Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary material for:

Facile Activation of Alkynes with a Boraguanidinato-Stabilized Germylene: A Combined Experimental and Theoretical Study.

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Table S1. Relevant crystallographic data for the studied compounds.

	1a	**1b**	**1c**	**2a**
Chemical formula	$C_{48}H_{70}B_2Ge_2N_6$	$C_{58}H_{74}B_2Ge_2N_6$	$C_{52}H_{70}B_2Ge_2N_6$	$C_{56}H_{74}B_2FeGe_2N_6$
Cryst syst	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	*P-1*	*C2/c*
a[Å]	10.1640(12)	19.659(2)	15.3900(7)	52.0662(4)
b[Å]	21.9981(17)	10.8410(8)	18.312(2)	10.3231(2)
c[Å]	23.169(3)	28.649(4)	36.856(5)	21.2294(4)
α[°]	90	90	91.094(11)	90
β[°]	112.354(12)	114.791(10)	97.193(5)	112.682(3)
γ[°]	90	90	91.257(8)	90
Z	4	4	8	8
μ[mm^{-1}]	1.293	1.126	1.206	1.449
D_x [Mg m^{-3}]	1.245	1.225	1.220	1.330
Cryst size [mm]	0.59x0.47x0.19	0.37×0.21×0.15	0.48x0.19x0.11	0.46×0.23×0.11
θ range, [deg]	1-27.5	1-27.5	1-27.5	1-27.5
T_{min}, T_{max}	0.599, 0.837	0.820, 0.878	0.725, 0.884	0.703, 0.867
no. of reflns measd	34717	37747	150 941	97484
no. of unique reflns, R_{int}	10461, 0.037	12326, 0.064	46094, 0.074	12046, 0.053
no. of obsd reflns	8045	8407	29450	8940
no. of params	592	613	2224	604
S all data	3.191	1.131	1.100	1.153
final R indices [$I>2\sigma(I)$]	0.042	0.050	0.067	0.044
wR2 indices (all data)	0.084	0.081	0.111	0.076
$\Delta\rho$, max., min. [e Å^{-3}]	0.805, -0.654	0.485, -0.506	0.938, -0.626	0.679, -0.684

	2c	**3a**	**3b**	**4**
Chemical formula	$C_{62}H_{78}B_2FeGe_2N_6 \cdot C_6H_{14}$	$C_{60}H_{74}B_2Ge_2N_6.0.5(C_6H_{14})$	$C_{56}H_{82}B_2Ge_2N_6$	$C_{114}H_{146}B_4FeGe_4N_{12} \cdot 6(C_7H_8)$
Cryst syst	Triclinic	monoclinic	monoclinic	Triclinic
Space group	*P-1*	*P21/c*	*P21/c*	*P-1*
a[Å]	10.7590(8)	22.5261(14)	11.1579(7)	10.8838(8)
b[Å]	14.9720(14)	13.2680(15)	19.2531(19)	16.8256(12)
c[Å]	21.213(2)	21.209(2)	27.690(2)	19.8906(16)
α[°]	75.454(9)	90	90	77.578(3)
β[°]	78.047(8)	112.060(9)	110.450(6)	78.671(3)
γ[°]	85.108(7)	90	90	72.523(3)
Z	2	4	4	1
μ[mm^{-1}]	1.189	1.067	1.119	1.048
D_x [Mg m^{-3}]	1.249	1.231	1.199	1.299
Cryst size [mm]	0.39×0.33×0.16	0.52×0.32×0.18	0.39x0.17x0.13	0.161×0.073×0.073
Θ range, [deg]	1-26.5	1-27	1-27	1-26
T_{min}, T_{max}	0.748, 0.857	0.762, 0.878	0.6567, 0.7455	0.849, 0.927
no. of reflns measd	54709	50365	67651	54930
no. of unique reflns, R_{int}	13191, 0.095	12445, 0.065	12138, 0.060	11525, 0.088
no. of obsd reflns	9144	8543	8509	8415
no. of params	658	667	625	684
S all data	1.121	1.133	1.081	1.134
final R indices [$I>2\sigma(I)$]	0.068	0.048	0.048	0.082
wR2 indices (all data)	0.142	0.081	0.085	0.158
$\Delta\rho$, max., min. [e Å^{-3}]	1.239, -0.896	0.600, -0.595	0.877, -0.586	0.920, -0.695

