Ni-Catalyzed Double Gemylation of Alkynes and Alkenes

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The reaction of 1,2-bis(dimethylgermyl)carborane with Ni(PEt₃)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 $RC \equiv CR'$ 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 germylation² 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(PPh₃)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-

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(chlorogermyl)platinum has been structurally characterized by Tanaka and co-workers.⁵

Recently, we⁶ reported a variety of silvlation 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



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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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-(GeMe₂)₂C₂B₁₀H₁₀]Ni(PEt₃)₂ Complex 2. The synthesis of 1,2-bis(dimethylgermyl)carborane (1) was prepared by the salt elimination reaction of 1,2-Li₂C₂B₁₀H₁₀ and 2 equiv of Me₂GeCl₂, followed by reduction with a mild reducing agent, NaB(CN)H₃.⁷ 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(PEt₃)₄. The addition of 1.1 equiv of o-bis(dimethylgermyl)carborane to Ni(PEt₃)₄ in pentane gave a red solution. Standard workup and crystallization from toluenepentane 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(PPh₃)GeCl₃.⁹ The Ni–P bond distance [2.2188(10) Å] is comparable to those observed in other phosphine nickel compounds.¹⁰ The

¹H and ³¹P NMR spectra and mass spectrum were consistent with the structure determined by X-ray crystallography. In particular, the ³¹P NMR signal was shifted from -2.2 ppm in Ni(PEt₃)₃ to 6.18 ppm. The mass spectrum of **2** showed a molecular ion at m/z 642.

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(PEt₃)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

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 ¹H and ¹³C NMR spectra, mass spectra, and elemental analyses. The ¹H NMR spectrum of **6** showed the phenyl and methyl resonances in the expected 5:3:6:6 ratio. In the ¹³C 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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entry	Reactant	conditions	Product (yield, %)
1	PhC≕CPh	80 °C (8 h)	Ge Ph Ge Ph Ge Ph Me ₂
			3 (75 %) Mea
2	PhC≡CH	80 °C (8 h)	Ge H Me ₂ 4 (65 %)
3	EtC≕CEt	80 °C (8 h)	Me ₂ Ge Et Ge Et Me ₂ 5 (87 %)
4	PhC≡CMe	80 °C (8 h)	Me ₂ Ge Ph Ge Me Me ₂ 6 (85 %)
5	MeC≕CMe	80 °C (8 h)	Me ₂ Ge Me Ge Me Me ₂ 7 (72 %)
6	PhC≡CSiMe ₃	80 °C (8 h)	Me ₂ Ge SiMe ₃ Me ₂ 8 (72 %)
7	Me₃SiC≡CSiMe₃	110 °C (12 h)	Me ₂ Ge_SiMe ₃ Ge_SiMe ₃ Me ₂ 9 (72 %)
8	MeO₂CC≡CCO₂Me	rt (6 h)	Me ₂ Ge CO ₂ Me Ge CO ₂ Me Me ₂ 10 (58 %)

Table 1.	Nickel-Catal	yzed Reactions	of Alkynes	with 1,2-Bis(dimethylg	germyl)carborane

