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# Ni-Catalyzed Double Gemylation of Alkynes and Alkenes

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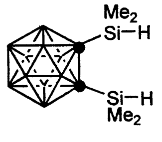
The reaction of 1,2-bis(dimethylgermyl)carborane with $Ni(PEt_3)_4$ yielded the cyclic bis(germyl)nickel complex **2**. **2** was found to be a good catalyst for the double germylation reaction. Thus, the reaction of **1** with RC≡CR′ in the presence of a catalytic amount of **2** yielded the six-membered digermyl ring compounds $B_{10}H_{10}C_2(GeMe_2)_2(RC{=}CR')$ (R = R′= Ph (**3**); R = Ph, R′ = H (**4**); R = R′ = Et (**5**); R = Ph, R′ = Me (**6**); R = R′ = Me (**7**); R = Ph, R′ = $SiMe_3$ (**8**); R = R′ = $SiMe_3$ (**9**); R = R′ = $CO_2Me$ (**10**)). In contrast, the reaction of **1** with 1-hexyne under the same reaction conditions yielded the five-membered digermyl ring compound $B_{10}H_{10}C_2(GeMe_2)_2(C{=}C(C_4H_9)H)$ (**11**). The intermediate was also found to be a good reactant for the double germylation of some alkenes. Thus, the stoichiometric reaction of **2** with 4-vinylanisole and 1,1-diphenylethylene gave the five-membered digermylene compounds (**14** and **15**). However, the stoichiometric reaction of **2** with 2,3-dimethylbutadiene afforded a different type of five-membered digerma compound **17** via the 1,4-migration of the hydride. The crystal structures of **2**, **6**, **12**, **14**, and **17** are described.

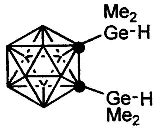
## Introduction

Although the transition metal-catalyzed double silylation of unsaturated organic substrates has been well documented for three decades,[1] little is known about the double germylation[2] because the synthetic methods available for organogermanium compounds are quite limited compared with those for organosilicon compounds. The double germylation reactions were mainly carried out in the presence of $[Pd(PPh_3)_4]$ as a catalyst.[3] Recently, Mochida and co-workers reported on the platinum-catalyzed bis-germylation of alkynes with organodigermanes and cyclic oligogermanes.[4] In the catalytic cycle, the bis(germyl) complexes have been implicated as important intermediates. However, there are only a few precedents for such species and only bis(chlorogermyl)platinum has been structurally characterized by Tanaka and co-workers.[5]

Recently, we[6] reported a variety of silylation reactions of a bis(silyl)nickel complex containing an *o*-bis(dimethylsilyl)carboranyl unit (**A**). We were also successful in preparing its congener, *o*-bis(dimethylgermyl)carborane (**1**).[7]



**A**



**1**

The property of moderate reactivity makes **1** a good choice for the double germylation reaction. Accordingly, we have started an investigation of the synthesis of the bis(germyl)nickel complex bearing a bulky *o*-carboranyl unit. We found that the bis(germyl)nickel complex is the most efficient and reactive catalyst for the double germylation reaction. This study includes the first crystal structure of a cyclic bis(germyl)nickel complex and a variety of double germylation reactions with alkynes and alkenes. Early results of this study have already been communicated.[8]

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(6) (a) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Chem. Commun.* **1998**, 2343. (b) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1772. (c) Kang, Y.; Kim. J.; Kong, Y. K.; Lee, S. W.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 5027. (d) Kim. J.; Kang, Y.; Lee, J.; Kong, Y. K.; Gong, M. S.; Kang, S. O.; Ko, J. *Organometallics* **2001**, *20*, 937.

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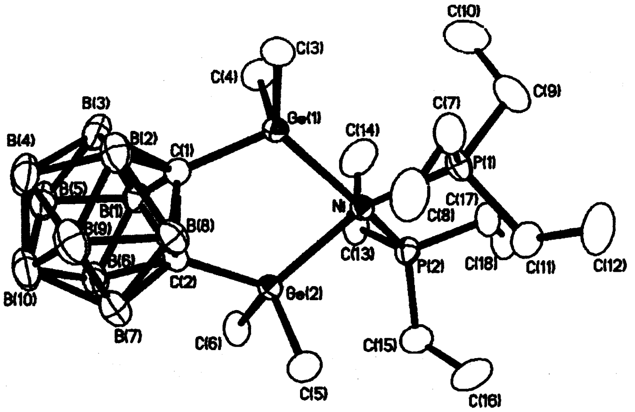
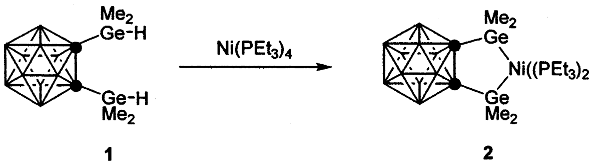


**Figure 1.** X-ray crystal structure of **2** with 50% probability thermal ellipsoids depicted. Selected bond lengths [Å] and angles [deg]: Ni−Ge(1) 2.3316(5), Ni−Ge(2) 2.3264(5), Ni−P(1) 2.2146(10), Ni−P(2) 2.2230(10), Ge(1)−C(1) 2.028(3), C(1)−C(2) 1.659(5), Ge(2)−C(2) 2.035(3), Ge(1)−Ni−Ge(2) 84.231(18), P(1)−Ni−P(2) 103.10(4), P(1)−Ni−Ge(2) 146.73(3), P(2)−Ni−Ge(2) 92.08(3), Ge(2)−C(1)−C(2) 110.4(2).

## Results and Discussion

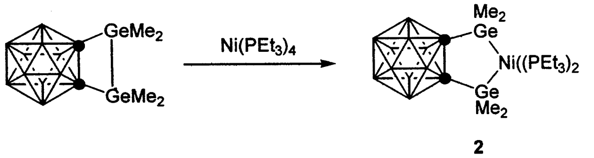
**Synthesis of [*o*-$(GeMe_2)_2C_2B_{10}H_{10}$]Ni$(PEt_3)_2$ Complex 2.** The synthesis of 1,2-bis(dimethylgermyl)carborane (**1**) was prepared by the salt elimination reaction of 1,2-$Li_2C_2B_{10}H_{10}$ and 2 equiv of $Me_2GeCl_2$, followed by reduction with a mild reducing agent, $NaB(CN)H_3$.[7] Compound **1** is a crystalline solid that is relatively stable in air and to brief heating to 108−110 °C. Compound **1** is soluble in toluene and THF. In an attempt to synthesize a stable bis(germyl)nickel complex, we investigated the reaction of **1** with $Ni(PEt_3)_4$. The addition of 1.1 equiv of *o*-bis(dimethylgermyl)carborane to $Ni(PEt_3)_4$ in pentane gave a red solution. Standard workup and crystallization from toluene−pentane gave [*o*-$(GeMe_2)_2C_2B_{10}H_{10}$]Ni$(PEt_3)_2$ (**2**) as a spectroscopically pure, red crystalline solid that is very sensitive to air and water in 60% yield (eq 1). Compound **2** is soluble in toluene and THF. The structure of **2** was unambiguously established by single-crystal X-ray analysis and is shown in Figure 1. The crystallographic data and processing parameters are given in Table 1. Complex **2** has a distorted tetrahedral geometry with the dihedral angle between Ge(1)−Ni−Ge(2) and P(1)−Ni−P(2) being 84.60°. This unstable bis(germyl)nickel complex is the first such compound as indicated by a search of the Cambridge Crystallographic Database. The average Ni−Ge bond length [2.3290(5) Å] is slightly longer than 2.248(1) Å found in $CpNi(PPh_3)GeCl_3$.[9] The Ni−P bond distance [2.2188(10) Å] is comparable to those observed in other phosphine nickel compounds.[10] The $^1$H and $^{31}$P NMR spectra and mass spectrum were consistent with the structure determined by X-ray crystallography. In particular, the $^{31}$P NMR signal was shifted from −2.2 ppm in $Ni(PEt_3)_3$ to 6.18 ppm. The mass spectrum of **2** showed a molecular ion at *m*/*z* 642.



