Ruthenium(0) Nanoparticle-Catalyzed Isotope Exchange between ^{10}B and ^{11}B Nuclei in Decaborane(14)

Zhu Yinghuai,*,[†] Effendi Widjaja,[†] Shirley Lo Pei Sia,[†] Wang Zhan,[†]
Keith Carpenter,[†] John A. Maguire,[‡] Narayan S. Hosmane,[§] and
M. Frederick Hawthorne[||]

*Contribution from the Institute of Chemical and Engineering Sciences, No. 1 Pesek Road,
Jurong Island, Singapore 627833, Department of Chemistry, Southern Methodist University,
Dallas, Texas 75275-0314, Department of Chemistry and Biochemistry, Northern Illinois
University, DeKalb, Illinois 60115-2862, and International Institute of Nano and Molecular
Medicine, University of Missouri—Columbia, 202 Schlundt Hall, Columbia, Missouri 65211*

Received January 11, 2007; E-mail: zhu_yinghuai@ices.a-star.edu.sg

Abstract: Well dispersed ruthenium(0) nanoparticles, stabilized in the ionic liquid agent, trihexyltetrade-cylphosphonium dodecylbenzenesulfonate, have been successfully prepared via a reduction reaction of the precursor [CpRuCp*RuCp*]PF$_6$ (Cp* = C$_5$Me$_5$). The ruthenium(0) nanoparticles were shown to catalyze the isotope exchange reaction between ^{10}B enriched diborane and natural abundant B$_{10}$H$_{14}$ to produce highly ^{10}B enriched ($\sim$90%) decaborane(14) products. The ruthenium(0) nanoparticles were characterized by TEM, XRD, and XPS. The ^{10}B enriched decaborane(14) has been analyzed by Raman spectroscopy, NMR, and high-resolution MS.

Introduction

Boron neutron capture therapy (BNCT) is based on the nuclear reaction that occurs when ^{10}B is irradiated with low-energy thermal neutrons to yield high linear energy transfer α particles and recoiling lithium-7 nuclei.[1,2] Clinical interest in BNCT has focused primarily on the treatment of high-grade gliomas and either cutaneous primaries or cerebral metastases of melanoma, and more recently, head, neck, and liver tumors.[3]

Over the past 20 years, various boron delivery agents have been designed and synthesized. These include boron-containing amino acids, biochemical precursors of nucleic acids, DNA-binding molecules, porphyrin derivatives, and high molecular weight delivery agents, such as monoclonal antibodies and their fragments, carbon nanotubes and liposomes.[4−11] It is unlikely that any single agent will be able to target all, or even most,

tumor cells. For a boron delivery agent to be successful, the following criteria must be met: (1) low systemic toxicity and normal tissue uptake with high tumor uptake and concomitantly high tumor/tissue and tumor/blood concentration ratios (>3−4:1); (2) tumor concentrations of $\sim$20 μg ^{10}B/g tumor; (3) rapid clearance from blood and normal tissues along with persistence in the tumor during BNCT. To date, there is no single boron delivery agent that fulfils all these criteria. One of the problems is that only the ^{10}B isotope, which is of minor abundance ($\sim$20%), is therapeutically effective. To reach higher ^{10}B concentration in the tumors, ^{10}B enriched compounds are needed, and, thus, the search for convenient and effective methods to prepare such compounds is an extremely important area of both pharmacological and academic research interests.

Decaborane(14) (B$_{10}$H$_{14}$), is one of the most useful of the precursor boron hydrides in the syntheses of high boron containing compounds. It is a fairly stable solid that can be manipulated using standard Schlenk techniques.[12−14] Prior to the late 1970s, the principal methods for the preparation of

[†] Institute of Chemical and Engineering Sciences.
[‡] Southern Methodist University.
[§] Northern Illinois University.
[||] University of Missouri—Columbia.
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Scheme 1. Synthesis of $^{10}B_{10}H_{14}$ and $closo$-1-R^1-2-R^2-$C_2$$^{10}B_{10}H_{10}$

