DOI: 10.1002/ejic.200800083

Silylene and Germylene Intermediates in the Reactions of Silole and Germole Dianions with *N*,*N*′-Di-*tert*-butylethylenediimine

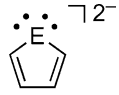
Irina S. Toulokhonova,[a] Vitaly I. Timokhin,[a] David N. Bunck,[a] Ilia Guzei,[a] Robert West,*[a] and Thomas Müller*[b]

Keywords: Silole dianion / Germole dianion / *N*,*N*′-Di-*tert*-butylethylenediimine / Silylene / Germylene / Metallation

Spiro-diazasilole (germole) adducts were observed in reactions of dilithium salts of silole and germole dianions with *N*,*N*′-di-*tert*-butylethylenediimine in THF at room temperature. A proposed mechanism of the reaction includes metallation of *N*,*N*′-di-*tert*-butylethylenediimine and the formation of an intermediate silylene or germylene. This reaction mechanism was supported by experimental data and theoretical calculations.

Introduction

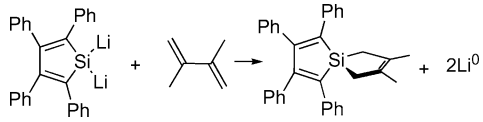
The silole[1] and germole[2] (metallole) dianions **I** (Figure 1) are interesting compounds both from theoretical and practical points of view due to their aromaticity[3,4] and unique reactivity. Metallole dianions act as strong reducing agents[5] and nucleophiles.[1]



I

Figure 1. Metallole dianions **I** (E = Si, Ge).

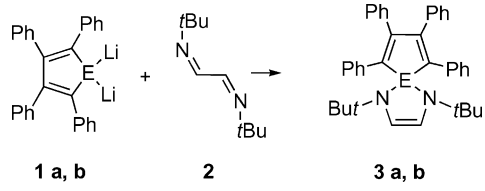
The tetraphenylsilole dianion is a precursor of a stable diradical[6] and a silene.[7] Recently, we found that silole dianions undergo novel oxidative cyclization reactions with 1,4-butadienes with formation of a spiro adduct and release of free lithium metal[8] (Scheme 1).



Scheme 1. Oxidative cyclization of 1,3-dimethyl-1,4-butadiene with 1,1-dilithio-2,3,4,5-tetraphenylsilole.

[a] Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave.,
Madison, WI 53706, USA
[b] Institut für Reine und Angewandte Chemie der Carl von Ossietzky Universität Oldenburg,
Carl von Ossietzky Str. 9-11, 26129 Oldenburg, Federal Republic of Germany
Fax: +49-441-798 3352
E-mail: thomas.mueller@uni-oldenburg.de
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

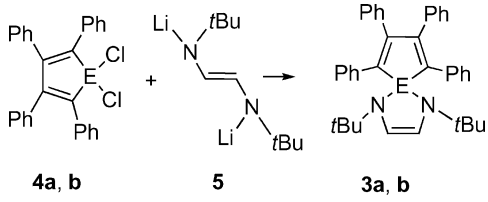
Here we report that the reaction of the dilithiosilole **1a** and the dilithiogermole **1b** with *N*,*N*′-di-*tert*-butylethylenediimine (**2**) in THF at room temperature also leads to the formation of novel spiro adducts **3a** and **3b** (Scheme 2).



1 a, b **2** **3 a, b**

Scheme 2. Reaction of dilithio compounds **1a**,**b** with *N*,*N*′-di-*tert*-butylethylenediimine (**2**) (a, E = Si; b, E = Ge).

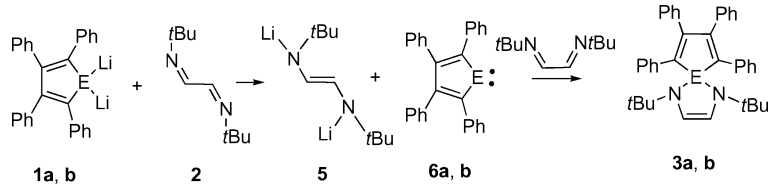
These products were characterized by ^{29}Si, ^{13}C, and ^{1}H NMR spectroscopy, and the formation of **3a**,**b** was confirmed by synthesis via an independent route. The reaction of the dichlorosilole **4a** or the dichlorogermole **4b** with the dilithium salt of the diimine **5** in THF at room temperature also yielded **3a**,**b** (Scheme 3).



