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Theoretical Calculations of the Effects of 2-Heavier Group 14 Element and Substituents on the Singlet−Triplet Energy Gap in Cyclopentane-1,3-diyls and Computational Prediction of the Reactivity of Singlet 2-Silacyclopentane-1,3-diyls

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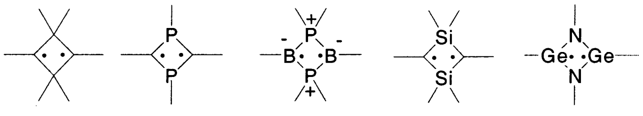
UDFT and CASSCF calculations with the 6-31G(d) basis set were performed to investigate the heavier group 14 element (M) effect on the ground-state spin multiplicity of cyclopentane-1,3-diyls and their reactivity. The calculations find that 2-metallacyclopentane-1,3-diyls (M = Si, Ge) that possess a variety of substituents (X = H, Me, F, OR, SiH_3) at M(2) are singlet ground-state molecules. The energies of the 1,3-diphenyl-substituted singlet 2-silacyclopentane-1,3-diyls are calculated to be ca. 5 kcal/mol lower than those of the intramolecular ring-closure products, i.e., 1,4-diphenyl-5-silabicyclo[2.1.0]pentanes, at the B3LYP/6-31G(d) level of theory. The energy barrier for the disrotatory ring closure of singlet 2,2-dimethyl-1,3-diphenyl-2-silacyclopentane-1,3-diyl ($\lambda_{calcd} = 757$ nm, $f = 1.01$ at RCIS/6-31G(d)) to the corresponding 5-silabicyclo[2.1.0]pentane is computed to be 11.6 kcal/mol, which is 13.1 kcal/mol lower in energy than that for the conrotatory ring-opening to a 3-silapenta-1,4-diene. The computational work predicts that singlet 1,3-diaryl-2-silacyclopentane-1,3-diyls are persistent molecules under conditions without trapping agents.

Introduction

Substituents and heteroatom effects on the ground-state spin multiplicity of diradicals and their reactivity have been a topic of timely current interest. Taking advantage of the kinetic stability of four-membered ring systems, considerable effort has been devoted to understand the electronic structure and reactivity of singlet cyclobutane-1,3-diyls **A**,[1] **B**,[2] **C**,[3] **D**,[4] and **E**.[5] The open-shell molecules **B**, **C**, and **E** were even isolated under certain conditions. In five-membered ring systems, Borden and our group[6] found the notable substituents (X) effects at C(2) on the ground-state spin multiplicity of localized 1,3-diradicals **DR1** (M = C) and have investigated the reactivity of the singlet diradicals (Scheme 1). Thus, strong electron-withdrawing substituents (X = F, OR) or -donating silyl groups (X = SiR_3) allow us to locate energetically the singlet states below the triplet states (Table 1).[6] The substituents effects were concluded to be due to the hyperconjugative stabilization of the singlet



A **B** **C** **D** **E**

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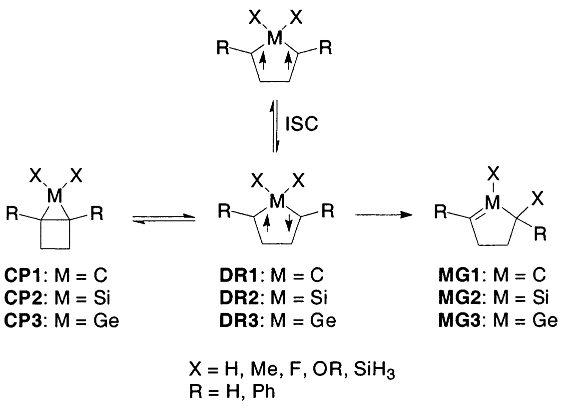
TABLE 1. Group 14 Element and Substituents Effects on the Singlet−Triplet Energy Gap, ΔE_{ST}, in Cyclopentane-1,3-diyls DR1-3