$(R = Alkyl, R^1, R^2 = H, Alkyl, Aryl)$
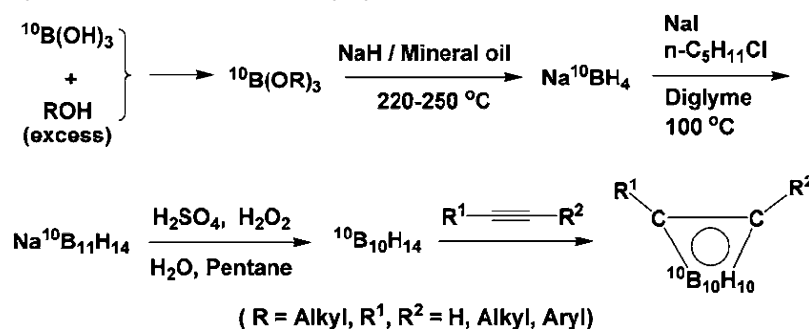
decaborane(14) involved pyrolytic or high-pressure reactions using difficult to handle lower boron hydrides, such as diborane (B_2H_6) or tetraborane (B_4H_{10}).[15] Later, a nonpyrolytic method, involving the reaction of an alkali metal pentaborane with diborane at temperatures below −20 °C, was developed.[16] These methods all require specialized equipment and involve the use of potentially hazardous reagents.

Currently, the syntheses of ^{10}B enriched decaborane(14) follow a rather circuitous route, beginning with the synthesis of $^{10}B(OR)_3$ from ^{10}B enriched boric acid, followed by reduction to give $Na^{10}BH_4$. The borohydride could undergo further reaction as shown in Scheme 1 to give the desired $^{10}B_{10}H_{14}$ in ∼50% yield.[17a] Alternately, the $Na^{10}BH_4$ could be oxidized by I_2 in a diglyme/dioxane mixture to give $Na[^{10}B_3H_8]\cdot3(C_4H_8O_2)$, which could then undergo oxidative cage fusion with $NiCl_2$ in heavy mineral oil to produce $^{10}B_5H_9$, which on further reaction with $NiCl_2$ or $FeCl_2$ gives the final product, $^{10}B_{10}H_{14}$.[17b,c] Since none of the steps involve routine chemistry, there is a need to find new, convenient, high-yield synthetic routes for the preparation of ^{10}B-enriched boron cage molecules.

Nanoscale metal particles have been attracting much attention and are widely explored for their intriguingly chemical and physical properties, as well as potential applications.[18] The extremely high surface areas and the subsequent high density of active sites make these nanoparticales more attractive than the bulk metals as catalysts.[19,20] It has been observed that transition metals such as Ru, Os, Ir, and Rh, could interact with boron clusters to form metal−boron (M−B) bonds and thus activate B−H bonds.[21] Also, carboranes and boron hydrides were found to undergo catalytic isotopic exchange of their terminal hydrogens with deuterium gas with $(PPh_3)_3RuHCl$ as

catalyst.[22] These examples of B−H activation and the enhanced catalytic activity of nanoscale metal particles encouraged us to investigate the possibility of synthesizing ^{10}B-enriched decaborane(14) via isotope exchange between natural abundant decaborane(14) and ^{10}B-enriched diborane, in the presence of Ru(0) nanoparticles as catalysts. Herein, we report the preliminary results of this investigation.

The preparation and stabilization of metal nanoparticles with controlled size and composition have opened new avenues of investigation.[23] In general, particle size is closely related to particle synthesis, which has given rise to the descriptions of a number of synthetic approaches, such as, chemical reduction,[24] UV photolysis,[25] thermal decomposition,[26] metal vapor deposition,[27] electrochemical reduction,[28] sonochemical decomposition,[29] microwave irradiation,[30] and rapid expansion of supercritical fluid solutions.[31] Since the nanoparticles tend to aggregate, forming bulk particles with reduced catalytic activity, stabilization methods become equally important. The main methods used for the stablization of metallic nanoparticles in solution involve electrostatic or steric protection by the use of water-soluble polymers, quaternary ammonium salts, surfactants, or polyoxoanions.[32] It has recently been reported that mild hydrogenation reduction of metal complexes such as $[IrCl(cod)]_2$ and Ru(cod)(cot) (cod = 1,5-cyclooctadiene, coe = 1,3,5-cyclooctatriene) in the ionic liquids, such as 1-n-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6], produced active and recyclable biphasic C=C hydrogenation systems with the Ir(0) particles of around 2.5 nm and Ru(0)

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around 2.6 nm diameters acting as catalysts. The room-temperature ionic liquid was thought to act as a stabilizing medium.[33−35] This general procedure was adopted in the present study.

