To our knowledge, it is for the first time to have shown that the reaction selectivity in photocatalysis can be controlled clearly by this kind of surface modification.

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A New Type of Stabilized Carbonucleophiles with A Carboranyl Group(I)

Sang Chul Shim*, Jae Goo Shim‡, Dong Yub Lee, Young Zoo Youn, and Valery N. Kalinin†

Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701, Korea
‡*Fuel & Combustion Team, Korea Electric Power Corporation Research Center, Taejon 305-380, Korea*
†*Institute of Organoelement Compounds of Russian Academy of Science, Vavilov 28, Moscow, 117813*

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One area of interests concerns the carboranes or boron-carbon cage molecules, upon which a large part of the recent research in the boron field has centered. A significant aspect of carborane chemistry is its considerable overlap with organic, organometallic and transition metal coordination chemistry.[1]

Recently, the selective synthesis of monosubstituted icosahedral 1,2-$C_2B_{10}H_{12}$ carborane derivatives is currently of great synthetic importance. Noteworthiness is their use in the boron-neutron capture reaction as the basis of a method for cancer therapy.

Hawthorne,[2] Yamamoto,[3] and Gabel[4] reported on the synthetic methods of 1,2-dicarba-*closo*-dodecaborane (*o*-carborane) derivatives.

Meanwhile, we investigated a new type of stabilized carbonucleophiles based on the strong electron-withdrawing effect of carboranyl group.[5] Especially in order to test the ability of carboranylacetic esters to form stabilized carbanions, the palladium catalyzed C-allylation of carbonucleophiles was carried out under neutral conditions using allylic carbonates.[6]

In this article, the palladium catalyzed reaction of carbonucleophiles containing a carboranyl group was studied.

Experimental

Reagent and Instruments. Melting points were checked by using a Yamato Model MP-21 and were uncorrected. FT-IR spectra were recorded on a Mattson Galaxy 6030E FT-IR Spectrophotometer using a thin film of the sample sandwitched between NaCl plates or KBr pellets. Mass spectra were determined on a Shimadzu-QP 1000 spectrometer at 70 eV by the electron impact (EI) method. ^{1}H NMR spectra were obtained at 60 MHz on a Varian EM 360 or at 300 MHz on a Bruker AM 300 spectrometer. All chemical shifts were measured relative to TMS (δ=0.00). ^{13}C NMR spectra were obtained at 75.5 MHz on a Bruker AM 300 spectrometer with $CDCl_3$ as solvent and internal standard (δ=77.0). Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F_{254}. Preparative thin layer chromatography was prepared using Merck silica gel 60 HF_{254}, calcium sulfate and water (weight ratio=10 : 1 : 30) on 20×20 cm^2 glass plate. Column chromatography was performed using Merck silica gel 60 (70-230 mesh). Elemental analyses were performed by a Carlo Erba 1108 Elemental analyzer.

Employed 1,2-dicarba-*closo*-dodecaboranes were received from the Institute of Organoelement Compounds in Russia and identified by ^{1}H NMR, FT-IR, and GC-MS spectrometer before use.

Dibenzylideneacetone[7], ethylcinnamyl carbonate[8], ethyl allyl carbonate[8], and bis(dibenzylidene-acetone)palladium(O)[9] were prepared according to the method descrived in previous papers.

Preparation of Methyl 2-(2-phenyl-o-carboran-1-yl) acetate. To a solution of sodium metal (0.46 g, 20 mmol) and iron nitrate nonahydrate (0.20 g, 0.5 mmol) in a liq. NH_3 (200 mL) at −45 ℃ was added 1-phenyl-*o*-carborane (4.4 g, 20 mmol) in dry diethyl ether (10 mL) dropwise over 10 minutes. The reaction mixture was allowed to stir for 15 minutes, and then added sodium bromoacetate (3.3 g, 20 mmol). The reaction mixture was allowed to stir for 15 minutes, and then added sodium bromoacetate (3.3 g, 20 mmol). The mixture was allowed to stir 10 minutes in an ice bath. After the ice bath was removed, the reaction mixture was allowed to stir for 1 hour, and then quenched with

water (100 mL), and transferred to a separatory funnel, and extracted with diethyl ether. The aqueous layer was acidified by the concentrated hydrochloric acid (100 mL) to pH 4-5, then extracted with diethyl ether. The organic layer was washed with brine, and dried over magnesium sulfate, and concentrated *in vacuo*. The carboxylic acid was converted directly into ester by Fisher esterification. The crude white solid was purified by recrystallization with *n*-hexane (5.02 g, 86%). white crystal; mp. 79.0-79.5 ℃; Mass (m/e) : 292 (M^+); IR (KBr) : υ_{B-H} 2577 cm^{-1}, υ_{CO} 1744 cm^{-1}; ^1H NMR (CCl_4): δ 2.68 (s, 2H, $C\underline{CH_2}CO_2$), 3.66 (s, 3H, $CO_2\underline{CH_3}$), 7.47 (m, 5H, Ar.).

