CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200500576

The Transfer of Tin and Germanium Atoms from *N*-Heterocyclic Stannylenes and Germylenes to Diazadienes

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Abstract: New *N*-heterocyclic stannylenes and germylenes were synthesized by transamination of $E\{N(SiMe_3)_2\}$ (E = Ge, Sn) with α-amino-aldimines or ethylidene-1,2-diamines and were characterized by spectroscopic methods and in the case of the germylene **10g** by X-ray diffraction. The reactions of several germylenes and stannylenes with diazadienes were studied by using dynamic NMR and computational methods. Experimental and theoretical studies confirmed that metathesis with exchange of the Group 14 atom is feasible for both stannylenes and germylenes, with exchange rates being generally higher for stannylenes. The metathesis of the diazadiene **3b** and the stannylene **1b** follows second-order kinetics and exhibits a sizeable negative entropy of activation. The transfer reaction is inhibited by bulky substituents in both reactants and surprisingly coincides with a suppression of the fragmentation of the stannylene into tin and diazadiene. A connection between oxidative addition and ring fragmentation was also observed in the reaction of **1f** with sulfur. Density functional theory (DFT) calculations suggest that all metathesis reactions proceed via transient spirocyclic [1+4] cycloaddition products, the formation of which is generally endothermic and endergonic. The spirostannanes display a distorted *Ψ*-tbp geometry at the tin atom and their cycloreversion requires low or nearly negligible activation energies; spirogermanes exhibit distorted tetrahedral central atoms and sizeable energy barriers with respect to the same reaction. Complementary studies of cycloadditions of diazadienes to triplet germylenes or stannylenes indicate that these reactions are exothermic. The lowest triplet state in the carbene homologues results from promotion of an electron from an n(N) orbital with π character rather than the n(C)-σ orbital as in carbenes, and singlet–triplet excitation energies decrease from carbon to tin. Spirostannanes exhibit a triplet ground-state multiplicity that implies that the energy hypersurfaces for the reactions of singlet and triplet stannylenes with diazadienes intersect; for germylenes, the singlet hypersurface is always lower in energy. A reaction mechanism explaining the different thermal stabilities of *N*-heterocyclic germylenes and stannylenes, and the coincidence between ring metathesis and thermal decomposition of the latter, is proposed based on the different separation of the singlet and triplet energy hypersurfaces.

Keywords: atom transfer · carbenoids · germanium · stannanes · triplet states

Introduction

The discovery of isolable singlet carbenes has initiated significant and ongoing research activities aimed at the comprehensive characterization of the physical and chemical properties of these compounds[1] and the development of new applications of carbenes and their complexes in synthesis and catalysis.[1,2] Among several molecular frameworks that are suitable for the electronic stabilization of a divalent carbon atom, *N*-heterocyclic imidazoylidenes of type **IC**[3] received particular interest and stimulated the advancement of carbene chemistry as well as investigations on carbene homologues with heavier Group 14 elements. These studies showed silylenes **I*Si*** to be the first stable compounds with a dicoordinate silicon atom,[4] and stimulated the further de-

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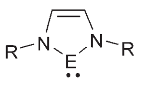
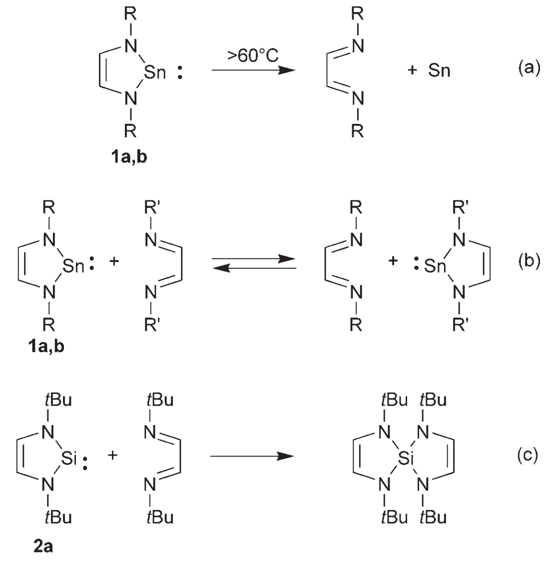


I*E*

(*E* = C, Si, Ge, Sn)

velopment of the chemistry of germylenes **I*Ge***.[5] Unsaturated cyclic stannylenes **I*Sn*** were unknown apart from a few annelated $1,3,2\lambda^2$-diazastannole derivatives,[6] although stable tin(II) amides and related stannylenes are an abundant class of compounds.[7]

We have previously described the monocyclic, CC-unsaturated stannylenes **1a** (**I*Sn***, R = *t*Bu) and **1b** (**I*Sn***, R = Mes), which represent the first genuine tin analogues of the carbenes **I*C***. The synthesis of these compounds proved challenging, not only because of the need to suppress redox reactions competing with the ring formation but also because the products proved to be thermolabile and decomposed at slightly elevated temperatures to yield tin and the corresponding diazadiene (Scheme 1a).[8] Both the ease and the pathway of this formal [1+4] cycloreversion is unprecedented for lighter carbene analogues **I***E* (E = C, Si, Ge) that are renowned for their high thermal stability.[1–5] Initial reactivity studies showed that **1a,b** undergo a unique metathesis with diazadienes that permitted interconversion between different cyclic stannylenes through formal transfer of a single tin atom (Scheme 1b).[8] Although this reaction was considered to proceed via an initial [1+4] cycloaddition, its outcome differs markedly from that of the reaction of the silylene **2a** that forms a stable spirocyclic cycloadduct under the same conditions (Scheme 1c).[9]



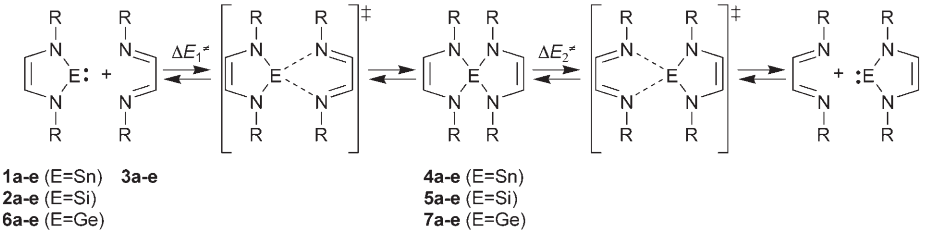
Scheme 1. R = *t*Bu (**1a**), Mes (**1b**); R′ = *t*Bu, Mes.

In contrast to derivatives of the type **I*C*** and **I*Si***,[1,2,4] and considering further that **1a,b** do not tend to coordinate to transition-metal atoms, these preliminary results clearly demonstrate a quite remarkable chemical diversity in the series of isoelectronic carbene analogues **I*E*** that certainly warrants further investigation.

To pursue this goal we performed a more extensive survey of the reactivity of cyclic stannylenes of the type **I*Sn***. Considering that reactions involving the formal transfer of a "naked" tin atom might exhibit a significant potential in synthesis for the assembly of novel heterocycles or cage compounds, we focused on the elucidation of the mechanism of the reaction of Scheme 1b by using both computational and experimental approaches. We extended these studies to include germylenes **I*Ge*** because, to our knowledge, similar reactions involving the transfer of germanium atoms have not been reported. Our results suggest that a reaction according to Scheme 1b is indeed not restricted to stannylenes but may also occur with germylenes, and allows us to further propose some interesting suggestions regarding the mechanism of the cycloreversion shown in Scheme 1a. In addition, we report on a generalized synthesis of carbene analogues **I*E*** from α-amino-aldimine precursors and on the reaction of a stannylene **I*Sn*** with sulfur.

Results

Computational studies: Assuming that the Sn-transfer reaction in Scheme 1b follows an associative mechanism, we performed an initial computational study of the degenerate reaction of the *N*H-substituted model stannylene **1c** with the diazadiene **3c** and identified the oxidative addition product **4c** (Scheme 2) as a possible intermediate. In contrast to the strongly exothermic formation of the stable spirosilane **5c** from **3c** and the silylene **2c**, the reaction leading to **4c** was slightly endothermic and the product featured an unusual Ψ-trigonal-bipyramidal coordination at the tin atom.[8] To obtain better estimates for reactions of species such as **1a,b** and **2a,b,** the bulky substituents of which should have an effect on geometries and relative energies of the cycloadducts, we extended these studies to substrates with more realistic substitution patterns. Furthermore, we studied the corresponding reactions of the germylenes **I*Ge***. Computations were performed at the B3LYP/SDD(pol) level (see Experimental Section). We assigned a structure as local min-



Scheme 2. R = *t*Bu (**1a**–**7a**), Mes (**1b**–**7b**), H (**1c**–**7c**), Me (**1d**–**7d**), 2,6-Me_2-C_6H_3 (**1e**–**7e**).

imum or transition state on the potential energy hypersurface by analyzing the second derivatives (minima have no negative eigenvalues and transition states have one negative eigenvalue of the Hessian matrix). Harmonic vibrational frequencies and zero-point vibrational energies (zpe) were calculated at the same level.

