

Radical anions of carbenes and carbene homologues. DFT study and preliminary experimental results

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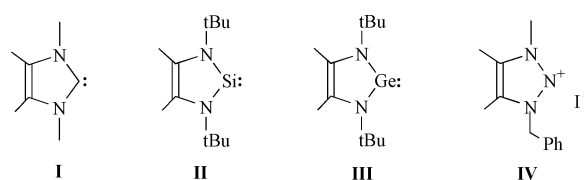
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In the course of exploring the electronic properties and chemistry of stable non-annulated and annulated heterocyclic carbenes and carbene analogues (silylenes, germynes and nitrenium ions), we investigated ground state configurations of such structures as well as their one-electron reduction by means of *ab initio* calculations. We used a DFT approach, which proved to be reliable for obtaining the geometries of the ground state molecules and was thus employed for all calculations. The compounds investigated are presented in Scheme 2. Injection of one electron into these molecules leads to the formation of radical anions, except for with cation **4a**, which gives a neutral radical. For all molecules, ground states are singlet states and comparison has been made in terms of geometrical parameters with known experimental structures and results obtained at the MP2 level of calculation. These results, along with experimental data on the reduction of carbenes, nitrenium ions and germynes obtained by cyclic voltammetry, give some clues about their stability, properties and potential redox activity.

Introduction

During the past ten years, the chemistry of stable species containing a divalent atom from either group 14 (C, Si, Ge, Sn) or 15 (N) has developed enormously and in many directions, including the synthesis of various crystals, the study of their structure and bonding by theoretical calculations, their use as synthons in organic synthesis (additions, insertions, *etc.*) as well as their coupling to metals to obtain new and powerful catalysts (mainly with carbenes for this last class of reactions). The electronic deficient molecules mentioned above are usually short lived and involved as reaction intermediates. This is the case for example with carbenes in organic chemistry¹ and with silylenes in thermal and photochemical silicon chemistry.² But following the initial work of Wanzlick *et al.*^{3a-c} during the sixties, the first crystalline and stable heterocyclic carbene at room temperature in the absence of air and moisture was synthesized by Arduengo *et al.* in 1991,^{3d} opening the route to a rich coordination chemistry.⁴ Reports on the study of the chemistry of silylenes, the silicon counterparts to carbenes, started in 1986 with the isolation by Jutzi *et al.*⁵ of the π complex $(Me_5C_5)_2Si$ and was followed later by the synthesis of the first stable two-coordinate structure by Denk *et al.* in 1994.⁶ The germanium and tin analogues of silylenes were first isolated by Lappert *et al.* in 1974.⁷ Finally, nitrenium ions, species containing a divalent nitrogen atom, were also characterized as stable compounds at room temperature and clearly identified by their X-ray crystal structure by Boche *et al.* in 1996.⁸ All of these molecules are in the singlet spin state. The divalent atom contains a filled, in plane, orbital and an empty, out of plane, pure p orbital (or a formally $p(\pi)$ orbital in the case of the nitrenium ions), which is strongly stabilized by donating atoms (for instance nitrogen atoms) adjacent to the divalent center. This type of structure is thermodynamically favored over a triplet configuration. A few examples of such stable N-heterocyclic carbenes and analogues are presented in Scheme 1. Another strategy, kinetic stabilization using steric protection, has been recently used in order to obtain stable triplet carbenes, since the introduction of steri-



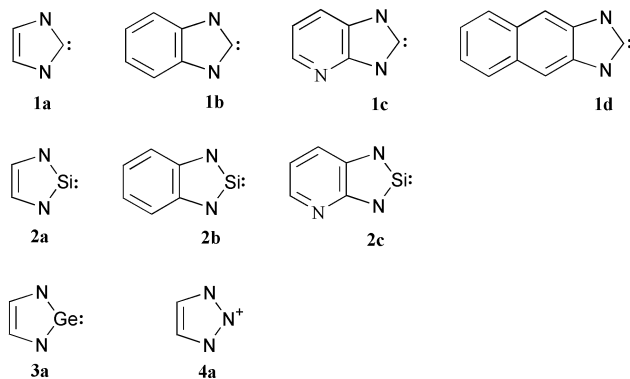
Scheme 1 Some stable carbenes and analogues.

cally bulky groups around a carbenic center results in an increase of the carbene bond angle, thus giving a thermodynamic advantage to the triplet form.⁹ A limitation of this approach lies in the necessity of introducing groups that do not react with the carbene center itself by intramolecular radical type reactions (mainly H atom abstraction). Until now, no stable crystalline triplet carbenes have been synthesized, and the longest lifetimes obtained are around 2 seconds at room temperature with the triplet bis[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-9-anthryl]carbene.^{9b}