		ΔE_{ST} (kcal/mol) = $E_S - E_T$							
		DR1 M = C	**DR2** M = Si			**DR3** M = Ge			
X	sym	UDFT[a]	UDFT[a]	CASSCF[b]	MP2//CASSCF[c]	UDFT[a]	CASSCF[b]	[d]$\Delta\Delta E_{ST}{}^{C,X}$	[e]$\Delta\Delta E_{ST}{}^{Si,X}$
H	C_{2v}	+1.3	−5.2	−3.8	−1.0	−1.8[g,h]	−1.8[g,h]	0.0	0.0
Me	C_2	+0.2[f]	−5.7	−3.1	−3.7	−2.5[g]	−2.1[g]	+1.1	+0.5
F	C_{2v}	−11.4	−11.3	−7.5	−10.8	_[i]	_[i]	+12.7	+6.1
OH	C_2	−6.4	−8.1	−5.5	−6.5	_[i]	_[i]	+7.7	+2.9
$-O(CH_2)_2O-$	C_2	−10.7	−11.4	_[i]	_[i]	_[i]	_[i]	+12.0	+6.2
SiH_3	C_2	−5.4	−1.6	−0.7	_[i]	_[i]	_[i]	+6.7	−3.6

[a] The calculations were performed at the UB3LYP/6-31G(d) level of theory. The energy gaps were calculated after correction for spin contamination in the singlet by using Yamaguchi and Houk's formula (ref 16). The energy gaps for **DR1** are taken from our previous work; see refs 1 and 6h. [b] The energy gaps were calculated at the (6/6)CASSCF/6-31G(d) level of theory. [c] The energy gaps were calculated at the MP2/6-31G(d)//(6/6)CASSCF/6-31G(d) level of theory. [d] $\Delta\Delta E_{ST}{}^{C,X} = 1.3$ (for $\Delta E_{ST}{}^{C,H}$) − $\Delta E_{ST}{}^{C,X}$, whose values were calculated at UB3LYP/6-31G(d). [e] $\Delta\Delta E_{ST}{}^{Si,X} = -5.2$ (for $\Delta E_{ST}{}^{Si,H}$) − $\Delta E_{ST}{}^{Si,X}$, whose values were calculated at UB3LYP/6-31G(d). [f] This work. [g] LANTZ2 basis set was used for Ge. [h] In C_2 symmetry. [i] Not calculated.

SCHEME 1. Reactivity of Cyclopentane-1,3-diyls



states, i.e., electron delocalization of in-phase p−π orbitals at C(1) and C(3) to low-lying C−X (X = F, OR) σ* orbitals or electron delocalization of high-lying C−Si σ orbital to in-phase p−π orbitals at C(1) and C(3) (Figure 1). The spectroscopic detection of persistent singlet diradicals (X = F, OR) in a matrix (77 K) was achieved by the introduction of aryl groups (R = Ph) at the C(1) and C(3) positions.[6e,h,i,k] However, the lifetime of the species is still short at room temperature (τ = ns − μs), since the intramolecular cyclization and migration reactions are fast processes to give **CP** and **MG** (Scheme 1). If the rates of the two pathways are retarded, the lifetime of open-shell singlet molecules could increase. The elongation of the lifetime should provide us more opportunities to investigate precisely the character of carbon-centered localized singlet diradicals.

In the present study, we designed 2-metallacyclopentane-1,3-diyls **DR2** (M = Si) and **DR3** (M = Ge), considering the following advantages to generate the singlet ground-state molecules and retard the rates of the intramolecular cyclization and 1,2-migration reaction: (1) M (= Si, Ge)−X σ* orbitals are lower in energy than C−X σ* orbitals.[7] (2) The strain energies of silirane and germirane (SE = ca. 40 kcal/mol) are much higher than that of cyclopropane (SE = ca. 27 kcal/mol).[8] (3) The π-bond energies of $CH_2{=}MH_2$ (M = Si: $D_{C=SiH2}$ = ca. 40 kcal/mol, M = Ge: $D_{C=GeH2}$ = ca. 30 kcal/mol) are much smaller than that of $CH_2{=}CH_2$ double bond ($D_{C=C}$ = ca. 65 kcal/mol).[9] Here, we report computational investigations regarding heavier group 14 element (M) and substituents (X) effects on the singlet−triplet energy spacing in 2-metallacyclopentane-1,3-diyls.[10] In connection with future experimental studies, the reactivity of a singlet 1,3-diphenyl-substituted 2-silacyclopentane-1,3-diyl was also investigated at the UB3LYP/6-31G(d) level of theory.