4a, b **5** **3a, b**

Scheme 3. Synthesis of **3a**,**b** from the dichlorosilole **4a** and the dichlorogermole **4b** with *N*,*N*′-dilithio-*N*,*N*′-di-*tert*-butylethene (**5**) (a, E = Si; b, E = Ge).

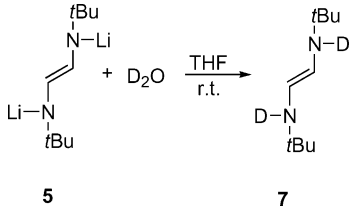
Although the cycloaddition reactions in Schemes 1 and 2 are formally similar, they appear to proceed by quite different mechanistic pathways. The reaction of Scheme 1 is believed to take place through nucleophilic addition of the silole to the diene, assisted by complexing of the diene to



Scheme 4. Proposed mechanism of the reaction of the dianions **1a**,**b** with the diimine **2** (a, E = Si; b, E = Ge).

lithium.[8] In contrast, the cycloaddition of Scheme 2 appears to involve lithium transfer to the diimine to give **5**, generating the silylene or germylene **6a**,**b**, which then adds to the excess diimine (Scheme 4).[9]

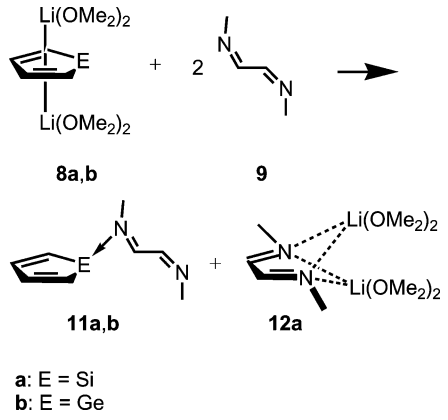
The dilithiodiamine **5** was identified in the reaction mixture by ^{7}Li NMR spectroscopy, as well as by derivatization with D_2O to give the dideuteriodiamine **7** (Scheme 5).



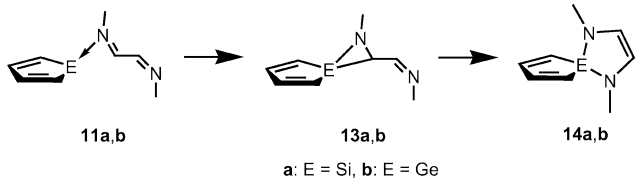
Scheme 5. Treatment of **5** with D_2O.

^{7}Li NMR for the reaction mixtures of the dianions **1a** and **1b** with the diimine **2** was similar to that obtained for the dilithiodiamine salt **5**, prepared independently from the diimine **2** and metallic lithium,[10] and different from that for the silole dianion **1a**.

This mechanistic proposal is consistent with the results of density functional computations at the B3LYP/6-311+G(d,p) level (see Computational Methods for details). Note that the electron affinity E_A which is computed for 1,4-diazabutadiene is significant [E_A = –0.24 eV at B3LYP/6-311+G(d,p)]. This suggests that for the reactivity of dianions **1a**,**b** towards diazabutadienes, electron transfer is a plausible reaction mode. For the calculation of the reaction path we used as model compounds the unsubstituted η^5,η^5-dilithium complex of the silole or germole dianion, **8a**,**b**,[3,8] and the methylated diazabutadiene **9**, to reduce the complexity of the theoretical problem. As solvation is important for the reactivity and stability of organolithium compounds in solution[11] we used dimethyl ether as a model for the THF used in the synthesis, to complete the coordination sphere of the lithium ions in **8a**,**b**. The computed structures of reactants, products, and intermediates are given in the case of the silicon compounds in Figure 3 and the complete data set can be found in the Supporting Information. The reaction course is summarized in Schemes 6 and 7 and the computed reaction profiles for the complete transformation **8a**,**b**/**9**→**14a**,**b** are shown in Figure 4.



