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Palladium-Catalyzed Heck Reactions of Styrene Derivatives and 2-Iodo-*p*-carborane

Ludvig Eriksson, Karl Johan Winberg, Rodrigo Tascon Claro, and Stefan Sjöberg*

Uppsala University, Institute of Chemistry, Department of Organic Chemistry, Box 599,
S-751 24 Uppsala, Sweden

ssj@kemi.uu.se

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p-Carborane has been vinylated on the 2-*B*-atom in high yields using the Heck reaction. Thus, the reaction between 2-iodo-*p*-carborane and various styrenes [4-H-, 4-C_6H_4-, 4-Cl-, 4-Br-, 4-NO_2-, 4-CH_3O-, and 4-CH_3-] resulted in the production of the corresponding *trans*-β-(2-*B*-*p*-carboranyl)-styrene in DMF solution when reacted in the presence of silver phosphate and the palladacycle Herrmann's catalyst.

Introduction

The carboranes $C_2B_{10}H_{12}$ exhibit remarkable chemical stability and are generally biologically inactive.[1] The use of carboranes in boron neutron capture therapy (BNCT) for cancer has attracted much interest in recent years. For this purpose, numerous carborane-containing derivatives of biomolecules have been synthesized.[2−5] Until recently, only a few cases, besides the BNCT application, have been described where use has been made of the carborane cages as hydrophobic pharmacophores in biologically active molecules. One example of the most explored compounds is *o*-carboranylalanine, the *o*-carboranyl analogue of phenylalanine, which has been used to replace phenylalanine and tyrosine in a number of biological active peptides. This work has recently been reviewed.[6] Research on the use of carboranes as hydrophobic pharmacophores has recently been intensified,[7−9] particularly by Endo.[10−13] One of the most frequently used procedures for the synthesis of functionalized carborane derivatives is to let a pre-functionalized acetylene react with decaborane. This leads to the formation of an *o*-carborane derivative. However, these *o*-carboranes are generally easily degraded to the corresponding anionic *nido*-analogue in a nucleophilic environment.[14−19] Attachment of functional groups to the C-1 carbon and the B-2 boron of *p*-carborane can form compounds with similar geometry as a corresponding C-1/C-2-functionalized *o*-carborane and will be more stable toward degradation than the analogous *o*-carborane derivatives. A B-2 monofunctionalized *p*-carborane possesses two nonequivalent carbons that may allow a selective introduction of a second functional group at either the C-H ortho or the C-H meta position to the B-2 boron atom. Furthermore, B-2 functionalized *p*-carborane might also find applications in the material science field. High chemical and thermal stability in combination with the rigid structure of the carborane cage and the possibility of attachment of different types of substituents make them good candidates for the synthesis of new and interesting materials.[20−26]

In previous work, we have demonstrated that it is feasible to react the boron-iodinated 2-iodo-*p*-carborane

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* To whom correspondence should be addressed. Fax: +46 18-4713818.

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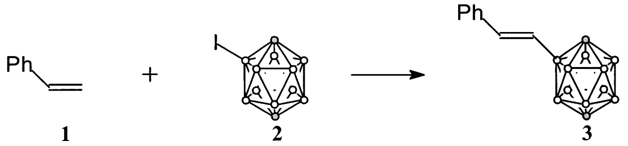
TABLE 1. Heck Coupling of 2-Iodo-*p*-carborane and Styrene



entry[a]	catalyst (mol %)	base	ratio of boronated products[b] (**3**/**2**/side products)
1	$Pd_2(dba)_3$/dppb (2/4)	CsF, 3 equiv	∼5/73/∼22
2	$Pd_2(dba)_3$/dppb (2/4)	K_2CO_3, 1.5 equiv	∼5/89/∼5
3	$Pd_2(dba)_3$/dppb (2/4)	NaOAc, 1.5 equiv	0/100/0
4	$Pd_2(dba)_3$/dppb (2/4)	Ag_3PO_4, 2 equiv	15/81/4
5	**4** (1)	CsF, 3 equiv	32/49/19
6	**4** (4)	CsF, 3 equiv	62/19/19
7	**4** (1)	Cs_2CO_3, 2 equiv	0/60/40
8	**4** (1)	Ag_3PO_4, 2 equiv	4/96/0
9	**4** (1)	$K_3PO_4 \cdot nH_2O$, 2 equiv	33/50/17
10[c]	**4** (1)	KOAc, 1.5 equiv	50/34/16
11[c]	**4** (1)	$K_3PO_4 \cdot nH_2O$, 2 equiv	0/0/100
12[c]	**4** (1)	Ag_3PO_4, 2 equiv	>95/0/<5

