# Insertion of a Cationic Metallogermylene into E−H Bonds (E = H, B, Si)

Koya Inomata,[†] Takahito Watanabe,[‡] Yoshikazu Miyazaki,[‡] and Hiromi Tobita[*,‡]

[†]Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
[‡]Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

**S** *Supporting Information*

**ABSTRACT:** A cationic germylene containing tungsten and N-heterocyclic carbene units reacted with $H_2$ in fluorobenzene at 60 °C, resulting in its insertion into the H−H bond. It also activated the Si−H bond of ethyldimethylsilane and the B−H bond of pinacolborane at ambient temperature to give the insertion products. The latter insertion reactions against hydrosilane and hydroborane were found to be reversible.

There is considerable current interest in the activation of $\sigma$ bonds such as H−H, B−H, C−H, N−H, etc., by coordinatively unsaturated group 14 element centers.[1] In particular, the activation of $H_2$ has been discovered and intensively studied in the past decade. In 2005, Power and co-workers showed that the digermyne ArGe≡GeAr (Ar = 2,6-$(Dipp)_2C_6H_3$, Dipp = 2,6-$^iPr_2C_6H_3$) reacts with $H_2$ at ordinary temperature and pressure to give a mixture of its hydrogenation products Ar(H)Ge=Ge(H)Ar, Ar(H)$_2$GeGe(H)$_2$Ar, and ArGeH$_3$.[2] Then, in 2007, Bertrand and co-workers reported that stable singlet (alkyl)(amino)carbenes such as C($^tBu$)N$^iPr_2$ readily react with $H_2$ and $NH_3$ to afford the insertion products.[3] Several other low-valent group 14 compounds have also been found to activate $H_2$ since these discoveries.[4]

Activation of $H_2$ with germylenes was first reported by Power and co-workers in 2009.[4c] Namely, the reaction of :Ge(2,6-Mes$_2$C$_6$H$_3$)$_2$ with $H_2$ at 60−70 °C gave the insertion product (2,6-Mes$_2$C$_6$H$_3$)$_2$GeH$_2$. Interestingly, the corresponding reaction did not proceed in the case of the tin analogue :Sn(2,6-Mes$_2$C$_6$H$_3$)$_2$.[4c] A proposed mechanism for this insertion reaction based on density functional theory (DFT) calculations is illustrated in Scheme 1.[4c] $H_2$ approaches the Ge atom via a weak interaction between the $\sigma$ orbital of $H_2$ and the empty p orbital of Ge, and subsequent interaction between the lone pair of Ge and the $\sigma^*$ orbital of $H_2$ yields the dihydrogermane. They also suggested that the lack of reactivity of the stannylene
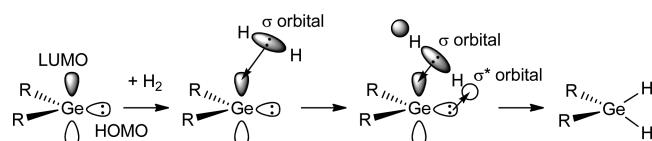
toward $H_2$ is due to the larger energy separation between the lone-pair orbital and the empty p orbital of the stannylene in comparison with that of the germylene.

We recently succeeded in the synthesis of the N-heterocyclic carbene (NHC)-stabilized chlorometallogermylene Cp*-(CO)$_3$WGeCl(IPr) (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) and its conversion to the cationic metallogermylene [Cp*(CO)$_3$WGe(IPr)](BAr$^F_4$) (**2**) (Ar$^F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) by chloride abstraction with NaBAr$^F_4$.[5] The UV/vis spectrum of **2** in fluorobenzene showed an absorption maximum assignable to the HOMO−LUMO transition at 671 nm. This value indicates that the HOMO−LUMO gap of **2** is smaller than that of the neutral germylene :Ge(2,6-Mes$_2$C$_6$H$_3$)$_2$ (578 nm)[4c] and therefore suggests that **2** could have higher reactivity toward $H_2$.[6] In addition, the energies of both the HOMO and LUMO of cationic metallogermylene **2** are expected to be lower than those of neutral germylenes because of the positive charge of **2**.[7] The lowered LUMO would be more susceptible to the interaction with the $\sigma$-bonding orbital of $H_2$. On the basis of these hypotheses, we began to study the reactions of **2** with $H_2$ and also with compounds having a B−H or Si−H bond. In this paper, we report the insertion of cationic metallogermylene **2** into not only the H−H bond but also the Si−H and B−H bonds.