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

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	v			
2	6	12	14	17
$C_{18}H_{52}B_{10}P_2Ge_2Ni$	$C_{15}H_{30}B_{10}Ge_2$	$C_{14}H_{34}B_{10}Ge_2$	$C_{15}H_{32}B_{10}Ge_2O$	$C_{12}H_{32}B_{10}Ge_2$
641.52	463.67	455.69	481.69	429.66
monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
P2(1)/n	P2(1)/c	P2(1)/n	Pbca	P2(1)/c
11.2880(10)	8.481(3)	11.431(2)	16.6363(9)	13.1554(9)
14.2049(3)	15.592(5)	13.249(3)	15.3576(8)	12.6872(9)
20.6930(4)	17.342(6)	14.957 (3)	18.9404(10)	13.2244(9)
104.7760(10)	97.870(7)	90.000(4)		103.915(2)
3208.52(10)	2271.8(14)	2265.3(8)	4839.2(4)	2142.4(3)
4	4	4	8	4
1.328	1.356	1.336	1.322	1.332
1324	936	928	1952	872
2.550	2.644	2.650	2.488	2.798
$0.30\times0.30\times0.30$	0.25 imes 0.35 imes 0.40	$0.10\times0.10\times0.20$	$0.20\times0.30\times0.40$	$0.20\times0.35\times0.40$
$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
1.88 - 24.10	1.76 - 28.33	2.05 - 28.34	2.10 - 28.30	1.59 - 28.33
5038	14270	14258	30403	13641
338	5521	5433	5992	5140
0.0339	0.0300	0.0826	0.0378	0.0396
0.0809	0.0796	0.2289	0.0781	0.1071
1.059	1.002	1.111	0.951	1.021
	$\begin{array}{c} \textbf{2} \\ \hline C_{18}H_{52}B_{10}P_2Ge_2Ni \\ 641.52 \\ monoclinic \\ P2(1) \ /n \\ 11.2880(10) \\ 14.2049(3) \\ 20.6930(4) \\ 104.7760(10) \\ 3208.52(10) \\ 4 \\ 1.328 \\ 1324 \\ 2.550 \\ 0.30 \times 0.30 \times 0.30 \\ \omega - 2\theta \\ 1.88 - 24.10 \\ 5038 \\ 338 \\ \hline 0.0339 \\ 0.0809 \\ 1.059 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

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

to the vinyl proton. The characteristic high-field $^{13}\mathrm{C}$ 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 Me₂Si(o-C₂B₁₀H₁₀)SiMe₂Pt(PPh₃)₂ with 1-hexyne¹¹ and the reaction of chloro(triisopropyl-phosphine)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 ¹³C NMR spectra together with the mass spectrometric analysis. In the olefinic region of the ¹³C NMR spectrum of **12**, one



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).

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°).

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.

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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-digerma-cyclopentane (**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 ¹H NMR spectrum of 15 are assigned to the two methine protons. A large coupling contant ($J_{\rm HH} = 13.50$ Hz) indicates that the two methine protons are in a trans configuration due to the steric hindrance of the phenyl groups. A lowfrequency ¹³C 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 C2Ge2C five-



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).

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

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 ¹H NMR



spectrum of **16** includes a singlet at 6.72 ppm assigned to the vinyl proton. A characteristic high-frequency ¹³C NMR resonance at 135.4 ppm provided evidence for a tethered sp² 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-1,1,3,3tetramethyl-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

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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).



Compounds 17 and 18 were characterized by ¹H and ¹³C NMR and elemental analyses. Three singlets (δ 1.63, 1.56, 1.48) in the ¹H NMR spectrum and three singlets $(\delta 21.5, 21.3, 20.9)$ in the ¹³C 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 ¹H NMR spectrum of **17** shows a single resonance at δ 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 ¹³C NMR spectrum of compound 17 exhibits resonances for the olefinic carbons at δ 124.1 and 122.3, a methine carbon at δ 30.1, and the methyl carbons of germanium at δ 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 1,4migration of hydride **D** and reductive elimination of the





nickel fragment lead to compound **17**. Such a 1,4migration 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

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 1,2bis(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 sixmembered-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 CaH₂. The ¹H and ¹³C, ³¹P 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, PEt₃, and GeMe₂Cl₂ were purchased from Strem Chemicals. The alkynes were purchased from Aldrich. 1,2-Bis-(chlorodimethylgermyl)carborane,⁷ Ni(PEt₃)₄,²⁰ cyclooctyne,²¹