Within this large variety of extraordinary molecules,¹⁰ little is known about their electrochemical activity and their participation in electron transfer reactions. Some elusive diarylcarbene cation radicals have been characterized in a solid matrix at low temperatures^{11a} and in solution at room temperature by nanosecond flash photolysis.^{11b} Some recent work also tends to demonstrate that, in some cases, carbene radical anions or cations could be obtained by the unimolecular loss of nitrogen from the corresponding reduced or oxidized diazo precursors, although the formation of these short lived intermediates was inferred from isolation of the final stable products of the process and not from direct observation.^{11c} As concerns stable carbenes and analogous structures, few examples have been described. One is the synthesis, by Fox *et al.*, of a contact charge transfer complex between an imidazol-2-ylidene (compound I, Scheme 1) and $Ru(bpy)_3^{2+}$, in which the carbene is oxidized by a one electron exchange.^{11d} A second example is the generation and characterization by fast cyclic voltammetry of nitrogen radicals resulting from one electron reduction of the corresponding nitrenium

ions.¹² The last and most recent example is the synthesis in tetrahydrofuran by West *et al.* of the stable *N,N'*-di-*tert*-butyl-1,2,3-diazasilol-2-ylidene, its subsequent overreduction to a dimeric dianion and finally the cleavage of the dimer to a pair of silyl dianions.^{10a,o}

To gain further insight into the electronic structure and properties of such species, we have investigated the ground state configurations of a series of heterocyclic carbenes and analogues (Scheme 2). The effect of annelation is discussed on both



Scheme 2 Carbenes, silylenes, germynes and nitrenium ions investigated (missing atoms are hydrogen).

carbenes and silylenes. Injection of one electron into these structures leads to the formation of the corresponding radical anions (or neutral radical in the case of the nitrenium). The geometry and electronic structure of these products are analyzed and an estimation of the standard potential of the redox couples is given. Based on experimental results previously obtained with nitrenium ions and on original results gathered by cyclic voltammetry with the carbene **VII** and the two germynes **XII** and **XV**, it is shown that depending on the nature of the divalent atom, radical anionic chemistry could be initiated.

Computational methods

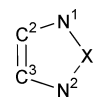
All calculations on geometries and energies were carried out with the program package Gaussian98.¹³ The B3LYP method was used for the density functional theory (DFT) approach and the MP2 (UMP2) method for the *ab initio* approach. A standardized 6-31G basis set was used together with diffuse (+) and polarization (*) function for carbenes, silylenes and nitrenium ions. The 6-311+G** basis set was employed for the germanium related compounds. For all optimized geometries, no imaginary frequencies were found from the analytical second derivatives of the energies, confirming that stationary points were true minima on the potential energy surface. The second derivatives were also used to obtain various thermodynamic parameters, including the zero-point energy and the entropy term from the usual relationships within an ideal gas, rigid rotor and harmonic oscillator models. The standard enthalpies and free enthalpies were corrected by a scaling factor (0.9804 at the B3LYP/6-31G* level) applied to the zero-point energies and thermal energy corrections. The charges on atoms were obtained by a Mulliken population analysis. Solvation energies were estimated with the isodensity polarized continuum model (IPCM), that defines a cavity for the solute as an isodensity surface.

Results and discussion

Geometries of carbenes and analogues and of their one electron reduction products

Key features concerning the geometries of **1a**, **2a**, **3a** and **4a** are

presented in Table 1. The classification of the various atoms is as given in the model compound below (Scheme 3). For the sake

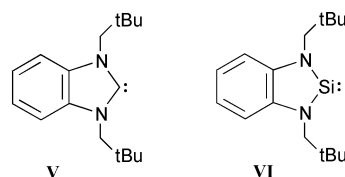


Scheme 3 Model compound.

of comparison, various molecules **I**,^{10b} **II**,⁶ **III**^{10p} and **IV**⁸ (see Scheme 1) whose structures have been experimentally determined, are compared to the models. All the calculated structures are planar. Some theoretical calculations have been done for these models.^{8,10c,12,14} It emerged that all of these do benefit, in addition to the p(π) donation of the two nitrogen atoms next to the carbene or carbene like center, from some cyclic delocalization of the two π electrons of the C=C double bond, this effect being less extensive in the silylenes and germynes compared to their carbene analogs. π Bonding decreases on going from carbene to silylene and germylene, while the s character of the lone pair increases. In the case of the nitrenium ion **4a**, stabilization occurs mainly through strong donation of the two adjacent amino groups, as reflected by the low partial positive charge born by the nitrenium center (about 0.1 in the gas phase).

It is interesting to note that our calculations at the B3LYP level, even when using the modest 6-31G* basis set, do lead to results as good as the MP2 level of calculation (see Table 1, compound **1a** for example). Quantitative agreement with known structures becomes quite close with the 6-31+G* basis set, which has been employed in most of the calculations with these models. In the case of germylene (model **3a** and **III**), results at the B3LYP/6-311+G** level give a better agreement than previous calculations done at the MP2 level with a relativistic pseudo potential for Ge.¹⁴ The former level will thus be employed for calculations related to germanium containing molecules. One may also notice the slight tendency of the calculations, as at the MP2 level, to overestimate the length of the N₁-X bond and to underestimate the value of the N₁-X-N₂ angle.

