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Amidinate bromogermylene resulting from carbodiimide insertion into Ar–GeBr bond

Takahiro Sasamori,*[a,b] Tomohiro Sugahara[c] and Norihiro Tokitoh[c]

[a] *Division of Chemistry, Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan. E-mail: sasamori@chem.tsukuba.ac.jp*

[b] *Graduate School of Science, Nagoya City University, Mizuho-cho, Mizuho-ku, Nagoya, Aichi 467-8501, Japan*

[c] *Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

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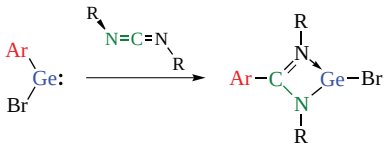
The reaction of diaryldibromodigermene Tbb(Be)Ge=Ge(Br)Tbb (Tbb = 4-Bu^t-2,6-[CH(SiMe$_3$)$_2$]$_2$C$_6$H$_2$) with *N*,*N*′-diisopropylcarbodiimide afforded the corresponding amidinato-supported bromogermylene *via* the insertion of the C=N moiety into the Ge–C(Tbb) σ-bond. The formation mechanism of the amidinato-supported bromogermylene was revealed by DFT calculations. This type of insertion reaction toward a metal–carbon bond can be interpreted in analogy to the reactivity of transition-metal complexes.



Keywords: carbenoids, germylenes, 1,2-insertion, main group elements, an amidinato ligand.

Dedicated to Emeritus Professor Shigeru Nagase on the occasion of his 75th birthday

Over the last few decades, interest has intensified in the chemistry of heavier tetrylenes, *i.e.*, divalent species of heavier group-14 elements (>Si**:**, >Ge**:**, >Sn**:**, >Pb**:**); this is hardly surprising given the parallels and differences compared to the ubiquitous divalent carbon analogues, *i.e.*, carbenes.[1] As in the case of isolable carbenes,[2] N-substituted tetrylenes and especially N-heterocyclic tetrylenes are known to be isolable in monomeric form due to the effective electronic stabilization provided by the lone pairs of the neighboring N atoms toward the vacant p-orbital of the tetrylene.[1,3] Among the numerous examples of isolable N-substituted tetrylenes, those supported by monovalent bidentate N-ligands such as β-diketiminato and amidinato ligands have attracted much attention due to their strong σ-donating character, which has already been systematically investigated in the context of classic transition-metal complexes.[3] Particularly, the isolable β-diketiminato and amidinato halotetrylenes are of great importance in tetrylene chemistry, because they can be further functionalized *via* replacement of the halogen atom for other functional groups, which allows controlling the properties of the resulting compounds.[3,4] Among stable tetrylenes that bear an N,N′-bidentate monovalent ligand (*e.g.*, structures **1** and **2a**,**b**; Figure 1),[4,5] germylenes and stannylenes can be easily prepared due to the availability of E^{II}X$_2$ species (E = Ge Sn, X = Cl, Br) as precursors. For example, amidinato-supported chlorogermylenes can be obtained from the reaction of lithium amidinate (available from the reaction of RLi with a carbodiimide) with GeCl$_2$ in a one-pot reaction.[5(c)] Herein, we report the synthesis of an amidinato-supported bromogermylene (Scheme 1). The reaction of dibromodigermene **1**, (*E*)-Tbb(Br)Ge=Ge(Br)Tbb (Tbb = 4-Bu^t-2,6-[CH(SiMe$_3$)$_2$]$_2$C$_6$H$_2$),[6] which is dissociated into the corresponding bromogermylene in solution, with *N*,*N*′-diisopropylcarbodiimide resulted in the corresponding amidinato-supported bromogermylene *via* the C=N insertion into the Ge–C(Tbb) σ-bond.

