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Article

Evidence That Imidazolium-Based Ionic Ligands Can be Metal(0)/Nanocluster Catalyst Poisons in at Least the Test Case of Iridium(0)-Catalyzed Acetone Hydrogenation

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This study begins with the question of whether ionic liquids (ILs), such as 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], can be catalyst poisons for transition-metal catalysts rather than a preferred stabilizing media as typically assumed in the literature. The test case of acetone (propanone) hydrogenation is picked for two reasons: (i) acetone hydrogenation is important for its applications in heat pumps, H_2 storage schemes, and fuel cells and for the commercial value of the resultant product, propan-2-ol, and (ii) two recent, independent studies have reported putative $Ir(0)_n$ nanocluster-catalyzed hydrogenations of acetone beginning in each case with the identical precursor, [{(COD)IrCl}$_2$] (where COD = 1,5-cyclooctadiene) (**1**). A close comparison of the results of those two literature studies and their related, but different, experimental conditions (vide infra) suggests the hypothesis that the IL is actually a catalyst poison. Indeed, the investigations herein (i) find that 1.0 equiv of added IL, [bmim][PF_6], completely inhibits the formation of $Ir(0)_n$ nanoclusters under conditions 1 in Table 1 in the main text (namely, 3.6 mM precatalyst **1**, 22 °C, and 2.76 bar H_2) and (ii) demonstrate that 0.1 and 1.0 equivs of this same IL, [bmim][PF_6], poisons 74 and 90%, respectively, of the acetone hydrogenation activity of premade, previously catalytically active nanoclusters. The above results in turn compelled a reinvestigation of the claim that $Ir(0)_n$ nanoclusters are the catalyst in what was reported as a colloidal suspension prepared under conditions 2 in Table 1 of the main text (namely, 52 mM precursor **1**, 92 equiv of IL, 75 °C, and 4.05 bar of H_2). We further (iii) find that the colloidal suspension prepared under conditions 2 is a mixture of unreacted precursor, **1**, some nanoclusters, and isolable bulk metal, and we also (iv) find, somewhat surprisingly, in light of the IL-poisoning results found under conditions 1, that the Ir(0) catalyst prepared under conditions 2 is active, precisely as reported, for acetone hydrogenation. This, in turn, further demanded that we go on to (v) investigate the nature of the true catalyst under conditions 2, the results of which we are able to interpret only by the hypothesis that bulk metal is the dominant, true catalyst under conditions 2. Overall, the results provide strong evidence that ILs can be potent inhibitors of metal(0)/nanocluster catalysis, rather than the often-assumed superior solvent for nanocluster catalysis. The results also fortify our recent report that, under conditions where stoichiometrically high amounts of coordinating ligands are present (vs the amount of surface metal atoms), bulk-metal catalysts can actually be superior to nanocluster catalysts of the same metal, a seemingly heretical finding prior to our recent experimental evidence for this (Besson, C.; Finney, E. E.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 8179; Besson, C.; Finney, E. E.; Finke, R. G. *Chem. Mater.* **2005**, *17*, 4925).

Introduction

Over the past decade, interest in the field of ionic liquids has grown enormously.[1,2] Ionic liquids (ILs) possess a wide range of properties that can be tailored to suit their applications; as a result, they have been dubbed "designer solvents".[3] Among the key properties of ILs are their negligible vapor pressure at room temperature (RT),[4] their wide range of viscosities, their high stability in many cases, and their range of combinations possible from a synthetic tool box of different cations and anions. They are often considered

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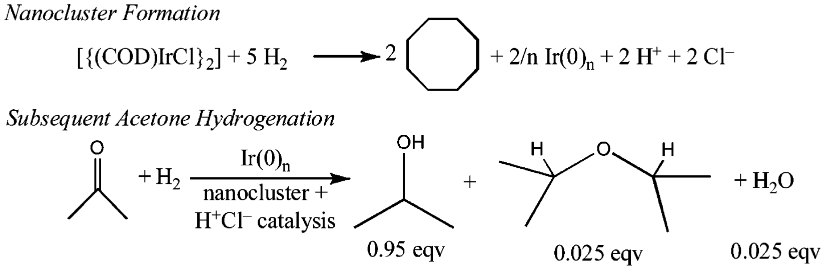
Scheme 1. Reactions Established in the Study,[10] Using Conditions 1 of Table 1, Which Are Important to the Present Studies



"green alternatives" to volatile organic solvents, although their toxicity and biodegradability are not yet well investigated. Ionic liquids are currently being investigated for use in several fields, including but not limited to solvents for catalysis,[5] biocatalysis,[6,7] and analytical applications,[1a] including chromatography, extraction, and spectrometry.[8]

Catalysis by nanoclusters,[9] including high selectivity and mild temperature acetone hydrogenation,[10] is also of considerable interest. Acetone hydrogenation is interesting because of its use in heat pumps, H_2 storage schemes, and fuel cells, as well as to satisfy the general demand for the end product, propan-2-ol.[10]

Two recent literature reports detail $Ir(0)_n$-catalyzed hydrogenation of acetone.[10,11] Both studies use the identical precursor, $[\{(COD)IrCl\}_2]$, **1**. However, one formation reaction and subsequent acetone hydrogenation was carried out in neat acetone and under the conditions of 3.6 mM precursor **1**, 22 °C, and 2.76 bar of H_2 (hereafter, conditions 1 of Table 1).[10] The nanocluster formation reaction and subsequent acetone hydrogenation established from the first study[10] is shown in Scheme 1.

The second study pregenerated what was termed a "colloidal suspension"[11] in the ionic liquid (hereafter, IL) 1-butyl-3-methylimidazolium hexafluorophosphate, $[bmim][PF_6]$, Figure 1, at 52 mM precursor, 75 °C, and 4.05 bar of H_2. That suspension was isolated, redissolved in acetone, and then studied for its acetone hydrogenation catalytic activity at 75 °C and 4.05 bar of H (conditions 2, Table 1).[11] Table 1 summarizes the two sets of reaction conditions used for acetone hydrogenation in the two studies.

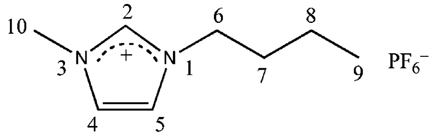


Figure 1. Ionic liquid 1-butyl 3-methyl imidazolium hexafluorophosphate, $[bmim][PF_6]$, used previously,[11] as well as herein.

Table 1. Reported Literature Conditions[10,11] and Results for Two Studies of Acetone Hydrogenation Beginning with $[\{(COD)IrCl\}_2]$, (**1**)

conditions	1[10]	2[11]
solvent	acetone	$[bmim][PF_6]$
reaction time	2 h	2 h
yield	95%	95%
T (°C)	22	75
H_2 P (bar)	2.76	4.05
[**1**] (mM)	3.6	52
av TOF[a]	1.92	0.033
selectivity	95%	not reported

[a] Turn-over frequency, TOF, = (mol product)/[(mol total catalyst loading) × sec].

