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Synthesis of carboranyl amides catalyzed by recyclable Pd (0) nanoparticles supported on carbon nanotubes (CNTs)

Algin Oh Biying [a], Karen Tang Yuanting [a], Narayan S. Hosmane [b], Zhu Yinghuai [a,*]

[a] Institute of Chemical and Engineering Sciences (ICES), 1 Pesek Road, Jurong Island 627833, Singapore
[b] Department of Chemistry and Chemical Biology, Northern Illinois University, DeKalb, Illinois 60115-2862, USA

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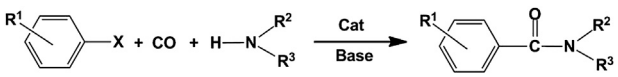
ABSTRACT

Palladium (0) nanoparticles with small size and narrow size distribution were synthesized conveniently and supported on CNTs. The supported nano-Pd^0 was found to be a highly efficient and recyclable catalyst for the aminocarboranylation reaction of aryl halide. Thus, a series of carboranyl amides, 1-R-2-[$CH_2NHC(=O)Ar$]-1,2-$C_2B_{10}H_{10}$ (R = H, Me; Ar = C_6H_5, 4-Me-C_6H_5, 4-MeO-C_6H_5 and 2-C_5NH_4), were synthesized and fully characterized. The catalyst was recyclable at least three times with sustained activity.

1. Introduction

Formation of amide bond (CON) remains one of the key steps in both the fine chemical and pharmaceutical industries [1–4]. However, the existing methods are either expensive or environmentally unfriendly and, therefore, a green and economical technology is highly desired. We are studying the catalytic aminocarbonylation of aryl halides to synthesize amides as shown in Eq (1) by constructing and screening various metal-supported heterogeneous catalysts. It has been demonstrated that both ionic liquid stabilized and metal-organic frameworks (MOF-5) supported palladium (0) nanoparticles are effective catalysts for the aminocarbonylation reactions of aryl halides [5,6]. Nevertheless, the inherent disadvantages of the catalyst composites such as moisture sensitivity of the commonly used ionic liquids, high-cost procedures of purification process for products of reactions involving ionic liquids [7], air and chemical instability of metal-organic frameworks (MOFs) [8,9] may hinder their wide applications in catalysis. Therefore, more robust and highly efficient catalyst composites are needed to be developed for the aminocarbonylation reactions for future applications.



Previous results showed that palladium nanoparticles supported on pristine inorganic supports such as SiO_2, Al_2O_3, molecular sieves and Celite, provided low yield [6], hence other frequently used support materials in heterogeneous catalysis were employed to construct catalyst nanocomposites for the target reaction. Carbon nanotubes (CNTs) have been well recognized as a promising and robust catalyst support due to their significant chemical and physical stability, nanometric size, opened hollow-sphere structure, low mass density and superb mechanical properties [10–12]. In addition, advanced developments in surface modification of CNTs with various functional groups further broaden their applications such as in biosensors [13], drug carriers [14], and catalysis [10,11,15,16]. The surface chemistry of the CNTs is playing an important role as well in tuning the catalytic behaviors, such as adjusting catalyst activity and strongly preventing leaching of the supported metallic nanoparticles. In this work, the commercially available CNTs were used as catalyst support after a slight pretreatment to immobilize palladium (0) nanoparticles for the aminocarbonylation reactions.

* Corresponding author. Tel.: +6567963801; fax: +6563166184.
E-mail address: zhu_yinghuai@ices.a-star.edu.sg (Z. Yinghuai).

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Carboranyl amide is one type of the most widely studied compounds in boron chemistry, which could be potentially used as promising boron carriers in boron neutral capture therapy [17–19]. Formation of amide bond is a commonly used strategy to conjugate carborane clusters with other functional species. An efficient method to form amide bond (C(=O)N) will definitely benefit the specific area and thus broaden the applications of boron-containing amides. In our current work, the catalytic amidocarbonylation procedure involving palladium (0) enriched multi-walled CNTs composite has been adopted to synthesize various carboranyl amides and herein we report the preliminary results of this investigation.