We found that once the crystals of **2** precipitated out from the reaction mixture, they became almost insoluble in organic solvents. Complex **2**, therefore, was prepared from **1** and NaBAr$^F_4$ in fluorobenzene immediately prior to the reactions with the substrates. The reaction of **2** with $H_2$ (1 atm) in fluorobenzene did not proceed at room temperature, but it did proceed slowly at 60 °C. The color of the reaction mixture gradually changed from green to yellow, and the insertion product [Cp*(CO)$_3$WGeH$_2$(IPr)](BAr$^F_4$) (**3**) was formed as the sole product (Scheme 2). Complex **3** was isolated in 92% yield as pale-yellow crystals by recrystallization from a fluorobenzene/hexane solution.

The molecular structure of **3** was determined by X-ray crystal structure analysis (Figure 1). There are two independent molecules with nearly identical structures in an asymmetric unit cell. The hydrogen atoms on Ge in one molecule were found from the difference Fourier map. The W−Ge bond length (2.6038(7) Å) and the W−Ge−C bond angle (120.8(2)°) are comparable to those of the closely related IPr-stabilized

**Scheme 1. Schematic Representation of a Proposed Mechanism for Insertion of a Germylene into the H−H Bond of $H_2$**

## Scheme 2. Reaction of 2 with H$_2$



## Scheme 3. Reactions of 2 with Hydrosilane and Hydroborane
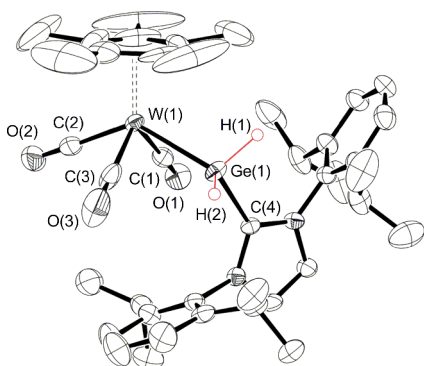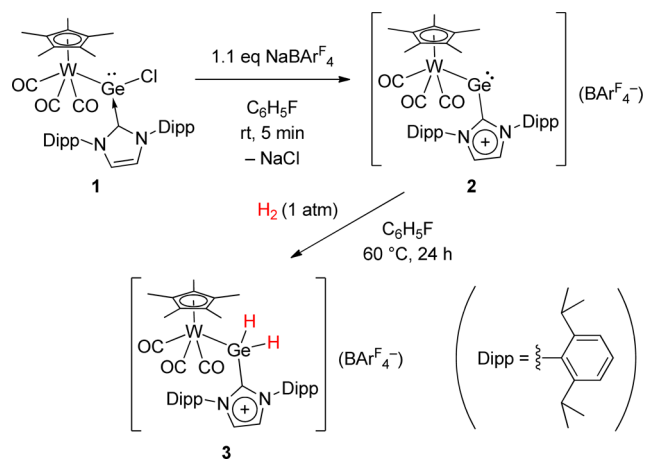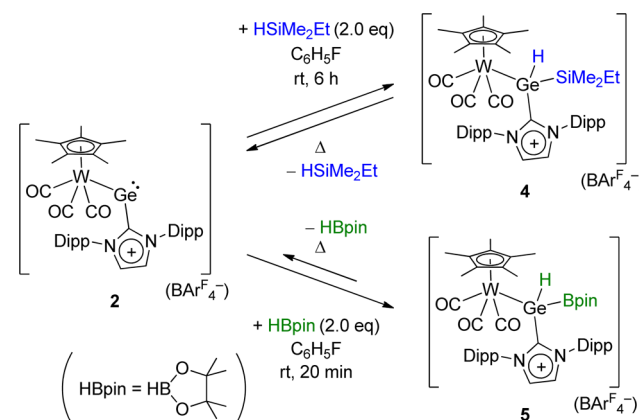




**Figure 1.** ORTEP drawing of one of the two independent cationic parts of **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity except for H(1) and H(2) on the Ge atom. Selected bond lengths (Å) and angles (deg): W(1)−Ge(1) 2.6038(7), Ge(1)−C(4) 1.998(6), Ge(1)−H(1) 1.42(7), Ge(1)−H(2) 1.59(6), W(1)−C(1) 1.977(7), W(1)−C(2) 1.979(8), W(1)−C(3) 1.983(7), C(1)−O(1) 1.153(8), C(2)−O(2) 1.154(9), C(3)−O(3) 1.155(9), W(1)−Ge(1)−C(4) 120.8(2).

germylene complex IPr·GeH$_2$·W(CO)$_5$ (2.6318(2) Å and 121.44(5)°).[8]

The $^1$H NMR spectrum of **3** shows a signal assigned to the GeH$_2$ moiety at 3.78 ppm. Four $^i$Pr groups in the IPr moiety exhibit only a single methyne signal at 2.44 ppm and two methyl signals at 1.02 and 1.30 ppm. This indicates that two methyne groups on the same Dipp group become equivalent but two methyl groups in each $^i$Pr group are inequivalent because of the diastereotopic relationship in solution. In the $^{13}$C{$^1$H} NMR spectrum of **3**, the signals of the corresponding four $^i$Pr groups are observed at 22.1, 26.0 (CH(CH$_3$)$_2$), and 29.0 ppm (CH(CH$_3$)$_2$). In the IR spectrum of **3**, the GeH$_2$ stretching bands could not be observed, probably because the bands overlap with three strong CO stretching bands (1919, 1950, and 2015 cm$^{-1}$).