Annelated heterocyclic diamino nucleophilic carbenes **V**,^{10h} **VIII**¹⁵ and **IX**¹⁵ and higher homologues **VI**,¹⁰ⁱ **X**,^{10j} **XIII** (this work, see Experimental section), **XIV** and **XV**^{10q} have also been synthesized recently (Schemes 4 and 5), giving access to benzo-



Scheme 4 Stable annelated heterocyclic carbene and silylene.

pyrido- and naphtho-annelated imidazolin-2-ylidene and their analogs, opening the route to their use in complex chemistry and catalysis, which is becoming of growing importance. The main geometric parameters for model structures **1b-d** and **2b** and **c** are given in Table 2, along with those of the characterized molecules shown in Scheme 4.

Owing to the size of the systems investigated, the 6-31G* basis set was employed for these annelated carbenes and analogs. The agreement between calculated structures **1b** and **V** on the one hand and between calculated **2b** and **VI** on the other hand proved to be satisfactory both in terms of bond lengths and angles, while geometries of carbenes **1c** and **1d** as well as silylene **2c** remain experimentally unknown. For both carbenes (**1b-d**) and silylenes (**2b** and **c**), one may notice that the planar geometries obtained are quite close to those of the non-annelated derivatives, with a slight increase of the C₂-C₃ distance, due to electronic delocalization over the aromatic ring.

Table 1 Optimized geometrical parameters for carbene and homologues at various levels and comparison with known structures

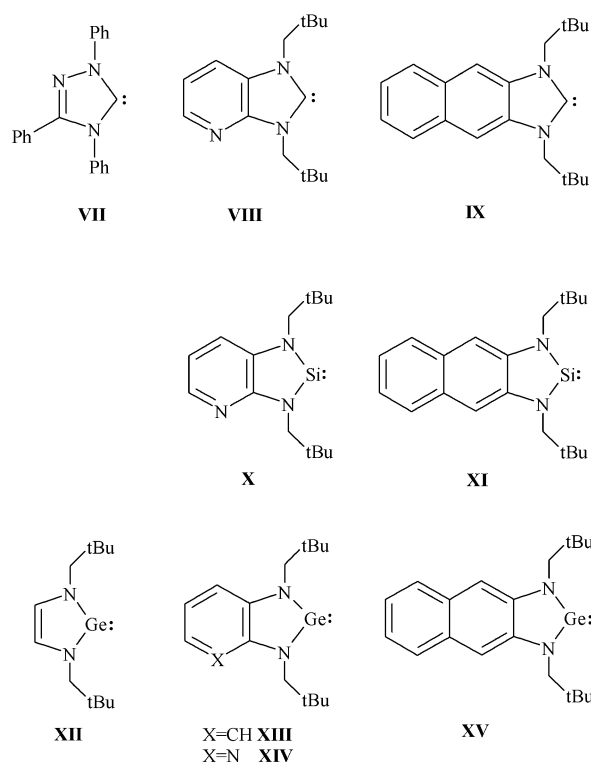
	1a				2a				4a				3a			
	<i>a</i>	<i>b</i>	<i>c</i>	I	<i>a</i>	<i>c</i>	II		<i>a</i>	<i>c</i>	IV		<i>d</i>	<i>e</i>	III	
N ₁ –X	137.1	137.2	136.9	136.3	177.2	177.9	175.3		133.1	131.3	131.9		192.5	189.0	185.9	
N ₁ –C ₂	138.4	139.3	139.3	139.4	138.4	138.8	140.0		135.3	136.1	134.3		137.2	138.0	138.4	
C ₂ –C ₃	136.3	135.6	135.8	135.2	136.3	136.0	134.7		138.3	137.5	135.5		137.1	136.0	136.4	
N ₁ –X–N ₂	99.4	99.9	100.5	101.5	84.7	84.9	90.5		102.2	103.2	103.8		80.1	81.5	84.8	
X–N ₂ –C ₃		114.6	114.3			115.5	115.5		114.4	113.8	112.4			115.5		
N ₁ –C ₂ –C ₃									104.6	104.6	105.4					

^a MP2/6-31G*. ^b B3LYP/6-31G*, this work. ^c B3LYP/6-31+G*, this work. ^d MP2/ECP/31/31/1. ^e B3LYP/6-311+G**, this work. For the exact structures of **I**, **II**, **III** and **IV**, refer to Scheme 1. Bond lengths in pm, bond angles in deg.

