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Catalytic Phenylborylation Reaction by Iridium(0) Nanoparticles Produced from Hydridoiridium Carborane

Zhu Yinghuai,*,† Koh Chenyan,† Ang Thiam Peng,† A. Emi,† Winata Monalisa,† Loo Kui-Jin Louis,† Narayan S. Hosmane,‡ and John A. Maguire§

Institute of Chemical and Engineering Sciences Ltd, 1 Pesek Road, Jurong Island, Singapore 627833, Department of Chemistry and Chemical Biology, Northern Illinois University, DeKalb, Illinois 60115-2862, and Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

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Well-dispersed iridium(0) nanoparticles stabilized with the ionic liquid, trihexyltetradecylphosphonium methylsulfonate, [THTdP][MS], have been successfully prepared by reduction of the precursor hydridoiridium carborane, $(Ph_3P)_2Ir(H)$-(7,8-*nido*-$C_2B_9H_{11}$). The iridium nanoparticles were found to be active catalysts for arylborylation, forming boric acids. The activity of the catalyst has been investigated as a function of the activating base, and reaction conditions. The highest yield of 91% was achieved in a microwave reactor using the base, *tetra*-2-pyridinylpyrazine, in the presence of [THTdP][MS]. The catalytic system could be recycled at least six times with less than a 0.5% loss of activity.

Introduction

The catalytic borylation of unreactive alkanes and arenes to form boric acids, is an important process in forming new C−C bonds and has found extensive use in pharmaceutical chemistry and organic synthesis.[1,2] The existing methods of preparation of arylboronic acids produce only modest yields (∼50%), have limited tolerance of other functional groups, and require restricted experimental conditions.[3] Complexes of rhenium, rhodium, and iridium have been reported to be capable of intermolecular C−H activation with both saturated and unsaturated hydrocarbons.[4–9] Despite the fact that these systems provide feasible synthetic conditions for arylborylation reactions, there are no reported indications of their reusability factor, which can contribute significantly to the cost of the catalyst and the environment. As such, the recycling of both ligand and metal is highly desirable for reducing raw material costs and engineering a greener process via limiting the amount of waste chemicals for disposal.

Because of their high surface areas and high density of active sites, nanoscaled metal particles have been widely explored as catalysts.[10–13] With the improved developments in nanochemistry, it is now possible to prepare soluble analogues of heterogeneous catalysts, materials that might have properties intermediate between those of the bulk metal

* To whom correspondence should be addressed. E-mail: zhu_yinghuai@ices.a-star.edu.sg. Phone: (+65)-6796-3801. Fax: (+65)-6316-6182.
† Institute of Chemical and Engineering Sciences Ltd.
‡ Northern Illinois University.
§ Southern Methodist University.

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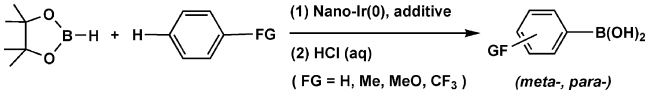
Scheme 1. Nano-Ir(0)-Catalyzed Borylation



and single metal-particle (homogeneous) catalysts. Because nanoparticle-based catalytic systems generally exhibit superior catalytic activities than the corresponding bulk materials, the application of transition-metal nanoparticles as catalysts for organic transformations has been attracting wide interest.[14,15] In these studies, the methods of preparation and stabilization of metallic nanoparticles, with controlled size and compositions, such as alloys or core−shell particles, present critical challenges.[16] It is also generally believed that the particle size is a function of the precise method of preparation.[17] To sustain catalytic activity, it is important to stabilize the metallic nanoparticles, preventing their aggregation to form bulk particles, thereby reducing, or even eliminating, their catalytic potency. Typical methods to stabilize metallic nanoparticles in solution include electrostatic or steric protection.[15] However, the problem of recycling the catalysts must be addressed before any nanocatalytic process can be effectively scaled-up.[18] It has been found that room-temperature ionic liquids have potential as stabilization reagents for transition-metal nanoparticles[15] and are easily separated from product mixtures by simple decantation.[19,20] Herein, we report our preliminary findings regarding the synthesis and characterization of ionic liquid-stabilized iridium(0) nanoparticles and their use as catalysts for the C−H borylation of arenes by pinacolborane (HBpin), as outlined in Scheme 1.

