J. Am. Chem. Soc. **1996,** *118,* 2039−2046

Electronic Structure of Stable Carbenes, Silylenes, and Germylenes

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Received August 9, 1995. Revised Manuscript Received December 15, 1995⊗

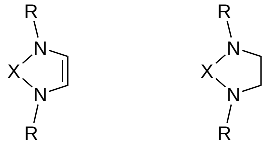
Abstract: Quantum mechanical ab initio calculations at the MP4/6-311G(d,p)//MP2/6-31G(d) level of theory have been carried out for the parent compounds of the stable carbenes imidazol-2-ylidene (**1**) and the silylene (**8**) and germylene (**9**) analogues. The energies of hydrogenation of **1**, **8**, and **9** and the structures of the saturated derivatives **2**, **10**, and **11** have also been calculated. The analysis of the electronic structure shows clearly that the higher stability of **1** than that of **2** is caused by the enhanced $p_\pi - p_\pi$ delocalization. However, a strong π-donor stabilization of the carbene p_π orbital by the nitrogen lone pairs is found already in the C−C-saturated imidazolin-2-ylidene **2**. This explains why the *N*-mesityl derivative of **2**, which is sterically protected against dimerization, could recently be synthesized. Also the silylene and germylene systems **8** and **9** are stabilized by enhanced $p_\pi - p_\pi$ delocalization. The method of electron density mapping as used by Arduengo et al. (*J. Am. Chem. Soc.* **1994**, *116*, 6812) as evidence for negligible π-delocalization in **1** is not very useful, because it predicts negligible π-delocalization even in pyridine and pyrrole. Energetic and magnetic criteria suggest that the cyclic electron delocalization in **1** has some aromatic character.

1. Introduction

One of the most astonishing results of organic structural chemistry in the recent past has been the successful isolation of a stable carbene reported by Arduengo and co-workers.[1] The 1,3-diadamantyl derivative of the imidazol-2-ylidene **1** can easily be handled under an inert atmosphere even at room temperature. In the following years a variety of stable carbenes in the imidazol-2-ylidene series such as the 1,3-dimethyl-substituted derivative of **1** were synthesized, which shows that steric effects are not the dominant factor for the high stability of these compounds.[2] Also the analogous silylene[3] and germylene[4] compounds have been prepared in the meantime.

The exciting chemistry of stable (isolable) carbenes has not come to an end with the synthesis of derivatives of **1** (Scheme 1). Very recently, Arduengo and co-workers[5] succeeded in isolating a derivative of the related C−C-saturated imidazolin-2-ylidene **2**, which has earlier been studied by Wanzlick.[6] The diaminocarbene **2** with R = mesityl melts without decomposition at 107−109 °C and is stable in the absence of oxygen and moisture.[5] Prior to this work it was believed that unsaturation in the imidazole ring is required to produce a stable diaminocarbene. In the report about the synthesis of the mesityl derivative of **2**, it was said, however, that π-interactions “undoubtedly enhance the stability of the unsaturated compounds over the saturated analogues”.[5] It follows that π-delocalization still appears to be an important factor to stabilize carbenes, although cyclic delocalization is not a conditio sine qua non for isolating such species. Wanzlick[6] recognized already the stabilization due to π-delocalization, which has later been modeled by Gleiter and Hoffmann using EHT calculations.[7]

Scheme 1. Investigated Imidazol-2-ylidenes **1**, **8**, and **9** and Imidazolin-2-ylidenes **2**, **10**, and **11**.



1: X = C; R = H
8: X = Si; R = H
9: X = Ge; R = H

2: X = C; R = H
10: X = Si; R = H
11: X = Ge; R = H

The peculiar stability of **1** has prompted several theoretical studies of the electronic structure of stable carbenes. Although the theoretical work was carried out with the believe that analogues of **2** cannot be isolated, the results are still important. The first ab initio investigation was reported by Dixon and Arduengo.[8] These authors reported Hartree−Fock and two-configurational SCF (TCSCF) calculations of the lowest lying singlet and triplet states of the parent imidazol-2-ylidene (**1**) and its protonated form. The analysis of the wave function of **1** and a comparison with the carbene center of CF$_2$ showed that the two carbenes are very similar. It was concluded that C−N π-interaction in **1** is *not* a dominant factor “...although such an interaction undoubtedly contributes some stability...”.[8] A subsequent analysis of the wave function of the 1,3-dimethyl derivative of **1** at the MP2/6-311++G(d,p) level of theory by Cioslowski[9] even came to the conclusion that the π-donation plays only a minor role, and that the unusual stability of the singlet carbene is related to the substantial σ-back-donation from the carbenic carbon atom to the adjacent nitrogen atoms. An

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

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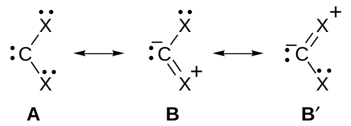
explanation for the difference in the stability between **1** and **2** was not given, however.

Another theoretical analysis of the C−C-unsaturated carbenes **1** and the saturated analogues **2** using high-level ab initio methods for calculating correlation energy (MP2, MP3, CISD+Q, CCSD(T)) was published in 1994 by Heinemann and Thiel.[10a] They found that the p_π population at the carbene carbon atom of **1** is 30% higher than that of **2**, which indicates that cyclic delocalization in the unsaturated carbene is clearly enhanced.[10a] The same authors published more recently a theoretical study about the structure of the corresponding silylenes and germylenes.[10b] The analysis of the electronic structure revealed that "electronic stabilization via $p_\pi-p_\pi$ delocalization is an important bonding feature in aminosubstituted silylenes and germylenes". In contrast to the homologous aminocarbenes, however, aminosilylenes and -germylenes were found to be thermodynamically stable with respect to the 1,2-rearranged isomers.[10b]

Three other theoretical studies were published in 1994 by Arduengo et al.[11−13] which were based on density functional theory (DFT). In the first work the electron density distribution of the perdeuterated tetramethyl derivative of **1** was compared with experimental results, which showed very good agreement between theory and experiment.[11] A particular focus of this study was the question whether **1** is a true carbene or whether ylidic resonance forms are important. Because the plot of the π-electron density with an outermost contour line 0.65 e Å^{-3} lying 0.7 Å above the molecular plane showed no electron density at the carbene carbon atom, the authors concluded that "π-delocalization does not play a dominant role in stabilization of the imidazol-2-ylidenes".[11] It is interesting to note that the plot using the chosen parameters showed a low density for the π-electrons of the C−C double bond, which means that even a truely π-bonded carbon atom has a low electron density at a distance of 0.7 Å above the molecular plane.[11]