[a] General conditions: 1 equiv (100 mg) of2-iodo-*p*-carborane **2**, 1.2 equiv of styrene **1**, and 2 mL of DME. The mixture was heated to reflux and left overnight with stirring under argon. [b] Determined by ^{11}B NMR. [c] 2 mL of DMF was used as solvent, and the reactions were performed at 120 °C.

with arylboronic acids under mild Suzuki−Miyaura reaction conditions.[27] Problems arising mainly from an unfavorably shifted equilibrium in the oxidative addition of the B−I bond to the Pd^0 species in the catalytic cycle could be overcome, which led us to further investigations of palladium-mediated couplings. There are several reports of olefinic attachments to carboranes in the literature.[28−37] However, the rather mild and straightforward Heck reaction has not been applied, to our knowledge, to a boron iodide of any species before.

In the present paper, we desribe the synthesis of a number of *trans*-*β*-(2-*B*−*p*-carboranyl)styrenes.

Results and Discussion

Styrene (**1**), which is a standard Heck-coupling reagent, was chosen as a substrate for the development of the 2-iodo-*p*-carborane (**2**) coupling. At an early stage, it was clear that the stability of the catalytic system would become the main obstacle to overcome. The catalytic system of the earlier reported work of Suzuki-type cross-couplings[27] of (**2**) and arylboronic acids was initially applied to give low yields of the trans isomer of *β*-(2-*B*-*p*-carboranyl) styrene (**3**) (entries 1−4, Table 1). Throughout these attempts, palladium precipitation was observed shortly after initiation of the reaction.

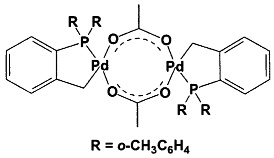


FIGURE 1. Palladacycle Herrmann's catalyst (**4**).

During the past decade, palladacycles have been shown to be highly efficient and robust in Heck-type reactions.[38,39] Therefore, the commercially available palladacycle Herrmann's catalyst (**4**, Figure 1) was introduced with different bases to the model reaction (entries 5−9).[40,41]

Using 1 mol % of **4** (vs 2-iodo-*p*-carborane) and CsF as a base in DME gave an increased conversion of the model reaction (entry 5). Increasing the catalyst loading to 4% of **4** enhanced the conversion further to give a rather high yield of the desired styrene derivative **3** (entry 6). Alternative bases gave poorer results (entries 7−9).

Since Heck-type reactions catalyzed by palladacycles often require temperatures higher than the boiling point of DME,[38] a few attempts were made to perform the coupling in DMF at 120 °C (entries 10−12). And by combining the catalyst **4** with silver phosphate in DMF, we obtained full conversion of the iodocarborane **2** and 95% of target compound **3** was formed (entry 12).

A suggested approximate mechanism of this application of the Heck reaction is given in Scheme 1. In the scheme, we have chosen to draw the catalytic cycle in a

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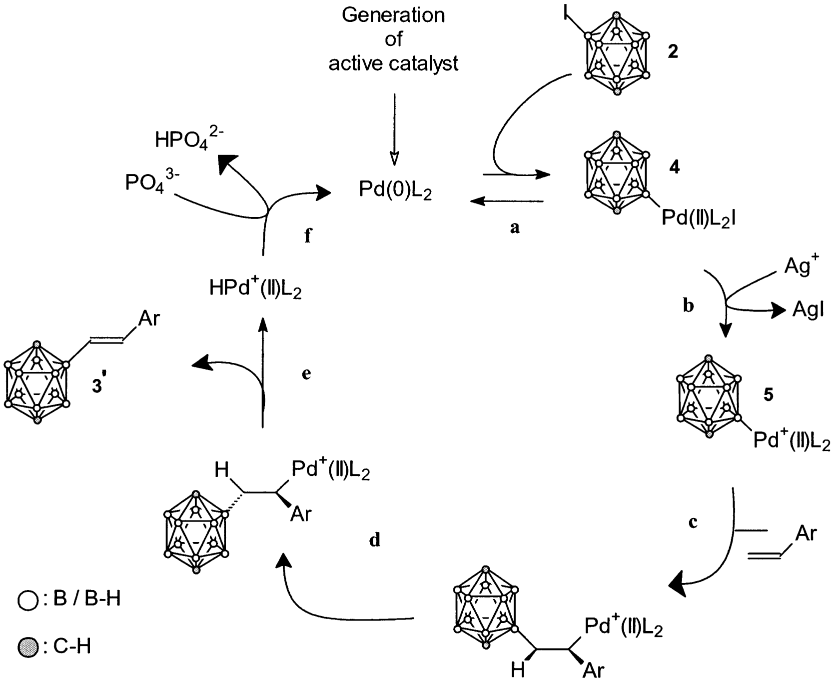
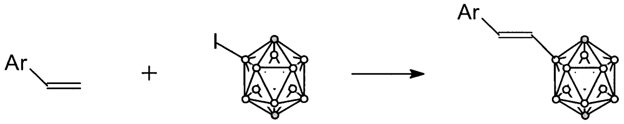
SCHEME 1. Plausible Mechanism of the Heck Reaction[a]