Modeling the interaction of the parent diazadiene **3c** with the germylene **6c**, allowed us to locate a reaction product **7c,** which, like the spirosilane **5c**, is best described as a spirocyclic [1+4] cycloaddition product. The distortion from regular (D_{2d}) symmetry is less pronounced than in **4c** and the coordination geometry at the germanium atom may still be classified as tetrahedral (see Figure 1; a close inspection suggests that the lowering from D_{2d} to C_2 symmetry is primarily due to the pyramidalization at the nitrogen atoms). The cycloaddition leading to **7c** is still exothermic ($\Delta E = -5.7\,\text{kcal}\,\text{mol}^{-1}$), although much less so than in the case of the spirosilane **5c** ($\Delta E = -57.8\,\text{kcal}\,\text{mol}^{-1}$[8]). In line with this result, cleavage of **7c** by [1+4] cycloreversion requires a sizeable activation energy ($\Delta E^{\ddagger}_{2} = 14.8\,\text{kcal}\,\text{mol}^{-1}$) but proceeds more smoothly than with **5c** ($\Delta E^{\ddagger}_{22} = 64.9\,\text{kcal}\,\text{mol}^{-1}$). In view of the fact that the computed Gibbs enthalpy for the formation of **7c** from **3c** and **6c** is positive ($\Delta G_{298} = +7.0\,\text{kcal}\,\text{mol}^{-1}$ versus $-44.0\,\text{kcal}\,\text{mol}^{-1}$ for **5c** at the same level), the spirogermane **7c** must be considered a possible intermediate in a Ge-transfer reaction between **2c** and **6c** rather than a stable adduct.

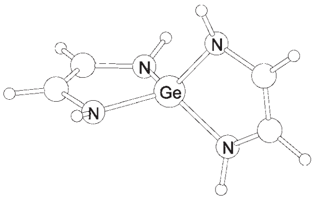


Figure 1. Computed C_2-symmetric molecular structure of the spirogermane **7c**

As expected, formal replacement of *N*H-hydrogen atoms by larger Me and *t*Bu groups has some effect on both molecular geometries and relative energies of the adducts **4**, **5**, and **7**. The structural changes in the spirocyclic cages of the silanes **5c**, **5d** (R = Me), and **5a** (R = *t*Bu), and germanes **7c,d,a** are not very significant; the central atoms maintain their distorted tetrahedral coordination sphere (see Figure 2; local D_{2d} symmetry except for **7c**, vide supra) and the E–N bonds lengthen slightly when the size of the substituents increases (Table 1).

In contrast, the tin-containing spirocycles **4** display both a marked lengthening of Sn–N bonds and substantial deformations of N-Sn-N bond angles with increasing substituent size. As a consequence, the coordination polyhedron of the tin atom changes from a distorted *Ψ*-trigonal-bipyramid whose axial bonds are bent towards the equatorial ones (**4c**) to one whose axial bonds are bent away from the equatorial ones (**4a**; Figure 2). Whereas the angular distortions are most likely attributable to growing steric hindrance between the peripheral substituents, the observation of parallel (although less-pronounced) changes in Sn–N lengths in the stannylenes **1** (Sn–N 2.098 (**1c**), 2.107 (**1d**), 2.123 Å (**1a**)) suggest that the increase of bond length may be partly at-

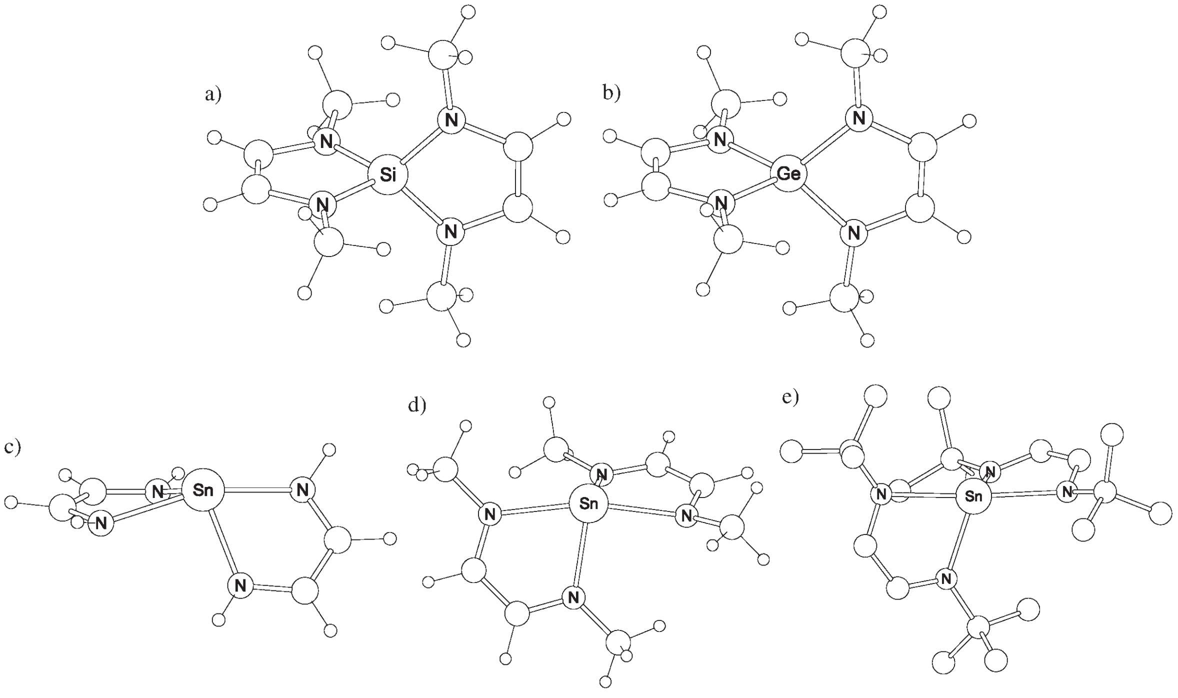


Figure 2. Computed molecular structures of the spirocyclic cycloadducts: a) **5d**, b) **6d**, c) **4c**, d) **4d**, and e) **4a** (H atoms omitted for clarity in **4a**). The molecular symmetry is D_{2d} for **5d**, **6d**, and C_2 for **4a,c,d**.

Table 1. Computed bond lengths in the spirocyclic frameworks ([Å] at the B3LYP/SDD(pol) level) of the stannanes **4a**,**c**,**d**, silanes **5a**,**c**,**d**, and germanes **7a**,**c**,**d**.

	E	R	Sym.	E–N		N–C		C–C
5c	Si	H	D_{2d}	1.742		1.416		1.352
5d	Si	Me	D_{2d}	1.745		1.411		1.357
5a	Si	*t*Bu	D_{2d}	1.762		1.413		1.353
7c	Ge	H	C_2	1.850	1.866	1.415	1.419	1.356
7d	Ge	Me	D_{2d}	1.852		1.408		1.359
7a	Ge	*t*Bu	D_{2d}	1.868		1.409		1.355
4c	Sn	H	C_2	2.157[a]	2.269[b]	1.359	1.359	1.398
4d	Sn	Me	C_2	2.203[a]	2.305[b]	1.348	1.350	1.402
4a	Sn	*t*Bu	C_2	2.200[a]	2.327[b]	1.358	1.366	1.388
4e	Sn	Mes′	C_2	2.215[a]	2.337[b]	1.352	1.364	1.393

[a] "Equatorial" bond. [b] "Axial" bond.

tributable to electronic influences such as a varying degree of hyperconjugation with exocyclic N–R bonds.

A more significant substituent influence was established for the energies of the intermediate cycloadducts and transition states in the oxidative additions of the diazadienes **3** to the carbene analogues **1**, **2**, and **6** shown in Scheme 2. Both the energies ΔE and free enthalpies ΔG_{298} of the cycloadducts increase relative to the values of the parent spirocycles (**4c**, **5c**, **7c**) by 6–8 kcal mol^{-1} upon introduction of methyl and by 12–17 kcal mol^{-1} upon introduction of *t*Bu groups at the nitrogen atoms (see Table 2); 2,6-dimethylphenyl (Mes′) groups which were chosen to simulate mesityl substituents appear to be less destabilizing than *t*Bu moieties in stannylenes. As a consequence, the formation of all *N*-substituted spirogermanes and spirostannanes with $R \neq H$ is both endothermic and endergonic. The changes in energies ($\Delta\Delta E$ and $\Delta\Delta G_{298}$) are considered to reflect growing steric strain between increasingly larger substituents in the spirocycles, and the higher degree of destabilization for the Si- than for Ge-centered adducts suggesting that the importance of this effect increases when the size of the tetrahedrally coordinated central atom decreases.