The second study published by Arduengo et al.[12] reported experimental and theoretical results about the electronic structure of the *tert*-butyl derivative of **1** and the silicon and germanium analogues. The theoretical part of this study is particularly interesting, because for the interpretation of the photoelectron spectra of the carbene/silylene/germylene series Koopman's theorem[14] in conjunction with Kohn−Sham orbitals[15] was applied for the assignment of the PE bands. The results were very surprising. The highest occupied molecular (Kohn−Sham) orbital (HOMO) of the carbene was the in-plane lone pair on the carbene carbon. This is in contrast to the results of the ab initio calculations by Heinemann and Thiel,[10] who found that the Hartree−Fock orbitals of the parent compound **1** give a delocalized π-orbital as the HOMO. For the silylene and germylene the highest occupied Kohn−Sham orbital has π-symmetry.[12] Another surprising feature of the Kohn−Sham orbitals was the shape of the highest lying π-orbital of the three compounds. The occupation of the formally "empty" p_π orbital at the ene center *increases* from carbene to silylene to germylene. There is a gradual shift toward the formation of a p_π orbital C < Si < Ge. This is opposite to the trend of the electronegativity of the atoms. It is also opposite to the general trend of the π-bonds between elements of the first full and higher rows of the periodic system.[16] In a recent ab initio study of the rotational barrier of the allyl cations $H_2CCHXH_2^+$ (X = C, Si, Ge, Sn, Pb) we could show that the degree of π-bonding and the rotational barrier of the C−X bond shows the order C ≫ Si > Ge > Sn > Pb.[17] Although this result was found for cations, it is in general agreement with chemical experience that conjugation in neutral systems shows the same trend. Arduengo et al.[12] suggested a "chelated atom" model for the silylene and germylene to account for the calculated trend in the π-electron density.

Scheme 2. Most Important Resonance Forms of π-Donor-Stabilized Carbenes (**A**, Carbene Form; **B** and **B′**, Ylide Forms)



The third paper by Arduengo et al. reported about a combined experimental/theoretical study of the chemical shielding tensor of **1**.[13] It was shown that the NMR chemical shifts of **1** were reasonably well reproduced at the HF/IGLO[18] and HF/LORG[19] level of theory if large basis sets were employed. The magnitude of the least-shielded tensor component was calculated poorly at the HF level, although the magnitude for the other components was in reasonable agreement with experiment.[13] It was demonstrated that a correlated treatment of the chemical shielding tensor is necessary for giving accurate results. Because the shielding tensor σ_{11} of **1** was found to be negative, it was concluded that the resonance structure **A** dominates over the fully π-bonded ylidic resonance structure **B** (Scheme 2).

After this study was completed, we learned about another theoretical investigation of imidazol-2-ylidenes and their silicon analogues by Heinemann, Müller, Apeloig, and Schwarz.[20] These workers found also that π-donation by the lone pairs of the nitrogen atoms is an important stabilizing factor for these compounds.

The previous theoretical studies give different explanations why the carbenes **1** can be isolated as stable compounds. The classical explanation considers the *thermodynamic* stabilization of the carbenes by electron delocalization of the six π-electrons into the formally "empty" p_π AO of C^2 as the dominating effect. In light of the recent discovery that the C−C-saturated analogue **2** is also a stable molecule,[5] this argument must be modified by saying that the electron donation of the neigboring lone pairs is sufficient (but necessary and still dominating) and that the delocalization of the six π-electrons in **1** provides merely an additional but not a necessary thermodynamic stabilization. In contrast to the thermodynamic arguments stands the *kinetic* reasoning given by Arduengo and co-workers. These workers argue that "the $C^4{=}C^5$ double bond is critical in amassing the necessary electron repulsion to deprive the carbene of electrophilic reactivity".[11] The stability of the C−C-saturated carbenes was rationalized by saying that "the bulky mesityl groups at nitrogen in **2** probably provide some measure of kinetic stability...".[5]

The conflicting interpretation of the electronic structure of the carbene **1** and the related silylene and germylene species

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prompted us to carry out a detailed ab initio study of the structure and peculiar stability of these compounds. In particular the importance of the π-delocalization for the stability of the compounds needs to be addressed in detail. Because of the recent report[5] about the stability of the mesityl derivative of **2**, we analyze also the difference in the π-interactions of C^2 with the neighboring nitrogen atoms between **1** and **2**. We present results of ab initio calculations of the geometries, barriers for intramolecular rearrangement, and hydrogenation energies of the carbene, silylene, and germylene parent compounds of the imidazol-2-ylidene and the imidazolin-2-ylidenes series and for related molecules.

We will focus on the following questions: (i) What difference in the electronic structure between the C−C-unsaturated carbenes/silylenes/germylenes and their saturated analogues is the reason for the observed stability difference? (ii) Is there aromatic stability in the 6π-electron system **1**? (iii) What structural properties of **1** and **2** are essential to isolate stable carbenes and which other carbenes might still be expected to be isolable as stable species in the future? (iv) What is the difference between the carbene **1** and the silicon and germanium analogues **8** and **9**?

Some aspects of the present topic have been addressed in the previous studies[8−13,20] and need not be discussed in detail. This concerns the geometries of the molecules and the discussion of the singlet and triplet states of the carbenes. There is general agreement that the stability of the molecules is related to the singlet ground state of the amino-substituted carbenes. However, this does not explain the peculiar stability of the derivatives of **1**.

The electronic structure of the molecules is examined using the natural bond orbital (NBO) partitioning scheme.[21] We are well aware that the interpretation of the electronic structure in terms of bonding models is determined by the method used for the analysis of the wave function. It is important to compare the results of different interpretations if they give conflicting results. Therefore, we present also a critical examination of the previous analyses of the electronic structure presented by Cioslowski[9] and by Arduengo et al.[11−13]

2. Methods

The geometries of the molecules have been optimized at the full MP2 level (Møller−Plesset perturbation theory terminated at second order)[22] using a 6-31G(d) basis set for carbon, hydrogen, oxygen, nitrogen, and silicon.[23] For Ge a relativistic pseudopotential with a (31/31/1) valence basis set was employed, which has the same valence shell quality as the 6-31G(d) basis set.[24] Higher-level energy calculations were carried out for some molecules at the MP4 level using a 6-311G(d,p) basis set.[25] Energies are discussed at the MP4/6-311G(d,p)//MP2/6-31G(d) level of theory, unless otherwise noted. Zero-point vibrational energies are not included in the calculated energies, because we are mainly concerned with the effects due to the different electronic structures.

