Synthesizability of the Heavy Analogues of Disubstituted Cyclopropenylidene: A Theoretical Study

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The thermodynamic and kinetic stability of bis(diisopropylamino)cyclopropenylidene and related molecules were investigated by quantum chemical methods. The main stabilizing factor in the amino-substituted cyclopropenylidene is the significant π-electron shift from the amino substituents, via a nonaromatic ylidic structure; however, its successful synthesis is based on its high kinetic stability. The silicon and germanium analogues show lower stabilization than the synthesized carbene. However, when investigating their reactions, we found that both amino-disubstituted three-membered silylene and germylene have considerable kinetic stability.
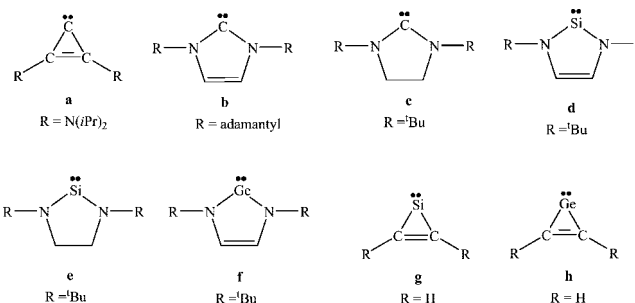
Introduction

The synthesis of bis(diisopropylamino)cyclopropenylidene (**a**) in 2006 gave a new twist to the story of carbenes.[1] The new carbene is a stable, yellow crystal with a melting point between 107 and 109 °C. As early as 1997 the same compound was mentioned as a transient carbene.[2] In 2007 the bis[bis(R-1-phenylethyl)amino]cyclopropenylidene, a chiral cyclopropenylidene derivative, was also reported.[3]

The first bottleable carbene was synthesized in 1991 by Arduengo's group (**b**).[4] In the following years the corresponding silylene (**d**)[5] and germylene (**f**)[6] analogues were also prepared. Since then, a few dozens of related compounds have been isolated.[7]

The effect of different substituents on the stability of carbene[8] and silylene[9] has been well investigated. It has been shown that

π-donating substituents are effective in stabilizing both silylene and carbene in the singlet state. The importance of the aromaticity in the case of cyclic carbene/silylene/germylene derivatives has also been shown;[10] for instance the aromaticity of imidazole-2-ylidene is about 60% of that of benzene.[10a] However, the existence of stable imidazolyn-2-ylidene (**c**)[11] and the related silylene derivative **e**[12] proved that it had no crucial role in the stabilization.

The questions of substituent effect, aromaticity, stability, and reactivity of carbenes[13] and silylenes[14] were discussed in several recent reviews.

The majority of the recently known stable carbenes are imidazole derivatives. For a long time, it was believed that these electron-deficient species could be stable only when at least one heteroatom connects to the divalent center.[15] The skeleton of the newly prepared cyclopropenylidene derivative is, however, a three-membered highly strained ring. Also, **a** is the only stable

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carbene, which has no heteroatom substituent directly linked to the carbene center.[16] It is easy to recognize that a compound with R = NH_2 is a structural isomer of the Arduengo carbene **b** (R = H); thus, on comparing their energies, one may get a simple explanation for the stability of the new compound. However, our first calculations showed that diamino-cyclopropenylidene is less stable than imidazole-2-ylidene by ca. 40 kcal/mol. Therefore, a deeper investigation of the conspicuous stability is required. This is the main aim of this article.

On the other hand, since **d** and **f** were bottled just after the first stable carbene **b**, the question of the relative stability of the related species **g** and **h** arises. Is the silicon (or germanium) analogue of cyclopropenylidene stable enough to be synthesized?

Methodology and Computation

All calculations were performed using the Gaussian03[17] software package. Geometry optimization and frequency analysis were performed at the B3LYP/cc-pVTZ[18,19] and MP2/cc-pVTZ[20] levels. All geometries were fully optimized, as verified by the frequency analysis. In order to obtain accurate energetic and geometric data, the investigated molecules were reoptimized at the CCSD/6-311++G(d,p)[21] level of theory. We compared the B3LYP/cc-pVTZ and MP2/cc-pVTZ energies to CCSD(T)/aug-cc-pVTZ calculations for **1-H**, **2-H**, **9-H**, **10-H**, **16-H**, and **17-H** and found that the B3LYP method underestimates the relative energy by ca. 0.83 kcal/mol, while the MP2 method overestimates it by ca. 2.17 kcal/mol (relative to the coupled cluster results).

