



Theoretical descriptions of novel triplet germynes $M_1\text{-Ge-}M_2\text{-}M_3$ ($M_1 = \text{H, Li, Na, K}$; $M_2 = \text{Be, Mg, Ca}$; $M_3 = \text{H, F, Cl, Br}$)

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Abstract

In a quest to identify new ground-state triplet germynes, the stabilities (singlet–triplet energy differences, ΔE_{S-T}) of 96 singlet (s) and triplet (t) $M_1\text{-Ge-}M_2\text{-}M_3$ species were compared and contrasted at the B3LYP/6–311++G**, QCISD(T)/6–311++G**, and CCSD(T)/6–311++G** levels of theory ($M_1 = \text{H, Li, Na, K}$; $M_2 = \text{Be, Mg, Ca}$; $M_3 = \text{H, F, Cl, Br}$). Interestingly, F-substituent triplet germynes ($M_3 = \text{F}$) appear to be more stable and linear than the corresponding Cl- or Br-substituent triplet germynes ($M_3 = \text{Cl}$ or Br). Triplets with $M_1 = \text{K}$ (i.e., the K-Ge- $M_2\text{-}M_3$ series) seem to be more stable than the corresponding triplets with $M_1 = \text{H, Li,}$ or Na . This can be attributed to the higher electropositivity of potassium. Triplet species with $M_3 = \text{Cl}$ behave similarly to those with $M_3 = \text{Br}$. Conversely, triplets with $M_3 = \text{H}$ show similar stabilities and linearities to those with $M_3 = \text{F}$. Singlet species of formulae K-Ge-Ca-Cl and K-Ge-Ca-Br form unexpected cyclic structures. Finally, the triplet germynes $M_1\text{-Ge-}M_2\text{-}M_3$ become more stable as the electropositivities of the α -substituents (M_1 and M_2) and the electronegativity of the β -substituent (M_3) increase.

Keywords Triplet germynes · Singlet–triplet energy gaps · Electronegativity · Electropositivity

Introduction

There is a growing interest in organogermanium chemistry [1–13]. Knowledge of the chemistry of organogermynes has significantly improved in recent years due to the critical role of germanium and its organic derivatives in electronics and other applications [14–16]. This rapid development of organogermanium chemistry has led to the increased production and utilization of elemental germanium and its derivatives, which in turn has reduced the prices of those materials [17].

The term “germylene” refers to a neutral species that possesses a divalent germanium atom with six electrons in its valence shell [18]. Germynes are used during the

manufacture of components of nanomaterials and as precursors in the low-temperature synthesis of Ge-rich semiconductors via chemical vapor deposition [1]. Germynes prefer to keep their nonbonding electrons in atomic orbitals with a high percentage of *s* character [19]. Hence, the covalent bonds to the two groups next to the divalent center often have greater *p* character than the corresponding carbene and silylene bonds, which accounts for the smaller bond angles seen in germynes than in carbenes and silylenes [20].

Due to the importance of triplet ground-state germylene radicals in chemical vapor deposition, semiconductor manufacturing, and the photonics and aerospace industries [21], the preparation of these species has become one of the most important topics in modern organogermanium chemistry [19, 22–26]. It is possible to calculate the IR and NMR spectra of these species, although this is beyond the scope of the work presented here. Recently, some studies have suggested that EPR and X-ray crystallography data provide unambiguous evidence for triplet ground states of silylenes and germynes [27, 28].

Aspects such as the electronic effects of different substituents can influence the ΔE_{S-T} (singlet–triplet energy difference) and $\Delta E_{\text{HOMO-LUMO}}$ (HOMO–LUMO energy difference) values of divalent species and hence the sizes of their nonbonding orbitals. It has been reported that electronegative

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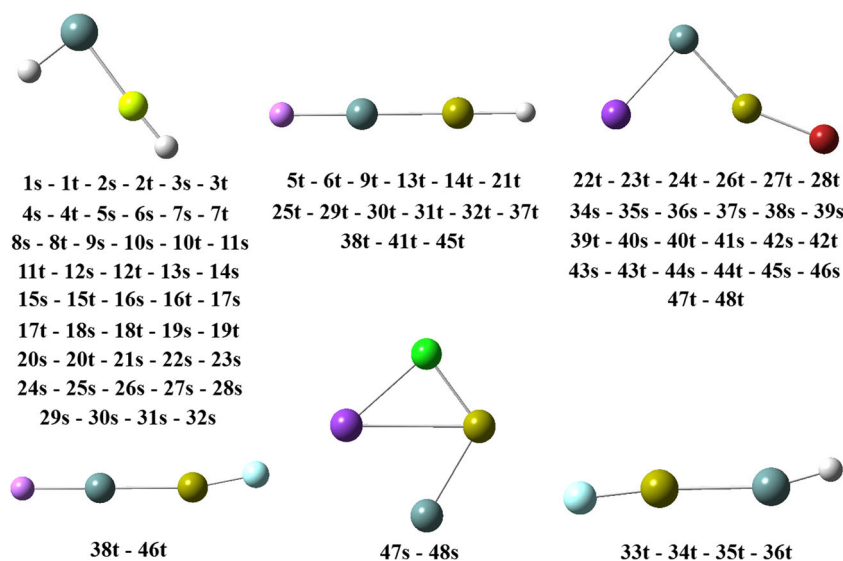
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groups increase ΔE_{S-T} and $\Delta E_{HOMO-LUMO}$, whereas electro-positive ones decrease them [13, 22, 23, 29, 41]. However, it is not possible to swiftly switch germylenes from singlet to triplet states by altering their substituents, in contrast to their carbene analogs [19, 30]. Following our quest for stable triplet germylenes containing two different metal substituents from groups 1 and 2 of the periodic table [32], here we report the results of our theoretical investigation of the singlet (s) and triplet (t) structures of 96 different germylenes divided into four families: H-Ge-M₂-M₃ (I), Li-Ge-M₂-M₃ (II), Na-Ge-M₂-M₃ (III), and K-Ge-M₂-M₃ (IV) (M₂ = Be, Mg, Ca; M₃ = H, F, Cl, Br) (Scheme 1).

Computational methods

Our computational study is confined to B3LYP calculations due to its excellent performance-to-cost ratio as compared with correlated wavefunction theory [31–34]. While some recent reports have questioned the reliability of the most popular density functional, B3LYP [35], we used B3LYP with the 6–311++G** basis set as the method of choice in the present work, in common with many other papers on germylenes [23, 36–40]. Triplet states were calculated using the unrestricted broken spin-symmetry UB3LYP/6–311++G** method implemented in the GAMMES software package [41, 42]. To obtain more accurate data on energetics, single-point calculations were performed at the QCISD(T) and CCSD(T) levels of theory using the 6–311++G** basis set [43]. Frequency calculations were carried out to characterize the resulting structures as minima (the number of imaginary frequencies (NIMAG) = 0) or transition states (NIMAG = 1) [44]. Density functional calculations with the B3LYP functional were implemented to compute the stability of the germylenes through appropriate isodesmic reactions [45].