The nature of the stationary points was determined by calculating the Hessian matrix. The program packages Gaussian 92[26a] and Turbomole[26b] were used for this study. The magnetic susceptibilities have been calculated with the direct IGLO program using basis set II.[18]

3. Results and Discussion

Figure 1 shows the optimized geometries of the investigated compounds. The energies are listed in Table 1.

The theoretically predicted geometry of the 1,3-dimethylimidazol-2-ylidene **1(Me)** at MP2/6-31G(d) is in very good agreement with the observed structure of the 1,3,4,5-tetramethyl derivative of **1** (Figure 1).[2] The calculated geometries of **1(Me)** and the parent imidazol-2-ylidene **1** are quite similar. Thus, the electronic structure of **1** may be used to analyze the reasons why 1,3-disubstituted derivatives of **1** are stable compounds. Figure 1 shows also the optimized geometry of the saturated carbene **2** and the experimental geometry of the mesityl derivative of **2**.[5] The theoretical and experimental values are in very good agreement. As expected, the $C^4{-}C^5$ and $N^3{-}C^4$ bonds of **2** are longer than those in **1**. The X-ray structure analysis and the calculations show that the angle at the carbene center $N^1{-}C^2{-}N^3$ is larger in **2** than in **1**, and that the bond between the carbene carbon atom and nitrogen $C^2{-}N$ in **2** is slightly *shorter* than in **1**. This will be important for the discussion of the differences between the electronic structures of the two molecules.

Figure 1 shows also the optimized geometries of the imidazoles **1a** and **2a**. The isomer **1a** is calculated as 27.0 kcal/mol more stable than **1**, while **2a** is 23.0 kcal/mol more stable than **2**. It follows that the thermodynamic stabilities of **1** and **2** toward tautomerization are of comparable magnitude. Also kinetic reasons can be excluded as stability factor. The barrier for rearrangement **1** → **1a** is nearly the same (44.1 kcal/mol) as for **2** → **2a** (44.7 kcal/mol). We want to point out, however, that the tautomerizations **1** → **1a** and **2** → **2a** are *not* the crucial reactions which determine the stability of these compounds.

A reaction which is more relevant for the stability of the carbenes is the nucleophilic addition reaction. We calculated the transition states for the addition of a hydride anion to **1** and **2**. Figure 1 shows the optimized structures of **1(H$^-$)TS** and **2(H$^-$)TS** at MP2/6-31++G(d,p). The transition state for the addition to the CC-saturated carbene is "earlier" than to the unsaturated carbene. The $C^2{-}H$ distance of the incipient bond of **2(H$^-$)TS** is 2.030 Å, while it is 1.928 Å for **1(H$^-$)TS**. The addition of the hydride anion to **1** has a higher barrier (13.2 kcal/mol) and is less exothermic (−8.4 kcal/mol) at MP2/6-31++G(d,p) than the H^- addition to **2**. The transition state **2(H$^-$)TS** is only 4.0 kcal/mol higher in energy than the educts, and the reaction is −27.7 kcal/mol exothermic.[36] This indicates that the CC-unsaturated carbene **1** is thermodynamically *and* kinetically more stable with respect to an attack by a nucleophile than the saturated carbene **2**, which is in agreement with experimental observations. The bond lengths of the incipient $C^2{-}H$ bonds of **1(H$^-$)TS** and **2(H$^-$)TS** are in agreement with the Hammond postulate, which suggests that a more exothermic reaction should have an earlier transition state. The transition states **1(H$^-$)TS** and **2(H$^-$)TS** look quite similar, except for the $C^2{-}H$ bond lengths.

The carbenes **1** can be isolated as stable compounds, because the dimerization of the compounds yielding the olefines is

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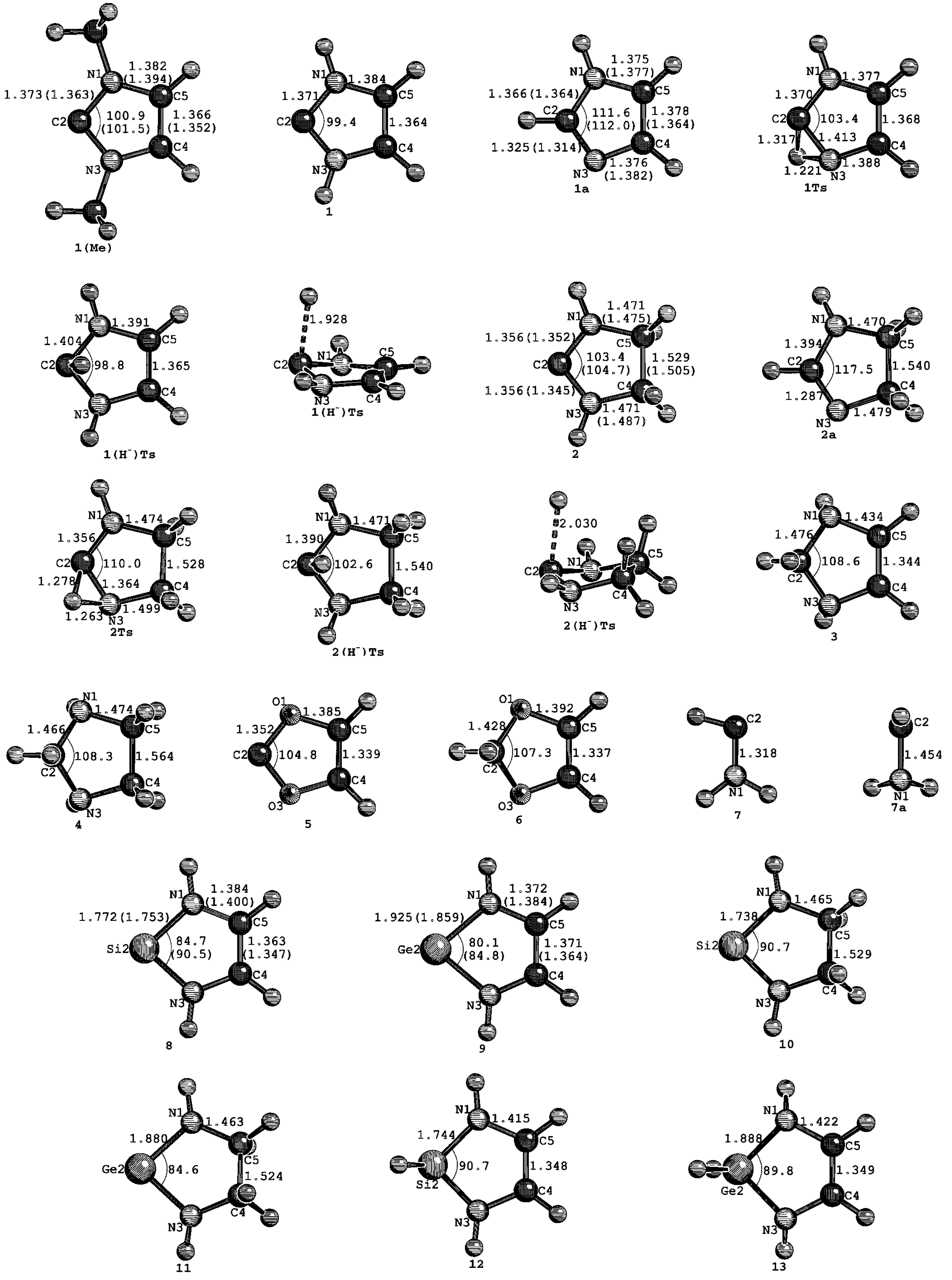