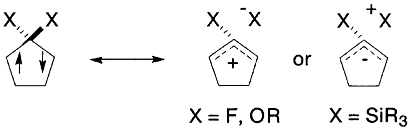


FIGURE 1. Hyperconjugated stabilization of singlet cyclopentane-1,3-diyls **DR1**.

Computational Methods

Geometry optimizations were performed at the UB3LYP[11] and/or (6/6)CASSCF[12] level of theory with the 6-31G(d)[13] basis set. The geometries of stationary points and transition states

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were all located, and vibrational analyses were performed with the Gaussian 98 suite of programs.[14] A multireference MP2 algorithm[15] that has been implemented in the Gaussian was used to correct the SCF energetics for dynamic correlation (without re-optimization for the geometries). The optimized geometries and their energies are available in the Supporting Information.

Results and Discussion

Table 1 summarizes group 14 element (M) and substituents (X) effects on the ground-state spin multiplicity of diradicals **DR1**−**3** at the UB3LYP/6-31G(d), (6/6)-CASSCF/6-31G(d), and MP2/6-31G(d)//(6/6)CASSCF/6-31G(d) levels of theory. The spin-corrected[16] singlet−triplet energy gaps (ΔE_{ST}) calculated using the UDFT method are known to be close to the energy gaps computed at a multiconfiguration self-consistent field method such as CASSCF and CASPT2 calculations.[6] The discussion in the present study will be done on the basis of the spin-corrected UDFT energies.

Singlet−Triplet Energy Gap in 2-Silacyclopentane-1,3-diyls DR2. In contrast to the substituents' (X) dependent change of the ground-state spin multiplicity in **DR1** (M = C),[6,17] singlet ground states were calculated for all the diradicals **DR2** (M = Si) that possess a variety of substituents (X) at Si(2). The results were qualitatively independent of the method of calculations (Table 1). It should be noted that the singlet states are energetically more stable than the triplet, $\Delta E_{ST} = E_S - E_T < 0$, even when the substituents (X) are hydrogen atoms or methyl groups. The notable substituents effects in **DR2** are rationalized in terms of the low-lying energy of Si−H/Me σ*orbitals.[7] The electron delocalization of the in-phase NBMO (ψ_S) to the low-lying Si−X σ* orbitals enhances the energy separation between ψ_S and the out-of-phase NBMO (ψ_A), and thus, the singlet falls below the triplet in energy, according to the Hund rule (Figure 2). The introduction of the electron-withdrawing substituents (X = F, OR) was found to increase the singlet−triplet energy gap (ΔE_{ST}), as calculated for **DR1**. However, the effect of the electron-withdrawing substituents on ΔE_{ST} in **DR2** were calculated to be about half in **DR1**, i.e., $\Delta\Delta E_{ST}{}^{C,X} > \Delta\Delta E_{ST}{}^{Si,X} > 0$ (Table 1). The small substituents (X) effects in **DR2** is not so easy to understand, because the effect of the electron-withdrawing substituents (X) on lowering the energy of Si-X σ* is known to be much larger than that on lowering the energy of C−X σ*.[18] The M═C double-bond character of the hyperconjugative structures $\mathbf{DR_{HC}}$ in the singlet states (Figure 2, vide infra in Table 2) reasonably explains the diminished effect of the substituents in **DR2**, because the electron-withdrawing substituents at silicon largely destabilize CH_2═SiX_2 double bonds ($D_{C=SiF2}$ = 26.3 kcal/mol, $D_{C=Si(OH)2}$ = 26.3 kcal/mol).[9c,h] In addition, the longer C−Si bond length is also the reason for the smaller substituents effects in **DR2**, since orbital interactions are largely dependent on the distance between interacting orbitals.

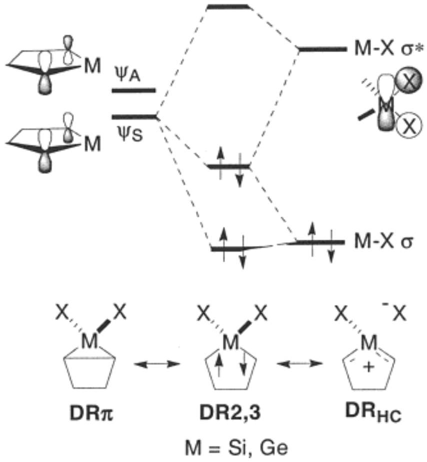

FIGURE 2. Orbital interaction diagram depicting the effect of hyperconjugative electron delocalization from the in-phase NBMO (ψ_S) to the M(2)−X bonds in **DR2** and **DR3** and resonance structures of singlet diradicals **DR2** and **DR3**.

