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Communication

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2,5-Digermaselenophenes: Germanium Analogues of Selenophenes

Tomohiro Sugahara,[1] Takahiro Sasamori,*[2] and Norihiro Tokitoh[1,3]

[1] Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

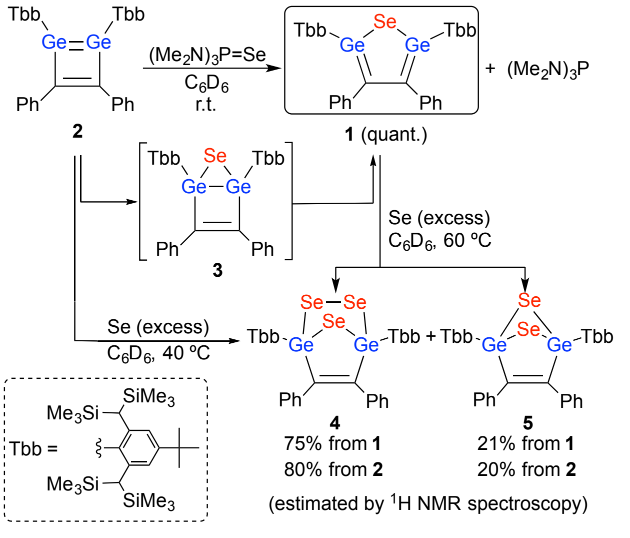
[2] Graduate School of Natural Sciences, Nagoya City University, Yamanohata 1, Mizuho-cho, Mizuho-ku, Nagoya, Aichi 467-8501, Japan.

[3] Integrated Research Consortium on Chemical Sciences, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

Supporting Information Placeholder

ABSTRACT: A stable crystalline 2,5-digermaselenophene was synthesized. In contrast to hitherto reported selenophenes, this digermaselenophene exhibits a *trans*-pyramidalized structure, which is due to its electronic properties. The practical utility of this 2,5-digermaselenophene is reflected in its ability to activate dihydrogen and acetylene at room temperature in the absence of a transition-metal complex, and this behavior can be rationalized on the basis of its physico-chemical properties, which are characterized by considerable electron-donating and -accepting abilities.

Organic optoelectronic materials are considered the next generation of electron-transporting materials.[1] Suitable building blocks for such advanced optoelectronic materials should be designed to exhibit the following physical properties: (i) a low LUMO level, (ii) a high HOMO level, and (iii) a corresponding small HOMO-LUMO gap in order to promote the transfer of electrons. These very requirements should also be advantageous for functional main-group-element-containing molecules that aim at the activation of small inert molecules.[2] On account of their potential electron-donating ability, thiophenes often serve as building blocks for organic optoelectronic materials[3] such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs). Much research has been focused on modifying thiophenes, *e.g.* *via* extension of their π-conjugation system and the introduction of π-conjugated functional substituents, which are expected to diminish the HOMO-LUMO gap under concomitant improvement of the electron-transporting ability.[4] Despite the small HOMO-LUMO gap of a thiophene, even such thiophene derivatives would not activate small inert molecules. Similarly, selenophenes, *i.e.*, selenium analogues of thiophenes, are also excellent building blocks for organic optoelectronic materials. Specifically, they exhibit a smaller ionization energy relative to thiophenes, *i.e.*, an effective electron-donating ability.[5] While the HOMO-LUMO gaps of thiophenes and selenophenes may be small enough as optoelectronic materials, but no example of a thiophene/selenophene derivative with very small HOMO-LUMO gap enough to activate small molecules. Moreover, the variety of available organic functional groups and molecular designs should be limited, since the physical properties of thiophenes and selenophenes predominantly reflect the π-electron-properties of the butadiene moiety, which suggests that substitution with organic substituents and/or replacement of the sulfur atom with selenium should not induce a remarkable improvement. The replacement of the carbon atoms in the butadiene moiety in thiophenes or selenophenes with heavier main-group elements has not yet been investigated in detail, mostly due to a lack of effective synthetic strategies or appropriate precursors.



Scheme 1. Synthesis of 2,5-digermaselenophene **1**, and subsequent treatment with elemental selenium to give **4** and **5**.

Recent developments in the area of main-group-element chemistry have allowed the preparation of stable π-bonded species of heavier-group-14 elements,[6] which demonstrates that the incorporation of heavier main-group elements into π-systems significantly increases the electron affinity of the latter due to their extremely low-lying π*-orbitals. Thus, a 2,5-dimetallaselenophene, which contains heavier-group-14 elements instead of carbon atoms at the 2- and 5-positions, should represent fascinating physical and chemical properties due to its unique electronic structure.[7] Herein, we report the synthesis of digermaselenophene **1** and its ability to activate small molecules, which renders **1** also a promising prospective building block for advanced optoelectronic materials.