2. Results and discussion

Commercially available multi-walled carbon nanotubes (MWCNTs) with an outside diameter of 6–9 nm and more than 1 μm length were pretreated with a concentrated H_2SO_4–HNO_3 mixture to remove trace of metal catalysts remained in the supplied products and create surface defects by forming carboxylic acid groups [20]. Palladium (0) nanoparticles were prepared *in situ* by reducing H_2PdCl_4 and then supported on MWCNTs according to literature [20]. The synthesized catalyst composite was analyzed using ICP, XPS as well as TEM to identify the loading amount, chemical oxidation state and particle size of the supported palladium species. As shown in TEM images (Fig. 1), the produced Pd particles are small crystalline in nanometric size with an average size of around 5.4 nm (Fig. 2(A), determined from the measurement of ~150 particles). The uniform nanoparticles are well dispersed on the MWCNTs support. Samples for XPS analysis were prepared in a glove box as described elsewhere [5,21–23]. The XPS samples The XPS spectrum (see Fig. 2(B)) shows typical Pd (0) absorptions at 335.28 and 340.48 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively, with a $\Delta = 5.2$ eV, which is consistent with the literature values for Pd (0) [5,22–24].

The prepared MWCNTs-supported palladium nanoparticles were examined as catalysts in the aminocarbonylation reaction between iodobenzene and aniline, which was selected as standard reaction. According to previous results, base plays the second important role in the reaction after catalyst [5,6]. Therefore, commonly used bases were investigated at reaction conditions of 130 °C and CO pressure of 150 psi, similar to those used in the literature procedures [5,6]. The base optimization results are summarized in Table 1.

It was found that among the screened bases, K_2CO_3 provided higher yield under the same conditions and the results are comparable with the previous reports [5,6]. After completion of the reaction, the solid residue was filtered off and washed with ethyl acetate to remove adherent organic composites. The combined organic phase was concentrated under reduced pressure and purified by thin-layer chromatography (TLC, SiO_2) to collect the corresponding products. Isolated amides were characterized by ^1H and ^{13}C, FT-IR and Mass spectroscopy.

Aminocarbonylation reactions between the carboranylmethyl ammonium salt and iodobenzene were performed with optimized base K_2CO_3 using Pd/MWCNTs as catalyst. After purification, air-stable waxy solid products, namely phenyl(carboranylmethyl)amides, 1-R-2-[$CH_2NHC(=O)Ar$]-1,2-$C_2B_{10}H_{10}$ (R = H, Me; Ar = C_6H_5, 4-Me-C_6H_5, 4-MeO-C_6H_5 and 2-C_5NH_4), were obtained in 57–91% yields as shown in Table 2. All the prepared new carboranyl amides were characterized by ^1H, ^{13}C, ^{11}B NMR and FT-IR spectroscopy as well as MS. The ^1H, ^{13}C, and ^{11}B NMR spectra of the resulting carboranyl amides appear normal relative to other related structures. In ^{11}B NMR spectra, amides of 1-[$CH_2NHC(=O)Ar$]-1,2-$C_2B_{10}H_{10}$ (Ar = C_6H_5, 4-Me-C_6H_5, 4-MeO-C_6H_5 and 2-C_5NH_4) showed a splitting pattern of 1:1:2:2:4. In comparison, the amides of 1-Me-2-[$CH_2NHC(=O)Ar$]-1,2-$C_2B_{10}H_{10}$ (Ar = C_6H_5, 4-Me-C_6H_5, 4-MeO-C_6H_5 and 2-C_5NH_4) showed varying splitting patterns, 1:1:5:3 (Ar = C_6H_5, 4-Me-C_6H_5), 1:1:8 (Ar = 4-MeO-C_6H_5), and 1:1:2:4:2 (Ar = 2-C_5NH_4) in ^{11}B NMR spectra. The results suggest that both substituted groups attached to carbon atoms of the carborane cage and Ar functionalities affect the ^{11}B splitting patterns. In the IR spectra, strong absorptions at 2575–2585 cm^{-1} are attributed to B–H stretching mode of vibrations (ν_{BH}).

It should be pointed out that the nano-Pd/MWCNTs-based catalyst can be separated conveniently by filtration and reused at least three times with the yield of 81%, 78% and 82% for the aminocarbonylation between iodobenzene and aniline in the presence of K_2CO_3. To investigate the leached Pd, the samples of the filtrate plus washings obtained from above standard reactions were subjected to ICP analysis that shown the concentrations of Pd were to be less than 4.0 ppm. In addition, the standard reaction was conducted with recovered filtrate, but no product could be isolated. The results suggested that the supported Pds, rather than the leached Pds, provide the high catalytic performance. The detailed study of the reaction mechanism on the Pd/MWCNTs catalyst surface, using various spectroscopy techniques, is currently undergoing in our laboratories.