Experimental Section

General Procedure. All reactions were carried out under an argon atmosphere using standard Schlenk line or glove box techniques. Diglyme, diethyl ether, and hexane were refluxed over sodium/benzophenone until a blue color was sustained, and distilled under argon just before use. Natural abundant decaborane(14) and $Na^{10}BH_4$ were obtained from Katchem Ltd and used as received. Iodine, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) and other reagents were purchased from Aldrich and used as received. The ionic liquid, trihexyltetradecylphosphonium dodecylbenzenesulfonate, [TH-TdP][DBS], was provided by IL-TECH Inc. (Dr. Rex Ren) as free gift. The complex [CpRuCp*RuCp*]PF_6 (Cp* = C_5Me_5) was prepared according to literature methods.[36] X-ray diffractometry (XRD) was measured on a Bruker XRD D8 Advance analyzer, X-ray photoelectron spectrometery (XPS) was analyzed with a ESCALAB 250 analyzer, and transmission electron microscopy scans (TEM) were obtained on a Tecnai TF 20 S-twin with Lorentz lens analyzer at 200 kV. The Raman scattering spectra were measured at room temperature using a JY Horiba LabRAM Raman microscope equipped with liquid-nitrogen-cooled charge-coupled device (CCD), multichannel detector (256 pixels × 1024 pixels) and a high grade Olympus microscope (objective 100×). The spectra were measured using the visible 514.5 nm argon ion laser as the scattering excitation source. The laser power on the sample was about 6 mW. The spectral acquisition time for each Raman spectrum was about 120 s with spectral resolution around $1.5−2$ cm^{-1}. The high-resolution MS was measured on a Thermo Finnigan MAT XP95 analyzer using EI-HR model (70 eV, source temperature 150 °C). $^{10}B/^{11}B$ NMR spectra were recorded on a Bruker 400 analyzer at 128.38 MHz.

(1) Synthesis of Ruthenium Nanoparticle in Ionic Liquid. Nanoscale ruthenium was prepared by the reduction of (13.5 mg) [(η^5-C_5H_5)Ru(μ,η^5-C_5Me_5)Ru(η^5-C_5Me_5)][PF_6] in 15.0 mL of ethylene glycol under a hydrogen atmosphere to produce a red-brown solution. The solution was heated to 180 °C and kept at that temperature until the color of the mixture changed to black (about 5 h). Ionic liquid, trihexyltetradecylphosphonium dodecylbenzenesulfonate (5.0 mL), was then added, and the system was cooled to room temperature. After removal of the excess ethylene glycol in vacuum and washing with a mixture of hexane and diethyl ether, a black sticky residue was obtained. To isolate Ru nanoparticles, the black residue was dissolved in 10.0 mL of dichloromethane and subjected to centrifugation (4000 rpm, 35

min) followed by washing with dichloromethane (2 × 10.0 mL) and drying under reduced pressure. The resulting ruthenium nanoparticles were subjected to analysis by XRD, XPS, and TEM.

(2) Synthesis of $^{10}B_2H_6$. ^{10}B enriched diborane ($^{10}B_2H_6$) was produced according to the literature method using ^{10}B-enriched sodium borohydride ($Na^{10}BH_4$).[37] In brief, under argon atmosphere, a solution of iodine (20 mmol) in dry diglyme (30 mL) was added dropwise to a solution of $Na^{10}BH_4$ (40 mmol) in dry diglyme 30 mL at room temperature with constant stirring. The resulting $^{10}B_2H_6$ and H_2 were carried off through a side tube and connected to a series of four cooling traps for purifying and trapping the product. The first trap was immersed in a −78 °C bath to remove traces of diglyme and iodine which were entrained in the diborane stream. The other three traps were cooled with liquid nitrogen (−196 °C) to collect diborane. The outlet from the last trap was vented through a mercury bubbler and a trap containing an adequate amount of isopropanol/acetone to destroy excess diborane. When the reaction had finished, the bubbler was removed under argon and replaced by a reactor for the next step in the synthesis.

