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Transition metal-catalyzed double silylation and germylation with 1,2-bis(dimethylsilyl)carborane and 1,2-bis(dimethylgermyl)carborane

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Abstract

The reaction of 1,2-bis(dimethylsilyl)carborane **1** with Ni(PEt_3)$_4$ yielded the cyclic bis(silyl)nickel complex **7**. Compound **7** was found to be a good catalyst for the double silylation reaction of alkynes, alkenes, aldehydes, and nitriles. The reaction of 1,2-bis(dimethylgermyl)carborane **2** with Ni(PEt_3)$_4$ afforded the reactive intermediate, $[o\text{-}(GeMe_2)_2C_2B_{10}H_{10}]Ni(PEt_3)_2$ **41**. The facile double germylation of unsaturated organic substrates catalyzed by **41** afforded novel class of heterocyclic compounds. The 1,2-bis(dimethylsilyl)- and 1,2-bis(dimethylgermyl)carborane also reacted with palladium and platinum complexes to give the corresponding cyclic bis(silyl) or bis(germyl)metal complexes, which were found to be good catalysts in the double-silylation and germylation reactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Double silylation; Double germylation; Reactive intermediates

1. Introduction

The double-silylation reaction, pioneered by Kumada and co-workers [1], is a convenient synthetic route to obtain compounds in which two Si–C bonds are created by the addition of two silicon units to unsaturated organic substrates such as alkynes [2], alkenes [3], 1,3-dienes [4], aldehydes [5], and nitriles [6].

Nickel, palladium, and platinum complexes are excellent catalysts for the transformation of silicon-containing linear compounds [7] and for hydrosilylation [8]. Bis(silyl)M complex (M = Ni, Pd, and Pt) have been

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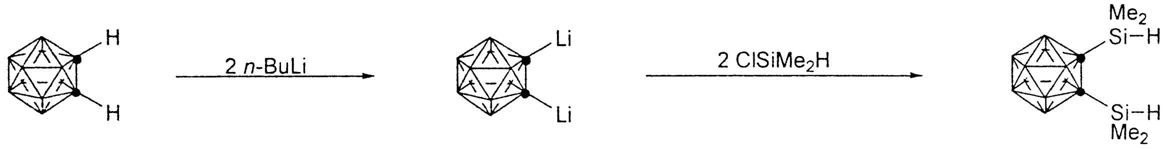
implicated as key intermediates in the metal-catalyzed double silylation.

In this account, we describe our recent study on the double silylation and germylation by nickel, palladium, and platinum complexes. In particular, the bis(silyl)- and bis(germyl)nickel complexes have been crucially important to achieve effective double silylation and germylation reactions. We begin with the synthesis of three ligands **1**–**3** with *o*-carboranylene units and several bis(silyl) and bis(germyl)metal complexes, and then describe catalytic reactions with a variety of unsaturated organic substrates.

2. Synthesis and properties of 1,2-bis(dimthylsilyl)carborane, 1,2-bis(dimethylgermyl) carborane, and 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene

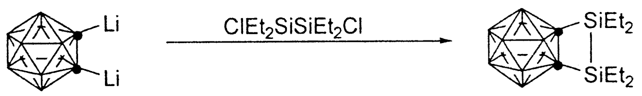
1,2-Bis(dimethylsilyl)carborane **1** can readily be prepared from the reaction of 1,2-$Li_2C_2B_{10}H_{10}$ and two equivalents of $SiMe_2ClH$. 1,2-Bis(dimethylgermyl)carborane **2** used in this study was prepared using a simple two-step methodology by allowing dilithio-*o*-carborane to react with two equivalents of dimethylgermanium dichloride to form 1,2-bis(chlorogermyl)carborane, followed by displacement of the chlorine atoms by hydrides with $NaBH_3CN$.



1

Compounds **1** and **2** are crystalline white solids and can be handled in air for a few hours. However, they are gradually oxidized at room temperature to give 4,5-carboranylene-1,1,3,3-tetramethyl-2-oxa-1,3-la or 1,3-digermylacyclopent-4-ene.

The reaction of 1,2-dilithiated carborane with dichlorotetraethyldisilane yielded the strained 3,4-carboranylene-1,1,2,2,-tetraethyl-1,2-disilacyclobut-3-ene **3**. In contrast to 3,4-carboranylene-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene reported by de Rege [9], compound **3** is quite stable. However, compound **3** is rapidly oxidized in oxygen gas to give 4,5-carboranylene-1,3-disila-2-oxacyclopent-4-ene. We examined the chemical behavior of **3** towards palladium complexes. The palladium-catalyzed reaction of **3** in refluxing benzene afforded 1-(diethylphenylsilyl)-2-(diethylsilyl)carborane **4** in 38% yield.



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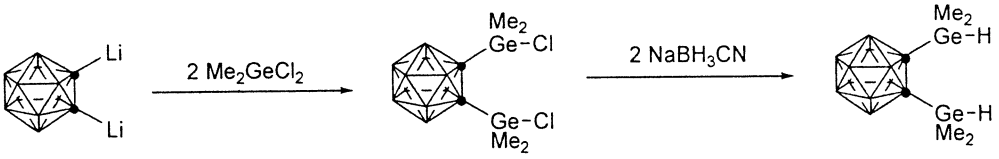

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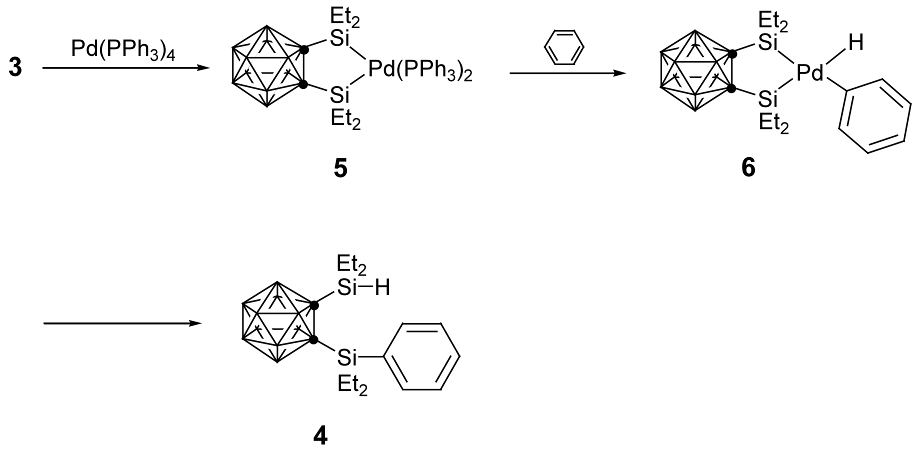
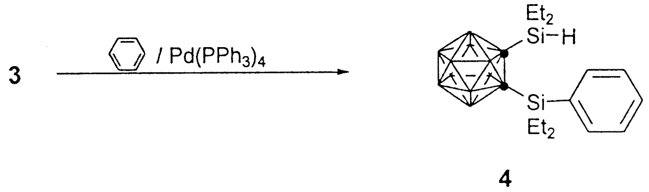
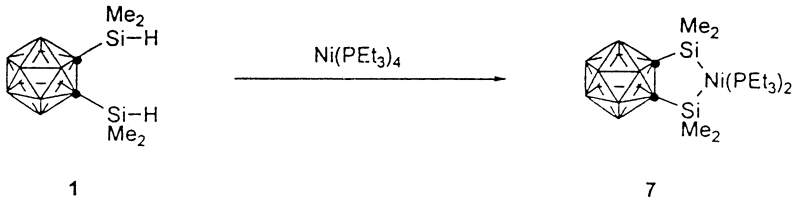


Scheme 1.





The formation of this benzene adduct may be interpreted in terms of C–H activation of benzene by a palladium complex (Scheme 1). A key intermediate is 3,4-carboranylene-2,2,5,5-tetraethyl-1-pallada-2,5-disilacyclopent-3-ene **5**, which after oxidative addition of the C–H bond in the coordinated benzene gives intermediate **6**. Reductive elimination of a palladium species then leads to the benzene adduct **4**. Such a C–H bond activation of arenes by transition metal complexes has been well documented [10].

3. Nickel-catalyzed double silylation with alkynes

Since bis(silyl)nickel complexes have been implicated as intermediates in the nickel-catalyzed double silylation of unsaturated organic substrates, the isolation of bis(silyl)nickel complexes is essential to understand their role as catalytic intermediates. We prepared the bis(silyl)nickel complex **7** by the reaction of **1** with $Ni(PEt_3)_4$ in 86% yield as a crystalline solid, which is quite air-sensitive. The structure of **7** was confirmed by X-ray analysis.