Scheme 1 Schematic of the germylenes scrutinized in this study



Results and discussion

During our continued search for rare triplet ground-state heavy divalents [19, 20, 22, 23], we compared and contrasted the thermodynamic and geometrical parameters for 96 new germylenes of formula M₁-Ge-M₂-M₃ at the B3LYP/6–311++G**, CCSD(T)/6–311++G**, and QCISD(T)/6–311++G** levels of theory, where M₁ = H, Li, Na, K; M₂ = Be, Mg, Ca; M₃ = H, F, Cl, Br (see Fig. S1 in the “Electronic supplementary material,” ESM). Here we illustrate how bond lengths, bond angles, symmetries, and interatomic interactions vary from one germylene to another, and more specifically from a singlet germylene (**1_s**–**48_s**) to its corresponding triplet state (**1_t**–**48_t**). We compare their relative energies (calculated at three levels of theory) along with their B3LYP/6–311++G**-computed dipole moments (*D*) and their vibrational zero-point energies in Table 1. We show the frontier molecular orbital energies (HOMO and LUMO) for singlet M₁-Ge-M₂-M₃ germylenes along with their band gaps ($\Delta E_{HOMO-LUMO}$) and relative stabilities (ΔE_{S-T}) in Table 2.

We also employed appropriate isodesmic reactions to determine the relative thermal energies for singlet (ΔE_S) and triplet (ΔE_T) germylenes and the thermal energy difference between each singlet and its corresponding triple ($\Delta\Delta E_{S-T}$) at the B3LYP/6–311++G** level (see Table 3). Data for the hydrogenation of germylenes (Scheme 1) along with heats of hydrogenation (ΔH_H) are given for singlet M₁-Ge-M₂-M₃ species in Table 4. Finally, the B3LYP/6–311++G**-calculated natural bond orbitals (NBOs) of the M₁-Ge-M₂-M₃ germylenes are provided in Table 5. Computed harmonic frequencies are omitted here to save space, but they are available upon request. Our force constant calculations show that only **33_s** has one imaginary frequency and exists as a transition state. Among our 96 germylene isomers, only two singlet structures, **47_s** (K-Ge-Ca-Cl) and

Table 1 Thermodynamic parameters for singlet (s) and triplet (t) states of M_1 -Ge- M_2 - M_3 ($M_1 = \text{H, Li, Na, K}$; $M_2 = \text{Be, Mg, Ca}$; $M_3 = \text{H, F, Cl, Br}$) germynes, including relative energies (kcal/mol, calculated at three levels of theory), their B3LYP/6-311++G***-computed dipole moments (D), and their vibrational zero-point energies (kcal/mol)

Germynes	Structures Singlet (s) and triplet (t)	B3LYP/6-311++G***- computed dipole moments (D)	B3LYP/6-311++G***-computed vibrational zero-point energies	Relative energies		
				B3LYP/6- 311++G**	QCISD(T)/6- 311++G**	CCSD(T)/6- 311++G**
1 _s	H-Ge-Be-H (s)	0.18	8.26	0	0	0
1 _t	H-Ge-Be-H (t)	0.56	8.75	4.23	1.68	1.71
2 _s	H-Ge-Be-F (s)	1.13	6.29	0	0	0
2 _t	H-Ge-Be-F (t)	1.19	6.64	9.26	6.21	6.23
3 _s	H-Ge-Be-Cl (s)	0.82	5.59	0	0	0
3 _t	H-Ge-Be-Cl (t)	1.06	5.89	7.90	5.12	5.14
4 _s	H-Ge-Be-Br (s)	0.72	5.31	0	0	0
4 _t	H-Ge-Be-Br (t)	0.98	5.68	7.64	4.90	4.93
5 _s	Li-Ge-Be-H (s)	5.57	5.56	9.11	9.62	9.63
5 _t	Li-Ge-Be-H (t)	7.72	6.03	0	0	0
6 _s	Li-Ge-Be-F (s)	5.90	14.82	8.18	8.40	8.41
6 _t	Li-Ge-Be-F (t)	8.40	15.79	0	0	0
7 _s	Li-Ge-Be-Cl (s)	5.96	12.04	2.48	3.88	3.83
7 _t	Li-Ge-Be-Cl (t)	5.77	11.96	0	0	0
8 _s	Li-Ge-Be-Br (s)	5.96	10.97	2.48	3.83	3.78
8 _t	Li-Ge-Be-Br (t)	5.76	10.94	0	0	0
9 _s	Na-Ge-Be-H (s)	5.70	5.35	5.82	8.45	8.45
9 _t	Na-Ge-Be-H (t)	9.05	5.59	0	0	0
10 _s	Na-Ge-Be-F (s)	6.01	13.55	4.58	7.34	7.34
10 _t	Na-Ge-Be-F (t)	9.61	13.95	0	0	0
11 _s	Na-Ge-Be-Cl (s)	6.16	10.78	0.48	3.59	3.56
11 _t	Na-Ge-Be-Cl (t)	7.07	10.31	0	0	0
12 _s	Na-Ge-Be-Br (s)	6.22	9.71	0.58	3.61	3.57
12 _t	Na-Ge-Be-Br (t)	7.06	9.32	0	0	0
13 _s	K-Ge-Be-H (s)	8.40	5.21	10.15	11.72	11.72
13 _t	K-Ge-Be-H (t)	11.70	5.41	0	0	0
14 _s	K-Ge-Be-F (s)	8.61	13.01	9.58	11.53	11.54
14 _t	K-Ge-Be-F (t)	12.59	13.47	0	0	0
15 _s	K-Ge-Be-Cl (s)	8.86	10.23	6.71	8.76	8.75
15 _t	K-Ge-Be-Cl (t)	9.72	9.78	0	0	0
16 _s	K-Ge-Be-Br (s)	8.95	9.16	7.14	9.65	9.63
16 _t	K-Ge-Be-Br (t)	8.82	8.99	0	0	0
17 _s	H-Ge-Mg-H (s)	0.48	6.63	0	0	0
17 _t	H-Ge-Mg-H (t)	0.55	6.93	2.99	0.53	0.59
18 _s	H-Ge-Mg-F (s)	2.94	4.87	0	0	0
18 _t	H-Ge-Mg-F (t)	1.85	5.13	7.83	3.42	3.43
19 _s	H-Ge-Mg-Cl (s)	3.15	4.50	0	0	0
19 _t	H-Ge-Mg-Cl (t)	1.84	4.72	7.58	3.13	3.14
20 _s	H-Ge-Mg-Br (s)	3.07	4.28	0	0	0
20 _t	H-Ge-Mg-Br (t)	1.65	4.53	7.52	3.18	3.20
21 _s	Li-Ge-Mg-H (s)	5.45	4.08	8.72	9.64	9.66
21 _t	Li-Ge-Mg-H (t)	7.13	4.31	0	0	0
22 _s	Li-Ge-Mg-F (s)	6.76	9.45	2.94	7.91	7.93
22 _t	Li-Ge-Mg-F (t)	1.85	5.13	0	0	0
23 _s	Li-Ge-Mg-Cl (s)	7.10	7.84	2.79	5.12	4.98
23 _t	Li-Ge-Mg-Cl (t)	6.92	7.78	0	0	0
24 _s	Li-Ge-Mg-Br (s)	7.13	7.16	2.77	5.07	4.93
24 _t	Li-Ge-Mg-Br (t)	6.93	7.17	0	0	0
25 _s	Na-Ge-Mg-H (s)	5.50	3.76	6.33	8.69	8.71
25 _t	Na-Ge-Mg-H (t)	8.18	3.79	0	0	0