3. Conclusions

It can be concluded that the well-dispersed, MWCNTs-supported palladium nanoparticle composite was found to be efficient and recyclable catalyst for the aminocarbonylation reactions. A series of carboranyl amides were synthesized using the prepared

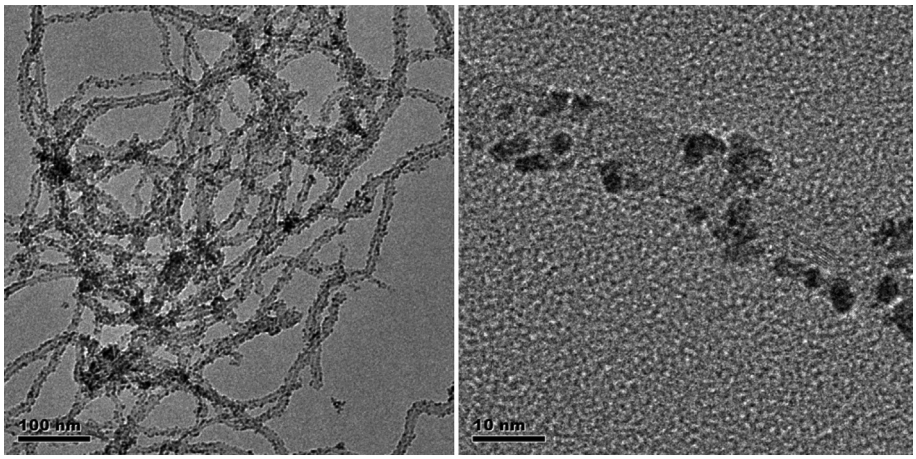

Fig. 1. TEM images of nano-Pd/MWCNTs.

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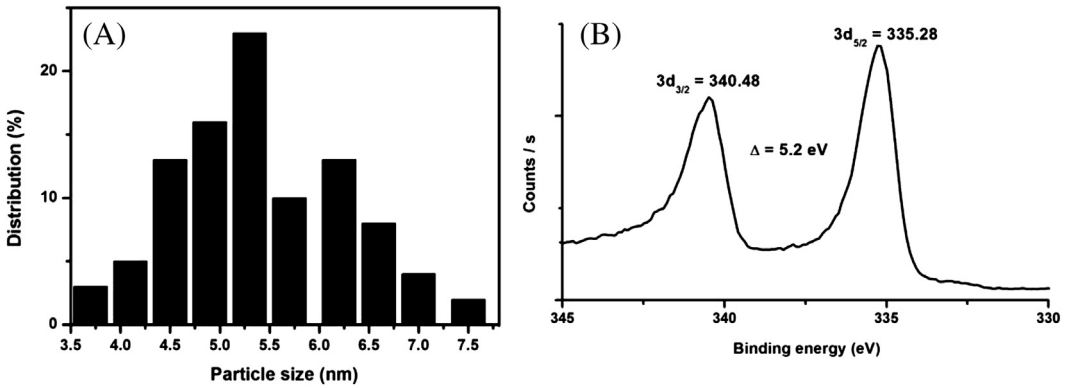


Fig. 2. Size histogram (A) and XPS spectrum (B) of supported Pd nanoparticles.

Pd/MCNTs catalyst in medium to good yields. Considering the high thermal and chemical stability of MWCNTs support and high activity of the catalyst, we expect our prototype catalyst to find broader applications in both academia and fine chemical industry, particularly in the area of pharmaceutical research such as in BNCT, to construct carboranyl-containing hybrids.