Experimental Section

General Procedures. All synthetic procedures were carried out in an inert atmosphere using standard Schlenk techniques. $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$ was prepared as described in the literature.[21] Solvents were dried using standard methods. All other reagents were used as received. FTIR spectra were measured using a BIO-RAD spectrophotometer with KBr pellets or organic solvent films. Scanning electron microscopy (SEM) images were obtained on a JSM-6700F field-emission microscope. Transmission electron microscopy (TEM) measurements were carried out on a JEOL Tecnai-G,[2] FEI analyzer at 200 kV. The elemental analyses were measured on a EURO EA. Proton, carbon-13, and boron-11 NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.13, 100.62, and 128.38 MHz, respectively.

Synthesis of the Iridium(0) Nanoparticles in Ionic Liquid. A 0.85 g (1.00 mmol) sample of $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$ was placed in 30 mL of ethylene glycol, and the resulting solution was heated to 160 °C for 8 h under a hydrogen atmosphere (10 bar). A 4 mL sample of the ionic liquid was then added to extract the generated nanoscale-sized iridium, and the reaction mixture was further reacted for 12 h before being cooled to room temperature. After the removal of ethylene glycol via syringe, the residue was washed with EtOH (2 × 3 mL), diethyl ether (2 × 3 mL), and deionized water (2 × 2 mL) in sequence, followed by drying in vacuum. To isolate the iridium nanoparticles, the black ionic liquid residue was diluted with 20 mL of dichloromethane and subjected to centrifugation (4500 rpm, 40 min), followed by washing with dichloromethane (2 × 15 mL) and drying in vacuum. The nanoparticles were analyzed by XRD, XPS, and TEM.

Evaluation of Catalytic Activity. The borylation of benzene was performed in dichloromethane (CH_2Cl_2) and the ionic liquid, trihexyltetradecylphosphonium methylsulfonate [THTdP][MS], in the presence of an iniating ligand base. The reactants were used in the following amounts: 1.0 mmol HBpin, 0.006 mmol nano-Ir(0), 0.01 mmol of base, 5 mL benzene (or benzene-d_6), and 2 mL each of dichloromethane and the ionic liquid [THTdP][MS]. The reaction was carried out at a temperature of 80 °C for 20 h. After borylation, the solvent was removed under reduced pressure and diethyl ether (2 × 15 mL) was added to extract the crude mixture of boroxines. The ionic-liquid phase, containing the nano-Ir(0), was washed with deionized water and dried under reduced pressure for subsequent runs. In addition to these conventional conditions, the catalytic reactions were repeated under the following conditions: (a) in a high pressure reactor (Parr stirred high pressure reactor) at 180 °C for 12 h; (b) under ultrasonic irradiation (Transsonic T750 Ultrasonic Bath) for 4 h; and (c) under microwave irradiation (Milestone Microsynth Microwave Laboratory station with Laboratory Terminal 800 Controller) with the temperature increasing from room temperature to 130 °C within 2 min and maintained at 130 °C for 1 h. After borylation, the solvent was removed under reduced pressure. Prior to hydrolysis, diethyl ether (2 × 15 mL) was added to dissolve the obtained residue, after which 20 mL of 10% HCl (aq) was added and the mixture stirred for 4 h. Two layers formed, and the organic layer was isolated and dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residual product was purified with flash column chromatography (SiO_2) to obtain the phenylboronic acids, which were confirmed by NMR spectroscopy. For catalyst recycle runs, after the borylation reaction and removal of the solvent, the crude product of boroxines was extracted with diethyl ether and separated via decantation. The ionic liquid residue containing nano-Ir(0) could be used for future runs.

In an effort to further characterize the nature of the catalytic species, borolation reactions were carried out in the presence of the precursor, $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$. For such runs, 1.0 mmol HBpin, 0.03 mmol of the precursor, 0.03 mmol of base (TPy),

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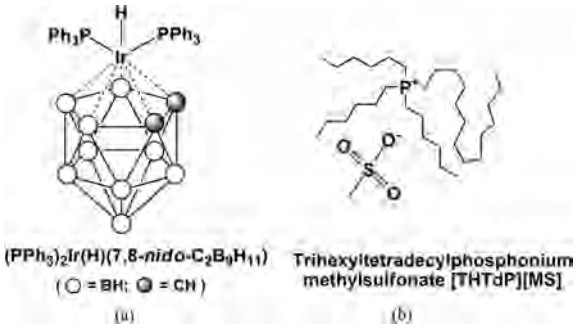

Figure 1. Structures of precursor and used ionic liquid.

and 10 mL of benzene were used. The borylation products were isolated and analyzed as described above for the nanoparticle catalysts. The results are plotted in Figure 4.