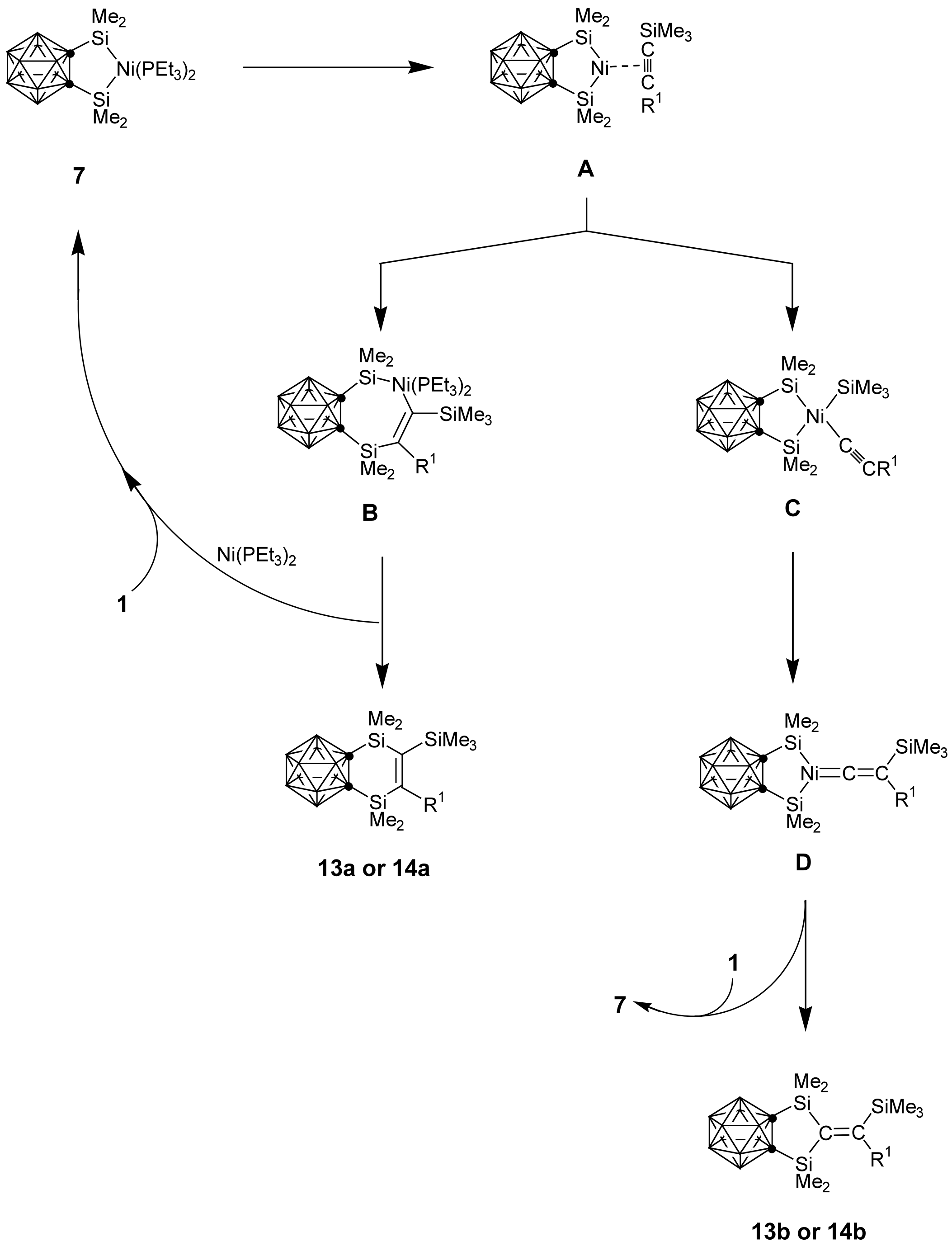
The nickel complex **7** was found to be a good catalyst for the double silylation reaction [11].

Thus, the nickel-catalyzed reaction of **1** with non-activated alkynes such as diphenylacetylene, phenylacetylene, 3-hexyne, 2-butyne afforded the corresponding 5,6-carboranylene-1,1,4,4-tetramethyl-1,4-disilacyclohex-2-enes by insertion of the carbon-carbon triple bond into a silicon-nickel bond of **7**. However, activated alkynes such as 1-phenyl-1-propyne and dimethyl acetylenedicarboxylate react with **1** in the presence of a catalytic amount of **7** to give the trimerization products as the major products 11b.

When 1-hexyne was employed as a terminal alkyne in the nickel-catalyzed reaction of **1**, the five membered ring compound **12** was isolated. It seems likely that a 1,2-hydrogen shift must be involved in its formation [11]. A similar reaction of **1** with alkynes containing a trimethylsilyl group such as 1-phenyl-2-(trimethylsilyl)acetylene afforded both five- and six-membered cyclic products.

The formation of the five- and six-membered disilylene ring compounds **13** and **14**, respectively, may be explained by a series of steps, as shown in Scheme 2.

In the first stage, the intermediate **7** coordinates to an alkyne **A**. This is followed by insertion of the triple bond into a Ni–Si bond to give a seven-membered intermedi-

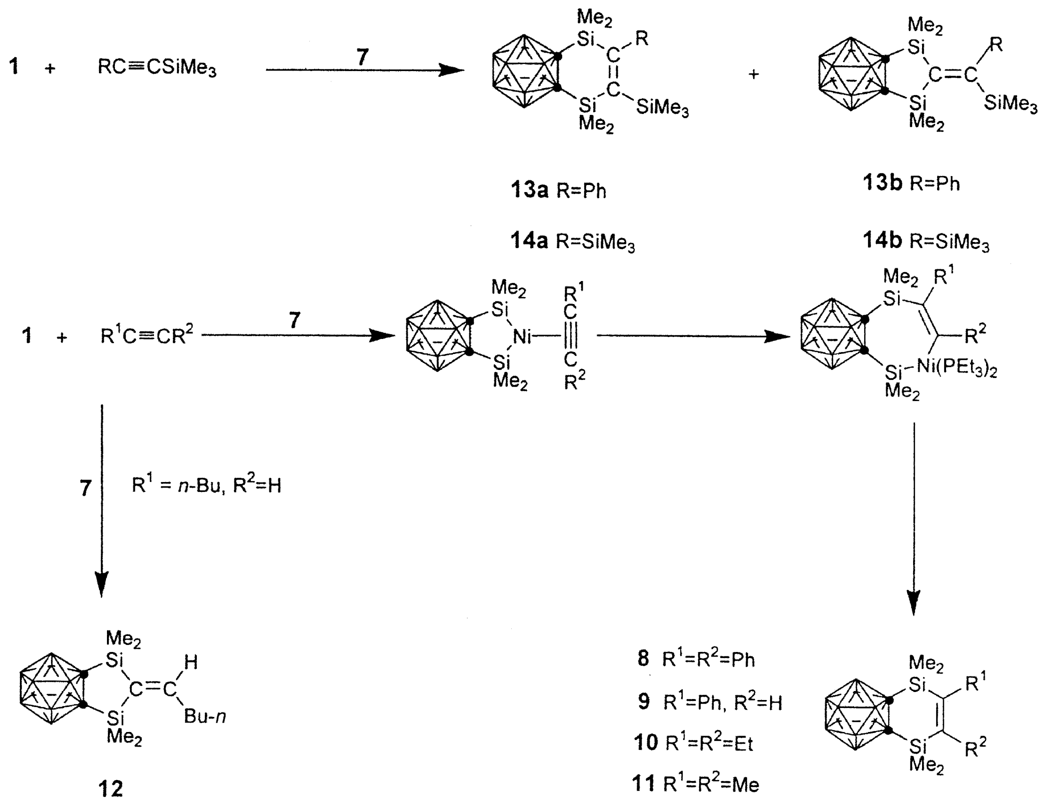


Scheme 2.

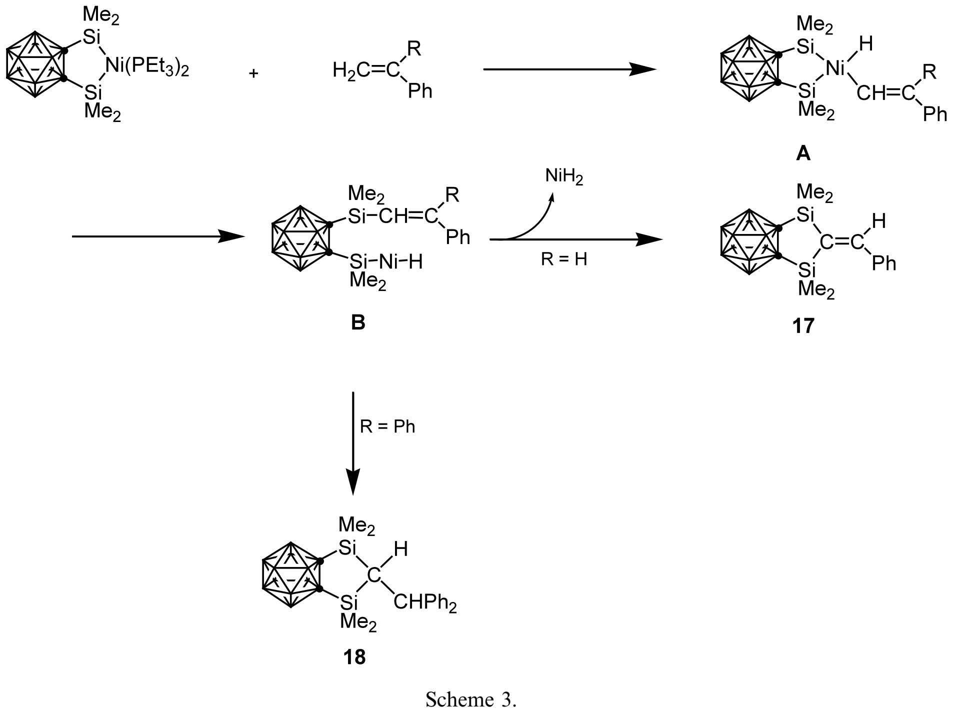
ate **B** or by oxidative addition of the Si–C bond to a nickel center to give **C**. Reductive elimination of the nickel fragment from intermediate **B** leads to the six-membered disilylene ring compound **13a** or **14a**. On the other hand, formation of the five-membered disilylene ring compound **13b** or **14b** may be explained in terms of a shift of the trimethylsilyl group to the CR^1 carbon atom, giving a (vinylidene)nickel intermediate **D**. Such a trimethylsilyl shift has previously been observed in nickel- [12] and rhodium-catalyzed reactions [13].