As we have observed, the notable effect of the ethylene ketal functionality on ΔE_{ST} in **DR1**,[6k] the singlet−triplet energy gap in ethylene-ketal substituted **DR2** (X = $-O(CH_2)_2O-$, $\Delta E_{ST} = -11.4$ kcal/mol) was calculated to be larger than that in dihydroxy-substituted **DR2** (X = OH, $\Delta E_{ST} = -8.1$ kcal/mol). The spiroconjugation, i.e., electron delocalization of the n-orbital at oxygen to the out-of-phase NBMO ψ_A, is responsible for the notable effect of the ethylene-ketal functionality.[6k] As for the silyl-substituted diradicals (X = SiH_3), the opposite effect of the substituents on ΔE_{ST} was calculated between **DR1** and **DR2**, i.e., $\Delta\Delta E_{ST}{}^{C,Si} > 0$ and $\Delta\Delta E_{ST}{}^{Si,Si} < 0$. The substituent effects are not due to the energetic destabilization of the hyperconjugative structure $\mathbf{DR}_{HC}$ because it is known that the silyl-substitution at silicon rather stabilizes C═Si double bond.[19] The small energy gap between Si−Si σ and σ* orbital is proposed to be responsible for the opposite substituent effect in **DR2**.[20] Thus, the interaction of the high-lying Si−Si σ orbital with the in-phase ψ_S, which destabilizes ψ_S in energy, competes with the interaction of ψ_S with Si−Si σ* orbital to reduce the singlet−triplet energy gap (Figure 2).

Singlet−Triplet Energy Gap in DR3 (M = Ge). The singlet ground state was also calculated for **DR3** (M =

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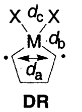
(20) $\sigma_{C-Si} = -12.3$ eV, $\sigma^*_{C-Si} = 4.3$ eV.; $\sigma_{Si-Si} = -10.9$ eV, and σ^*_{Si-Si} = 3.8 eV, which were calculated for MH_3-MH_3 molecules at the RHF/6-31G(d) level of theory.

TABLE 2. Ratios (ψ_S/ψ_A) of Occupation Numbers of ψ_S and ψ_A Orbitals in the Singlet DR2 and Structural Differences between the Singlet and Triplet Diradicals DR2



DR

M	X	spin multiplicity[b]	occupation numbers[a] ψ_S	ψ_A	ψ_S/ψ_A	atom lengths (Å)[a] d_a	d_b	d_c
Si	H	S	1.36	0.65	2.1	2.646	1.878	1.483
		T				2.694	1.881	1.481
Si	Me	S	1.36	0.64	2.1	2.639	1.883	1.895
		T				2.690	1.894	1.894
Si	F	S	1.47	0.54	2.7	2.646	1.842	1.591
		T				2.710	1.856	1.589
Si	OH	S	1.43	0.57	2.5	2.643	1.856	1.654
		T				2.703	1.872	1.650
Si	Si	S	1.27	0.73	1.7	2.657	1.892	2.367
		T				2.694	1.896	2.363
Ge	H	S	1.26	0.74	1.7	2.723	1.960	1.550
		T				2.753	1.964	1.548
Ge	Me	S	1.28	0.72	1.8	2.715	1.966	1.974
		T				2.748	1.971	1.973

[a] The calculated values were obtained at the (6/6)CASSCF/6-31G(d) level of theory. [b] S: singlet state, T: triplet state.