Definitions: $R_{\text{int}} = \sum|F_o^2 - F_{o,\text{mean}}^2|/\sum F_o^2$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{\text{diffrs}} - N_{\text{params}})]^{½}$ for all data, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

Computational results

Possible additional pathways of the 3,4-Me$_2$-1,2-digermacyclobut-3-ene (**1a**) formation

Complex **D3** can also be obtained from dimer **D1** found in the solid phase[S1] (**D1→D4→D3**). However, in alkyne complex **D4** (Scheme S1) the Ge-C_2Me_2 interaction is weaker than that in intermediate **M2**, the averaged Ge-C distances are, respectively, 3.907 and 3.058 Å (Table S2). This is caused by mutual repulsion between the methyl groups of the Ge-containing fragment and the alkyne (Figure S2). On the other hand, the averaged Ge-C distance in dimer **D3** (3.014 Å) is close to that in **M2**. To form complex **D3** from **D4**, the C_2Me_2 fragment has to overcome the Me-Me repulsion which makes the **D1→D4→D3→1a** pathway less favourable. The formation of the 3,4-R,R′-1,2-digermacyclobut-3-enes with more bulky substituents (**1b-e**, **2a-d**) also testifies to the preferable pathway via monomeric species **M2**. The **D1→D5** stage (Scheme S1) leading to digermene is accompanied by an increase in both electronic and Gibbs energies (ΔE_{el} = 12.5, ΔG = 3.5 kcal mol^{-1}). Accordingly, no **D5** species are detected both in the crystal state and in solution.[S1]

Furthermore, the insertion of the **M1** species into the Ge-N bond of another **M1** molecule can produce dimer **D6** (Scheme S1). The calculated solution-phase electronic energy of **D6** is 3.7 kcal mol^{-1} higher than that of **D1**, but the **D1→D6** ΔG value is only 1.3 kcal mol^{-1} so the **D6** dimer might participate in the reactions leading to the **1a** product. The addition of C_2Me_2 to this dimer (**D6→D7**) is endergonic (ΔG = 5.8 kcal mol^{-1}). Alternatively, the **D7** adduct can be obtained from the monomer **M2** with the ΔE_{el} = -18.6, ΔG = 2.7 kcal mol^{-1} energy changes (Scheme S1).

The transformations of **D7** into the alkene complex **D8** and then to the product **1a** lead to a decrease of the free energy (ΔG = -8.4 and ΔG = -18.4 kcal mol^{-1}, respectively). The pathway involving the **D7** and **D8** species thus appears to be thermodynamically favoured. Moreover, the activation energy (ΔE_{a}) of the **D7→D8** reaction is rather low (5.9 kcal mol^{-1}, Scheme S3). However, the **D8→1a** transformation requires a substantial rearrangement of the molecular fragments including the Ge-N and Ge-C bond cleavages, ligand rotations and formations of new bonds.

In the course of a search for the corresponding transition state, additional stable intermediates **D9** - **D13** with electronic energies E_{el} lying between those of **1a** and **D7** (Figure S4) were found. The **D9** complex with the MeC≡C and Me fragments coordinated to a Ge atom appears to have an even lower E_{el} value than **1a** (Table S3). The dimethylacetylene MeC≡C-Me bond cleavage necessary for the formation of **D9** (**D7→D9**) corresponds, however, to a high activation energy of 73.4 kcal mol^{-1}. This barrier prevents the formation of dimer **D9** in the germylene reaction with C_2Me_2. Our DFT analysis shows, therefore, that among the numerous possible mechanisms of the 3,4-Me$_2$-1,2-digermacyclobut-3-ene (**1a**) formation the **M1→M2→D3→1a** pathway is energetically favourable. The gas-phase reaction parameters (Scheme S2) reveal similar trends and suggest the same mechanism.

QTAIM analysis of Ge-Ge bonding in D5 and 1a.

Like MO, NBO and ELF approaches, the QTAIM analysis also reveals large differences in the **D5** and **1a** Ge-Ge bonding. The electron density in the Ge-Ge (3, −1) critical point increases from 0.035 a.u. in **D5** to 0.078 a.u. in **1a** which agrees with the shorter **1a** interatomic distance. The corresponding

Laplacian value decreases from +0.006 to −0.064 a.u., respectively, whereas the ratio of the local potential-energy density and local kinetic-energy density $|V(\mathbf{r}_c)|/G(\mathbf{r}_c)$increases from 1.778 to 2.938. The nature of bonding interactions can be classified according to the $|V(\mathbf{r}_c)|/G(\mathbf{r}_c)$ ratio at the bonding critical points.[S1] Closed-shell interactions display $|V(\mathbf{r}_c)|/G(\mathbf{r}_c)$ values less than 1.0, intermediate interactions $1<|V(\mathbf{r}_c)|/G(\mathbf{r}_c)<2$ and covalent interactions $|V(\mathbf{r}_c)|/G(\mathbf{r}_c)>2$.The observed changes suggest stronger covalent character of the Ge-Ge bond in **1a**.