[a] Key: (a) Reversible oxidative addition of 2-iodo-*p*-carborane (**2**); (b) silver-mediated iodide abstraction; (c) styrene complexation and *syn*-insertion; (d) Internal rotation; (e) *syn*-elimination to form *trans-β-(2-B-p*-carboranyl)styrene derivative **3′**; (f) base-promoted proton scavenging and regeneration of Pd^0.

Pd^0/Pd^{II} pathway as argued for by Herrmann and co-workers;[38] however, a Pd^{II}/Pd^{IV} pathway also has been suggested and may be present.[42] The cationic-like palladium species **5** in the scheme, formed from **4** by halogen abstraction, is given in accordance with work presented by Hallberg and co-workers.[43,44] They propose that the silver phosphate has a dual function in these types of reactions. Besides the proton-scavenging role of the phosphate, it has been proposed that the silver ion can abstract the iodide (step b, Scheme 1) from the Pd^{II} complex formed by the oxidative addition of an aryl halide (in this case the boron−iodide bond of **2**, step a). This would generate an electrophilic, cationic Pd^{II} complex. It has been shown that the oxidative addition of the boron−iodide bond of **2** and 9-iodo-*m*-carborane to Pd^0 complexes is a reversible process, with the equilibrium shifted to disfavor formation of the Pd^{II} complex[27,45] (complex **4** in Scheme 1). The complex **4** enters the next step of the cycle to give the cationic complex **5**. A cationic Pd^{II} complex, such as **5**, would likely shift the equilibrium of the oxidative addition, which could explain the high formation of the styrene derivative **3** in the model reaction.

TABLE 2. Screening of 2-Vinylstyrene and Various Styrene Derivatives



2 **3, 6-11**

entry	substrate Ar-CH=CH$_2$	reaction time, h	product β-(2-*B*-*p*-carboranyl)-styrene	isolated yield (%)
1	Ph	4	**3**	91
2	4-Ph-Ph	12	**6**	80
3	4-Cl-Ph	4	**7**	82
4	4-Br-Ph	12	**8**	64
5	4-NO$_2$-Ph	12	**9**	75
6	4-CH$_3$O-Ph	6	**10**	73
7	4-CH$_3$-Ph	8	**11**	94
8	2-pyridine			no reaction

The best reaction conditions found (entry 12, Table 1) were used for the reaction with various styrene derivatives containing both electron-donating and electron-withdrawing substituents. The reaction time and the *isolated yield* of the respective *trans*-β-(2-*B*-*p*-carboranyl) styrenes **3** and **6**−**11** are shown in Table 2. As shown in the entries, most reactions proceeded with high yields. The *p*-chlorostyrene (entry 3) reacted cleanly and afforded no detectable (by GC−MS) homocoupled side product. The *p*-bromostyrene, however, partially reacted by homocoupling (to give $CH_2{=}CHC_6H_4CH{=}CHC_6H_4$-*p*-Br), and the yield of compound **8** (entry 4) was thus lower than for the chloro compound. 2-Vinylpyridine did not react (entry 8), which may be due to palladium complexation of the pyridinium nitrogen.

Besides 2-vinylpyridine, also butyl acrylate and acrylonitrile, which often readily react in these types of reactions, were not converted under the parent reaction conditions. Moreover, the more electron-deficient styrenes, such as 4-nitrostyrene (entry 5), reacted more slowly than the more electron-rich styrene analogues.