Ge). However, the singlet−triplet energy gaps were computed to be smaller than those in **DR2** (Table 1). The small singlet preference calculated in **DR3** is reasonably proposed to be due to the following two reasons: (1) C−Ge bond (ca. 2.0 Å) is longer than that of C−C and C−Si bonds. Thus, the longer the distance between the interacting orbitals, the smaller the energetic change of ψ_S will be, and the more likely it is that the singlet−triplet energy gaps in **DR3** are smaller than those in **DR2**. (2) Energy gap between the C−Ge σ and σ^* orbital is smaller than that in C−C and C−Si σ bond.[7a] Thus, the interaction of the Ge−H/Me σ orbital with the in-phase ψ_S, which destabilizes ψ_S in energy, competes with the interaction of ψ_S with Ge−H/Me σ^* orbital, which stabilizes ψ_S in energy, to reduce the singlet−triplet energy gap.

Electronic and Structural Features of Singlet DR2 and DR3. Table 2 summarizes the ratios (ψ_S/ψ_A) of the electron occupation number of ψ_S and ψ_A in the singlet diradicals **DR2** and **DR3** and the characteristic differences in the structures (atom distances d_a, d_b, and d_c) between the singlet and triplet states. The calculated values were obtained at (6/6)CASSCF/6-31G(d) level of theory. The ratios of the occupation numbers were computed to be largely deviated from unity, $\psi_S/\psi_A \gg 1.0$. The larger the energy difference between the ψ_S and ψ_A NBMOs, the larger the occupation number in the lower energy ψ_S NBMO will be, and the more likely it is that the singlet will fall below the triplet in energy. The deviations from unity clearly indicate the selective occupancy of electrons in the C(1)−C(3) π-bonding orbital (ψ_S). The π-bonding character (**DR**$_\pi$ in Figure 2) between C(1) and C(3) in the singlet states of **DR2** and **DR3** is unequivocally supported by comparing the atom C(1)−C(3) distances (d_a) between the singlet and triplet state. Thus, all the distances d_a in the singlet diradicals is significantly shorter than those in the triplet diradicals. The hyperconjugative resonance structures (**DR**$_{\mathbf{HC}}$ in Figure 2) of the singlet diradicals are also clarified by comparing the values of d_b and d_c in the singlet and triplet diradicals. The C(1)−M(2) bond lengths (d_b) of the singlet states are shorter than those of the triplet states, while the M(2)-X lengths (d_c) in the singlet states are longer than those in the triplet states. The two resonance structures are strongly proposed to be responsible for the stabilization of the lowest singlet state.

Reactivity of Singlet 2-Silacyclopentane-1,3-diyls. To confirm the above-mentioned theoretical predictions, it is important to design experimentally feasible molecules and compute their reactivity and spectroscopic characteristic. To this end, we noticed 2-silacyclopentane-1,3-diyl derivatives, since silicon compounds are more familiar than germanium compounds, and the substituents (X) effects on the singlet−triplet energy gaps in **DR2** were computed to be more drastic than those calculated in **DR3**. First of all, the electronic energies of the possible products from **DR2**, i.e., intramolecular cyclization products **CP2** and the migration products **MG2** (M = Si; X = F, Me; R = H, Ph), were calculated at B3LYP/6-31G(d) level of theory (Table 3). The energies for compounds **CP1** and **MG1** (M = C; X = F, Me; R = H, Ph) were also computed at the same revel of theory (entries 1−3) to examine the effect of silicon on the reactivity of **DR2**. As mentioned in the Introduction, three-membered com-