Figure 1. Optimized geometries at MP2/6-31G(d) (MP2/ECP/31/31/1 for Ge) for structures **1**−**13**. The geometries of **1(H⁻)TS** and **2(H⁻)TS** have been optimized at MP2/6-31++G(d,p). Bond lengths are given in angstroms. Experimental values for **1(Me)** (taking the 1,3,4,5-tetrametyl derivative of **1**),[2] **1a**,[35] the *N*-mesityl derivative of **2**,[5] and the *N*-*tert*-butyl derivatives of **8**[3] and **9**[4] are given in parentheses.

Table 1. Total Energies E_{tot} (au) and Relative Energies E_{rel} (kcal/mol)[a]

		MP2/6-31G (d)			MP4/6-311G (d,p)[b]	
no.	sym	E_{tot}	E_{rel}	i	E_{tot}	E_{rel}
1	C_{2v}	−225.469 86	0.0	0	−225.744 80	0.0
1a	C_s	−225.522 14	−32.8	0	−225.787 75	−27.0
1Ts	C_1	−225.398 39	44.8	1	−225.674 60	44.1
1 (Me)	C_{2v}	−303.800 48		0		
1 (H^-) Ts	C_s	−226.010 27[c]		1		
2	C_2	−226.635 44	0.0	0	−226.938 57	0.0
2a	C_1	−226.679 65	−27.7	0	−226.975 27	−23.0
2Ts	C_1	−226.563 32	45.3	1	−226.867 31	44.7
2 (H^-) Ts	C_s	−227.206 92[d]		1		
3 (cis)	C_s	−226.646 14	0.0	0	−226.945 73	0.0
3 (trans)	C_1	−226.646 68	−0.3		−226.946 40	−0.4
4 (cis)	C_s	−227.844 96	0.0		−228.169 60	0.0
4 (trans)	C_1	−227.843 32	1.0	0	−228.167 39	1.4
5	C_{2v}	−265.119 89		0	−265.401 32	
6	C_s	−266.328 08		0	−266.630 29	
7	C_s	−94.248 21	0.0	0	−94.388 81	0.0
7a	C_s	−94.161 16	54.6	1	−94.305 14	52.5
8	C_{2v}	−476.560 92		0	−476.944 02	
9[d]	C_{2v}	−191.313 87		0	−191.371 16	
10	C_2	−477.727 13		0		
11[d]	C_2	−192.472 46		0		
12	C_s	−477.712 87		0	−478.127 32	
13[d]	C_s	−192.422 51		0	−192.485 18	
CH_2 ($^1A_1$)	C_{2v}	−38.970 24		0	−39.049 26	
CH_4	T_d	−40.333 49		0	−40.424 74	
SiH_2 ($^1A_1$)	C_{2v}	−290.072 01		0	−290.260 98	
SiH_4	T_d	291.311 80		0	−291.52 616	
GeH_2 ($^1A_1$)[d]	C_{2v}	−4.859 26		0	−4.881 85	
GeH_4[d]	T_d	−6.06021		0	−6.08457	
H_2	$D_{\infty h}$	−1.144 14		0	−1.167 72	

[a] i gives the number of imaginary frequencies. [b] Using geometries optimized at MP2/6-31G (d). [c] MP2/6-31++G(d,p). [d] For germanium a relativistic ECP with a valence basis set of (31/31/1) has been used.[24]

Table 2. Results of the NBO Analysis at MP2/6-31G (d)[a]

no.	p_π (X^2)	%N ($X^2-N)_\sigma$[b]	q (X^2)	q (N)[c]
1	0.67	66.9	0.06	−0.59
1a	1.03	61.3	0.15	−0.56
2	0.53	66.7	0.17	−0.68
3	1.21	60.9	−0.08	−0.71
4	1.15	60.4	−0.08	−0.69
5	0.46	74.3	0.44	−0.49
6	1.14	68.7	0.22	−0.56
7	0.42	66.9	−0.13	−0.77
7a	0.10	65.2	0.11	−1.02
8	0.54	85.0	0.87	−1.00
9	0.63	85.1	0.78	−0.94
10	0.33	85.0	1.05	−1.12
11	0.33	83.9	1.02	−1.09
12	0.69	81.5	1.58	−1.09
13	0.67	78.5	1.43	−1.03

[a] p_π (X^2) gives the occupation of the p_π orbital at carbon, silicon, and germanium, respectively. %N($X^2-N)_\sigma$ gives the polarity of the X^2-N σ-bond. $q(X^2)$ and q(N) give the partial charges at X^2 and nitrogen, respectively. [b] For **5** and **6** the values refer to the C^2-O bonds. [c] For **5** and **6** the values refer to the oxygen atoms.

energetically not a favorable process. Arduengo et al.[11] consider the electron density amassed by the double bond as crucial for the stability of the carbenes. Heinemann and Thiel studied the thermodynamic stability of **1** and **2**. These workers estimated the C═C bond dissociation energy of the dimer of **1** using a model suggested by Carter and Goddard[27] as only 1 kcal/mol, while the estimated C═C bond dissociation energy of the dimer of **2** was 31.2 kcal/mol.[10a] Calculations at MP2/TZ2P//HF/TZ2P gave a similar difference (32.8 kcal/mol) for the C═C bond of the dimers, the dimer of **1** being less stable than the dimer of **2**.[10a] The calculations supported the model[27] that the bond strength of the dimer is mainly determined by the monomer properties.