To study the effects of stabilization on the different structures, appropriate isodesmic reactions were designed. The reaction energies and Gibbs free energies were calculated at the B3LYP/cc-pVTZ level. In order to characterize the extent of aromaticity in the ring structures, we used the NBO framework; natural resonance theory[22] (NRT) analysis was performed at the B3LYP/cc-pVTZ level. This methodology was recently successfully applied in the study of the aromaticity of mono-, di-, tri-, and tetraphosphatriafulvenes.[23]

To investigate the kinetic stability of divalent species, the energies of isomerization, hydride ion addition, and dimerization reactions were studied for carbenes, while isomerization, nucleophilic complexation, and dimerization were considered for silylenes. The isomerizations were calculated at the MP2/cc-pVTZ level. For the hydride ion addition and complexations the 6-311++G(d,p) basis set was used with the MP2 level of theory. Because of the size problem, dimerization calculations were performed at the B3LYP/cc-pVTZ level.

Results and Discussion

This section is divided into two major sections according to the two investigated C_3R_2 and XC_2R_2, (X = Si, Ge) systems.

Scheme 1

The first part of each section deals with the thermodynamic stability of the three-membered divalent species. The relative energies of the observed isomers are compared to those of stable five-membered imidazole derivatives. The data of isodesmic reactions and NRT analysis are also discussed in the first part. The kinetic stability of cyclopropenylidene derivatives and their heavy analogues is investigated in the second part of the section.

The molecules studied are marked and numbered continuously from **1** to **21**. The suffixes H and NH_2 distinguish the hydrogen- and diamino-substituted species in the text. For instance **1-H** symbolizes cyclopropenylidene, while **1-NH₂** is diaminocyclopropenylidene. We will discuss the potential energy surfaces based on the most sophisticated CCSD/6-311++G(d,p) results. The optimized geometries at the B3LYP/cc-pVTZ, MP2/cc-pVTZ, and CCSD/6-311++G(d,p) levels are available in the Supporting Information.

I. Stability of Cyclopropenylidene Derivatives. The parent cyclopropenylidene (**a**, R = H) prepared first by high-vacuum flash pyrolysis was detected in 1984.[24] Gleiter and Hoffmann had already predicted in 1968 that it had a singlet ground state and was stabilized by the interaction between the carbene center and the unsaturated part of the molecule.[25] Pople et al. attributed its stability to the 2π electron cycle.[26] Also, the surprising stability of **a** was attributed to the π donation from the amino groups to the electron-deficient ring.[1,27] Two additional C_3H_2 isomers, vinylidenecarbene[28] and propargylene,[29] are also known, and the interconversion among the three isomers was demonstrated.[30]

The computed relative energies and Gibbs free energies for the observed isomers (Scheme 1) of the C_3H_2 and $C_3(NH_2)_2$ potential energy surfaces are summarized in Table 1. Our calculations provide the same stability order on the C_3H_2 PES that was previously reported;[31] the global minimum appears to be at cyclopropylidene (**1-H**), while vinylidenecarbene (**2-H**) and propargylene (**3-H**) seem to be less stable by 14.40 and 30.01 kcal/mol, respectively. The MP2 method gives definitely better results than the B3LYP.

Although different halogen (R = F, Cl, Br)[32] and alkyl (R = CH_3, $(CH_3)_2CH$, $(CH_3)_3C$)[33] substituents have already been tested on the stability of the C_3R_2 system, the effect of the amino groups remains undiscovered. Four isomers, **2-NH₂** and **3-NH₂**