Scrutiny of the two sets of conditions and catalytic activity catches one's eye: conditions 2 from the IL-prepared catalyst employ a 53 °C higher temperature, a 1.29 bar higher H_2 pressure, and a 14.4-fold higher initial concentration of **1**, yet achieve a *58-fold slowe*r *TOF*. The implied $\geq$835 (i.e, $\geq$58 × 14.4) times *slower* catalytic activity of conditions 2 in Table 1 suggests that (i) the IL *inhibits* catalysis, (ii) the nature of the catalyst in the two systems is different, or (iii) both (or (iv) possibly some other, at present unseen, explanation). Evidence was provided that at least the initial catalysis under conditions 1 is caused by nanoclusters.[10] However, convincing evidence is lacking for the claim that nanoclusters are the true catalyst under conditions 2.[11]

The above data demands a test of the implied, repeated claim, one rigorously untested until now, that ILs are a

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superior medium for nanocluster synthesis and catalysis.[12−18] The results in Table 1 offer an important, alternative hypothesis to be tested, namely, *that ILs can be potent poisons of nanocluster catalysts*, at least at lower temperatures and H_2 pressures (e.g., in conditions 1 in Table 1).

Further support for the hypothesis that ILs can be nanocluster poisons is the report that ILs with hydrogens in the 2-position such as [bmim][PF_6], Figure 1, can form *N*-heterocyclic carbenes (NHCs) atop $Ir(0)_n$ nanoclusters.[19] This fact was demonstrated by D_2-labeling studies that exchange D for H at the 2-position, along with kinetic evidence that the true olefin hydrogenation catalyst in that study[10] is not the precatalyst, **1**, but, instead, is both nanoclusters and then probably also some bulk-metal catalysis late in the reaction (see the Supporting Information for a summary of the evidence for the true catalyst under conditions 1). The alternative hypothesis of “IL-derived nanocluster poisoning” is also quite reasonable in light of the fact that NHCs are well established to be strongly coordinating ligands, at least for single transition-metal centers.[20−24]

Herein, we begin by testing the hypothesis that the prototype 1,3-substituted imidazolium-based IL, [bmim][PF_6], can be a catalyst poison for $Ir(0)_n$-catalyzed acetone hydrogenation. This led us in turn to a re-examination of the literature catalyst under conditions 2, with the finding that the reported[11] colloidal suspension is actually a mixture of precursor **1**, some nanoclusters, plus bulk Ir(0) metal. A deeper probing of the true catalyst in the case of that mixture led to evidence that the bulk metal is a kinetically significant catalyst in the IL system and that catalysis is not just by the nanoclusters. The insights from the studies herein and their expected impact on IL, nanocluster, and IL/nanocluster catalysis are summarized and briefly discussed.

Experimental Section

Materials. All reaction solutions were prepared under oxygen- and moisture-free conditions in a Vacuum Atmospheres drybox (≤5 ppm O_2 as continuously monitored by a Vacuum Atmospheres O_2 monitor). [{(COD)IrCl}$_2$] (**1**, Strem, 99%) was stored in the drybox and used as received. Acetone (Burdick and Jackson, 0.26% H_2O) was purged with Ar for 30 min and transferred into the drybox. The IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was prepared at the Queen’s University Ionic Liquid Laboratories (QUILL).[25] The IL was dried under vacuum (≤100 mmHg) at 60 °C for ≥5 h and stored in the drybox. [NBu_4][PF_6] (Aldrich, 98%) was dried under vacuum (≤100 mmHg) at 22 °C for ≥12 h and stored in the drybox.

^{1}H NMR spectroscopy was performed on a Varian Inova 300 spectrometer. Spectra were obtained in CD_2Cl_2 (Cambridge Isotope Laboratories, 99%) in predried (≥160 °C for ≥24 h) 5 mm o.d. NMR tubes. Spectra were referenced to the residual CH_2Cl_2 impurity. ^{2}H NMR spectroscopy was performed on a Varian Inova 400 spectrometer; spectra were obtained in CH_2Cl_2 (Aldrich, 99+%). XPS spectra were collected using a Physical Electronics (PHI) Model 5800XPS system equipped with a monochromator (Al Kα source operating at 1486.8 eV; system pressure $\leq 1 \times 10^{-8}$ Torr) and a hemispherical analyzer to detect the ejected electrons. An Eppendorf 5415c 18-well centrifuge was used for nanocluster isolation.

Hydrogenation Apparatus. Hydrogenation experiments were carried out in a previously described[2,26,27] apparatus designed to continuously monitor H_2 pressure loss. This apparatus consists of a Fisher−Porter (FP) bottle, which connects via Swagelok quick-connects to both a dihydrogen line and an Omega PX621 pressure transducer. The pressure transducer is interfaced with a PC by means of an Omega D1131 5V A/D converter with a RS-232 connection. The pressure uptake data is collected using LabView 7.1. The FP bottle is placed in an oil-filled jacketed reaction flask with temperature control by means of a recirculating water bath. The reaction solution is stirred by a Fisher Jumbo magnetic stirrer with a 5/8” × 5/16” Teflon-coated octagon shaped spin bar at speeds of ≥600 rpm to avoid H_2 gas-to-solution mass-transfer limitations.[28]

Catalyst Formation Under Conditions 1 in Table 1 (3.6 mM 1, 22 °C, 2.76 bar H_2 in Neat Acetone).[10] In the drybox, **1** (1.2 mg, 3.6 μmol Ir) was weighed into a predried 2 dram glass vial. Acetone (1.0 mL, 13 mmol) was added with a 1.0 mL gastight syringe. The reaction solution was then agitated with a disposable polyethylene pipet until the precursor had dissolved (approximately 5 min), resulting in a clear, bright-yellow solution. Next, the reaction solution was transferred with the pipet into a new culture tube with a new stir bar. The culture tube was sealed in the FP bottle, brought out of the drybox, and attached to the H_2 line. To initiate the reaction, the FP bottle was purged 13 times with H_2 (2.76 ± 0.07 bar, 15 s/purge). Five min after the first purge, the pressure was set at 2.76 ± 0.07 bar, $t = 0$ was noted, and pressure vs time data was collected at 2.5 min intervals.

Acetone/IL Stock Solutions. Stock solutions of IL in acetone were prepared containing both 1 and 5 equiv of IL in predried 25 mL volumetric flasks. For each solution, approximately half the acetone was first transferred into the flask with a disposable polyethylene pipet. The necessary volume of IL (7.5 μL for 1 equiv, 37.6 μL for 5 equiv) was added next with a 10 or 50 μL gastight

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syringe. The solution was swirled, and the remaining acetone was added with the same polyethylene pipet to reach 25 mL. The volumetric flask was then capped with a lightly greased, ground glass stopper and sealed with Parafilm. All IL stock solutions were used within 2 days of being prepared.

Catalyst Formation Under Conditions 1 in Table 1 in Acetone with Added [bmim][PF_6]. These experiments were carried out exactly as described for conditions 1 with the following exception: instead of neat acetone, a stock solution containing the desired number of equivalents of [bmim][PF_6] in acetone was used.

Acetone Hydrogenation Under Conditions 1 in Table 1 in Acetone with Added [bmim][PF_6] or [NBu_4][PF_6]. These experiments were initiated exactly as described for conditions 1, except this time only 0.8 mL acetone was used to dissolve **1**. A hydrogenation experiment was initiated exactly as described in the section titled Catalyst Formation Under Conditions 1 in Neat Acetone. After approximately 0.3 bar of H_2 had been consumed, the FP bottle was sealed and removed from the H_2 line. The pressure in the line was adjusted to 2.46 bar, and the bottle then re-attached to the line. Under this adjusted, reduced flow of H_2, 0.2 mL of a solution of [bmim][PF_6] or [NBu_4][PF_6] in acetone (86 mM, 1 equiv) was added to the culture tube for a total reaction volume of 1.0 mL. The FP bottle was then purged 3 times, and data collection was reinitiated.