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and ferrocenylacetylene $^{\rm 22}$ 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. ¹H NMR (C₆D₆): δ 4.23 (sept, 2H, ³*J*_{HH} = 3.04 Hz, Ge–*H*), 0.13 (d, 12H, ³*J*_{HH} = 3.04 Hz, Ge–*CH*₃). ¹³C{¹H} NMR (C₆D₆): δ –1.5. MS: *m*/*z* 349 [M⁺]. Anal. Calcd for C₆H₂₄B₁₀Ge₂: 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(PEt₃)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). ¹H NMR (C₆D₆): δ 1.14 (dq, 12H, $J_{HP} = 7.42$ Hz, $J_{HH} = 5.48$ Hz, PCH_2), 0.86 (dt, 18H, $J_{HP} = 7.04$ Hz, $J_{HH} = 5.48$ Hz, CH_3), 0.21 (s, 12H, GeC H_3). ³¹P{¹H}</sup> NMR (C₆D₆): δ 6.18. MS (EI): m/z 642 [M⁺]. Anal. Calcd for C₁₈H₅₂B₁₀NiP₂Ge₂: 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: $115-117 \,^{\circ}$ C. ¹H NMR (CDCl₃): $\delta 7.09-6.72 \,(m, 10H, Ph), 0.42$ (s, 12H, GeC*H*₃). ¹³C{¹H} NMR (CDCl₃): $\delta 154.0 \,(\text{Ge}C=), 142.0, 128.0, 127.6, 126.2 (Ph), -1.0 (Ge-CH₃). MS: <math>m/z 526 \,[\text{M}^+]$. Anal. Calcd for C₂₀H₃₂B₁₀Ge₂: 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. ¹H NMR (CDCl₃): δ 7.32–7.04 (m, 5H, *Ph*), 6.49 (s, 1H, =*CH*), 0.54 (s, 6H, GeC*H*₃), 0.50 (s, 6H, Ge-*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 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*H₃), -0.6 (Ge-*C*H₃). MS: *m*/*z* 450 [M⁺]. Anal. Calcd for C₁₄H₂₈B₁₀Ge₂: 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. ¹H NMR (CDCl₃): δ 2.28 (q, 4H, $J_{HH} = 7.50$ Hz, CH_2), 0.95 (t, 6H, $J_{HH} = 7.50$ Hz, CH_3), 0.47 (s, 12H, GeC H_3). ¹³C{¹H} NMR (CDCl₃): δ 150.9 (*C*=*C*), 67.6 (*carborane carbons*), 25.3 (*C*H₂), 14.8 (*C*H₃), -0.2 (Ge-*C*H₃). MS: *m*/*z* 430 [M⁺]. Anal. Calcd for C₁₂H₃₂B₁₀Ge₂: 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. ¹H NMR (CDCl₃): δ 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). ¹³C{¹H} NMR (CDCl₃): δ 158.3 (=*C*Ph), 156.7 (=*C*Me), 128.7, 127.2, 126.6 (*Ph*), 20.3 (*C*H₃), -1.3 (Ge– *C*H₃), -1.6 (Ge–*C*H₃). MS: *m*/*z* 464 [M⁺]. Anal. Calcd for C₁₅H₃₀B₁₀Ge₂: 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. ¹H NMR (CDCl₃): δ 1.18 (s, 3H, =C-CH₃), 1.16 (s, 3H, C-CH₃), 0.51 (s, 3H, Ge-CH₃), 0.49 (s, 3H, Ge-CH₃), 0.46 (s, 3H, Ge-CH₃), 0.26 (s, 3H, Ge-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 148.4 (*C*=C), 29.5 (CH₃), 12.6 (CH₃), -2.1 (Ge-CH₃), -2.4 (Ge-H₃), -3.4 (Ge-CH₃), -6.8 (Ge-CH₃). MS: *m*/*z* 402 [M⁺]. Anal. Calcd for C₁₀H₂₈B₁₀Ge₂: 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. ¹H NMR (CDCl₃): δ 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). ¹³C{¹H} NMR (CDCl₃): δ 152.6 (=*C*Ph), 146.0 (=*C*SiMe₃), 129.8, 128.6, 127.0, 126.3 (*Ph*), 2.2 (Ge–*C*H₃), 1.9 (Ge–*C*H₃), -0.9 (Si–*C*H₃). MS: *m*/*z* 522 [M⁺]. Anal. Calcd for C₁₇H₃₆B₁₀Ge₂Si: 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. ¹H NMR (CDCl₃): δ 0.58 (s, 6H, Ge–C H_3), 0.45 (s, 6H, Ge–C H_3), 0.13 (s, 18H, Si–C H_3). ¹³C{¹H} NMR (CDCl₃): δ 144.3 (=CSiMe₃), 1.1 (Ge–CH₃), -0.2 (Ge–CH₃), -1.0 (Si–CH₃). MS: m/z 518 [M⁺]. Anal. Calcd for C₁₄H₄₀B₁₀-Ge₂Si₂: 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.¹H NMR (CDCl₃): δ 3.77 (s, 6H, CO₂CH₃), 0.62 (s, 12H, Ge–CH₃). ¹³C{¹H} NMR (CDCl₃): δ 168.0 (CO_2 CH₃), 151.0 (C=C), 52.6 (OCH₃), -0.5(Ge–CH₃). MS: m/z 490 [M⁺]. Anal. Calcd for C₁₂H₂₈B₁₀O₄-Ge₂: 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). ¹H NMR (CDCl₃): δ 6.28 (s, 1H, =CH), 2.16 (t, 2H, $J_{\text{HH}} = 8.8$ Hz, =CC H_2), 1.59–1.27 (m, 4H, -C H_2 –), 0.90 (t, 3H, $J_{\text{HH}} = 5.2$ Hz, C H_3), 0.48 (s, 6H, Ge–C H_3), 0.43 (s, 6H, Ge–C H_3). ¹³C{¹H} NMR (CDCl₃): δ 159.2 (=CH), 142.8 (GeC=), 41.0, 31.4, 22.6, 14.2 (Bu), -0.6 (GeCH₃), -0.8 (GeCH₃). MS: m/z 415 [M⁺ – CH₃]. Anal. Calcd for C₁₂H₃₂B₁₀-Ge₂: 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.¹H NMR (CDCl₃): δ 2.38 (br, 4H, =C H_2), 1.45 (br, 8H, -C H_2), 0.45 (s, 12H, Ge–C H_3). ¹³C{¹H} NMR (CDCl₃): δ 140.6 (=*C*CH₂), 30.7, 29.2, 26.2 (*C*H₂), -1.6 (Ge–*C*H₃). MS: *m*/*z* 456 [M⁺]. Anal. Calcd for C₁₄H₃₄B₁₀Ge₂: 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. ¹H NMR (CDCl₃): δ 6.70 (s,