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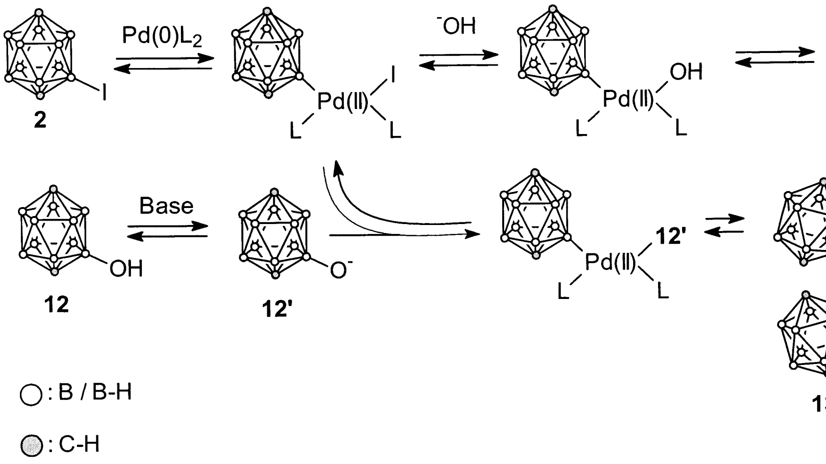
SCHEME 2 Palladium-Catalyzed Formation of 12 and 13



Electron-poor compounds such as these, with better π-accepting and poorer π-donating properties than the more electron-rich styrene analogues, have been shown to coordinate slower to cationic complexes (such as **5**, Scheme 1) than to a neutral complex.[46] One explanation for this phenomenon is that there exists a competition between the coordination of the olefin and good σ-donors which slows down the reaction rate.[47] Thus, coordination of complex **5** to other species in the reaction mixture such as the anionic phosphate is likely dominating in the case of butyl acrylate and acrylonitrile.

As mentioned earlier, a clear difference in reaction time can be seen among the various styrene derivatives. This indicates that the styrene derivatives used in this screening are involved in a rate-limiting reaction step. Most likely, this rate-limiting reaction step is the alkene complexation step.[48]

Boron-iodinated carboranes has been shown to undergo palladium-catalyzed nucleophilic substitutions,[45,49] and analyzing the side products formed under conditions shown in entry 11, Table 1, two major components could be detected, 2-hydroxy-*p*-carborane (**12**) and the previously unreported bis(2-*B*-*p*-carboranyl) ether (**13**). The hydroxide is likely generated from water-contaminated potassium phosphate. Compounds **12** and **13** were also isolated when the experiment was repeated on a larger scale. A blank experiment, without influence of catalyst, led to no product formation. As suggested in Scheme 2, the formation of **12** and **13** are two other examples of this substitution reaction, which under controlled conditions allow a variety of nucleophiles.

Conclusions

In this paper, we have shown that by a proper choice of reaction conditions it is possible to use the Heck-type reaction for preparation of a number of *trans*-β-(2-*B*-*p*-carboranyl)styrenes. Furthermore, 2-hydroxy-*p*-carborane and the previously unreported di-2-*p*-carboranyl ether can be formed by palladium-catalyzed nucleophilic substitution in the presence of a hydroxide. Regarding the use of electron-poor olefins for the coupling reaction, it is likely that the development of a catalytic system with nonionic intermediates is required. Work on the corresponding cross-coupling reaction using other halogenated carboranes such as 9-iodo-*m*-carborane and development of a catalytic system which allows the introduction of acrylates is in progress.

Experimental Section

General Details. All experiments were performed under argon atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectra were recorded in $CDCl_3$ at 400, 100.6, and 128.3 MHz, respectively. ^{11}B NMR chemical shifts were referenced to external boron trifluoride etherate (0.00 ppm). Coupling constants (*J*) are reported in Hz. Broad carborane BHs are not reported. For column chromatography, 35−70 μm silica gel was used. Mass analyses were performed by direct inlet using ESI. Mikro Kemi AB performed elemental analyses. DMF was first distilled from Na_2SO_4 followed by distillation from molecular sieves (4 Å). Reaction chemicals were used as purchased unless otherwise noted. 2-Iodo-*p*-carborane was prepared according to the procedure described by Jones and co-workers.[50]