Table 2 Optimized geometrical parameters for annelated heterocyclic carbenes and silylenes at various levels and comparison with some known structures

	1b		1c	1d	2b		2c	
	<i>a</i>	V	<i>a</i>	<i>a</i>	<i>a</i>	VI	<i>b</i>	<i>a</i>
N ₁ –X	137.3	136.1	137.7	137.3	177.2	175.2	176.6	177.9
(N ₂ –X)			(137.3)				(177.7)	(177.3)
N ₁ –C ₂	139.5	138.8	139.1	139.7	139.1	138.5	138.5	138.6
(N ₂ –C ₃)			(139.0)				(138.1)	(138.4)
C ₂ –C ₃	140.5	139.5	140.9	142.2	141.5	141.7	141.4	141.9
N ₁ –X–N ₂	101.3	103.5	101.6	101.7	86.0	88.2	86.2	86.2
X–N ₂ –C ₃	114.4	112.8	114.1	114.5	115.9	114.1		115.7

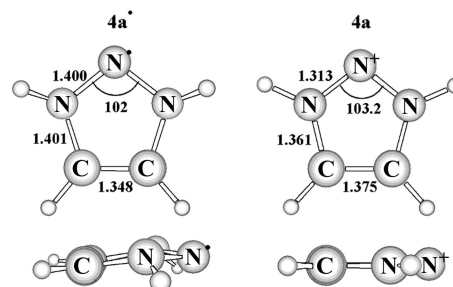
^a B3LYP/6-31G*, this work. ^b MP2/6-31G*. For the exact structures of **V** and **VI**, see Scheme 4. Bond lengths in pm, bond angles in deg.

**Scheme 5** Some stable carbenes, silylenes and germylenes.

It is also interesting to note the concomitant enlargement of the N₁–X–N₂ angle when passing from **1a** (or **2a**) to annelated molecules. For example, at the B3LYP/6-31G* level, this angle passes from 100.5° in carbene **1a** to 101.3° in benzo-annelated **1b**, to 101.6° in pyrido-annelated **1c** and finally to 101.7° in naphtho-annelated **1d**. Even if small, this increase stands in line with the recent X-ray crystal structure analysis of crystals of **V**, which reveals a N₁–C–N₂ angle value of 103.5°, a value closer to that obtained for saturated N-heterocyclic carbenes rather than for unsaturated compounds. This indicates a lack of aromatic

Table 3 Optimized geometrical parameters for anion radicals of a carbene and its homologues at the B3LYP/6-31+G* level or B3LYP/6-311+G** (**3a**^{•–}) [bond lengths in pm, bond angles in deg]

	1a ^{•–}	2a ^{•–}	3a ^{•–}	4a [•]
N ₁ –X	136.9	184.5	195.5	140.0
N ₁ –C ₂	138.7	139.2	138.6	140.1
N ₁ –X–N ₂	100.4	83.0	80.3	102.0
X–N ₂ –C ₃	114.1	115.4	114.8	110.6

**Fig. 1** Optimized geometries (at the B3LYP/6-31+G* level) of the radical **4a**[•] (left) and of the nitrenium ion **4a** (right) (bond lengths in pm, bond angles in deg).

stabilization of the carbene center and should lead to experimental spectroscopic activity and chemical reactivity similar to carbenes containing a saturated N-heterocyclic ring. In the case of **VIII** and **IX** this similarity is even stronger. We observed the same structural trend in the case of the silylenes (**2a–c**) and thus the same consequences are postulated for their reactivity.

To gain further insight into the electronic structures and chemical reactivity of these carbenes and homologues, ion radicals of compounds **1a–d**, **2a–c** and **3a** as well as the radical form of **4a** have been computed. Addition of one electron to the ground state molecules leads to the desired structures. The main characteristics of the non-annelated molecules are given in Table 3. These reduced compounds are found to be no longer planar. The clearest example is given by radical **4a**[•] (see Fig. 1)

Table 4 Optimized geometrical parameters for annelated heterocyclic anion radicals of carbenes and silylenes at the B3LYP/6-31+G* level (bond lengths in pm, bond angles in deg)

	1b^{•-}	1c^{•-}	1d^{•-}	2b^{•-}	2c^{•-}
N ₁ -X	139.6	139.2	138.4	185.7	185.4
(N ₂ -X)		(138.9)			(184.8)
N ₁ -C ₂	139.4	139.5	140.0	137.2	136.9
(N ₂ -C ₃)		(139.6)			(136.4)
C ₂ -C ₃	139.9	139.5	139.9	143.3	143.8
N ₁ -X-N ₂	98.3	99.0		82.1	80.3
X-N ₂ -C ₃	116.0	115.7	115.3	117.5	117.7

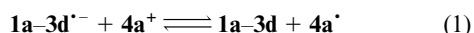
for which the geometry around the N₁ and N₂ atoms becomes pyramidal, with a pronounced sp³ hybridization character and little electronic delocalization over the three nitrogen atoms. The N₁-N[•] and N₂-N[•] bond lengths elongated from 131.3 pm in **4a** to 140.0 pm in **4a[•]**. Parallel, N₁-C₂ and N₂-C₃ bond lengths increased from 136.1 to 140.1 pm, while the N[•]-N₁-C₂ angle narrows from 113.9 to 110.6 deg. It should also be noted that the C₂-C₃ bond shortens from 137.5 to 134.8 pm. The spin density on the nitrogen radical center is important, and is about 60%, the remaining part being equally shared between N₁ and N₂ (these values were obtained after solvation of the optimized geometries in *N,N*-dimethylformamide (DMF) using the isodensity surface polarized continuum model as implemented in Gaussian98). The same trends are observed with germylene **3^{•-}** and to a lesser extent with silylene **2a^{•-}**. For example, with the germylene, the N₁-Ge and N₁-C₂ bond lengths increase from 189.0 to 195.5 pm and from 138.0 to 138.6 pm respectively, on going from the neutral state to the radical anion. The Ge-N₁-C₂ angle slightly narrows (115.5 deg in **3a** vs. 114.8 deg in **3a^{•-}**) and the C₂-C₃ bonds remain unchanged. With both radical anions, spin densities are almost completely localized onto the carbene like center.