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1H, =C*H*), 4.28 (br, 4H, C₅*H*₄), 4.07 (s, 5H, C₅*H*₅), 0.65 (s, 6H, Ge-C*H*₃), 0.51 (s, 6H, Ge-C*H*₃). ¹³C{¹H} NMR (CDCl₃): δ 142.4 (=*C*H), 134.4 (=*C*C), 69.8, 69.1, 67.0 (*Cp*), 1.2 (Ge-*C*H₃), -0.5 (Ge-*C*H₃). MS: *m*/*z* 558 [M⁺]. Anal. Calcd for C₁₈H₃₂B₁₀-Ge₂Fe: 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 (CDCl₃): δ 7.05 (d, 2H, $J_{\rm HH}$ = 8.96 Hz, *Ph*), 6.83 (d, 2H, $J_{\rm HH} = 8.96$ Hz, *Ph*), 3.79 (s, 3H, OCH₃), 2.80 (d, 2H, $J_{\text{HH}} = 8.74$ Hz, CH₂), 1.34 (t, 1H, $J_{\text{HH}} = 8.74$ Hz, CH), 0.38 (s, 6H, Ge-CH₃), 0.33 (s, 6H, Ge-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 139.2, 134.1, 128.9, 114.1, 55.4 (OCH₃), 31.5 (CH₂), 21.29 (CH), -0.3 (Ge-CH₃), -3.2 (Ge-CH₃). MS: m/z 482 [M⁺]. Anal. Calcd for C₁₅H₃₂B₁₀Ge₂O: 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 (CDCl₃): δ 7.35–7.18 (m, 10H, *Ph*), 4.07 (d, 1H, *J*_{HH} = 13.50 Hz, *CH*Ph₂), 1.68 (d, 1H, *J*_{HH} = 13.50 Hz, *CH*Ge₂), 0.26 (s, 6H, Ge–*CH*₃), -0.05 (s, 6H, Ge–*CH*₃). ¹³C{¹H} NMR (CDCl₃): δ 145.5, 129.1, 127.9, 127.7, 50.3 (*C*HPh₂), 23.1 (*C*HGe₂), -0.1 (Ge–*C*H₃), -2.7 (Ge–*C*H₃). MS: *m*/*z* 528 [M⁺]. Anal. Calcd for C₂₀H₃₄B₁₀Ge₂: 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 (CDCl₃): δ 6.72 (t, 1H, $J_{\rm HH} = 13.86$ Hz, =C*H*), 2.17 (dt, 2H, $J_{\rm HH} = 13.86$ Hz, $J_{\rm HH} = 5.02$ Hz, C*H*₂), 1.48–1.27 (m, 8H, C*H*₂), 0.88 (t, 3H, $J_{\rm HH} = 4.62$ Hz, C*H*₃), 0.37 (s, 6H, Ge–C*H*₃), 0.28 (s, 6H, Ge–C*H*₃). ¹³C{¹H} NMR (CDCl₃): δ 152.5, 135.4, 36.9, 30.1, 27.4, 27.2, 20.9, 12.5, -2.7 (GeCH₃), -2.9 (GeCH₃). MS: m/z 458 [M⁺]. Anal. Calcd for C₁₄H₃₆B₁₀Ge₂: C, 36.74; H, 7.92. Found: C, 36.46; H, 7.72.