Mercury Poisoning Tests. Two experiments were conducted to study the effects of mercury on the precatalyst and the preformed nano-Ir(0) catalysts. In the first experiment, after the formation of nano-Ir(0), a large excess (300 equivalents) of mercury was added to the ionic liquid solution.[22] After stirring for 2 h at room temperature under an argon atmosphere, the mixture containing mercury was used in the phenylborylation reaction, and any products were collected as described above. No isolable products were obtained in this experiment. In the second study, excess mercury was added to an active catalyst solution. In these experiments, after an 8 h reaction process, the reaction was interrupted by cooling the mixture to room temperature and carefully adding 300 equivalents of mercury under an argon atmosphere. After stirring for about 1 h at room temperature, the mixture was reheated to 80 °C and further reacted for 14 h. Only a 30% yield of the phenyl boric acid product was collected. These results confirm that the catalyst was deactivated by mercury.

Results and Discussion

Synthesis of Iridium(0) Nanoparticles. The iridium(0) noanparticles were produced by the slow reduction of the air-stable hydridoiridium carborane, $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$ (part a in Figure 1).[21] The $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$ was reduced in ethylene glycol under a hydrogen atmosphere to produce nano-Ir(0) particles. After addition of the ionic liquid, the iridium(0) nanoparticles could be extracted from the ethylene glycol, which was found not to be a suitable stabilization reagent. The ionic liquid mixture was washed with EtOH, Et_2O, and deionized water, in sequence, to remove all byproduct. Our choice of the water-stable and environmentally benign ionic liquid trihexyltetradecylphosphonium methylsulfonate [THTdP][MS] (part b of Figure 1) to stabilize nano-Ir(0) particles was dictated by the following considerations. We wished to avoid ionic liquids derived from $[BF_4]^-$ or $[PF_6]^-$ anions, which are moisture-sensitive and can decompose and release highly corrosive HF.[23] In addition, it is known that imidazolium-based ionic liquids may produce *N*-heterocyclic carbenes, which are poisons to nanometal catalysts.[24]

Characterization of Iridium(0) Nanoparticles. The produced iridium(0) nanoparticles were analyzed by TEM,

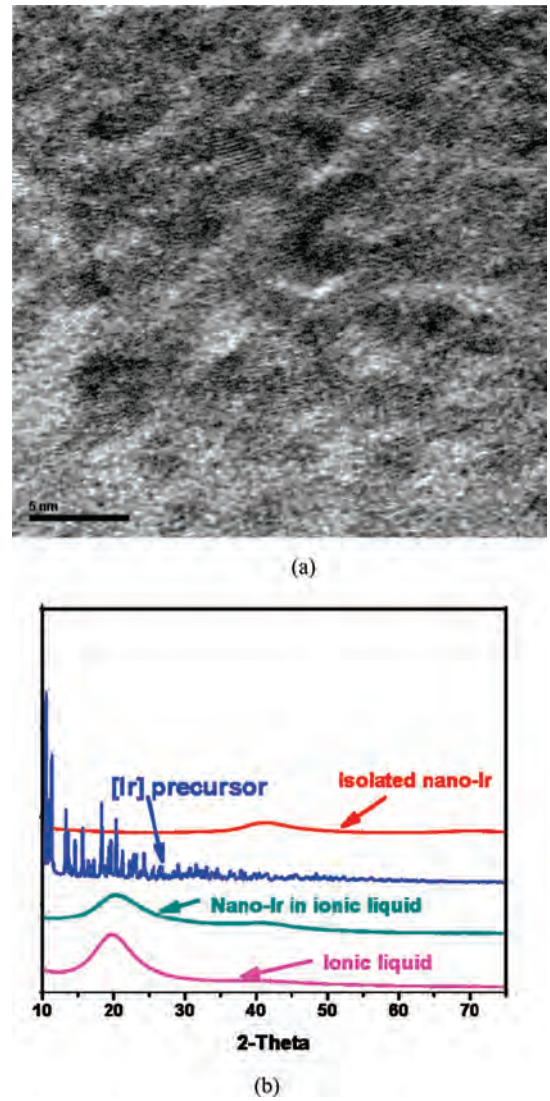

Figure 2. (a) TEM, (b) XRD, patterns of the iridium(0) nanocatalyst.