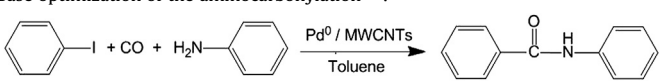
4. Experimental

All synthetic procedures and operations were carried out in an argon atmosphere using standard Schlenk techniques or a glove box. Organic solvents such as toluene and hexane were dried using standard procedures and distilled under argon before use [25]. Iodobenzene was pre-dried before use. 1-(CH_2NH_3Cl)-1,2-$C_2B_{10}H_{11}$ and 1-Me-2-(CH_2NH_3Cl)-1,2-$C_2B_{10}H_{10}$ were prepared according to the literature procedures [26]. Multi-walled carbon nanotubes were purchased from Sigma–Aldrich. ^1H, ^{13}C and ^{11}B NMR were recorded on a Bruker Fourier-Transform multinuclear NMR spectrometer at 400, 100.6 and 128.4 MHz, relative to external Me_4Si (TMS) and $BF_3 \cdot OEt_2$ standards. Infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with KBr pellets technique and presented in the sequence of signal strength as strong (s), medium (m) and weak (w), and peak pattern as single (s), multiple (m) and broad (br). MS (ESI) analyses were carried out on a Thermo Finnigan MAT XP95 analyzer using ESI model. Transmission electron microscopy (TEM) measurements were carried out on a JEOL Tecnai-G^2, FEI analyzer at 200 kv. Inductively coupled plasma (ICP) analysis was determined using a VISTA-MPX, CCD Simultaneous ICP-OES analyzer. X-Ray photoelectron spectrometer (XPS) was performed with an ESCALAB 250 analyzer.

4.1. Synthesis of supported catalyst namely nano-Pd^0/MWCNTs

A literature method was used with slight modification to prepare the supported catalyst [20]. The purchased MWCNTs (2.0 g) were first dispersed in a concentrated H_2SO_4–HNO_3 mixture (250 mL, 8.0 M for each acid) and then placed in an ultrasonic bath for treatment at a bath temperature of 60 °C over a period of 8 h. The acid-treated MWCNTs were then separated by centrifugation and washed with de-ionized water (4 × 15 mL) and dried in a vacuum oven at 70 °C for about 12 h before use. To an aqueous fresh H_2PdCl_4 solution of the desired concentration, the required amount of a polyvinylalcohol (PVA) (Aldrich, MW = 10,000, 80% hydrolyzed) solution (1 wt%) was added (PVA/(Pd) (wt/wt) = 1.2); a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/(Pd) (mol/mol) = 5) was then added to form a dark-brown solution. After 30 min of sol generation, the colloid was immobilized by adding above prepared MWCNTs under vigorous stirring conditions. The amount of support material required was calculated so as to have a total final metal loading of 5 wt%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight. The obtained catalyst composites were analyzed by XPS, TEM, ICP and XRD.

Table 1
Base optimization of the aminocarbonylation[a,b].



Base	K_2CO_3	Na_2CO_3	Cs_2CO_3	Na_3PO_4	NaOAc	NaOH	Et_3N	Pyridine
Yield	83	48	51	57	43	15	61	36

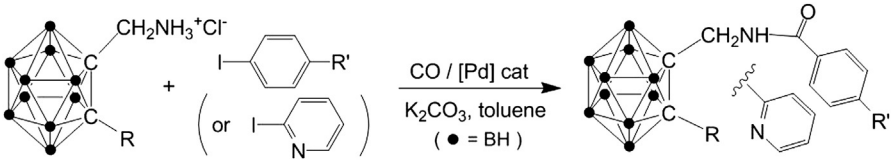
[a] Reaction conditions: 1.0 mmol of iodobenzene, 1.1 mmol of aniline, 3.0 equiv. of base, 1 mol% Pd catalyst loading in 7 mL anhydrous toluene, P_{CO} = 150 psi, Temperature = 130 °C, time = 5 h.
[b] Isolated yield (%).

4.2. Procedures of catalytic aminocarbonylation of iodobenzene

Catalyst examination was performed in a stainless steel reactor, CAT-7 with 7 vials and K-type thermocouple. The aminocarbonylation of iodobenzene was conducted in toluene (7 mL) in the presence of a base. The aminocarbonylation reaction between aniline and iodobenzene was selected as a standard reaction to study the base effect. Commercially available bases, namely K_2CO_3, Na_2CO_3, Cs_2CO_3, Na_3PO_4, NaOAc, NaOH, Et_3N and pyridine, were tested at 130 °C for 5 h under the CO pressure of 150 psi following the similar reaction conditions used in the literature [5]. The product mixtures were purified with thin-layer chromatography (TLC, SiO_2, developed with mixture of hexane and ethyl acetate). The known products were analyzed by ^1H and ^{13}C NMR spectra and compared with the corresponding spectra of standards. The screening results are summarized in Table 1.