With carbene **1a^{•-}**, only marginal changes occur upon electron injection and the carbene center is just slightly out of the plane formed by the two nitrogen atoms and the two carbon atoms of the double bond. Spin density on the carbene center is again close to 1. Thus, despite the additional charge, the p(π) donation of the two nitrogen atoms and the partial cyclic delocalization of the two π electrons of the C=C double bond tend to remain identical, reflecting the poor stability of the radical anion form.

The main geometrical features of the annelated radical anions are presented in Table 4. These molecules are found to be mainly planar. In the carbene series (**1b^{•-}**-**d^{•-}**) it can be seen that no major changes occur when comparing them with the neutral corresponding states, except for a small increase of the N-C: bond length. Spin density is mainly delocalized over the aromatic part of the molecule while only 20 to 30% is located on the carbene center. In contrast, the spin is more concentrated at the silicon atom in the silylene series (about 75% for both **2b^{•-}** and **2c^{•-}**), which reflects its better electron acceptance. The Si-N bonds are also slightly elongated compared with the neutral compounds.

Redox properties of the carbenes and their analogues

From frequency calculations (that give access to the Gibbs standard free energy in the gas phase) and solvation of the optimized geometries, evaluation of the standard redox potentials of the couples **1a-3d/1a-3d^{•-}** could be done by calculating the standard free energy change associated with the electron exchange reaction with the nitrenium ion **4a⁺**/radical **4a[•]** couple (see reaction (1) below). Absolute values of the *E*⁰'s are then

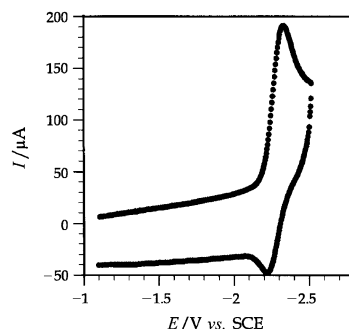


estimated taking -1.84 V vs. SCE as *E*⁰ for the **4a⁺**/**4a[•]** couple. This latter value is taken equal to the experimental value

Table 5 Estimated standard redox potentials for carbenes and analogues

Redox couple	<i>E</i> ⁰ (in V vs. SCE) ^d
1a/1a^{•-} ^a	-4.41
2a/2a^{•-} ^a	-2.97
3a/3a^{•-} ^b	-2.88
1b/1b^{•-} ^c	-3.63
1c/1c^{•-} ^c	-3.10
1d/1d^{•-} ^c	-2.97
2b/2b^{•-} ^c	-2.88
2c/2c^{•-} ^c	-2.69

^a At the B3LYP/6-31+G* level, solvent: DMF. ^b At the B3LYP/6-311+G** level, solvent: DMF. ^c At the B3LYP/6-31G* level, solvent: tetrahydrofuran. ^d The result, obtained in Hartrees, was first converted to Joules and then to V.

**Fig. 2** Cyclic voltammogram of carbene **VII** (2.4 mM) in DMF and at 100 V s⁻¹ on a 1 mm diameter carbon disk.

obtained in a previous study of the **IV⁺**/**IV[•]** couple.¹² The results are summarized in Table 5.

Even though approximate (the absolute numbers in Table 5 should be considered as rough estimations while the differences between the various couples are certainly more accurate), several features are worth noting from these values, giving some insights into the question of stability of these molecules. In the carbene series (**1a-d**), one can see that all compounds are very resistant to one electron reduction and thus should prove to be stable even in extreme conditions. Since non-annelated carbenes are resistant toward dimerization,¹⁶ it comes as no surprise that **1a** remains intact even in the presence of an extremely strong reductive agent, like KC₈. It also explains the fact that carbene **I^{11d}** and the carbene center of **VII¹⁷** could not be electrochemically reduced, even at very negative potentials. In the case of **VII**, we observed a mono-electronic reduction wave (Fig. 2) which appeared to be chemically reversible with an *E*⁰(**VII/VII^{•-}**) close to -2.35 V vs. SCE in acetonitrile (on a glassy carbon electrode) and to -2.31 V in DMF (on both a glassy carbon electrode and at a mercury drop). This behaviour mirrors the electroactivity of the substituents on the ring (mainly the C=N double bond and the phenyl ring link to it) and not the redox activity of the carbene center.