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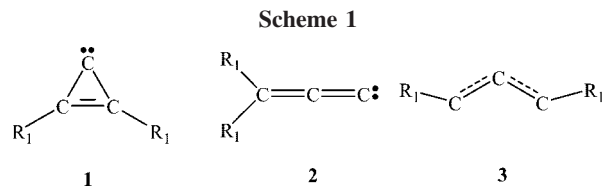
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Table 1. Relative Energies and Gibbs Free Energies (in kcal/mol) of the Investigated Isomers on the C_3H_2 and $C_3(NH_2)_2$ Potential Energy Surfaces

| | B3LYP/cc-pVTZ | | | | MP2/cc-pVTZ | | | | CCSD/6-311++G(d,p) | |
| | H | | NH₂ | | H | | NH₂ | | H | NH₂ |
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔE
cis-1	0.00	0.00	0.08	0.00	0.00	0.00	0.13	0.00	0.00	0.23
trans-1			0.00	0.24			0.00	0.08		0.00
2	11.15	10.15	1.23	0.69	19.56	18.44	3.48	1.89	14.40	3.99
3	20.14	17.42	1.34	0.11	32.80	30.02	9.49	8.68	30.01	8.23
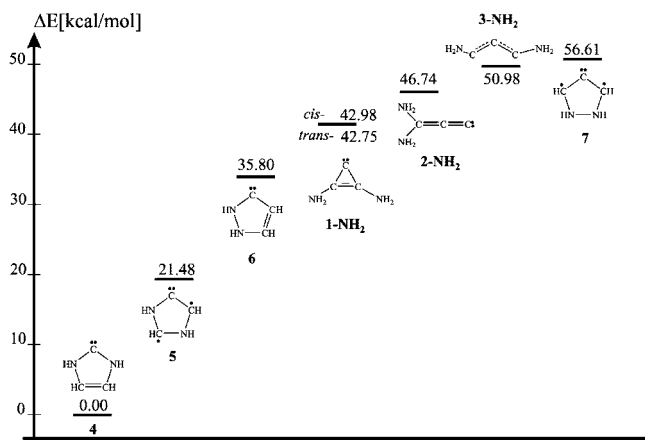
Figure 1. Stability order of the structural isomers of imidazole-2-ylidene derivatives, at the CCSD/6-311++G** level.

Scheme 2

$\delta = \delta_1 + \delta_2 + \delta_3 = 347.8°$ $\delta = 349.0°$
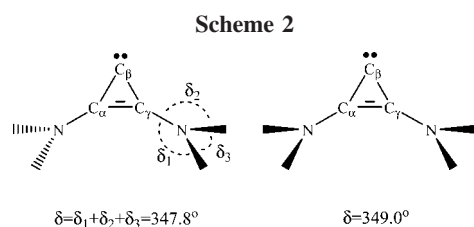
and the two conformers of the cyclopropylidene derivative, were found by replacing the hydrogen substituents with NH_2 groups. The sum of the bond angles around N is 349.0° and 347.8° in the case of *cis*-**1-NH₂** and *trans*-**1-NH₂** conformations (Scheme 2). Their energy difference is negligible (0.23 kcal/mol). The stability order is the same as in the case of the C_3H_2 system; however, the energy differences between the first few isomers are definitely smaller.

Since diaminocyclopropenylidene is a structural isomer of the Arduengo carbene, the comparison of their potential energies may provide a simple rationalization of the stability of the newly synthesized three-membered-ring carbene. The relative stability of the $C_3N_2H_4$ carbene derivatives is depicted in Figure 1. As expected, the Arduengo carbene, **4**, is the most stable isomer due to the known strong stabilizing effect of the nitrogens neighboring the carbene center.[34] It is followed in energy by two hitherto unknown five-membered rings (**5** and **6**). Diaminocyclopropenylidene (**1-NH₂**) is only the fourth in line, lying a considerable 42.75 kcal/mol higher than **4**.

Thus, it is somewhat surprising that bis(diisopropylamino)cyclopropenylidene was possible to synthesize. To answer this obvious contradiction, we studied the different factors of the stability in detail.