(1)

The formation **2** may be interpreted in terms of the insertion of nickel into one of the Ge−H bonds of **1** and subsequent insertion of another Ge−H bond. The silicon analogue has been reported to undergo a similar type of dehydrogenation to give the bis-silyl metal complex.[6b]

For an alternate synthesis of complex **2**, we have also carried out the reaction of $Ni(PEt_3)_4$ with 3,4-carboranylene-1,1,2,2-tetramethyl-1,2-digermacyclobutane,[7] prepared from the Würtz reaction of 1,2-bis(chlorogermyl)carborane and sodium in toluene, which was isolated as orange crystals in 88% yield (eq 2). A similar cyclic bis(silyl)platinum complex has been reported.[11] Such an alkyne insertion by the reaction of digermylacyclohexadienes with acetylenedicarboxylate in the presence of $[PdCl_2(PPh_3)_2]$ was observed by Sakurai and co-workers.[12]



(2)

**Nickel-Catalyzed Reaction with Alkynes.** As expected, the nickel complex **2** was found to be an efficient catalyst for the double germylation reaction under mild conditions. Thus, the reaction of **1** (0.10 g, 0.29 mmol) with diphenylacetylene (0.06 g, 0.35 mmol) in the presence of a catalytic amount of **2** (0.01 g, 0.016 mmol) was heated under the conditions specified in Table 2. Subsequent recrystallization gave 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-digermacyclohex-2-ene (**3**) by insertion of the carbon−carbon triple bond into a germanium−nickel bond of **2** (entry 1). In a similar fashion, the reaction of **2** with other alkynes such as phenylacetylene, 3-hexyne, 1-phenyl-1-propyne, 2-butyne, and 1-phenyl-2-(trimethylsilyl)acetylene under the same reaction conditions also yielded the six-membered insertion products. Such alkyne insertion reactions in Ge−M have been reported for the palladium-catalyzed double germylation reactions of 3,4-benzo-1,2-germacyclobut-3-ene,[3a] digermiranes,[3b] and 1,2-dichloro-1,1,2,2-tetramethyldigermane.[2c]

Compounds **3**−**9** were identified on the basis of their $^1$H and $^{13}$C NMR spectra, mass spectra, and elemental analyses. The $^1$H NMR spectrum of **6** showed the phenyl and methyl resonances in the expected 5:3:6:6 ratio. In the $^{13}$C NMR spectrum of **6**, two resonances at 158.3 and 156.7 ppm could be assigned to the olefinic carbon atoms. The mass spectrum of **6** showed a molecular ion at *m*/*z* 464.

To provide structural information for one of the newly prepared compounds (**3**−**9**), a single-crystal X-ray diffraction study of the 1-phenyl-1-propyne insertion product **6** was undertaken. The molecular structure of **6** is

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[8] Lee, J.; Lee, C.; Lee, S. W.; Kang, S. O.; Ko, J. *Chem. Commun.* **2001**, 1730.

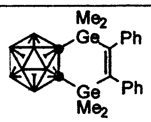
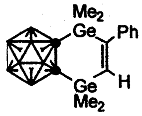
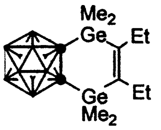
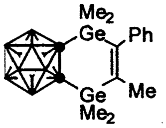
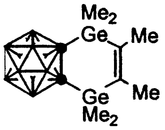
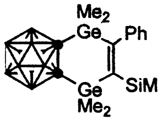
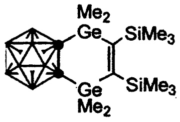
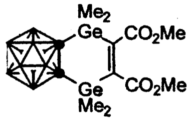
[9] Glockling, F.; Mcgredor, A.; Schneider, M. L.; Shearer, H. M. M. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3101.

[10] Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636.

[11] Kang, Y.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1217.

[12] Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 932.

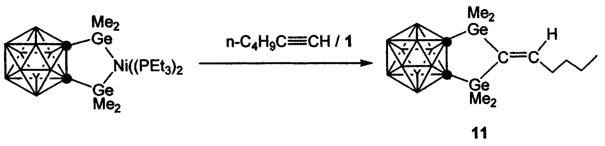
**Table 1. Nickel-Catalyzed Reactions of Alkynes with 1,2-Bis(dimethylgermyl)carborane**

| entry | Reactant | conditions | Product (yield, %) |
|---|---|---|---|
| 1 | $PhC{\equiv}CPh$ | 80 °C<br>(8 h) | <br>**3** (75 %) |
| 2 | $PhC{\equiv}CH$ | 80 °C<br>(8 h) | <br>**4** (65 %) |
| 3 | $EtC{\equiv}CEt$ | 80 °C<br>(8 h) | <br>**5** (87 %) |
| 4 | $PhC{\equiv}CMe$ | 80 °C<br>(8 h) | <br>**6** (85 %) |
| 5 | $MeC{\equiv}CMe$ | 80 °C<br>(8 h) | <br>**7** (72 %) |
| 6 | $PhC{\equiv}CSiMe_3$ | 80 °C<br>(8 h) | <br>**8** (72 %) |
| 7 | $Me_3SiC{\equiv}CSiMe_3$ | 110 °C<br>(12 h) | <br>**9** (72 %) |
| 8 | $MeO_2CC{\equiv}CCO_2Me$ | rt<br>(6 h) | <br>**10** (58 %) |

shown in Figure 2. A summary of the cell constants and data collection parameters is included in Table 1. The X-ray crystal structure of **6** confirmed the presence of a six-membered ring comprising a carboranylene, two germanium atoms, and an unsaturated hydrocarbon unit containing a C=C bond. The C7−C9 bond length (1.332(3) Å) is comparable to that of 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene (1.33(1) Å)[11] and the tricyclic product (1.346(3) Å) formed from the reaction between diphenylacetylene and tetrakis(dimethylsilyl)benezene.[13]

The nickel-catalyzed reaction with alkynes was quite sensitive to the reaction conditions. When the reaction of *o*-bis(dimethylgermyl)carborane **1** with dimethyl acetylenecarboxylate in the presence of a catalytic amount of **2** was carried out at 80 °C, the major product was identified as the alkyne cyclotrimerization product. However, the reaction of the nickel intermediate **2** with dimethyl acetylenecarboxylate at room temperature yielded the six-membered-ring compound **10** in 58% yield.