1,2-Digermacyclobutadiene **2** can serve as a suitable precursor for heterocycles, given that insertion reactions may occur at the reactive Ge=Ge π-bond.[8,9] When **2**, which was obtained from the reaction between the stable digermyne TbbGe≡GeTbb (Tbb = 2,6-$[CH(SiMe_3)_2]_2$-4-*t*-butyl-phenyl) with diphenylacetylene,[10] was treated with an equimolar amount of $(Me_2N)_3P$=Se in C_6D_6 at room temperature, the color of the reaction mixture changed from dark red to purple. Removal of the solvent and $(Me_2N)_3P$ under reduced pressure afforded 2,5-digermaselenophene **1** as purple crystals (Scheme 1).[11] While **1** is extremely sensitive toward air and moisture, which results in complicated product mixtures, **1** is thermally stable in benzene upon heating to 80 ˚C under an atmosphere of inert gas. The formation of **1** should most likely be interpreted in terms of the formation of selenadigermirane **3** as an intermediate, which could easily undergo transformation into **1**.[12] Although the reaction of **2** with $(Me_2N)_3P$=Se was carefully monitored by ^1H NMR spectroscopy, only the signals of **1** and **2** were observed under light shielding conditions, due to the facile conversion of **2** into **1**. In a previous study, the selenization of **2** with elemental selenium resulted in the formation of heterocycles **4** and **5**.[9c] Since further selenization of **1** with elemental selenium afforded **4** and **5** exclusively, **1** could be conceived as an intermediate in the reaction of **2** with elemental selenium that affords **4** and **5**.

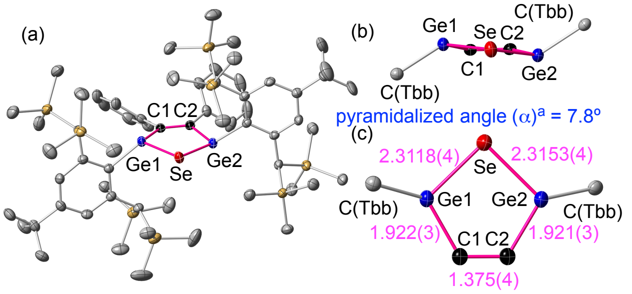
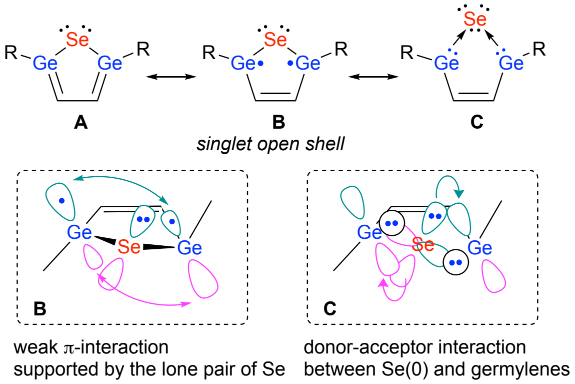


Figure 1. Molecular structure of **1** (ORTEP drawing with thermal ellipsoids set to 50% probability). The minor parts of the disordered moieties, hydrogen atoms, and the solvents are omitted for clarity; (a) entire molecule, (b) side view of the $[SeGe_2C_2]$ ring, and (c) top view of the $[SeGe_2C_2]$ ring; selected bond lengths are shown in Å. [a]The pyramidalized angle (α) is defined as the angle between the Se–Ge1–Ge2 and Se–C1–C2 planes.

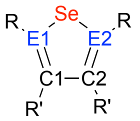
An X-ray crystallographic analysis (Figure 1)[13] revealed that 2,5-digermaselenophene **1** exhibits a non-planar structure with a *trans*-pyramidalized geometry of the five-membered $[SeGe_2C_2]$ ring with a *trans*-pyramidalized angle (α) of 7.8˚, which stands in sharp contrast to the completely planar structure of previously reported selenophenes.[14] However, the bent structure of **1** should not be attributed to the sterically demanding Tbb substituents on the Ge atoms, but rather to the intrinsic nature of the 2,5-digermaselenophene. The results of theoretical calculations on the parent 2,5-digermaselenophene $SeGe_2C_2H_4$ suggested that its planar structure is a transition state; the energy minimum is the *trans*-pyramidalized structure, which is 7.2 kcal/mol lower in SCF-energy relative to the planar geometry. This result can be rationalized in terms of the weakness of the Ge-containing π-bond, *i.e.*, given the small overlap of the 4p orbitals, a 2,5-digermaselenophene would adopt a *trans*-pyramidalized geometry to form a C1=C2 π-bond rather than keeping its Ge1=C1 and Ge2=C2 π-bonds. In other words, the contribution of resonance structures **B** or **C** (Scheme 2) should become dominant.