Three main factors determine the stability of carbenes: the substituent effect, the delocalization and possible aromaticity of the ring, and the ring strain. Using appropriate isodesmic reactions (Scheme 3) one can quantify the extent of these effects. The energy of reaction 1 (ΔE_1) measures the net stabilization,[35] including the contribution of π electron donation of nitrogens, the electron delocalization (including aromaticity), and ring strain, relative to the triplet ground-state carbene (X=C) and the singlet ground-state silylene (Si) and germylene (Ge). In reaction 2 the strain and the delocalization are considered assuming that the substituent effect on both sides of the equation is the same. In both reactions 1 and 2 all the reactants and products were fully optimized. To estimate the ring strain (ΔE_{strain}), reaction 3 was designed where the molecules on the left-hand side were optimized with bond angles fixed at the values found in the respective ring, while on the right-hand side they were fully optimized in *cis* form. To compare the extent of the individual factors, the subtituent effect can be defined as the difference between the reaction energies of eqs 1 and 2 ($\Delta E_{subs} = \Delta E1 - \Delta E2$), while the ring effect is estimated by subtracting the reaction energy of 3 from that of 2 ($\Delta E_{ring} = \Delta E2 - \Delta E_{strain}$).

The calculated data are summarized in Table 2. The total stabilization energies meet the expectation; the Arduengo carbene ($\Delta E_1^4 = 119.3$ kcal/mol) is more stable than the newly synthesized three-membered carbene ($\Delta E1\textbf{1-NH2} = 64.4$ kcal/mol). This suggests that the resulting stabilization of the three factors is 55 kcal/mol higher in the five-membered ring than in the three-membered-ring carbene. Comparing to the 42.95 kcal/mol, which is the energy difference between the two compounds on the PES, the difference (12 kcal/mol) can be attributed to the bond strength difference of the two C−C bonds in **1-NH₂** and two C−N bonds in **4**.

It can be recognized that the stabilization effect of π electron donation from the nitrogen atoms is about 3 times larger in the Arduengo carbene ($\Delta E_{subs}^4 = 81.8$ kcal/mol) than in the **1-NH₂** ($\Delta E_{subs}^{\textbf{1-NH2}} = 27.8$ kcal/mol). This is not surprising, as in the former molecule the nitrogen lone pair acts directly, while in the latter it has only an indirect interaction. In contrast, the effect of the ring is almost double in the three-membered ring (97.2 kcal/mol) than in the Arduengo carbene (49.4 kcal/mol). In the parent molecule **1-H** it is considerably smaller but also overcomes that of **4**. The stabilization effect of the ring involves two feasible processes; the π electron shift toward the divalent center and the cyclic delocalization. As expected, the ring strain destabilizes both molecules; however, it is significantly larger in the three-membered ring (−60.5 kcal/mol) than in **4** (−25.4 kcal/mol).

Since the ring stabilization is surprisingly large in **1-NH₂**, we tried to gain more insight in the possible aromaticity using the natural resonance theory. Five Lewis structures (**A**, **B**, **C**, **D**, and **E**), shown in Scheme 4, are relevant for describing the resonance hybrid of **1-NH₂**. In the parent molecule **1-H**

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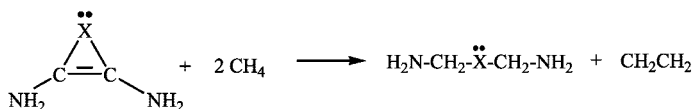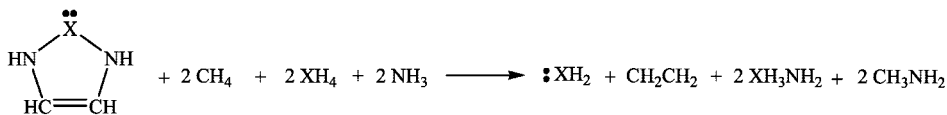
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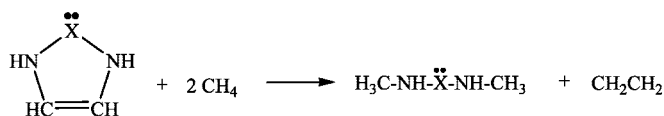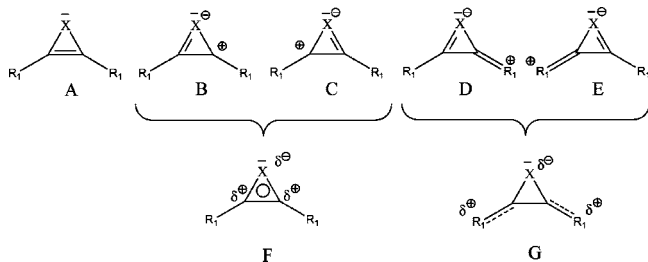(35) In this reaction methene was calculated in its ground triplet state.