4. Nickel-catalyzed double silylation with alkenes

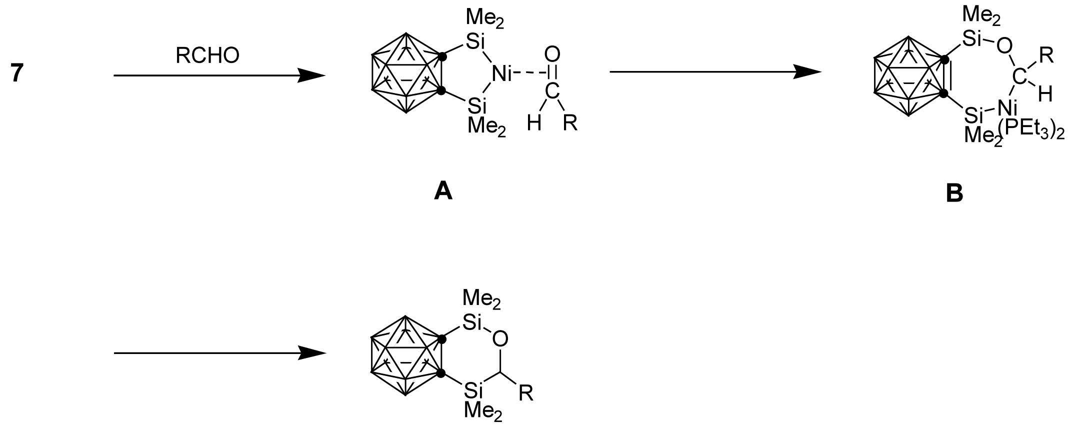
Reaction of **1** with two equivalents of 4-vinylanisole in the presence of a catalytic amount of **7** afforded a



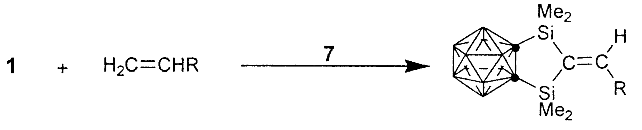
moderate yield of the five-membered disilylene compound **15**. A similar reaction of **1** with 1-octene gave a five-membered disilylene ring compound **16**. Although the intermediate **7** is not effective in the nickel-catalyzed double silylation of styrene, the stoichiometric reaction of **7** with styrene afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-phenylmethylene-1,3-disilacyclopent-4-ene **17**. On the other hand, treatment of **1** with



Scheme 3.



Scheme 4.

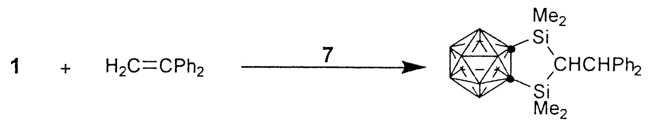


15 $R{=}C_6H_4\text{-}4\text{-}OCH_3$

16 $R{=}CH_2(CH_2)_4CH_3$

17 $R{=}C_6H_5$

1,1-diphenylethylene in the presence of a catalytic amount of **7** gave the five-membered disilylene ring compound **18**, which contained a saturated side chain.



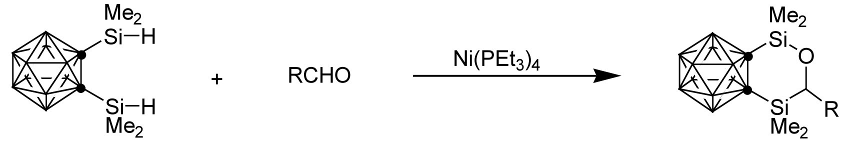
18

The formation of **17** and **18** may involve an initial oxidative addition reaction of an olefinic C–H bond to the nickel center to give **A**, followed by shift of a phenylethenyl group from the nickel atom to one of two silicon atoms to give **B**, as shown in Scheme 3. Another olefinic C–H oxidative addition followed by elimination of nickel dihydride could lead to compound **17**. On the other hand, when R is phenyl in **B**, such a second C–H oxidative addition may not be possible and an intramolecular hydrosilylation takes place instead, leading to compound **18**.

5. Nickel-catalyzed double silylation with carbonyl compounds

Isobutyraldehyde readily reacted with **1** in the presence of a catalytic amount of $Ni(PEt_3)_4$ to give 5,6-carboranylene-1,1,4,4-tetramethyl-2-oxa-3-isopropyl-1,4-disilacyclohex-5-ene **19**. In a similar fashion, the nickel-catalyzed reaction of **1** with other aldehydes such as trimethyl acetaldehyde, 5-norbornene-2-carboxaldehyde, and benzaldehyde yielded the corresponding six-membered cyclic insertion products [14].

Such dehydrogenative 1,2-double silylation reactions have been reported using a platinum complex as the catalyst with *o*-bis(dimethylsilyl)benzene as the sub-



1

19 $R{=}C_3H_7\text{-}i$

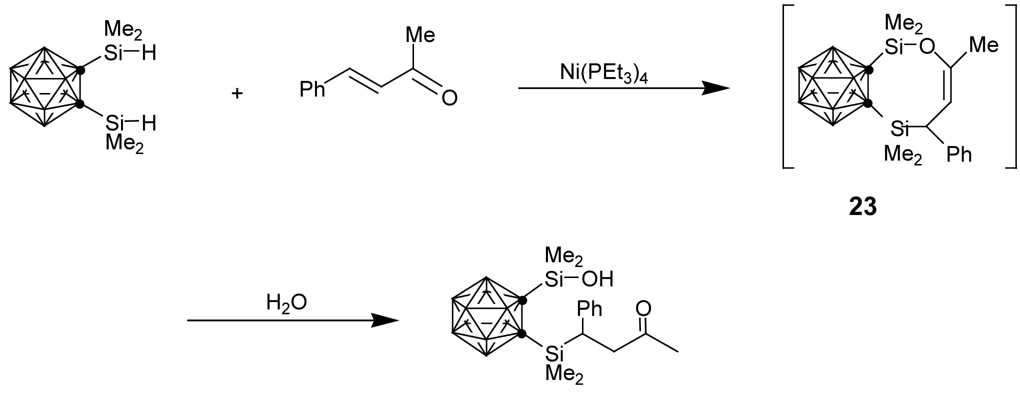
20 $R{=}CMe_3$

21 R=norbornene

22 R=Ph

strate [5]. The insertion of an aldehyde carbonyl group into the Si–Si bond was also found to be promoted by fluoride ion [15].

A reasonable mechanism for the formation of **19**–**22** involves the initial formation of bis(silyl)nickel complex **7** as a key intermediate. Intermediate **7** then coordinates to a carbonyl group **A**, followed by insertion of the carbonyl bond into a Ni–Si bond to give a seven-memberded cyclic intermediate **B**. Analogous reactions of a silyl-substituted transition metal complex with



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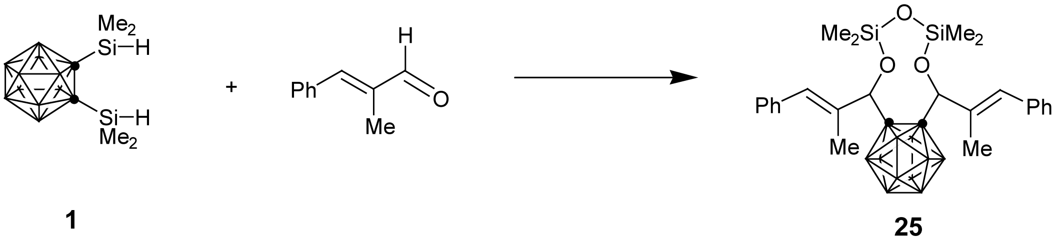
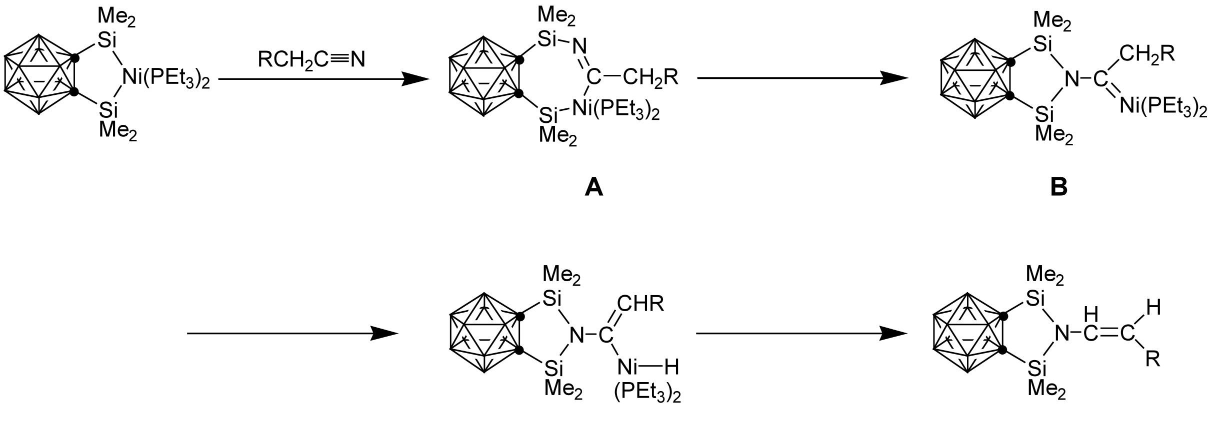