Scheme 6.



Scheme 7.

According to our model computations the initial step of the reaction cascade is the reduction of the diazabutadiene **9** by the lithiated metalloles **8a**,**b** which yields the cyclic 1-metallacyclopenta-2,4-dienylidenes **10a**,**b**.[9] Under the reaction conditions carbene analogues such as **10a**,**b** (Figure 2) will form Lewis acid-base complexes either with the solvent THF or with the reactant diazabutadiene **2**. In the case of the silicon compound **10a**, the computations predict that the complexation with diazabutadiene **9** to form compound **11a** is favored compared to the reaction with dimethyl ether by 30.6 kJ mol^{-1} and complex **11a** is stabilized compared to its two independent components by 96.3 kJ mol^{-1} (Figure 3). Encounter complex **11a** undergoes an intramolecular [2+1] addition giving the silaaziridine **13a** as the product (Scheme 7). In a subsequent reaction step the silaaziridine **13a** is transformed by facile nucleophilic ring extension into

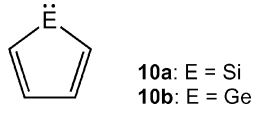


Figure 2. Carbene analogues **10a**,**b**.

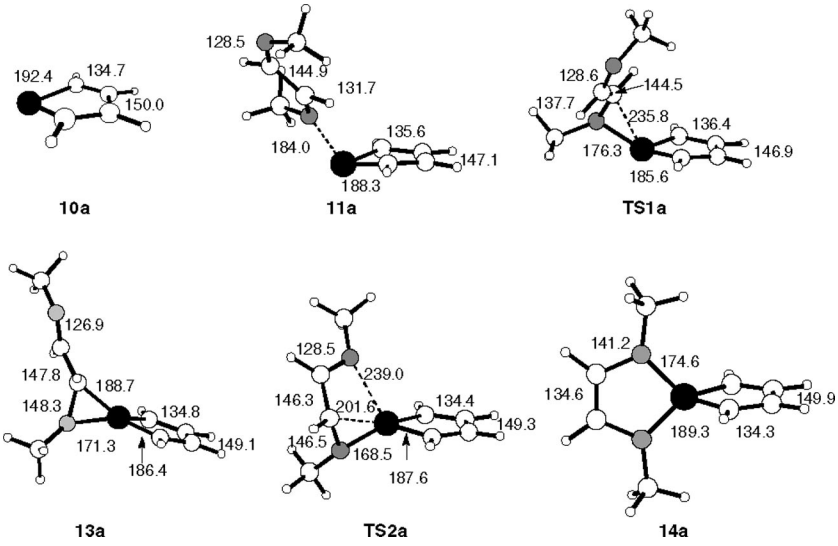


Figure 3. Calculated molecular structures for compounds **10a**–**14a** and for the transition states **TS1a** and **TS2a** [at B3LYP/6-311+G(d,p)]. Selected bond lengths in pm; color code: C white, large; Si black; N grey; H, white, small.