Dibromodigermene **3** was prepared according to literature procedure.[6] Heating of a C$_6$D$_6$ solution of **3** in the presence of 2.5 equiv. of *N*,*N*′-diisopropylcarbodiimide at 70 °C for 7 h

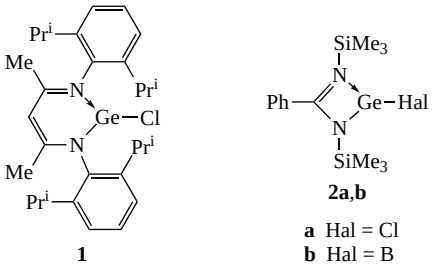
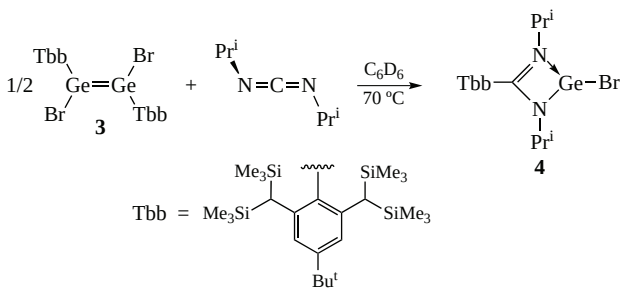


Figure 1 Halogermylenes bearing β-diketiminato (**1**) or a amidinato (**2a**,**b**) ligands.



Scheme 1

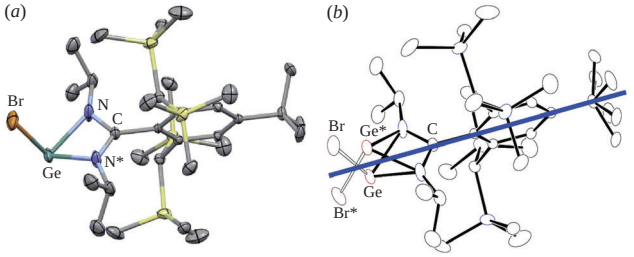


Figure 2 (*a*) Molecular structure of amidinato-supported bromogermylene **4** with thermal ellipsoids at 50% probability. (*b*) Depiction of the pseudo *C*2 axis generated due to the severe disorder. Selected bond lengths (Å) and angles (°): Ge–Br, 2.4189(8), Ge–N (Ge–N*), 2.057(3), C–N (C–N*), 1.332(3), N–Ge–N*, 62.7(1), Br–Ge–N, 93.30(9), N–C–N*, 107.1(3).

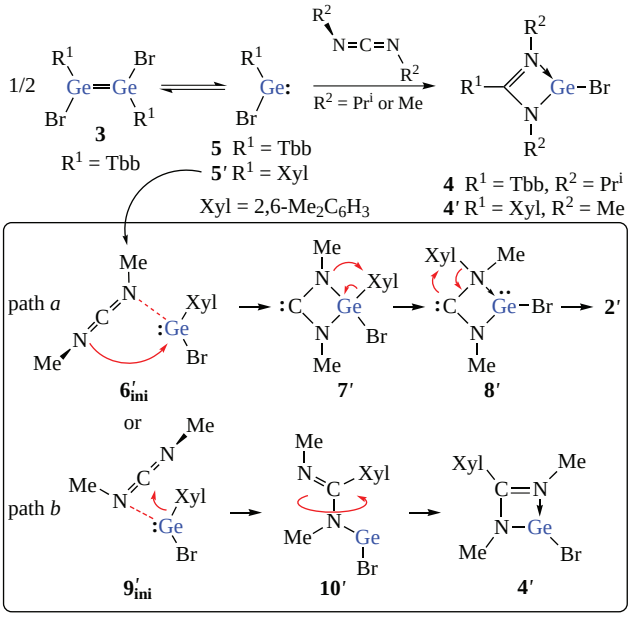
afforded amidinate bromogermylene **4** as the sole product, which was purified by recrystallization from hexane to furnish stable colorless crystals in 84% isolated yield (see Scheme 1).

The molecular structure of bromogermylene **4** was unequivocally determined by a single-crystal X-ray diffraction analysis [Figure 2(*a*)].† Bromogermylene **4** crystallizes in the *Pbcn* (#60) space group and contains only four molecules per unit cell ($Z = 4$), as the pseudo *C*2 axis that passes through the center of the Tbb group and the central C atom of the amindinato ligand is generated due to the severe disorder of the Ge–Br and $C(SiMe_3)_3$ moieties [see Figure 2(*b*)].