XRD (parts a and b in Figure 2), XPS, and IR spectra (parts a and b in Figure 3). The TEM image shows small and uniform crystalline nanoparticles with an average particle size of ~3.5 nm. Using this average diameter and assuming a close packing arrangement of the iridium atom, a particle composition of Ir_{1100}, and a resulting surface population of from 360 to 400 iridium particles. These results are in general agreement with those of Lin and Finke prepared by the reduction of $(Bu_4N)_5Na_3[1,5\text{-}(COD)Ir\cdot P_2W_{15}Nb_3O_{62}]$ (1,5-COD is 1,5-cyclooctadiene) by H_2.[25] The XRD spectra of the nano-Ir(0)/ionic liquid shows two broad peaks at $2\theta = 40.60$ and 20.23°, which are characteristic of the isolated iridium(0) nanoparticle and [THTdP][MS], respectively (part b in Figure 2). The XPS spectrum shows typical iridium(0) absorptions at 60.75 and 63.65 eV for $4f_{7/2}$ and $4f_{5/2}$, respectively, with a $\Delta = 2.90$ eV (part b of Figure 3); these values are consistent with those reported in the literature.[26] Samples for XPS analysis were prepared and transferred

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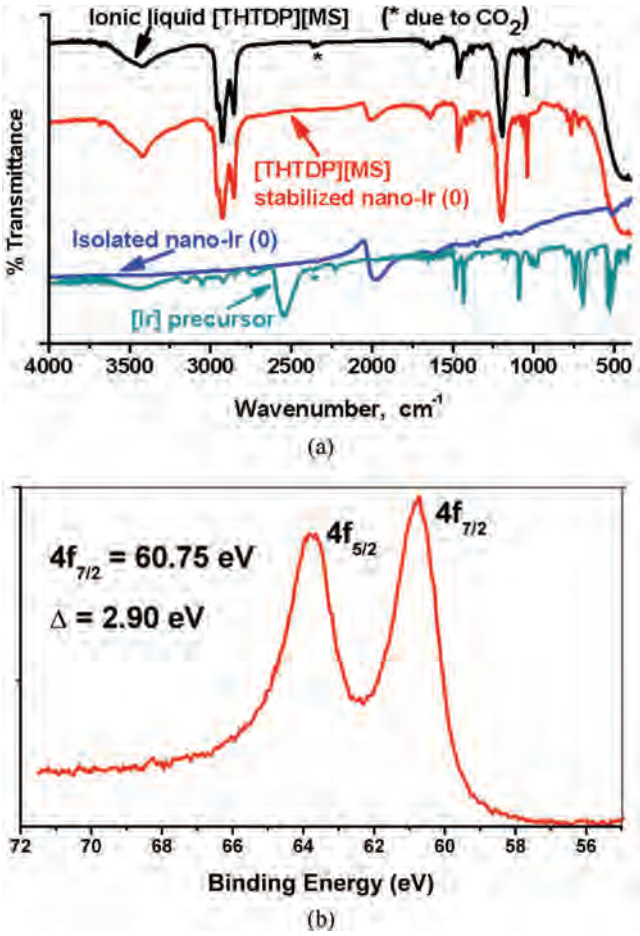

Figure 3. (a) IR and (b) XPS of the nano-Ir(0) catalyst.