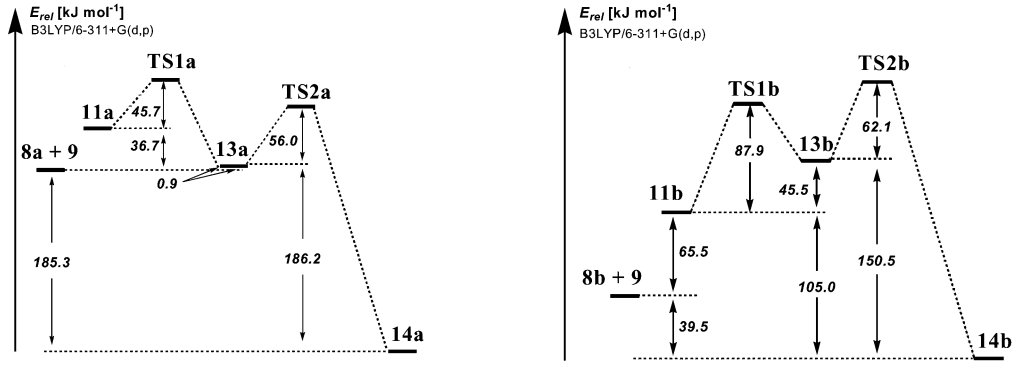
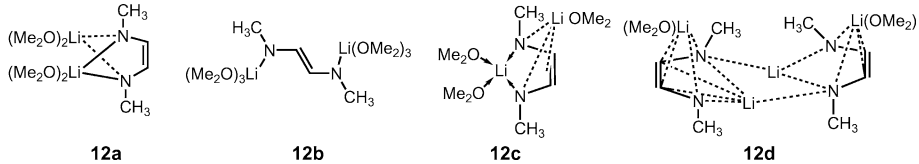


Figure 4. (left and right). Calculated reaction coordinates for the reactions of the dianions **8a**,**b** with the diazabutadiene **9**. The energetic relation between **8a**,**b**/**9** and **11a**,**b** is calculated from Scheme 6 using the absolute energies of reactants and products.

the spirocyclic compound **14a**. Both barriers, that for the [2+1] addition **11a**→**13a** and that for the consecutive ring extension reaction **13a**→**14a** are relatively small (45.7 kJ mol^{-1} and 56.0 kJ mol^{-1}, see Figure 4, left). This suggests that both intermediates, the encounter complex **11a** and the silaaziridine **13a**, would be difficult to detect in the experiments which were conducted at room temperature. The overall reaction **8a** + 2 **9**→**14a** + **12a** is strongly exothermic (185.3 kJ mol^{-1}). Therefore, the computation for the model compounds **8a** and **9** suggests that the reaction of equimolar amounts of **1a** and **2** will give exclusively spirocycle **3a** in a theoretical yield of 50% yield, in qualitative agreement with the experimental results.

A qualitatively similar reaction course is predicted by the computations for the dilithiogermole **8b**, although the reaction and activation energies for the individual reaction steps differ significantly (see Figure 4, right). As a result of the generally higher relative stability of dicoordinated states in germanium chemistry the dilithiogermole **8b** as well as the germylene complex **11b** are lower in energy compared to the tetravalent compounds **13b** and **14b**. Consequently, the computed overall reaction energy is much smaller in the germanium case (39.5 kJ mol^{-1}) than in the silicon case and also the barrier predicted for the cycloaddition to form germaaziridine **13b** is significantly higher (87.9 kJ mol^{-1} vs. 45.7 kJ mol^{-1}).

A crucial point in the computations is a good prediction of the structure of the dilithiated diazabutadiene **12**. Although it is only a byproduct, **12** influences the thermodynamics of the initial electron-transfer process significantly.



The solution structures of organolithium compounds in general, and lithiated imines in particular, are complex and in many cases not known.[11,12] For the lithium and potassium salt of the radical monoanion of **2**, ESR and structural studies indicate metalladiazacyclopentene structures.[13] The molecular structure of a related dilithiated diazabutadiene featured a *s-cis*-configured diazadiene dianion which coordinates to each of the two lithium ions in a chelating fashion.[14] The molecular structure of dilithiodiamine **5** as obtained from a X-ray structure analysis, is that of an unsymmetrical dimer with four lithium atoms in two different binding modes.[10] ^{7}Li NMR spectroscopy did not provide significant information on the structure of **5** in solution. Therefore several possible structures **12a**–**d** of dilithiated diazabutadiene were optimized and the computed energies were compared. This study included the bis-chelate complex **12a**, the (*E*)-configured complex **12b**, a mixed chelate/η^4 complex **12c** and a dimeric structure **12d**. The structures **12a** and **12d** are reminiscent of solid states structures of strongly related compounds,[10,14] while **12b** and **12c** emerged as possible structures from test calculations. The optimized structures of **12a**–**d** are given in the Supporting Information. The results of DFT computations for the gas phase and in solution (modelled by a PCM computation using as solvent THF) identified uniformly the bis-chelate complex **12a** as the energetically preferred structure, and the energy of this structure was used to compute the heat of reaction for Scheme 6. However, in view of the crude model and the complex problem arising from aggregation of the lithiated species in solution, the thermodynamics of the initial electron transfer step should be regarded only as an estimate.