The observed structural parameters of compound **4** are in good agreement with those obtained from the theoretical optimization at the B3PW91/6-311G(2d) level of theory (Ge–Br, 2.443 Å, Ge–N, 2.013 Å, C–N, 1.334 and 1.335 Å, N–Ge–N, 64.5°, Br–Ge–N, 98.6 and 99.2°, N–C–N, 107.1°), suggesting a reliable solution of the reflection data despite the severe levels of disorder. While there is only one example of a structurally characterized amidinate bromogermylene in the CCDC database (structure **2b**, see Figure 1),[5(*b*)] the observed structural parameters for the $BrGeN_2C$ moiety of **4** are comparable to those of **2b** [Ge–Br, 2.4239(12) Å, Ge–N, 2.037(5) and 2.049(6) Å, C–N, 1.316(8) and 1.351(8) Å, N–Ge–N, 66.0(2)°, Br–Ge–N, 97.55(17) and 95.81(16)°],[5(*b*)] suggesting that the steric/electronic perturbation toward the germylene center from the substituents on the amidinato ligand can be expected to be negligible.

We also theoretically investigated the formation mechanism of bromogermylene **4** (Scheme 2). As dibromodigermene **3** is known to undergo Ge=Ge dissociation upon heating to afford the corresponding germylene **5**,[6,7] the formation of amidinato bromogermylene **4** should most likely be interpreted in terms of the reaction of germylene **5** with *N*,*N*′-diisopropylcarbodiimide. The potential energy surfaces (PESs) of the model reaction of bromogermylene **5**′, which bears a 2,6-dimethylphenyl group, and *N*,*N*′-dimethylcarbodiimide to give amidinato-supported bromogermylene **4**′ at the B3PW91/6-311G(2d)//B3PW91/3-21G level of theory revealed two possible pathways *a* and *b* (see Scheme 2).

As shown in Scheme 2, the two initial complexes, $\mathbf{6}'_{\mathbf{ini}}$ and $\mathbf{9}'_{\mathbf{ini}}$, which are formed by the coordination of the N atom of the carbodiimide to the vacant p orbital of **5**′ in different directions,



Scheme 2

leads to the formation of **4**′ *via* pathways *a* or *b*. From $\mathbf{6}'_{\mathbf{ini}}$ (path *a*), carbene **7**′ was formed *via* a formal [1 + 3] cycloaddition between germylene **5**′ and the carbodiimide with the barrier of $\Delta E^{\ddagger}_{ZPE}$ = 20.9 kcal mol^{-1} (Figure 3). Then the Xyl group of **7**′ could migrate from Ge to N to give **8**′, which is the rate-determining step with the large barrier of $\Delta E^{\ddagger}_{ZPE}$ = 63.0 kcal mol^{-1}, followed by the further migration of the Xyl group from N to C to give product **4**′ with a barrier of $\Delta E^{\ddagger}_{ZPE}$ = 35.1 kcal mol^{-1}. As for path *b*, the initial complex $\mathbf{9}'_{\mathbf{ini}}$ is transformed to germylene **10**′ *via* the 1,2-insertion of the C=N moiety of the carbodiimide into the Ge–C(aryl) bond with a small barrier of $\Delta E^{\ddagger}_{ZPE}$ = 7.5 kcal mol^{-1}. The barrier of the 1,2-insertion of an acetylene into the Ge–C bond of a bromo(mesityl)germylene to give the corresponding bromo(vinyl)germylene was calculated to be $\Delta E^{\ddagger}_{ZPE}$ = 6.7 kcal mol^{-1},[7] which is similar to the barrier from $\mathbf{9}'_{\mathbf{ini}}$ to **10**′ *via* $\mathbf{TS}_{910}$ (see Figure 3), suggesting that the 1,2-insertion of a π-bond compound is a general reactivity pattern of arylbromogermylenes. Then, the C–N bond rotation of **10**′ could afford **4**′ with a barrier of $\Delta E^{\ddagger}_{ZPE}$ = 13.5 kcal mol^{-1}, which is the rate-determining step for path *b*. An analysis of both PESs for pathways *a* and *b* reveals that path *b* should be more favorable, and that the formation of bromogermylene **4** should thus be most likely interpreted in terms of a 1,2-insertion of the C=N π-bond of *N*,*N*′-diisopropylcarbodiimide into the Ge–C(Tbb) bond of

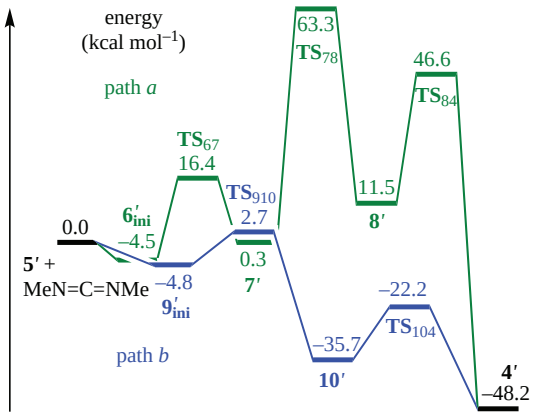


Figure 3 Calculated potential energy surfaces (PESs) for pathways *a* and *b* (see Scheme 2) with zero-point corrected energies (ΔE_{ZPE} in kcal mol^{-1}) for the reaction of **5**′ with *N*,*N*′-dimethylcarbodiimide.