Catalyst Formation Under Conditions 2 in Table 1 (52 mM 1, 75 °C, 4.05 bar H_2 in Neat [bmim][PF_6]). Repeating the Literature as Precisely as Possible.[11] In the drybox, **1** (35.0 mg, 0.052 mmol) was weighed into a predried 2 dram glass vial. Because this complex is insoluble at room temperature in the ionic liquid [bmim][PF_6], the red crystalline complex was transferred as a solid into a new borosilicate culture tube (22 × 175 mm) with a new 5/8 × 5/16 in. Teflon-coated octagon-shaped spin bar. Next, [bmim][PF_6] (1.0 mL) was added to the culture tube with a 1.0 mL gastight syringe. The culture tube was placed in the FP bottle, and the bottle was sealed and brought out of the drybox. The reaction solution was stirred in the oil-filled, jacketed reaction flask at 75 °C for ≥10 min before being exposed to H_2 to raise the reaction solution temperature to the reported literature temperature of 75 °C (a necessary step in our hands, albeit one not reported in the prior study).[11] At the end of the ≥10 min of stirring, **1** had dissolved, resulting in a clear yellow-orange solution.

Next, the reaction solution was exposed to 4.05 bar of H_2 for 10 min. After approximately 2 min, the reaction solution turned brown. At the end of the 10 min exposure, the reaction solution was opaque and black, with *bulk metal* visible on the sides of the culture tube [this mixture is, apparently, the colloidal suspension[11] cited in the literature, namely, unreacted **1**, a brown[29] $Ir(0)_n$ nanocluster solution (as judged by TEM, vide infra) and bulk metal, as confirmed by XPS, vide infra]. The FP bottle was disconnected from the H_2 line, vented, sealed, and brought back into the drybox. Once the FP bottle was opened in the drybox, visual examination of the stir bar revealed that it was also coated with bulk metal.

Isolation of the nanoclusters was carried out as closely as possible to the literature report.[11] In the drybox, the 1.0 mL solution of nanoclusters in IL was decanted into a 1.5 mL snap-cap centrifuge tube. Acetone (0.5 mL) was added with a polyethylene pipet, and the brown-black solution was shaken vigorously. The tube was sealed with Parafilm and brought out of the drybox. Next, the tube was centrifuged for 10 min at 10 000 rpm and brought back into the drybox. The bright-yellow supernatant liquid (a color characteristic of **1** dissolved in acetone) was removed with a new polyethylene pipet, leaving a brown-black powder at the bottom of the vial. Acetone (1.5 mL) was added to the powder at the bottom of the vial. The solution was shaken vigorously, producing a brown-black solution. This cycle of centrifugation and addition of fresh acetone was repeated twice more, after which the brown-black powder was dried under vacuum overnight. The yield, beginning from 35 mg of [{(COD)IrCl}$_2$], was 5.5 mg of brown/black powder.

Next, the dark brown powder (still in the centrifuge tube) was dissolved in 1.0 mL of acetone and agitated with a polyethylene pipet until the solution was brown and apparently homogeneous. With the same polyethylene pipet, the solution was transferred into a new culture tube with a new stir bar. The culture tube was sealed into the FP bottle, and the bottle brought out of the drybox. The FP bottle was attached via its Swagelok quick-connects to the H_2 line, and the mixture was again stirred under N_2 for 10 min in the oil-filled jacketed reaction flask to raise the temperature of the reaction solution. First, under conditions chosen to repeat the originally reported[11] conditions as closely as possible (see ref 39), the FP bottle was maintained at a constant H_2 pressure of 4.05 bar by opening the valve between the FP bottle and the H_2 tank but keeping the valve between the FP bottle and the pressure transducer closed. This ensures a constant H_2 pressure of 4.05 bar, but eliminates the valuable kinetic information normally gathered[10,26−28] via the pressure transducer. The reaction was maintained at 4.05 bar and 75 °C for 2 h, during which time the reaction solution

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(36) (a) The reasons to expect that the such a direct spectroscopic detection of surface-coordinated IL-derived NHCs will be challenging and therefore worthy of its own, separate effort and study, are severalfold: (i) There are only a small number of active sites on nanoclusters in the few cases where they have been titrated (e.g., ≤1.8% for polyoxoanion-stabilized Ir(0) nanoclusters)[37b,c] so that one will presumably be trying to detect a small number of surface-coordinated NHCs. The findings herein confirm this prediction since even 0.1 equiv of IL poisons acetone hydrogenation catalysis. Second, (ii) in previous experiments we were not able to detect any surface-coordinated NHC even when 100 equiv of IL per equiv of Ir was added, despite the fact that H/D exchange studies demonstrate that they are formed, and third (iii) the literature of, for example, NMR studies of ligands atop nanoclusters indicates that such signals are often broadened, subject to facile ligand exchange, or simply not observed.[36c] In short, considerably more development of surface-ligation studies of transition-metal nanoclusters, by whatever proves to be the best physical methods, will be required before low levels of surface-coordinated poisons can be routinely detected. (b) Schmid, G. *Struct. Bonding* **1985**, *62*, 51. (c) (i) Pelzer, K.; Philippot, K.; Chaudret, B. *Z. Phys. Chem.* **2003**, *217*, 1539. (ii) Pery, T.; Pelzer, K.; Buntkowsky, G.; Philippot, K.; Limbach, H.-H.; Chaudret, B. *ChemPhysChem* **2005**, *6*, 605. (d) (i) Foos E. E.; Snow A. W.; Twigg M. E. *J. Cluster Sci.* **2002**, *13*, 543. (ii) Fu, X.; Wang, Y.; Wu, N.; Gui, L.; Tang, Y. *J. Colloid Interface Sci.* **2001**, *243*, 326.

(37) (a) Hornstein, B. J.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 1625. (b) Vargaftik, M. N.; Zargorodnikov, V. P.; Stolarov, I. P.; Moiseev, I. I.; Kochubey, D. I.; Likholobov, V. A.; Chuvilin, A. L.; Zamaraev, K. I. *J. Mol. Catal.* **1989**, *53*, 315.

changed from an apparently homogeneous brown to clear with suspended bulk metal visible to the naked eye. Additionally, a bulk-metal mirror formed on the side of the culture tube.

A second reaction solution was prepared exactly as described above (i.e., the brown colloidal suspension was generated and centrifuged, and the brown powder was isolated under vacuum). However, this time a reaction was carried out to monitor to kinetics of acetone hydrogenation. In this procedure, the valve between the H_2 line and the FP bottle is closed, and the valve between the FP bottle and the pressure transducer is opened. Hence, the H_2 pressure-loss kinetics can now be measured. To initiate the acetone hydrogenation reaction, the FP bottle was purged 5 times with H_2 (4.05 ± 0.07 bar, 5 s/purge; this shorter purging cycle was employed to minimize the loss of the acetone); 1.5 min after the first purge, the pressure was set at 4.05 ± 0.07 bar, $t = 0$ was noted, and pressure versus time data were collected at 2.5 min intervals.