Scheme 2. Conceivable resonance structures for a 2,5-digermaselenophene.

It should be noted that the results of NBO calculations[15] revealed a double-bond character for the C1=C2 bond, and π-type bonding interaction between the Ge atoms, thus supporting a 3-center-4-electron π-bonding[16] through the stabilization of the electron-deficient Ge atoms by coordination of lone pairs of the Se atoms in resonance structure **B**. Conversely, the results of NPA calculations revealed a negative charge at the Se atom and a positive charge at the Ge atoms, supporting electron donation from the Ge atoms to the central Se atom, indicative of non-negligible contributions from the donor-acceptor model **C** (NPA charges for **1**: $q_{Se} = –0.35$; $q_{Ge} = +0.90$). In their entirety, these results suggest that such a 2,5-digermaselenophene should exhibit a *trans*-pyramidalized structure at the energetic minimum due to the predominant contribution of **B** together with minor contributions from the donor-acceptor interactions of **C**. The results of the theoretical calculations on the real model (**1**) and the parent models of selenophene derivatives (**1’**, **6**, **7**) are summarized in Table 1. The C1–C2 bond length of **1** is relatively short [1.375(4) Å], suggesting a partial π-bond character, while the Ge–C bond lengths in the five-membered ring are elongated relative to those of previously reported Ge=C bonds (*ca*. 1.83 Å).[17] In addition, a comparison of the structural parameters of the simple models [$SeE_2C_2H_4$] (E = C (**7**), Si (**6**), Ge(**1’**)) clearly suggests an increasing contribution of resonance structure **A** as the E atom descends the periodic table.

Table 1. Results of the theoretical calculations.

	**1**[a] E=Ge R=Tbb R’=Ph	**1**[b] E=Ge R=Tbb R’=Ph	**1’**[c] E=Ge R=H R’=H	**6**[c] E=Si R=H R’=H	**7**[c] E=C R=H R’=H
Se–E1/Å	2.3118(4)	2.325	2.345	2.258	1.856
Se–E2/Å	2.3153(4)	2.325	2.344	2.258	1.856
E1–C1/Å	1.922(3)	1.918	1.915	1.809	1.376
E2–C2/Å	1.921(3)				
C1–C2/Å	1.375(4)	1.390	1.368	1.385	1.420
E1–Se–E2/°	91.21(2)	92.5	90.9	89.4	87.6
α/° [d]	7.8	7.0	8.5	8.5	0.0
δ_{Se}/ppm	481.8[e]	520.6[f]	---	---	---
$\delta_{C1/2}$/ppm	176.8[e]	188.3[f]	---	---	---
NICS(0)	---	–11.2[f]	–12.5[i]	–12.6[i]	–13.4[i]
NICS(1)	---	–8.0[f]	–10.5[i]	–10.4[i]	–10.9[i]

[a]Observed by XRD analysis. [b]Optimized at the B3PW91/6-311G(3df)<Se,Ge,Si>/6-311G(d)<C,H> level of theory [c]Optimized at MP2/6-311G(3d) level of theory. [d]Defined as the angle between the Se–E1–E2 and Se–C1–C2 planes. [e]Measured at r.t. in C_6D_6. [f]Calculated at the GIAO-B3PW91/6-311G(3df)<Se,Ge,Si>/6-311G(d)<C,H> level of theory. [i]Calculated at GIAO-MP2/6-311G(3d) level of theory.

Based on the calculated NICS values (NICS(0) = –11.2; NICS(1) = –8.0), digermaselenophene **1** should, despite its *trans*-pyramidalized structure, exhibit considerable levels of aromaticity similar to parent selenophene **7**. In addition, NICSzz(r)[18] scan calculations delivered an NICSzz(1.3) value of –24.1 for **1’**, which is slightly smaller but still comparable to the NICSzz(1.0) value for a selenophene (–29.2). Accordingly, it can be concluded that 2,5-digermaselenophenes should exhibit aromaticity similar to that of selenophenes and 2,5-disilaselenophenes. Due to the aromatic π-conjugation system in digermaselenophene **1**, a small ionization energy and a high electron affinity were calculated, suggesting excellent electron-donating and -accepting abilities. The low-field shifted ^{77}Se NMR resonance (δ_{Se} = 481.8 in C_6D_6) for digermaselenophene **1**, which could be reproduced by GIAO calculations (δ_{Se} = 520.6), suggests that **1** retains its *trans*-pyramidalized structure in solution.[19]