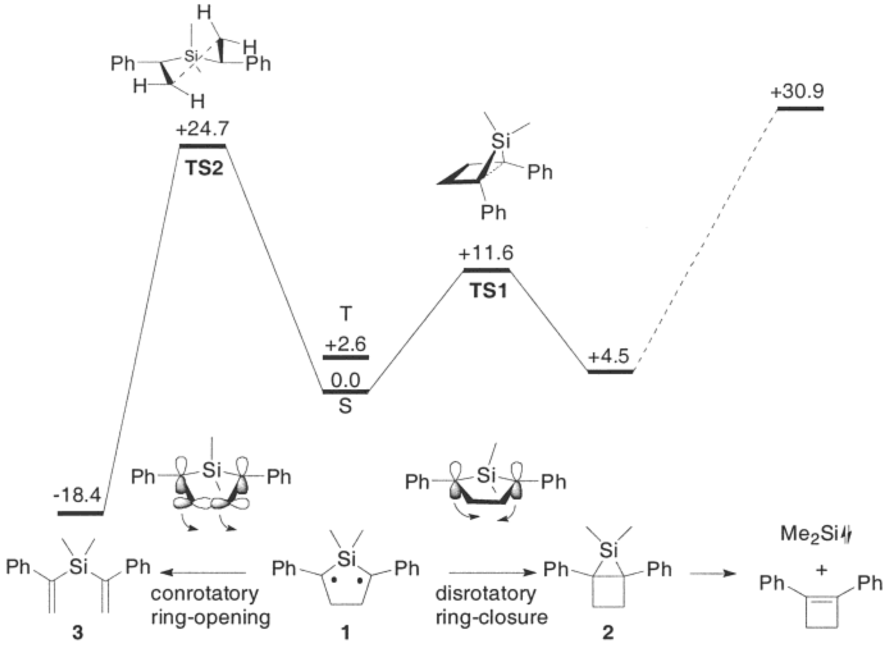


FIGURE 3. B3LYP/6-31G(d)-calculated energy profile for the reaction of the 2-silacyclopentane-1,3-diyl **1**; the energies are relative to the singlet diradical.

TABLE 3. Calculated B3LYP/6-31G(d) Energies (kcal/mol) of the Stationary Points for CP and MG, Relative to the Energies of Singlet Cyclopentane-1,3-diyls DR1 (M = C) and DR2 (M = Si)

entry	DR	X	R	ΔE_{CP}[a] (kcal/mol)	ΔE_{MG}[b] (kcal/mol)
1	**DR1** (M = C)	Me	H	33.4	65.8
2		F	H	21.2 (20.9[c])	48.1
3[d]		Me	Ph	15.0	45.5
4	**DR2** (M = Si)	Me	H	16.3	22.6
5		F	H	3.3	−36.1
6[e]		Me	Ph	−4.5	1.2
7[f]		F	Ph	−5.1	−51.0

[a] $\Delta E_{CP} = E$(singlet **DR**) − E(**CP**). [b] $\Delta E_{MG} = E$(singlet **DR**) − E(**MG**). [c] At the CASPT2N/6-31G(d) level of theory, see ref 6a. [d] The singlet−triplet energy gap in the diradical was calculated to be $\Delta E_{ST} = +0.3$ kcal/mol at UB3LYP/6-31G(d) with C_2 symmetry. [e] The singlet−triplet energy gap in the diradical was calculated to be $\Delta E_{ST} = -2.6$ (kcal/mol) at UB3LYP/6-31G(d) with C_2 symmetry. [f] The singlet−triplet energy gap in the diradical was calculated to be $\Delta E_{ST} = -6.6$ (kcal/mol) at UB3LYP/6-31G(d) with C_2 symmetry.

pounds and double-bonds that contain silicon atom are energetically less stable than the corresponding all carbon compounds. The significant effect of silicon atom was also calculated in the energy differences ΔE_{CP} (= $E_{DR} - E_{CP}$) and ΔE_{MG} (= $E_{DR} - E_{MG}$) (Table 3). Thus, the energy differences of $|\Delta E_{CP}|$ and $|\Delta E_{MG}|$ in 2-silacyclopentane-1,3-diyls **DR2** (entries 4−6) were calculated to be smaller than those in cyclopentane-1,3-diyls **DR1** (entries 1−3). It should be noted that the migration product **MG2** (X = F) was predicted to be less stable than the corresponding singlet diradical **DR2**, $\Delta E_{CP} < 0$ (entries 5 and 7). The weak C═Si(F) double bond might be the reason of the surprising results. Since the energy differences of ΔE_{CP} calculated in **DR2** molecules were predicted to be quite small (entries 4 and 5), diphenyl-substitutions at C(1) and C(3) might provide a significant stabilization of the singlet diradical **DR2** to make the diradical lower in energy than the ring-closure form **CP2**. In fact, the 1,3-diphenyl-substituted singlet diradicals **DR2** were calculated to be more stable in energy than the ring-closure products **CP2** (entries 6 and 7). Thus, the 1,3-diphenyl-substituted 2-silacyclopentane-1,3-diyls would be the target molecules for experimental studies to uncover the ground-state spin multiplicity and reactivity.