Scheme 3

$$+ 4\,CH_4 \quad + 2\,XH_4 \longrightarrow \mathbin{:}XH_2 + CH_2CH_2 + 2\,CH_3NH_2 + 2\,XH_3CH_3$$

(1)

$$+ 2\,CH_4 \quad + 2\,XH_4 + 2\,NH_3 \longrightarrow \mathbin{:}XH_2 + CH_2CH_2 + 2\,XH_3NH_2 + 2\,CH_3NH_2$$

$$+ 2\,CH_4 \longrightarrow H_2N\text{-}CH_2\text{-}\ddot{X}\text{-}CH_2\text{-}NH_2 + CH_2CH_2$$

(2)

$$+ 2\,CH_4 \longrightarrow H_3C\text{-}NH\text{-}\ddot{X}\text{-}NH\text{-}CH_3 + CH_2CH_2$$

$$\mathbin{:}XH_2 + NH_2\text{-}CH=CH\text{-}NH_2 \longrightarrow \mathbin{:}XH_2 + NH_2\text{-}CH=CH\text{-}NH_2$$

(3)

Table 2. Calculated Isodesmic Reaction Energies (in kcal/mol) at the B3LYP/cc-pVTZ Level

	ΔE_1	ΔE_2	ΔE_{strain}	ΔE_{subs}	ΔE_{ring}
1-H	18.34	1.29	−58.60	17.05	59.89
1-NH₂	64.40	36.65	−60.51	27.75	97.17
4	119.36	23.97	−25.44	95.39	49.41
9-H	−2.48	−4.54	−40.14	2.06	35.60
9-NH₂	34.28	33.60	−38.73	0.68	72.34
11	65.00	27.72	−7.47	37.28	35.19
16-H	−3.91	−6.99	−39.50	3.08	32.50
16-NH₂	31.48	29.47	−38.04	2.01	67.51
18	74.75	32.58	−5.67	42.17	38.25

Scheme 4

Scheme 5

structures. For instance, the weight of **G** equals the sum of weights of **D** and **E**.

In this theory, the criterion of aromaticity is that the ratio of the weight of aromatic and nonaromatic resonance structures should be larger than 1. The higher this fraction, the larger the aromatic character of the given molecule.

It can be seen from the data that, in agreement with the previous investigations,[10,36] **4** has strong aromatic character (the weight of **F** is $w_F = 72\%$), whereby the carbene center is also stabilized. In the case of **1-H** the localized form (**A**) is dominant ($w_A = 56\%$) and the molecule is only moderately aromatic ($w_F = 38\%$). This was also stated earlier considering the bond lengths and heats of bond separation reactions.[26] However, in the amino-substituted three-membered ring (**1-NH₂**) the weight of the localized **A** form is almost zero and the ylidic structures become more preferable. The contribution of the charge-separated form **G** is 44%, while the aromatic form **F** is represented only by 34%. Since the electrons of the amino groups are donated to the π system, a significant electron surplus is evolved in the ring and the Hückel rule is violated. The aromaticity is diminished, although an enhanced stabilization due to the ylidic charge separation takes place.

obviously only **A**, **B**, and **C** resonance structures can be assumed. Structure **A** corresponds to a nonaromatic carbene that contains a localized C=C double bond, while **B** and **C** indicate the possible resonance Lewis structures for the aromatic ring. **D** and **E** represent charge-separated electronic structures in which negative charge shift stabilizes the carbene center, like in **B** and **C**, but they are ylidic and nonaromatic structures. Similarly, five-membered rings can be described with the analogous nonaromatic (**A**) and two aromatic (**B** and **C**) Lewis structures (Scheme 5). Obviously, the ylidic structures are missing in this case. The total weights of the aromatic hybrid structure (**F**) and the ylide hybrid structure (**G**) have been calculated simply as a sum of the weights of the suitable Lewis