(xiv) 17 from the Reaction with 2,3-Dimethyl-1,3butadiene. Yield: 62%. Mp: $161-163 \,^{\circ}$ C. ¹H NMR (CDCl₃): δ 2.46 (s, 1H, CH), 1.63 (s, 3H, =CH₃), 1.56 (s, 3H, CCH₃), 1.48 (s, 3H, CCH₃), 0.50 (s, 6H, Ge-CH₃), 0.47 (s, 6H, Ge-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 124.1 (C=C), 122.3 (C=C), 30.1 (CH), 21.5, 21.3, 20.9 (C-CH₃), 0.6, -0.4 (GeCH₃). 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 (CDCl₃): δ 4.95 (d, 1H, $J_{HH} = 11.72$ Hz, =CH), 1.97 (d, 1H, $J_{HH} = 11.72$ Hz, CH), 1.69 (s, 3H, C–CH₃), 1.54 (s, 3H, C–CH₃), 0.48 (s, 6H, Ge–CH₃), 0.41 (s, 6H, Ge–CH₃). ¹³C{¹H} NMR (CDCl₃): δ 130.6, 119.0 (*C*=C), 26.3 (*C*H), 21.6 (*C*H₃), 0.6 (Ge*C*H₃), -1.1 (Ge*C*H₃). MS: m/z 416 [M⁺]. Anal. Calcd for C₁₁H₃₀B₁₀Ge₂: 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 \times 0.30 \times 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 graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å). The sample was first cooled to 130 K. The intensities were measured as a series of ϕ oscillation frames each of 0.4° for 30 s/frame. A colorless crystal of $\boldsymbol{6}$ with the dimensions of $0.25\times0.35\times0.40$ mm³ was mounted on the tip of a glass fiber. The cell parameters were obtained by least-squares refinement from 25 reflections in the range $1.76^\circ < 2\theta < 28.33^\circ$ measured with graphite-monochromated Mo Ka radiation on a Simens P4 diffractometer. The X-ray intensity data were collected by the ω -2 θ 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 $1.76^{\circ} < 2\theta < 28.33^{\circ}$ on a Simens P4 diffractometer. The X-ray intensity data were collected by the ω -2 θ 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. Nonhydrogen 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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