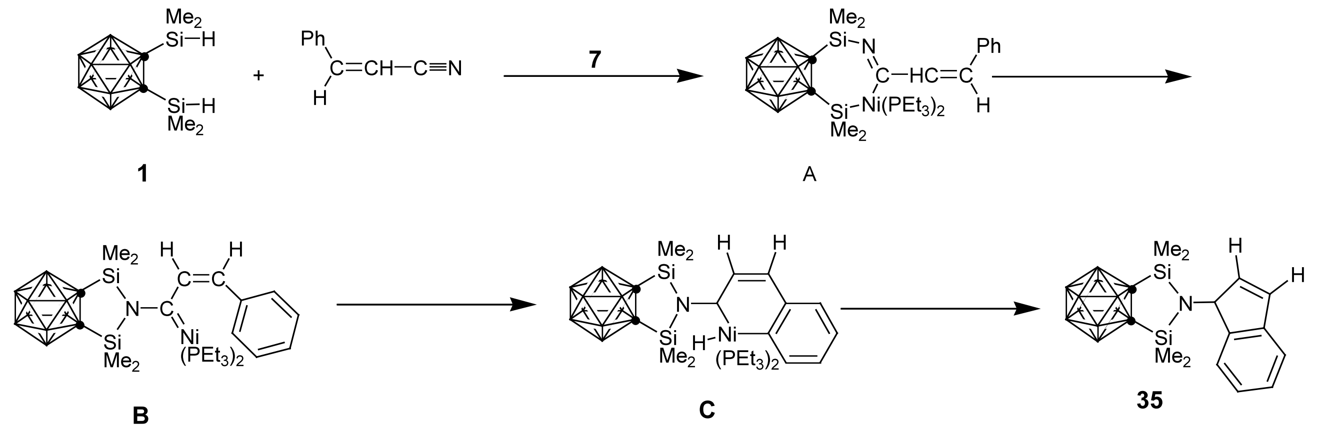
1

25



C

Scheme 5.

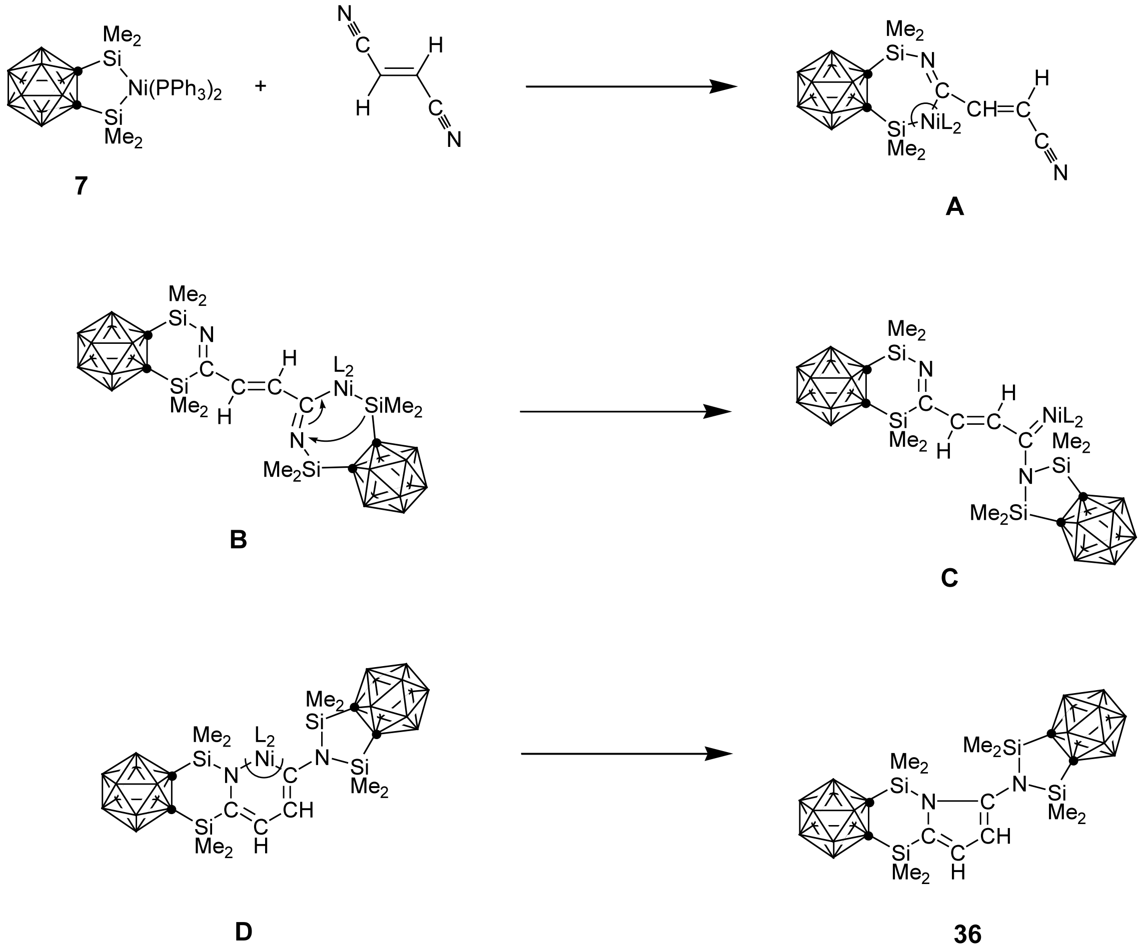


Scheme 6.

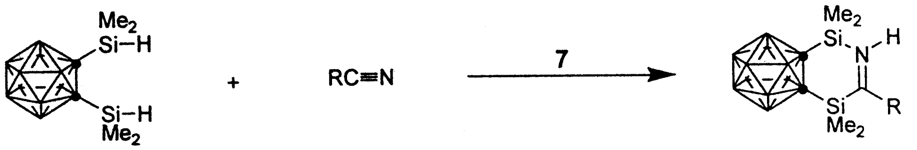
carbonyl compound have been reported previously. Reductive elimination of the nickel fragment from the latter intermediate then leads to products **19**–**22** (Scheme 4).

α,β-Unsaturated carbonyl compounds also reacted with **1** in the presence of a catalytic amount of Ni(PEt$_3$)$_4$ to give the 1,4-double silylated products. Reaction of **1** with the hindered *trans*-4-phenyl-3-buten-2-one in the presence of a nickel catalyst afforded **24**, presumably obtained by hydrolysis of 7,8-carboranylene-1,1,6,6-tetramethyl-3-methyl-5-phenyl-2-oxa-1,6-disilacyclooct-3-ene **23**.

Such 1,4-double silylations have been observed in the transition metal catalyzed silylation of α,β-unsaturated ketones and aldehydes [16]. These reactions were very sensitive to the substituents on the carbonyl group. When α-methyl-*trans*-cinnamaldehyde was employed in the reaction with **1** under certain reaction conditions, the



Scheme 7.



1

27 R= i-C_3H_7

28 R=C_6H_5

29 R=$C_6H_4CH_3$-p

30 R=β-naphthyl

di-insertion product **25** of a carbonyl group into each of the C–Si bonds was obtained.

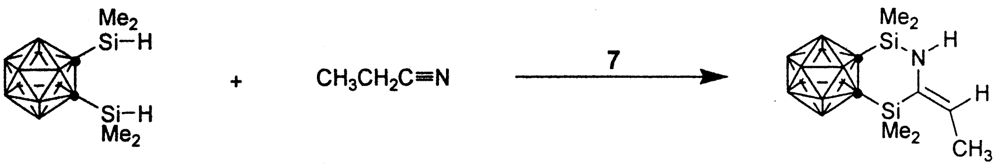
It had been demonstrated by a trapping experiment that the oxygen atom of the disiloxane unit was derived from the aldehyde [17]. Similar insertion was observed in the reactions of $(CO)FeSiMe_2CH_2CH_2SiMe_2$ [18], $(CO)_5MnSiMe_3$ [19], and $MeEt_2SiCo(CO)_3L$ [20] with benzaldehyde and of 3,4-benzo-1,1,2,2-tetraethyldisilacyclobut-3-ene with benzophenone in cyclohexene.

6. Nickel-catalyzed double silylation with nitriles

Propionitrile readily reacted with **1** in the presence of a catalytic amount of **7** in refluxing toluene to give the *N*-silyl enamine **26** [21].

Interestingly, the nickel catalyzed reactions of **1** with nitriles without an α-hydrogen such as benzonitrile, isobutyronitrile, and 1-cyanonaphthalene afforded six-membered cyclic imines **27**–**30**. Such a nitrile insertion reaction has been reported using a platinum complex as catalyst and *o*-bis(dimethylsilyl)benzene as the substrate [6].

In contrast to the double silylation of the above nitriles with **1**, reaction of **9**-anthracenecarbonitrile with **1** under the same reaction conditions gave the five-membered cyclic *N*,*N*-bis(silyl)amine **31**.



