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Reaction of 5-$(CH_3)_2S$-6-$[((CH_3)_3Si)_2C{=}CH]$-$B_{10}H_{11}$ with Cyclopentadienylnickel Carbonyl Dimer

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Introduction

The investigation of the chemistry of metallacarboranes derived from monocarbon carboranes has lagged behind that of metallacarboranes derived from the dicarbollide ligand due to the relatively few examples of monocarboranes available for conversion into metallacarboranes.[1−7]

Several years ago it was reported that the reaction of decaborane(14) with the silylated acetylene bis(trimethylsilyl)acetylene, in the presence of dimethyl sulfide, resulted in the formation of two products, an alkenyldecaborane and a monocarbon carborane.[8] In that communication and a subsequent paper, some reactions dealing with the chemistry of the monocarbon carborane[6,8] were reported, but none involving the alkenyldecaborane product.

The reaction of the alkenyldecaborane product with $[(\eta^5\text{-}C_5H_5)Ni(CO)_2]_2$ results in the formation of two products: 1-$(\eta^5\text{-}C_5H_5)$-2-$[((CH_3)_3Si)_2CH]$-1,2-$NiCB_{10}H_{10}$ (**I**) and 1-$(\eta^5\text{-}C_5H_5)$-7-$[((CH_3)_3Si)_2CH]$-1,7-$NiCB_{10}H_{10}$ (**II**). The formation of these products is the result of incorporation of the $(\eta^5\text{-}C_5H_5)Ni$ group as well as one carbon atom of the bis(trimethylsilyl)ethylene group initially present in the alkenylborane. Insertion of a metal fragment as well as of a ligand is rare but not unprecedented. For example photolysis of 6-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]B_{10}H_{13}$ in THF results in the formation of 1-$(\eta^5\text{-}C_5H_5)$-2-THF-1,2-$FeCB_{10}H_{10}$.[9] Reaction of $B_{10}H_{13}^-$ with $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ in the presence of NaH also results in the formation of monocarbon carboranes in which both the metal and one of the carbonyl groups is incorporated to form an icosahedral monocarbon carborane.[10]

Experimental Section

Reaction of 5-$(CH_3)_2S$-6-$[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ with Cyclopentadienylnickel Carbonyl Dimer. In a typical reaction, 0.50 g (1.4 mmol) of the alkenyldecaborane 5-$(CH_3)_2S$-6-$[((CH_3)_3Si)_2C{=}CH]$-$B_{10}H_{11}$, prepared according to the literature procedure,[8] was dissolved in 35 mL of dry THF. To the resulting solution, 0.43 g (1.4 mmol) of cyclopentadienylnickel carbonyl dimer dissolved in 10 mL of THF was added through an addition funnel. The red solution was then transferred to a 100 mL round bottom flask equipped with a high vacuum stopcock, frozen, and degassed three times before heating the solution at reflux temperature for 24 h. The volatile fraction was then removed in vacuo and the resulting red-brown solid extracted with dry methylene chloride. The methylene chloride solution was concentrated to approximately 3 mL, stirred with silica gel, transferred to a column, and eluted with benzene, resulting in the separation of two bands. The first band was identified as 1-$(\eta^5\text{-}C_5H_5)$-2-$[((CH_3)_3Si)_2CH]$-1,2-$NiCB_{10}H_{10}$ (**I**) [0.18 g, (0.44 mmol, 31% yield) by direct comparison to its ^1H and ^{11}B NMR with the reported data in the literature. The second band isolated was identified as 1-$(\eta^5\text{-}C_5H_5)$-7-$[((CH_3)_3Si)_2CH]$-1,7-$NiCB_{10}H_{10}$ (**II**) [0.13 g (0.31 mmol, 22% yield), yellow crystals, mp 195−7 °C]. Mass measurements for $^{12}C_{13}{}^{1}H_{34}{}^{11}B_{10}{}^{58}Ni^{28}Si_2$: calculated, 414.2483; found, 414.2482.