(3) Catalytic $^{10}B/^{11}B$ Isotope Exchange Between $^{10}B_2H_6$ and $B_{10}H_{14}$. Catalytic isotope exchange process took place in a solution of decaborane(14) (0.1 g, 0.82 mmol) dissolved in the above prepared catalytic system composed of 4.0 mg of Ru nanoparticles dispersed in 5.0 mL of ionic liquid trihexyltetradecylphosphonium dodecylbenzenesulfonate and 10.0 mL of dichloromethane. The pre-prepared ^{10}B enriched diborane (41.00 mmol) was introduced to the reaction flask. The resulting mixture was then heated to 50 °C to undergo reaction (*P* $\cong$ 1.08 atm) for 6 h. After the reaction process, the diborane was released and destroyed by bubbling through excess isopropanol/acetone. The residue was dried under reduced pressure, was extracted with hexane (25 mL × 3), and combined to dryness with a recovery of decaborane(14) > 97.3%. The recovered, partially substituted decaborane(14), was then redissolved in a new ionic liquid/dichloromethane/catalyst mixture and treated with additional ^{10}B-enriched diborane. This proceedure was repeated for a total of six times. The isolated ^{10}B-enriched $B_{10}H_{14}$ sample was then analyzed with Raman spectroscopy, ^{10}B-NMR spectra, and MS.

Results and Discussion

1. Synthesis and Spectra of Catalyst. The initial choice of ruthenium as the catalyst was dictated by earlier work and the relatively low price of the metal compared to other transition metals such as platinum, palladium, and rhodium.[38] It should be pointed out that other nanosized metals could also function as catalysts. In our work, the bimetallic metallocene complex [CpRuCp*RuCp*]PF_6 (Cp* = C_5Me_5)[36] was selected as a precursor to produce ruthenium nanoparticles via a reduction reaction, with trihexyltetradecylphosphonium dodecylbenzenesulfonate [THTdP][DBS] or [BMIM][PF_6] as the stabilizing ionic liquid agent. The diruthenium metallocene was reduced by hydrogen in a mixed solvent of ethylene glycol and the particular ionic liquid.

Because of differences in the densities of the ionic liquids, the ionic liquid containing nanoRu(0) could be either the top layer or the bottom layer of the biphasic mixture (see Figure 1a). As can be seen from the Figure, the [THTdP][DBS] stabilized nanoRu was the upper layer and the [BMIM][PF_6] was the lower layer. Ethylene glycol was used to dissolve metal complex precursor and to initially stabilize Ru nanoparticles.[34,35] Ruthenium nanoparticles stabilized with ethylene glycol could be easily extracted into ionic liquids to form two layers. Ethylene glycol can be separated by decantation, followed by further