The thermodynamic stability of carbenes can also be taken from the heats of hydrogenation. The higher stability of **1** over **2** is revealed by the calculated heats of hydrogenation of the carbene carbon atom yielding the compounds **3** and **4**[37] (Figure 1), respectively:

$$\mathbf{1} + H_2 \rightarrow \mathbf{3} \qquad \Delta E = -20.8 \text{ kcal/mol} \tag{1}$$

$$\mathbf{2} + H_2 \rightarrow \mathbf{4} \qquad \Delta E = -39.7 \text{ kcal/mol} \tag{2}$$

The heat of hydrogenation of ($^1A_1$) CH_2 calculated at the same level of theory (MP4/6-311G(d,p)//MP2/6-31G(d)) yielding CH_4 is $\Delta E = -130.4$ kcal/mol, which is in excellent agreement with the experimental value $\Delta E = -130.9$ kcal/mol.[28] It follows that both carbenes **1** and **2** are already significantly stabilized by the two amino substituents. It is important to recognize that, although the difference in the calculated heats of hydrogenation between the two carbenes is small compared with the difference to the heat of hydrogenation of methylene, **1** is more stable than **2**. Then what is the difference in the electronic structure which causes the significantly reduced reactivity of **1** over **2**?

Table 2 shows the results of the NBO analysis[21] for the investigated compounds. The degree of π-delocalization into the formally empty p_π AO of the carbene carbon atom is given by the $p_\pi(C^2)$ occupancy. The calculations show that **1** has an occupancy $p_\pi(C^2) = 0.67$ electrons, which is larger than in **2** ($p_\pi(C^2) = 0.53$). This is remarkable because the C^2-N bonds of **1** are slightly *longer* than those of **2** (Figure 1). For comparison, the imidazole isomer **1a** has $p_\pi(C^2) = 1.03$. An explanation for the trend in the C^2-N bond lengths of **1** and **2** is given below.

The calculated charge distribution of **1** and **2** at C^2 is in agreement with the $p_\pi(C^2)$ occupancy (Table 2). The carbene carbon atom of **1** has a positive charge of 0.06, while $q(C^2)$ of **2** is 0.17. If the six π-electrons of the five-membered ring were equally distributed over the ring atoms, each atom would have 1.20 π-electrons. A value of $p_\pi(C^2) = 0.67$ for **1** means that the p_π occupancy is 55.8% of a perfectly delocalized π-system. In **2**, there are four π-electrons for three atoms in the allyl− anion system. A perfect delocalization would mean that 1.33 electrons should be in each p_π orbital. The calculated value of $p_\pi(C^2) = 0.53$ means that the p_π occupancy is only 39.8% of the theoretical value. Thus, the π-delocalization in **1** is clearly enhanced over **2**. The NBO analysis shows also that the polarity of the C^2-N σ-bonds is nearly the same in **1** (66.9% at N) and **2** (66.7% at N). It follows that the difference of the σ-electron distributions between **1** and **2** is negligible, while the π-electron distribution of **1** has a clearly higher weight at the carbene carbon atom than that of **2**. This is opposite to the conclusion made by Cioslowski, who suggested that there is only a marginal π-donation from the nitrogens to the carbon atom.[9] This conclusion was made by inspection of the polarities of the σ and π localized natural orbitals (LNO) of **1(Me)**. Although the π-orbitals of the C−N bonds of **1** and **2** are indeed more polarized toward nitrogen than the σ-orbitals, the *trend*

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(27) Carter, E. A.; Goddard, W. A. *J. Phys. Chem.* **1986**, *90*, 998.

(28) This value is derived from the experimental heats of formation ΔH_f(0 K) of ($^3B_1$) CH_2 and CH_4: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. The ZPE data to convert the ΔH_f(0 K) values to ΔE were taken from MP2/6-31G(d) calculations. The ($^3B_1$) → ($^1A_1$) excitation energy for CH_2 was taken from Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.

of the σ- and π-polarization shows clearly that the difference between **1** and **2** is solely due to the N → C^2 π-donation.

If the polarization of the carbene σ-bonds was responsible for the higher stability as suggested by Cioslowski,[9] the dioxocarbene **5** (Figure 1) should be even more stable than **1**. Table 2 shows that the C^2−O bond of **5** has an even higher polarity (74.3% at O) than the C^2−N bond of **1**. However, the p_π occupancy at C^2 is only 0.46 electrons (Table 2). The calculated heat of hydrogenation at C^2 yielding **6** (Figure 1) indicates that **5** should have a comparable reactivity as **2**:

$$\mathbf{5} + H_2 \rightarrow \mathbf{6} \qquad \Delta E = -38.4 \text{ kcal/mol} \qquad (3)$$

While the p_π occupancy at C^2 is higher in the unsaturated carbene **2** than in **1**, the difference is not dramatical. The NBO analysis and the calculated heats of hydrogenation indicate that the electrophilic reactivity at the carbene carbon atom of **2** should not be much higher than that of **1**. This explains the success of the recently reported synthesis and isolation of the *N*-mesityl derivative of **2**.[5] Since numerous N-substituted analogues of **2** spontaneously dimerize when generated in solution,[6,29] while the related N-substituted species **1** are stable,[1,2] the bulky mesityl groups apparently hinder the dimerization of the carbene. The X-ray structure analysis of the C−C-saturated carbene shows that the aryl rings of the mesityl substituents are nearly orthogonal to the imidazole ring and that the mesityl substituents are clearly in a position which would cause severe steric repulsion in a hypothetic dimer.[5] It seems that the steric effect of bulky substitutents at the α-position of a carbene can compensate for the reduced electronic stabilization by the nitrogen atom, as indicated by the NBO analysis.