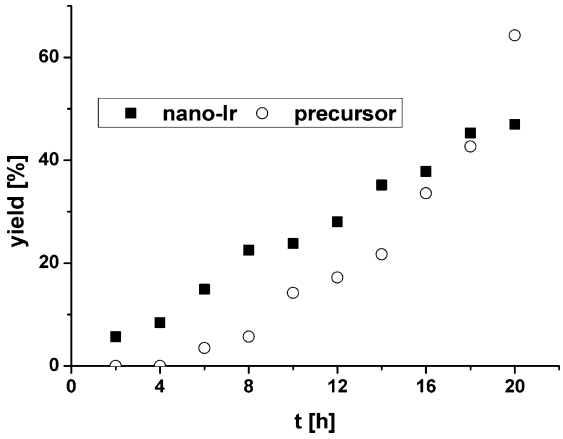

Figure 4. Plots of catalytic borylation of benzene with pinacoborane.

under a high pure argon atmosphere; no visible Ir−O absorptions have been observed.[27–29] The IR spectra, shown in part a in Figure 3, show peaks found in both the [THTdP][MS] ionic liquid and isolated iridium(0) nanoparticles. The absorption at ν = 2010 cm^{-1} found in the [THTdP][MS]-stabilized nano-Ir(0), was identified as a blue-shifted nano-Ir(0) peak that was originally at ν = 1982 cm^{-1}.

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Table 1. Effects of Auxiliaries on the Phenylborylation Reaction[a]

auxiliary[b]	PPh_3	Py	BPy	TPy	Cs_2CO_3	Na_2CO_3
yield (%)[c]	11	17	32	47	<5[d]	<5[d]

[a] All catalytic reactions were conducted under argon atmosphere at 80 °C for 20 h. Reaction mixture consisted of 1.0 mmol HBpin, 0.006 mmol of nano-Ir(0), and 0.01 mmol ligand, 5.0 mL benzene and 2.0 mL each of CH_2Cl_2 and IL. [b] Py = pyridine, Bpy = 2,2′-bipyridine, TPy = *tetra*-2-pyridinylpyrazine. [c] Isolated yield (%) after hydrolysis and flash chromatography. [d] Based on ^{1}HNMR spectra.

Table 2. Phenylborylation with Different Methodology Using Nano-Ir(0) Catalyst and TPy Ligand in Ionic Liquid[a]

method	MW[b]	((((c	autoclave[d]	IL[e]	B_2pin_2[f]
yield (%)	91	61	50	47	26

[a] Conditions are same as described in Table 1. [b] Reaction mixture was heated at 130 °C using microwaves for 1 h. [c] Reaction mixture was heated at 80 °C in ultrasonic bath for 4 h. [d] Reaction mixture was heated at 180 °C in high pressure reactor for 12 h. [e] 5.0 mL benzene with additional 2.0 mL each of dichloromethane and the ionic liquid [THTdP][MS] as solvent at 80 °C for 20 h. [f] Same conditions with e method except using B_2pin_2 instead HBpin.

Table 3. Phenylborylation with Different Substituted Groups Using Nano-Ir(0) Catalyst and TPy Ligand in Ionic Liquid[a]

FG	H	Me	OMe	CF_3
yield (%, *m*:*p*)[b,c]	47	39 (1.7)	40 (1.4)	89 (1.5)