Separately, under the literature's biphasic conditions,[11] acetone was added (1.0 mL, 13 mmol) to the same culture tube used for the nanocluster formation reaction, resulting in a total volume of 2.0 mL. (In our hands, [bmim][PF_6] and acetone are miscible, and we only observe one phase.) The culture tube used is the one which already contained the nanocluster solution, in 1.0 mL of IL, with bulk metal present both on the sides of the culture tube and on the stir bar. The culture tube was sealed in the FP bottle, and the bottle was brought out of the drybox. The FP bottle was attached via its Swagelok quick-connects to the H_2 line, and the mixture was again stirred under N_2 for 10 min in the oil-filled, jacketed reaction flask to raise the temperature of the reaction solution. To initiate the acetone hydrogenation reaction, the FP bottle was purged 13 times with H_2 (4.05 ± 0.07 bar, 15 s/purge). Five minutes after the first purge, the pressure was set at 4.05 ± 0.07 bar, $t = 0$ was noted, and pressure versus time data were collected at 2.5 min intervals.

X-ray Photoelectron Spectroscopy (XPS) of the Reaction Vessel from Conditions 2 in Neat [bmim][PF_6]. A nanocluster formation reaction was carried out exactly as described under conditions 2. After the 10 min reaction time, bulk metal was visible on the sides of the culture tube. The FP bottle was vented, resealed, and brought into the drybox. In the drybox, the FP bottle was opened, and the culture tube was removed. After the IL was decanted from the culture tube into a beaker, the culture tube was rinsed three times with acetone to remove any remaining IL/nanocluster solution. Next, the culture tube was broken with a hammer. A piece of the culture tube with the visible metal film was sealed in an oven-dried glass scintillation vial, and the vial was sealed with electrical tape before being removed from the drybox. Under flowing N_2, the metal-coated glass was mounted onto a XPS sample holder with Scotch tape. After the sample chamber was thoroughly evacuated ($\leq 10^{-9}$ Torr), sample analysis was initiated. Bulk $Ir(0)_n$ metal was confirmed in a high-resolution XPS scan (see the Supporting Information for further details).

Testing the Kinetic Competence of the Bulk-Metal Film Produced Under Conditions 2 in Neat [bmim][PF_6]. A nanocluster formation reaction was carried out exactly as described for conditions 2. The resultant colloidal suspension was decanted, and the bulk-metal film inside the culture tube was washed with acetone exactly as described above with the exception that the stir bar was kept in the culture tube. (Washing the culture tube to remove any remaining IL following the decanting procedure is necessary to avoid an ill-determined, variable amount of remaining IL between experiments, especially since we find that even 0.1 equiv of IL is a catalyst poison, vide infra). Next, acetone (1.0 mL) was added to the culture tube. The culture tube was then sealed in the FP bottle, and hydrogenation was initiated exactly as described.

Catalyst Formation Under Conditions 2 in Neat [bmim][PF_6] with D_2 in Place of H_2.[11] This reaction was carried out exactly as described for conditions 2,[11] except D_2 was used in place of H_2.

Results and Discussion

Initial Control Experiment: Repeating Conditions 1 of Table 1 (3.6 mM Precatalyst 1, 22 °C, and 2.76 bar of H_2 in Neat Acetone).[10] A control experiment was performed repeating the results obtained under conditions 1 in Table 1 in 1.0 mL of acetone.[10] After the expected induction period,[10] known to be caused by the nucleation and initial growth of $Ir(0)_n$ nanoparticles,[26] acetone hydrogenation took off smoothly with the same general H_2 uptake curve as previously reported (see Figure 2 herein, which is similar to Figure S1 of our prior work).[10] The solution acquired a brown color characteristic of $Ir(0)_n$ nanoclusters as the catalysis ensued and the solution remained homogeneous to the eye for at least the first 2 h. The kinetic and TEM evidence presented previously (and which is summarized in the Supporting Information herewith for the convenience of the interested reader), provide evidence for nanocluster catalysis, at least initially.[10] The visual homogeneity throughout the first 2 h of the catalysis is also consistent with catalysis by a soluble species. An overall 95% complete hydrogenation was observed after 2 h, with 100% hydrogenation after approximately 10 h. However, and as reported earlier,[10] after the 10 h period, the final reaction solution becomes clear, with non-redispersable bulk metal present as the final metal product. It follows that some bulk-metal catalysis is almost surely part of the high, 164 000 total turnovers for acetone hydrogenation seen after 10 h, a point noted previously.[10]

Poisoning of Nanocluster Formation and Catalysis Under Conditions 1 of Table 1 by the Addition of [bmim]-[PF_6] IL. In a series of separate experiments with 0, 1, and 5 equiv of added [bmim][PF_6], we observed that just *1 equiv* of added IL per Ir atom in **1** poisons ≥90% of the acetone hydrogenation catalysis, Figure 2. Only 10% conversion after 22 h is observed with 1 equiv of added IL (in comparison to

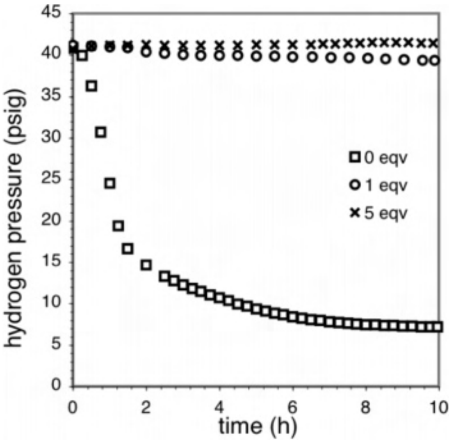


Figure 2. Hydrogen uptake curves for 3.6 mM **1** under 2.76 bar of H_2 in acetone with 0, 1, and 5 equiv of added [bmim][PF_6]. The results demonstrate that even 1 equiv of [bmim][PF_6] is a strong poison of the acetone hydrogenation catalysis derived from 3.6 mM **1** at 22 °C and 2.76 bar of H_2 (conditions 1, Table 1).

100% conversion in less than half the time (10 h) in neat acetone with no added IL). Five equivalents of added IL further poisons the hydrogenation activity; even after a 7-fold longer reaction time (70 h), only one-tenth the previous conversion (i.e., just 10% conversion) is observed. Additionally, the solutions with 1 or 5 equiv of added IL remain the brilliant-yellow color characteristic of the precatalyst **1** dissolved in acetone; no change to a brown solution characteristic of $Ir(0)_n$ nanoclusters is observed.[29] It seems clear that the added IL is poisoning the formation of nanoclusters; an educated guess is that the added IL poisons the critical nuclei,[30] which otherwise lead to the formation of larger, catalytically active nanoclusters.

Next, an experiment with just 0.1 equiv of IL added to **1** was tried under conditions 1 of Table 1. Significant poisoning of the acetone hydrogenation catalysis was again observed: only 26% conversion of acetone to 2-propanol occurred even after a 2.4-fold longer period (24 h) than is normally required for 100% conversion.

In short, *1,3-substituted imidazolium-based ILs are a potent poison of the formation of* $Ir(0)_n$ *nanocluster-catalyzed acetone hydrogenation initiated with* ***1***, under the specific conditions of 22 °C and 2.76 bar of H_2.