1

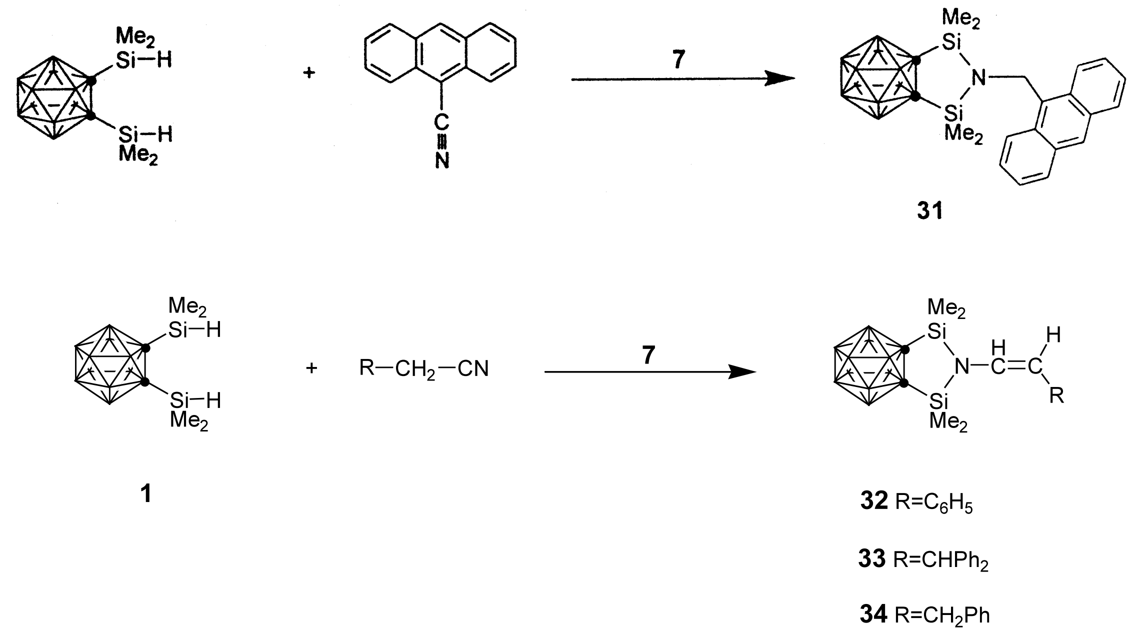
26

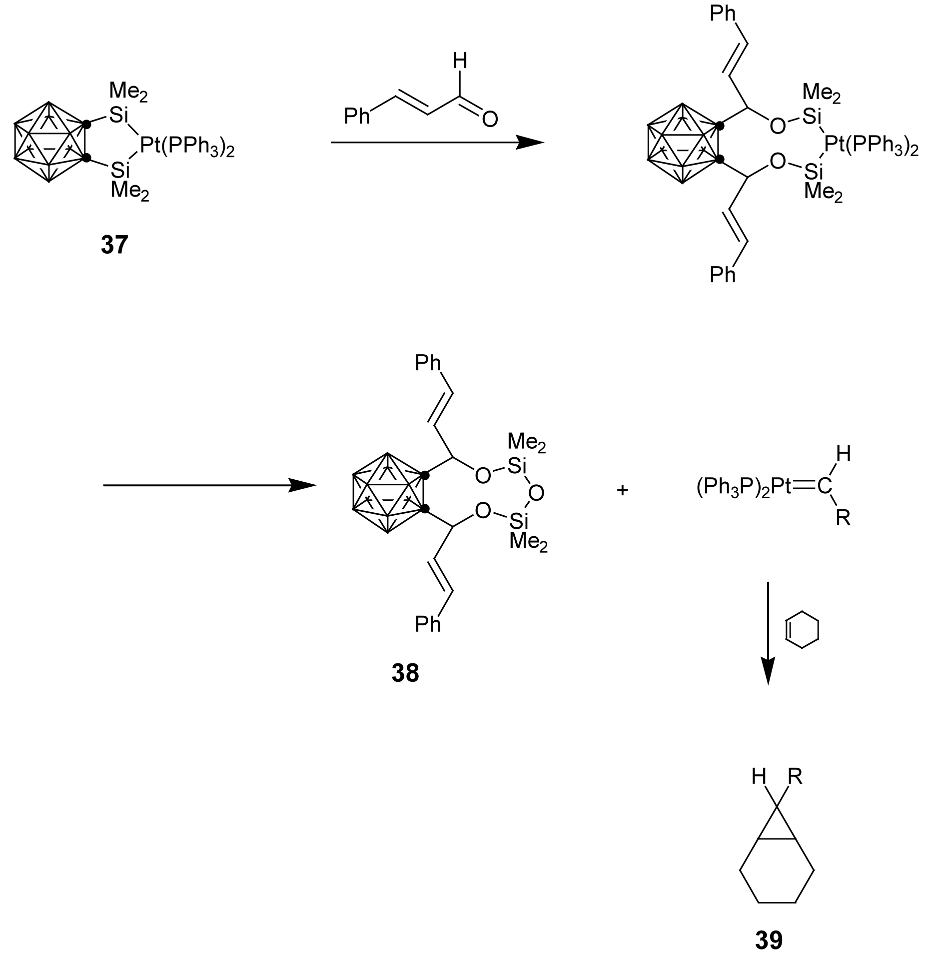
The formation of **31** is interesting because sequential hydrosilylation of the carbon–nitrile triple bond by the Si–H bond in **1** must be involved during the course of the reaction. A similar hydrosilylation has been observed in the rhodium- [22] and platinum-catalyzed double silylation of nitriles with a bis(hydrosilane) [6].

The nickel catalyzed reaction with more activated nitriles with an α-hydrogen afforded *N*,*N*-bis(silyl)enamines **32**–**34**. Thus, treatment of **1** with benzyl cyanide in the presence of a catalytic amount of **7** gave the *N*,*N*-bis(silyl)enamine **32**. Such a selective conversion of nitriles into *N*,*N*-bis(silyl)enamines has been observed in the iron-catalyzed double silylation [23].

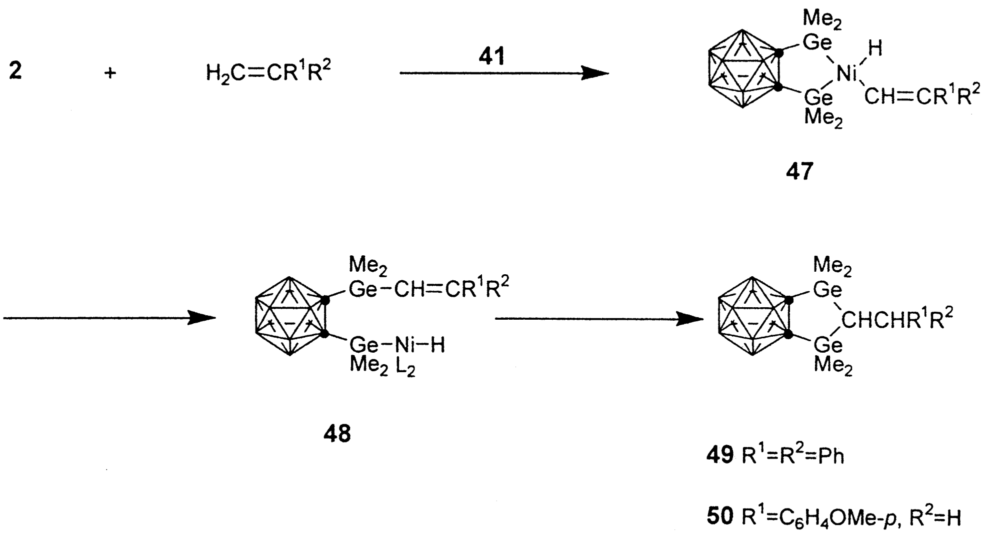
On the basis of our results and those of other [23], a plausible reaction pathway for the above reactions may be proposed as shown in Scheme 5. In the first stage, insertion of the cyano group into one Ni–Si bond in **7** gives a seven-membered intermediate **A**. The migration of the other silicon atom to the nitrogen affords the carbene intermediate **B**. The σ-vinyl complex **C** can be obtained by a migration of one hydrogen atom α to the cyano group of the nitrile to the carbon α to the nitrogen atom. The *N*,*N*-bis(silyl)enamine is then formed in a reductive elimination step.

Surprisingly, when cinnamonitrile was employed in the catalytic reaction with **7**, a five-membered cyclopentanone enamine **35** was isolated in 68% yield (Scheme 6).


Me2
Si–H
Si–H
Me2
+
C
N
7
Me2
Si
N
Si
Me2
31
1
R–CH2–CN
H
N–C=C
R
32 R=C6H5
33 R=CHPh2
34 R=CH2Ph


Me2
Si
Pt(PPh3)2
Si
Me2
37
H
Ph
O
Ph
O
Ph
O
O
38
(Ph3P)2Pt=C
H
R
H R
39

Scheme 8.



Scheme 9.

The structure of **35** was confirmed by a single-crystal X-ray diffraction [21]. Such a transformation of nitrile to enamine has been observed in the photochemical reaction of iron with 4-cyanobut-1-ene [24].