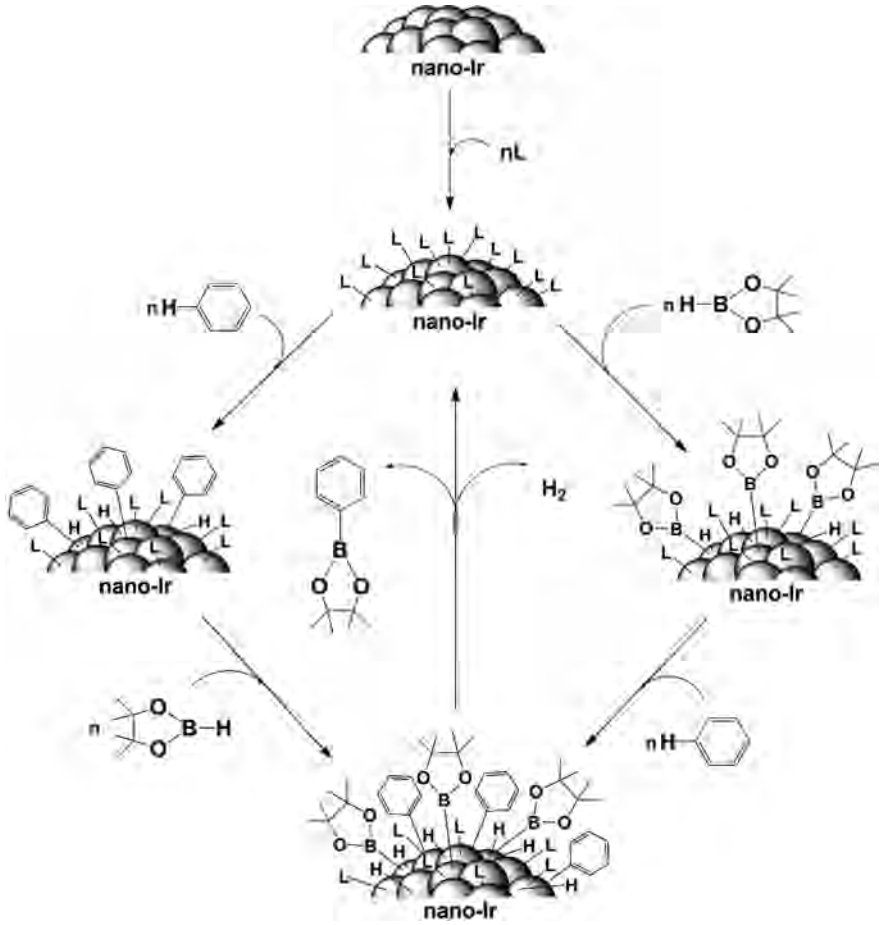
[a] Conditions are the same as described in Table 1 except for CF_3, which was operated for 12 h. [b] Obtained from 10-fold of arenes with HBpin with similar standard processes. [c] Isolated yield (%) after hydrolysis and flash chromatography.

This shift might be caused by multiple interactions between ionic liquid and iridium nanoparticles. There are no peaks due to the precursor complex. In addition, the ^{1}H, ^{31}P NMR spectra (Supporting Information) of [THTdP][MS]-stabilized nano-Ir(0) show only the normal [THTdP][MS] absorptions. All spectral evidence confirms the complete reduction of the precursor $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$ to nano-Ir(0).

Evaluation of Catalytic Activity. The prepared ionic liquid-stabilized iridium(0) nanoparticles were used as catalysts for phenylborylation to produce phenyl boric acids. In these reactions, a large excess of benzene, or substituted arenes, was used to minimize the formation of any diborylation products. The catalytic runs were initiated by the addition of a base. At the end of the catalytic runs, all solvents were removed under reduced pressure to produce a crude residue containing a mixture of boroxines, which were then extracted with diethyl ether and hydrolyzed by the addition of aqueous HCl. After purification, the structures of the phenylboronic acids were ascertained using NMR spectroscopy. The results of the catalytic runs as a function of the auxiliary base are listed in Table 1. From the table, one can see that our system is generally active for phenylborylation, with yields highly dependent on the nature of the activating base. The yields ranged from <5% for the inorganic bases Cs_2CO_3 and Na_2CO_3 to a modest 47% obtained for *tetra*-2-pyridinylpyrazine (TPy) (TOF = 3.9 h^{-1} based on total nano-Ir(0) or 11.3 h^{-1} corrected from the exposed iridium(0) atoms on the nanoparticle surface (~34.5%)[25]).

Because the most advantageous reaction mixture was the nano-Ir(0) catalyst with TPy in the ionic liquid [THTdP][MS], this combination was used to investigate the effects of different reaction conditions; the results of this study are

Scheme 2. Proposed Catalyst Sequence



given in Table 2. As can be seen, normal reaction aids such as ultrasonocation and increased temperature had positive effects on the yields. The highest yield was obtained using microwave irradiation in the ionic liquid medium, giving a yield of 91% with a TOF of 151.7 h^{-1} (439.7 h^{-1} corrected from the exposed iridium(0) atoms on the nanoparticle surface (~34.5%)[25]). It has been reported that a system of nanoparticle-stabilized electrostatic reagents, such as ionic liquids, is very sensitive to thermal motion.[30] Therefore, the beneficial effects of microwave irradiation might be due to an increased local temperature,[31] a disturbance in the stabilizing [THTdP][MS]-Ir(0) interactions, or a combination of the two. The results in Table 2 indicate that the yield enhancement resulting from microwave irradiation is due to more than just temperature. When bis(pinacolato)diboron (B_2pin_2) was used in place of pinacolborane (HBpin), a lower yield (26%) was obtained, which suggests that the nano-Ir(0) catalyst is not as effective in activating a B−B bond as it is a B−H bond. When benzene-d_6 was used as borylation substrate, only 14.3% yield of deuterated phenyl boric acid was isolated under the same conditions, suggesting an isotope effect in the catalytic process.