Preparation of methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-cinnamylacetate catalyzed by Pd(dba)$_2$ and DPPE. A mixture of ethyl cinnamyl carbonate (0.21 g, 1 mmol), methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate (0.29 g, 1 mmol), Pd (dba)$_2$ (0.03 g, 5 mol%), 1,2-bis(diphenylphosphino)ethane (DPPE) (0.04 g, 10 mol%) and dry THF (5 mL) was stirred under atmospheric nitrogen at room temperature for 5 hours. After addition of water the mixture was extracted by diethyl ether. The organic layer was dried over magnesium sulfate. After the solvent was removed, methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-cinnamyl-acetate was isolated by preparative TLC (silica gel, *n*-hexane : $CHCl_3$ = 1 : 1) or column chromatography. The crude solid was purified by recrystallization with hot *n*-hexane (0.361 g, 88%).

Methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-allylacetate could also be synthesized as described method above (0.315 g, 95 %).

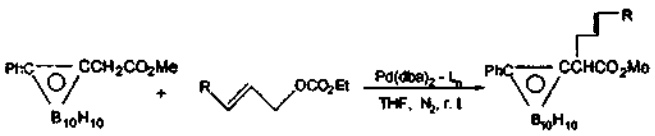
Methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-cinnamylacetate (3a). White crystal. mp. 130-131 ℃; ^1H NMR ($CDCl_3$) δ 2.35 (dd, 1H), 2.61 (m, 2H), 3.62 (s, 3H), 5.67 (m, 1H), 6.17 (d, 1H), 7.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 36.9, 49.2, 52.1, 80.6, 84.9, 123.9, 126.1, 127.6, 128.4, 129.9, 131.1, 131.4, 133.9, 136.4, 169.3; mass (m/e) 408 (M^+); IR (KBr) : υ_{B-H} 2550-2560 cm^{-1}, υ_{CO} 1744 cm^{-1}. Anal. Cald for $C_{10}H_{10}O_3$: C, 58.80; H, 6.91. Found : C, 59.80; 6.98.

Methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-allylacetate (3b). White crystal. mp. 51 ℃; ^1H NMR ($CDCl_3$ δ 2.18 (dd, 1H), 2.54 (m, 2H), 3.63 (s, 3H), 4.85 (dd, 2H), 5.29 (m, 1H), 7.53 (m, 5H); ^{13}C NMR ($CDCl_3$ δ 37.5, 49.0, 52.0, 80.7, 84.8, 118.7, 128.9, 130.0, 131.1, 131.4, 132.9, 169.3; mass (m/e) 332 (M^+); IR (KBr): υ_{B-H} 2580-2590 cm^{-1}, υ_{CO} 1750 cm^{-1}. Anal. Cald for $C_{10}H_{10}O_3$: C, 50.58; H, 7.28. Found: C, 50.65; H, 7.42.

Results and Discussion

Treatment of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate (**1**), ethyl allylic carbonate (**2a** : R=Ph, **2b** : R=H), and Pd (dba)$_2$-phosphine complex as a catalyst in THF at room temperature under the nitrogen atmosphere for 2-5 hours gave the corresponding mono C-allylated products (**3**) in good to excellent yields (Scheme 1).

The palladium-catalyzed C-alkylation reaction of *o*-carboranylacetic ester with the corresponding carbonates under neutral condition was very sensitive to the CH-acidity of carbonucleophiles. At first, we investigated the optimum condition for the allylation of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate with ethyl cinnamyl carbonate. Yields of product were affected significantly by reaction conditions as shown



1 **2** **3**

a, R=Ph b, R=H

a, R=Ph b, R=H

Scheme 1.