Aminocarbonylation reactions between aryl iodides and carboranyl ammonium salts were carried out under the same conditions as described above. In general, the reactants were used in the following amounts: 1.0 mmol aryl iodide, 1.1 mmol of carboranyl ammonium chloride, 4.0 equiv of base, 0.01 mmol Pd nanoparticles and 7 mL of anhydrous toluene. For catalyst recycle runs, the reaction mixture was filtered off and solid residue was washed with oxygen-free ethyl acetate (2 × 10 mL) and de-ionized water (2 × 10 mL) to recover adherent organic substrates and remove both excess K_2CO_3 and other inorganic salts. The resulting residue was dried *in vacuo* at 60 °C for 20 h before being used for next runs. The combined solution from filtrate and washings of ethyl acetate was dried under reduced pressure using a rotary evaporator, the

Table 2
Nano-Pd^0/MWCNTs-catalyzed carbonylation of carboranyl ammonium salts[a,b] .



R′		H	Me	OMe	Pyridine
R	H	85	74	68	57
	Me	91	88	77	63

[a] Reaction conditions: 1.0 mmol of iodobenzene, 1.1 mmol of aniline, 4.0 equiv. of base, 1 mol% Pd catalyst loading in 7 mL anhydrous toluene, P_{CO} = 150 psi, Temperature = 130 °C, time = 5 h.
[b] Isolated yield (%).

resulting crude products were purified with flash column chromatography (SiO_2, eluted with solvent mixture of hexane and ethyl acetate in a ratio of 5:1–20:1) to obtain the corresponding amide products; the reaction scheme and yields are summarized in Table 2. All products were analyzed by ^1H and ^{13}CNMR spectra, FT-IR, and mass spectra (MS).

1-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{11}$ (Ar = C_6H_5). Yield 85%. MS (ESI) for $C_{10}H_{19}B_{10}NO$: m/z = 300.24 $[M + Na]^+$, 278.25 $[M + H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.69–7.32 (m, 5H, $C_6\underline{H}_5$), 6.60 (s, 1H, N$\underline{H}$), 4.06 (d, 2H, $C\underline{H}_2$–N), 3.99 (s, 1H, $\underline{H}C_{cage}$), 1.18–2.66 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 168.06 ($\underline{C}O$), 132.64, 132.59, 128.96, 127.02 ($\underline{C}_6H_5$), 74.20 and 60.61 ($\underline{C}_{cage}$), 45.00 (–$\underline{C}H_2$–N). ^{11}B NMR ($CDCl_3$, ppm), δ = –1.61 (1B, $^1J_{BH}$ = 148 Hz), –5.11 (1B, $^1J_{BH}$ = 153 Hz), –9.82 (2B, $^1J_{BH}$ = 154 Hz), –11.82 (2B, $^1J_{BH}$ = 148 Hz), –12.72 (4B, $^1J_{BH}$ = 151 Hz). IR (KBr pellet, cm^{-1}), 3307 (vs, s), 3048 (vs, s), 2626 (m, s), 2575 (vs, s), 1792 (m, m), 1645 (vs, s), 1555 (s, s), 1540 (s, s), 1507 (m, s), 1469 (m, s), 1311 (m, s), 1128 (w, s), 1090 (w, s), 1018 (w, s), 927 (w, s), 832 (w, s), 780 (w, s), 724 (m, s), 693 (m, s).

1-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{11}$ (Ar = 4-Me-C_6H_5). Yield 74%. MS (ESI) for $C_{11}H_{21}B_{10}NO$: m/z = 314.25 $[M + Na]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.58–7.11 (m, 4H, $C_6\underline{H}_4$), 6.67 (s, 1H, N$\underline{H}$), 4.02 (d, 2H, $C\underline{H}_2$-N), 3.96 (s, 1H, $\underline{H}C_{cage}$), 2.31 (s, 3H, $C\underline{H}_3$), 2.50–1.57 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 168.08 ($\underline{C}O$), 143.30, 129.76, 129.59, 127.06 ($\underline{C}_6H_4$), 75.08 and 60.56 ($\underline{C}_{cage}$), 44.96 (–$\underline{C}H_2$–N), 21.55 ($\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = –1.60 (1B, $^1J_{BH}$ = 145 Hz), –5.07 (1B, $^1J_{BH}$ = 147 Hz), -9.77 (2B, $^1J_{BH}$ = 157 Hz), -11.71 (2B, $^1J_{BH}$ = 139 Hz), -12.64 (4B, $^1J_{BH}$ = 154 Hz). IR (KBr pellet, cm^{-1}), 3346 (vs, s), 3065 (m, s), 3040 (m, s), 2918 (w, s), 2849 (w, s), 2580 (vs, s), 1699 (m, s), 1635 (vs, s), 1541 (vs, s), 1504 (s, s), 1419 (m, s), 1363 (w, s), 1303 (s, s), 1193 (m, s), 1119 (m, s), 1017 (m, s), 835 (m, s), 751 (s, s), 725 (m, s), 664 (m, s), 629 (m, s).