In contrast to the above reactions, the reaction of *o*-bis(dimethylgermyl)carborane (**1**) with 1-hexyne in the presence of a catalytic amount of **2** at room temperature afforded the five-membered-ring compound **11** in 62% yield (eq 3). All the spectral data of **11** were consistent with the proposed formulation. A key feature in the $^1H$ NMR spectrum includes a singlet at 6.24 ppm assigned



(3)

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[13] Uchimaru, Y.; Brandl, P.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744.

**Table 2. Crystal Data for 2, 6, 12, 14, and 17**

| | **2** | **6** | **12** | **14** | **17** |
|---|---|---|---|---|---|
| empirical formula | $C_{18}H_{52}B_{10}P_2Ge_2Ni$ | $C_{15}H_{30}B_{10}Ge_2$ | $C_{14}H_{34}B_{10}Ge_2$ | $C_{15}H_{32}B_{10}Ge_2O$ | $C_{12}H_{32}B_{10}Ge_2$ |
| mol wt | 641.52 | 463.67 | 455.69 | 481.69 | 429.66 |
| cryst syst | monoclinic | monoclinic | monoclinic | orthorhombic | monoclinic |
| space group | *P*2(1)/*n* | *P*2(1)/*c* | *P*2(1)/*n* | *Pbca* | *P*2(1)/*c* |
| a (Å) | 11.2880(10) | 8.481(3) | 11.431(2) | 16.6363(9) | 13.1554(9) |
| *b* (Å) | 14.2049(3) | 15.592(5) | 13.249(3) | 15.3576(8) | 12.6872(9) |
| *c* (Å) | 20.6930(4) | 17.342(6) | 14.957 (3) | 18.9404(10) | 13.2244(9) |
| $\beta$ (deg) | 104.7760(10) | 97.870(7) | 90.000(4) | | 103.915(2) |
| $V$ (Å$^3$) | 3208.52(10) | 2271.8(14) | 2265.3(8) | 4839.2(4) | 2142.4(3) |
| *Z* value | 4 | 4 | 4 | 8 | 4 |
| $D$(calcd) (g cm$^{-3}$) | 1.328 | 1.356 | 1.336 | 1.322 | 1.332 |
| $F$(000) | 1324 | 936 | 928 | 1952 | 872 |
| abs coeff (mm$^{-1}$) | 2.550 | 2.644 | 2.650 | 2.488 | 2.798 |
| cryst size (mm$^3$) | 0.30 × 0.30 × 0.30 | 0.25 × 0.35 × 0.40 | 0.10 × 0.10 × 0.20 | 0.20 × 0.30 × 0.40 | 0.20 × 0.35 × 0.40 |
| scan type | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ | $\omega-2\theta$ |
| 2 $\theta$ range, deg | 1.88−24.10 | 1.76−28.33 | 2.05−28.34 | 2.10−28.30 | 1.59−28.33 |
| no. of reflns | 5038 | 14270 | 14258 | 30403 | 13641 |
| no. of obsd reflns ($I > 3.00\sigma(I)$) | 338 | 5521 | 5433 | 5992 | 5140 |
| $R$ | 0.0339 | 0.0300 | 0.0826 | 0.0378 | 0.0396 |
| $R_w$ | 0.0809 | 0.0796 | 0.2289 | 0.0781 | 0.1071 |
| goodness of fit | 1.059 | 1.002 | 1.111 | 0.951 | 1.021 |

to the vinyl proton. The characteristic high-field $^{13}C$ NMR signal at 142.8 ppm provided evidence for the tethered carbon atom of the two germanium moieties. The formation of the digerma ring compound can be related to the nickel-catalyzed double silylation. The isolation of **11** is interesting because a 1,2-hydrogen shift must be involved in its formation. A similar 1,2-shift in the alkynes has been observed in the stoichiometric reaction of $Me_2Si(o\text{-}C_2B_{10}H_{10})SiMe_2Pt(PPh_3)_2$ with 1-hexyne[11] and the reaction of chloro(triisopropylphosphine)rhodium(I) with trimethylsilyl-substituted alkynes.[14]

When cyclooctyne was employed as an angle-strained cycloalkyne in the nickel-catalyzed reaction of **1** at 80 °C, the six-membered-ring compound **12** was isolated as colorless crystals in 82% yield (eq 4). The structure of **12** is fully consistent with its $^1H$ and $^{13}C$ NMR spectra together with the mass spectrometric analysis. In the olefinic region of the $^{13}C$ NMR spectrum of **12**, one resonance at 140.6 ppm was present. In addition, three peaks were observed at 30.7, 29.2, and 26.2 ppm due to the symmetrically substituted methylene carbons. The $^1H$ NMR data for **12** conform to the structure determined by the X-ray structural study. The structure of **12** is closely related to the double silylating adducts of the 1,2-bis(dimethylsilyl)carborane.[6b] The ORTEP diagram in Figure 3 shows the molecular structure of **12** and confirms the six-membered-ring geometry containing the two germanium atoms. The C=C bond length of C(7)−C(8) is 1.331(12) Å, which is in good agreement with the existing values in the literature for a wide variety of C=C bonds. An interesting structural feature of **12** is that the two planes consisting of Ge1, C1, C2, Ge2 and Ge2, C7, C8, Ge1 are slightly bent (168.4°).

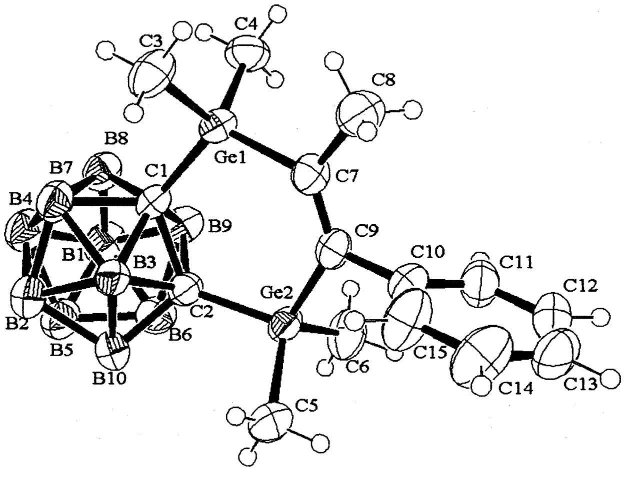
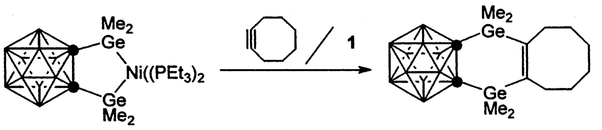
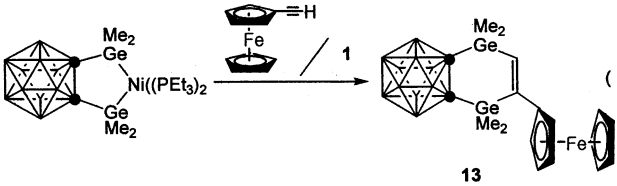


**Figure 2.** X-ray crystal structure of **6** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ge(1)−C(1) 1.986(2), Ge(2)−C(2) 1.989(2), C(1)−C(2) 1.671(3), Ge(1)−C(7) 1.950(2), Ge(2)−C(9) 1.947(2), C(7)−C(9) 1.332(3), C(9)−C(10) 1.501(3), C(1)−Ge(1)−C(7) 111.61(10), Ge(1)−C(7)−C(9) 126.86(18), C(7)−C(9)−Ge(2) 127.61(18), C(1)−C(2)−Ge(2) 120.43(14).