Table 1 (continued)

Germynes	Structures Singlet (s) and triplet (t)	B3LYP/6-311++G**- computed dipole moments (<i>D</i>)	B3LYP/6-311++G**-computed vibrational zero-point energies	Relative energies		
				B3LYP/6- 311++G**	QCISD(T)/6- 311++G**	CCSD(T)/6- 311++G**
26 _s	Na-Ge-Mg-F (s)	6.92	8.16	1.31	7.24	7.26
26 _t	Na-Ge-Mg-F (t)	1.85	5.13	0	0	0
27 _s	Na-Ge-Mg-Cl (s)	7.31	6.55	1.21	4.93	4.79
27 _t	Na-Ge-Mg-Cl (t)	7.96	6.31	0	0	0
28 _s	Na-Ge-Mg-Br (s)	7.35	5.87	1.21	4.93	4.78
28 _t	Na-Ge-Mg-Br (t)	8.02	5.63	0	0	0
29 _s	K-Ge-Mg-H (s)	8.23	3.62	10.15	11.98	12.01
29 _t	K-Ge-Mg-H (t)	10.90	3.77	0	0	0
30 _s	K-Ge-Mg-F (s)	9.49	7.67	9.46	11.34	11.37
30 _t	K-Ge-Mg-F (t)	14.10	7.98	0	0	0
31 _s	K-Ge-Mg-Cl (s)	9.92	6.04	9.44	11.30	11.34
31 _t	K-Ge-Mg-Cl (t)	14.75	6.25	0	0	0
32 _s	K-Ge-Mg-Br (s)	9.94	5.35	9.40	11.20	11.24
32 _t	K-Ge-Mg-Br (t)	14.87	5.54	0	0	0
33 _s	H-Ge-Ca-H (s)	-	-	-	-	-
33 _t	H-Ge-Ca-H (t)	1.08	5.50	-	-	-
34 _s	H-Ge-Ca-F (s)	2.85	4.39	4.75	7.66	7.65
34 _t	H-Ge-Ca-F (t)	0.80	4.37	0	0	0
35 _s	H-Ge-Ca-Cl (s)	4.11	3.98	0	0	0
35 _t	H-Ge-Ca-Cl (t)	1.75	3.18	13.64	11.41	11.45
36 _s	H-Ge-Ca-Br (s)	3.06	3.87	0	0	0
36 _t	H-Ge-Ca-Br (t)	1.46	3.05	12.17	11.29	11.34
37 _s	Li-Ge-Ca-H (s)	5.84	2.96	11.42	11.54	11.59
37 _t	Li-Ge-Ca-H (t)	6.00	3.01	0	0	0
38 _s	Li-Ge-Ca-F (s)	5.27	7.81	10.48	11.25	11.30
38 _t	Li-Ge-Ca-F (t)	6.55	7.77	0	0	0
39 _s	Li-Ge-Ca-Cl (s)	5.75	6.21	4.69	6.44	6.48
39 _t	Li-Ge-Ca-Cl (t)	5.81	6.17	0	0	0
40 _s	Li-Ge-Ca-Br (s)	6.23	5.66	4.66	6.05	6.11
40 _t	Li-Ge-Ca-Br (t)	5.67	5.51	0	0	0
41 _s	Na-Ge-Ca-H (s)	6.20	2.68	10.39	11.25	11.30
41 _t	Na-Ge-Ca-H (t)	4.17	2.67	0	0	0
42 _s	Na-Ge-Ca-F (s)	5.80	6.55	5.08	8.73	8.75
42 _t	Na-Ge-Ca-F (t)	5.75	6.20	0	0	0
43 _s	Na-Ge-Ca-Cl (s)	6.62	4.88	4.97	8.57	8.56
43 _t	Na-Ge-Ca-Cl (t)	6.35	4.72	0	0	0
44 _s	Na-Ge-Ca-Br (s)	6.35	4.35	4.97	8.53	8.52
44 _t	Na-Ge-Ca-Br (t)	6.53	4.22	0	0	0
45 _s	K-Ge-Ca-H (s)	9.06	2.50	12.74	13.46	13.53
45 _t	K-Ge-Ca-H (t)	9.60	2.47	0	0	0
46 _s	K-Ge-Ca-F (s)	8.04	6.05	11.93	13.60	13.69
46 _t	K-Ge-Ca-F (t)	10.26	5.76	0	0	0
47 _s	K-Ge-Ca-Cl (s)	3.70	5.12	7.24	8.22	8.30
47 _t	K-Ge-Ca-Cl (t)	12.34	4.48	0	0	0
48 _s	K-Ge-Ca-Br (s)	3.33	4.45	2.08	6.89	6.93
48 _t	K-Ge-Ca-Br (t)	11.52	3.70	0	0	0

48_s (K-Ge-Ca-Br), undergo rearrangement upon optimization, forming rather long linkages from K to Ca (3.88 Å and 3.92 Å, respectively) and transforming into cyclic structures (Fig. S1 in the ESM).

This phenomenon is consistent with the convergence reported for XGeCBr₃ and XGeCCl₃ molecules (X = H, F, Cl, Br, I) to unexpected structures when the same DFT functionals were used [45].