Table 3 summarizes the effect of aromatic substituent groups on the borylation using the nano-Ir(0) catalyst and TPy ligand in the ionic liquid. It can be seen that the electron poor arenes increase the reactivity, which was found in the homogeneous catalyst systems.[32,33] The highest yield, 89% after 12 h, was found for the electron-withdrawing CF_3 group, whereas the electron donating OMe group led to a yield of 40% after 20 h. Table 3 also shows that the electronic properties of the substituents have no dramatic influence on regioselectivity. The lack of formation of any ortho products seems to be due to the high sensitivity of the catalyst to steric hindrance.

The nano-Ir(0) catalysts are not as effective as homogeneous catalysts. The homogeneous $[Ir(cod)Cl]_2$/2,2′-bipyridine (bpy) catalyst system, gave an 80% conversion of HBpin after 16 h at 80 °C,[32] whereas our nanocatalyst produced only 47% isolated yields of phenyl boric acid after 20 h at 80 °C. However, our catalyst has the advantage of being recyclable; the catalyst was reused more than 6 times with essentially no loss in activity. After 4 runs were carried out on a particular catalyst, the catalyst was isolated via centrifugation and analyzed by TEM and XPS. These analyses showed that the nano-Ir(0) catalyst had similar particle size and the same chemical composition as a freshly prepared nano-Ir catalyst (Supporting Information, Figure S-13). The concentrations of iridium leached into the aqueous

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solution obtained from the hydrolysis reaction were found to be less than 1.0 ppm, based on ICP results.

Although analytical data showed a complete reduction of the original $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$ precursor, the catalytic properties of the precursor were studied and compared with those of the [THTdP][MS] stabilized nano-Ir(0) catalyst. The results are shown in Figure 4. The figure shows that both of the composites are effective for phenylborylation reactions with the TOF of 11.3 h^{-1} and 1.1 h^{-1} for nano-Ir(0) and $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$, respectively. There is an induction period of about 4 h for the precursor catalyst that is not found in the nanometal catalyst. Although it is difficult to distinguish homogeneous from heterogeneous catalysis, the lack of an induction period, the results of the mercury poisoning studies, and the TEM analyses are all consistent with the [THTdP][MS] stabilized nano-Ir(0) as being the true catalyst.[34–37]

Although the definitive mechanism is not yet clear, based on previous reports[4,37] and our present observations, the catalytic cycle, shown in Scheme 2, can be proposed. Accordingly, the basic ligands can coordinate with ionic liquid-stabilized nano-Ir(0) to form ligand-stabilized species $Ir(L_n)$. The iridium(0) metal has been reported to be able to active C−H bond in benzene to form active species of [Ph-Ir], [Ir−H], and so forth,[38] it is reasonable for nano-Ir(0) to activate benzene to give an oxidation addition intermediate. It is also reasonable that HBpin can undergo oxidative addition process, ending ultimately with the iridium being associated with both the arene and HBpin reactants. Reductive elimination could then lead to release the boroxine and H_2 products and regeneration of the catalyst. Scheme 2 should be taken more as a diagrammatic summary of the reaction process, rather than a definitive mechanism.

Conclusions

Carboranyl coordinated iridium complex, $(Ph_3P)_2Ir(H)(7,8\text{-}nido\text{-}C_2B_9H_{11})$, has been used as precursor to prepare well dispersed iridium(0) nanoparticles. In the presence of auxiliary ligands or bases, the nano-Ir(0) particles stabilized with the ionic liquid, trihexyltetradecylphosphonium methylsulfonate [THTdP][MS], were found to be active catalysts for phenylborylation reaction. Importantly, the catalyst can be easily recovered and reused. Microwave irradiation benefits the reaction process significantly. Detailed mechanistic studies and the effects of modification of catalyst components are currently underway in our laboratories.

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Supporting Information Available: Characterization data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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