**12** (4)

The treatment of **1** with ferrocenylacetylene in the presence of a catalytic amount of **2** resulted in the formation of the six-membered-ring compound containing a ferrocenyl unit **13** (eq 5). The structure of **13** was determined on the basis of its spectral data as well as elemental analysis. The $^1H$ NMR spectrum of **13** exhibited a single and broad proton signal assignable to a coordinated cyclopentadienyl ligand. In addition, a characteristic feature in the $^1H$ NMR spectrum includes a singlet at 6.70 ppm assigned to the olefinic proton.



**13** (5)

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[14] (a) Schneider, D.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, 700. (b) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089.

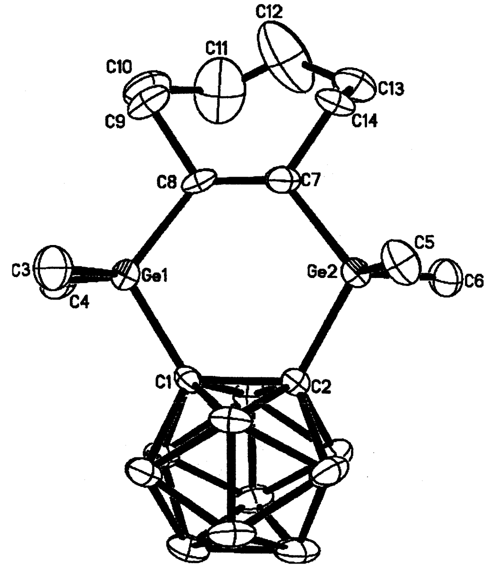
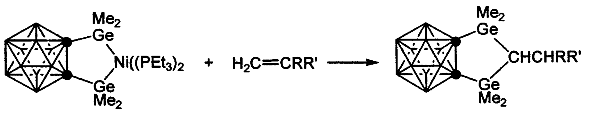


**Figure 3.** X-ray crystal structure of **12** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ge(1)−C(1) 1.974(8), Ge(1)−C(8) 1.940(9), C(7)−C(8) 1.331(12), Ge(2)−C(7) 1.933(9), Ge(2)−C(2) 2.013(8), C(1)−C(2) 1.692(11), C(1)−Ge(1)−C(8) 111.6(3), Ge(1)−C(8)−C(7) 127.4(6), C(8)−C(7)−Ge(2) 126.4(7), C(7)−Ge(2)−C(2) 112.6(4), Ge(2)−C(2)−C(1) 117.9(5).

**Stoichiometric Reaction of 2 with Alkenes.** The digermanickela compound **2** is not effective in the nickel-catalyzed double germylation reaction with alkenes. However, the stoichiometric reaction of **2** with some alkenes and dienes afforded five-membered digerma ring compounds. Thus, the stoichiometric reaction of **2** with 4-vinylanisole afforded 4,5-carboranyl-1,1,3,3-tetramethyl-2-(4-methoxymethyl)-1,3-digermacyclopentane (**14**), which contained a saturated side chain in 55% yield (eq 6). A similar reaction of **2** with 1,1-diphenylethylene also gave a five-membered digermylene compound **15**. The formulation of **14** and **15** was confirmed by spectroscopic analysis. The two characteristic doublets at 4.07 and 1.68 ppm in the $^1$H NMR spectrum of **15** are assigned to the two methine protons. A large coupling contant ($J_{HH}$ = 13.50 Hz) indicates that the two methine protons are in a trans configuration due to the steric hindrance of the phenyl groups. A low-frequency $^{13}$C NMR resonance at 23.1 ppm provided evidence for the tethered carbon atom of the germanium moieties. These values are comparable to those observed for 4,5-carboranylene-1,1,3,3-tetramethyl-2-diphenylmethylene-1,3-disilacyclopentane[6b] and *cis*-4,5-benzo-1,1,3-triethyl-2-methyl-1,3-disilacyclopent-4-ene.[15] The structure of **14** has been determined by X-ray crystallography. The molecular structure of **14** is shown in Figure 4. The molecule contains one $C_2Ge_2C$ five-membered ring comprised of a carboranylene, two germanium atoms, and a saturated carbon atom. The formation of **14** and **15** may involve the initial oxidative addition reaction of an olefinic C−H bond to the nickel center, followed by the shift of a phenyl group from the nickel atom to one of the two germanium atoms. Such a C−H activation has been observed in the Ni-catalyzed double silylation.[16]



**14** R = H, R' = 4-$C_6H_4OMe$
**15** R = R' = Ph

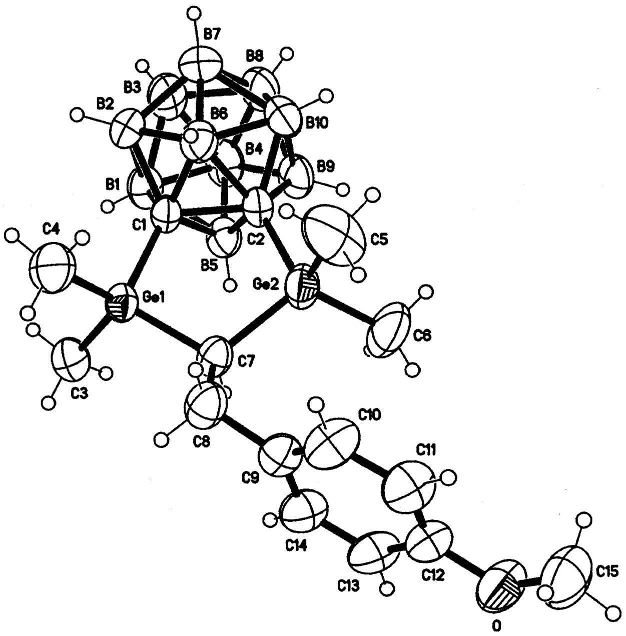
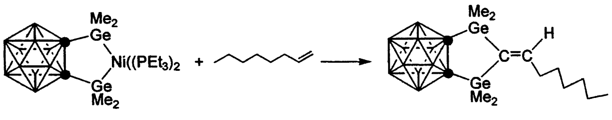


**Figure 4.** X-ray crystal structure of **14** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ge(1)−C(7) 1.967(3), Ge(2)−C(7) 1.954(3), Ge(2)−C(2) 1.997(3), C(1)−C(2) 1.679(3), C(1)−Ge(1) 1.990(3), C(7)−C(8) 1.539(4), Ge(1)−C(7)−Ge(2) 110.04(14), C(7)−Ge(2)−C(2) 100.39(10), Ge(2)−C(2)−C(1) 112.92(16), C(2)−C(1)−Ge(1) 112.30(16).