References

S1. (a) E. Espinosa, I. Alkorta, J. Elguero and E. Molins, *J. Chem. Phys.*, 2002, **117**, 5529; (b) G. V. Gibbs, D. F. Cox, T. D. Crawford, K. M. Rosso, N. L. Ross and R. T. Downs, *J. Chem. Phys.*, 2006, **124**, 084704.

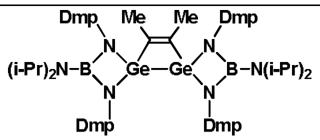
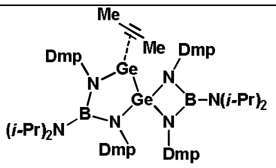
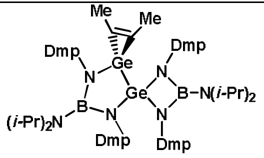
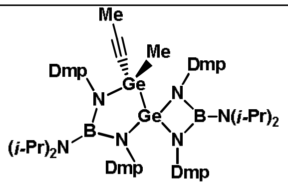
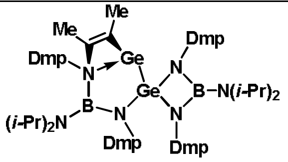
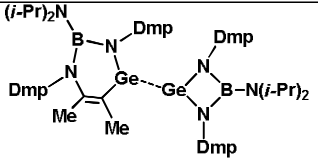
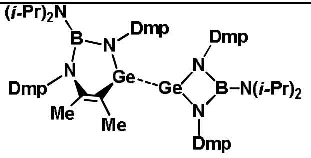
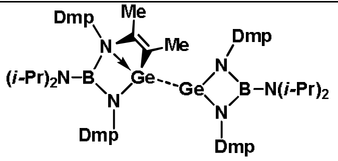
Table S2. Selected M06-2X/DGDZVP interatomic distances and bonding angles in the optimized structures of reactants, products, intermediates and transition states corresponding to the interaction between germylene [(*i*-Pr)$_2$NB(N-2,6-Me$_2$C$_6$H$_3$)$_2$]Ge (**M1**)and C$_2$Me$_2$.