Consistent with the proposed mechanism involving metallation of the diimine **2** is the fact that a polar solvent is required. When THF as the solvent was replaced by toluene, no reaction was observed. We did not observe products of addition of silole or germole dianions to the double carbon–nitrogen bond (C=N) of diimine **2**, as is observed in the reaction of methyllithium with *N*,*N*′-di-*tert*-butylethylenediamine.[15,16] The addition of the dilithio compounds **1a** and **1b** to **2** is sterically hindered and instead metallation of the diimine **2** takes place. Addition of more than one equivalent of the diimine **2** in the reaction with the dilithiosilole **1a** resulted in decreased yields of spirocompound **3a**. This is most probably due to increased formation of the radical anion $[\mathbf{2}_2\mathrm{Li}]^{\cdot-}$ by the reaction of the initially formed dilithio compound **5** with diimine **2**[13c] and subsequent follow-up reactions of the radical anion.

Attempts to obtain crystals of **3a** suitable for X-ray crystal analysis were unsuccessful. However, upon column chromatography **15**, a product of oxidation of **3a**, was separated and characterized. The crystal structure of **15** is shown in Figure 5 and the crystallographic data in Table 1. Evidently **15** arises via C-oxidation of spirocyclo-enediamine **3** (Scheme 8). Similar oxidation of enamines, enhanced in presence of molecular sieves was described previously by Blau et al.[17–19]

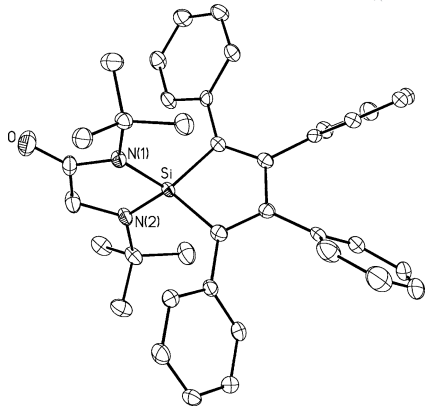
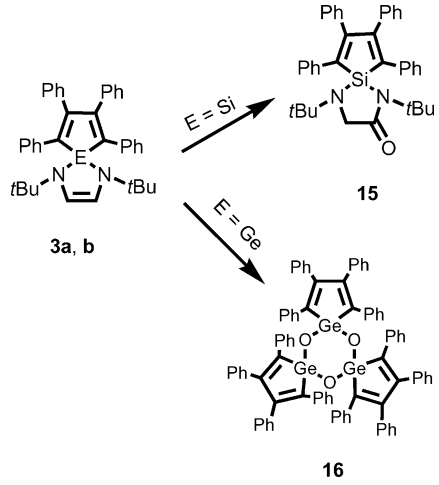


Figure 5. Molecular structure of 1,4-di-*tert*-butyl-6,7,8,9-tetraphenyl-1,4-diaza-5-silaspiro[4,4]nona-6,8-diene-2-one (**15**) shown with 50% probability thermal ellipsoids.

Table 1. Crystal data and structure refinement for **15**.