Poisoning of a Preformed, Active $Ir(0)_n$ Nanocluster Catalyst by 1 equiv of IL at 22 °C and 2.76 bar of H_2. Next, we hypothesized that added IL would also poison a preformed, active nanocluster catalyst. To test this hypothesis, we started by initiating a normal nanocluster formation and concomitant acetone hydrogenation experiment in neat acetone under conditions 1 of Table 1 (i.e., with no added IL). Once the solution became catalytically active, 5 equiv of [bmim][PF_6] was added. Acetone hydrogenation was completely arrested. In the next experiment, 1 equiv of [bmim][PF_6] was added. As Figure 2 shows, just 1 equiv of IL also completely halts the catalytic activity of preformed, otherwise record, activity and selectivity acetone hydrogenation catalysis[10] at 22 °C and 2.76 bar of H_2 (specifically, $\leq$5% activity was seen after 24 h following the addition of the IL). No bulk metal was visible at the end of either of these experiments.

These results demonstrate that added 1,3-substituted imidazolium-based IL is a poison and therefore is not a preferred solvent, for at least $Ir(0)_n$ nanocluster-catalyzed acetone hydrogenation under the milder conditions 1 in Table 1. This is an important, previously unreported result, one which likely has broader implications for putative nanocluster catalysis in ILs. Elsewhere we have shown that added IL poisons $Ir(0)_n$ nanocluster catalysis of (in that study) cyclohexene hydrogenation.[19] We conclude, therefore, that at least hydrogenation catalysis by Ir(0) is probably generally poisoned by added ILs such as [bmim][PF_6], at least at 22 °C and $\leq$2.7 bar H_2.

Control Experiments Testing If It is the Cationic or Anionic Component of the IL that Leads to the Observed Poisoning. There are two limiting sub-hypotheses for what is actually key to the poisoning: (a) the cationic, $[bmim]^+$, component of the IL or (b) the anionic, $[PF_6]^-$, component of the IL. Relevent to the second limiting hypothesis is literature showing that even traditionally weakly coordinating anions can coordinate surprisingly strongly to electrophilic nanocluster surfaces;[32] specifically, recent XPS evidence shows that PF_6^- is present on the surface of dried $Pd(0)_n$ nanoclusters prepared in [bmim][PF_6].[33]

Hence, we carried out a control experiment in which 1 equiv of [NBu_4][PF_6] was added in place of the previous 1 equiv of [bmim][PF_6] (but with the other conditions identical to the poisoning experiment just described). Acetone hydrogenation continued uninhibited to completion (Figure S1 of the Supporting Information).[34] Hence, given that added [bmim][PF_6] poisons catalysis (Figure 3), but $[NBu_4][PF_6]^-$ does not (Figure S1), it follows that the poisoning is caused by the presence of the $[bmim]^+$ counterion portion of the IL (or, conceivably and to keep the logic complete, that both components are necessary for the poisoning or, also conceivably, that some impurity in the IL is the true posion). However, given our recent work showing that $Ir(0)_n$ nanoclusters oxidatively add to the cationic component of ILs such as $[bmim]^+$ to form surface-coordinated *N*-heterocyclic carbenes (NHCs), Scheme 2, the most plausible, precedented, and simplest (i.e., the Ockham's razor) interpretation is that the actual poison derived from the IL is a surface-coordinated NHC derived from the cationic, $[bmim],^+$ component of the IL.

To summarize to this point, the results demonstrate that the cationic component of the IL, [bmim][PF_6], is a poison to the otherwise record[10] catalytic activity and selectivity acetone hydrogenation under conditions 1 in Table 1 of 22 °C and 2.76 bar of H_2. This finding of IL cation-derived poisoning is a non-trivial insight in contrast to prior studies of nanoclusters in IL, where the typical starting hypothesis, of "ionic liquids are a superior solvent for nanocluster catalysis" is assumed, but never subjected to an attempt at its disproof as science requires.[35] Remaining to be accomplished, however, is the challenging goal[36] of the direct detection of the expected small[37] number of nanocluster surface active sites with coordinated NHC ligands by, say, NMR, IR, or other spectroscopies.

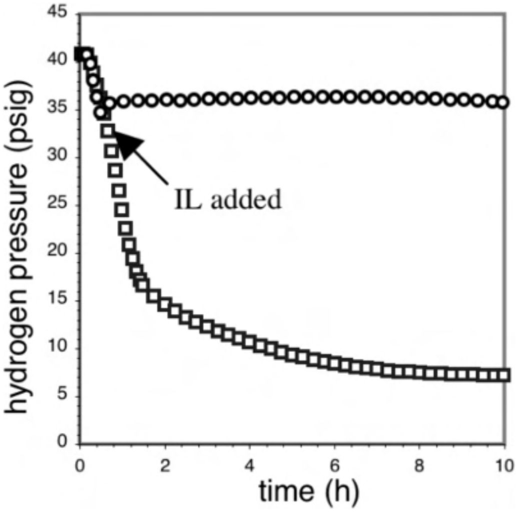
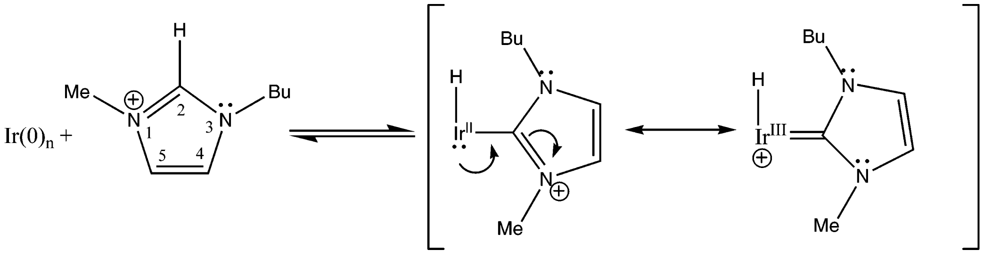


Figure 3. Acetone hydrogenation with no added IL (squares) and then with 1 equiv [bmim][PF_6] added (circles) after the formation of nanoclusters under conditions 1 of Table 1 (the IL was added where arrow indicates; the barely visible rise in pressure after the lowest circle just below 35 psig (2.46 bar) is caused by the acetone vapor re-equilibration with the gas-phase post flushing the system with H_2 to restart the reaction).[31]

Scheme 2. Precedented *N*-heterocyclic Carbene Formation on $Ir(0)_n$ Nanoclusters



Reinvestigation of the Literature Conditions 2 of Table 1 (Namely, 52 mM Precursor 1 in [bmim][PF_6] at 75 °C and 4.05 bar of H_2). Initial Control Experiment.[11] Given our finding that even 0.1 equiv of IL completely poisons acetone hydrogenation catalysis under conditions 1 in Table 1, an important question is why is any acetone hydrogenation seen at all under conditions 2?

Under conditions 2 in Table 1, the literature reports formation of a colloidal suspension after an initial, "around 10 min"[11] reaction time. In our hands (i.e., repeating the literature conditions as exactly as we could), we were able to repeat the literature's report of acetone hydrogenation under conditions 2. Moreover, after just 10 min, the sides of the reaction vessel were covered with a metal film (this bulk-metal mirror was verified as Ir metal by XPS; a spectrum is supplied in the Supporting Information); the stir bar was also coated with appreciable quantities of bulk metal, and the dark brown solution contained bulk metal particles visible to the naked eye. In the course of 9 repetitions, a bulk metal film was always formed, although the amount of bulk metal varied somewhat from run to run. The observation of visible bulk metal means that the amount of nanoclusters/colloids in the suspended material must be variable as well.

