1.005584	2.601615
H	-2.725069	0.412101	3.074362
H	-1.793470	-0.043888	4.514291
H	-3.308809	-0.863388	4.153695

H	-2.183328	-3.212319	4.095962
H	-0.737203	-2.369554	4.679996
H	-0.640152	-3.414493	3.251921
H	-0.493937	-2.752224	-1.913906
H	-3.140656	-2.912656	-3.456955
H	-1.518020	-2.757258	-4.131344
H	-2.216853	-1.428785	-3.184198
H	-0.940265	-5.126956	-1.255508
H	-0.848382	-4.941084	-3.016243
H	-2.421190	-5.117095	-2.221264
H	1.636164	2.857843	-1.375244
H	2.609309	2.596553	0.083838
H	1.549398	4.007133	-0.033052
H	0.347662	3.166867	2.684883
H	1.084926	1.567427	2.790213
H	-0.680264	1.731133	2.797535
H	-4.149623	3.046197	-1.674685
H	-4.588777	4.543506	-0.857193
H	-4.482841	3.043222	0.067984
H	-2.442879	4.424058	2.077330
H	-2.606775	5.921766	1.151595
H	-1.005146	5.246156	1.444619
H	-0.402896	5.217543	-1.649555
H	-1.987522	5.940242	-1.949201
H	-1.536138	4.435487	-2.762287

3.5) DFT Calculations: Supplementary Data to 3

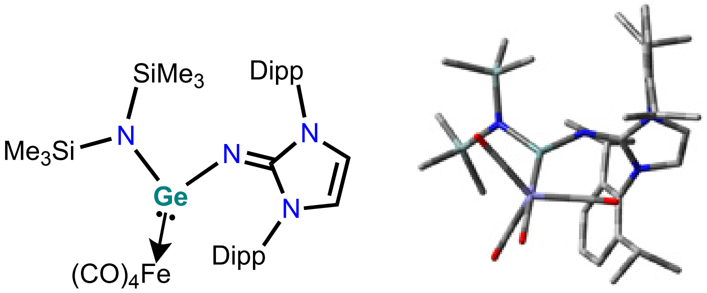
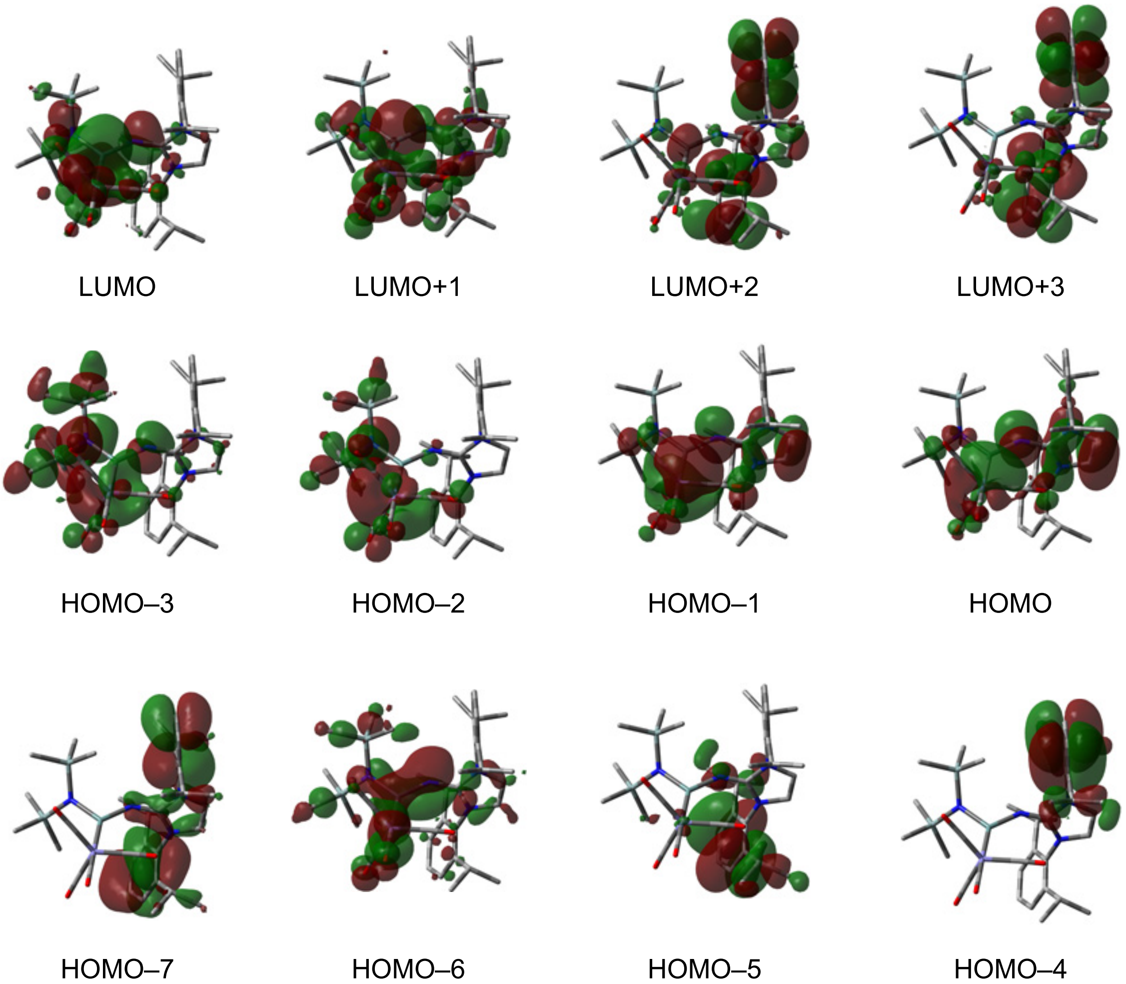


Figure S21. Lewis structure (left) and optimized structure (right) for **3**.