To provide further mechanistic insight, we also located transition states for the individual reactions. The energies and free enthalpies of activation ($\Delta E_1^{\ddagger}$, $\Delta G_{1,298}^{\ddagger}$) increase with increasing substituent size for each class of compounds parallel to the energies of the spirocycles (Table 2). Quite remarkably, the activation energies ($\Delta E_1^{\ddagger}$) and free enthalpies ($\Delta G_{1,298}^{\ddagger}$) for the cycloadduct formation are higher for germylenes **6** than for corresponding stannylenes **1**, even though the energies and Gibbs enthalpies of the adducts themselves (ΔE, ΔE_{298}) display a reverse order (Table 2). This means that transfer of a tin atom between two diazadiene fragments requires a lower activation barrier than transfer of a germanium atom although the formation of the transient adducts is more endothermic and endergonic. As a consequence of this trend, the energy barrier $\Delta E_2^{\ddagger}$ required for cleavage of a spirocycle decreases from the germanium compounds **7** to the spirostannanes **4**, and in particular the latter are located in extremely shallow local minima of the energy hypersurface (<1 kcal mol^{-1}) and must therefore be considered very short-lived species. Although the implications of these results are currently not fully understood, the energy profile of the stannylene cycloaddition bears a formal resemblance to reactions that pass through a structureless transition region rather than a well-defined transition state, and display energy profiles with a broad "plateau" rather than a well-defined maximum (Figure 3).[10]

Computational studies on oxidative additions between the *N*-substituted stannylenes **1** with diazadienes revealed that the unique distortion of the tin coordination sphere in the parent spirocycle **4c**[8] survives even in the presence of bulky substituents with significant steric repulsion. Although the origin of this deformation was acceptably explained as resulting from the geometric constraints imposed by the incorporation of two long geminal Sn–N bonds in a rigid five-membered ring,[8] we have further analyzed the impact of

Table 2. Computed relative energies and Gibbs enthalpies (in kcal mol^{-1} at the B3LYP/SDD(pol) level) of transition states and spirocycles formed in the cycloadditions of the carbene analogues **1**, **2**, and **6** with the diazadienes **3** shown in Scheme 2. The given figures of ΔE (ΔG_{298}) denote the difference in energies (Gibbs enthalpies) between cycloadducts and reactants (free carbene analogue and *trans*-diazadiene). $\Delta E_1^{\ddagger}$($\Delta G_{298,1}^{\ddagger}$)and $\Delta E_2^{\ddagger}$ are the energies (Gibbs enthalpies) required to reach the transition state from the side of the reactants or the spirocycle, respectively.

Reactants	E	R		Cycloadduct		Transition state		
				ΔE[a]	ΔG_{298}[a]	$\Delta E_1^{\ddagger}$[a]	$\Delta G_{298,1}^{\ddagger}$[a]	$\Delta E_2^{\ddagger}$
2c + 3c	Si	H	**5c**	−57.8	−44.0	7.1	17.1	64.9
2d + 3d	Si	Me	**5d**	−49.0 *(8.8)*	−34.8 *(9.2)*	10.4 *(3.3)*	21.9 *(4.8)*	59.4
2a + 3a	Si	*t*Bu	**5a**	−40.9 *(16.9)*	−22.6 *(21.4)*	23.2 *(16.1)*	37.4 *(20.4)*	64.1
6c + 3c	Ge	H	**7c**	−5.7	7.0	9.2	20.6	14.9
6d + 3d	Ge	Me	**7d**	2.8 *(8.5)*	14.5 *(7.5)*	14.3 *(5.1)*	26.0 *(5.4)*	11.5
6a + 3a	Ge	*t*Bu	**7a**	6.9 *(12.6)*	23.0 *(16.0)*	27.7 *(18.5)*	42.2 *(21.6)*	20.8
1c + 3c	Sn	H	**4c**	1.1	13.4	5.6	15.3	4.5
1d + 3d	Sn	Me	**4d**	6.8 *(5.7)*	18.4 *(5.0)*	7.4 *(1.8)*	18.6 *(3.1)*	0.6
1a + 3a	Sn	*t*Bu	**4a**	21.7 *(20.6)*	34.3 *(20.9)*	21.8 *(16.2)*	35.4 *(20.1)*	0.1
1e + 3e	Sn	Mes′	**4e**	15.4 *(14.3)*	-	-	-	

[a] Values in parentheses denote substituent-induced excess energies (Gibbs enthalpies) $\Delta\Delta E$ ($\Delta\Delta G_{298}$) relative to the parent compounds with R=H.

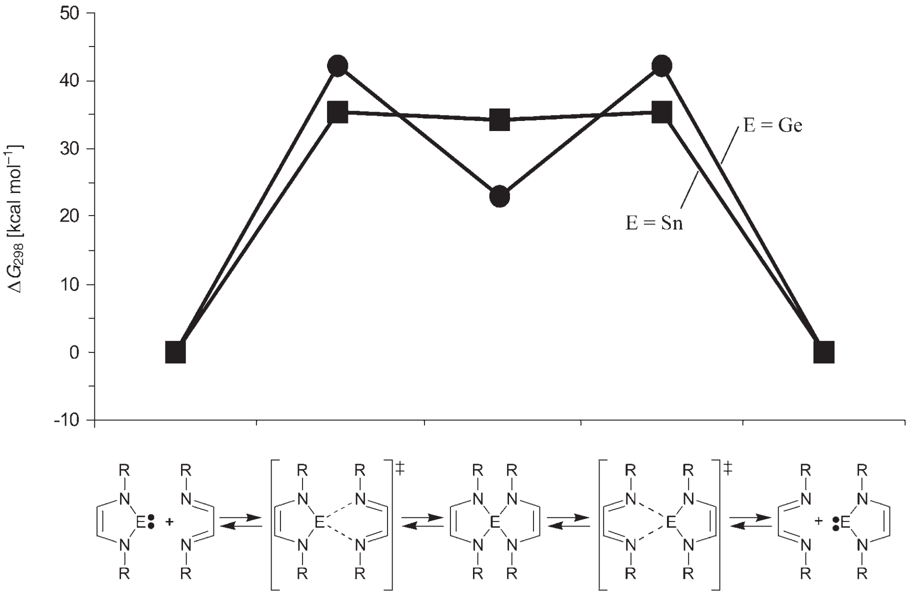


Figure 3. Comparison of computed Gibbs enthalpies ΔG_{298} of intermediates and transition states in reactions of the stannylene **1a** (squares) and germylene **6a** (circles) with the diazadiene **3a** (R = *t*Bu).

this distortion on the electronic structure. Taking into account that the resemblance with the molecular structure of Sn^{II}–amidinates[11] and a natural bond orbital (NBO) analysis suggested a description of the C_2-symmetric **4c** as a donor-stabilized tin(II) amide with a lone pair of electrons at the tin atom;[8] the molecule can be formally decomposed into a Sn^{2+} ion and two chelating diazadiene radical anions (the existence of stable diazadienyl radical anions and their ability to act as chelate ligands have been independently established by ESR studies[12]). It is evident that attaching two radical ligands to a central tin(II) ion may occur with or without spin-pairing to yield a complex in a singlet or triplet state. The energetic order of both states is not a priori clear and either one may represent the molecular ground state. To elucidate the relation between singlet and triplet states of the cycloadducts **4** in more detail, we have also explored the properties of the triplet complexes, and their formation by cycloaddition of a singlet diazadiene to a triplet stannylene.[13]

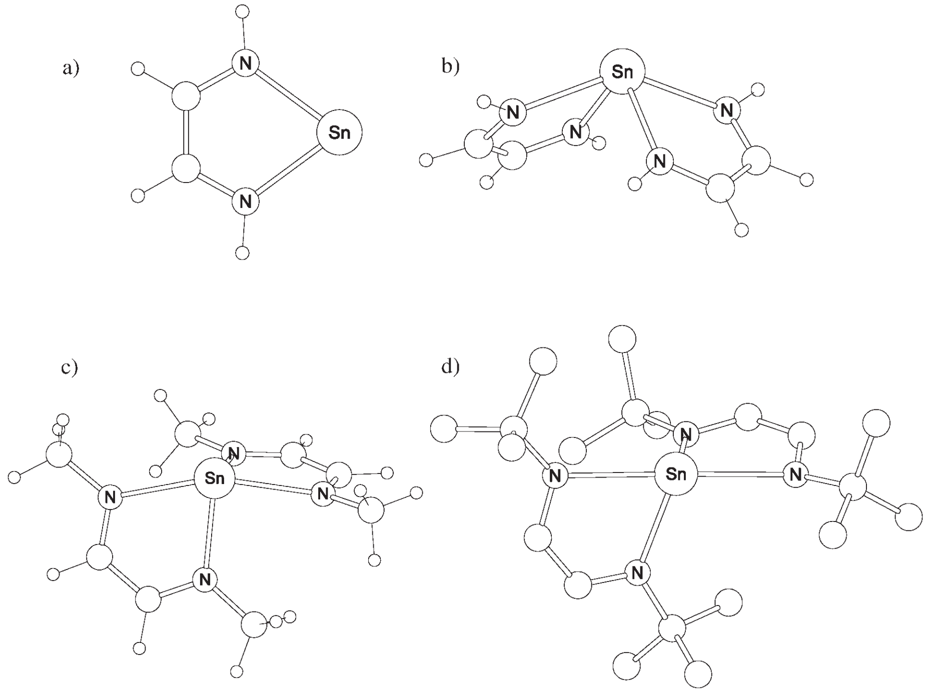


Figure 4. Computed molecular structures for the triplet states of a) the stannylene **1c**, and the spirocyclic cycloadducts b) **4c**, c) **4d**, and d) **4a** (H atoms omitted for clarity for **4a**).