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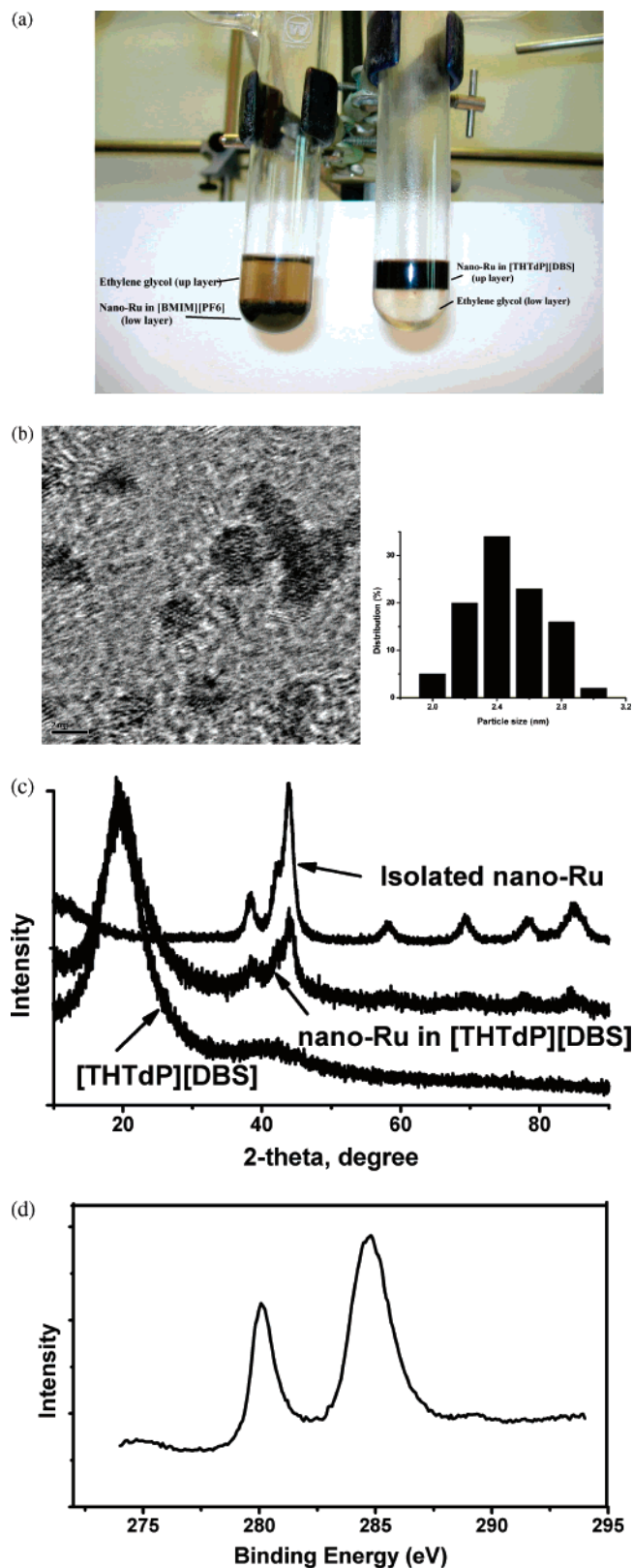
Figure 1. Ionic liquid systems, TEM, XRD and XPS of Ru Nanoparticles: (a) Ru nanoparticles in different ionic liquids: (b) TEM picture and histogram of Ru nanoparticles: (c) XRD spectra: (d) XPS spectrum.

vacuum drying. Complete removal of alcohol is important for our system because any remaining alcohol will destroy both decaborane(14) and ^{10}B-enriched diborane. The fluoride containing ionic liquid, [BMIM][PF$_6$], might release HF under
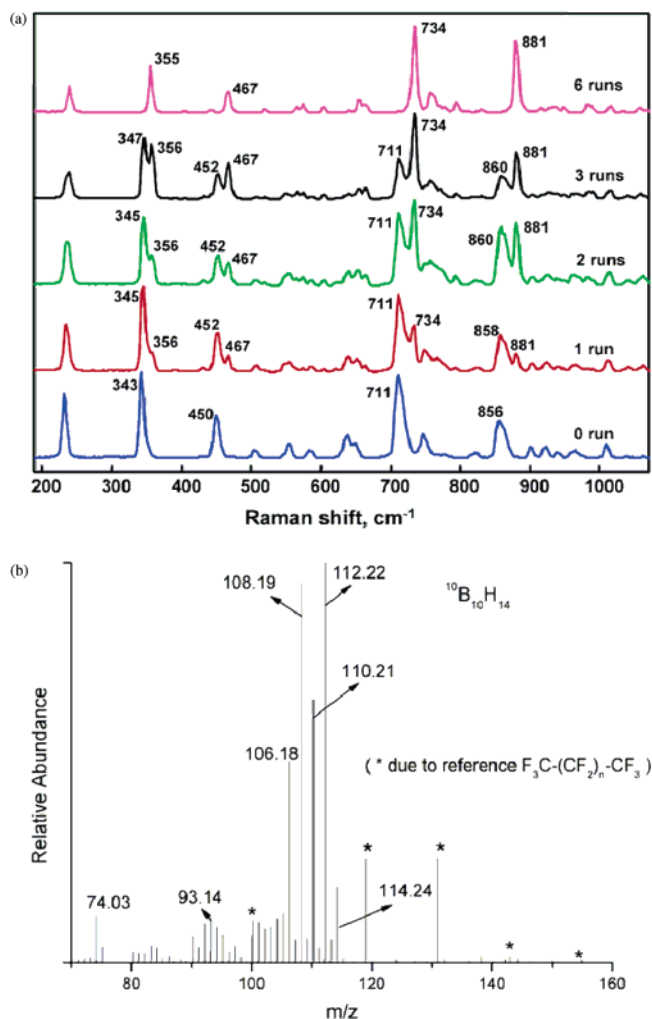
Figure 2. Raman spectra in different runs and MS spectra of ^{10}B$_{10}$H$_{14}$: (a) Raman spectra in different runs; (b) analyzed MS of ^{10}B-enriched decaborane(14).