Due to the *trans*-pyramidalized structure of **1**, the energy levels of the slipped π-type HOMO (–5.04 eV) and LUMO (–2.69 eV) are raised and lowered, respectively.[6] In addition, the small HOMO-LUMO gap of **1** (2.35 eV)[7] is responsible for its purple color, which stands in contrast to conventional selenophenes, which are typically colorless/pale yellow. The UV/vis spectrum of **1** in hexane reveals a strong absorption at λ_{max} = 536 nm (ε 7,800), which was assigned to the HOMO-LUMO transition based on TDDFT calculations (533.6 nm; *f* = 0.2164).[19] Such an absorption at longer wavelengths suggests that 2,5-digermaselenophenes could serve as promising building blocks for optoelectronic materials.

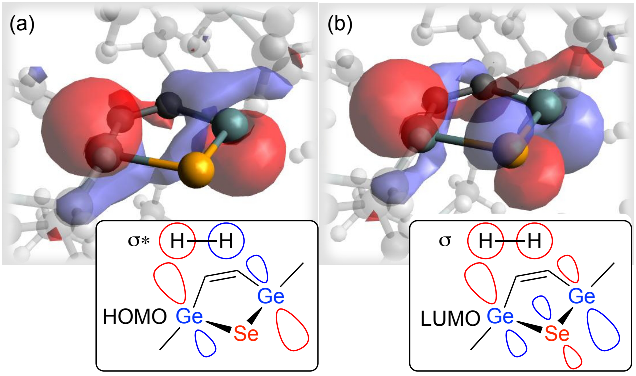
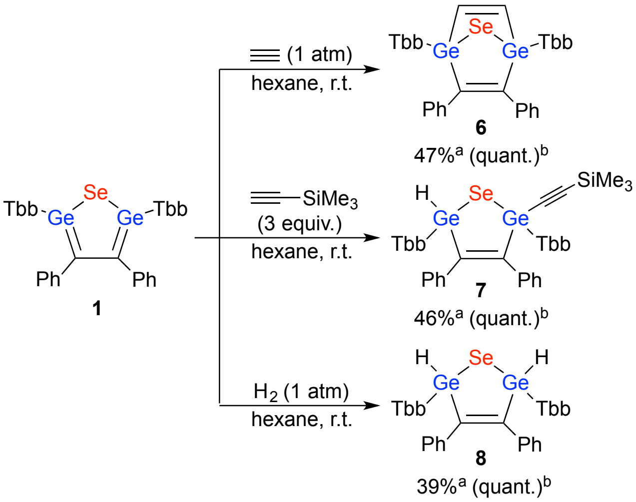


Figure 2. (a) HOMO of **1** (–5.04 eV) and schematic illustration of the interaction with the σ* orbital of H_2. (b) LUMO of **1** (–2.69 eV) and schematic illustration of the interaction with the σ orbital of H_2. B3PW91/6-311G(3df)<Se,Ge,Si>/6-311G(d)<C,H> level of theory.



Scheme 3. Reactions of 2,5-digermaselenophene **1** with small molecules. [a]Isolated yield. [b]Yield estimated based on the ^1H NMR spectrum of the crude mixture.

Considering the frontier orbitals of **1**, and especially the small HOMO-LUMO gap, **1** could be highly susceptible toward pericyclic or addition reactions. The HOMO and LUMO of **1** (Figure 2) exhibit a predominant contribution of the p-type Ge–Se–Ge 3-center-4-

electron π-bond.[16] As expected, digermaselenophene **1** readily reacts with alkynes and H_2 under ambient conditions to form the corresponding adducts in moderate yield (Scheme 3). Notably, **1** is able to activate and fix molecular hydrogen and acetylene in the absence of any transition metal.[2a,20]

In conclusion, we have demonstrated the synthesis of stable 2,5-digermaselenophene **1**, and demonstrated its ability to activate small molecules such as dihydrogen and acetylenes. Given the electronic structure of **1** and its high reactivity toward the activation of small molecules, **1** is also a promising prospective building block for advanced optoelectronic materials. Further investigations into the electrochemical properties of such digermaselenophenes are currently in progress in our laboratories.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental section (PDF), spectral data (PDF) crystallographic data (CIF), and theoretically optimized coordinates (XYZ) are included in the SI.