A point which needs to be addressed concerns the C^2−N bond lengths of **1** and **2**. **2** has slightly shorter C^2−N bonds than **1**, although the NBO analysis indicates that the C^2−N bonds of **1** have a higher π-character than those of **2**. The shorter C^2−N bonds of **2** as compared to those of **1** can be explained by the change in the hybridization of the C^2−N σ-bonds at C^2. The C^4−C^5 single bond of **2** is clearly longer than the C^4−C^5 double bond of **1** (Figure 1). This leads to an opening of the N^1−C^2−N^3 angle, yielding a higher percent s character for the C^2−N bonds of **2** (the NBO analysis gives 38.8% s at C^2) than those of **1** (NBO: 36.6% s at C^2). Additional factors which support shorter C^2−N bonds in **2** are the release of ring strain and the calculated charge distribution, which indicates higher Coulomb attraction between C^2 and nitrogen in **2** than in **1** (Table 2).

The conclusion that the significant π-delocalization is the dominant reason for the enhanced stability of **1** compared with that of **2** stands in contrast to the results of Arduengo et al. who employed the method of electron density mapping for analyzing the electronic structure of the tetramethyl derivative of **1**.[11] These authors showed that the theoretical and experimental valence electron density 0.70 Å above the molecular plane using intervals of 0.05 e $Å^{-3}$ and an outermost contour level of 0.65 e $Å^{-3}$ vanishes in the region of the C^2−N bond.

In order to examine the method of density mapping chosen by Arduengo et al.,[11] we calculated the electronic structure of the aminocarbene **7** and plotted its electron density distribution at the MP2/6-31G(d) level.[30] Figure 1 shows the optimized geometry of planar **7** and the transition state for rotation around the C−N bond **7a**. The calculated C−N bond length of **7** is 1.318 Å. The transition state **7a** has a much longer C−N bond of 1.454 Å. The shorter C−N bond of **7** has a significant π-contribution due to the N → C charge donation from the nitrogen lone pair into the formally empty carbon p_π AO. Table 2 shows that in **7** the p_π AO of carbon has an occupancy p_π = 0.42 electrons, while in **7a** it is only p_π = 0.10 electrons. Figure 2 displays the electron density distribution of **7** in the molecular plane (Figure 2a) and 0.70 Å above the molecular plane (Figure 2b), using the same parameters as chosen by Arduengo et al.[11] (intervals of 0.05 e $Å^{-3}$, outermost contour level 0.65 e $Å^{-3}$). *The contour line diagram of Figure 2b suggests that there is no significant π-electron distribution between the nitrogen and carbon atom of 7!* Even more striking is the result for pyridine. Figure 2 shows also the electron density distribution for pyridine 0.7 Å above the molecular plane. Following the reasoning by Arduengo et al.,[11] there would be no significant π-delocalization even among the carbon atoms of pyridine! Since the density mapping is a very sensitive method which may depend on the number of π-electrons per center, we calculated also the electron density distribution of pyrrole, which has six π-electrons in a five-membered ring. The result is shown in Figure 2d. Again, the contour line diagram shows no π-electron distribution between N and C^2 and between C^3 and C^4. We conclude that the method of density mapping is not very reliable for the indication of electron delocalization.

In order to investigate the degree of aromaticity in the π-delocalized carbene **1**, we calculated the magnetic susceptibilities χ of **1**, **1a**, and **2**. It has been shown that the anisotropy of the magnetic susceptibility $\Delta\chi$ given by the difference of the in-plane and out-of-plane components can be used as an indication for a ring current.[31] Table 3 shows the calculated values for $\Delta\chi$ at the IGLO/II level[18] for **1**, **1a**, **2**, and pyridine. The latter has been included as a reference. The $\Delta\chi$ values show a significant anisotropy for **1**, which is only slightly lower than for imidazole **1a** (Table 3). The calculated $\Delta\chi$ value for **2** is significantly below the results for **1** and **1a**. Using the theoretical $\Delta\chi$ value for pyridine (50.27) as a reference it can be seen that **1** and **1a** have partial aromatic character. This result may be criticized, because the HF/IGLO calculations have been shown to reproduce the magnetic shielding tensors of **1** only poorly.[13] Although the magnetic susceptibility χ is calculated in a different way than the NMR chemical shielding,[32] it seems possible that the absolute values for χ are not very accurate. However, since we compare the differences of the results for **1**, **1a**, and **2**, some error cancelation may occur. The *difference* in the $\Delta\chi$ values at HF/IGLO should be reliable.

The next topic concerns the comparison of the carbene/silylene/germylene series **1**, **8**, and **9**. Figure 1 shows the calculated geometries of the silylene **8** and germylene **9**. We will not discuss the geometries and bonding features of **8** and **9** in detail, because this has been done already by Heinemann et al.[10b] Table 2 shows that the p_π occupancy at Si and Ge is quite high (0.54 electrons for **8**, 0.63 electrons for **9**). Like the carbenes **1** and **2**, the p_π occupancy at Si and Ge is significantly lower in the respective saturated silylene **10** and **11** (Table 2).

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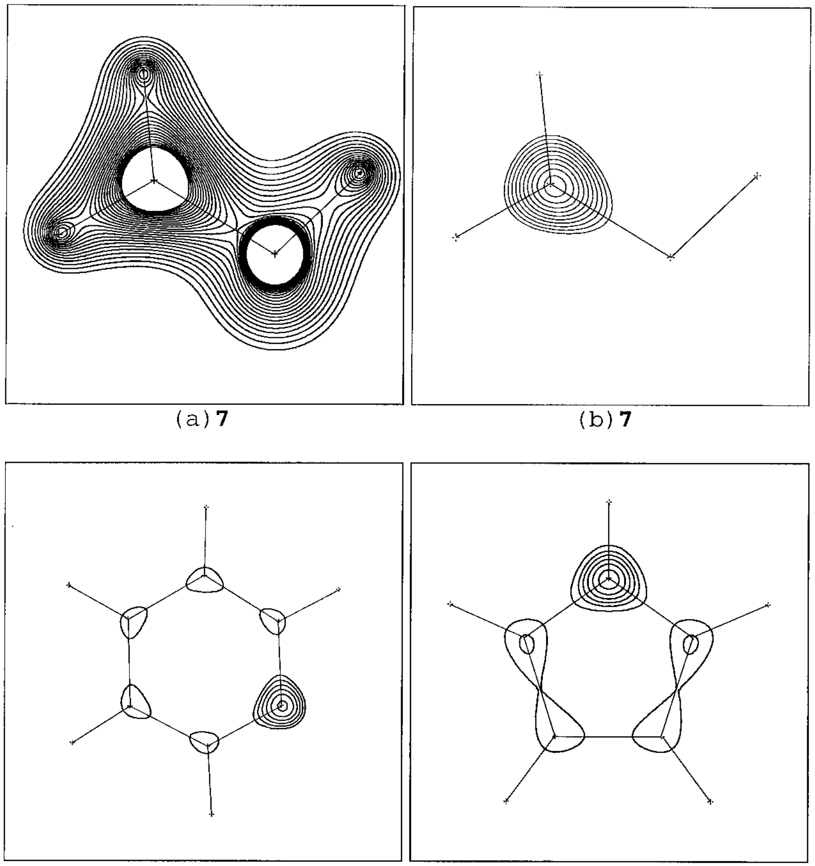
(29) (a) Schönherr, H.-J.; Wanzlick, H. W. *Chem. Ber.* **1970**, *103*, 1037. (b) Schönherr, H.-J., doctoral thesis, Technische Universität Berlin, 1970. (c) Schikora, E. doctoral thesis, Technische Universität Berlin, 1961.