This picture, which has already been proposed,¹² is clearly reinforced by our calculations. In contrast, the experimental observation that carbene **VIII** (Scheme 5) (for which **1c** stands as a model) could only be obtained in small yields (40% in the crude product) may not be related to the redox properties of the corresponding couple.¹⁵ The lower symmetry and decreased aromatic stabilization of **VIII** and **IX** (the ¹³C(π) signals are even more downfield shifted than in **V**) may be responsible for the easier decomposition and a possible dimerization shown recently for less bulky substituted analogues of **V**¹⁸ may enable the slow reduction of **VIII**¹⁵ by excess potassium.

In the silylene series (**2a-c**), the couples also have very negative redox potentials, which is in line with the successful synthesis of similar structures that prove to remain stable in

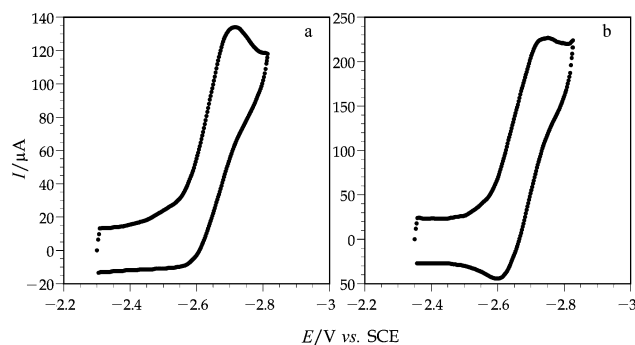


Fig. 3 Cyclic voltammogram of germylene **XII** (≈ 4.5 mM) in DMF, at 0.5 V s^{-1} (a) and at 5 V s^{-1} (b) on a 3 mm diameter carbon disk.

very reductive conditions.^{10*ij*} In the case of the naphtho-1,3,2 λ^2 -diazasilole **XI**, even though the standard redox potential was not calculated, it's very likely to be slightly more positive than -2.69 V vs. SCE , by comparison with the $2\text{c}/2\text{c}^{\cdot-}$ couple and by analogy to the difference observed in the carbene series between the two couples $1\text{c}/1\text{c}^{\cdot-}$ and $1\text{d}/1\text{d}^{\cdot-}$. Failed attempts at its synthesis by reduction of the respective heterocyclic Si(IV) dichloride with potassium^{10*g*} may not be due to an instability connected with a further one-electron reduction process, especially in conditions where the starting material is less concentrated than the reducing agent. However, since Si–Cl are extremely strong bonds, it may well be possible that the diazasilole ring opens during the course of the reaction, at the level of the starting material and/or at the level of the silyl radical anion, an intermediate that could be obtained after a one electron reduction followed by the expulsion of a chloride anion. Polymeric agglomeration may also be a cause of the instability of **XI**. It is also worth noting, as mentioned in the introduction, that West *et al.* very recently succeeded in synthesizing 1,3-di-*tert*-butyl-1,2,3-diazasilol-2-ylidene in tetrahydrofuran and its dianion form, obtained after a two electron overreduction in the presence of potassium in excess.^{10*n,o*} The intermediate between these two structures, namely a radical anion, was obtained as a dimer dianion, the product of the coupling of two individual molecules. These results indicate that some ionic chemistry using silylene may be possible.

In the case of germylene **3a**, the E^0 value we estimated indicates that this compound should be much more easily reducible than the corresponding carbene **1a** and significantly more reducible than the silylene **2a** (Table 5), opening a potential window for a redox chemistry. These predictions were confirmed with two stable diaminogermylene molecules, namely 1,3-dineopentyl-1,3,2-diazagermol-2-ylidene **XII**, a new stable germylene monomer, and the naphtho-annelated analogue **XV**, whereas the benzo- and the pyrido-annelated derivatives **XIII** and **XIV** could not be reduced. Cyclic voltammograms of **XII** obtained in DMF do lead to the observation of an irreversible monoelectronic wave located at -2.81 V vs. SCE at low scan rates (Fig. 3). Increasing the scan rate up to a few V s^{-1} was sufficient to catch a reversible wave, *i.e.* a stable radical anion. The standard redox potential of the corresponding couple was thus found to equal -2.75 V vs. SCE , close to the rough theoretical estimation.