† *Crystallographic data for* **4**. $C_{31}H_{63}BrGeN_2Si_4$, FW 728.69, crystal size 0.05 × 0.05 × 0.02 mm^3, temperature –170 °C, λ = 0.71073 Å, monoclinic, space group *Pbcn* (#60), a = 19.0423(5), b = 13.8557(4) and c = 14.9376(4) Å, V = 3941.20(19) Å^3, Z = 4, D_{calcd} = 1.228 g cm^{-3}, μ = 1.934 mm^{-1}, θ_{max} = 28.223°, 32529 reflections measured, 4513 independent reflections (R_{int} = 0.0693), 201 parameters refined, GOF = 1.188, completeness to θ_{max} = 97.1%, R_1 [$I > 2\sigma(I)$] = 0.0530, wR_2 (all data) = 0.1180, largest diff. peak and hole 0.335 and –0.348 e Å^{-3}.

CCDC 2103198 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

bromogermylene **5**, which would be a characteristic π-bond insertion of an arylbromogermylene in analogy to transition-metal complexes.[7,8]

In conclusion, amidinato-supported bromogermylene **4** was formed in the reaction of dibromodigermene **3** with *N*,*N'*-diisopropylcarbodiimide. We used DFT calculations to examine the formation mechanism, including the 1,2-insertion of the C=N moiety of the carbodiimide into the Ge–C bond of intermediate arylbromogermylene **5**, which was thermally generated from **3**. This reaction could be a unique synthetic method for the amidinato-supported halogermylenes exploiting the transition-metal-like reactivity of an arylbromogermylene toward the π-bond compounds.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.020.

References

1 (*a*) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479; (*b*) C. Shan, S. Yao and M. Driess, *Chem. Soc. Rev.*, 2020, **49**, 6733; (*c*) S. Fujimori and S. Inoue, *Eur. J. Inorg. Chem.*, 2020, 3131.

2 (*a*) A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361; (*b*) S. Díez-González and S. P. Nolan, *Coord. Chem. Rev.*, 2007, **251**, 874; (*c*) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485.

3 (*a*) M. Bayat and E. Soltani, *Polyhedron*, 2017, **123**, 39; (*b*) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354; (*c*) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457.

4 O. Kühl, *Coord. Chem. Rev.*, 2004, **248**, 411.

5 (*a*) Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt and P. P. Power, *Organometallics*, 2001, **20**, 1190; (*b*) D. Matioszek, N. Katir, N. Saffon and A. Castel, *Organometallics*, 2010, **29**, 3039; (*c*) S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmüller, A. Pal and R. Herbst-Irmer, *Organometallics*, 2008, **27**, 5459; (*d*) J. A. Cabeza, P. García-Álvarez and D. Polo, *Dalton Trans.*, 2013, **42**, 1329.

6 (*a*) T. Sasamori, T. Sugahara, T. Agou, J.-D. Guo, S. Nagase, R. Streubel and N. Tokitoh, *Organometallics*, 2015, **34**, 2106; (*b*) T. Sugahara, J.-D. Guo, T. Sasamori, Y. Karatsu, Y. Furukawa, A. Espinosa Ferao, S. Nagase and N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 1375; (*c*) T. Sasamori, Y. Sugiyama, N. Takeda and N. Tokitoh, *Organometallics*, 2005, **24**, 3309.

7 T. Sugahara, A. E. Ferao, A. R. Planells, J.-D. Guo, S. Aoyama, K. Igawa, K. Tomooka, T. Sasamori, D. Hashizume, S. Nagase and N. Tokitoh, *Dalton Trans.*, 2020, **49**, 7189.

8 (*a*) P. P. Power, *Nature*, 2010, **463**, 171; (*b*) T. Chu and G. I. Nikonov, *Chem. Rev.*, 2018, **118**, 3608.

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