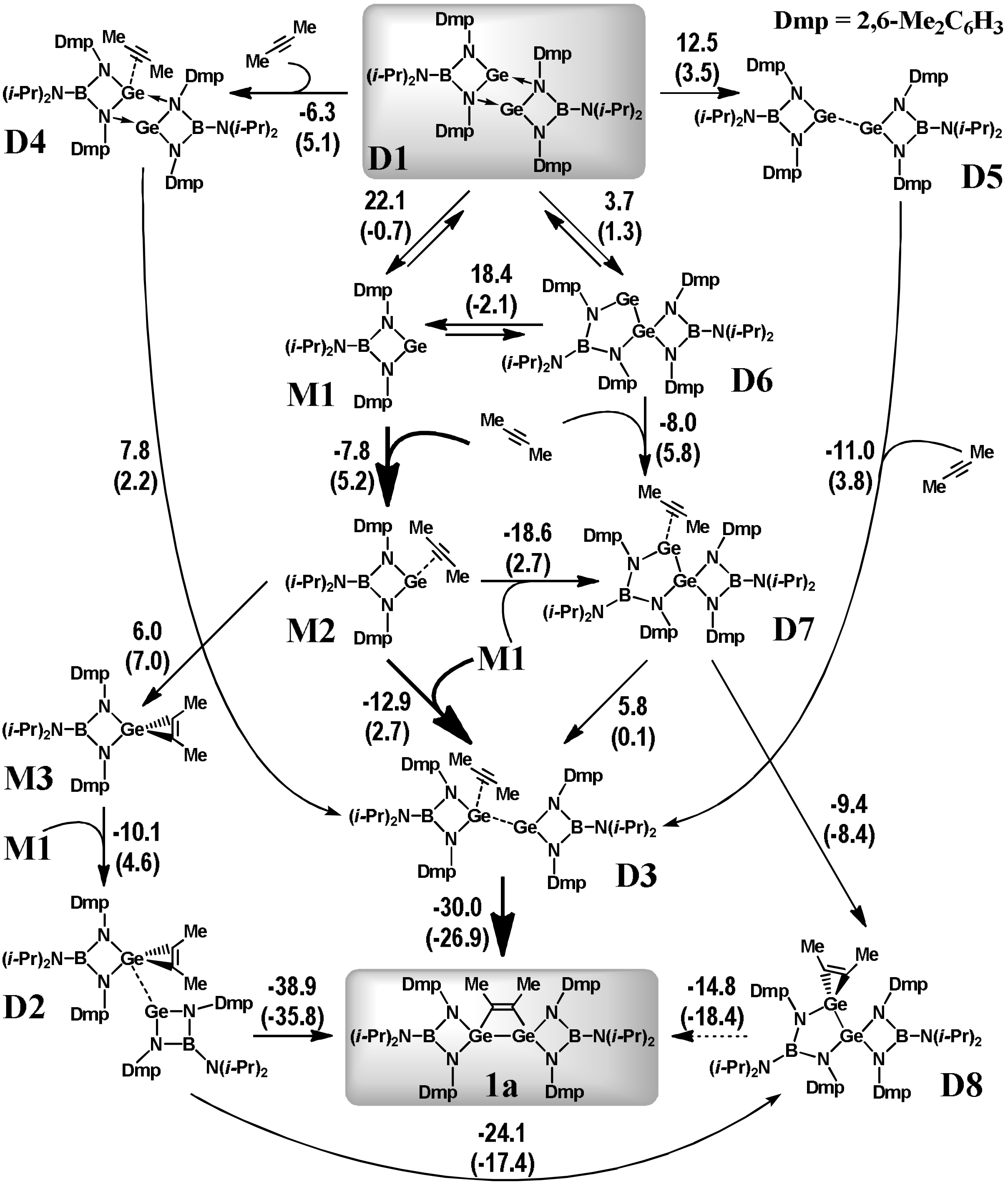
Compound	Phase	Bond lengths [Å]					Bonding angles [°]			
		Ge–Ge	Ge–N	Ge–C	C=C	C≡C	C–Ge–Ge	C–C–Ge	C–Ge–C	C–C–CH$_3$
1a	gas	2.442	1.864, 1.865; 1.868, 1.874	1.979, 1.980	1.357	–	73.94, 74.00	105.66, 105.69	–	126.92, 127.31
	C$_6$H$_6$	2.445	1.864, 1.869; 1.869, 1.877	1.978, 1.980	1.357	–	73.78, 74.09	105.58, 105.96	–	126.78, 127.21
M1	gas	–	1.886, 1.886	–	–	–	–	–	–	–
	C$_6$H$_6$	–	1.885, 1.889	–	–	–	–	–	–	–
M2	gas	–	1.898, 1.903	2.993, 3.127	–	1.214	–	72.41, 84.85	22.75	177.58, 178.53
	C$_6$H$_6$	–	1.899, 1.904	2.991, 3.124	–	1.215	–	72.47, 84.75	22.78	177.63, 178.53
M3	gas	–	1.864, 1.865	1.892, 1.892	1.364	–	–	68.86, 68.89	42.25	133.92, 133.93
	C$_6$H$_6$	–	1.865, 1.866	1.891, 1.891	1.364	–	–	68.86, 68.87	42.28	133.98, 133.99
D1	gas	3.017	1.961, 2.125, 2.112; 1.961, 2.125, 2.112	–	–	–	–	–	–	–
	C$_6$H$_6$	3.016	1.960, 2.126, 2.112; 1.960, 2.126, 2.111	–	–	–	–	–	–	–
D2	gas	3.622	1.866, 1.869; 1.892, 1.892	1.889, 1.897; 3.873	1.364	–	–	68.56, 69.21	42.23	134.03, 134.72
	C$_6$H$_6$	3.638	1.867, 1.870; 1.892, 1.894	1.888, 1.896; 3.882	1.364	–	–	68.54, 69.20	42.23	134.01, 134.71
D3	gas	2.918	1.898, 1.890; 1.885, 1.896	2.994, 3.033	–	1.214	–	76.61, 80.16	23.23	176.46, 179.00
	C$_6$H$_6$	2.923	1.897, 1.890; 1.885, 1.896	2.999, 3.042	–	1.214	–	76.43, 80.40	23.18	176.62, 178.96
D4	gas	3.013	1.965, 2.124; 1.965, 2.129	3.693, 3.997	–	1.212	–	66.85, 95.60	17.56	179.15, 179.29