AUTHOR INFORMATION

Corresponding Author

sasamori@nsc.nagoya-cu.ac.jp

ORCID

Takahiro Sasamori: 0000-0001-5410-8488
Norihiro Tokitoh: 0000-0003-1083-7245

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7. The HOMO/LUMO levels of selenophene (–8.79/2.91), 2,5-disilaselenophene (–6.79/–0.04), and 2,5-digermaselenophene (–6.84/–0.61 eV) were calculated at the MP2/6-311G(d) level of theory. Thus, calculated HOMO-LUMO gaps of parent molecules of a selenophene and a 2,5-digermaselenophene are 11.7 eV and 6.23 eV.
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11. Compound **1**: purple crystals, mp 102 °C (dec), δ_{Se} = 481.8 (C_6D_6), UV–vis (*n*-hexane) λ_{max} (nm, ε) = 530 (7,800). For detailed data, see Supporting Information.
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13. [**1**·hexane] ($C_{62}H_{108}Ge_2SeSi_8$, C_6H_{14}): $M = 1388.51$, $\lambda = 0.71069$ Å, $T = -170$ °C, triclinic, P–1 (no. 2), $a = 13.3399(2)$ Å, $b = 17.1478(3)$ Å, $c = 19.6332(3)$ Å, $\alpha = 95.455(1)^\circ$, $\beta = 108.200(1)^\circ$, $\gamma = 105.365(2)^\circ$, $V = 4035.66(12)$ Å^3, $Z = 2$, $D_{calc} = 1.143$ g cm^{-3}, $\mu = 1.348$ mm^{-1}, $2\theta_{max} = 50.0^\circ$, measd./unique refls. = 71755/14184 ($R_{int} = 0.0557$), param = 769, GOF = 1.145, R_1 = 0.0401/0.0560 [$I > 2\sigma(I)$/all data], wR_2 = 0.1041/0.1108 [$I > 2\sigma(I)$/all data], largest diff. peak and hole 1.989 and –1.137 e.Å^{-3} (CCDC-1849658).
14. For examples, see: (a) Masuda, T.; Inagaki, Y.; Momma, H.; Kwon, E.; Setaka, W., *New. J. Chem.* **2016**, *40*, 8593-8599. (b) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M., *Org. Lett.* **2009**, *11*, 1487-1490. (c) Hua, G.; Henry, J. B.; Li, Y.; Mount, A. R.; Slawin, A. M. Z.; Woollins, J. D., *Org. Biomol. Chem.* **2010**, *8*, 1655-1660. (d) Beswick, M. A.; Harmer, C. N.; Raithby, P. R.; Steiner, A.; Tombul, M.; Wright, D. S., *J. Organomet. Chem.* **1999**, *573*, 267-271.
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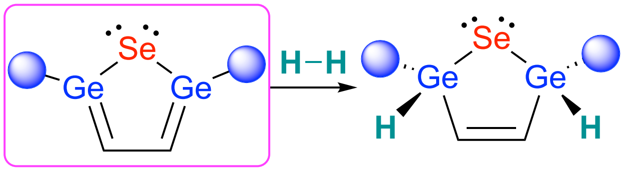
19. TDDFT calculations were carried out at the B3PW91/6-311G(3df)<Se,Ge,Si>, 6-311G(d)<C,H> level of theory.
20. Spikes, G. H.; Fettinger, J. C.; Power, P. P., *J. Am. Chem. Soc.* **2005**, *127*, 12232-12233.



Dihydrogen Activation by a Digermaselenophene

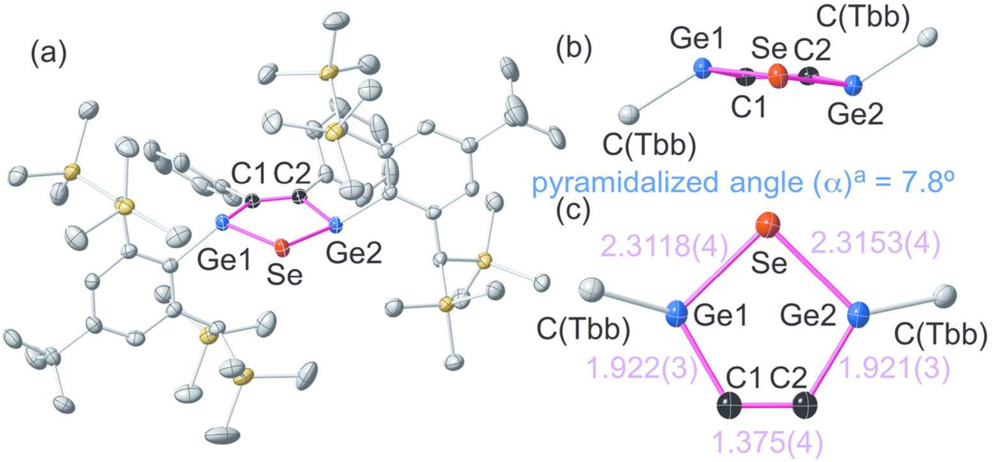


Figure 1

65x30mm (600 x 600 DPI)