1-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{11}$ (Ar = 4-MeO–C_6H_5). Yield 68%. MS (ESI) for $C_{11}H_{21}B_{10}NO_2$: m/z = 330.35 $[M + Na]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.66–6.86 (m, 4H, $C_6\underline{H}_4$), 6.62 (s, 1H, N$\underline{H}$), 4.02 (d, 2H, $C\underline{H}_2$-N), 3.97 (s, 1H, $\underline{H}C_{cage}$), 3.81 (s, 3H, $OC\underline{H}_3$), 2.28-1.36 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 167.58 ($\underline{C}O$), 163.04, 128.99, 124.75, 114.14 ($\underline{C}_6H_4$), 75.19 and 60.54 ($\underline{C}_{cage}$), 55.53 ($O\underline{C}H_3$), 44.97 (–$\underline{C}H_2$–N). ^{11}B NMR ($CDCl_3$, ppm), δ = –1.64 (1B, $^1J_{BH}$ = 145 Hz), –5.11 (1B, $^1J_{BH}$ = 153 Hz), –9.80 (2B, $^1J_{BH}$ = 156 Hz), –11.69 (2B, $^1J_{BH}$ = 128 Hz), –12.70 (4B, $^1J_{BH}$ = 145 Hz). IR (KBr pellet, cm^{-1}), 3337 (s, s), 3059 (m, s), 3037 (m, s), 2963 (m, s), 2839 (m, s), 2579 (vs, s), 2050 (w, br), 1844 (w, s), 1669 (w, s), 1769 (w, s), 1699 (m, s), 1634 (s, s), 1606 (s, s), 1541 (s, s), 1507 (s, s), 1457 (s, s), 1419 (s, s), 1319 (s, s), 1302 (s, s), 1264 (s, s), 1180 (s, s), 1117 (m, s), 1020 (s, s), 843 (s, s), 768 (s, s), 722 (m, s), 631 (m, s), 610 (m, s).

1-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{11}$ (Ar = 2-C_5NH_4). Yield 57%. MS (ESI) for $C_9H_{18}B_{10}N_2O$: m/z = 323.14 $[M+2Na]^+$, 173.07 $[M-COC_5H_4N + H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 8.53–7.44 (m, 4H, $C_5\underline{H}_4$), 7.20 (s, 1H, N$\underline{H}$), 4.08 (d, 2H, $C\underline{H}_2$–N), 3.89 (s, 1H, $\underline{H}C_{cage}$), 2.2.81–1.18 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 166.4 ($\underline{C}O$), 149.18, 148.20, 136.55, 125.06, 124.11 ($\underline{C}_5H_4N$), 79.46 and 66.20 ($\underline{C}_{cage}$), 47.47 (–$\underline{C}H_2$–N). ^{11}B NMR ($CDCl_3$, ppm), δ = –2.92 (1B, $^1J_{BH}$ = 155 Hz), –5.53 (1B, $^1J_{BH}$ = 139 Hz), –9.04 (2B, $^1J_{BH}$ = 148 Hz), –11.72 (2B, $^1J_{BH}$ = 133 Hz), –13.21 (4B, $^1J_{BH}$ = 160 Hz). IR (KBr pellet, cm^{-1}), 3331 (m, s), 3050 (m, s), 2952 (w, s), 2583 (vs, s), 1669 (s, m), 1521 (s, m), 1309 (m, s), 1236 (w, s), 1173 (w, s), 1121 (w, s), 1093 (w, s), 1020 (w, s), 908 (w, s), 836 (w, s), 725 (m, s), 683 (m, s).