XV is expected to be more easily reducible than **XII** by a few hundred millivolts. Cyclic voltammograms of **XV** obtained in DMF indeed lead to the observation of an irreversible wave located at -2 V vs. SCE at low scan rates (Fig. 4). This wave does correspond to the formation of a germylene centered radical anion and not to the reduction of the aromatic part of the molecule (we indeed checked that 1,8-diaminonaphthalene is not reducible before the supporting electrolyte discharge). The change in the wave location upon variation of the scan rate v (the peak potential is negatively shifted by about 35 mV per decade of log v) does indicate that irreversibility is due to an

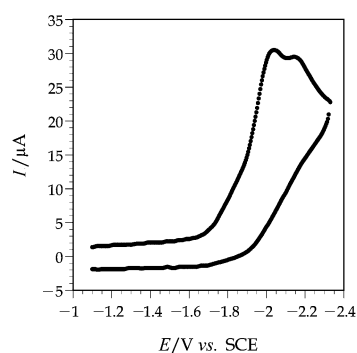


Fig. 4 Cyclic voltammogram of germylene **XV** (≈ 0.3 mM) in DMF and at 0.2 V s^{-1} on a 3 mm diameter carbon disk.

irreversible and fast chemical reaction following the first charge transfer ($E + C$ mechanism), that drives the wave to a substantially more positive potential than the standard potential (a few hundreds of mV at low scan rate).[†] Thus, peak wave location is consistent with a value around -2.5 V for E^0 , in agreement with our prediction.

The favorable redox properties of **XII** show that, as for nitrenium ions, a redox chemistry along a germylene series could be envisaged.

Conclusion

The structures of several heterocyclic and annelated heterocyclic carbenes, silylenes, germylenes and nitrenium ions have been calculated by *ab initio* calculations, as well as the products of their one electron reduction. The density functional approach used at the B3LYP level proved to give reliable geometries for the singlet ground state molecules when compared to known structures. Standard potentials of the various redox couples in solution have been roughly estimated. These values give some clues about the various synthetic attempts at these low-coordinate molecules and especially on their resistance to the very reductive medium employed for their building. Moreover, results suggest that, while in the carbene series no radical anionic chemistry could be envisaged due to the extreme reluctance of the carbene center to accept an extra electron, reduced forms of some silylenes and germylenes may be obtained in a polar medium. For example, preliminary results show that both 1,3,2 λ^2 -diazagermole (**XII**) and naphtho-1,3,2 λ^2 -diazagermole (**XV**) are reducible in DMF, leading to the corresponding radical anions. Further experiments will explore the properties and chemistry triggered by these anions.

Experimental

Chemicals

For the electrochemical investigations, acetonitrile (Merck Uvasol), *N,N*-dimethylformamide (Fluka, >99.5%, stored over molecular sieves and under an argon atmosphere), the supporting electrolyte NEt_4BF_4 (Fluka, puriss), 1,8-diaminonaphthalene (Aldrich, 99%), stable compound **VII** (Acros) were used as received. Salt concentration was 0.1 M .

Compounds **XIV** and **XV** were synthesized as reported earlier.^{10*g*}

Compound **XII** was obtained from equimolar amounts of GeCl_2 (dioxane) and the dilithium reagent formed by treating *N,N'*-dineopentylethylenediimine with 2 Li in THF and sublimation in vacuum (10^{-2} Torr, 50°C), mp $68\text{--}69^\circ\text{C}$, yield 53%. Compound **XIII** was prepared from GeCl_2 (dioxane) and

[†] Experiments were not performed in a dry box as for **XII** and water traces may be the cause of the fast chemical reaction consuming the initially formed radical anion.

N,N'-dilitio-*N,N'*-dineopentyl-*o*-phenylenediamide¹⁰ⁱ in 71% yield, mp 120–122 °C. Elemental analyses are in accordance with the structures. A detailed description of the preparation, spectroscopic data and crystal structure analysis is given separately.¹⁹

Cyclic voltammetry

Most of the cyclic voltammetric experiments were carried out with a 3 mm diameter glassy carbon disk. The 1 mm diameter carbon electrode was obtained by mechanical abrasion of the original one. The mercury electrode was obtained from adsorption of an hemispheric mercury drop onto a 1 mm diameter gold disk. Experiments were performed in a conventional electrochemical cell designed for use on a vacuum line, the solution volume being between 5 and 10 mL. Solutions of compound **X** were prepared in a dry box, in which the water content was held under 5 ppm. Positive currents are cathodic. The electrodes were carefully polished and ultrasonically rinsed with absolute ethanol. The counter electrode was a platinum wire and the reference electrode an aqueous saturated calomel electrode (SCE). The potentiostat, equipped with a positive feedback compensation, and current measurer used at low or moderate scan rates, were the same as previously described.²⁰ All experiments were performed at 18 °C, the double-wall jacket cell being thermostated by circulation of water.