Table 2 Frontier molecular orbital energies (HOMO and LUMO in eV) for singlet M_1 -Ge- M_2 - M_3 germylenes ($M_1 = \text{H, Li, Na, K}$; $M_2 = \text{Be, Mg, Ca}$; $M_3 = \text{H, F, Cl, Br}$) along with their $\Delta E_{\text{HOMO-LUMO}}$ (eV) and $\Delta E_{\text{S-T}}$ (kcal/mol) values calculated at the B3LYP/6-311++G** level

Germylenes	Structures	$\Delta E_{\text{S-T}}$	HOMO	LUMO	$\Delta E_{\text{HOMO-LUMO}}$
1 _s	H-Ge-Be-H (s)	4.23	-3.66	-5.96	-2.29
2 _s	H-Ge-Be-F (s)	9.26	-3.78	-6.37	-2.21
3 _s	H-Ge-Be-Cl (s)	7.90	-3.78	-6.31	-2.52
4 _s	H-Ge-Be-Br (s)	7.64	-3.79	-6.29	-2.50
5 _s	Li-Ge-Be-H (s)	-9.11	-4.65	-3.12	1.52
6 _s	Li-Ge-Be-F (s)	-8.18	-4.68	-3.15	1.52
7 _s	Li-Ge-Be-Cl (s)	-2.48	-4.73	-3.21	1.52
8 _s	Li-Ge-Be-Br (s)	-2.48	-4.76	-3.26	1.49
9 _s	Na-Ge-Be-H (s)	-5.82	-4.48	-3.04	1.44
10 _s	Na-Ge-Be-F (s)	-4.58	-4.51	-3.07	1.44
11 _s	Na-Ge-Be-Cl (s)	-0.48	-4.57	-3.12	1.44
12 _s	Na-Ge-Be-Br (s)	-0.58	-4.59	-3.15	1.44
13 _s	K-Ge-Be-H (s)	-10.15	-3.86	-2.66	1.19
14 _s	K-Ge-Be-F (s)	-9.58	-3.89	-2.69	1.19
15 _s	K-Ge-Be-Cl (s)	-6.71	-3.94	-2.75	1.19
16 _s	K-Ge-Be-Br (s)	-7.14	-3.97	-2.80	1.17
17 _s	H-Ge-Mg-H (s)	2.99	-3.47	-5.38	-1.91
18 _s	H-Ge-Mg-F (s)	7.83	-3.84	-6.06	-2.21
19 _s	H-Ge-Mg-Cl (s)	7.58	-3.88	-6.07	-2.19
20 _s	H-Ge-Mg-Br (s)	7.52	-3.87	-6.04	-2.16
21 _s	Li-Ge-Mg-H (s)	-8.72	-4.51	-3.02	1.49
22 _s	Li-Ge-Mg-F (s)	-2.94	-4.78	-3.29	1.49
23 _s	Li-Ge-Mg-Cl (s)	-2.79	-4.84	-3.34	1.49
24 _s	Li-Ge-Mg-Br (s)	-2.77	-4.84	-3.34	1.49
25 _s	Na-Ge-Mg-H (s)	-6.33	-4.38	-2.96	1.41
26 _s	Na-Ge-Mg-F (s)	-1.31	-4.62	-3.21	1.41
27 _s	Na-Ge-Mg-Cl (s)	-1.21	-4.68	-3.26	1.41
28 _s	Na-Ge-Mg-Br (s)	-1.21	-4.70	-3.26	1.44
29 _s	K-Ge-Mg-H (s)	-10.15	-3.80	-2.64	1.17
30 _s	K-Ge-Mg-F (s)	-9.46	-3.99	-2.82	1.17
31 _s	K-Ge-Mg-Cl (s)	-9.44	-4.08	-2.91	1.17
32 _s	K-Ge-Mg-Br (s)	-9.40	-4.08	-2.91	1.17
33 _s	H-Ge-Ca-H (s)	-	-	-	-
34 _s	H-Ge-Ca-F (s)	-4.75	-3.21	-4.76	-1.54
35 _s	H-Ge-Ca-Cl (s)	13.64	-3.38	-4.96	-1.58
36 _s	H-Ge-Ca-Br (s)	12.17	-3.42	-4.99	-1.56
37 _s	Li-Ge-Ca-H (s)	-11.42	-4.21	-2.91	1.30
38 _s	Li-Ge-Ca-F (s)	-10.48	-4.35	-2.91	1.44
39 _s	Li-Ge-Ca-Cl (s)	-4.69	-4.54	-3.10	1.44
40 _s	Li-Ge-Ca-Br (s)	-4.66	-4.59	-3.12	1.46
41 _s	Na-Ge-Ca-H (s)	-10.39	-4.16	-2.83	1.33
42 _s	Na-Ge-Ca-F (s)	-5.08	-4.27	-2.85	1.41
43 _s	Na-Ge-Ca-Cl (s)	-4.97	-4.43	-3.02	1.41
44 _s	Na-Ge-Ca-Br (s)	-4.97	-4.46	-3.04	1.41
45 _s	K-Ge-Ca-H (s)	-12.74	-3.70	-2.55	1.14
46 _s	K-Ge-Ca-F (s)	-11.93	-3.72	-2.55	1.17
47 _s	K-Ge-Ca-Cl (s)	-7.24	-3.48	-2.44	1.03
48 _s	K-Ge-Ca-Br (s)	-2.08	-3.53	-2.50	1.03

To ensure that the cyclized structures **47_s** and **48_s** are not artifacts of the particular level of computation and basis set used, they were optimized at two levels of theory (see Table S1 in the ESM). Consequently, the relative stabilities of our 96 novel germylenes were compared and contrasted at the B3LYP/6-311++G**, CCSD(T)/6-311++G**, and QCISD(T)/6-311++G** levels of theory. The trends in the singlet-triplet energy gaps computed using the high-level QCISD(T) and CCSD(T) single-point energies are similar to that computed using the B3LYP-optimized energy. For example, the structures with $M_1 = \text{Li}$ can be ordered according to their singlet-triplet energy gaps calculated at the B3LYP/6-

311++G**, QCISD(T)/6-311++G**, and CCSD(T)/6-311++G** levels of theory (respectively) as follows: $\Delta E_{\text{S-T}}^{(5)}$ (-9.11, -9.62, -9.63 kcal/mol) > $\Delta E_{\text{S-T}}^{(6)}$ (-8.18, -8.40, -8.41 kcal/mol) > $\Delta E_{\text{S-T}}^{(7)}$ (-2.48, -3.88, -3.83 kcal/mol).