Table 1. Reaction of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate with ethyl cinnamyl or ethyl allyl carbonates catalyzed by Pd(O) at various conditions[a]

Exp. No.	Cat (mol%)	Time (hr)	Yield[b]
1	1	10	53
2	3	10	81
3	5	10	89
4	10	10	89
5	5	5	88
6[c]	5	24	86
7[d]	5	24	85
8[e]	5	5	95

[a] Methyl 2-(2-phepyl-*o*-carboran-1-yl)acetate (0.292 g, 1 mmol), ethyl cinnamylcarbonate (0.206 g, 1 mmol) or ethyl allylcarbonate (0.130 g, 1 mmol), Pd(dba)$_2$, DPPE, THF (3 mL) were stirred under atmospheric N_2 at room temperature. [b] Isolated yield. [c] Molar ratio; *o*-carborane : carbonate = 1 : 2 at 60 ℃. [d] Atmospheric CO at room temperature. [e] Ethyl allyl carbonate instead of ethyl cinnamyl carbonate.

in Table 1.

The yield of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate was influenced by the molar ratio of Pd(dba)$_2$. A small amount of the catalyst slowed down the overall reaction rate. Increasing the molar ratio of Pd(dba)$_2$ over methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate from 1 mol% to 3, 5 and 10 mol% in 10 h at room temperature enhanced the yields of the C-allylated products to 53, 81, 89 and 89% respectively (Exp. Nos. 1-4). When the molar ratio of the catalyst over methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate was 5 mol%, the most effective reaction time was 5 hours in the formation of methyl 2-(2-phenyl-*o*-carboran-1-yl)-2-cinnamylacetate (Exp. No. 5). A longer reaction time gave a similar result (Exp. No. 3).

At 60 ℃ even with the molar ratio of ethyl cinnamyl carbonate over methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate of 2, diallylation on the active methylene in methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate did not take place (Exp. No. 6), presumably due to the steric hindrance of carbonucleophile as well as the low acidity of the monoallylated methine group. Furthermore, we could not obtained the carbonylated product under atmospheric pressure of carbon monoxide at room temperature (Exp. No. 7). This may be due to the reductive elimination of the π-allylpalladium complex induced by carbon monoxide[10] as well as the high reactivity of π-allylpalladium intermediates toward carbonucleophiles.[11] The allylation product of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate with ethyl allyl carbonate under these optimum condition

Table 2. Ligand effect on the reaction of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate with ethyl cinnamyl or ethyl allyl carbonates catalyzed by Palladium[a]

Exp. No.	Ester (R=)	Cat.	Product	Yield[b]
5	Ph	$Pd(dba)_2$+2DPPE	**3a**	88
8	H	$Pd(dba)_2$+2DPPE	**3b**	95
9	Ph	$Pd(dba)_2$	**3a**	0
10	Ph	$Pd(dba)_2$+2DPPM	**3a**	88
11	Ph	$Pd(dba)_2$+2DPPP	**3a**	82
12	Ph	$Pd(dba)_2$+4PPh_3	**3a**	79
13	Ph	$Pd(dba)_2$+4PBu_3	**3a**	77
14	Ph	$Pd(dba)_2$+4PhCN	**3a**	trace
15	Ph	$Pd(dba)_2$+4$P(OEt)_2$	**3a**	0

[a]Methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate (1 mmol), ethyl cinnamyl carbonate (0.206 g, 1 mmol), or ethyl allyl carbonate (0.130 g, 1 mmol) $Pd(dba)_2$ (0.029 g, 5 mol%), ligand, THF (3 mL) were stirred under atmospheric N_2 at room temperature for 5 hours. [b]Isolated yield.

Table 3. Solvent effects on the reaction of methyl 2-(2-phenyl-*o*-carboran-1-yl)acetate with ethyl cinnamyl or ethyl allyl carbonates catalyzed by $Pd(dba)_2$ and DPPE[a]

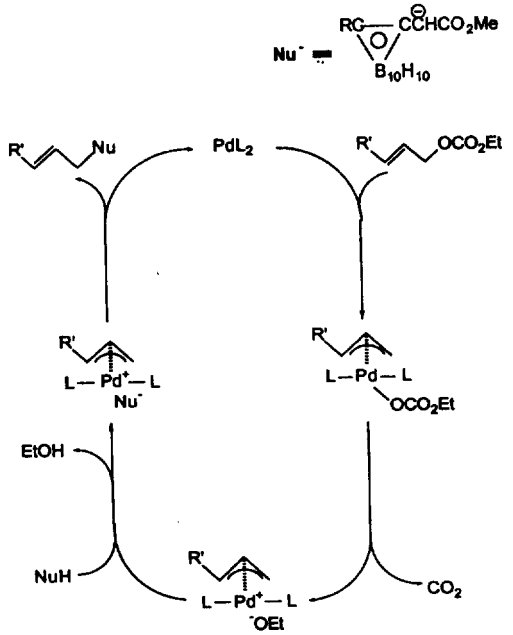
Exp. No.	Solvent	Product	Yield[b]
5	THF	**3a**	88
8	THF	**3b**	95
15	Ether	**3a**	85
16	Benzene	**3a**	74
17	DMF	**3a**	0
18	Acetonitrile	**3a**	0