1-Me-2-(CH_2NH_3Cl)-1,2-$C_2B_{10}H_{10}$. The compound was synthesized according to literature in 69% yield [26]. MS (ESI) for $C_4H_{18}B_{10}NCl$: m/z = 188.25 $[M - Cl]^+$. ^1H NMR (DMSO-d_6, ppm), δ = 3.85 (s, 2H, $C\underline{H}_2$–N), 2.49 (s, 3H, C_{cage}–CH_3) 1.51–2.67 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR (DMSO-d_6, ppm), δ = 77.04 and 74.0164 ($\underline{C}_{cage}$), 40.91 (–$\underline{C}H_2$–N), 22.38 (C_{cage}–$\underline{C}H_3$). ^{11}B NMR (DMSO-d_6, ppm), δ = –4.05 (1B, $^1J_{BH}$ = 108 Hz), –6.33 (1B, $^1J_{BH}$ = 156 Hz), –10.71 (8B, $^1J_{BH}$ = 122 Hz). IR (KBr pellet, cm^{-1}), 3204 (s, br), 2997 (vs, br), 2889 (vs, br), 2588 (vs, s), 2017 (m, s), 1559 (s, br), 1193 (m, s), 1124 (m, s), 1030 (m, s), 1002 (m, s), 730 (s, s), 682 (m, s), 641 (m, s).

1-Me-2-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{10}$ (ArC_6H_5). Yield 91%. MS (ESI) for $C_{11}H_{21}B_{10}NO$: m/z = 314.25 $[M + Na]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.70–7.32 (m, 5H, $C_6\underline{H}_5$), 6.59 (s, 1H, N$\underline{H}$), 4.15 (d, 2H, $C\underline{H}_2$–N), 3.10–1.30 (m, br, 10H, $B_{10}\underline{H}_{10}$). 2.14 (s, 3H, $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), δ = 166.95 ($\underline{C}O$), 133.16, 132.38, 128.83, 126.87 ($\underline{C}_6H_5$), 77.84 and 76.10 ($\underline{C}_{cage}$), 41.84 (–$\underline{C}H_2$–N), 23.50 ($\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = –3.48 (1B, $^1J_{BH}$ = 152 Hz), –5.78 (1B, $^1J_{BH}$ = 150 Hz), –9.77 (5B, $^1J_{BH}$ = 136 Hz), –10.52 (3B, $^1J_{BH}$ = 114 Hz). IR (KBr pellet, cm^{-1}), 3245 (s, br), 3064 (s, br), 2866 (m, br), 2590 (vs, br), 1962 (w, s), 1785 (vs, s), 1722 (vs, s), 1646 (s, s), 1599 (m, s), 1541 (s, s), 1451 (s, s), 1424 (m, s), 1314 (s, s), 1277 (m, s), 1213 (vs, s), 1173 (s, s), 1075 (m, s), 1017 (s, s), 1009 (s, s), 993 (s, s), 940 (m, s), 798 (w, s), 777 (w, s), 702 (vs, s), 615 (m, s).

1-Me-2-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{10}$ (Ar = 4-Me-C_6H_5). Yield 88%. MS (ESI) for $C_{12}H_{23}B_{10}NO$: m/z = 328.27 $[M + Na]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.97–7.19 (m, 4H, $C_6\underline{H}_4$), 6.48 (s, 1H, N$\underline{H}$), 4.14 (d, 2H, $C\underline{H}_2$–N), 2.64–1.57 (m, br, 10H, $B_{10}\underline{H}_{10}$), 2.39 (s, 3H, $C\underline{H}_3$), 2.15 (s, 3H, C_{cage}–$C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), δ = 166.78 ($\underline{C}O$), 143.04, 130.64, 129.57, 126.98 ($\underline{C}_6H_4$), 77.94 and 76.14 ($\underline{C}_{cage}$), 41.78 (–$\underline{C}H_2$–N), 23.51 (C_{cage}–$\underline{C}H_3$), 21.53 ($\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = –3.53 (1B, $^1J_{BH}$ = 150 Hz), –5.80 (1B, $^1J_{BH}$ = 149 Hz), –9.80 (5B, $^1J_{BH}$ = 135 Hz), –10.56 (3B, $^1J_{BH}$ = 116 Hz). IR (KBr pellet, cm^{-1}), 3256 (vs, br, s), 3061 (m, s), 2947 (m, s), 2923 (m, s), 2864 (w, s), 2588 (vs, s), 1921 (w, s), 1773 (m, s), 1641 (vs, s), 1555 (s, s), 1507 (s, s), 1448 (m,

s), 1314 (s, s), 1169 (m, s), 1037 (m, s), 1018 (m, s), 836 (m, s), 723 (s, s), 689 (s, s), 635 (m, s).