LUMO LUMO+1 LUMO+2 LUMO+3

HOMO–3 HOMO–2 HOMO–1 HOMO

HOMO–7 HOMO–6 HOMO–5 HOMO–4

Figure S22. Kohn-Sham depictions of selected molecular orbitals of **3**.

Table S5. Cartesian coordinates (x, y, z) for the optimized structure of **3**.

Ge	1.098822	-0.532285	0.061367
Fe	2.468979	-0.156046	1.958118
Si	0.704519	-3.328168	-1.313054
O	0.285181	1.409366	3.138407
N	-0.572539	-0.050829	-0.260591
C	-1.472409	0.834560	0.034404
Si	2.982573	-1.441727	-2.271695
O	2.889183	-3.070113	1.960703
N	-2.722287	0.591584	0.603827
C	-3.453693	1.780998	0.665510
O	3.930460	0.038938	4.485547
N	-1.473611	2.203338	-0.246611
C	-2.695354	2.763625	0.140139
O	4.485634	1.425315	0.531403
N	1.556758	-1.764886	-1.255688
C	-3.285803	-0.697278	0.932736
C	-4.008169	-1.394952	-0.063717
C	-4.592711	-2.616218	0.290144
C	-4.477162	-3.124686	1.581284
C	-3.780739	-2.410759	2.549479
C	-3.174096	-1.182832	2.251756
C	-4.219985	-0.830711	-1.465927
C	-5.570597	-0.087993	-1.557988
C	-4.129270	-1.896213	-2.572157
C	-2.481008	-0.399023	3.358408
C	-1.463982	-1.250047	4.140555
C	-3.520114	0.224331	4.313908
C	-0.483315	2.908608	-1.022553
C	-0.461141	2.719545	-2.423205
C	0.504307	3.415080	-3.161030
C	1.393279	4.288978	-2.542561
C	1.319674	4.497677	-1.169076

C	0.383838	3.818806	-0.377137
C	-1.476961	1.851619	-3.159848
C	-2.355206	2.711268	-4.092387
C	-0.816165	0.694028	-3.930416
C	0.287416	4.134899	1.112700
C	-0.476840	5.458089	1.337369
C	1.660520	4.200541	1.806473
C	3.136961	0.417850	-2.595750
C	2.792706	-2.255865	-3.974039
C	4.586275	-2.063462	-1.481806
C	-0.388769	-3.468370	-2.852879
C	-0.380899	-3.541049	0.222391
C	1.944614	-4.762719	-1.295796
C	1.126492	0.772284	2.651365
C	2.703486	-1.926233	1.930852
C	3.355868	-0.038757	3.487925
C	3.671203	0.785318	1.051275
H	-4.441189	1.804616	1.096861
H	-2.896178	3.813208	0.002145
H	-5.151027	-3.175722	-0.453583
H	-4.938541	-4.075918	1.833325
H	-3.708558	-2.807201	3.557700
H	-3.426735	-0.102345	-1.656279
H	-6.404114	-0.772314	-1.359519
H	-5.709282	0.331191	-2.561870
H	5.632871	0.734979	-0.838897
H	-3.210020	-2.482749	-2.492280
H	-4.141206	-1.412162	-3.555623
H	-4.978034	-2.589496	-2.546175
H	-1.927212	0.422047	2.899418
H	-1.947182	-2.064096	4.693557
H	-0.938095	-0.623107	4.868386
H	-0.715490	-1.690361	3.473894

H	-4.222932	0.872523	3.777691
H	-3.018696	0.829090	5.078436
H	-4.105120	-0.549767	4.825387
H	0.547997	3.280673	-4.238122
H	2.135079	4.819186	-3.133728
H	2.001279	5.200157	-0.700263
H	-2.143501	1.405041	-2.418509
H	-2.856880	3.514266	-3.540662
H	-3.125358	2.091281	-4.566540
H	-1.762704	3.173506	-4.890315
H	-0.134156	1.061767	-4.706589
H	-1.581918	0.086308	-4.427616
H	-0.253979	0.044056	-3.253566
H	-0.281361	3.335098	1.593622
H	0.055310	6.299960	0.878419
H	-0.573768	5.663738	2.409838
H	-1.484171	5.430607	0.907879
H	2.254301	3.303117	1.612960
H	1.522665	4.287627	2.889845
H	2.242833	5.070226	1.480395
H	2.223429	0.829764	-3.038577
H	3.953047	0.585995	-3.311121
H	3.377364	1.007944	-1.706352
H	2.725165	-3.347817	-3.937276
H	3.672568	-2.006265	-4.581512
H	1.909558	-1.880850	-4.503704
H	4.756913	-1.597337	-0.505078
H	5.448002	-1.826124	-2.119231
H	4.570950	-3.148866	-1.331514
H	-1.033923	-2.588002	-2.944581
H	-1.032039	-4.355896	-2.790899
H	0.196347	-3.548202	-3.774953

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