	C_6H_6	3.014	1.963, 2.135; 1.965, 2.124	3.753, 4.060	–	1.212	–	66.83, 95.90	17.27	179.07, 179.20
D5	gas	2.933	1.887, 1.905; 1.869, 1.875	–	–	–	–	–	–	–
	C_6H_6	2.943	1.889, 1.907; 1.869, 1.874	–	–	–	–	–	–	–
D6	gas	2.515	1.877, 1.891 1.873; 1.873	–	–	–	–	–	–	–
	C_6H_6	2.516	1.878, 1.892, 1.874; 1.873	–	–	–	–	–	–	–
D7	gas	2.527	1.888, 1.903, 1.887; 1.892	2.842, 2.965	–	1.215	–	72.32, 83.65	24.03	177.24, 178.16
	C_6H_6	2.527	1.889, 1.904, 1.888; 1.893	2.818, 2.943	–	1.216	–	72.09, 83.67	24.24	176.65, 177.65
D8	gas	2.402	1.863, 1.876, 1.859; 1.883	1.906, 1.914	1.345	–	–	69.09, 69.69	41.22	137.50, 136.82
	C_6H_6	2.403	1.863, 1.876, 1.859; 1.884	1.906, 1.913	1.345	–	–	69.11, 69.67	41.23	137.32, 136.83
D9	gas	2.422	1.879, 1.895, 1.870; 1.864	1.930, 1.974	–	1.218	–	179.78	107.70	178.65
TS1	gas	–	1.893, 1.898	2.018, 2.190	–	1.277	–	65.11, 79.88	35.02	146.31, 153.30
TS2		2.702	1.874, 1.851; 1.891, 1.898	1.861, 2.130; 2.663	1.357	–	46.78, 103.91	81.28, 126.03	–	126.11, 132.43
TS3		2.598	1.876, 1.883; 1.902, 1.905	2.444, 2.495	–	1.253	71.38, 72.68	98.00, 104.88	–	151.64, 156.16
TS4		2.431	1.876, 1.886, 1.870; 1.916	2.075, 2.281	–	1.265	–	64.37, 82.27	33.35	155.06, 153.84
TS5		2.547	1.891, 1.888, 2.421; 1.856, 2.384	2.876, 3.026	–	1.216	–	71.27, 85.12	23.61	176.53, 180.00