The brown-black suspended material was isolated after the 10 min reduction according to the reported centrifugation method.[11] Shaking of the dark-brown reaction IL solution with 0.5 mL of acetone in a 1.5 mL centrifuge tube yielded a dark-brown, apparently homogeneous solution. After centrifugation, a brown-black material collected at the bottom of the tube along with a bright-yellow supernatant liquid, the latter the color *of remaining, unreacted precursor, **1**,* in acetone (a ^1H NMR spectrum confirmed that unreacted precursor was in solution). Hence, the 10 min initial reaction time detailed in the literature[11] is insufficient to completely reduce the precursor, at least in our hands. After removal of the yellow supernatant liquid, the brown-black isolated solid was redissolvable in fresh acetone with shaking, resulting in a dark-brown, apparently homogeneous solution as reported.[11] Two identical, subsequent centrifugation cycles yielded equivalent results: each time a bright-yellow supernatant liquid containing the precatalyst **1** was formed (and, hence, subsequently removed by decantation), and a dark-brown material collected at the bottom of the tube. Transmission electron microscopy (TEM) images of the dark-brown material redissolved in acetone and then placed on a TEM grid, Figure 4, reveal that agglomerated, polydisperse colloids are a third product of the above synthesis and isolation procedure.

To summarize this section, the literature Ir(0) catalyst, prepared under conditions 2 in Table 1, is active in our hands as reported and consists of an Ir bulk-metal mirror (plus some suspended bulk metal visible to the naked eye), agglomerated nanoclusters by TEM, and unreacted **1**. That is, a catalytically active, 3-detectable-component mixture is formed from [{(COD)IrCl}$_2$], **1**, under the literature conditions 2 in Table 1. It follows that the product is not solely "iridium nanoparticles"[11] as previously claimed, at least in our hands.

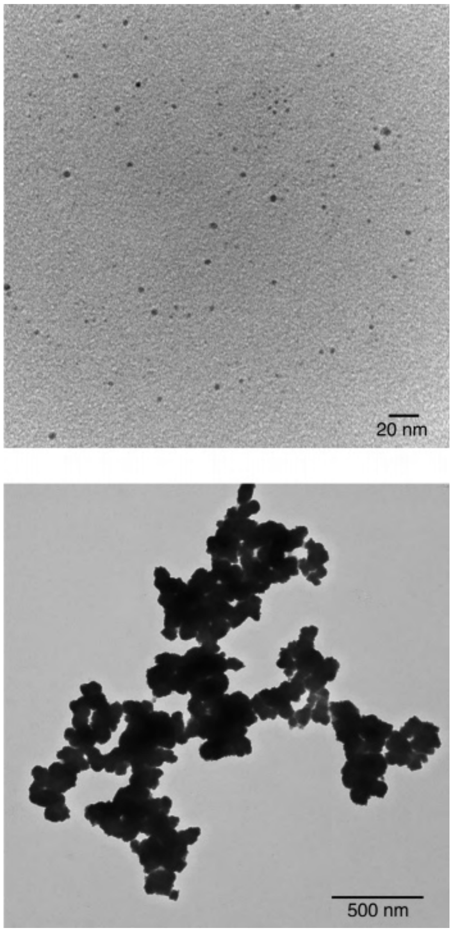


Figure 4. Two TEM micrographs of *soluble* portion of a reaction solution generated from 52 mM **1**, 75 °C, and 4.05 bar H_2 in neat IL (conditions 2 in Table 1). The results reveal the formation of some polydisperse nanoclusters (top TEM), but considerable agglomerated Ir(0) colloidal nanoclusters (bottom TEM). Recall that bulk, insoluble Ir(0) metal is a third product under conditions 2 as demonstrated herein. Hence, these (ex situ) TEMs are not representative of the entire sample; instead, these TEMs are primarily useful for visualizing the polydisperse, agglomerated colloids, which are present in the 3-component colloidal suspension.

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(38) For an example the history and complexity of the "is it homogeneous or heterogeneous catalysis?" question, see: Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317−341.

(39) Dupont, J. Personal communication. October, 2006.

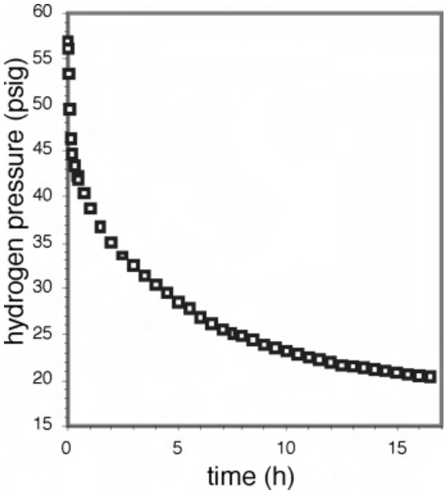

Figure 5. Acetone hydrogenation beginning with acetone-washed bulk metal, the bulk metal being collected from the sides of the culture tube and stir bar after decanting off the soluble part of the catalyst and any unreacted **1**, then washing the bulk-metal film to remove any remaining (acetone soluble) IL. Note the lack of any discernible induction period; note also that the initial rate of acetone hydrogenation by the acetone-washed bulk metal is 4.5 ± 0.2 bar H_2/h for ∼190-fold larger than the initial rate in Figure 5 (vide infra) for the 3-component mixture of 0.2 ± 0.01 bar H_2/h.

The reader probably has already realized that remaining, unreacted **1** is just what is expected in light of the IL-poisoning of the formation of nanoclusters from **1** found above. It also follows that (i) the poisoning by the NHC is reversed under conditions 2 (e.g., under the 53 °C higher temperature and 1.3 bar higher H_2 pressure), (ii) there is a different catalyst from the two, seemingly close sets of conditions, or (iii) some other explanation (such as both i and ii are occurring). This demanded that we determine the true catalyst in the 3-component system under conditions 2. Relevant here is that the literature teaches that the identification of the "true catalyst"[38] is a challenging venture even for a 1-component system.

Investigation of the Acetone Hydrogenation Catalysis by Particles Isolated from the 3-Component System. The isolated, agglomerated (by TEM, vide supra) particles can be redispersed in 1.0 mL of fresh acetone with vigorous shaking or sonication as reported[11] to yield an apparently homogeneous brown solution (note that we did not purify the particles further, as our goal was to reinvestigate the literature report of acetone hydrogenation; note also, therefore, that the particles are also likely still contaminated with some residual **1**). Following the original report,[39] an acetone hydrogenation reaction was carried out under the specified conditions[39] of 75 °C and a constant pressure of 4.05 bar H_2. The acetone was 90−95% hydrogenated after the reported reaction time[11] of 2 h (as verified by ^{1}H NMR). The final metal product from starting with the isolated particles is bulk metal visible on the stir bar and the culture tube plus a clear and colorless solution. This experiment shows that the system beginning with agglomerated particles (plus some unreacted **1**, vide supra) is a competent catalyst but that the IL-derived particles are not stable under the reaction conditions.