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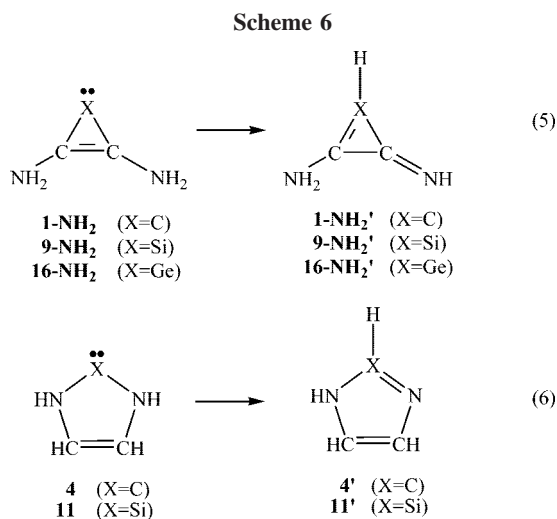
Scheme 6

Scheme 7

Table 3. Weights of Main Resonance Structures in Percentages Calculated at B3LYP/cc-pVTZ Level

	A	B	C	D	E	F	G
1-H	56	19	19			38	
1-NH₂	7	17	17	22	22	34	44
4		36	36			72	
9-H	83	5	5			10	
9-NH₂	52	8	8	7	7	16	14
16-H	84	5	5			10	
16-NH₂	52	8	8	7	7	16	14

Kinetic Stability. Reactions of singlet carbenes can be sorted into three classes: structural isomerization, nucleophilic attack on the unfilled p orbital of the carbene, and dimerization. The ability of cyclopropenylidene derivatives for these reactions was investigated by the rearrangement of **1-NH₂** to **1-NH₂′** (Scheme 6), addition of a hydride ion, and calculating the dimerization energy ΔE_{dim}, respectively.

We found that the isomerization (5) of **1-NH₂** to **1-NH₂′** is a slightly favorable process (ΔE_{Iso} in Table 4) and occurs in one step with a huge barrier ($\Delta E^{\ddagger}_{\mathrm{Iso}}$). The activation barrier of the hydride ion addition of **1-NH₂**, which is more relevant for the kinetic stability of carbenes, is comparable with that of imidazol-2-ylidene (**4**) and much higher than that of imidazolin-2-ylidene (**8**). We also studied the complex formation of carbenes with ammonia using MP2/aug-cc-pVTZ level of theory, but the calculations suggest that these carbenes do not form nucleophilic complexes.

The estimated dimerization Gibbs free energy for bis(amino)cyclopropenylidene, considering the general route of dimerization in which a double bond is formed between the two monomers, is 0.7 kcal/mol, similar to that of the Arduengo

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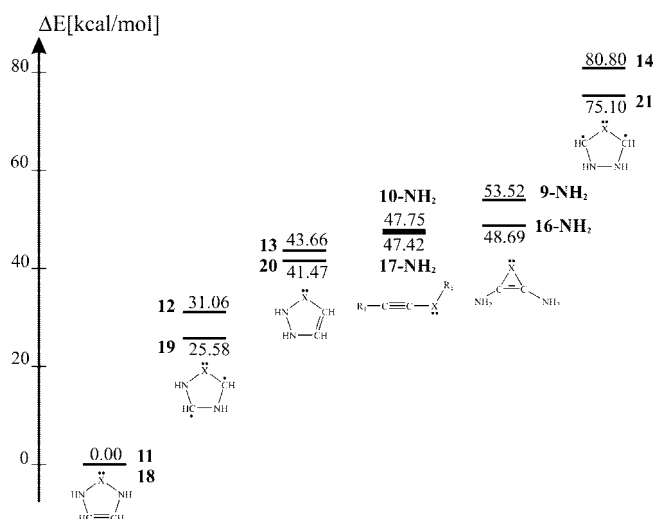
$\Delta E[\mathrm{kcal/mol}]$

Figure 2. Stability order of the $XC_2N_2H_4$ silylene and germylene (X = Si, Ge) derivatives at the CCSD/6-311++G** level. Upper numbers refer to the silylene series, while lower numbers symbolize the germylene species.

carbene (1.20 kcal/mol).[37] In contrast, **1-H** dimerizes in a very exothermic reaction (−39.3 kcal/mol).