Results and Discussion

The major product obtained from the reaction mixture was the previously known nickelacarborane, but the other product obtained in significant amounts warrants discussion about how both products could have formed. The formation of **II** is somewhat surprising since thermolysis of **I** at 350 °C results in decomposition. Furthermore reaction at lower temperatures yielded unreacted **I** only. A probable explanation for the formation of **I** and **II** could be that the initial attack of the $(\eta\text{-}C_5H_5)Ni$ unit on the open face of the alkenylborane results in the formation of an initial intermediate in which the alkene group interacts with the Ni atom. This intermediate can rearrange into the two observed products, depending on which side of the molecule incorporates the $(\eta\text{-}C_5H_5)Ni$ and the carbon atom of the alkenyl group. If the incorporation of the $(\eta^5\text{-}C_5H_5)Ni$ unit is on the side closer to the bis(trimethylsilyl)ethylene group, namely the belt of boron atoms composed of B_6, B_7, B_8, and B_9, compound **I** is formed as depicted on reaction A shown in Figure 1. On the other hand, if the $(\eta^5\text{-}C_5H_5)Ni$ unit is incorporated on the side further away from the bis(trimethylsilyl)ethylene group, namely the belt of boron atoms composed of B_5, B_7, B_8, B_9, and B_{10}, compound **II** should be result of the reaction as depicted on reaction B also shown in Figure 1. In both cases, incorporation of one of the carbon atoms into the borane structure was observed. This could be a result of a reactive intermediate which involves coordination of the incoming nickel atom to the double bond of the bis(trimethylsilyl)ethylene group and rearrangement to the observed products as explained. The numbering scheme shown in Figure 1 for both products is that of the alkenylborane precursor, in order to account for every single boron atom present in the metallacarborane products.

A preliminary X-ray study of compound **II** afforded its gross geometry but due to twinning of the crystal it could not be refined below $R = 0.094$ and $R_w = 0.240$. The space group assigned was C_2/c. Cell constants obtained were $a = 16.300(4)$ Å. $b = 7.267(2)$ Å, $c = 38.376(10)$ Å, $\beta = 95.26(2)°$. The crystal diffracted poorly, of the 5816 collected reflections only 2919 were observed; nonetheless, it allowed confirmation of the proposed structure. An ORTEP picture of compound **II** is shown in Figure 2.

The $^{11}B\{^1H\}$ NMR spectrum of **II** shows six resonances of relative intensities 1:1:2:2:1:3, which is similar to the $^{11}B\{^1H\}$ NMR spectrum reported by Hawthorne and coworkers for the parent compound of **II**, 1-$(\eta^5\text{-}C_5H_5)$-1,7-$NiCB_{10}H_{11}$.[4] It is important to note that under ideal conditions the $^{11}B\{^1H\}$ NMR should consist of six resonances having relative intensities 1:1:2:2:2:2. Clearly the presence of the bulky trimethylsilyl group somehow affects the local symmetry of the molecule and the $^{11}B\{^1H\}$ NMR signals reflect this fact. Indeed, even in the parent compound, the ideal number of signals is not observed.[4]

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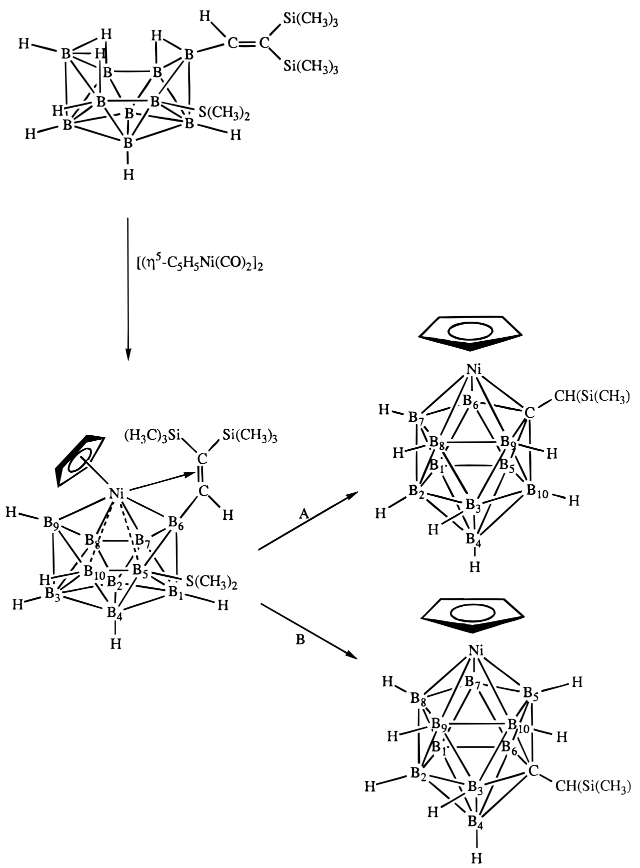

Figure 1. Proposed reaction sequence for the formation of compounds **I** and **II**.

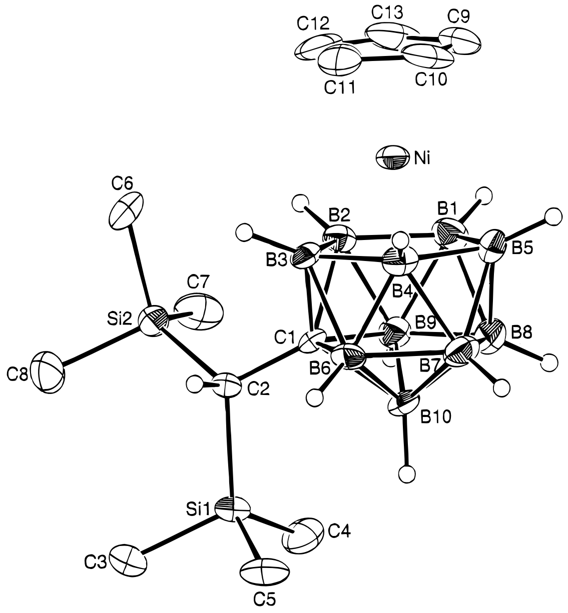

Figure 2. ORTEP drawing of compound **II**, showing 30% probability thermal ellipsoids.