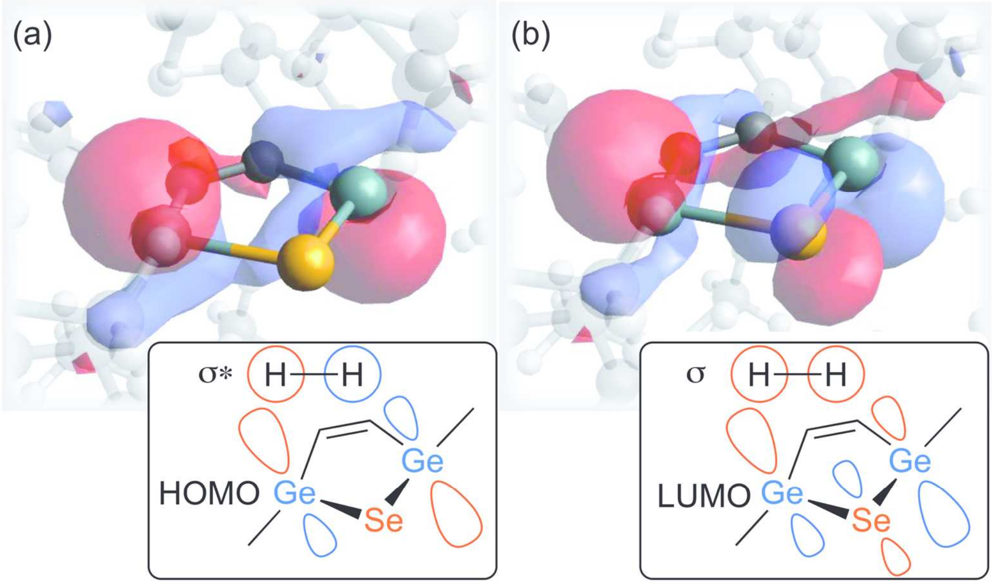
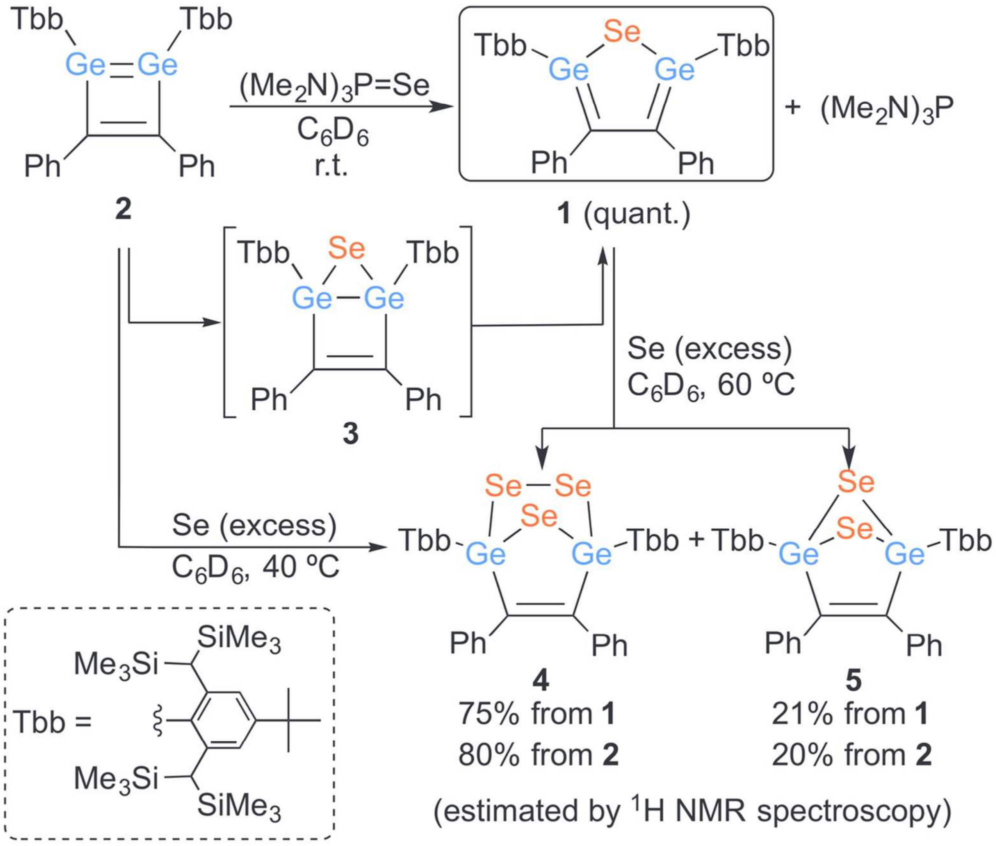