In contrast to the double germylation reaction of **2** with the above alkenes, when 1-octene was employed in the reaction of **2** under the same reaction conditions, the five-membered digerma compound **16** was isolated in 45% yield (eq 7). A key feature in the $^1$H NMR spectrum of **16** includes a singlet at 6.72 ppm assigned to the vinyl proton. A characteristic high-frequency $^{13}$C NMR resonance at 135.4 ppm provided evidence for a tethered sp$^2$ carbon atom between the two germanium atoms, in addition to a low-frequency resonance at 152.5 ppm assigned to the terminal olefinic carbon. These values are close to those of 4,5-carboranylene-1,1,3,3-tetramethyl-2-(*n*-butylmethylene)-1,3-disilacyclopentane.[6b] The formation of **16** is of interest because two olefinic C−H bond activations must have occurred during the course of the reaction. Such C−H activations have been observed in the nickel-catalyzed double silylation reaction with alkenes.[17]



**16**

(7)

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(15) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987.

(16) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114.

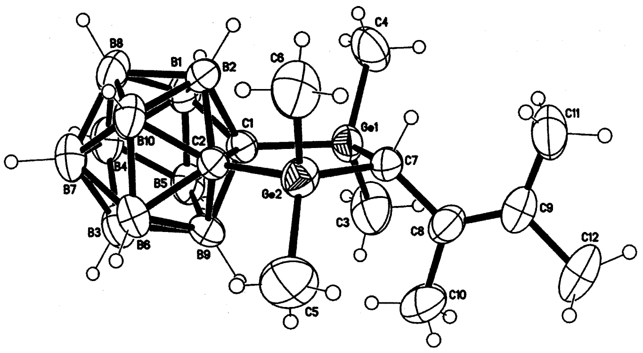
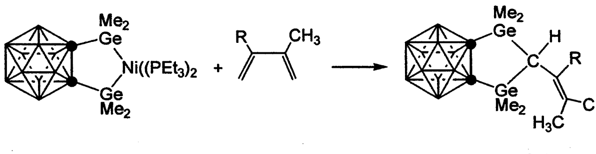


**Figure 5.** X-ray crystal structure of **17** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Ge(1)−C(7) 1.976(3), Ge(1)−C(1) 1.983(2), Ge(2)−C(7) 1.971(3), Ge(2)−C(2) 1.979(2), C(1)−C(2) 1.669(4), C(8)−C(9) 1.330(4), Ge(1)−C(7)−Ge(2) 109.21(13), C(7)−Ge(1)−C(1) 102.34(11), Ge(1)−C(1)−C(2) 112.88(14), C(1)−C(2)−Ge(2) 113.11(14), C(2)−Ge(2)−C(7) 102.44(11), C(7)−C(8)−9(2) 122.9(3).

The stoichiometric reaction of **2** with 2,3-dimethylbutadiene afforded the five-membered digerma compound. A similar reaction of **2** and isoprene also gave a five-membered digerma compound **18** (eq 8).



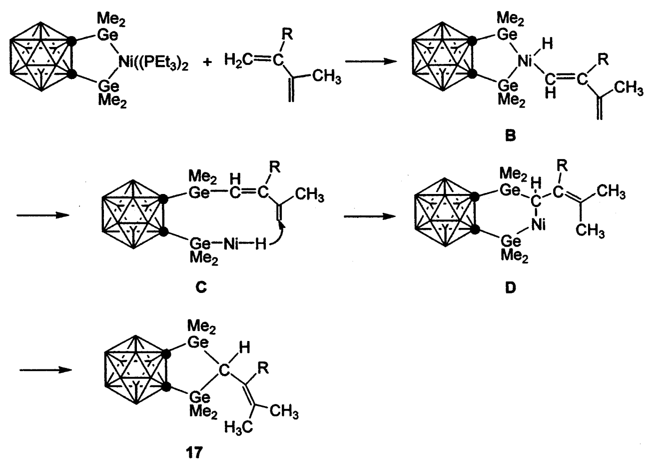
(8)

**17** R = CH$_3$
**18** R = H

Compounds **17** and **18** were characterized by $^1$H and $^{13}$C NMR and elemental analyses. Three singlets ($\delta$ 1.63, 1.56, 1.48) in the $^1$H NMR spectrum and three singlets ($\delta$ 21.5, 21.3, 20.9) in the $^{13}$C NMR spectrum of **17** could be assigned to the methyl groups on the diene, which indicated that the three methyl groups are not equivalent. The $^1$H NMR spectrum of **17** shows a single resonance at $\delta$ 2.46 assigned to the methine proton, as well as two resonances due to the methyl protons on germanium which show the presence of two nonequivalent methyl protons. The $^{13}$C NMR spectrum of compound **17** exhibits resonances for the olefinic carbons at $\delta$ 124.1 and 122.3, a methine carbon at $\delta$ 30.1, and the methyl carbons of germanium at $\delta$ 0.6 and −0.4. These spectral features are wholly consistent with the proposed structure of **17**. Structural confirmation was provided by an X-ray crystallographic analysis of **17**. The molecular structure of **17** is shown in Figure 5. The X-ray crystal structure of **17** confirmed the presence of a five-membered ring comprised of an *o*-carboranylene, two germaniums, and a saturated hydrocarbon fragment.

A reasonable mechanism for the formation of **17** and **18** (Scheme 1) involves the initial oxidative addition reaction of an olefinic C−H bond to the nickel center **B**, followed by the shift of a diene group from the nickel atom to one of the two germanium atoms **C**. The 1,4-migration of hydride **D** and reductive elimination of the nickel fragment lead to compound **17**. Such a 1,4-migration has been observed in the thermal reaction of *o*-bis(dimethylsilyl)benzene and isoprene.[18] It is interesting to note that the Ni-, Pd-, and Pt-mediated cycloaddition reactions of disilabutenes to conjugated dienes proceed via a 1,4-addition reaction.[19]

**Scheme 1**



In summary, we have prepared a cyclic bis(germyl)-nickel complex **2**. The complex **2** was found to be a good catalyst for the double germylation reaction of a variety of alkynes. Thus, the nickel-catalyzed reactions of 1,2-bis(dimethylgermyl)carborane with alkynes such as diphenylacetylene, phenylacetylene, 3-hexyne, 1-phenyl-1-propyne, 2-butyne, 1-phenyl-2-(trimethylsilyl)acetylene, bis(trimethylsilyl)acetylene, dimethyl acetylenedicarboxylate, 1-hexyne, and cyclooctyne afforded six-membered-ring compounds. The complex **2** is not effective in the nickel-catalyzed double germylation reaction with alkenes. However, the stoichiometric reaction of **2** with some alkenes and dienes afforded five-membered-ring compounds. Thus, the cyclic bis(germyl)nickel complex as a catalyst or reactant has been further exploited in a series of novel chemical transformations.

## Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene, THF, and benzene were distilled from sodium benzophenone. *n*-Hexane and pentane were dried and distilled from CaH$_2$. The $^1$H and $^{13}$C, $^{31}$P NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. Chemical shifts were referenced relative to TMS. The IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a Shimadzu Model QP-1000 spectrophotometer and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

*o*-Carborane was purchased from Callery Chemical Co. and used without purification. The starting materials Ni(COD)$_2$, PEt$_3$, and GeMe$_2$Cl$_2$ were purchased from Strem Chemicals. The alkynes were purchased from Aldrich. 1,2-Bis(chlorodimethylgermyl)carborane,[7] Ni(PEt$_3$)$_4$,[20] cyclooctyne,[21]

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and ferrocenylacetylene[22] were prepared according to the known procedures.

**Synthesis of *o*-Bis(dimethylgermyl)carborane (1).** To a stirred THF solution (15 mL) of the 1,2-bis(chlorodimethylgermyl)carborane (0.10 g, 0.24 mmol) was added a solution of sodium cyanoborohydride (0.15 g, 2.4 mmol) in THF (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was evaporated and the residue was extracted with *n*-hexane (20 mL). The extracts were concentrated to 3 mL and cooled to −20 °C to give 0.076 g (92%) of a white crystalline solid. Mp: 185−188 °C. $^1$H NMR ($C_6D_6$): $\delta$ 4.23 (sept, 2H, $^3J_{HH} = 3.04$ Hz, Ge−*H*), 0.13 (d, 12H, $^3J_{HH} = 3.04$ Hz, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ −1.5. MS: *m/z* 349 [M$^+$]. Anal. Calcd for $C_6H_{24}B_{10}Ge_2$: C, 20.61; H, 6.91. Found: C, 20.24; H, 6.68.

**Synthesis of [*o*-(GeMe$_2$)$_2$C$_2$B$_{10}$H$_{10}$]Ni(PEt$_3$)$_2$ (2).** Compound **1** (0.14 g, 0.38 mmol) in 5 mL of pentane was added to a stirred solution of Ni(PEt$_3$)$_4$ (0.19 g, 0.37 mmol) in 10 mL of pentane at −15 °C. The solution was warmed to room temperature and stirred for 2 h. The solution was then evaporated in vacuo and the residue was extracted with toluene (8 mL). The solution was then covered with a layer of pentane (10 mL) at −5 °C. Red crystals of **2** were formed over a period of several days in 60% yield (0.14 g). $^1$H NMR ($C_6D_6$): $\delta$ 1.14 (dq, 12H, $J_{HP} = 7.42$ Hz, $J_{HH} = 5.48$ Hz, PC*H*$_2$), 0.86 (dt, 18H, $J_{HP} = 7.04$ Hz, $J_{HH} = 5.48$ Hz, C*H*$_3$), 0.21 (s, 12H, GeC*H*$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 6.18. MS (EI): *m/z* 642 [M$^+$]. Anal. Calcd for $C_{18}H_{52}B_{10}NiP_2Ge_2$: C, 33.66; H, 8.16. Found: C, 33.28; H, 7.92.

**Nickel Complex-Catalyzed Reaction of 1 with Various Alkynes. General Procedure.** Compound **3**−**15** were prepared by the reaction of **1** with the corresponding alkynes in the presence of a catalytic amount of **2**. In a typical preparation, a mixture of diphenylacetylene (0.06 g, 0.35 mmol), **1** (0.1 g, 0.29 mmol), and **2** (0.01 g, 0.016 mmol) in toluene (20 mL) was stirred at room temperature for 1 h and then warmed to 80 °C for 8 h. The mixture was filtered through a short silica gel column to remove the nickel species. The solvent was removed in vacuo, and the residue was chromatographed with benzene/hexane (1:4) as the eluent ($R_f = 0.6$). Recrystallization from hexane at −20 °C afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-digermacyclo-hex-2-ene (0. 11 g, 75%).

**(i) 3 from the Reaction with Diphenylacetylene.** Mp: 115−117 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.09−6.72 (m, 10H, *Ph*), 0.42 (s, 12H, GeC*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 154.0 (Ge*C*=), 142.0, 128.0, 127.6, 126.2 (*Ph*), −1.0 (Ge−CH$_3$). MS: *m/z* 526 [M$^+$]. Anal. Calcd for $C_{20}H_{32}B_{10}Ge_2$: C, 45.69; H, 6.13. Found: C, 45.26; H, 6.02.

**(ii) 4 from the Reaction with Phenylacetylene.** Yield: 65%. Mp: 133−135 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.32−7.04 (m, 5H, *Ph*), 6.49 (s, 1H, =C*H*), 0.54 (s, 6H, GeC*H*$_3$), 0.50 (s, 6H, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 159.3 (=*C*Ph), 145.0 (=*C*H), 130.3, 128.7, 127.6, 126.2 (*Ph*), 68.9, 67.0 (*carborane carbons*), −0.1 (Ge−*C*H$_3$), −0.6 (Ge-*C*H$_3$). MS: *m/z* 450 [M$^+$]. Anal. Calcd for $C_{14}H_{28}B_{10}Ge_2$: C, 37.39; H, 6.27. Found: C, 37.02; H, 6.12.

**(iii) 5 from the Reaction with 3-Hexyne.** Yield: 87%. Mp: 120−124 °C. $^1$H NMR (CDCl$_3$): $\delta$ 2.28 (q, 4H, $J_{HH} = 7.50$ Hz, C*H*$_2$), 0.95 (t, 6H, $J_{HH} = 7.50$ Hz, C*H*$_3$), 0.47 (s, 12H, GeC*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 150.9 (*C*=*C*), 67.6 (*carborane carbons*), 25.3 (*C*H$_2$), 14.8 (*C*H$_3$), −0.2 (Ge−*C*H$_3$). MS: *m/z* 430 [M$^+$]. Anal. Calcd for $C_{12}H_{32}B_{10}Ge_2$: C, 33.54; H, 7.49. Found: C, 33.86; H, 7.58.

**(iv) 6 from the Reaction with 1-Phenyl-1-propyne.** Yield: 85%. Mp: 142−144 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.35−6.90 (m, 5H, *Ph*), 1.65 (s, 3H, C−C*H*$_3$), 0.53 (s, 6H, Ge−C*H*$_3$), 0.29 (s, 6H, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 158.3 (=*C*Ph), 156.7 (=*C*Me), 128.7, 127.2, 126.6 (*Ph*), 20.3 (*C*H$_3$), −1.3 (Ge−*C*H$_3$), −1.6 (Ge−*C*H$_3$). MS: *m/z* 464 [M$^+$]. Anal. Calcd for $C_{15}H_{30}B_{10}Ge_2$: C, 38.85; H, 6.51. Found: C, 38.46; H, 6.36.

**(v) 7 from the Reaction with 2-Butyne.** Yield: 72%. Mp: 114−118 °C. $^1$H NMR (CDCl$_3$): $\delta$ 1.18 (s, 3H, =C−C*H*$_3$), 1.16 (s, 3H, C−C*H*$_3$), 0.51 (s, 3H, Ge−C*H*$_3$), 0.49 (s, 3H, Ge−C*H*$_3$), 0.46 (s, 3H, Ge−C*H*$_3$), 0.26 (s, 3H, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 148.4 (*C*=C), 29.5 (CH$_3$), 12.6 (CH$_3$), −2.1 (Ge−*C*H$_3$), −2.4 (Ge−H$_3$), −3.4 (Ge−*C*H$_3$), −6.8 (Ge−*C*H$_3$). MS: *m/z* 402 [M$^+$]. Anal. Calcd for $C_{10}H_{28}B_{10}Ge_2$: C, 29.91; H, 7.03. Found: C, 29.58; H, 6.91.