General Procedure for the Heck Coupling Reactions. Preparation of *trans*-β-(2-*B*-*p*-Carboranyl)styrene (3). To a solution of 2-iodo-*p*-carborane (300 mg, 1 equiv), silver phosphate (700 mg, 1.5 equiv), and Herrmann's catalyst (*trans*-di-μ-acetatobis[2-(di-*o*-tolylphosphino)benzyl]dipalladium)(II) (10.4 mg, 0.01 equiv) in dry DMF (6 mL) was added styrene (1.3 mmol, 1.2 equiv). The mixture was then immersed in a preheated oil bath (120 °C) for 6 h. The reaction was monitored by TLC using pentane as eluent. The reaction was stopped *either* after precipitation of palladium-black and decolorization of the supernatant *or* when all 2-iodo-*p*-caborane was consumed. The resulting mixture was diluted with methylene chloride and filtered through a pad of Celite, which was carefully washed with methylene chloride. DMF was removed by water extraction, and the resulting solution was dried over sodium sulfate, filtrated, and concentrated under reduced pressure. The crude product was purified by flash chromatography using pentane as eluent to give 246 mg (91%) of **3** as white crystals. A sample for elementary analysis was obtained by recrystallization from hexane. Mp: 47−48 °C. ^{1}H NMR

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MHz ($CDCl_3$): δ 7.43 (m, 2H, arom), 7.33 (m, 2H, arom), 7.26 (m, 1H, arom) 6.89 (d, 1H, vinyl CH, *J* = 18), 6.37 (d, 1H, vinyl CH, *J* = 18), 2.95 (s, 1H, HC-cage) and 2.84 (s, 1H, HC-cage). ^{13}C NMR ($CDCl_3$): δ 142.8, 138.2, 128.8, 128.2, 126.6, 123.0 (br.), 65.8 and 63.6. ^{11}B NMR ($CDCl_3$): δ −6.4 (1B), −13.9 (2B), −15.0 (6B) and −17.9 (1B). IR (KBr) ν_{max}/cm^{-1}: 3058 (m) and 2608 (s). MS (IE): *m*/*z* calcd for M$^+$ of the highest intensity signal of the boron cluster 246, found 246. Anal. Calcd for $C_{10}H_{18}B_{10}$: C, 48.75; H, 7.36. Found: C, 48.73; H, 7.33.

2-Hydroxy-*p*-carborane (12) and Bis(2-*B*-*p*-carboranyl) Ether (13). To a solution of 500 mg (1.85 mmol) of 2-iodo-*p*-carborane, 786 mg (3.70 mmol) of anhydrous K_3PO_4, and 17.4 mg (18.5 μmol) of Herrmann's catalyst in DMF (10 mL) was added 2 drops of water. The resulting mixture was heated with stirring to 120 °C for 6 h. After cooling, the mixture was diluted with 100 mL of CH_2Cl_2, washed with water (4 × 30 mL), dried with anhydrous $MgSO_4$, filtered, concentrated, and put on a silica column. A 91 mg (0.301 mmol) portion of **13** was isolated as a white solid by using pentane as eluent. Compound **12** (139 mg, 0.869 mmol) could be isolated as a white solid by subsequent eluation with a 1:4 mixture of diethyl ether and pentane. The analytical data of **12** were consistent with those reported in the literature (mp, MS, and elementary analysis).[51,52] NMR data of **12** have not been reported previously and are given here. ^{1}H NMR MHz ($CDCl_3$): δ 3.12 (s, 1H, HC-cage), 2.70 (s, 1H, HC-cage) and 2.50 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 65.7, 60.4. ^{11}B NMR ($CDCl_3$): δ 2.1 (1B), −14.7 (2B), −16.6 (4B), −18.3 (2B) and −24.8 (1B).

13. Mp: 146−147 °C. ^{1}H NMR MHz ($CDCl_3$): δ 3.12 (s, 2H, HC-cage), and 2.65 (s, 2H, HC-cage). ^{13}C NMR ($CDCl_3$): δ 64.5, 59.1. ^{11}B NMR ($CDCl_3$): δ 1.3 (2B), −14.8 (4B), −17.0 (8B), −18.4 (4B) ,and −24.8 (2B). IR (KBr) ν_{max}/cm^{-1}: 3053 (m), 2613 (bs), 1343 (bs) and 1159. MS (IE): *m*/*z* calcd for M$^+$ of the highest intensity signal of the boron cluster 302, found 302.

Acknowledgment. This work was supported by the Swedish Cancer Foundation and by INTAS (Grant No. 99-00806).

Supporting Information Available: Synthesis of **6**−**11**; ^{1}H, ^{13}C, and ^{11}B NMR spectra of **3** and **6**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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