[a]1-Phenyl-2-(carbomethoxy)methyl-*o*-carborane (0.292 g, 1 mmol), ethyl cinnamyl-carbonate (0.206 g, 1 mmol), or ethyl allyl carbonate (0.130 g, 1 mmol) $Pd(dba)_2$ (5 mol%, 0.029 g), DPPE (10 mol%, 0.040 g), solvent (3 mL) were stirred under atmospheric N_2 at room temperature for 5 hours. [b]Isolated yield.

described above gave in 95% yield (Exp. 8).

Table 2 shows the ligand dependence of the yield of C-allylation. As shown in Table 2, it was found that the ligand had a critical effect in the reaction. $Pd(dba)_2$-1,2-bis(diphenylphosphino)ethane(DPPE) and $Pd(dba)_2$-bis(diphenylphosphino)methane(DPPM) complexes were found to be the best catalysts among bis(dibenzylideneacetone)palladium-phosphorous complexes employed (Exp. Nos. 5, 10).[12] In the case of Pd(dba)-DPPE catalyst-ethyl allyl carbonate system, C-allylation product of carboranylacetic ester was obtained in 75% yield (Exp. No. 8). $Pd(dba)_2$-1,3-bis(diphenylphosphino)propane(DPPP), $Pd(dba)_2$-PPh_3 complex and $Pd(dba)_2$-PBu_3 complexes had some catalytic activity (Exp. Nos. 11-13), but they were inferior to $Pd(dba)_2$-1,2-bis(diphenylphosphino)ethane (DPPE) and $Pd(dba)_2$-bis(diphenyl-phosphino)methane (DPPM) complexes respectively.

However, when other ligands such as PhCN and $P(OEt)_3$ were chosen, the catalytic activity was reduced drastically (Exp. No. 14). In addition, $Pd(dba)_2$-$P(OEt)_3$ system was not active (Exp. No. 15). In the cases of ligand such as benzonitrile or triethyl phosphite, most of substrates were recovered quantitatively. $Pd(dba)_2$ without phosphorous ligand did not show catalytic activity (Exp. No. 9). This fact suggests that $Pd(dba)_2$ was immediately dissociated to metallic palladium and dibenzylideneacetone in solution.



Scheme 2.

Accordingly, remarkable ligand effect was observed and 1,2-bis(diphenylphosphino)ethane(DPPE) and bis(diphenylphosphino)methane(DPPM) seem to be the best ligands for the C-allylation.

Table 3 exhibits some solvent dependence for the yield of C-allylation. As shown in Table 3, THF was found to be the best solvent among the solvents employed (Exp. No. 5). In the cases of other solvents such as diethyl ether and benzene the product was obtained in 85% and 74% yields, respectively (Exp. Nos. 16 and 17). But in the cases of DMF and acetonitrile the expected C-allylation did not take place (Exp. Nos. 18 and 19). This may be due to the high polarity of DMF and acetonitrile. Among these solvents, remarkable difference was observed. Diethyl ether and benzene were also an acceptable solvents, but they were inferior to THF.

As shown in Scheme 2, the mechanism of C-allylation was proposed by several authors.[13,14] The reason why the palladium-catalyzed C-allylation reaction of carboranylacetic ester with ethyl allylic carbonates can be carried out under neutral conditions is explained by the following mechanism.

Oxidative addition of Pd(0)-phosphine complex to ethyl allylic carbonates gives the π-allylpalladium carbonate, which undergoes decarboxylation to form π-allylpalladium ethoxide. The ethoxide anion formed *in situ* then abstracts active hydrogen from an active methylene in carboranylacetic ester to generate a carbanion. The *in situ* formation of the carbanion in this way explains why the allylation reaction with allylic carbonates can be carried out without addition of bases. Nucleophilic attack of carbanion on π-allylpalladium gives the allylated product, and Pd(0)-phosphine is regenerated.