Triplet complex **4c** features a Ψ-tbp C_2-symmetric molecular structure (Figure 4) that is distinguished from that of the singlet by longer Sn–N and C=C bonds and slightly shorter C–N bonds in the rings (Table 3). As a consequence of these changes, the deviation of the N-Sn-N "axis" from linearity is even larger than in the singlet state. A negative singlet–triplet excitation energy suggests that the triplet state has a lower energy than the singlet state. Comparison of molecular structures and energies of singlet and triplet states of the *N*-substituted spirocycles **4a,d** reveals similar geometric changes, and the triplet remains always lower in energy. The analysis of the computed spin densities reveals that each of the two unpaired electrons resides in a delocalized π orbital extending over the NCCN-moiety of one diazadiene fragment and thus agrees with the aforementioned description of the spirocycles **4** as complexes of a Sn^{2+} cation with two diazadiene radical anion ligands.

Although the DFT calculations on singlet and triplet spirostannanes appear to favor the assignment of triplet ground states for all adducts **4**, this result must be considered preliminary with regard to the low magnitudes of ΔE-

Table 3. Computed endocyclic bond lengths in the triplet state [Å] and singlet–triplet excitation energies $\Delta E(S\rightarrow T)$ and Gibbs enthalpies $\Delta G_{298}(S\rightarrow T)$ (in kcal mol^{-1}) for the stannylenes **1a**,**c**,**d**, and the spirostannanes **4a**,**c**,**d** at the B3LYP/SDD(pol) level.

	R	Sym.	$\Delta E(S\rightarrow T)$	$\Delta G_{298}(S\rightarrow T)$	E–N		N–C		C–C
1c	H	C_{2v}	33.8	31.2	2.296		1.341		1.416
1d	Me	C_{2v}	29.8	26.9	2.292		1.338		1.414
1a	*t*Bu	C_{2v}	30.2	26.8	2.313		1.339		1.413
4c	H	C_2	−9.0	−10.6	2.222[a]	2.415[b]	1.345	1.339	1.414
4d	Me	C_2	−9.5	−11.3	2.256[a]	2.417[b]	1.343	1.334	1.411
4a	*t*Bu	C_2	−6.5	−7.6	2.296[a]	2.532[b]	1.353	1.334	1.408

[a] "Equatorial" bond. [b] "Axial" bond.

(S→T): as the singlet spirocycles can be viewed as singlet biradicals or biradicaloids,[16] it may not necessarily be viable to describe their electronic structure in terms of a state originating from a single-electron configuration, and we may envisage that by using an adequate approach (for example by using MCSCF) we may see a stabilization of the singlet up to the point where the relative order of singlet and triplet states is again reversed. We have undertaken the first steps into a more elaborate investigation of this question but a full discussion is beyond the scope of the present work and will be presented elsewhere.

The triplet stannylenes **1a**,**c**,**d** feature planar five-membered rings and an even more pronounced lengthening of Sn–N and C=C, and shortening of C–N bonds than the spirocyclic adducts. The positive singlet–triplet excitation energies confirm singlet ground states but their magnitude of 30–34 kcal mol^{-1} is much smaller than the values of more than 80 kcal mol^{-1} for imidazoyl carbenes.[1,14] These results seem to contradict the trend that $\Delta E(S\rightarrow T)$ increases in a series of isoelectronic carbene analogues ER_2 with the atomic number of E (as a result of the improved stabilization of a lone-pair in a molecular orbital with high s character), but the apparent contradiction is easily resolved if we consider that the triplet states of a stannylene **1c** and a carbene **I*C*** represent different electronic states. The triplet carbene is, in simple terms, formed by promoting one electron from a molecular orbital of a_1 symmetry (representing the carbon "lone-pair") to the lowest π* MO of b_1 symmetry and corresponds thus to a $^3B_1$ state; in contrast, the lowest triplet state of the stannylene **1c** results from promotion of an electron from an a_2 orbital (representing the antisymmetric combination of the nitrogen lone pairs) into the same $b_1(\pi^*)$ MO and represents a $^3A_1$ state.

The finding of a triplet ground state for the spirostannanes **4** can be considered a highly interesting result as it implies an intersection of the potential energy hypersurfaces that represent the interaction of a diazadiene **3** with singlet or triplet stannylenes, respectively (Figure 5). If we imagine that the reaction of **3** with singlet **1** passes through a region of the hypersurface near the crossing point, there is a certain probability that a spin crossover occurs and a triplet adduct is formed.[17] Considering further that a) reconversion of this species into a diazadiene and a singlet stannylene requires another spin inversion and is therefore also considered a rather unlikely process, and b) fragmentation into a diazadiene and a triplet stannylene is highly endothermic, we can envisage that the actual decay of the transient triplet adduct follows a different path and yields completely different products. A mechanism of this type could provide an explanation for the thermal decomposition of the *N*-heterocyclic stannylenes **1a,b** under deposition of elemental tin and will be discussed later in the context of further experimental evidence that supports this hypothesis.

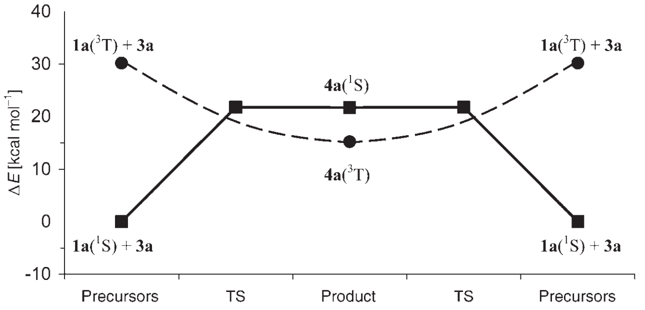


Figure 5. Schematic representation of the relative energies of stationary points on the energy hypersurfaces for the reactions of the diazadiene **3a** with the singlet (squares) and triplet (circles) states of the stannylene **1a** to give the singlet and triplet states of the spirocycles **4a**.

To assess if a reversed order of singlet and triplet states is also viable for the spirogermanes and spirosilanes **5** and **7**, we also studied the triplet states of these species. The parent compounds **5c** and **7c** feature C_2-symmetric structures with a relative elongation of two E–N bonds (see Figure 6) but may still be described as having distorted tetrahedral coordination of the central atoms. The triplet states of the silylene **2c** and the germylene **6c** contain nonplanar five-membered rings with flat-envelope conformations the bond lengths of which show similar deviations from those in the correspond-

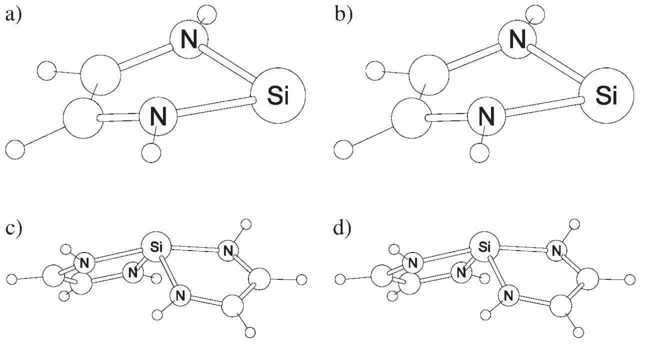


Figure 6. Computed molecular structures for the triplet states of a) silylene **2c** and b) germylene **6c**, and the spirocyclic cycloadducts c) **5c**, and d) **7c**.

ing singlet species as were noted for **1c**. The $^3A'$ electronic state of both species may be rationalized, as in **1c**, as arising from formal promotion of an electron from an a_2 (nitrogen lone pair) into a b_1 MO (π^*); additional studies suggest that the deviation from planarity arises from mixing of the $^3A_1$ and $^3B_1$ states of a C_{2v} symmetric molecule that are much closer in energy than in **1c**. The singlet–triplet splittings (Table 4) in both two- and four-coordinate germanium compounds **6c**, **7c** are larger (by some 13–18 kcal mol^{-1}) than in the corresponding tin compounds, and a further increase is observed for the appropriate silicon-containing molecules **2c**, **5c**. All species have thus a singlet ground state, and the participation of triplets in the reactions of diazadienes with the cyclic germylenes or silylenes **4c, 6c** seems unlikely.

Table 4. Computed endocyclic bond lengths [Å] and singlet–triplet excitation energies ΔE(S→T) and Gibbs enthalpies ΔG_{298}(S→T) (in kcal mol^{-1}) for the triplet states of the silylene **2c**, germylene **6c**, and the spirocycles **5c**, **7c,** at the B3LYP/SDD(pol) level.

	E	Sym.	ΔE (S→T)	E−N		N−C		C−C
2c	Si	C_s	60.8	1.958		1.346		1.413
6c	Ge	C_s	45.8	2.122		1.340		1.416
5c	Si	C_2	54.2	1.829[a]	1.961[b]	1.361	1.367	1.390
7c	Ge	C_2	9.5	2.025[a]	2.292[b]	1.347	1.339	1.411

[a] "Equatorial" bond. [b] "Axial" bond.

Summarizing the computational results we can state that products arising from oxidative addition of diazadienes to *N*-heterocyclic germylenes and stannylenes are, unlike the corresponding silylenes, predicted to be transient intermediates in a formal atom-transfer reaction rather than stable species. The transfer of a Ge-atom requires a higher activation energy, and thus proceeds at a lower rate, than the transfer of a Sn atom in a compound with identical substituents. Last, but not least, triplet states might interfere in reactions of diazadienes with stannylenes, but not in those with germylenes.