certain reaction conditions, which could cause severe corrosion problems. In addition, this imidazolium-based ionic liquid may produce N-heterocyclic carbenes, which have toxicity to nanometal catalysts,[32a] therefore, only the environmentally benign non-imidazolium ionic liquid, [THTdP][DBS], was used in catalytic runs. Well-dispersed ruthenium nanoparticles with a uniform size (2~4 nm) were obtained from [THTdP][DBS], these were analyzed by TEM, XRD, and XPS (Figure 1b−d).

The TEM shows that the prepared ruthenium nanoparticles are extremely small with an average size of ~2.5 nm and narrow size distribution (Figure 1b, as determined from the measurement of ~150 particles). These results are comparable with other reported results.[34,35] The XRD spectra (Figure 1c) show bulk Ru(0) model with broad peaks owing to the small particle size. The XPS spectrum (Figure 1d) shows typical Ru(0) absorptions at 280.08 and 284.48 eV for 3d$_{5/2}$ and 3d$_{3/2}$, respectively, with a $\Delta = 4.40$ eV, which is consistent with literature results.[39] In the preparation of these samples for analysis all work was done in an argon atmosphere to guard against oxide formation; no evidence was found in the XPS results for the existence of RuO contamination.[34] The [THTdP][DBS] protected ruthenium nano-

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Scheme 2. Catalytic ^{10}B-^{11}B Isotope Exchange

($\bigcirc$ = $^{11/10}$BH; $\bullet$ = ^{10}BH)   (^{10}B$_{10}$H$_{14}$)
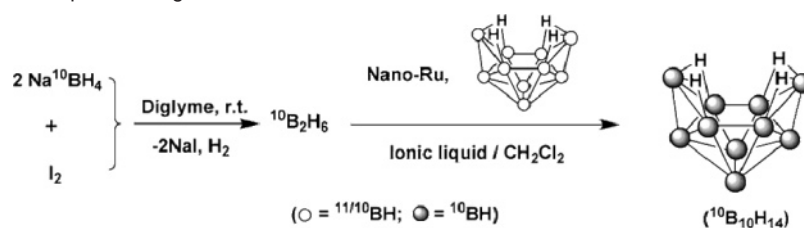
particles were found to be stable for more than 1 month under an argon atmosphere.

2. Catalytic Isotope Exchange. The boron-10 enriched cluster B$_{10}$H$_{14}$ was prepared from the boron exchange reaction of ^{10}B enriched diborane, ^{10}B$_2$H$_6$ and natural abundant B$_{10}$H$_{14}$, catalyzed by ruthenium nanoparticles that were well dispersed in the ionic liquid [THTdP][DBS] as outlined in Scheme 2. The ^{10}B$_2$H$_6$ was introduced to the system and the reaction was continued for 6 h at 50 °C and ca. 1 atm. After purification, a ^{10}B enriched product was obtained with a recovery of 97.3% decaborane(14). The procedure was repeated six times for each sample and the products were analyzed by Raman spectroscopy (Figure 2a). The last obtained ^{10}B enriched B$_{10}$H$_{14}$ was also analyzed with ^{10}B{^{1}H-decoupled}-NMR and high-resolution MS. The recyclable biphasic catalytic system could be used at least three times without showing obvious changes in activity.

Figure 2a shows the Raman spectra, from 200 to 1000 cm^{-1}, of the product boranes after the different runs. Decaborane(14) is a 24 atom molecule with C_{2v} symmetry, resulting in 64 fundamental frequencies in the IR/Ramon spectra. The Raman spectrum is complex and has not been analyzed in detail. However, the fundamental frequencies can be grouped as follows: 200−400 cm^{-1} (B−B skeletal bending), 400−1100 cm^{-1} (B−B skeletal stretching), 600−800 cm^{-1} (B−H bending || to C$_2$).[40] The measured Raman spectra consist of five major peaks at ∼230, 343, 450, 711, and 856 cm^{-1} (see Figure 2a). There is a steady shift to higher cm^{-1} of about 3% in going from the natural abundant to the product after six runs. Although the specific transitions cannot be identified, a shift to higher wave numbers by about that percent would be what is expected from the substitution of ^{10}B atoms for ^{11}B in B$_{10}$H$_{14}$. The ^{10}B-NMR of the final product shows the same peaks as did the ^{11}B-NMR of the starting borane, which confirms identical structures for the beginning and final borane clusters (see the NMR spectra in the Supporting Information).