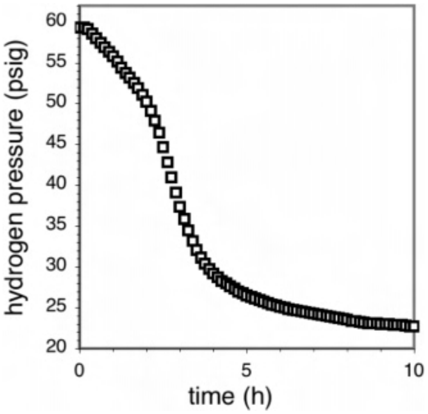

Figure 6. Hydrogen uptake kinetic curve for acetone hydrogenation after 1 mL of acetone was added to the 3-component mixture formed under conditions 2 in Table 1. These kinetic data were qualitatively reproducible in 4 independent experiments. An induction period of ∼20 min is observed before catalysis begins, an important observation which indicates that the most active catalyst is not the dominant species present in the 3 component mixture, but rather is being generated as a function of time from one or more of the 3 components. However, the hydrogenation rate, measured after the induction period (so as to favor the rate reported for the 3-component material), still produces a factor of ∼1/19 of that for the acetone-washed bulk metal, Figure 5, vide supra. The rate after the second increase in activity (i.e., after the second downturn in the figure) is still only 0.92 ± 0.05 bar H_2/h or 1/5 that of the 4.5 ± 0.2 bar H_2/h seen for the acetone-washed bulk metal, Figure 5, vide supra. An overall 95% hydrogenation is achieved after approximately 2 h (as reported[11]), followed by complete hydrogenation after approximately 10 h. Overall, the evidence indicates that at least the acetone-washed bulk metal is a superior acetone hydrogenation catalyst.

Evidence That the Bulk Metal Formed Under the Reaction Conditions is An Excellent Catalyst under Conditions 2. Given that visible, suspended bulk metal plus a bulk-metal mirror are formed under conditions 2, it is important to test whether or not bulk metal is an active catalyst under conditions 2. Noteworthy here is that the idea that bulk metal can be a good, if not superior, catalyst to even the smaller, higher-surface area nanoclusters has precedent in our recent work. Specifically, we found that Ir(0) bulk metal is a superior cyclohexene hydrogenation catalyst, in comparison to an $Ir(0)_n$ nanocluster catalyst, when an excess of coordinating ligands are present.[40,41]

To test the hypothesis that the bulk metal prepared under conditions 2 is an active, if not superior catalyst, we carried out an acetone hydrogenation reaction using only the bulk metal that is formed on the sides of the culture tube and stir bar after the synthesis under conditions 2. (Note that it is *this* source of bulk metal that we want to test and not, for example, commercial or other, unknown surface area or unknown surface ligation bulk metal.) The in situ-produced bulk metal was isolated by decanting the soluble portion containing the colloidal suspension[11] (including any nanoclusters) and unreacted **1**, followed *by washing the bulk-metal mirror with acetone to remove any excess IL present*. This washing step is crucial to achieve a reproducible experiment, in which the amount of IL present is more controlled. Experiments with this bulk metal under conditions 2 of Table 1 had variable and irreproducible kinetics (3

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(40) Besson, C.; Finney, E. E.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 8179.

(41) Besson, C.; Finney, E. E.; Finke, R. G. *Chem. Mater.* **2005**, *17*, 4925.

experiments), but each proceeded without an induction period and at a kinetically competent rate (i.e., at around the same rate seen for the catalysis at 75 °C and 4.05 bar of H_2, following correction for the fact that not all the Ir is present as bulk metal). The additional difference in these experiments versus those in the literature is that the valve to the H_2 line was closed, and the valve to the pressure transducer was left open, to enable monitoring of the hydrogenation kinetics, —that is, a constant pressure of 4.05 bar of H_2 as used originally[11] is not repeated (cannot be repeated) in these kinetic experiments.

The results of control experiment reusing the bulk metal formed in the catalysis proved telling: as noted above, acetone hydrogenation commenced immediately (i.e., without an induction period), as Figure 5 demonstrates. In addition, the observed initial rate for the acetone-washed bulk metal is ~19-fold higher than the initial rate of hydrogenation observed when beginning with the 3-component mixture, Figure 6, vide infra (see also Figure S3 of the Supporting Information where the rate data is coplotted for an easy visual comparison). Note that the rate enhancement for bulk metal is underestimated because the catalysis in Figure 6 using the 3-component mixture involves all the Ir, whereas that in Figure 5 involves just the Ir(0) bulk-metal component.

In separate experiments designed to assay the catalytic effectiveness of the 3-component mixture,[11] acetone was added to the culture tube containing the 3-component mixture, and the loss of H_2 pressure was monitored versus time, Figure 6.

The observation of an induction period in Figure 6, even when beginning with the 3-component mixture, is important and requires that generation of the true catalyst must occur prior to kinetically competent catalysis.

In short, the above studies indicate that bulk metal is not only a kinetically competent catalyst but also a fast, powerful catalyst in the absence of excess IL. The 19-fold slower rate starting from the 3-component mixture, in which the bulk metal is present, means that our washing the (excess) IL from the bulk metal for the experiment shown in Figure 5 must have enhanced its ability to do catalysis. This is independent evidence that the IL is a catalyst poison in this reaction (and, thus, in the conditions 2 system). In addition, the prior claim that nanoclusters are the sole catalyst in the IL system would seem, therefore, to be hereby refuted. Most important for the focal point of the present paper is the ≥19-fold higher rate by the acetone-washed, excess IL depleted, bulk metal, which provides further confirming evidence that [bmim][PF_6] leads to catalyst poisoning of at least Ir(0) acetone hydrogenation.

D_2-Labeling Evidence for the Formation of Surface Coordinated *N*-Heterocyclic Carbenes Under Conditions 2. The above evidence strongly suggests that NHC formation, as shown back in Scheme 2, is occurring on the catalyst prepared under conditions 2 in Table 1. This, therefore, is a prediction that needed to be tested using the D_2-labeling/exchange experiment that we developed previously. The expected (precedented)[19] result is D incorporation into several positions of the [bmim]$^+$ counterion of the IL (those previous experiments being similar to those under conditions 1).[19]

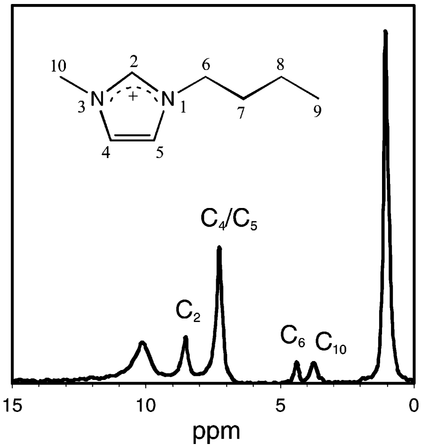

Figure 7. ^{2}H NMR spectrum of the reaction solution prepared from conditions 2 with D_2 substituted for H_2. The peak at δ 8.5 is attributable to substitution at C_2, indicative of NHC formation atop the $Ir(0)_n$ catalyst. The peaks at δ 1.0 and 10 are attributable to deuteration of the methyl groups and the alcohol group, respectively, of propan-2-ol.

To investigate whether or not surface-coordinated NHCs are also formed under conditions 2, we performed a catalyst formation and subsequent acetone hydrogenation reaction under conditions 2 (i.e., 52 mM **1**, 75 °C, 4.05 bar pressure, for 10 min), except that we substituted D_2 for H_2. The key result from the ^{2}H NMR, taken after the 10 min reaction time, shown in Figure 7, is the incorporation of deuterium into the C2-position (as well as at the other positions of the [bmim]$^+$ counterion exactly as seen previously). These NMR data indicate the reversible formation of NHCs under conditions 2.