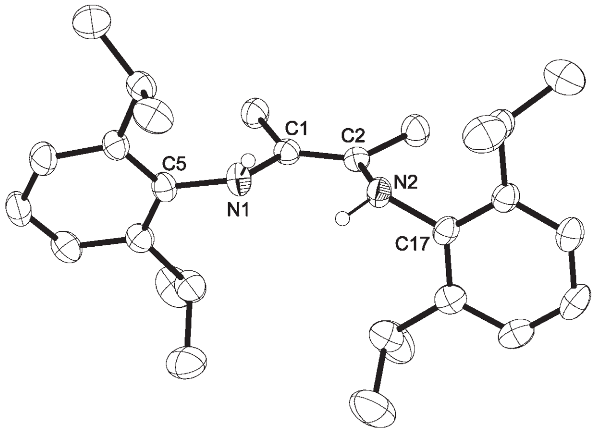
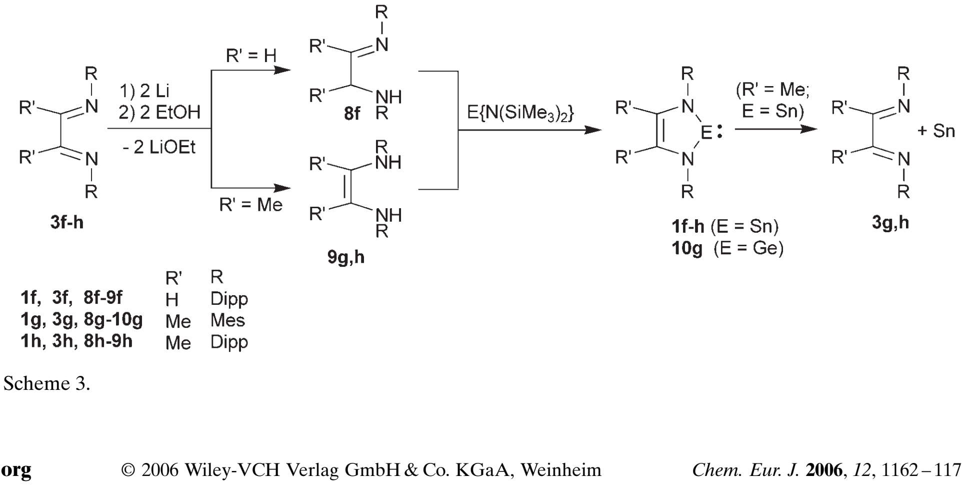


Figure 7. Molecular structure of **9h** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, hydrogen atoms of CH_n moieties omitted for clarity; selected bond lengths [Å]: N1−C5 1.425(2), N1−C1 1.433(2), N2−C2 1.428(2), N2−C17 1.446(2), C1−C2 1.339(2).

Syntheses of *N*-heterocyclic germylenes and stannylenes: Having found that the 1,3-disubstituted stannylenes **1a,b** can be accessed through transamination of tin(II) amides with α-amino-aldimines[8] we set out to extend this approach to the synthesis of *N*-heterocyclic stannylenes with other substitution patterns. To prepare appropriate aldimine precursors, we reduced the *N*-arylated diazadienes **3f–h**[18] with excess Li and the resulting dianions were then quenched with ethanol. We isolated tautomeric ene-diamines (**9g,h**) by workup of the reaction mixtures and we obtained the expected α-amino-aldimine only in one case (**8f**). All products were characterized by using analytical and spectroscopic data, and the ene-diamine **9h** was confirmed by a single-crystal X-ray diffraction study. The molecule (Figure 7) contains a *Z*-configured double bond with two pyramidal amino substituents ($\Sigma N_1 = 346°$, $\Sigma N_2 = 340°$); the C=C (1.339(2) Å) bonds are similar and the C−N bonds (1.428(2), 1.433(2) Å) slightly longer than known lengths in acyclic secondary ene-diamines (C=C 1.34±0.01, C−N 1.39±0.02 Å[19]).



Scheme 3.

Transamination of **8f** with $Sn\{N(SiMe_3)_2\}_2$ at 60 °C in hexane afforded the expected stannylene **1f** as an orange, air- and moisture-sensitive, crystalline solid (Scheme 3). In contrast to solid **1b**, which decomposes around 100 °C, pure **1f** was stable up to 130 °C before decomposing slowly with deposition of elemental tin. Although we could not obtain suitable crystals for an X-ray diffraction study, we established the identity of **1f** by using spectroscopic and analytical data. Of particular significance was the presence of the molecular ion in the mass spectrum, the similarity of solution

^{13}C, ^{15}N, and ^{119}Sn NMR data with those of **1b**, and the observation of a signal with a large chemical shift anisotropy ($|\delta_{11}-\delta_{33}|=1324$ ppm) in a solid-state slow-spinning ^{119}Sn CP/MAS NMR spectrum. Large anisotropies of the shielding tensors caused by strong deshielding of a single principal component as observed here are typical for *N*-heterocyclic carbene analogues.[20]

The analogous condensation of $Sn\{N(SiMe_3)_2\}_2$ with the ene-diamines **9g**,**h** required temperatures of 100–120 °C and gave mixtures of several products. NMR studies showed the formation of a product that we assigned as the stannylene **1h** beside tin and the diazadiene **3h** from the precursor **8h** although none of the products could be isolated in pure form. Only tin and the diazadiene **3g** were identified in the corresponding reaction of **8g**.

The suitability of the transamination method for the preparation of germylenes was demonstrated by the synthesis of the novel *C*-methylated derivative **10g** from **9g** and $Ge\{N(SiMe_3)_2\}_2$ (Scheme 3). The product was isolated as an orange crystalline solid and was characterized by analytical and spectroscopic data, and a single-crystal X-ray diffraction study. The molecular structure (Figure 8) features a planar five-membered ring with endocyclic bond distances (average values: Ge–N 1.864, C–N 1.384, C=C 1.364 Å) that are in close agreement with the known data of **10a** (Ge–N 1.856, C–N 1.391, C=C 1.368 Å[21]). Solutions of **10g** showed no evidence of thermal decomposition up to 120 °C.

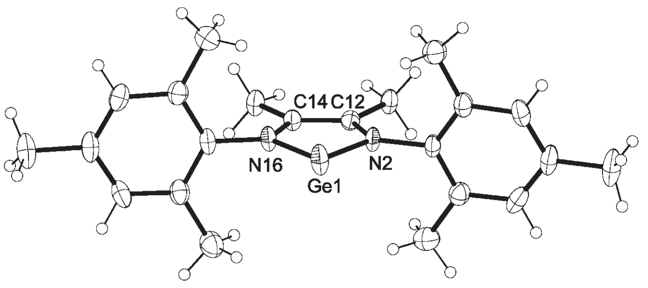


Figure 8. Molecular structure of **10g** in the crystal, ORTEP view thermal ellipsoids are at the 50 % probability level; selected bond lengths [Å] and angles [°]: Ge1–N2 1.864(2), Ge1–N16 1.864(2), C12–N2 1.390(3), C14–N16 1.391(3), C12–C14 1.368(3); N16-Ge1-N2 82.8(1).

Reactions of carbene analogues with diazadienes: Reactions of *N*-heterocyclic carbene analogues with diazadienes were studied to establish both if the transformation under formal single-atom-transfer is a general scheme for stannylenes and germylenes, and to obtain experimental data giving insight into the energetics and mechanism of the reaction. Having previously detected the "degenerate" interconversion between stannylenes **1a**,**b** and diazadienes **3a**,**b** bearing like-substituents using dynamic NMR spectroscopy,[8] we used the same approach to explore the reactions of the new stable carbene analogues **1f** and **10g** with the corresponding diazadienes **3f**,**g**, respectively. In contrast to the previously studied cases where interchange on a subsecond timescale was easily detectable in two-dimensional (2D) EXSY NMR spectra at around room temperature, we saw no evidence in spectra of mixtures of **1f**/**3f** in [D$_8$]toluene for intermolecular exchange on a second timescale up to 110 °C. Quite surprisingly, under these conditions no cycloreversion of **1f** under formation of tin and diazadiene was detected whereas a noticeable decay of **1a**,**b** occurred at much lower temperatures (around 60 °C). We noticed the immediate onset of a "nondegenerate" exchange reaction, however, upon addition of a small amount of diazadienes **3a** or **3b**, respectively, to a solution of **1f**; under these conditions, both formation of the cross-products **1a** (**1b**)/**3f**, and (above 60 °C) the deposition of tin were observed.

Analogous 2D EXSY NMR studies of mixtures containing either the germylene **10g** and the diazadiene **3g**, or a mixture of the sterically less-hindered species **10a**[21]/**3a**, gave no evidence for reaction under formal transfer of germanium atoms below 110 °C. Similar negative results were obtained for the nondegenerate cross-reactions between **10a** and **3g**. In the ^{1}H NMR spectra of a solution of the germylene **10g** and the diazadiene **3a** in [D$_8$]toluene, we observed small signals attributable to the expected transformation products **10a**/**3g** after the solution had been heated to 70 °C for a short time. Near quantitative conversion ($>98\,\%$) into the cross-products was observed when this temperature was maintained for 12 h. Careful monitoring of the spectra throughout the reaction showed that, apart from the decay of the signals of the starting materials and the growth of those of the products, no further changes indicating the formation of intermediates or decomposition products occurred.