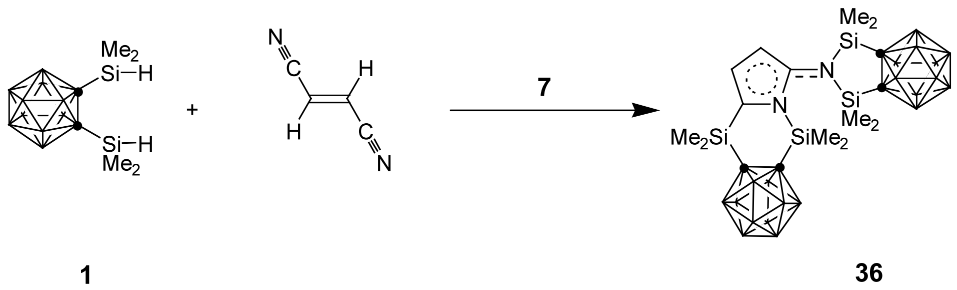
A reasonable mechanism for the formation of **35** involves the initial insertion of the cyano group into one of the nickel–silicon bonds, leading to the seven-membered intermediate **A**. The migration of the silicon atom to the nitrogen atom would afford an amine and the carbene **B**. The intramolecular aromatic C–H activation would occur to give the nickel hydride intermediate **C**. The nickelacyclohexene thus formed can liberate the cyclic enamine by reductive elimination with extrusion of $Ni(PEt_3)_2$. Such a formation of a nickel carbene intermediate is indirectly supported by the isolation of iron carbene complexes as reported by Gladysz and co-workers [25].

Fumaronitrile was found to react with **1** in the presence of a catalytic amount of **7** to afford the cyclization product **36**, which contained two types of disilyl moieties, imine and *N*,*N*-bis(silyl)amine.

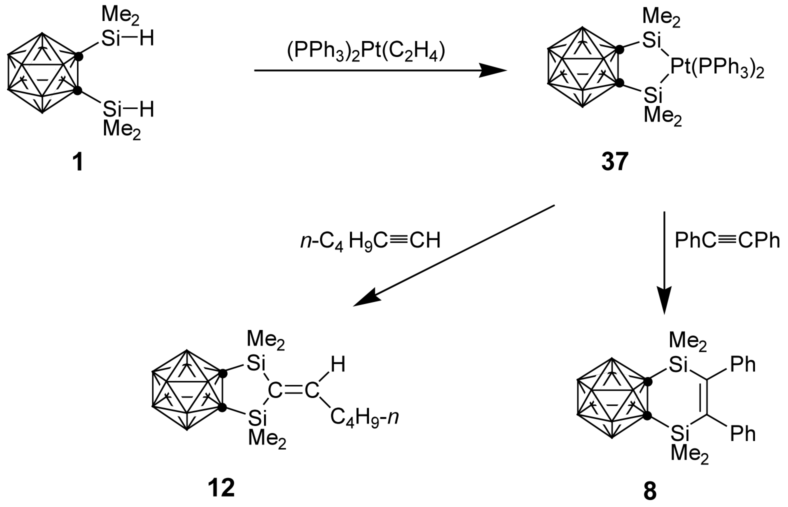
A reasonable mechanism for the formation of **36** involves the initial insertion of the cyano group into one of the nickel–silicon bonds, leading to seven-membered intermediate **A**, followed by cyclization to imine **B** and concomitant with another insertion of the cyano group into the remaining Ni–Si bond (Scheme 7). The platinum-catalyzed reaction of 1,2-bis(dimethylsilyl)benzene with nitriles without an α-hydrogen such as cyanoarenes is well established to give imines of type **B** [6]. The migration of the silicon atom to the nitrogen atom in this case then would afford the carbene **C**. This lends some credence to the notion that the nucleophilic attack of the imine occurs at a vinyl Ni intermediate **D**. The cyclization product **36** then is formed by the reductive elimination extrusion of NiL_2.

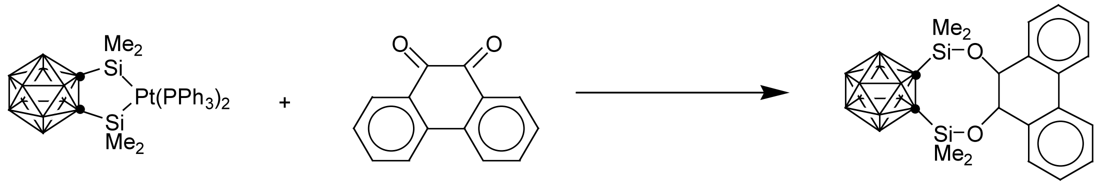
7. Platinum complex-mediated double silylation

The platinum-catalyzed reactions of **1** with diphenylacetylene and phenylacetylene produce no alkyne adducts, but instead afford platinum silyl compounds. After careful workup, the product was found to be a cyclic bis(silyl)platinum complex **37** [26]. The yellow compound **37** is relatively stable in air and to brief heating to 120–130 °C. Although the cyclic bis(si-



lyl)platinum complex is not a catalyst for the double silylation of unsaturated organic substrates, owing to its strong Pt–Si bonds and the high thermal stability, compound **37** was found to be a good reactant in stoichiometric double-silylation reactions. Thus, thermolysis of a toluene solution of **37** and diphenylacetylene in a 1:8 molar ratio at 120 °C afforded 5,6-carboranylene-1,1,4,4-tetramethyl-2,3-diphenyl-1,4-disilacyclohex-2-ene in 92% yield. Such acetylene insertion reactions have been effected using palladium and platinum complexes as catalysts with *o*-(dimethylsilyl)benzene as the substrate 8b. In contrast to the double silylation reaction of **37** with the above diphenylacetylene, reaction of 1-hexyne with **37** under the same reaction conditions gave the five-membered disila ring compound **12** in 54% isolated yield. The formation of **12** is of interest because a 1,2-hydrogen shift must have occurred during the course of the reaction as in the nickel catalyzed double silylation with 1-hexyne.





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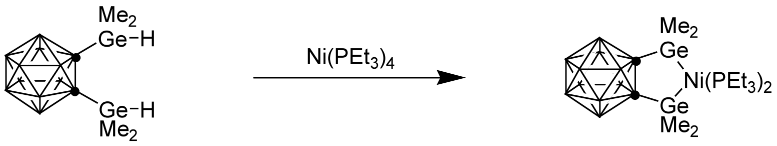
In stoichiometric reactions of **37** with carbonyl compounds such as benzaldehyde and ketones, only decomposition occurred. However, *trans*-cinnamaldehyde reacted with **37** to give the disilylation product **38** in 56% yield (Scheme 8). The formation of **38** is of considerable interest, because the siloxane oxygen atom in **38** must come from aldehyde analogous to the formation of **25**. To prove the presence of a carbene–platinum intermediate generated during the reaction, a trapping experiment was designed. Thus, when a mixture of **37** and *trans*-cinnamaldehyde in 1:8 molar ratio was heated at reflux in cyclohexene as a trapping agent, 7-(β-styrenyl)norcarane **39** was obtained in 14% yield, together with compound **38**. The formation of **39** indicates that the oxygen atom in **38** was derived from the aldehyde.

The insertion of phenanthrenequinone into **37** proceeds to give the eight-membered ring compound **40** with a 1,2-vinylenedioxy group. The reaction of hexamethyldisilane with diones in the presence of a Pd catalyst has been reported to give an insertion product of a carbonyl group into the Si–Si bond [27].

8. Nickel-catalyzed double germylation with unsaturated organic compounds

The catalytic double germylation of the Ge–Ge bond to unsaturated organic compounds has been developed to provide new methodologies for the efficient preparation of organic germanium compounds [28]. A bis(germyl)nickel complex was found to serve as the most efficient and reactive catalyst for the double germylation reaction. The reactive intermediate [*o*-(GeMe$_2$)$_2$C$_2$B$_{10}$H$_{10}$]Ni(PEt$_3$)$_2$ **41** can be readily prepared by the reaction of *o*-bis(dimethylgermyl)carborane **2** with Ni(PEt$_3$)$_4$ [29].



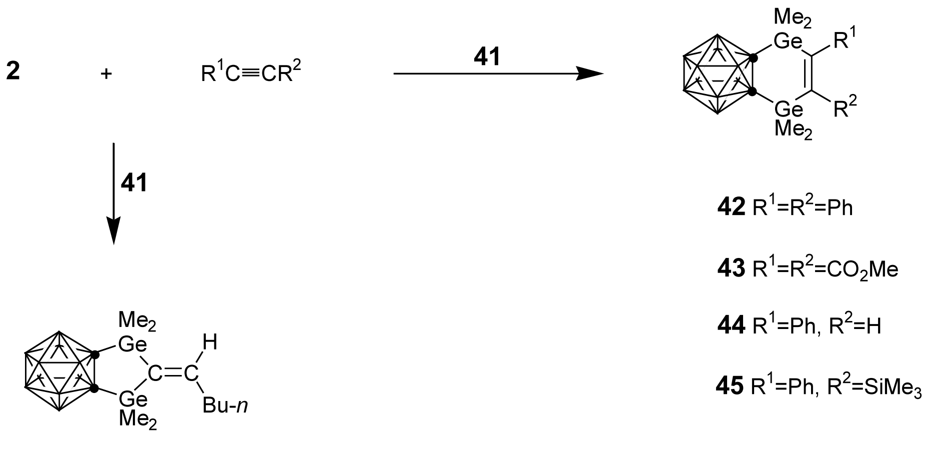
2 **41**

The nickel-catalyzed reaction of **2** with alkynes afforded 5,6-carboranylene-1,1,4,4-tetramethyl-1,4-digermylacyclohex-2-enes by the insertion of the carbon–carbon triple bond into a germanium–nickel bond of **41**. The reaction of **2** with 1-hexyne in the presence of a catalytic amount of **41** at room temperature afforded the double-germylated product **46** in 62% yield. Formation of the digermyl ring compound **46** can be related to the nickel-catalyzed double silylation and the formation of **12** [11].