**(vi) 8 from the Reaction with 1-Phenyl-2-(trimethylsilyl)acetylene.** Yield: 72%. Mp: 138−139 °C. $^1$H NMR (CDCl$_3$): $\delta$ 7.29−6.83 (m, 5H, *Ph*), 0.63 (s, 6H, Ge−C*H*$_3$), 0.26 (s, 6H, Ge−C*H*$_3$), −0.21 (s, 9H, Si−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 152.6 (=*C*Ph), 146.0 (=*C*SiMe$_3$), 129.8, 128.6, 127.0, 126.3 (*Ph*), 2.2 (Ge−*C*H$_3$), 1.9 (Ge−*C*H$_3$), −0.9 (Si−*C*H$_3$). MS: *m/z* 522 [M$^+$]. Anal. Calcd for $C_{17}H_{36}B_{10}Ge_2Si$: C, 39.13; H, 6.95. Found: C, 39.46; H, 7.04.

**(vii) 9 from the Reaction with Bis(trimethylsilyl)acetylene.** A mixture of bis(trimethylsilyl)acetylene (0.12 mL, 0.50 mmol), **1** (0.10 g, 0.29 mmol), and **2** (0.01 g, 0.015 mmol) in toluene (20 mL) was refluxed overnight. The solvent was removed in vacuo, and the residue was chromatographed with hexane as eluent ($R_f = 0.5$). Recrystallization from hexane at −10 °C afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-di(trimethylsilyl)-1,3-digermacyclohex-2-ene (**9**) in 62% yield. Mp: 106−108 °C. $^1$H NMR (CDCl$_3$): $\delta$ 0.58 (s, 6H, Ge−C*H*$_3$), 0.45 (s, 6H, Ge−C*H*$_3$), 0.13 (s, 18H, Si−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 144.3 (=CSiMe$_3$), 1.1 (Ge−*C*H$_3$), −0.2 (Ge−*C*H$_3$), −1.0 (Si−*C*H$_3$). MS: *m/z* 518 [M$^+$]. Anal. Calcd for $C_{14}H_{40}B_{10}Ge_2Si_2$: C, 32.46; H, 7.77. Found: C, 32.38; H, 7.58.

**(viii) 10 from the Reaction with Dimethyl Acetylenedicarboxylate.** A mixture of dimethyl acetylenedicarboxylate (0.04 mL, 0.30 mmol) and **2** (0.10 g, 0.20 mmol) in toluene (15 mL) was stirred at room temperature for 6 h. The solvent was removed in vacuo, and the residue was chromatographed with ethyl acetate/hexane (1:10) as eluent ($R_f = 0.62$). Recrystallization from hexane at −20 °C afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-dicarbomethoxy-1,4-digermacyclohex-2-ene (**10**) in 58% yield. Mp: 126−128 °C.$^1$H NMR (CDCl$_3$): $\delta$ 3.77 (s, 6H, CO$_2$C*H*$_3$), 0.62 (s, 12H, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 168.0 (*C*O$_2$CH$_3$), 151.0 (*C*=*C*), 52.6 (O*C*H$_3$), −0.5 (Ge−*C*H$_3$). MS: *m/z* 490 [M$^+$]. Anal. Calcd for $C_{12}H_{28}B_{10}O_4Ge_2$: C, 29.43; H, 5.76. Found: C, 29.08; H, 5.58.

**(ix) 11 from the Reaction with 1-Hexyne.** A mixture of 1-hexyne (0.04 mL, 0.30 mmol), **1** (0.08 g, 0.22 mmol), and **2** (0.01 g, 0.016 mmol) in toluene (20 mL) was stirred at room temperature for 14 h. The solvent was removed in vacuo. Pure **11** was isolated by chromatographic workup (eluent = hexane, $R_f = 0.6$, 62% yield). $^1$H NMR (CDCl$_3$): $\delta$ 6.28 (s, 1H, =C*H*), 2.16 (t, 2H, $J_{HH} = 8.8$ Hz, =CC*H*$_2$), 1.59−1.27 (m, 4H, −C*H*$_2$−), 0.90 (t, 3H, $J_{HH} = 5.2$ Hz, C*H*$_3$), 0.48 (s, 6H, Ge−C*H*$_3$), 0.43 (s, 6H, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 159.2 (=*C*H), 142.8 (Ge*C*=), 41.0, 31.4, 22.6, 14.2 (*Bu*), −0.6 (Ge*C*H$_3$), −0.8 (Ge*C*H$_3$). MS: *m/z* 415 [M$^+$ − CH$_3$]. Anal. Calcd for $C_{12}H_{32}B_{10}Ge_2$: C, 33.54; H, 7.50. Found: C, 33.22; H, 7.38.

**(x) 12 from the Reaction with Cyclooctyne.** To a stirred solution of **2** (0.20 g, 0.30 mmol) in toluene (15 mL) was added cyclooctyne (0.07 g, 0.6 mmol) at room temperature. The solution was heated to 80 °C for 14 h and then evaporated in vacuo, and the residue was chromatographed with benzene/hexane (1:4) as eluent ($R_f = 0.8$). Recrystallization from hexane at −10 °C afforded **12** as colorless crystals in 82% yield. Mp: 168−169 °C.$^1$H NMR (CDCl$_3$): $\delta$ 2.38 (br, 4H, =C*H*$_2$), 1.45 (br, 8H, −C*H*$_2$), 0.45 (s, 12H, Ge−C*H*$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 140.6 (=*C*CH$_2$), 30.7, 29.2, 26.2 (*C*H$_2$), −1.6 (Ge−*C*H$_3$). MS: *m/z* 456 [M$^+$]. Anal. Calcd for $C_{14}H_{34}B_{10}Ge_2$: C, 36.89; H, 7.51. Found: C, 36.66; H, 7.38.

**(xi) 13 from the Reaction with Ferrocenylacetylene.** Yield: 78%. Mp: 135−137 °C. $^1$H NMR (CDCl$_3$): $\delta$ 6.70 (s,

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1H, =C*H*), 4.28 (br, 4H, $C_5H_4$), 4.07 (s, 5H, $C_5H_5$), 0.65 (s, 6H, Ge−C*H*$_3$), 0.51 (s, 6H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 142.4 (=*C*H), 134.4 (=*C*C), 69.8, 69.1, 67.0 (*Cp*), 1.2 (Ge−*C*H$_3$), −0.5 (Ge−*C*H$_3$). MS: *m*/*z* 558 [M$^+$]. Anal. Calcd for $C_{18}H_{32}B_{10}Ge_2Fe$: C, 38.77; H, 5.78. Found: C, 38.46; H, 5.62.