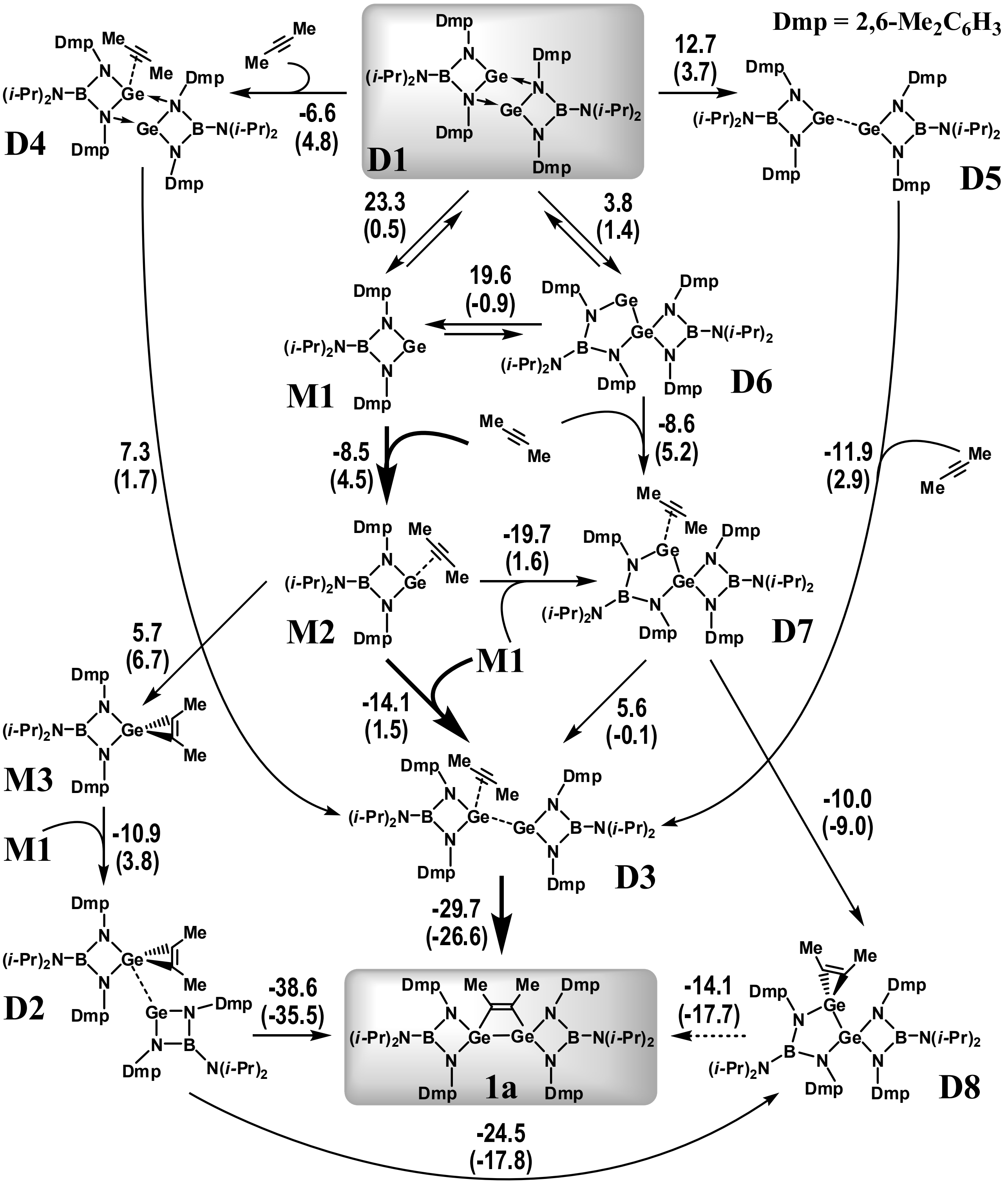
[a] See Scheme 5 (Main Text) and Schemes S1 -S3 (Supporting Information) for the compound notations.

Table S3. Calculated electronic energies E_{el} (a.u.) of the **D7** - **D14** intermediates and their separations ΔE_{el} (kcal mol^{-1}) from the **1a** energy.

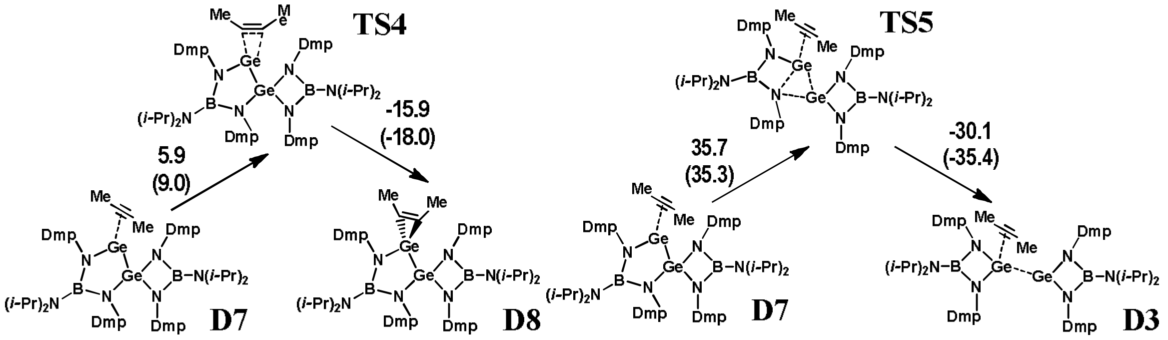
Compound	Structural formula	E_{el}	ΔE_{el}
1a		-6402.06096087	0
D7		-6402.02870354	20.2
D8		-6402.04470540	10.2
D9		-6402.06366861	-1.7
D10		-6402.03862449	14.0
D11		-6402.05455066	4.0
D12		-6402.02640299	21.7
D13		-6402.02487783	22.6



Scheme S1. Theoretical analysis of possible pathways of the interaction between germylene [(*i*-Pr)$_2$NB(N-2,6-Me$_2$C$_6$H$_3$)$_2$]Ge (**M1**) and C$_2$Me$_2$ in C$_6$H$_6$ solution. The calculated changes of the electronic energy Δ*E* and Gibbs free energy Δ*G* (in parentheses) are given in kcal mol^{-1}.The DFT-suggested favourable pathway (**M1**→**M2**→**D3**→**1a**) is shown by the bold arrows.