Complex **2** was also found to react with a hydrosilane under conditions milder than those for the reaction with H$_2$ (Scheme 3). Treatment of **2** with 2 equiv of ethyldimethylsilane at room temperature for 6 h gave [Cp*(CO)$_3$WGeH(SiMe$_2$Et)(IPr)]-(BAr$^F_4$) (**4**) through insertion of **2** into the Si−H bond. Interestingly, this Si−H bond activation is reversible. When the reaction mixture was heated to 60 °C, the hydrosilane was slowly eliminated from the Ge center of **4**. After 1 h, this

reaction achieved equilibrium to give a mixture of **4** and **2** in a 7:2 ratio. The equilibrium ratio changed to 7:8 at 80 °C, but at higher temperatures, decomposition of both **4** and **2** occurred, forming a complicated mixture. Although the insertion of in situ-generated germylenes into Si−H bonds is well-known,[9] to our knowledge, no reversible insertion of isolable germylenes into Si−H bonds has been reported to date.

The molecular structure of **4** was determined by X-ray crystal structure analysis. The ORTEP drawing of one of the two cationic parts in an asymmetric unit, which are nearly identical to each other, is depicted in Figure 2. It clearly demonstrates
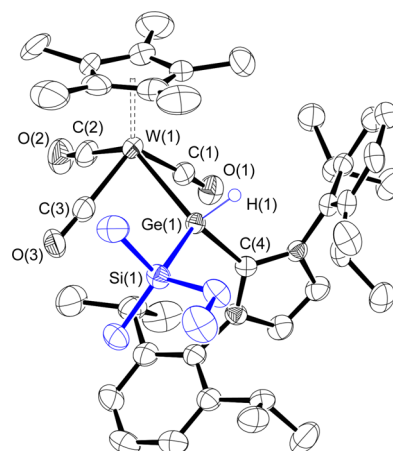


**Figure 2.** ORTEP drawing of one of the two independent cationic parts of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity except for H(1) on the Ge atom. Selected bond lengths (Å) and angles (deg): W(1)−Ge(1) 2.6934(6), Ge(1)−Si(1) 2.431(2), Ge(1)−C(1) 2.025(6), Ge(1)−H(1) 1.32(6), W(1)−C(1) 1.990(7), W(1)−C(2) 1.975(8), W(1)−C(3) 1.976(7), C(1)−O(1) 1.142(8), C(2)−O(2) 1.149(9), C(3)−O(3) 1.153(9), W(1)−Ge(1)−Si(1) 119.77(5), W(1)−Ge(1)−C(4) 115.8(2), Si(1)−Ge(1)−C(4) 113.5(2).

the existence of a Ge−Si bond and a Ge−H bond, whose hydrogen atom was found from the difference Fourier map. The bond lengths of the W−Ge−Si linkage of **4** (W−Ge, 2.6934(6) Å; Ge−Si; 2.431(2) Å) are both longer than those in the related complex IPr·H$_2$SiGeH$_2$·W(CO)$_5$ (W−Ge, 2.6479(6) Å; Ge−Si, 2.3717(14) Å).[10] The W−Ge bond in **4** is also significantly longer than that in **3**. These elongations

undoubtedly reflect steric repulsion between the tungsten fragment and the silyl group.

The $^1H$ NMR spectrum of **4** shows the GeH signal at 3.56 ppm and two signals for diastereotopic SiMe groups at −0.22 and −0.14 ppm. In the $^{13}C\{^1H\}$ NMR spectrum of **4**, the signals for eight methyl carbons of four $^iPr$ groups in IPr all appear inequivalently. These are inequivalent because the Ge center is chiral and the Ge−C(IPr) and N−C(Dipp) bonds cannot rotate or the rotation is very slow on the NMR time scale, reflecting the steric congestion of substituents surrounding these bonds. This steric congestion around Ge is also probably responsible for the facile elimination of the hydrosilane upon gentle heating.