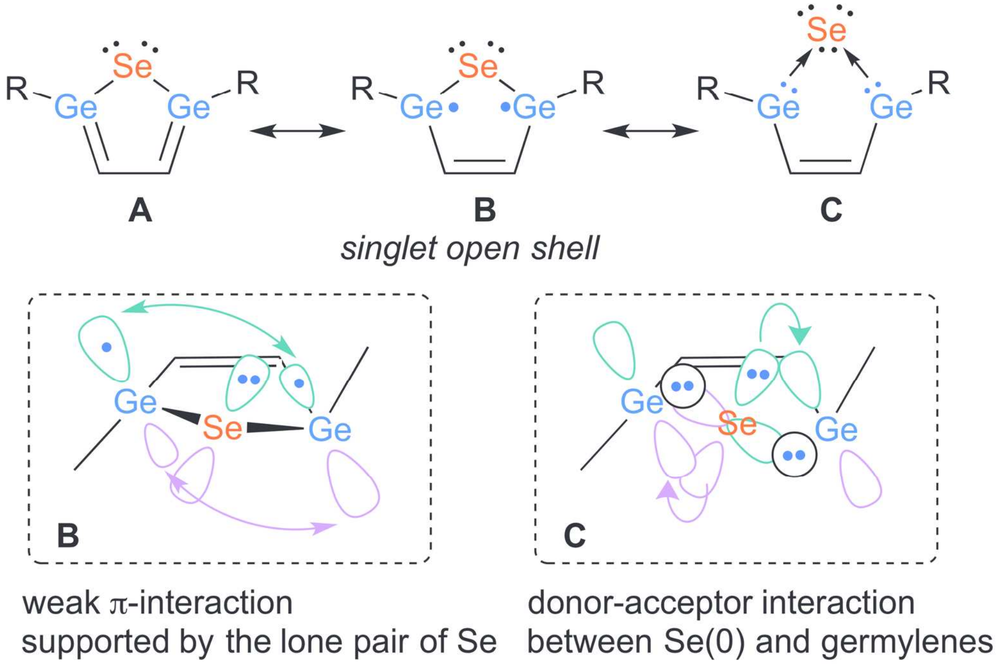
Figure 2

75x44mm (600 x 600 DPI)



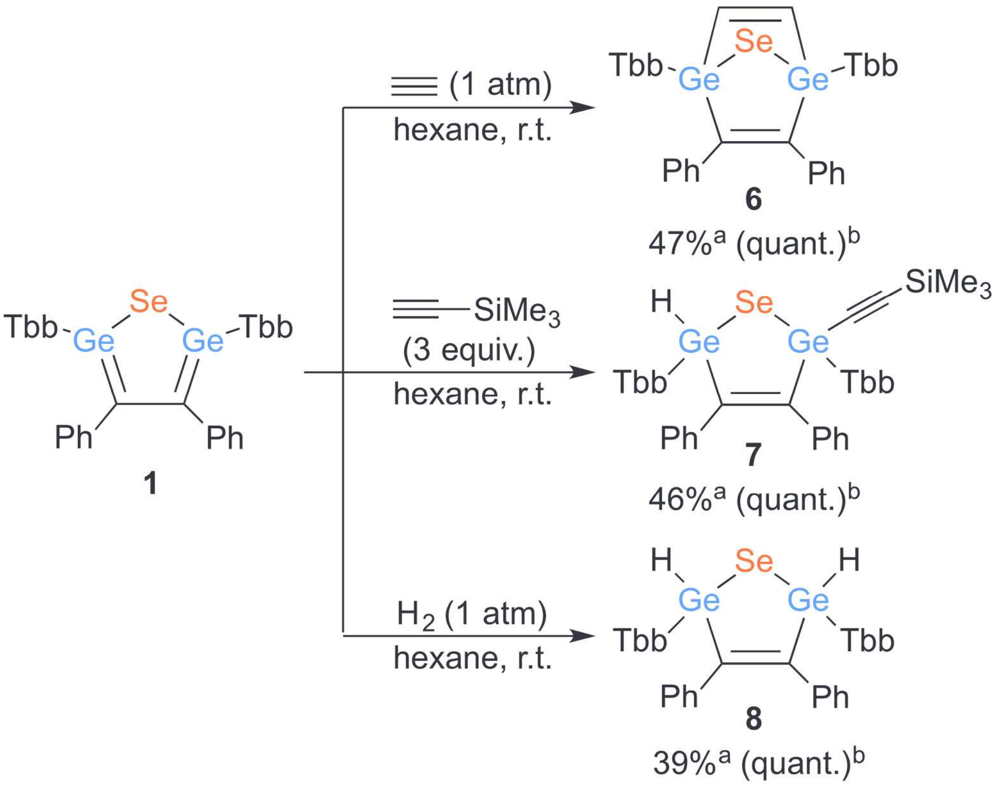
Scheme 1

114x97mm (300 x 300 DPI)