Scheme S2. Theoretical analysis of possible pathways of the interaction between germylene [(*i*-Pr)$_2$NB(N-2,6-Me$_2$C$_6$H$_3$)$_2$]Ge (**M1**) and C$_2$Me$_2$ in the gas phase. The calculated changes of the electronic energy Δ*E* and Gibbs free energy Δ*G* (in parentheses) are given in kcal mol^{-1}.The DFT-suggested favourable pathway (**M1**→**M2**→**D3**→**1a**) is shown by the bold arrows.



Scheme S3. Calculated activation energies ΔE_a and Gibbs free energies of activation $\Delta^{\ddagger}G$ (in parentheses) for the **D7→D8** (left) **and D7→D3** (right) stages of interaction between germylene [(*i*-Pr)$_2$NB(N-2,6-Me$_2$C$_6$H$_3$)$_2$]Ge (**M1**) and C_2Me_2 in the gas phase. The energy values are given in kcal mol^{-1}.

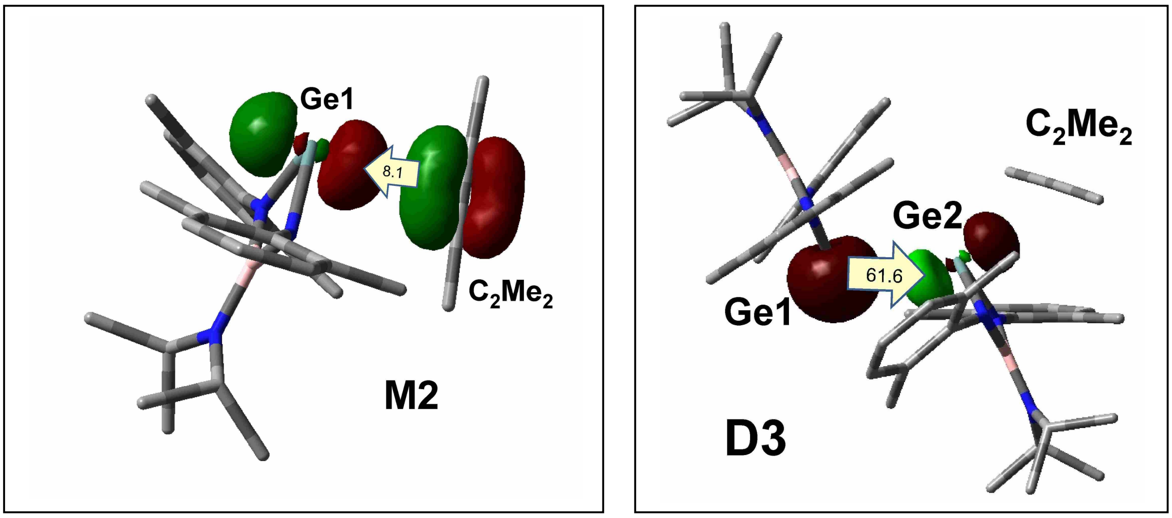


Figure S1: The donor-acceptor interactions responsible for the Ge---C_2Me_2 bonding in **M2** (left) and for Ge-Ge bonding in **D3** (right) revealed by NBO analysis. Hydrogen atoms are omitted for clarity. The NBO isosurfaces correspond to the 0.1 isovalue. For the **D3** molecule, there is also a similar donor-acceptor interaction involving the lone pair of Ge2 and empty p orbital of Ge1. The corresponding energies obtained from the second order perturbation theory analysis of the Fock matrix in the NBO basis (kcalmol^{-1}) are shown on the arrows.