The nickel-catalyzed reaction of **2** with 1,1-diphenylethylene afforded 4,5-carboranylene-1,1,3,3-tetramethyl-1,3-digermylacyclopent-2-ene **49** in 63% yield (Scheme 9).

With 4-vinylanisole under the same reaction conditions, **2** produced 4,5-carboranylene-1,1,3,3-tetramethyl-2-(*p*-methoxyphenyl)-1,3-digermylacyclopent-2-ene **50** in 54% yield. The formation of **49** and **50** would involve oxidative addition of a terminal sp^2-hybridized C–H bond to **41**. A shift of an alkenyl group from the nickel atom to a germanium atom in **47** produces the nickel–hydride complex **48**. Intramolecular hydrogermylation of **48** gives products **49** and **50**. A similar process has been observed in the platinium-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with styrene [30].

The nickel-catalyzed reaction of **2** with 2,3-dimethylbutadiene afforded 4,5-carboranylene-1,1,3,3-tetramethyl-2-(1,2,2-trimethylethenyl)-1,3-digermylacyclopent-4-ene **52** in 68% yield (Scheme 10). A plausible mechanism for the formation of **52** involves C–H bond activation of the diene. The migration of a diene group



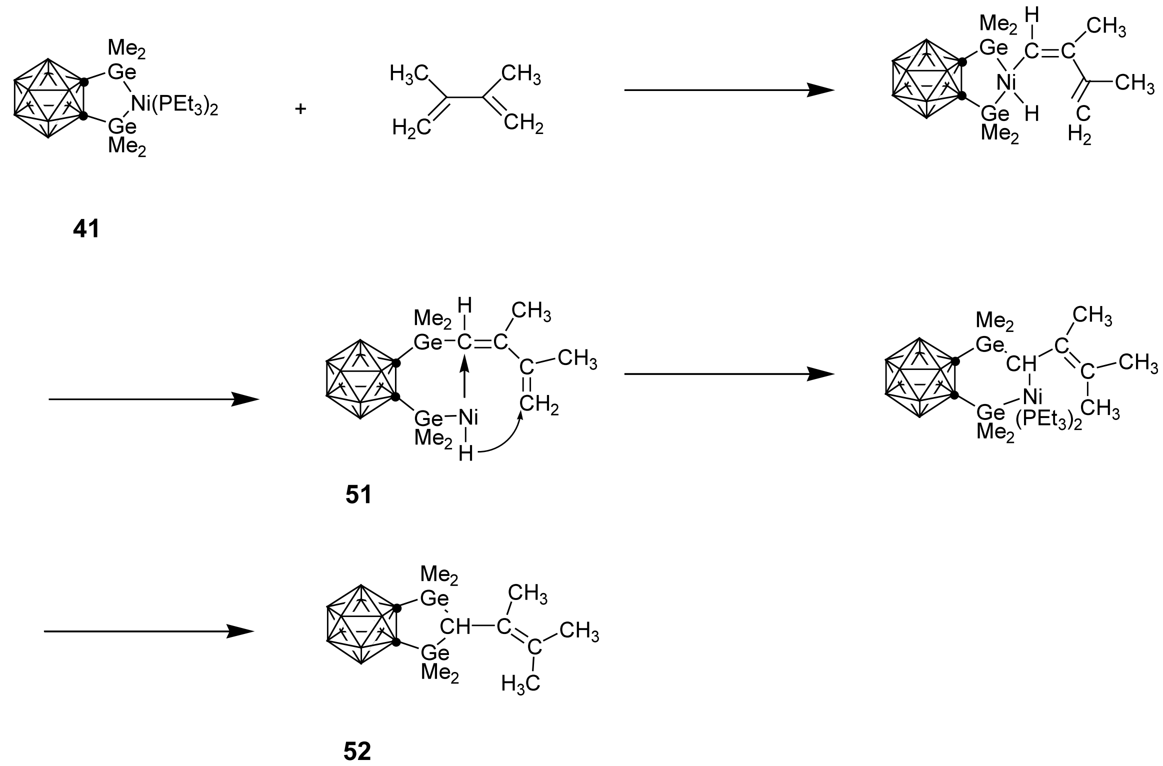
42 R^1=R^2=Ph

43 R^1=R^2=CO$_2$Me

44 R^1=Ph, R^2=H

45 R^1=Ph, R^2=SiMe$_3$

46



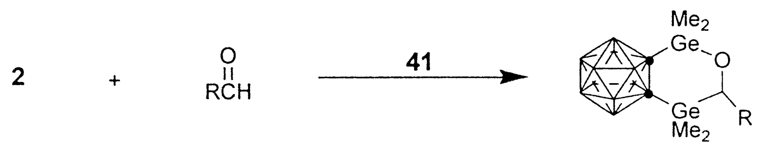
Scheme 10.

in the nickel complex to one of two germanium atoms gives complex **51**. Intramolecular addition of the Ni–H bond across the terminal carbon–carbon double bond then affords **52**. A similar situation has been observed in the nickel-catalyzed reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene with dienes [31].

Isobutyraldehyde readily reacted at room temperature with **2** in the presence of a catalytic amount of **41** to give 5,6-carboranylene-1,1,4,4-tetramethyl-2-oxa-3-isopropyl-1,4-digermylacyclohex-5-ene **53**. In a similar fashion, the nickel-catalyzed reactions of **2** with aromatic aldehydes such as 4-cyanobenzaldehyde and *p*-methoxybenzaldehyde yielded the corresponding six-membered cyclic insertion products **54** and **55**.

In marked contrast to the nickel catalyzed double silylation of **1** with *trans*-cinnamaldehyde, which gives the insertion product of a carbonyl group into each of the C–Si bonds [14], the nickel-catalyzed double germylation of **2** with *trans*-cinnamaldehyde afforded the six-membered cyclic insertion product **56**. Accordingly, the double germylation seems to be quite different from the double silylation under the same reaction conditions, owing probably to the difference in Si–O and Ge–O bond strengths and steric hindrance.

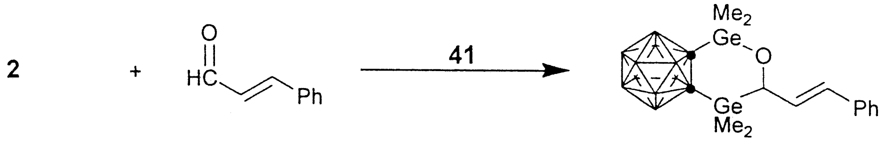
The nickel-catalyzed reactions of **2** with non-activated nitriles such as propionitrile and benzonitrile produce no nitrile adducts. However, activated nitriles such as diphenylacetonitrile react with **2** in the presence of a



53 R=$CHMe_2$

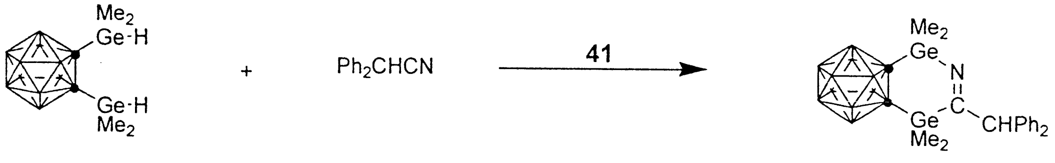
54 R=C_6H_4CN-*p*

55 R=C_6H_4OMe-*p*



56

catalytic amount of **41** to give the six-membered cyclic insertion product **57**. Such nitrile insertions have been observed in the nickel catalyzed double silylation reactions of **1** with nitriles without an α-hydrogen.



2

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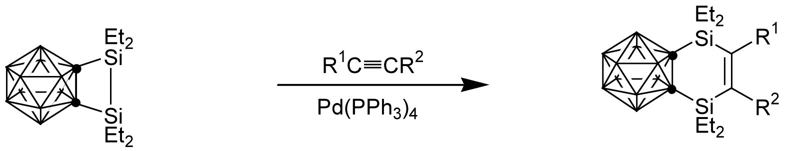
9. Palladium-catalyzed double silylation of 3,4-carboranylene-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene



3

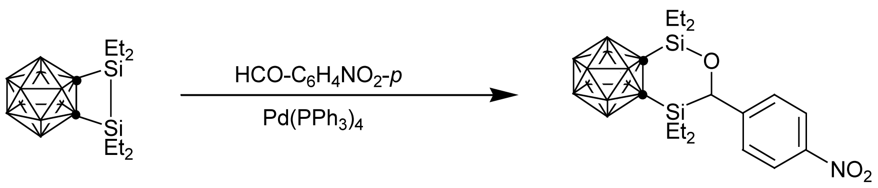
58 R^1=Ph, R^2=H

59 R^1=Ph, R^2=Me

60 R^1=n-C_4H_9, R^2=H

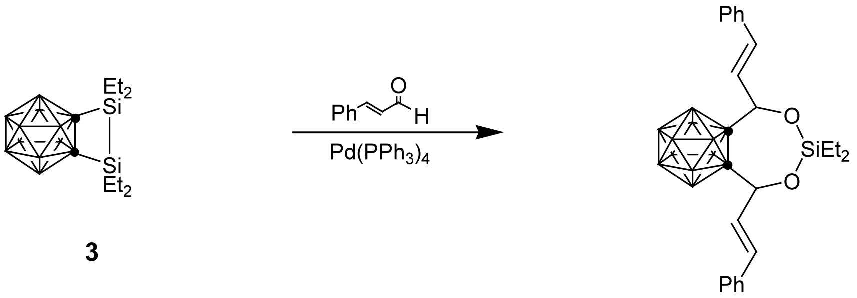
While the Pd complex readily catalyzed the double silylation with **3**, Pt and Ni complexes proved to be much less efficient owing probably to inertness and extreme instability, respectively. Thus, the palladium-catalyzed reaction of **3** with phenylacetylene afforded 5,6-carboranylene-1,1,4,4-tetraethyl-2-phenyl-1,4-disilacyclohex-2-ene **58** in 62% yield [32]. In a similar fashion, the palladium catalyzed reaction of **3** with other alkynes such as 1-phenyl-1-propyne, and 1-hexyne yielded the six-membered cyclic insertion products **59** and **60**. The formation of **58**–**60** can be explained by the reaction of the intermediate 4,5-carboranylene-1,1,3,3-tetraethyl-1-pallada-2,3-disilacyclopent-4-ene with alkynes. It is also noted that the palladium catalyzed reaction of **3** with 1-hexyne is quite different from the analogous catalyzed reaction of **1** in that the former gives the six-membered cyclic insertion product.