Empirical formula	$C_{38}H_{40}N_2OSi$
Formula weight	568.81
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.832(3) Å
	b = 10.127(4) Å
	c = 17.651(6) Å
	α = 76.411(6)°
	β = 78.750(7)°
	γ = 73.232(6)°
Volume	1620.4(10) Å^3
Z	2
Density (calculated)	1.166 Mg/m^3
Absorption coefficient	0.104 mm^{-1}
F(000)	608
Crystal size	0.49 × 0.46 × 0.40 mm^3
Theta range for data collection	2.14 to 26.40°
Index ranges	$-12 \le h \le 12$
	$-12 \le k \le 12$
	$-20 \le l \le 21$
Reflections collected	11097
Independent reflections	6143
	[R(int) = 0.0864]
Completeness to θ = 26.40°	92.4%
Absorption correction	multi-scan with SADABS
Max. and min. transmission	0.9595 and 0.9507
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	6143/0/385
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0506, wR_2 = 0.1351
R indices (all data)	R_1 = 0.0672, wR_2 = 0.1436
Largest diff. peak and hole	0.663 and –0.233 e Å^{-3}

The germanium–nitrogen bond in **3b** (E = Ge) is less stable than a silicon–nitrogen bond and rapidly decomposes in the presence of air to give the cyclo-trigermoletrioxane **16** (Scheme 8), identified by X-ray crystallography and ^{1}H, and ^{13}C NMR analysis. The data for **16** are consistent with those reported in the literature.[20]



Scheme 8. Oxidation of **3a**,**b**.

Computational Details

All calculations were done using the Gaussian03 program.[21] The structures of all compounds were optimized at the hybrid density functional B3LYP level of theory[22] in connection with 6-311+G(d,p) basis set. Every stationary point was identified either as intermediate or transition state (TS) by a subsequent frequency calculation. Intrinsic reaction coordinate (IRC) computations were used to connect the TS with the appropriate minima. Solvent effects were included by using the PCM model.[23] All calculated data are presented in the Supporting Information.

Experimental Section

General: All procedures with air- and moisture-sensitive compounds were carried out using a Schlenk line under nitrogen and argon. Solvents were distilled from sodium benzophenone ketyl.

NMR spectroscopic data were recorded with a Varian UNITY-500 spectrometer at 499.89 MHz for ^{1}H, 125.71 MHz for ^{13}C, 99.31 MHz for ^{29}Si, 194.28 MHz for ^{7}Li NMR and 76.71 MHz for ^{2}H NMR spectroscopy.

1,1-Dilithio-2,3,4,5-tetraphenylsilole (1a) and 1,1-Dichloro-2,3,4,5-tetraphenylsilole (4a): These compounds were synthesized as described in the literature.[3] 1,1-Dilithio-2,3,4,5-tetraphenylgermole (**1b**) and 1,1-dichloro-2,3,4,5-tetraphenylgermole (**4b**) were obtained as described by Boudjouk et al.[2] *N*,*N*′-Di-*tert*-butylethylenediimine (**2**) and *N*,*N*′-dilithio-*N*,*N*′-di-*tert*-butylethenediamine (**5**) were prepared as described previously.[10]

Reaction of Dilithiosilole 1a with *N*,*N*′-Di-*tert*-butylethylenediimine (2): The dilithiosilole **1a** (1.1 mmol, 0.44 g) in 10 mL of THF was added to **2** (1.1 mmol, 0.18 g) at room temperature. The reaction mixture has a dark red color; after 1 h solvent was evaporated and the product **3a** (spectroscopic yield 55%) was characterized by NMR spectroscopy. ^{1}H NMR ($C_6D_5CD_3$): δ = 1.26 (s, 18 H, *t*Bu), 5.98 [s, 2 H, N–C(*H*)=C], 6.85–6.98 (m, 20 H, Ar) ppm. ^{13}C NMR ($C_6D_5CD_3$): δ = 153.22, 140.12, 138.63, 137.38, 137.33, 130.2–126.5 (m, Ar), 113.88 (N–*C*=C–N, J_1 = 9.1, J_2 = 179.8 Hz), 51.89 (N–*C*Me$_3$), 30.05 [C(*C*H$_3$)$_3$] ppm. ^{29}Si NMR ($C_6D_5CD_3$): δ = –16.20 ($J_{Si–CH}$ = 6 Hz) ppm.