The assigments of ^1H- and ^{13}C NMR spectrum for carbor-

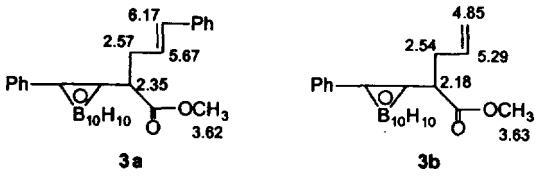


Figure 1. ^1H NMR assigment of C-allylated carboranyl acetic ester.

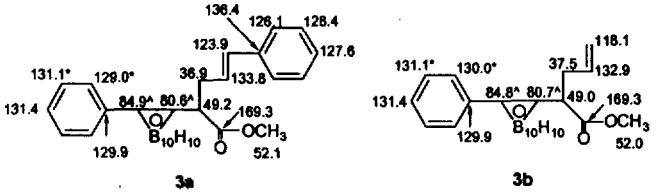


Figure 2. ^{13}C NMR assignment of C-allylated carboranyl acetic ester.

ances (**3a**, **3b**) showed in Figure 1 and Figure 2, respectively.

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The Synthesis of Bis-(2,2′-bipyridine) [4,4′-di-(hexadecyloxycarbonyl)-2,2′-bipyridine] ruthenium(II) and Its Application for Photolysis of Water

Yong-Tae Park and Sang-Gyun Noh

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

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For the solar energy storage, many studies have been concerned with mimicking the plant photosynthetic system. A vesicle system of water photolysis has been designed by several groups.[1-3] For that purpose a photosensitizer, an electron donor and an electron acceptor are needed and must be oriented properly in the vesicle system, just like chlorophyll, O_2-evolving complex, and ferredoxin in plant membrane. However, few authors have made a vesicle system which generates hydrogen and oxygen from water by visible light.

In this study, we synthesized tris(bipyridine) ruthenium(II) with two long hydrocarbon chains, **6** $[Ru(bipy)_2\ (lhcbipy)]^{2+}$, as a photosensitizer to be inserted into the vesicle system. For the first time, a vesicle system prepared with photosensitizer itself was examined for the water photolysis.

We planed to coordinate *cis*-dichloro-bis(bipyridine) ruthenium(II) with 4,4′-di-(hexadecyloxycarbonyl)-2,2′-bipyridine (**4**) to prepare bis-(2,2′-bipyridine) [4,4′-di-(hexadecyloxycarbonyl)-2,2′-bipyridine] ruthenium(II) $[Ru(bipy)_2\ (lhcbipy)^{2+}$, **6**]. Thus, 4,4′-di-(hexadecyloxycarbonyl)-2,2′-bipyridine (**4**) was first prepared as follows. A key intermediate, 4,4′-dimethyl-2,2′-bipyridine (**1**, 10 g, yield 6%) was prepared by reacting 4-picoline (175 m*l*) with palladium (10% charcoal, 9.5 g) as previously described in ref. (4). The oxidation of the methyl groups of bipyridine **1** (8 g) with potassium permanganate (25 g) afforded 4,4′-dicarboxy-2,2′-bipyridine (**2**), (2.7 g, yield 26%), using the reported method.[5] The carboxylic acid group of the bipyridine **2** was converted to acyl chloride **3** by heating the mixture of 4,4′-dicarboxy-2,2′-bipyridine **2** (700 mg) and thionyl chloride (7 m*l*) to reflux. The esterification of 4,4′-di-(chlorocarbonyl)-2,2′-bipyridine (**3**) (700 mg) was performed by heating it with cetyl alcohol (1.45 g) in benzene (25 m*l*) to reflux for 2 hrs. Adding 40 m*l* of chloroform, the mixture was washed with aqueous sodium bicarbonate. The organic layer was dried with magnesium sulfate. Evaporation of the solvent produced a colorless crystal. The recrystallization from acetone/chloroform afforded 4,4′-di-(hexadecyloxycarbonyl)-2,2′-bipyridine (**4**), as colorless crystal, (950 mg, yield 48%) with mp. 78 ℃.

The esterified bipyridine **4** was confirmed by ^1H NMR, UV, and elemental analysis.[6] The ultraviolet absorption (λ_{max} 300 nm in $CHCl_3$) spectra of this compound were found to be very similar to that of 2,2′-bipyridine (λ_{max} 280 nm in MeOH). In the ^1H NMR of compound **4**, the signal for terminal protons appeared as a triplet at 0.89 ppm, middle methylene protons as a multiplet at 1.10-1.60 ppm, homomethoxy protons as a quintet at 1.80 ppm, and methoxy protons as a triplet at 4.40 ppm. Protons (6- and 6′-) on the pyridine