The B3LYP/6-311++G** results as well as those gained using QCISD(T)/6-311++G** show that structures with $M_1 = \text{H}$ have a stable singlet ground state (except for **34**). Although a more electronegative substituent is generally considered to stabilize singlet states more than their corresponding triplet states, we actually find here that $M_3 = \text{F}$ leads to more stable triplets than those obtained when $M_3 = \text{Cl}$ or Br . Natural bond orbital (NBO) analysis shows that among all the

Table 3 Isodesmic reactions showing the relative thermal energies of singlet (ΔE_S) and triplet (ΔE_T) germylenes M_1 -Ge- M_2 - M_3 , ($M_1 = H, Li, Na, K$; $M_2 = Be, Mg, Ca$; $M_3 = H, F, Cl, Br$) as well as the ΔE_{S-T} values for the germylenes, all in kcal/mol and calculated at the B3LYP/6-311++G** level

Numbers	Isodesmic reactions	Germylenes	Structures	Relative thermal energies		
				ΔE_S^a	ΔE_S^b	$\Delta \Delta E_{S-T}^c$
		1	H-Ge-Be-H	-	-	-
1		2	H-Ge-Be-F	1.3	13.4	12.1
		3	H-Ge-Be-Cl	1.2	15.7	14.5
		4	H-Ge-Be-Br	1.3	15.7	14.4
2		5	Li-Ge-Be-H	10.3	-21.4	-31.7
		6	Li-Ge-Be-F	10.3	-21.4	-31.7
		7	Li-Ge-Be-Cl	9.5	-22.5	-32.0
		8	Li-Ge-Be-Br	9.0	-22.9	-31.9
3		9	Na-Ge-Be-H	10.7	-1.7	-12.4
		10	Na-Ge-Be-F	9.6	3.4	-6.2
		11	Na-Ge-Be-Cl	9.1	24.8	15.7
		12	Na-Ge-Be-Br	10.7	-1.7	-12.4
4		13	K-Ge-Be-H	10.7	-1.7	-12.4
		14	K-Ge-Be-F	9.6	3.4	-6.2
		15	K-Ge-Be-Cl	9.1	24.8	15.7
		16	K-Ge-Be-Br	10.7	-1.7	-12.4
5		17	H-Ge-Mg-H	-	-	-
		18	H-Ge-Mg-F	2.6	0.9	-1.7
		19	H-Ge-Mg-Cl	2.6	3.2	0.6
		20	H-Ge-Mg-Br	2.7	2.8	0.1
6		21	Li-Ge-Mg-H	8.8	-22.6	-31.4
		22	Li-Ge-Mg-F	8.8	-22.6	-31.4
		23	Li-Ge-Mg-Cl	8.7	-3.2	-11.9
		24	Li-Ge-Mg-Br	8.7	-23.6	-32.3

^a Singlet germylenes are employed in both sides of the isodesmic reactions

^b Triplet germylenes are employed in both sides of the isodesmic reactions

^c $\Delta \Delta E_{S-T} = \Delta E_S - \Delta E_T$

7		25	Na-Ge-Mg-H	8.6	-24.7	-33.3
		26	Na-Ge-Mg-F	8.6	-24.7	-33.3
		27	Na-Ge-Mg-Cl	8.5	-17.4	-25.9
		28	Na-Ge-Mg-Br	8.4	-19.1	-27.5
8		29	K-Ge-Mg-H	8.8	2.1	-6.7
		30	K-Ge-Mg-F	8.8	2.1	-6.7
		31	K-Ge-Mg-Cl	8.7	17.4	8.7
		32	K-Ge-Mg-Br	8.6	15.1	6.5
9		33	H-Ge-Ca-H	-	-	-
		34	H-Ge-Ca-F	-	10.1	10.1
		35	H-Ge-Ca-Cl	-	-6.2	-6.2
		36	H-Ge-Ca-Br	-	-4.4	-4.4
10		37	Li-Ge-Ca-H	7.6	-31.2	-38.8
		38	Li-Ge-Ca-F	6.2	-21.1	-27.3
		39	Li-Ge-Ca-Cl	7.4	-21.1	-28.5
		40	Li-Ge-Ca-Br	7.6	-31.2	-38.8
11		41	Na-Ge-Ca-H	16.0	-4.4	-20.4
		42	Na-Ge-Ca-F	7.8	-14.0	-21.8
		43	Na-Ge-Ca-Cl	15.8	-4.3	-20.1
		44	Na-Ge-Ca-Br	16.0	-4.4	-20.4
12		45	K-Ge-Ca-H	2.8	9.7	6.9
		46	K-Ge-Ca-F	5.9	3.2	-2.7
		47	K-Ge-Ca-Cl	2.0	4.1	2.1
		48	K-Ge-Ca-Br	2.8	9.7	6.9

Table 4 Heats of hydrogenation (ΔH_H^a) for singlet M_1 -Ge- M_2 - M_3 ($M_1 = H, Li, Na, K$; $M_2 = Be, Mg, Ca$; $M_3 = H, F, Cl, Br$) in kcal/mol, as calculated at the B3LYP/6-311++G** level

Germlylenes	Structures	ΔH_H^a
1 _s	H-Ge-Be-H (s)	-40.72
2 _s	H-Ge-Be-F (s)	-41.82
3 _s	H-Ge-Be-Cl (s)	-40.97
4 _s	H-Ge-Be-Br (s)	-47.22
5 _s	Li-Ge-Be-H (s)	-39.58
6 _s	Li-Ge-Be-F (s)	-40.41
7 _s	Li-Ge-Be-Cl (s)	-39.66
8 _s	Li-Ge-Be-Br (s)	-40.72
9 _s	Na-Ge-Be-H (s)	-41.15
10 _s	Na-Ge-Be-F (s)	-42.61
11 _s	Na-Ge-Be-Cl (s)	-42.50
12 _s	Na-Ge-Be-Br (s)	-50.30
13 _s	K-Ge-Be-H (s)	27.61
14 _s	K-Ge-Be-F (s)	27.61
15 _s	K-Ge-Be-Cl (s)	27.61
16 _s	K-Ge-Be-Br (s)	26.98
17 _s	H-Ge-Mg-H (s)	-41.38
18 _s	H-Ge-Mg-F (s)	-40.89
19 _s	H-Ge-Mg-Cl (s)	-40.92
20 _s	H-Ge-Mg-Br (s)	-48.31
21 _s	Li-Ge-Mg-H (s)	-40.29
22 _s	Li-Ge-Mg-F (s)	-39.61
23 _s	Li-Ge-Mg-Cl (s)	-39.61
24 _s	Li-Ge-Mg-Br (s)	-49.18
25 _s	Na-Ge-Mg-H (s)	-42.70
26 _s	Na-Ge-Mg-F (s)	-41.52
27 _s	Na-Ge-Mg-Cl (s)	-42.40
28 _s	Na-Ge-Mg-Br (s)	-46.23
29 _s	K-Ge-Mg-H (s)	26.98
30 _s	K-Ge-Mg-F (s)	26.98
31 _s	K-Ge-Mg-Cl (s)	26.98
32 _s	K-Ge-Mg-Br (s)	26.98
33 _s	H-Ge-Ca-H (s)	-49.26
34 _s	H-Ge-Ca-F (s)	-40.40
35 _s	H-Ge-Ca-Cl (s)	-40.84
36 _s	H-Ge-Ca-Br (s)	-48.47
37 _s	Li-Ge-Ca-H (s)	-41.70
38 _s	Li-Ge-Ca-F (s)	-39.17
39 _s	Li-Ge-Ca-Cl (s)	-39.51
40 _s	Li-Ge-Ca-Br (s)	-49.35
41 _s	Na-Ge-Ca-H (s)	-52.34
42 _s	Na-Ge-Ca-F (s)	-40.99
43 _s	Na-Ge-Ca-Cl (s)	-42.30
44 _s	Na-Ge-Ca-Br (s)	-46.98
45 _s	K-Ge-Ca-H (s)	26.35
46 _s	K-Ge-Ca-F (s)	26.98
47 _s	K-Ge-Ca-Cl (s)	23.84
48 _s	K-Ge-Ca-Br (s)	23.84