We interpret the conversion of **10g**/**3a** into the cross-products **10a**/**3g** as proof that *N*-heterocyclic germylenes undergo similar exchange reactions with diazadienes as their heavier homologues; we did not detect the reverse reaction presumably because of the higher thermodynamic stability of **10a**/**3g** as compared to **10g**/**3a**. Furthermore, the failure to observe "degenerate" exchange between germylenes and diazadienes with identical substituents does not necessarily disprove that such processes take place at all, but suggests simply that their rate is too low to be detected by dynamic NMR spectroscopy. Thermal decomposition of the stannylenes **1a**,**b** has been previously found to be facilitated by catalytic amounts of nucleophilic impurities,[8] and the coincidence between the simultaneous onset of intermolecular metathesis of **1f** with the diazadienes **3a**,**b** and thermal decomposition of the stannylene is further interpreted as evidence that the deposition of tin from *N*-heterocyclic stannylenes at low temperatures implies no simple monomolecular [1+4] cycloreversion. Instead, we suggest that this reaction is associated with the bimolecular tin atom transfer process. On the basis of the previously discussed computational results, we propose a mechanism in which the transient singlet spirocyclic adduct is a key intermediate for both the atom-transfer and the decomposition processes. The first reaction proceeds straightforwardly by a simple retro-[1+4] addition, whereas the second one is initiated by spin-conversion to yield the triplet spirocycle that cannot undergo cycloreversion because of energetic reasons but decays via a different route. It should be noted that this mechanistic proposal accounts as well for the markedly different thermal stabilities of *N*-heterocyclic stannylenes and germylenes as the conversion of a singlet into a triplet germaspirocycle is inhibited because of the higher singlet–triplet separation in this case so that the decomposition pathway is blocked.

Assuming that the exchange between diazadienes and *N*-heterocyclic germylenes and stannylenes follows a common mechanism, further mechanistic studies focused on the stannylene system as here the higher reaction rates allowed the use of dynamic NMR spectroscopy as a tool for kinetic studies. A comprehensive investigation of the "degenerate" interconversions between **1a**/**3a** and **1b**/**3b**, respectively, showed that the exchange between stannylenes and diazadienes is not restricted to the previously reported[8] temperature range of 30–60 °C (where the onset of decomposition precluded further studies), but can be detected in 2D EXSY ^{1}H NMR spectra obtained with mixing times between 500 and 1000 ms at temperatures as low as −20 °C. Careful examination of the spectra of mixtures of **1b**/**3b** revealed, beside cross-peaks connecting the two reactants, further exchange correlations to a third species present in low concentration (approximately 1–2 % relative to **3b**).[22] The signals of this species were also detected in ^{1}H NMR spectra of pure **3b** and are assigned to a stereoisomer with *E*/*Z*-configured C=N double-bonds that is in dynamic equilibrium with the *E*/*E*-configured major isomer. Acquisition of 2D EXSY spectra of solutions to which small amounts of amines such as $HN(SiMe_3)_2$ or the α-amino aldimine **9b** had been deliberately added gave no evidence for the participation of these species in the exchange and allowed us to conclude that the stannylene/diazadiene interconversion proceeds at a much faster rate than a conceivable substituent metathesis via transamination reactions.

Beside the evaluation of exchange pathways, the measurement of rate constants may provide further mechanistic information. By the nature of dynamic NMR spectroscopy, measurable site-to-site rate constants are pseudo first-order and have to be divided by the equilibrium concentrations of all other reactants to obtain figures that give a correct description of the chemical process.[23] In the case of dynamic exchange between a stannylene and a diazadiene, the occurrence of a spirocyclic adduct as transition state or transient intermediate as outlined in Scheme 2 requires that the rate determining step obeys a second-order rate law. Assuming the validity of this hypothesis, the ratio of the observable rate constant k_{obs}(s→d) for the stannylene→diazadiene conversion and the equilibrium concentration of the diazadiene (and, vice versa, the ratio of the reverse rate constant k_{obs} (d→s) and the concentration of the stannylene) must be constant, and a measurable deviation from this relation would allow us to disprove the proposed mechanism. To clarify this issue we have carried out one-dimensional (1D) magnetization transfer experiments[24] to determine the pseudo first-order rate constants for the conversion of the stannylenes **1a**,**b** into the diazadienes **3a**,**b** over a range of concentrations. We found that solutions containing **1b**/**3b** were sufficiently stable to give the desired kinetic information, whereas mixtures of **1a**/**3a** decomposed erratically in the course of the experiments and no meaningful results were obtained. Evaluation of the calculated ratio $k_{12} = k_{obs}$ (**1b**→**3b**)/m(**3b**) (see Experimental Section) illustrates that, within the available experimental accuracy, k_{12} does not change and the data are thus compatible with the postulated reaction mechanism.

Magnetization transfer experiments at different temperatures allowed us to further evaluate the temperature dependence of the rate constant for the exchange between **1b** and **3b** (see Supporting Information) and to compute values for the activation enthalpy ($\Delta H^{\pm} = 8(1)$ kcal mol^{-1}) and entropy ($\Delta S^{\pm} = -26(3)$ cal K^{-1} mol^{-1}). Even though the results must be regarded with some skepticism owing to a noticeable correlation between both parameters that results from the rather small range of temperatures covered, it appears that the energetic contribution to the free enthalpy of activation $\Delta G^{\pm}$ is rather small but is accompanied by a sizeable negative activation entropy. The latter suggests a highly ordered transition state and agrees well with the proposed associative reaction mechanism which implies considerable steric crowding at the stage of the intermediate adduct. The magnitudes of the experimental values of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ are substantially smaller than those obtained from the computational studies on the reaction of **1a**/**3a** ($\Delta H^{\pm}_{298} = 21.5$ kcal mol^{-1}, $\Delta S^{\pm}_{298} = 46.7$ cal K^{-1} mol^{-1}). In assessing this difference it must be considered, however, that the deviation is partly attributable to the effect of formally replacing the *t*Bu groups in **1a**/**3a** by Mes substituents (like the decrease of the computed relative energy of the adduct **4e** (R = Mes′) versus **4a** (R = *t*Bu) by 6.4 kcal mol^{-1}; see Table 2), and that the computational model is far from being very sophisticated and neglects, among other factors, the influence of solvent effects.

Reaction of a *N*-heterocyclic stannylene with sulfur: It has recently been reported that reactions of sterically crowded stannylenes with sulfur or selenium yield tetrachalcogenostannolanes, which can be disassembled to give isolable products containing tin=sulfur and tin=selenium double bonds.[25] To explore if similar reactions are viable for *N*-heterocyclic stannylenes, we studied the reaction of **1f**, which was chosen as the thermally most stable and sterically best-protected derivative available, with one equivalent of sulfur. The reaction required slight warming to 40 °C and afforded a clear yellow solution and a brown precipitate. The diazadiene **3f** was the only species detectable by ^{1}H NMR spectroscopy in the supernatant solution, and energy dispersive X-ray (EDX) analysis gave an elemental composition of $SnS_{1.05}$ for the solid; attempts to characterize this material by powder diffraction studies produced featureless diffractograms that suggest a low-degree of crystallinity. The analytical data suggest that the reaction of **1f** with sulfur proceeds with quantitative formation of the diazadiene **3f** and tin(II) sulfide. Although both species represent the products of a formal

[1+4] cycloreversion of a hypothetical stannylene sulfide formed by oxidative sulfurization of **1f**, the spectroscopic detection of such a species was not possible and the mechanistic proposal remains speculative. Quantitative conversion of **1f** into the diazadiene **3f** was also observed in reactions of the former with air or selenium; in these cases, however, no satisfactory analytical data of the solid by-products were obtained and their exact composition remains unknown.

Conclusion

We have shown that synthesis of *N*-heterocyclic carbene analogues by transamination of $E(NR_2)_2$ with α-amino-aldimines and ring metathesis of the cyclic products with diazadienes under formal exchange of the divalent central atom is feasible for both stannylenes and germylenes. Qualitative kinetic studies indicated that exchange rates are generally higher for stannylenes, and measurement of rate constants indicated that metathesis of the diazadiene **3b** and the stannylene **1b** is characterized by second-order kinetics and a sizeable negative entropy of activation. Studies of the reactivity of the stannylene **1f** towards diazadienes disclosed that the tin transfer reaction is inhibited by the presence of bulky substituents at the ring nitrogen atoms and that this inhibition coincides, quite surprisingly, with a suppression of the fragmentation of the *N*-heterocyclic stannylene into tin and diazadiene. Another example hinting to a connection between oxidative addition and fragmentation reactions is given by the reaction of **1f** with sulfur to yield SnS and a diazadiene.