The reaction of **2** with pinacolborane at room temperature resulted in activation of the B−H bond to give the insertion product $[Cp^*(CO)_3WGeH(Bpin)(IPr)](BAr^F_4)$ (**5**) within 20 min (Scheme 3). This B−H bond activation was also found to be reversible, and the elimination of pinacolborane from **5** in solution was observed at 80 °C by variable-temperature NMR spectroscopy, although the proportions of **2** and pinacolborane to **5** were still low even at this temperature (see Figures S13 and S14 in the Supporting Information). Insertion of germylenes into B−H bonds is very rare, and only one example of this type of reaction has been reported to date for in situ-generated dimethylgermylene.[11]

The $^1H$ NMR spectrum of **5** shows the GeH signal at 3.35 ppm. Two diastereotopic Me groups on each of the two equivalent quaternary C atoms in Bpin are observed inequivalently at 0.99 and 1.03 ppm. The $^{13}C$ NMR spectrum shows only two sets of signals for four $^iPr$ groups of IPr at 21.8, 22.5, 25.9, 26.4 $(CH(CH_3)_2)$ and 28.7, 29.1 ppm $(CH(CH_3)_2)$. These observations indicate that the Ge center of **5** is chiral but the rotation around the Ge−C(IPr) bond is fast on the NMR time scale, in contrast to that in **4**. This is obviously the case because the steric congestion around the Ge center of **5** is smaller than that of **4**, which makes the elimination of HBpin unfavorable in comparison with that of $HSiMe_2Et$.

In summary, the cationic metallogermylene **2** activated H−H, Si−H, and B−H $\sigma$ bonds to afford the insertion products $[Cp^*(CO)_3WGeHR(IPr)](BAr^F_4)$ (**3**, R = H; **4**, R = $SiMe_2Et$; **5**, R = Bpin). Such a high reactivity of **2** toward small molecules is attributable to the small HOMO−LUMO gap and the very high electrophilicity of the Ge atom caused by the high distribution of positive charge at the Ge center. The effect of substituents of Ge on these insertion reactions is currently under investigation.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08169.

> X-ray crystallographic data for **3** and **4** (CIF)
> Synthetic procedures and characterization data for **3**−**5**, including $^1H$, $^{11}B$, $^{13}C$, $^{19}F$, and $^{29}Si$ NMR spectra, details of the crystal structure refinement for **3** and **4**, and details of the calculations for a model complex of **2** (PDF)

## AUTHOR INFORMATION

### Corresponding Author
*tobita@m.tohoku.ac.jp

### Notes
The authors declare no competing financial interest.

## REFERENCES

(1) (a) Power, P. P. *Organometallics* **2007**, *26*, 4362−4372. (b) Power, P. P. *Nature* **2010**, *463*, 171−177. (c) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389−399. (d) Yao, S.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, 1748−1767. (e) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627−637. (f) Asay, M.; Sekiguchi, A. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 1245−1261.

(2) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232−12233.

(3) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439−441.

(4) (a) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 12268−12269. (b) Peng, Y.; Brynda, M.; Ellis, B. D.; Fettinger, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 6042−6044. (c) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettinger, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 16272−16282. (d) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2011**, *133*, 18622−18625. (e) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2012**, *134*, 6500−6503. (f) Hadlington, T. J.; Hermann, M.; Li, J.; Frenking, G.; Jones, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 10199−10203. (g) Lui, M. W.; Merten, C.; Ferguson, M. J.; McDonald, R.; Xu, Y.; Rivard, E. *Inorg. Chem.* **2015**, *54*, 2040−2049.

(5) Inomata, K.; Watanabe, T.; Tobita, H. *J. Am. Chem. Soc.* **2014**, *136*, 14341−14344.

(6) Wilfling, P.; Schittelkopf, K.; Flock, M.; Herber, R. H.; Power, P. P.; Fischer, R. C. *Organometallics* **2015**, *34*, 2222−2232.

(7) DFT calculations for model complexes support the hypothesis that the positive charge in **2** lowers the energies of the frontier orbitals (see Figure S23 in the Supporting Information).

(8) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E. *J. Am. Chem. Soc.* **2011**, *133*, 777−779.

(9) (a) Mochida, K.; Hasegawa, A. *Chem. Lett.* **1989**, 1087−1088. (b) Baines, K. M.; Cooke, J. A.; Vittal, J. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1484−1485. (c) Baines, K. M.; Cooke, J. A. *Organometallics* **1992**, *11*, 3487−3488. (d) Tokitoh, N.; Kishikawa, K.; Okazaki, R.; Sasamori, T.; Nakata, N.; Takeda, N. *Polyhedron* **2002**, *21*, 563−577.

(10) Al-Rafia, S. M. I.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8354−8357.

(11) Mayer, E. P.; Nöth, H.; Rattay, W.; Wietelmann, U. *Chem. Ber.* **1992**, *125*, 401−405.