To assess quantitatively the extent of ^{10}B enrichment, the sample was subjected to analysis with high-resolution MS (see Figure 2b). The absence of peaks in the m/z region of 114.24∼123.99, which were dominant in the natural abundance spectrum (see the MS spectra in the Supporting Information), shows extensive exchange. The peak at m/z = 114.24 is consistent with a radical molecular ion (M$^{+\bullet}$). From Figure 2b, it can be seen that the main fragmentation process for ^{10}B enriched decaborane(14) is the dissociation of hydrogen to form strong peaks such as m/z = 112.22, 110.21, 108.19, and 106.18. The mass spectrum of the sample obtained after three runs (see the Supporting Information) was quite complex and did not provide any useful information. From the combined data, it is reasonable to conclude that the isotope exchange

between ^{10}B and ^{11}B nuclei in decaborane(14) is quite complete and ^{10}B enrichment is not less than 90% (based on Raman assessment).

At present, the mechanism for this reaction is not known. However, some observations in this, and other, laboratories offer some insight. (1) The Ru(0) is the active catalyst. Runs in the presence of Hg poison did not result in isotopic exchange (see Supporting Information). (2) While isotopic exchange between B$_2$H$_6$ and B$_{10}$H$_{14}$ is not known, complete isotopic exchange between ^{10}B$_2$H$_6$ and NaB$_{10}$H$_{13}$ had been reported some 40 years ago by Schaeffer and Tebbe.[41] (3) It is known that ruthenium complexes, such as [Cp*RuCl$_2$]$_2$ and Cp*RuCl(TMEDA) (Cp* = -C$_5$Me$_5$), are active precatalysts for the borylation of alkanes with bis(pinacolato)diboron (B$_2$pin$_2$), which suggests that [Ru] based catalysts are able to activate B−B bond cleavage.[42] (4) The ruthenium(0) complexes Ru(cod)(cot) (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) show catalytic activity for dehydrogenative borylation of vinylarenes with pinacolborane (H-Bpin).[43] (5) Diborane is active for isotopic exchange reactions involving D and ^{10}B, and some intermediates such as BH$_3$, BH$_2$ (twice as abundant as BH$_3$), and B$_3$H$_n$ were found to be present in the pyrolysis of B$_2$H$_6$.[44,45] Therefore, a likely sequence could involve the decaborane interacting with a Ru-(0) with B−H bond cleavage, giving a partially anionic boron species that could react with a ^{10}BH$_2$ or ^{10}BH$_3$ forming a metal bound *nido*-B$_{11}$H$_{14}^-$ species, in which the ^{10}B could migrate from a facial position to one within the complex; the *nido*-B$_{11}$H$_{14}^-$ is known. Removable of an unlabeled B vertex would lead to a monosubstituted B$_{10}$ cage. This process could be repeated. It should be pointed out that the overall exchange reaction is essentially thermoneutral and the reaction is driven by mass-action. The large excess in ^{10}B$_2$H$_6$ (>40:1) and the repetition of runs, ensure that essentially complete (90%) substitution is achieved. At the current stage of our investigation, the possibility of completely different, new mechanism cannot be excluded.

Conclusions

In summary, we report herein the first preparation of well dispersed, ionic liquid stablized ruthenium(0) nanoparticles from their corresponding metallocene precursor. The resulting Ru(0) nanoparticles were shown to catalyze the isotope exchange reaction between ^{10}B enriched diborane and natural abundant B$_{10}$H$_{14}$ to produce highly ^{10}B enriched (∼90%) decaborane(14) products. This novel performance of

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the catalytic system warrants further synthetic and mechanistic investigations; such studies are currently underway in our laboratories.

Supporting Information Available: Hg poisoning test results; NMR, HRMS, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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