(30) We also calculated the electron density distribution for **1** at MP2/6-31G(d) and plotted the contour line diagram in the molecular plane and 0.7 Å above the molecular plane using the same cutoff parameters as Arduengo et al.[11] The plots were practically the same as shown by these authors. The results are not very dependent on the size of the basis set and the presence of the core-electron density. The density maps at MP2/6-311G-(d,p) with and without the core electrons are practically undistinguishable from the MP2/6-31G(d) plots.

(31) (a) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337. (b) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.

(32) The NMR magnetic shielding is calculated as derivative of the energy with respect to (i) the magnetic moments of the nuclei and (ii) the external magnetic field. The shielding conctant is given as an *asymmetric* 3 × 3 tensor. The magnetic susceptibility is calculated as second derivative of the energy with respect to the external field. The result is a *symmetric* 3 × 3 tensor.


(a) **7**

(b) **7**

(c) **Pyridine**

(d) **Pyrrole**

Figure 2. Contour line diagrams of the electron density distribution at MP2/6-31G(d): (a) in the molecular plane of **7**; (b) 0.7 Å above the molecular plane of **7**; (c) 0.7 Å above the molecular plane of pyridine; (d) 0.7 Å above the molecular plane of pyrrole. The outermost contour line indicates a density of 0.65 e $Å^{-3}$; the increments between adjacent lines are 0.05 e $Å^{-3}$.

Table 3. Calculated Reaction Energies ΔE (kcal/mol) of Reaction 8 at MP2/6-31G (d) and Calculated Anisotropies of the Magnetic Susceptibility $\Delta\chi$ (ppm cgs) at IGLO/II

	ΔE (reaction 8)	$\Delta\chi$
1	27.8	27.71
1a	32.8	31.25
2		9.00
8	27.4	20.79
9	32.1	
pyridine	48.1	50.27

It follows that p_π–p_π delocalization is also operative in **8** and **9**. This is in agreement with the conclusion made by Heinemann and Thiel that p_π–p_π delocalization is an important bonding factor in amino-substituted silylenes and germylenes.[10b] The calculated p_π occupancy at Si and Ge in **8** and **9** is *lower* than $p_\pi(C^2)$ of **1**.[33] This is in agreement with theoretical evidence[16,17] that π-bonding between elements of the first full row of the periodic system is stronger than between first-row and heavier atoms. The opposite conclusion was made by Arduengo et al.[12] These workers showed the contour line diagrams of the highest lying Kohn–Sham orbitals of the *tert*-butyl derivatives of **1**, **8** and **9** 0.7 Å above the molecular plane. They found that the relative contribution of the C=C double bond to the highest lying π-orbital *decreases* and the π-charge at the two-coordinate group IV atom *increases* in the order $C^2 < Si < Ge$.[12] The authors suggested a "chelated-atom" model in order to account for the trend suggested by the Kohn–Sham orbitals. According to this model a gradual intramolecular electron transfer from the diaminoethylene backbone to the two-coordinate atom occurs. This would mean that the oxidation strength increases in the order Ge > Si > C, which is difficult to understand.[38] An explanation for the physical origin of this trend was not given.[12] Table 2 shows the calculated charge distribution of the molecules. The partial charges at Si(**8**) and Ge(**9**) are much more positive than at C^2(**1**). This is in agreement with the electronegativities of the elements.

We calculated the heats of hydrogenation at Si and Ge for **8** and **9**:

$$\mathbf{8} + H_2 \rightarrow \mathbf{12} \qquad \Delta E = -9.8 \text{ kcal/mol} \tag{4}$$

$$\mathbf{9} + H_2 \rightarrow \mathbf{13} \qquad \Delta E = +23.2 \text{ kcal/mol} \tag{5}$$

The less exothermic reaction 4 and even endothermic reaction 5 compared with the hydrogenation of **1** (reaction 1) is due to

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(33) The higher p_π occupancy and less positive partial charge of Ge than Si can be explained by the electronegativities. Ge is more electronegative (2.0) than Si (1.7).

(34) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

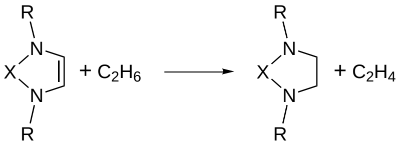
(35) Christen, D.; Griffiths, S. H.; Sheridan, J. *Z. Naturforsch. A* **1981**, *36*, 1378.

(36) The MP2/6-31++G(d,p) energies of the optimized educts and products are as follows. **1** + H^-, −226.031 24 au; **2** + H^-, −227.213 31 au; **1(H$^-$)**: −226.044 69 au; **2(H$^-$)**, −227.257 49 au.

(37) Figure 1 shows the cisoid structures of **3** and **4**. The energy calculations predict that the cisoid form of **3** is marginally more stable than the transoid form, while the opposite holds for **4**. The X-ray structure analyses of derivatives of **3** and **4** show the cisoid forms (A. J. Arduengo, personal communication to G.F.). The reaction energies for reactions 1 and 2 are calculated with respect to the more stable isomers, resepctively.