**Reaction of Nickel Intermediate 2 with Various Alkenes. General Procedure.** Compounds **14**−**18** were prepared by the reaction of **2** with the corresponding alkenes. In a typical preparation, a mixture of **2** (0.1 g, 0.15 mmol) and 4-vinylanisole (0.02 mL, 0.16 mmol) in toluene (15 mL) was heated to 80 °C and stirred for 14 h. The solvent was removed in vacuo, and the residue was chromatographed with benzene/hexane (1:4) as eluent. Recrystallization from hexane at −10 °C afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-(4-methoxymethyl)-1,3-digermacyclopenane, **14**, in 55% yield. Mp: 138−141 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.05 (d, 2H, $J_{HH}$ = 8.96 Hz, *Ph*), 6.83 (d, 2H, $J_{HH}$ = 8.96 Hz, *Ph*), 3.79 (s, 3H, OC*H*$_3$), 2.80 (d, 2H, $J_{HH}$ = 8.74 Hz, C*H*$_2$), 1.34 (t, 1H, $J_{HH}$ = 8.74 Hz, C*H*), 0.38 (s, 6H, Ge−C*H*$_3$), 0.33 (s, 6H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 139.2, 134.1, 128.9, 114.1, 55.4 (O*C*H$_3$), 31.5 (*C*H$_2$), 21.29 (*C*H), −0.3 (Ge−*C*H$_3$), −3.2 (Ge-*C*H$_3$). MS: *m*/*z* 482 [M$^+$]. Anal. Calcd for $C_{15}H_{32}B_{10}Ge_2O$: C, 37.40; H, 6.68. Found: C, 37.08; H, 6.52.

**(xii) 15 from the Reaction with 1,1-Diphenylethylene.** Yield: 48%. Mp: 176−179 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 7.35−7.18 (m, 10H, *Ph*), 4.07 (d, 1H, $J_{HH}$ = 13.50 Hz, C*H*Ph$_2$), 1.68 (d, 1H, $J_{HH}$ = 13.50 Hz, C*H*Ge$_2$), 0.26 (s, 6H, Ge−C*H*$_3$), −0.05 (s, 6H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 145.5, 129.1, 127.9, 127.7, 50.3 (*C*HPh$_2$), 23.1 (*C*HGe$_2$), −0.1 (Ge−*C*H$_3$), −2.7 (Ge−*C*H$_3$). MS: *m*/*z* 528 [M$^+$]. Anal. Calcd for $C_{20}H_{34}B_{10}Ge_2$: C, 45.51; H, 6.49. Found: C, 45.22; H, 6.32.

**(xiii) 16 from the Reaction with 1-Octene.** A mixture of **2** (0.10 g, 0.15 mmol) and 1-octene (0.05 mL, 0.32 mmol) in toluene (15 mL) was refluxed for 14 h. The solvent was removed in vacuo, and the residue was chromatographed with benzene/hexane (1:4) to give **16** as a colorless oil in 45% yield. $^1H$ NMR ($CDCl_3$): $\delta$ 6.72 (t, 1H, $J_{HH}$ = 13.86 Hz, =C*H*), 2.17 (dt, 2H, $J_{HH}$ = 13.86 Hz, $J_{HH}$ = 5.02 Hz, C*H*$_2$), 1.48−1.27 (m, 8H, C*H*$_2$), 0.88 (t, 3H, $J_{HH}$ = 4.62 Hz, C*H*$_3$), 0.37 (s, 6H, Ge−C*H*$_3$), 0.28 (s, 6H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 152.5, 135.4, 36.9, 30.1, 27.4, 27.2, 20.9, 12.5, −2.7 (Ge*C*H$_3$), −2.9 (Ge*C*H$_3$). MS: *m*/*z* 458 [M$^+$]. Anal. Calcd for $C_{14}H_{36}B_{10}Ge_2$: C, 36.74; H, 7.92. Found: C, 36.46; H, 7.72.

**(xiv) 17 from the Reaction with 2,3-Dimethyl-1,3-butadiene.** Yield: 62%. Mp: 161−163 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 2.46 (s, 1H, C*H*), 1.63 (s, 3H, =C*H*$_3$), 1.56 (s, 3H, CC*H*$_3$), 1.48 (s, 3H, CC*H*$_3$), 0.50 (s, 6H, Ge−C*H*$_3$), 0.47 (s, 6H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 124.1 (*C*=C), 122.3 (C=*C*), 30.1 (*C*H), 21.5, 21.3, 20.9 (C−*C*H$_3$), 0.6, −0.4 (Ge*C*H$_3$). MS: *m*/*z* 430 [M$^+$]. Anal. Calcd for $C_{12}H_{32}B_{10}Ge_2$: C, 33.58; H, 7.50. Found: C, 33.26; H, 7.34.

**(xv) 18 from the Reaction with Isoprene.** Yield: 48%. Mp: 146−149 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 4.95 (d, 1H, $J_{HH}$ = 11.72 Hz, =C*H*), 1.97 (d, 1H, $J_{HH}$ = 11.72 Hz, C*H*), 1.69 (s, 3H, C−C*H*$_3$), 1.54 (s, 3H, C−C*H*$_3$), 0.48 (s, 6H, Ge−C*H*$_3$), 0.41 (s, 6H, Ge−C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 130.6, 119.0 (*C*=C), 26.3 (*C*H), 21.6 (*C*H$_3$), 0.6 (Ge*C*H$_3$), −1.1 (Ge*C*H$_3$). MS: *m*/*z* 416 [M$^+$]. Anal. Calcd for $C_{11}H_{30}B_{10}Ge_2$: C, 31.82; H, 7.28. Found: C, 31.54; H, 7.14.

**X-ray Crystallography.** Details of the crystal data and a summary of the intensity data collection parameters for **2**, **6**, **12**, **14**, and **17** are given in Table 1. A reddish-orange crystal of **2** with the dimensions of 0.30 × 0.30 × 0.30 mm$^3$ was selected for structural analysis. The intensity data for **2** were collected with a Siemens SMART ccd area detector mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). The sample was first cooled to 130 K. The intensities were measured as a series of $\phi$ oscillation frames each of 0.4° for 30 s/frame. A colorless crystal of **6** with the dimensions of 0.25 × 0.35 × 0.40 mm$^3$ was mounted on the tip of a glass fiber. The cell parameters were obtained by least-squares refinement from 25 reflections in the range $1.76° < 2\theta < 28.33°$ measured with graphite-monochromated Mo Kα radiation on a Simens P4 diffractometer. The X-ray intensity data were collected by the $\omega-2\theta$ scan method for ranges $-11 < h < 10$, $-20 < k < 19$, and $-11 < l < 23$. The cell parameters of **12** were obtained by least-squares refinement in the range $1.76° < 2\theta < 28.33°$ on a Simens P4 diffractometer. The X-ray intensity data were collected by the $\omega-2\theta$ scan method for the ranges $-14 < h < 14$, $-17 < k < 11$, and $-13 < l < 19$. The structures were solved by direct methods and refined by the full-matrix least-squares method on $F^2$. The hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined by using anisotropic displacement parameters.

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**Supporting Information Available:** Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **2**, **6**, **12**, **14**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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