^a Calculated via $M_1 G^+ e^- M_2 M_3 + H_2 \rightarrow M_1 GeH_2 M_2 M_3$

germylenes investigated here, only **34_t** presents a $LP_F \rightarrow \sigma^*_{Ge-H}$ interaction, which stabilizes its triplet state (Table 1). The main difference between **34_t**, **35_t**, and **36_t** is their H-Ge-Ca angles (Fig. S1 in the ESM). In **34_t** (with $M_3 = F$), the H-Ge-Ca angle is smaller than the corresponding angles in **35_t** and **36_t** (with $M_3 = Cl$ and Br , respectively), which increases the probability of a $LP_F \rightarrow \sigma^*_{Ge-H}$ interaction.

Ordering the structures with $M_1 = Li$ according to their B3LYP/6-311++G**^a-calculated and QCISD(T)/6-311++

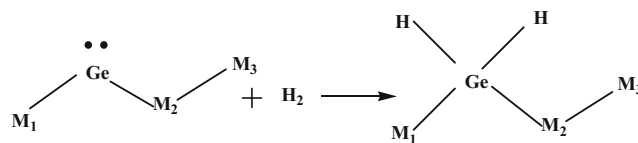
Table 5 The B3LYP/6-311++G**^a-calculated NBO atomic charges on M_1 -Ge- M_2 - M_3 ($M_1 = H, Li, Na, K$; $M_2 = Be, Mg, Ca$; $M_3 = H, F, Cl, Br$) germlylenes

Germlylenes	Structures	M_1	Ge	M_2	M_3
1 _s	H-Ge-Be-H (s)	-0.25	0.14	0.56	-0.45
1 _t	H-Ge-Be-H (t)	-0.15	-0.01	0.59	-0.42
2 _s	H-Ge-Be-F (s)	0.16	-0.25	0.79	-0.70
2 _t	H-Ge-Be-F (t)	-0.63	-0.15	-0.90	-0.69
3 _s	H-Ge-Be-Cl (s)	0.21	-0.25	0.50	-0.46
3 _t	H-Ge-Be-Cl (t)	0.03	-0.15	0.55	-0.43
4 _s	H-Ge-Be-Br (s)	0.21	-0.24	0.43	-0.39
4 _t	H-Ge-Be-Br (t)	0.05	-0.15	0.46	-0.36
5 _s	Li-Ge-Be-H (s)	0.39	-0.12	0.11	-0.38
5 _t	Li-Ge-Be-H (t)	0.66	-0.45	0.17	-0.38
6 _s	Li-Ge-Be-F (s)	-0.12	0.39	0.11	-0.38
6 _t	Li-Ge-Be-F (t)	-0.45	0.66	0.17	-0.38
7 _s	Li-Ge-Be-Cl (s)	0.05	0.40	-0.09	-0.36
7 _t	Li-Ge-Be-Cl (t)	-0.10	0.57	-0.11	-0.35
8 _s	Li-Ge-Be-Br (s)	0.02	0.40	-0.19	-0.24
8 _t	Li-Ge-Be-Br (t)	-0.13	0.58	-0.20	-0.23
9 _s	Na-Ge-Be-H (s)	0.35	-0.07	0.11	-0.38
9 _t	Na-Ge-Be-H (t)	0.52	-0.34	0.20	-0.38
10 _s	Na-Ge-Be-F (s)	-0.07	0.35	0.11	-0.38
10 _t	Na-Ge-Be-F (t)	-0.34	0.52	0.20	-0.38
11 _s	Na-Ge-Be-Cl (s)	0.11	0.36	-0.09	-0.37
11 _t	Na-Ge-Be-Cl (t)	-0.04	0.57	-0.15	-0.37
12 _s	Na-Ge-Be-Br (s)	-0.07	0.36	-0.17	-0.26
12 _t	Na-Ge-Be-Br (t)	-0.09	0.58	-0.22	-0.26
13 _s	K-Ge-Be-H (s)	0.60	-0.30	0.09	-0.39
13 _t	K-Ge-Be-H (t)	0.72	-0.55	0.21	-0.39
14 _s	K-Ge-Be-F (s)	-0.30	0.60	0.09	-0.39
14 _t	K-Ge-Be-F (t)	-0.55	0.72	0.21	-0.39
15 _s	K-Ge-Be-Cl (s)	-0.11	0.60	-0.08	-0.40
15 _t	K-Ge-Be-Cl (t)	-0.25	0.73	0.15	-0.32
16 _s	K-Ge-Be-Br (s)	-0.18	0.60	-0.12	-0.29
16 _t	K-Ge-Be-Br (t)	-0.30	0.72	-0.25	-0.16
17 _s	H-Ge-Mg-H (s)	-0.27	0.02	0.83	-0.58
17 _t	H-Ge-Mg-H (t)	-0.18	-0.24	0.98	-0.55
18 _s	H-Ge-Mg-F (s)	0.03	-0.27	1.10	-0.86
18 _t	H-Ge-Mg-F (t)	-0.28	-0.17	1.31	-0.86
19 _s	H-Ge-Mg-Cl (s)	0.09	-0.27	0.89	-0.72
19 _t	H-Ge-Mg-Cl (t)	-0.21	-0.17	1.08	-0.69
20 _s	H-Ge-Mg-Br (s)	0.11	-0.27	0.83	-0.66
20 _t	H-Ge-Mg-Br (t)	-0.20	-0.17	1.01	-0.63
21 _s	Li-Ge-Mg-H (s)	0.34	-0.19	0.42	-0.58
21 _t	Li-Ge-Mg-H (t)	0.61	-0.62	0.58	-0.57
22 _s	Li-Ge-Mg-F (s)	-0.19	0.34	0.42	-0.58
22 _t	Li-Ge-Mg-F (t)	-0.62	0.61	0.58	-0.57
23 _s	Li-Ge-Mg-Cl (s)	-0.19	0.36	0.08	-0.24
23 _t	Li-Ge-Mg-Cl (t)	-0.36	0.51	0.09	-0.24
24 _s	Li-Ge-Mg-Br (s)	-0.18	0.36	0.13	-0.30
24 _t	Li-Ge-Mg-Br (t)	-0.35	0.51	0.14	-0.30
25 _s	Na-Ge-Mg-H (s)	0.34	-0.15	0.39	-0.58
25 _t	Na-Ge-Mg-H (t)	0.56	-0.57	0.57	-0.56
26 _s	Na-Ge-Mg-F (s)	-0.15	0.34	0.39	-0.58
26 _t	Na-Ge-Mg-F (t)	-0.57	0.56	0.57	-0.56
27 _s	Na-Ge-Mg-Cl (s)	-0.13	0.35	0.03	-0.24
27 _t	Na-Ge-Mg-Cl (t)	-0.24	0.54	-0.04	-0.25
28 _s	Na-Ge-Mg-Br (s)	-0.10	0.35	0.06	-0.31
28 _t	Na-Ge-Mg-Br (t)	-0.21	0.54	0.00	-0.33
29 _s	K-Ge-Mg-H (s)	0.63	-0.36	0.31	-0.58
29 _t	K-Ge-Mg-H (t)	0.78	-0.80	0.57	-0.55
30 _s	K-Ge-Mg-F (s)	-0.36	0.63	0.31	-0.58
30 _t	K-Ge-Mg-F (t)	-0.80	0.78	0.57	-0.55
31 _s	K-Ge-Mg-Cl (s)	-0.30	0.65	-0.09	-0.26
31 _t	K-Ge-Mg-Cl (t)	-0.81	0.76	0.26	-0.21
32 _s	K-Ge-Mg-Br (s)	-0.24	0.65	-0.07	-0.32