Computational studies at the DFT level suggest that all metathesis reactions between singlet *N*-heterocyclic carbene analogues and diazadienes proceed via transient spirocyclic [1+4]-cycloaddition products whose formation is (with the exception of the *N*H-substituted spirogermane **6c**) endothermic and endergonic and agrees with the experimentally observed negative entropy of activation for these reactions. The properties of spirostannane and spirogermane intermediates differ notably: the former display a distorted *Ψ*-tbp geometry at the tin atom and their cleavage into stannylene and diazadiene requires low or nearly negligible activation energies, whereas the latter resemble known spirosilanes in exhibiting distorted tetrahedral central atoms and the need to overcome sizeable energy barriers to undergo appropriate fragmentation. Complementary studies of hypothetical cycloadditions of diazadienes to triplet germylenes or stannylenes indicate that these reactions are exothermic and yield interesting results concerning relative energies for singlet and triplet states of both carbene analogues and spirocycles: the germylenes and stannylenes exhibit the expected singlet ground states but the nature of the lowest triplet state differs from that of *N*-heterocyclic carbenes (resulting from promotion of an electron from an n(N) orbital with π character rather than the n(C)-σ orbital, to a π* orbital), and singlet–triplet excitation energies are lower than in carbenes and decrease from 60 $kcal\,mol^{-1}$ for the silylene to 45 $kcal\,mol^{-1}$ for the germylene and 30–33 $kcal\,mol^{-1}$ for stannylenes. For spirostannanes, the geometric distortion towards *Ψ*-tbp coordination at the tin atom coincides with a change from singlet to triplet ground state multiplicity that implies that the energy hypersurfaces for the reactions of singlet and triplet stannylenes with a diazadiene intersect. Although further validation of this finding by more sophisticated theoretical models (for example, by using an MCSCF approach) is certainly required, its consideration suggests a way to rationalize the different thermal stabilities of *N*-heterocyclic germylenes and stannylenes, and the coincidence between ring metathesis and thermal decomposition of the latter. The key to this explanation is the hypothesis that the proximity of singlet and triplet energy hypersurfaces in the stannylene–diazadiene system facilitates spin crossover to give a triplet species that may then disproportionate to give tin and diazadiene rather than decay via [1+4] cycloreversion; in contrast, in the germanium case, triplet species are much higher in energy than the corresponding singlet species and their participation need not be considered.

Experimental Section

General remarks: All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker Avance 300 (^1H: 300.1 MHz, ^{13}C: 75.4 MHz, ^{119}Sn: 111.9 MHz) and Avance 400 (^1H: 400.1 MHz, ^{119}Sn: 148.7 MHz) at 303 K; chemical shifts were referenced to external TMS (^1H, ^{13}C), Me_4Sn ($\Xi = 37.290632$ MHz, ^{119}Sn); coupling constants are given as absolute values; prefixes *i*, *o*, *m*, *p* denote atoms of *N*-aryl substituents. MS: VG-Instruments VG 12–250. Elemental analyses: Perkin–Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries.

Computational studies: DFT calculations were carried out with the Gaussian 98 program suite[26] using Becke's three-parameter exchange functional with a Lee–Yang–Parr correlation energy functional (B3LYP) and SDD basis sets that were augmented by one set of polarization functions on all heavy atoms. The basis set employs a D95V split-valence basis for the lighter atoms, and Stuttgart/Dresden ECP at Ge and Sn. Harmonic vibrational frequencies and zero-point vibrational energies (ZPE) were calculated at the same level. All structures reported are minima (only positive eigenvalues of the Hessian matrix) or transition states (one negative eigenvalue) on the potential energy surface. Analyses of electron populations and spin densities were carried out with the NBO 5.0 module.[27] Listings of atomic coordinates and relative molecular energies are given as Supporting Information.

The diazadienes **3f–h** were prepared by condensation of the appropriate aniline derivative with 2,3-butanedione or glyoxal using established procedures.[18]

General procedure for the preparation of α-aldimino-aldimines (8f) and ene-diamines (9g,h): Lithium turnings (500 mmol) were added to a solution of the appropriate diazadiene **3f–h** (200 mmol) in THF (150 mL) and the mixture was stirred for 2 days under strict exclusion of oxygen. Unreacted lithium was then filtered off and the filtrate evaporated in vacuum. The solid residue was suspended in hexane, the solvent filtered off, and the remaining solid was dried in vacuum. Between 50 and 100 mmol of the crude salt were then dissolved in THF (150–200 mL) and transferred into a dropping funnel that was placed on top of a flask containing THF (ca. 50 mL). A small volume of the lithium diazadienide solution was added to the flask and the mixture stirred until a dark brown-red solution formed. Then, dry ethanol was added dropwise by means of a syringe until the color turned yellow. This procedure was repeated until the required amount of ethanol (120–200 mmol) had been consumed. After completion of the reaction, solvents were evaporated in vacuum. The yellow residue was dissolved in hexane (100 mL) and precipitated LiOEt was filtered off. The filtrate was concentrated to a volume of 50 mL and stored overnight at a temperature of −2 °C. The crystalline precipitate formed was collected by filtration and dried in vacuum. A second batch of product was obtained in the same way after further concentration of the mother liquor.

[2-(2,6-Diisopropylphenyl)iminoethyl]-(2,6-diisopropylphenyl)amine (8 f): Yield 57 %; m.p. 91 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.85$ (t, ^3J(H,H) = 2.1 Hz, 1 H; N=CH), 7.17 (m, 3 H; C$_6$H$_3$), 7.15 (m, 3 H; C$_6$H$_3$), 4.71 (t, ^3J(H,H) = 5.2 Hz, 1 H; NH), 4.10 (dd, ^3J(H,H) = 5.2, 2.1 Hz, 2 H; NCH$_2$), 3.48 (septet, ^3J(H,H) = 6.9 Hz, 2 H; CH), 2.99 (septet, ^3J(H,H) = 6.9 Hz, 2 H; CH), 1.32 (d, ^3J(H,H) = 6.9 Hz, 12 H; CH$_3$), 1.22 ppm (d, ^3J(H,H) = 6.9 Hz, 12 H; CH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): $\delta = 163.4$ (N=*C*), 148.6 (*i*-C), 144.3 (*i*-C), 142.0 (*o*-C), 134.0 (*o*-C), 128.3 (*p*-C), 124.7 (*p*-C), 124.0 (*m*-C), 123.4 (*m*-C), 56.0 (N*C*H$_2$), 28.4 (*C*H(CH$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 23.9 ppm (CH(*C*H$_3$)$_2$); MS (16 eV, EI): *m*/*z* (%): 378 (56) [M^+], 334 (4) [$M^+ - C_3H_7$], 333 (16) [$M^+ - C_3H_8$].

***N,N'*-Di-(2,4,6-trimethylphenyl)-but-2-ene-2,3-diamine (9 g)**: Yield 31 %; m.p. 80 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 6.80$ (s, 4 H; *m*-H), 4.53 (s, 2 H; NH), 2.18 (s, 6 H; *p*-CH$_3$), 2.18 (s, 12 H; *o*-CH$_3$), 1.50 ppm (s, 6 H; CCH$_3$); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): $\delta = 139.9$ (*p*-C), 132.9 (*o*-C), 132.5 (*i*-C), 129.7 (*m*-C), 126.9 (=C−N), 21.1 (*p*-CH$_3$), 18.8 (*o*-CH$_3$), 14.6 ppm (*o*-CH$_3$); MS (16 eV, EI): *m*/*z* (%): 322 (25) [M^+], 305 (41) [$M^+ - $2H, −CH$_3$], 162 (100) [$M^+ - $H, −MesCN].

***N,N'*-Di-(2,6-diisopropylphenyl)-but-2-ene-2,3-diamine (9 h)**: Yield 41 %; m.p. 85 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.17$ (s, 6 H; C$_6$H$_3$), 4.84 (s, 2 H; NH), 3.41 (septet, ^3J(H,H) = 6.5 Hz, 4 H; CH), 1.58 (s, 6 H; =CCH$_3$), 1.29 ppm (d, ^3J(H,H) = 6.5 Hz, 12 H; CH); IR (CH$_2$Cl$_2$, NaCl): $\tilde{\nu} =$ 1666(s), 1650(w), 1638(m), 1621(w) cm^{-1}; MS (16 eV, EI): *m*/*z* (%): 406 (4) [M^+], 362 (5) [$M^+ - C_3H_7$], 362 (19) [$M^+ - C_3H_8$].

1,3-Di(2,6-diisopropylphenyl)-2,3-dihydro-1-*H*-[1,3,2]-diazastannol-2-ylidene (1 f): α-Amino-aldimine **8 f** (3.40 g, 9.0 mmol) and Sn{N(SiMe$_3$)$_2$}$_2$ (3.96 g, 9.0 mmol) were dissolved in hexane (50 mL) and a few drops of HN(SiMe$_3$)$_2$ were added. The solution was stirred for 4 h at 60 °C. The warm reaction mixture was then filtered and its volume slightly reduced in vacuum. The resulting solution was stored overnight at −30 °C. An orange crystalline precipitate formed that was collected by filtration and dried in vacuum to yield 3.10 g of **1 f** (68 %); m.p. 130 °C (decomp); elemental analysis calcd (%) for C$_{26}$H$_{38}$N$_2$Sn (497.3): C 63.07, H 7.28, N 5.66; found: C 62.22, H 7.70, N 5.43; ^{1}H NMR (300 MHz, C$_6$D$_6$): $\delta = 7.04$ (s, ^3J(^{119}Sn,H) = 9.2 Hz, 2 H; =CH), 7.19 (s, 6 H; C$_6$H$_3$), 3.31 (septet, ^3J(H,H) = 7 Hz, 4 H; CH), 1.21 (d, ^3J(H,H) = 7 Hz, 12 H; CH$_3$), 1.19 ppm (d, ^3J(H,H) = 7 Hz, 12 H; CH$_3$); ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): $\delta = 144.9$ (*o*-C), 144.7 (*i*-C), 130.3 (*p*-C), 126.9 (=CH), 123.7 (*m*-C), 28.4 (CH), 26.2 (CH$_3$), 25.1 ppm (CH$_3$); ^{119}Sn{^{1}H} NMR (111.9 MHz, C$_6$D$_6$): $\delta =$ 260.1 ppm; ^{119}Sn{^{1}H} NMR CP/MAS (148.7 MHz, solid): $\delta_{\text{iso}} = 259.5$ ppm, $\delta_{ii} = -222, -91, 1092$ ppm; MS (16 eV, EI): *m*/*z* (%): 492 (6) [M^+], 378 (12) [$M^+ - $Sn].