To predict the energy barriers from singlet 2-silacyclopentane-1,3-diyl **DR2** to **CP2** and **MG2**, 2,2-dimethyl-1,3-diphenyl-2-silacyclopentane-1,3-diyl **1** was selected and the transition states for the bond-forming and -breaking processes were calculated at UB3LYP/6-31G(d) level of theory (Figure 3).[21] The disrotatory ring-closure from **1** to housane **2** was found to have an activation energy of 11.6 kcal/mol. However, the transition state for the bond-breaking process of the Si−Me bond was not located at the same level of theory. The potential energy surface analysis for the bond-breaking process suggests that the activation energy is considerably higher than the energy barrier of the ring-closure process.[22] We found additionally the conrotatory ring-opening reaction of the singlet diradical **1** to the 2-sila-penta-1,4-diene **3** with an activation-energy of 24.7 kcal/mol, which is 13.1 kcal/mol higher in energy than the ring-closure process (Figure 3). Since silacyclopropanes (siliranes) are known to be the precursors of silylenes,[23] the reaction energy from silirane **2** to dimethylsililene

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[21] UDFT calculations are known to reproduce closely the results calculated by CASPT2 level of theory. However, CASSCF energies were reported to be largely deviated from CASPT2 calculations; see: Sinicropi, A.; Page, C. S.; Adam, W.; Olivucci, M. *J. Am. Chem. Soc.* **2003**, *125*, 10947−10959.

[22] The potential energy surface analysis for the Si−Me bond-breaking process is shown in the Supporting Information.

[23] (a) Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics*, **1991**, *10*, 2095−2096. (b) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gasper, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281−1288. (c) Jiang, P.; Trieber, D., II; Gasper, P. P. *Organometallics*, **2003**, *22*, 2233−2239. (d) Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 10659−10663.

and 1,2-diphenylcyclobutene was calculated at the same level of theory. The highly endothermic reaction, ca. 25 kcal/mol, was calculated (Figure 3). Thus, the theory predicts that singlet diradical **1** would be the persistent molecule under conditions without trapping agents.

To confirm experimentally the generation of the singlet diradical **1**, a spectroscopic detection of the molecule is necessary. To this end, we calculated the UV−visible spectrum of singlet diradical **1** at RCIS/6-31G(d)[24] level of theory. It is known that the computational method closely reproduces the spectra ($\lambda_{\max} \sim 600$ nm) obtained experimentally for singlet 1,3-diphenylcyclopentane-1,3-diyls **DR1** (M = C; X = F, OR; R = Ph).[6k] As expected, a strong absorption maximum was calculated to be $\lambda_{\text{calcd}} = 757$ nm ($f = 1.01$) in the visible region. The absorption band may be easily distinguishable from the spectrum of the triplet state, which was calculated to be $\lambda_{\max} = 381$ nm ($f = 0.007$) at the TD-UB3LYP level of theory.[25] Thus, UV−vis spectroscopic analysis should provide strong evidence for the formation of singlet diradical **1**, as observed for singlet 1,3-diphenylcyclopentane-1,3-diyls.[6g,h,k] Efforts directed toward the preparation of 2-silacyclopentane-1,3-diyls are in progress.

Conclusions

UDFT and CASSCF calculations find the singlet ground state of 2-metallacyclopentane-1,3-diyls (M = Si, Ge) that possess a variety of substituents at M(2). The striking findings are as follows: (i) The 2-metalla-1,3-diradicals that possess even hydrogen (X = H) or methyl groups (X = Me) at M(2) are singlet ground-state molecules, although it is known that the substituents make the triplet ground state of cyclopentane-1,3-diyls **DR1** (M = C). (ii) The diradicals **DR2** and **DR3** are kinetically stabilized due to the high strain energy of the ring-closure products **CP2** and **CP3** and the weak π-bonding energy of the migration products **MG2** and **MG3**. (iii) The thermodynamic stabilization by the diphenyl substitutions at C(1) and C(3) makes the singlet diradicals more stable compounds than the ring-closure products. The notable heavier group 14 element effects would provide a worthwhile focus for future calculations and subsequent experiments.

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Supporting Information Available: Optimized geometries and their energies for all the compounds studied in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135−149.

[25] The absorption max of ca. 320 nm was reported for the triplet state of **DR1** (M = C, X = Me, R = Ph); see; Kita, F.; Adam, W.; Jordan, P.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1999**, *121*, 9265−9275.