Table 5 (continued)

Germynes	Structures	M ₁	Ge	M ₂	M ₃
32 _t	K-Ge-Mg-Br (t)	-0.78	0.80	0.29	-0.32
33 _s	H-Ge-Ca-H (s)	-	-	-	-
33 _t	H-Ge-Ca-H (t)	-0.18	-0.48	1.38	-0.71
34 _s	H-Ge-Ca-F (s)	-0.15	-0.29	1.29	-0.85
34 _t	H-Ge-Ca-F (t)	-0.53	-0.18	1.56	-0.84
35 _s	H-Ge-Ca-Cl (s)	-0.10	-0.29	1.18	-0.78
35 _t	H-Ge-Ca-Cl (t)	-0.05	-0.61	1.37	-0.70
36 _s	H-Ge-Ca-Br (s)	-0.10	-0.29	1.16	-0.76
36 _t	H-Ge-Ca-Br (t)	-0.10	-0.55	1.35	-0.69
37 _s	Li-Ge-Ca-H (s)	0.17	-0.34	0.94	-0.77
37 _t	Li-Ge-Ca-H (t)	0.42	-0.63	0.97	-0.77
38 _s	Li-Ge-Ca-F (s)	-0.34	0.17	0.94	-0.77
38 _t	Li-Ge-Be-F (t)	-0.45	0.66	0.17	-0.38
39 _s	Li-Ge-Ca-Cl (s)	-0.36	0.20	0.72	-0.56
39 _t	Li-Ge-Ca-Cl (t)	-0.44	0.17	0.84	-0.57
40 _s	Li-Ge-Ca-Br (s)	-0.36	0.19	0.75	-0.58
40 _t	Li-Ge-Ca-Br (t)	-0.46	0.19	0.86	-0.58
41 _s	Na-Ge-Ca-H (s)	0.16	-0.28	0.89	-0.77
41 _t	Na-Ge-Ca-H (t)	0.16	-0.40	1.02	-0.77
42 _s	Na-Ge-Ca-F (s)	-0.28	0.16	0.89	-0.77
42 _t	Na-Ge-Ca-F (t)	-0.40	0.16	1.02	-0.77
43 _s	Na-Ge-Ca-Cl (s)	-0.30	0.18	0.68	-0.57
43 _t	Na-Ge-Ca-Cl (t)	-0.37	0.14	0.81	-0.58
44 _s	Na-Ge-Ca-Br (s)	-0.33	0.19	0.72	-0.58
44 _t	Na-Ge-Ca-Br (t)	-0.38	0.15	0.81	-0.59
45 _s	K-Ge-Ca-H (s)	0.55	0.33	0.79	-0.77
45 _t	K-Ge-Ca-H (t)	0.65	-0.88	1.00	-0.78
46 _s	K-Ge-Ca-F (s)	0.33	0.55	0.79	-0.77
46 _t	K-Ge-Ca-F (t)	-0.88	0.65	1.00	-0.78
47 _s	K-Ge-Ca-Cl (s)	-0.41	0.54	0.22	-0.35
47 _t	K-Ge-Ca-Cl (t)	-0.87	0.62	0.82	-0.57
48 _s	K-Ge-Ca-Br (s)	-0.41	0.49	0.25	-0.32
48 _t	K-Ge-Ca-Br (t)	-0.47	0.70	0.35	-0.58

G^{**}-calculated singlet–triplet energy gaps yields ΔE_{S-T} (5) (-9.11, -9.62 kcal/mol) > ΔE_{S-T} (6) (-8.18, -8.40 kcal/mol) > ΔE_{S-T} (7) (-2.48, -3.88 kcal/mol) > ΔE_{S-T} (8) (-2.48, -3.83 kcal/mol); ΔE_{S-T} (21) (-8.72, -9.64 kcal/mol) > ΔE_{S-T} (22) (-2.94, -7.91 kcal/mol) > ΔE_{S-T} (23) (-2.79, -5.12 kcal/mol) > ΔE_{S-T} (24) (-2.77, -5.07 kcal/mol); and ΔE_{S-T} (37) (-11.42, -11.54 kcal/mol) > ΔE_{S-T} (38) (-10.48, -11.25 kcal/mol) > ΔE_{S-T} (39) (-4.69, -6.44 kcal/mol) > ΔE_{S-T} (40) (-4.66, -6.05 kcal/mol). Evidently, the structures with the most electronegative substituents have the smallest singlet–triplet energy gaps. This may be because the presence of F or H rather than Cl or Br at M₂ (LP_{F, H} → σ*_{Ge-M2}) leads to stronger hyperconjugation. We know that F⁻ is a better base than Cl⁻ and Br⁻. Clearly, the presence of a fluorine substituent destabilizes σ orbitals at M₂, meaning that triplets with fluorine substituents are more stable than triplets with chlorine and bromine substituents. In other words, all the odds are stacked in favor of the existence of triplet germynes. Apparently, in structures with M₁ = Na, the presence of fluorine has an extraordinary effect on ΔE_{S-T} (26), which may be due to the substantial difference in orbital size between Na and Mg. On the other hand, Na and Mg are in the