1,3-Di(2,6-diisopropylphenyl)-4,5-dimethyl-2,3-dihydro-1-H-[1,3,2]-diazastannol-2-ylidene (1 h): Compound **9 h** (900 mg, 2.2 mmol) to a solution of Sn{N(SiMe$_3$)$_2$}$_2$ (966 mg, 2.2 mmol) in toluene (15 mL). The mixture was stirred for 90 min at 120 °C until a precipitate of elemental tin began to separate. The precipitate was filtered off and volatiles were removed under vacuum. NMR spectroscopic analysis revealed that the residue contained **1 h** (36 % by integration of suitable ^{1}H NMR signals) that was identified by its ^{1}H and ^{119}Sn NMR data beside diazadiene **2 h** (13 %) and unreacted starting material. Attempts to purify the crude product failed. ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 7.18$ (s, 6 H; C$_6$H$_3$), 3.12 (septet, ^3J(H,H) = 6.9 Hz, 4 H; C*H*(CH$_3$)$_2$), 1.95 (s, ^4J(^{119}Sn,H) = 6.3 Hz, 6 H; =CC*H*$_3$), 1.22 (d, ^3J(H,H) = 6.9 Hz, 12 H; CH(C*H*$_3$)$_2$), 1.13 ppm (d, ^3J(H,H) = 7 Hz, 12 H; CH(C*H*$_3$)$_2$); ^{119}Sn{^{1}H} NMR (C$_6$D$_6$): $\delta = 256$ ppm.

1,3-Dimesityl-4,5-dimethyl-2,3-dihydro-1-*H*-[1,3,2]-diazagermol-2-ylidene (10 g): A solution of Ge{N(SiMe$_3$)$_2$}$_2$ (2.35 g, 6.0 mmol) and **9 g** (1.93 g, 6.0 mmol) in hexane (20 mL) was stirred for 3 h at 70 °C. The mixture was then allowed to cool to ambient temperature and was concentrated to a volume of approximately 10 mL. Storage at −30 °C produced a yellow crystalline precipitate that was collected by filtration and dried in vacuum to yield 1.00 g (41 %) of **10 g**; m.p. 60 °C (decomp); elemental analysis calcd (%) for C$_{22}$H$_{28}$N$_2$Ge (393.1): C 67.23, H 7.18, N 7.13; found: C 66.07, H 7.01, N 7.39; ^{1}H NMR (C$_6$D$_6$): $\delta = 6.87$ (s, 4 H; *m*-H), 2.18 (s, 6 H; *p*-CH$_3$), 2.13 (s, 12 H; *o*-CH$_3$), 1.72 ppm (s, 6 H; =CCH$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = 139.7$ (*p*-C), 133.8 (*i*-C), 133.5 (*o*-C), 127.7 (*m*-C), 125.5 (=*C*CH$_3$), 19.6 (*p*-CH$_3$), 17.4 ppm (*o*-CH$_3$); MS (12 eV, EI): *m*/*z* (%): 394 (56) [M^+], 305 (45) [$M^+ - $Ge−CH$_3$].

Reactions of *N*-heterocyclic carbene analogues with diazadienes: For qualitative monitoring of exchange reactions, between 0.1 to 0.2 mmol of a carbene analogue (**10 a,g** or **1 h**) and roughly one equivalent of diazadiene (**3 a,b,g,h**) were dissolved in C$_6$D$_6$ or [D$_8$]toluene (0.5 mL). Approximately 0.5 mL of the solution was transferred into a sure-seal NMR tube and analyzed by ^{1}H and 2D ^{1}H EXSY NMR spectroscopy. The results of these studies are described in detail in the text. The identity of the products **10 a**/**3 g** formed via Ge-transfer from **10 g**/**3 a** was established by comparison with the spectra of authentic samples.

Measurements of pseudo first-order rate constants for the exchange between the stannylene **1 b** and the diazadiene **3 b** were made on a solution prepared by dissolving **1 b** (70.0 mg) and **3 b** (30.0 mg) in [D$_8$]THF (500 μL). Inversion-recovery experiments were conducted with a pulse sequence (180°)$_{\text{sel}}$–τ–90°–acquire, where (180°)$_{\text{sel}}$ denotes a selective 20 ms Gaussian inversion pulse applied to the resonance of the olefinic hydrogen of **3 b** and τ is a delay for magnetization transfer. For each measurement, a series of experiments with different values of τ was performed. The intensities of the signals of the olefinic hydrogens of both exchanging species in each spectrum were determined from fits of the observed resonances to Lorentzian lines, and the pseudo first-order rate constant was evaluated by simultaneously fitting the time-dependent intensities of both signals with an expression derived from the solution of the McConnell equations.[28] The true rate constant was finally obtained by computing the ratio k(**1 b**→**3 b**)/m(**1 b**) (where m(**1 b**) denotes the molality, that is, number of moles per kg of solvent, of **1 b**), and the enthalpy and entropy of activation were computed from a fit of ln(k/T) versus $1/T$. For monitoring the concentration dependence of the exchange rate, a stock solution prepared by dissolving **1 b** (89.0 mg) and **3 b** (3.0 mg) in [D$_8$]THF (500 μL) was diluted three times in the ratio of 1:2, and pseudo first-order rate constants were measured as described. Calculation of k(**1 b**→**3 b**)/m(**1 b**) gave values of 18.8(2), 20.0(2), 19.0(2), 16(3) kg s^{-1} mol^{-1} for the four solutions thus confirming within experimental error the invariance of k with concentration.

Reaction of 1 f with sulfur: Sulfur (19 mg, 0.6 mmol) was added to a solution of **1 f** (300 mg, 0.6 mmol) in toluene (5 mL) and the mixture warmed to 40 °C for 90 min. A brown precipitate formed that was filtered off, washed with toluene, and dried in vacuum. EDX analysis of the solid gave a composition of 48.7 atom % Sn and 51.3 atom % S, in accord with an empirical formula of SnS$_{1.05}$. ^{1}H NMR spectroscopic analysis of the supernatant solution revealed the presence of **3 f** as the only detectable reaction product.

Crystal structure determinations of 9 h and 10 g: Data were collected on a Nonius Kappa CCD diffractometer at −150 °C using Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97[29]). Non-hydrogen atoms were refined anisotropically and hydrogen atoms with a riding model on F^2 (full-matrix least-squares, SHELXL-97[30]).

9 h: yellow crystals, C$_{28}$H$_{42}$N$_2$, $M_r = 406.6$, crystal size 0.30 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/n$, no. 14: $a = 16.1735(3)$ Å, $b = 9.0446(1)$ Å, $c = 18.4566(3)$ Å, $\beta = 106.403(1)°$, $V = 2590.00(7)$ Å^3, $Z = 4$, ρ(calcd) = 1.04 Mg m^{-3}, $F(000) = 896$, $\mu = 0.06$ mm^{-1}, 45 384 reflections measured, 4547 unique reflections ($R_{\text{int}} = 0.058$) used for structure solution and refinement with 279 parameters, no absorption correction, $R1$ ($I > 2\sigma(I)$) = 0.042, $wR2 = 0.115$, largest diff. peak and hole 0.215 and −0.182 e Å^{-3}.

10 g: orange crystals, C$_{22}$H$_{28}$GeN$_2$, $M_r = 393.1$, crystal size 0.30 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/c$, no. 14: $a = 11.8927(3)$ Å, $b = 13.4278(5)$ Å, $c = 13.1531(4)$ Å, $\beta = 104.439(2)°$, $V = 2034.1(1)$ Å^3, $Z = 4$, ρ(calcd) = 1.28 Mg m^{-3}, $F(000) = 824$, $\mu = 1.51$ mm^{-1}, 12 838 reflections measured, 4595 unique reflections ($R_{\text{int}} = 0.053$) used for structure solution and refinement with 234 parameters, empirical absorption correction with multiple reflections (max/min transmission 0.7775 and 0.7259), $R1$ ($I > 2\sigma(I)$) = 0.044, $wR2$ = 0.111, largest diff. peak and hole 1.509 and −0.465 e Å^{-3}.

CCDC-271502 (**9h**) and CCDC-271503 (**10g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Dr. U. Kessler, University of Bonn, for performing powder diffraction studies and EDX analysis on the tin sulfide samples. K. Nättinen thanks the SFB624 for financial support.

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Received: May 24, 2005