1-Me-2-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{10}$ (Ar = 4-MeO-C_6H_5). Yield 77%. MS (ESI) for $C_{12}H_{23}B_{10}NO_2$: $m/z = 344.27$ $[M + Na]^+$. ^1H NMR ($CDCl_3$, ppm), $\delta = 7.68–6.49$ (m, 4H, $C_6\underline{H}_4$), 6.50 (s, 1H, N$\underline{H}$), 4.10 (d, 2H, $C\underline{H}_2$–N), 3.79 (s, 3H, $OC\underline{H}_3$), 2.31–1.18 (m, br, 10H, $B_{10}\underline{H}_{10}$), 1.98 (s, 3H, C_{cage}–$C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), $\delta = 166.34$ ($\underline{C}O$), 132.85, 125.27, 121.25, 114.10 ($\underline{C}_6H_4$), 78.06, and 76.12 ($\underline{C}_{cage}$), 55.61 ($O\underline{C}H_3$), 41.78 (–$\underline{C}H_2$–N), 23.50 (C_{cage}–$\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), $\delta = -3.58$ (1B, $^1J_{BH} = 152$ Hz), −5.84 (1B, $^1J_{BH} = 150$ Hz), −9.79 (8B, $^1J_{BH} = 133$ Hz). IR (KBr pellet, cm^{-1}), 3273 (s, s), 3060 (m, s), 3017 (m, s), 2953 (m, s), 2843 (m, s), 2587 (vs, s), 2225 (w, s), 2046 (w, br), 1910 (w, s), 1865 (w, s), 1790 (s, s), 1713 (s, s), 1641 (s, s), 1607 (s, s), 1541 (s, s), 1508 (s, s), 1423 (m, s), 1358 (w, s), 1301 (s, s), 1260 (s, s), 1222 (s, s), 1159 (s, s), 1111 (w, s), 1039 (s, s), 999 (s, s), 839 (s, s), 760 (s, s), 729 (m, s), 687 (s, s), 604 (m, s).

1-Me-2-($CH_2NHC(=O)Ar$)-1,2-$C_2B_{10}H_{10}$ (Ar = 2-C_5NH_4). Yield 63%. MS (ESI) for $C_{10}H_{20}B_{10}N_2O$: $m/z = 292.27$ $[M + H]^+$. ^1H NMR ($CDCl_3$, ppm), $\delta = 8.53–7.42$ (m, 4H, $C_5N\underline{H}_4$), 7.19 (s, 1H, N$\underline{H}$), 4.17 (d, 2H, $C\underline{H}_2$-N), 2.2.77–1.36 (m, br, 10H, $B_{10}\underline{H}_{10}$), 2.39 (s, 3H, $C\underline{H}_3$), 1.96 (s, 3H, C_{cage}–$C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), $\delta = 168.75$ ($\underline{C}O$), 148.27, 148.27, 137.02, 126.89, 124.36 ($\underline{C}_5NH_4$), 80.42 and 74.18 ($\underline{C}_{cage}$), 46.46 (–$\underline{C}H_2$–N), 22.95 (C_{cage}–$\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), $\delta = -3.98$ (1B, $^1J_{BH} = 173$ Hz), −5.58 (1B, $^1J_{BH} = 169$ Hz), −9.67 (2B, $^1J_{BH} = 53$ Hz), −10.21 (4B, $^1J_{BH} = 74$ Hz), −11.25 (2B, $^1J_{BH} = 148$ Hz). IR (KBr pellet, cm^{-1}), 33381 (m, br), 3058 (w, s), 2944 (m, s), 2874 (w, s), 2585 (vs, s), 2302 (w, s), 1680 (s, m), 1647 (s, s), 1557 (s, s), 1521 (s, s), 1448 (s, s), 1393 (m, s), 1293 1154 (s, s), 1105 (m, s), 1018 (m, s), 921 (m, s), 729 (s, s), 660 (w, s), 621 (w, s).

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