15 was obtained as result of oxidation of **3** on silica gel, in 50% yield after column chromatography [eluent: hexane/Et_2O (1:1)]. **15:** ^{1}H NMR ($CDCl_3$): δ = 1.10 (s, 9 H, *t*Bu), 1.39 (s, 9 H, *t*Bu), 3.71 (s, 2 H), 6.76–6.78 (m, 4 H, Ar), 7.01–7.10 (m, 16 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 177.18 (C=O), 154.61, 140.12, 138.83, 137.62, 136.10, 129.47, 129.23, 128.41, 128.19, 127.16, 126.84 (m, Ar), 54.95, 51.72, 50.67, (N–*C*Me$_3$), 28.40, 27.99, [C(*C*H$_3$)$_3$] ppm. ^{29}Si NMR ($CDCl_3$): δ = –7.80 ppm. $C_{34}H_{40}N_2Si$ (504.79): calcd. C 80.90, H 7.99; found C 80.64, H 8.32. Yellow crystals of **15** suitable for X-ray analysis were obtained by crystallization from hexane.

^{7}Li NMR for the reaction mixtures of dilithiometalloles **1a** and **1b** with diimine **2** (broad multiple peaks at –1.9 to –0.8) were identical to that for the dilithiodiamine **5**, prepared independently from diimine **2** and metallic lithium,[10] and different from that for the silole dianion **1a** (–7.3 ppm, broad intense peak and broad shoulder with low intensity at –1.1 to –3.2 ppm).

Treatment of the Reaction Mixture with D_2O: The reaction mixture was cooled to 0 °C and D_2O (2.2 mmol, 0.044 g) in 10 mL of THF was added to the mixture. After raising the temperature of the mixture to 20 °C the reaction mixture was dried with $MgSO_4$, the solvent was removed, and the reaction mixture was analyzed. **7:** ^{2}H NMR (C_6D_6): δ = 5.39 (*D*–N) ppm. Similar chemical shift at 5.4 ppm was observed when the dilithiodiamine **5**, which was synthesized from the diimine **2** and metallic lithium in THF at room temperature, was treated with deuterated water.

Reaction of the 1,1-Dichlorosilole 4a with *N*,*N*′-Dilithio-*N*,*N*′-di-*tert*-butylethenediamine (5): A solution of *N*,*N*′-dilithio-*N*,*N*′-di-*tert*-butylethenediamine **5** (1.1 mmol) in 10 mL of THF was added to 1,1-dichlorosilole **4** at room temperature and the dark red reaction mixture was stirred during 3.5 h. Analysis by ^{1}H NMR showed **3a** (63%).

Reaction of Dilithiogermole 1b with *N*,*N*′-Di-*tert*-butylethylenediimine (2): This reaction was carried out similarly to the procedure for dilithiosilole **1a** and diimine **2**. The product **3b** (spectroscopic yield 45%) was determined by ^{1}H NMR, and ^{13}C NMR spectroscopy. ^{1}H NMR (C_6D_6): δ = 1.27 (s, 18 H, *t*Bu), 6.04 [s, 2 H, N–C(*H*)=C], 6.87–7.47 (m, 20 H, Ar) ppm. ^{13}C NMR (C_6D_6): δ = 148.68–122.99 (m, Ar), 112.62 (N–*C*=C–N), 52.67 (N–*C*Me$_3$), 30.48 [C(*C*H$_3$)$_3$] ppm.

Reaction of 1,1-Dichlorogermole 4b with *N*,*N*′-Dilithio-*N*,*N*′-di-*tert*-butylethenediamine (5): This was conducted and analyzed as for the reaction of **4a** with **5**. By ^{1}H NMR, 58% of **3b** was found. Product **16** was obtained after attempts to crystallize **3b** from hexane/Et_2O (10:4) mixture.

CCDC-673921 contains the supplementary crystallographic data for compound **15**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Calculated structures in Cartesian coordinates and absolute energies of all computed compounds. Selected details of the single-crystal structure analysis of compound **15**.

Acknowledgments

Research at the University of Wisconsin was supported by the National Science Foundation under grant no. CHE-0451536. The Cluster for Scientific Computation (CSC) at the Carl von Ossietzky University Oldenburg is thanked for computer time.

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Received: January 24, 2008
Published Online: April 4, 2008