(38) A. J. Arduengo pointed out to us that an increase of the oxidation strength P < As < Sb has been previously recognized and explained for a series of compounds: Arduengo, A. J., III; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 627. Arduengo, A. J., III; Dixon, D. A. Electron Rich Bonding at Low Coordination Main Group Element Centers. In *Heteroatom Chemistry: ICHAC-2*, Block, E., Ed.; VCH: New York, 1990; p 47.

Scheme 3. Isodesmic Reaction 8



the weaker Si−H and Ge−H bonds than the C−H bond. The stabilization of the divalent Si and Ge atoms in **8** and **9** is revealed by comparing the heats of hydrogenation with the values for SiH_2 and GeH_2:

$$(^1A_1)SiH_2 + H_2 \rightarrow SiH_4 \qquad \Delta E = -61.2 \text{ kcal/mol} \qquad (6)$$

$$(^1A_1)GeH_2 + H_2 \rightarrow GeH_4 \qquad \Delta E = -32.5 \text{ kcal/mol} \qquad (7)$$

The comparison of the reaction energies of reactions 6 and 7 with the values for 4 and 5 demonstrate that the silylene and germylene structures **8** and **9** are significantly stabilized by π-delocalization. Figure 1 shows that the Si−N and Ge−N bonds of **8** and **9** are longer than the respective interatomic distances of **10**, **11**, **12**, and **13**. Table 2 shows that the charge attraction between the group 14 atoms Si and Ge and the nitrogen atoms is much higher in **10**−**13** than in **8** and **9**, respectively. The Coulomb attraction overcompensates the effect of π-delocalization upon the Si−N and Ge−N bond lengths in the silylene and germylene structures.

Finally we compare the calculated reaction energies of the isodesmic reaction 8 (Scheme 3) for the molecules **1**, **1a**, **8**, **9**, and pyridine. The results are shown in Table 3. The calculated energies at MP2/6-31G(d)//MP2/6-31G(d) give the stabilization of the carbene, silylene, and germylene in a five-membered ring due to the conjugation with the C−C double bond. The results support the conclusions made above. There is clearly a stabilizing effect by replacing the saturated $-H_2CCH_2-$ moiety with the −HCCH− group. The stabilization of **1** (27.8 kcal/mol) is only slightly lower than the value calculated for **1a** (32.8 kcal/mol). Nearly the same stabilization is calculated for the silylene analogue **8** (27.4 kcal/mol), and an even higher stabilization is predicted for the germylene **9** (32.1 kcal/mol). The higher stabilization energy of **9** might be caused by less ring strain.

In summary, all theoretical evidence suggests that the higher stability of the imidazol-2-ylidene **1** than that of the imidazolin-2-ylidene **2** is due to the π-delocalization in the five-membered ring. The π-delocalization increases the p_π occupancy at C^2, which reduces the electrophilicity of the carbene. Since both structures are significantly stabilized by the electron donation from the nitrogen lone pairs into the formally "empty" $p_\pi(C^2)$ orbital, the electronically less stable carbene **2** can be isolated if additional steric protection of the carbene carbon atom is available. The same reasoning may be used for yet unknown carbenes, which might become isolable by a combination of electronic stabilization of the formally "empty" carbon p_π orbital and additional steric protection. This could even lead to the synthesis of carbenes with other π-donating atoms in the α-position. Also the isolation of acyclic carbenes is conceivable, provided that the substituents in the α-position are sufficiently stabilizing. The results of this study may help to direct experimental research toward new stable carbenes.

Should compounds like **1** and **2** be considered as true carbenes or as ylides? Since the peculiar stability of these compounds clearly correlates with the electronic stabilization of the formally "empty" p_π orbital of the carbene carbon atom by the lone pairs of the α-substituents, it is obvious that the resonance forms **B** and **B′** shown in Scheme 2 are important for the description of the electronic structure of **1** and **2**. The question "carbene or ylide?" asks for the more important resonance form for the description of the electronic structure of **1**. This study suggests that **A** is still the dominating resonance form for **1** and particularly for **2**, but the peculiar stability of these compounds is due to the crucial contributions of **B** and **B′**.

The crucial importance of the π-donor stabilization for the unusual chemical behavior of the carbenes **1** and **2** is in agreement with numerous other systems, where the same correlation can be made. BH_3 and BF_3 may serve as examples. BH_3 dimerizes spontaneously to diborane. BF_3 is a monomer and a significantly weaker Lewis acid than BH_3.[34] This is clearly a π-donor effect, since the higher electronegativity of fluorine than that of hydrogen should yield a higher Lewis acidity. Since nitrogen is a better donor than fluorine and since carbon is a stronger acceptor than boron, the π-donor stabilization in amino-substituted carbenes can be expected to be stronger than in fluoroboranes. Although there are only two nitrogen atoms as π-donor substituents in **1** and **2**, a significantly reduced Lewis acidity (electrophilic reactivity) should be observed. This is exactly what Arduengo and co-workers have found in their experiments, which open a new and exciting new field in synthetic chemistry.[1,2,5]

4. Conclusion

The higher stability of the unsaturated carbenes with imidazol-2-ylidene structure **1** as compared to the C,C-saturated imidazolin-2-ylidene carbenes **2** is caused by the enhanced $p_\pi-p_\pi$ delocalization of **1**, which leads to a significant electronic charge in the formally "empty" p_π orbital of the carbene carbon atom. The calculated p_π occupancy at the carbene carbon atom of **1** indicates 55.8% of a perfectly delocalized π-bond, while $p_\pi(C^2)$ in **2** has only 39.8% of a complete delocalization. However, both carbenes **1** and **2** are strongly stabilized by electron donation from the nitrogen lone pairs into the formally "empty" p_π orbital. Additional steric protection of the carbene carbon atom can compensate for the lower electronic stabilization calculated for **2**, which explains the successful isolation of the *N*-mesityl derivative of **2**. According to the energetic and magnetic analysis, the cyclic delocalization in **1** has partial aromatic character. Also the silylene **8** and the germylene **9** are significantly stabilized by $p_\pi-p_\pi$ delocalization.

Acknowledgment. We thank the reviewers for constructive criticism. In particular, we acknowledge very helpful comments and information about unpublished results by Dr. A. J. Arduengo, which made the present version of the paper possible. We also thank Prof. H. Schwarz for a preprint of ref 20 and Dipl. Chem. C. Heinemann for stimulating discussions and copies of refs 29b,c. This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Generous support and excellent service by the computer centers HRZ Marburg, HHLRZ Darmstadt, and HLRZ Jülich is gratefully acknowledged.

JA9527075