In conclusion, although bis(diisopropylamino)cyclopropenylidene is more stable than its parent cyclopropenylidene, it is an unstable compound in a thermodynamic sense. The successful synthesis is based on its high kinetic stability.

II. Stability of 1-Silacyclopropenylidene and 1-Germacyclopropenylidene Derivatives. Silacyclopropenylidene (**f**) and its 14 C_2SiH_2 isomers were theoretically investigated by Frenking et al.,[38] while the infrared spectra of several of these isomers were experimentally observed by Maier et al. using a matrix-spectroscopic technique.[39] The effects of different halogen substituents,[40] the ionization potentials, the electron affinities,[41] and the triplet isomers[42] were also studied for this system. The study of the related germanium compounds involving germacyclopropenylidene (**g**) belongs to a less explored field of chemistry.

The different isomers observed on the SiC_2R_2 and $GeSi_2R_2$ (R = H, NH₂) potential energy surfaces and their relative energies and Gibbs free energies are available in the Supporting Information.

The stability order of the $XC_2N_2H_4$ silylene and germylene (X = Si, Ge) derivatives are plotted in Figure 2. The relative stability and aromaticity of the diazasilole isomers were previously published by Veszprémi and co-workers.[10d] Extending this order with **9-NH₂/16-NH₂** and **10-NH₂/17-NH₂**, the three-membered-ring silylene/germylene are the fourth most stable structure and lie 53.5 and 48.7 kcal/mol higher than the most stable five-membered derivatives.

As it can be seen from Table 2, the total stabilization energy (ΔE_1) is found to be ca. 30 kcal/mol in both diamino-substituted three-membered rings, which is about half of that calculated for **1-NH₂**. This stabilization is significantly smaller than in the corresponding stable five-membered-ring compounds. Similarly to carbenes, the ring effect is high, about double that in **11** or **18**. The most conspicuous observation shown in Table 2 is that

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Table 4. Reaction Energies and Activation Energies for Isomerization (ΔE_{Iso} and $\Delta E^{\ddagger}_{Iso}$), Hydride Ion Addition/Ammonia Complexation (ΔE_{Nuc} and $\Delta E^{\ddagger}_{Nuc}$), and Dimerization (in kcal/mol)

	ΔE_{Iso}	ΔG_{Iso}	$\Delta E^{\ddagger}_{Iso}$	$\Delta G^{\ddagger}_{Iso}$	ΔE_{Nuc}	ΔG_{Nuc}	$\Delta E^{\ddagger}_{Nuc}$	$\Delta G^{\ddagger}_{Nuc}$	ΔE_{dim}	ΔG_{dim}
1-NH$_2$	−14.45	−15.01	65.34	60.51	−33.40	−29.58	9.42	8.93	−12.98	0.69
4	−29.47	−29.73	43.26	39.31	−11.42	−5.42	10.70	11.42	−10.68	1.20
8	−24.52	−24.35	43.53	39.90	−11.13	−4.70	1.54	2.00	−35.46	−19.84
9-NH$_2$	*a*	*a*	68.24	63.85	*b*	*b*			*c*	*c*
11	29.45	26.65	56.15	52.33	*b*	*b*			18.70	31.53
15	34.94	32.20	73.83	69.59	−2.99	6.26			−8.65	6.10
16-NH$_2$	*a*	*a*	65.63	61.14	−2.65	5.33			*c*	*c*

a No stable cyclic product was found. *b* No stable complex was found. *c* No stable dimer was found.

Scheme 8
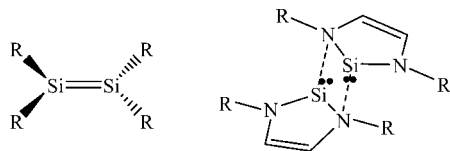
the substituents have a negligible effect in the three-membered rings, while they remarkably stabilize **11** and **18**. The stabilization caused by the delocalization plays an important role, but its effect is extremely diminished by the strain (ca. 38 kcal/mol).

The moderate stability of **9-NH$_2$** and **16-NH$_2$**, compared to the parent carbene **1-NH$_2$**, can be explained with both the reduced aromaticity and ylidic character (Table 3). As a matter of fact, the electron shift is considerably diminished compared to the respective carbene, and the highest contribution (52%) corresponds to the localized structure **A**.