Table 1. Spectroscopic Data

compound	^{11}B NMR, δ (J, Hz)	relative area
I^{a,b}	21.67 (102), 20.98 (121), 13.40 (156), 0.73 (147), −0.65 (135), −5.11 (157)	1:2:2:2:1:2
II^{c,d}	20.97 (148), 18.94 (155), 12.95 (145), 10.44 (157), −3.26 (168), −4.30 (151)	1:1:2:2:1:3

compound	^{1}H NMR, δ (relative area, assignment)
I	4.87 (5, C_5H_5), 1.35 (1, CH), 0.24 $(CH_3)_3Si$)
II	5.81 (5, C_5H_5), 1.14 (1, CH), 0.17 (18, $CH_3)_3Si$)

compound	IR, cm^{-1}
I	3030 (m), 2920 (m), 2510 (sh), 2470 (s), 1440 (s), 1280 (s), 1070 (sh), 1020 (s), 930 (sh), 840 (s), 750 (w)
II	3110 (w), 2960 (m), 2920 (m), 2890 (sh), 2860 (w), 2620 (m), 2560 (s), 2400 (m), 1450 (w), 1420 (m), 1260 (m), 1240 (s), 1210 (w), 1100 (m, br), 1040 (m), 1010 (w), 980 (m), 930 (w), 900 (m), 850 (w), 840)s, 830 (s), 810 (sh), 760 (w), 690 (m), 670 (w), 460 (m, br)

^{a} 115.5 MHz. ^{b} CD_2Cl_2 solvent. ^{c} 160.5 MHz. ^{d} C_6D_6 solvent.

Instead, five resonances of relative intensities 1:1:2:2:4 were observed, and it was attributed to signal overlap.The attempted thermolytic conversion of **I** into **II** failed. This is an unexpected result, since conversion of the parent metallacarborane 1-(η^5-C_5H_5)-1, 2-$NiCB_{10}H_{11}$ to 1-(η^5-C_5H_5)-1, 7-$NiCB_{10}H_{11}$ has been previously reported.[4] In other mixed metal metallacarboranes, migration of the metal has been observed.[11] One possible explanation for the failure of the conversion of **I** into **II** could be the bulkiness of the bis(trimethylsilyl)methyl group bonded to the carbon atom incorporated in the carborane cage. This steric interaction could prevent the 1,2- to 1, 7-rearrangement, which is possible in systems that are less sterically hindered.

Hawthorne has observed this type of rearrangement in monocarbon carboranes.[12] This rearrangement, known as the diamond−square−diamond mechanism, was first proposed by Lipscomb.[13] This mechanism involves a series of steps in which bond breaking, rotation, and bond formation result in the isomerization of the metallacarborane. The presence of the bis(trimethylsilyl)methyl group in **I**, in proximity to the cyclopentadienyl ligand of nickel, could prevent the diamond-square-diamond mechanism from taking place. Indeed, the X-ray structure of **I**,[6] shows that the cyclopentadienyl ligand is being pushed away from planarity with the open face of the monocarbon carborane by the bis(trimethylsilyl)methyl ligand. The dihedral angle between the cyclopentadienyl ligand and the open face of the carborane was found to be 9.5°. This clearly indicates that the bis(trimethylsilyl)methyl group is pushing the cyclopentadienyl ligand away by steric interactions. Since in the dsd mechanism these two groups will have to get closer to each other at some point, this clearly prevents the isomerization of **I** into **II**.

In summary, the reaction of 5-$S(CH_3)_2$-6-[($(CH_3)_3Si)_2C{=}CH$]-$B_{10}H_{11}$ with cyclopentadienylnickel carbonyl dimer resulted in the formation of the two above-mentioned products. The incorporation of the nickel group as well as one of the carbons of the bis(trimethylsilyl)ethylene unit to form two metallamonocarbon carboranes although not unprecedented is a rare occurrence. The relationship between **I** and **II** seems to be based on a common precursor, which, depending on which side of the proposed metallaborane intermediate is attacked by these groups, results in the formation of either **I** or **II**.

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Supporting Information Available: Tables of crystallographic data, bond lengths and angles, atomic coordinates, and thermal parameters (7 pages). Ordering information is available on any current masthead page.

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