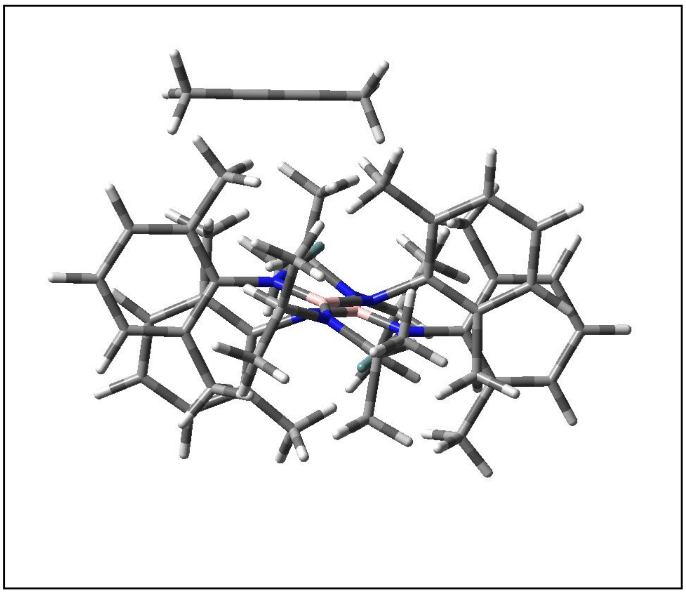


Figure S2: Optimised geometry of molecule**D4** in C_6H_6 solution.

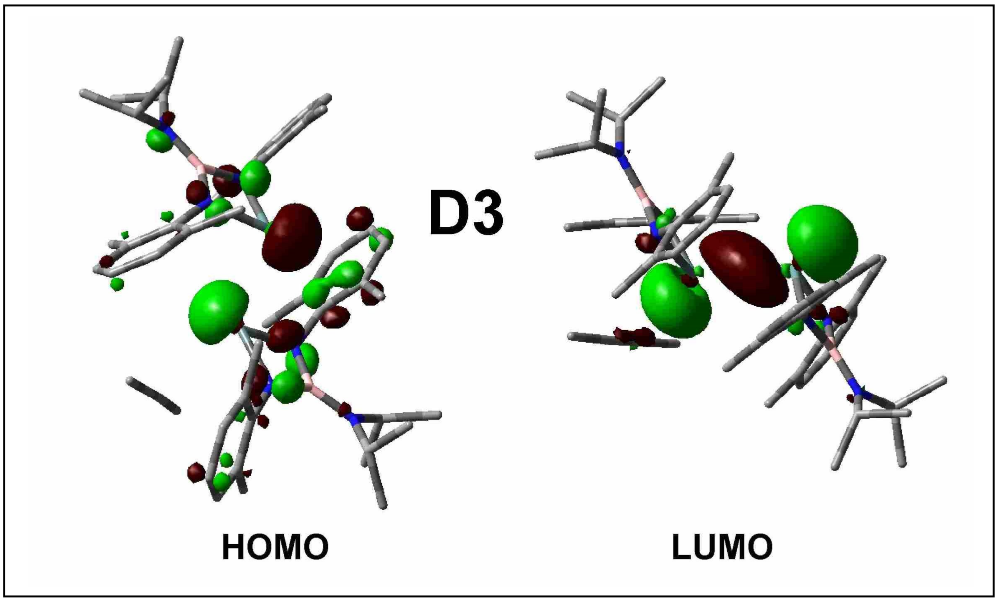


Figure S3. Isosurfaces (isovalue 0.05) of the frontier molecular orbitals of molecule **D3**.Hydrogen atoms are omitted for clarity.

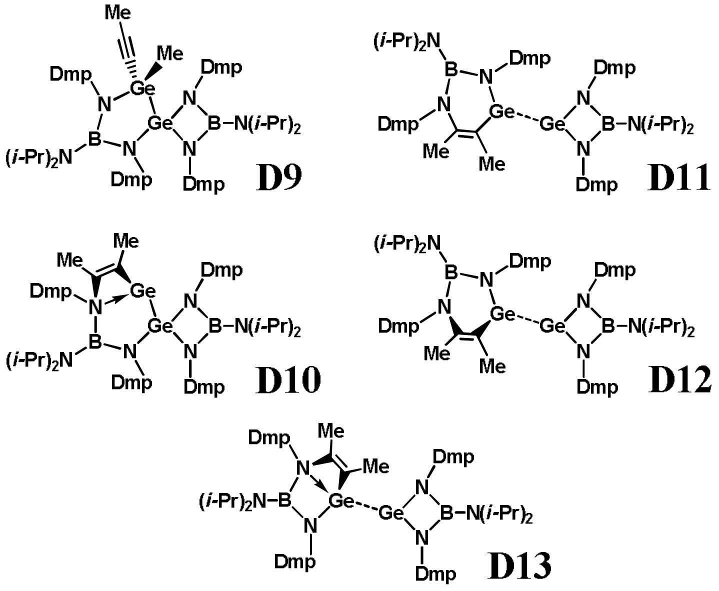


Figure S4. Structures of the **D9 - D13** intermediates identified by the DFT calculations.

Full reference to the Gaussian 09 program package:

M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, 2010.