To estimate the kinetic stability of **9-NH$_2$** and **16-NH$_2$**, their isomerization, dimerization, and nucleophilic complexation were considered. The latter is thought to predict the reactivity of heavy carbenes toward a nucleofilic attack.[43] From the calculations (Table 3) it can be recognized that the isomerization of **9-NH$_2$** and **16-NH$_2$** is not a likely process (Scheme 6); it occurs in a multistep process via open-chain intermediates. The products are not stable, and during the optimization they transformed into acyclic species. We found that the activation barriers are prohibitively high for the first, ring-opening step: for **9-NH$_2$** $\Delta G^{\ddagger}_{Iso}$ is 63.85 kcal/mol and $\Delta G^{\ddagger}_{Iso}$ is 61.14 kcal/mol for **16-NH$_2$**.

The immunity of silylenes and germylenes against nucleophilic attack is investigated via their complexation ability with ammonia. We found stable complexes for **15** and **16-NH$_2$**, and their formation is a slightly endothermic process (ΔE_{Nuc} are −2.99 and −2.65 kcal/mol) with positive ΔG_{Nuc} values. Therefore, their formation is not probable.

In accordance with the previous predictions no stable adduct exists between Denk silylene (**11**) and ammonia.[42] Similarly, during the MP2/6-311++G(d,p) calculations no stable Si···NH$_3$ bonded complex of the three-membered silylene (**9-NH$_2$**) has been found.

Generally, two major mechanisms are relevant for the dimerization reaction of silylenes and germylenes; the "classical" disilene formation (Scheme 8, left)[44] and a donor−acceptor adduct that is produced via the overlap of a substituent's lone pair and the p orbital of the divalent center ("bridge" way)

(Scheme 8, right).[45] The relationship between stability and dimerization ability of silylenes was investigated by Oláh et al.[46]

To investigate the dimerization ability of silylenes and germylenes, we calculated their dimerization Gibbs free energies. In every case the kinetically favorable route was considered. Accordingly, compounds **11** and **15**, which proved to be stable experimentally, have ΔG_{dim} values of 31.53 and 6.10 kcal/mol, respectively. No dimer was found in either case of aminodisubstituted three-membered rings (**9-NH$_2$** and **16-NH$_2$**), which supports the stability of these compounds against dimerization.

Conclusion

We studied the kinetic and thermodynamic stability of the recently synthesized bis(diisopropylamino)cyclopropenylidene and its silicon and germanium analogues. The three-membered cyclopropenylidene (**1-NH$_2$**) is less stable by 42.75 kcal/mol than the Arduengo carbene. The main stabilizing factor in **1-NH$_2$** is the significant π electron shift from the amino substituents, via a nonaromatic ylidic structure. It turns out that **1-NH$_2$** is stable against nucleophilic complexation, hydride ion addition, structural isomerism, and dimerization reactions. According to the data, its high kinetic stability is comparable with that of the known stable, five-membered-ring carbenes. The rational explanation for the synthesizability of bis(diisopropylamino)cyclopropenylidene is its substantial kinetic stability.

The silicon (**9-NH$_2$**) and germanium (**16-NH$_2$**) analogues show lower stabilization than **1-NH$_2$**. The three-membered silicon and germanium species are less stable by 49−53 kcal/mol than the corresponding five-membered rings. In these molecules the localized divalent structure is dominant and both the π conjugation and aromaticity are weaker than in **1-NH$_2$**. Investigating their reactions we found that, however, both amino-disubstituted three-membered silylene and germylene have high kinetic stability. According to our results, in contrast to the general tendency of stability order, in cyclopropenylidene analogues stability decreases in the sequence carbene/silylene/germylene. Nevertheless, our results suggest that due to the appropriate kinetic stability, the silicon and germanium derivatives can be promising targets for synthetic chemists.

Supporting Information Available: Optimized geometries at the B3LYP/cc-pVTZ, MP2/cc-pVTZ, and CCSD/6-311++G** levels and relative energies are available free of charge via the Internet at http://pubs.acs.org.

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