References

- For instance see: W. Kirmse, *Carbene Chemistry*, 2nd Edn., Academic Press, New York, 1971; R. A. Moss, *Carbenes*, eds. M. Jones, Jr and R. A. Moss, Wiley, New York, 1973; M. S. Platz, *Kinetics and Spectroscopy of Carbenes and Biradicals*, Plenum, New York, 1990.
- For instance see: P. P. Gaspar, *Reactive Intermediates*, eds. M. Jones, Jr and R. A. Moss, Wiley, New York, 1978, Vol. 1, pp. 229–278; P. P. Gaspar and R. West, *Chemistry of Organosilicon Compounds*, eds. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, Vol. 2, pp. 2463–2568.
- (a) H.-W. Wanzlick and E. Schikora, *Chem. Ber.*, 1961, **94**, 2389; (b) H.-W. Wanzlick, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 75; (c) H.-W. Wanzlick and H. J. Schönherr, *Angew. Chem., Int. Ed. Engl.*, 1968, **80**, 153; (d) A. J. Arduengo, III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
- W. A. Hermann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162.
- P. Jutzi, D. Kanne and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 164.
- M. Denk, R. Lennon, R. Hayshi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
- D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895.
- G. Boche, P. Andrews, K. Harms, M. Marsch, K. S. Rangappa, M. Schimeczek and C. Willeke, *J. Am. Chem. Soc.*, 1996, **118**, 4925.
- (a) Y. Hu, K. Hirai and H. Tomioka, *J. Phys. Chem. A*, 1999, **103**, 9280; (b) H. Itakura, H. Mizuno, K. Hirai and H. Tomioka, *J. Org. Chem.*, 2000, **65**, 8797.
- For carbenes, see for instance: (a) A. J. Arduengo, III, H. V. Rasika Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530; (b) N. Kuhn and T. Kratz, *Synthesis*, 1993, 561; (c) A. J. Arduengo, III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6641; (d) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel and S. Brode, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1021; (e) R. W. Alder, P. R. Allen, M. Murray and A. G. Orpen, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1121; (f) K. M. Lee, C. K. Lee and I. J. B. Lin, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1850; (g) A. J. Arduengo, III, F. Davidson, H. V. Rasika Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall and T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12742; (h) F. E. Hahn, L. Wittenbecher, R. Boese and D. Bläser, *Chem. Eur. J.*, 1999, **5**, 1931; for silylenes, see for instance: (i) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese and D. Bläser, *J. Chem. Soc., Chem. Commun.*, 1995, 1931; (j) J. Heinicke, A. Oprea, M. K. Kindermann, T. Karpáti, L. Nyulászi and T. Veszprémi, *Chem. Eur. J.*, 1998, **4**, 541; (k) T. A. Schmedake, M. Haaf, Y. Apeloig, T. Müller, S. Bulakov and R. West, *J. Am. Chem. Soc.*, 1999, **121**, 9479; (l) M. Kira, S. Ishida, T. Iwamoto and C. Kabuto, *J. Am. Chem. Soc.*, 1999, **121**, 9722; (m) M. Haaf, T. A. Schmedake and R. West, *Acc. Chem. Res.*, 2000, **33**, 704 and references therein; (n) M. Haaf, T. A. Schmedake, B. J. Paradise and R. West, *Can. J. Chem.*, 2000, **78**, 1526; (o) T. A. Schmedake, M. Haaf, J. Becker, T. Mueller and R. West, *Chem. Lett.*, 2001, 68; for germylenes, see for instance: (p) W. A. Hermann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1485; (q) J. Heinicke and A. Oprea, *Heteroatom Chem.*, 1998, **9**, 439.
- (a) T. Bally, S. Matzinger, L. Truttman, M. S. Platz, A. Admasu, F. Gerson, A. Arnold and R. Schmidlin, *J. Am. Chem. Soc.*, 1993, **115**, 7007; (b) D. G. Stoub and J. L. Goodman, *J. Am. Chem. Soc.*, 1997, **119**, 11110; (c) D. Bethell and V. D. Parker, *Acc. Chem. Res.*, 1988, **21**, 400 and references therein; (d) Y. Zhang and M. A. Fox, *Acta Chem. Scand.*, 1999, **53**, 857.
- M. Robert, A. Neudeck, G. Boche, C. Willeke, K. S. Rangappa and P. Andrews, *New J. Chem.*, 1998, 1437.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, M. A. Scuseria, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, G. Ochterski, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. B. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, A. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian 98, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 1998.
- C. Heinemann, T. Müller, Y. Apeloig and H. Schwarz, *J. Am. Chem. Soc.*, 1996, **118**, 2023; C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1996, **118**, 2039.
- A. Oprea, PhD Thesis, University Greifswald, 2000.
- L. Nyulászi, T. Veszprémi and A. Forró, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3127.
- D. Enders, K. Breuer, G. Raabe, J. Simonet, A. Ghanimi, H. B. Stegmann and J. Henrique Teles, *Tetrahedron Lett.*, 1997, **38**, 2833.
- (a) F. E. Hahn, L. Wittenbecher, D. Le Van and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2000, **112**, 541; (b) Y. Liu, P. E. Lindner and D. M. Lemal, *J. Am. Chem. Soc.*, 1999, **121**, 10626; (c) V. P. W. Böhm and W. A. Herrmann, *Angew. Chem.*, 2000, **112**, 4200.
- O. Kühl, P. Lönnecke and J. Heinicke, manuscript in preparation.
- D. Garreau and J.-M. Savéant, *J. Electroanal. Chem.*, 1972, **35**, 309; D. Garreau, P. Hapiot and J.-M. Savéant, *J. Electroanal. Chem.*, 1989, **272**, 1.