Scheme 2

84x56mm (600 x 600 DPI)



Scheme 3

103x80mm (600 x 600 DPI)

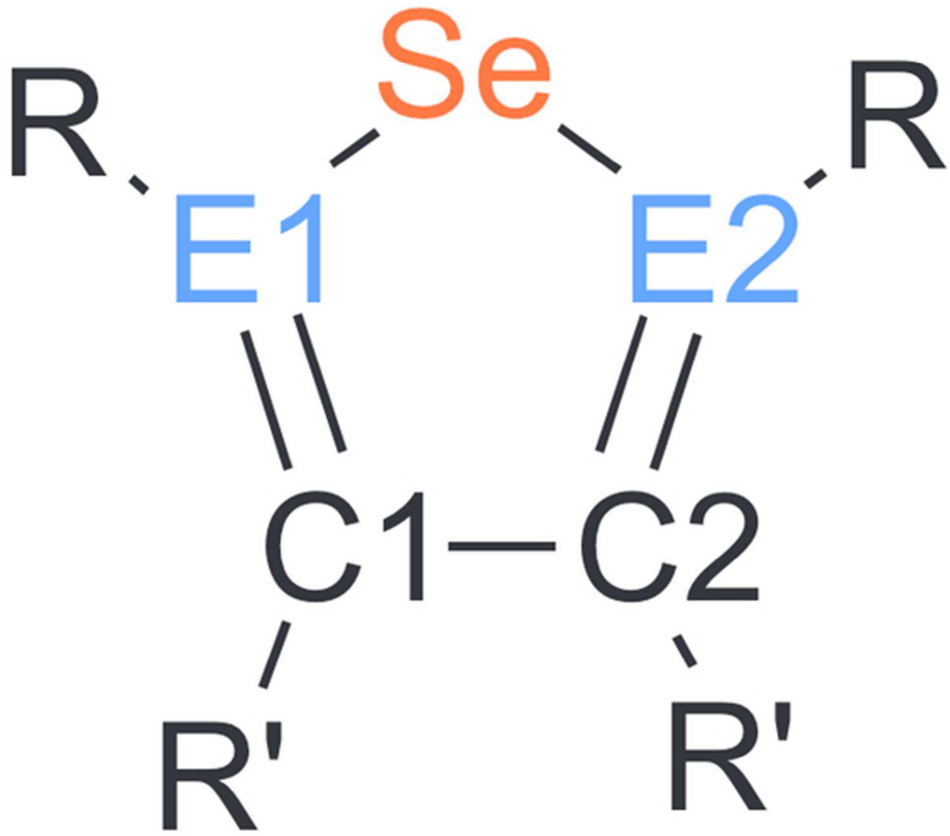
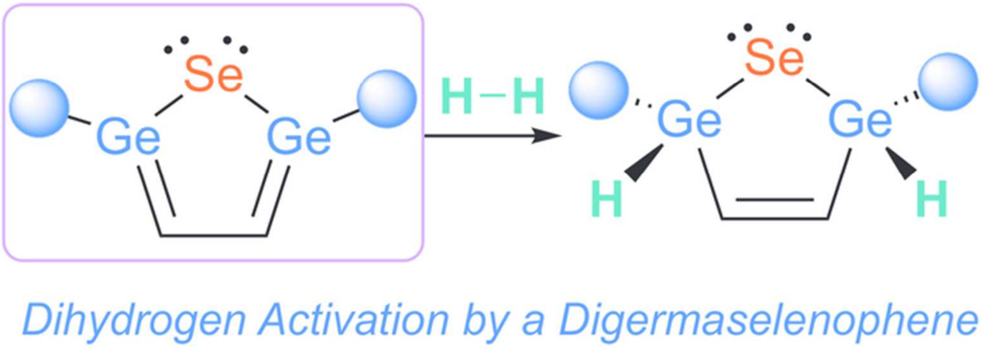


Table 1

25x22mm (600 x 600 DPI)



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29x10mm (600 x 600 DPI)