The observed H/D exchange is prima facie evidence that the IL has undergone C−H cleavage at its acidic 2-position.[19] The H/D exchange at the C6 and C10 positions is also highly suggestive evidence that the NHC sits atop a polymetallic catalyst able to do such facile H/D exchange at relatively unactivated C−H bonds.

Although the above experiment detects only *reversible* NHC formation (i.e, poisoning is presumably a largely *irreversible* process), four lines of evidence all suggest that NHCs are the nanocluster poison herein for both sets of catalyst conditions. That evidence is (i) the formation of NHCs under conditions 2, (ii) our earlier finding[19] that NHCs are formed and inhibit nanocluster catalysis of cyclohexene hydrogenation under conditions (1.2 mM Ir precursor, 22 °C, and 2.76 bar H_2 (D_2)) very similar to the acetone hydrogenation conditions 1 in Table 1, and (iii) the poisoning observed with added IL herein under conditions 1. The conclusion that the NHCs are the relevant nanocluster poison is also supported by (iv) the exclusion of PF_6 as the only other possible poison derived from [bmim][PF_6], and (v) the deduction that the poison must, therefore, be derived from the only remaining component of [bmim][PF_6], the [bmim]$^+$ cation (or, conceivably but unlikely, some impurity in the IL). In short, NHCs are the only obvious, the only precedented, as well as the simplest (Ockham's razor) explanation for the observed poisoning of catalysis.[42] Neverthless, further studies, ideally employing direct detection of the surface-bound poison, are needed. Such studies promise to be challenging,[36] however.

Literature Indicating Why Bulk Metal Can Be a Superior Catalyst to the Smaller Nanoclusters, Even Though the Nanoclusters Have a Greater Number of Exposed Surface Sites, as Well as a Greater Number of Lower Metal Coordination Number Active Sites. It was recently found that Ir(0) bulk metal can be a superior catalyst compared to Ir(0) nanoclusters present in the same system (in that case cyclohexene hydrogenation).[40,41] The key is that strongly coordinating ligands must be present (amines are the ligands present in the literature example).[40,41] The reader is probably wondering how can bulk metal be a superior catalyst in such systems when the smaller nanoclusters have more surface sites (and often intrinsically more active, lower metal coordination number edge, kink, and other highly active sites)? The recently given answer[40,41] is that metal–ligand bond-dissociation energies in nanoclusters can be as high as 2-fold stronger than those in the same bulk metal,[43] thereby rendering more coordinatively unsaturated sites and thus faster catalysis in the bulk-metal case at least when higher concentrations of coordinating ligands are also present! This important finding, which is counter to the "nanoclusters will always be superior catalysts" hypothesis, is noteworthy. Indeed, elsewhere it has been noted that this observation of a *particle-size-dependent fractional coverage of a nanocluster catalyst's surface* promises to be a significant insight for future nanocluster catalysis studies.[40,41] The 53 °C higher temperature of the conditions 2 catalyst system is also probably a factor in the catalytic activity seen for the 3-component system because reductive elimination of the NHC from the catalyst surface probably is endothermic and thus probably favored thermodynamically by higher temperatures.

Conclusions

The main findings of this contribution are the following: (1) Added [bmim][PF_6] IL at even the 0.1 equiv level poisons the formation of catalytically active nanoclusters formed from [{(COD)IrCl}$_2$] in neat acetone at 3.6 mM **1**, 22 °C, and 2.76 bar of H_2. Moreover, the otherwise record activity and selectivity of acetone hydrogenation nanocluster catalysts[10] preformed under conditions 1 are poisoned by $\leq$1 equiv of [bmim][PF_6] IL.

(2) The system produced under conditions 2 in Table 1 consists of three detectable components: unreacted **1**, agglomerated nanoclusters, and bulk metal either suspended or present as a metal mirror coating the reaction vessel and stir bar.

(3) Both the agglomerated particles and the bulk metal are acetone hydrogenation catalysts. In addition, the fact that acetone-washed (and thus less IL-containing) bulk metal is $\geq$19 times more reactive than the 3-component mixture provides further evidence that the IL hinders catalysis under conditions 2 (75 °C and 4.05 bar of H_2).

(4) H/D exchange studies under conditions 2, along with literature precedent,[19] provide highly suggestive evidence that the polymetallic Ir(0) catalyst poison is a NHC formed from the 2-poisition of the IL. Control experiments rule out the PF_6^- component of the IL as the catalyst poison, a result which provides further evidence that the cationic component of the IL is responsible for the observed poisoning. An important hypothesis for future research also appears here, namely, to test whether other ILs, notably 2-*alkyl*-ILs that have a blocked 2-position, are more-inert superior ILs for nanocluster catalysis. At present we have no plans to do such experiments and therefore invite others that might be interested to test this hypothesis.[42]

(5) The results also offer additional support for the finding that bulk metal can be a superior catalyst in comparison to even the smaller, greater surface area nanocluster catalysts.[40,41] This insight stands in direct opposition to the current widely held belief that smaller nanoclusters will almost always be the kinetically superior, dominant catalyst. The reason that bulk metal can be a superior catalyst, if larger amounts of coordinating ligands are present, is because of the lower fractional surface coverage on the bulk metal in comparison to that of a nanocluster catalyst.[40,41] This in turn results in more coordinative unsaturation, typically a prerequisite for transition-metal catalysis, in part, resulting from the up to 2-fold weaker metal–ligand bond energies for the bulk metal versus that of nanoclusters of that same metal.[43] As discussed elsewhere, this size-dependent fraction surface coverage of nanoclusters promises to be a very important insight from (and for) the study of nanocluster catalysis.[40,41]

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Supporting Information Available: Evidence for the true catalyst in the 3.6 mM **1**, 22 °C, and 2.76 bar of H_2 system in neat acetone; Figure S1 showing the kinetics of acetone hydrogenation at 3.6 mM **1**, 22 °C, and 2.76 bar of H_2 fit by the 2-step and 3-step[44] mechanisms; investigations of the metal film and the reaction solution prepared from 52 mM **1**, 75 °C, and 4.05 bar of H_2 in neat IL; Figure S2 showing the XPS spectrum of the metal film derived from 52 mM **1**, 75 °C, and 4.05 bar H_2; the reinvestigation of the kinetically dominant catalyst made under conditions 2 from the literature; Figure S3 showing a comparison of the initial rates of cyclohexene hydrogenation by the bulk metal isolated from the 52 mM **1**, 75 °C, 4.05 bar of H_2 conditions; Figure S4 showing acetone hydrogenation with 1 equiv of [NBu_4][PF_6] in 0.2 mL of added acetone; attempted nanocluster formation in neat [bmim]-[PF_6] with varying temperature and pressure; and a probe of the possible temperature dependence of IL poisoning of a conditions 2-prepared catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) We considered the potentially useful experiment of studying NHCs with butyl and methyl substitutions at the 1- and 3-positions, respectively. However, the preparation of such unbound NHCs is difficult and can usually only be accomplished when bulky ligands, such as mesitylene or norbornene, are present at the 1- and 3-positions of the imidazolium ring. Binding to the nanoclusters' surfaces and the subsequent nanocluster catalyst poisoning by these NHCs would presumably be hindered by these bulky ligands, complicating the interpretation of the results. Additionally, these bulky ligands might also hinder substrate access to the nanoclusters' surface, further complicating interpretation of the data. Hence, we decided not to pursue such experiments.

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