**Scheme 2** Hydrogenation of germynes of formula M₁-Ge-M₂-M₃ (M₁ = H, Li, Na, K; M₂ = Be, Mg, Ca; M₃ = H, F, Cl, Br)

same period, and their ionic radii are fairly similar (Na⁺ = 1.16 Å, Mg²⁺ = 0.85 Å) [46], which may explain the stability of ΔE_{S-T} (6). Clearly, the compounds with the most electropositive M₁ substituent (i.e., K, rather than H, Li, or Na) have the most stable triplets. The singlet–triplet energy gaps for the K-Ge-M₂-M₃ germynes, calculated at the B3LYP/6-311++G^{**} and QCISD(T)/6-311++G^{**} levels of theory, can be ordered as follows: ΔE_{S-T} (13) (-10.15, -11.72 kcal/mol) > ΔE_{S-T} (14) (-9.58, -11.53 kcal/mol) > ΔE_{S-T} (16) (-7.14, -9.65 kcal/mol) > ΔE_{S-T} (15) (-6.71, -8.76 kcal/mol); ΔE_{S-T} (29) (-10.15, -11.98 kcal/mol) > ΔE_{S-T} (30) (-9.46, -11.34 kcal/mol) > ΔE_{S-T} (31) (-9.44, -11.30 kcal/mol) > ΔE_{S-T} (32) (-9.40, -11.20 kcal/mol); and ΔE_{S-T} (45) (-12.74, -13.46 kcal/mol) > ΔE_{S-T} (46) (-11.93, -13.60 kcal/mol) > ΔE_{S-T} (47) (-7.24, -8.22 kcal/mol) > ΔE_{S-T} (48) (-2.08, -6.89 kcal/mol). The stabilities of **38_t**, **42_t**, and **46_t** compared to their corresponding singlet states can be explained by the electropositivity of the substituted divalent Ge atom with M₃ = Ca.

When comparing germynes with different β-substituents, the four structures **45** (-12.74 kcal/mol), **46** (-11.93 kcal/mol), **31** (-9.44 kcal/mol), and **32** (-9.40 kcal/mol) are found to possess higher triplet stabilities than the other structures. This can be attributed to the high electropositivity of potassium.

The LUMO–HOMO energy gap ($\Delta E_{HOMO-LUMO}$) varies as a function of M₃ as follows: F ≥ H ≥ Cl ≥ Br (see Table 2). This trend demonstrates that singlet germynes become increasingly stable as the electronegativity of the halogen atom increases. In addition, inspection of the calculated $\Delta E_{HOMO-LUMO}$ values for all of the singlet germynes seems to suggest that the value of this parameter is dictated by the size of the angle formed by the two substituents bound to the central germanium atom. The magnitude of this bond angle is also one of the main influences on the value of ΔE_{S-T} [45]. Except for two triplets, the Li–Ge–M₂ angles of corresponding singlets and triplets show negligible variation as a function of M₃, and this angle is bent in all cases. In almost all of the singlet Li–Ge–M₂-M₃ compounds, the Ge–M₂-M₃ bond angle trend as a function of the M₃ atom is: Br > Cl > F > H (Fig. S1 in the ESM).

However, the divalent angle (i.e., the angle M₁-Ge-M₂) in **6_t** and that in **38_t** are both about 180°, and both of these structures are linear. In all compounds of formula Na-Ge-

M_2 - M_3 , the Na-Ge- M_2 bond angle is bent to a degree that is (except in the case of one triplet) a function of the electronegativity of M_3 : $F > Cl > Br > H$. In the main, eight of the twelve triplet divalent angles in the K-Ge- M_2 structures are linear, which confirms the stability of the triplet states for these structures with $M_1 = K$ relative to the others. Although the Ge- M_2 bond length does vary significantly across this series of structures, the M_2 - M_3 bond lengthens notably as the size of the halogen substituent increases ($Br > Cl > F > H$).

Interestingly, the structure **6_t** belongs to the $C_{\infty v}$ point group, while all the other species belong to C_1 (Fig. S1 in the ESM).

Isodesmic reactions (Table 3) were employed to evaluate the electronic and thermal enthalpies of germynes with different substituents. The results suggest that triplet germynes with an electronegative substituent ($M_3 = F$) are slightly more stable than the corresponding triplet germynes with a less electronegative substituent ($M_3 = H$). Conversely, in the triplet K-Ge- M_2 - M_3 structures, as the electronegativity of the halogen decreases, the triplet germylene gradually becomes more stable.

Accordingly, the reactions of singlet M_1 -Ge- M_2 - M_3 structures with H_2 afford the dihydridogermane shown in Scheme 2.

Strikingly, **40_s**, **44_s**, and **46_s** are the most capable of activating dihydrogen, likely due to their relatively small singlet-triplet energy gaps. In close analogy, every singlet germylene can also undergo intramolecular H-H bond activation [36] (Table 4).

Finally, the NBO atomic charges were computed for the singlet and triplet states of the germylene species (Table 5). Charges on all the triplet germynes are less than those of their corresponding singlet species. The germanium atoms in the singlets tend to keep their nonbonding electrons in atomic orbitals with high s character. Consequently, electropositive substituents transfer charge from the corresponding Ge- M_1 and Ge- M_2 bonding orbitals with high p character to the partially populated s -type orbital on the Ge atom. Clearly, the particular halogen present influences the NBO atomic charge of the triplet Ge atom such that the charge on Ge varies as M_1 -Ge- M_2 -F > M_1 -Ge- M_2 -Cl > M_1 -Ge- M_2 -Br, which illustrates the effect of the substituent electronegativity on the stability of triplet germynes.

Conclusions

The effects of several metal substituents from the first and second groups of the periodic table on the singlet-triplet energy gaps and multiplicity of divalent germynes of formula M_1 -Ge- M_2 - M_3 were explored by performing calculations at the B3LYP/6-311++G**, QCISD(T)/6-311++G** and CCSD(T)/6-311++G** levels of theory. The results indicated that the presence of electropositive substituents

significantly reduces the excitation energy and singlet-triplet energy gap, which allows a triplet ground state to be obtained at a reasonable bond angle. The singlet-triplet energy gap (ΔE_{S-T}) varies as a function of M_3 as follows: $H \geq F \geq Cl \geq Br$, except when $M_1 = H$, in which case the trend becomes $F \geq Cl \geq Br \geq H$. Our calculations indicate that K-Ge- M_2 - M_3 shows the most promise as a candidate ground-state triplet germylene due to its small singlet-triplet energy gap and narrow band gap ($\Delta E_{HOMO-LUMO}$). The trend of $\Delta E_{HOMO-LUMO}$ as a function of M_3 is: $F \geq H \geq Cl \geq Br$. An inspection of NBO atomic charges highlighted the influence of electronegative substituents on triplet germylene stability, which varied as a function of M_3 is: M_1 -Ge- M_2 -F > M_1 -Ge- M_2 -Cl > M_1 -Ge- M_2 -Br.

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