The double silylation reactions of carbonyl compounds such as benzaldehyde, acetone, and acetopheneone with **3** in the presence of a palladium catalyst produced no carbonyl adducts. However, reactive aldehydes such as 4-nitrobenzaldehyde readily react with **3** to give **61** in 37% yield. The insertion of an aldehyde carbonyl group into the Si–Si bond promoted by a fluoride ion was noted [15].



3 **61**

Treatment of **3** with four equivalents of *trans*-cinnamaldehyde in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ gave 6,7-carboranylene-1,5-bis(styrenyl)-2,4-dioxa-3,3-diethyl-3-silacyclohept-6-ene **62**.

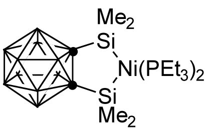


3 **62**

The X-ray study of **62** showed it to be the insertion product of two carbonyl ligands into the C–Si bond of **3**. The molecule contains a C$_4$SiO$_2$ seven-membered ring. Such an insertion of the carbonyl unit into *o*-carborane has observed in Yamamoto's work [33] on the chemoselective addition of *o*-carborane to aldehyde groups.

10. Isolation of bis(silyl)M and bis(germyl)M complexes (M = Pd and Pt)

Bis(silyl)- and bis(germyl)complexes (M = Ni, Pd, and Pt) are believed to be the key intermediates in a number of metal-catalyzed transformation of organosilanes and organogermanes, such as hydrosilylation and double silylation of unsaturated organic substrates [34]. Previously, we have mentioned the reactivity and isolation of two bis(silyl)metal complexes (**7** and **37**) and one



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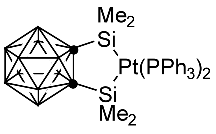

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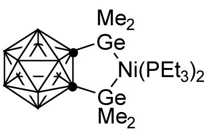
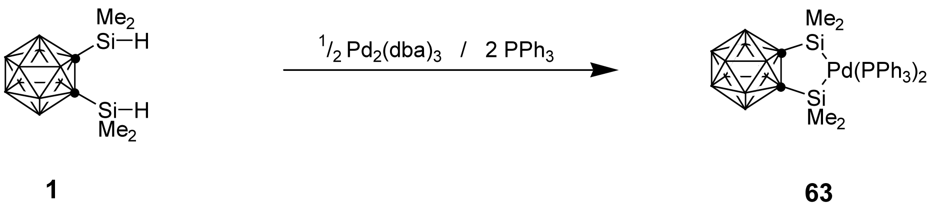


41

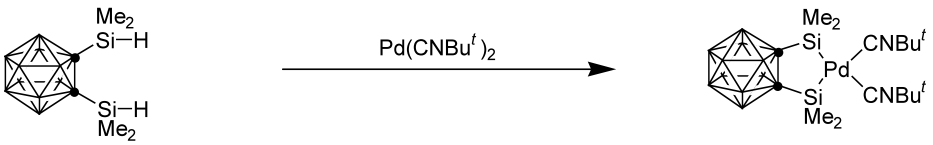
bis(germyl)nickel complex **41**. Other related complexes have been prepared in our laboratory. Thus, the bis(silyl)palladium complex **63** can be prepared by the reaction of **1** and $Pd_2(dba)_3$–$2PPh_3$ in 77% yield. Use of tetrakis(triphenylphosphine)palladium did not give the product **63**. The yellow product **63** was also found to be a good reactant in the double silylation reaction with a variety of alkynes.



1

63

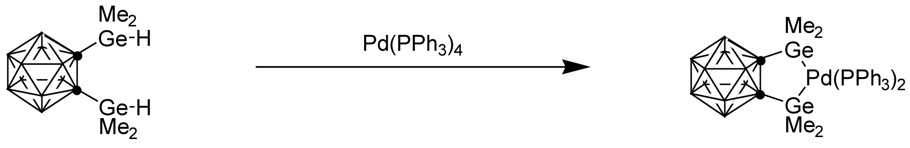
The ligand **1** reacted with bis(*t*-butylisocyanide)palladium to give the five-membered bis(silyl)palladium complex **64**, which is quite stable in air. The compound **64** was not reactive for double silylation reactions with any unsaturated organic substrates. Treatment of **2** with $Pd(PPh_3)_4$ in toluene resulted in the oxidative additon of Ge–H to the palladium to afford the bis(germyl)palladium complex **65** as yellow crystals in 80% yield



1

64

The palladium intermediate **65** readily reacted with alkynes to give the double-germylation products [35].

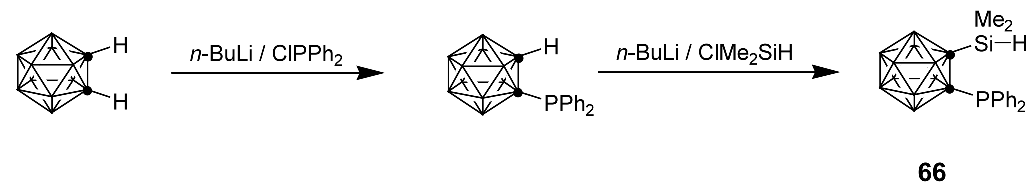


2

65

Phosphinoalkylsilanes as chelate ligands with transition metals have been well documented, in order to obtain a better understanding in some metal-catalyzed reactions such as hydrosilylation [36]. In this connection, we prepared a new class of *cis*-or *trans* bis-chelate metal complexes with a bulky *o*-carborane [37].

The phosphinosilane **66** has been synthesized using a two-step procedure. The reaction of $(PPh_3)_2Pt(C_2H_4)$ Pt and phosphinosilane **66** leads to *trans*-bis(silyl)platinum complex **67**. For **67**, a *trans*-arrangement for the phosphinosilyl ligands in a typical square–planar Pt(II) environment can be easily assigned by $^1J_{Pt-P}$ values in the range of 4049–4055 Hz. Initial attempts to isomerize the *trans* isomer have been unsuccessful. However, in the presence of dimethylacetylenedicarboxylate (DMAD) the *trans* isomer **67** rearranges to the *cis* isomer **68**.



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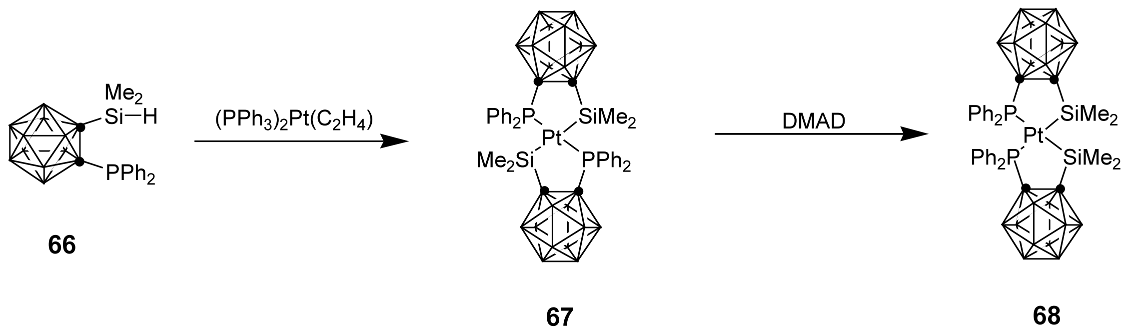

11. Conclusions

We have prepared three ligands **1**–**3** containing *o*-carboranylene units. The reactions of **1** and **2** with $Ni(PEt_3)_4$ afforded the bis(silyl)- and bis(germyl)nickel complexes **7** and **41**, which were found to be efficient catalysts in double-silylation and germylation reactions. The cyclic bis(silyl)nickel intermediate **7** catalyzed a variety of unsaturated organic substrates such as alkynes, alkenes, aldehydes, and nitriles, generating new classes of heterocycles. In marked contrast to the bis(silyl)palladium or platinum complexes reported previously, the intermediate **7** was found to exhibit unusual reactivities. The reactive intermediate, namely the cyclic bis(germyl)nickel complex **41** also reacts with unsaturated organic substrates such as alkynes, alkenes, aldehydes, and nitriles, giving a new class of heterocyclic compounds. Compared with the nickel intermediate **7**, the reactivity of the bis(silyl)palladium and platinum complexes is markedly decreased, owing probably to increased M–Si bond strength. We also isolated many bis(silyl)- and bis(germyl)complexes, which are believed to be the key intermediates in a number of metal-catalyzed double silylations. Indeed, the complexes were found to be highly effective for the activation of unsaturated organic substrates.

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