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In Situ Formed "Weakly Ligated/Labile Ligand" Iridium(0) Nanoparticles and Aggregates as Catalysts for the Complete Hydrogenation of Neat Benzene at Room Temperature and Mild Pressures

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"Weakly ligated/labile ligand" nanoparticles, that is nanoparticles where only weakly coordinated ligands plus the desired catalytic reactants are present, are of fundamental interest. Described herein is a catalyst system for benzene hydrogenation to cyclohexane consisting of "weakly ligated/labile ligand" Ir(0) nanoparticles and aggregates plus dry-HCl formed in situ from commercially available $[(1,5-\text{COD})\text{IrCl}]_2$ plus 40 ± 1 psig (~2.7 atm) H₂ at 22 ± 0.1 °C. Multiple control and other experiments reveal the following points: (i) that this catalyst system is quite active with a TOF (turnover frequency) of 25 h⁻¹ and TTO (total turnovers) of 5250; (ii) that the BF_4^- and PF_6^- iridium salt precursors, $[(1,5-COD)Ir(CH_3CN)_2]BF_4$ and $[(1,5-COD)Ir(CH_3CN)_2]PF_6$, yield inferior catalysts; (iii) that iridium black with or without added, preformed HCl cannot achieve the TOF of 25 h⁻¹ of the in situ formed Ir(0)/dry-HCl catalyst. However and importantly, CS₂ poisoning experiments yield the same activity per active iridium atom for both the Ir(0)/dry-HCl and Ir black/no-HCl catalysts (12.5 h^{-1} Ir¹⁻), but reveal that the Ir(0)/dry-HCl system is 10-fold more dispersed compared to the Ir(0) black catalyst. The simple but important and key result is that "weakly ligated/labile ligand" Ir(0)nanoparticles and aggregates have been made in situ as demonstrated by the fact that they have identical, per exposed Ir(0) activity within experimental error to Ir(0) black and that they have no possible ligands other than those desired for the catalysis (benzene and H₂) plus the at best poor ligand HCl. As expected, the in situ catalyst is poorly stabilized, exhibiting only 60% of its initial activity in a second run of benzene hydrogenation and resulting in bulk metal precipitation. However, stabilization of the Ir(0) nanoparticles with a ca. 2-fold higher catalytic activity and somewhat longer lifetime for the complete hydrogenation of benzene was accomplished by supporting the Ir(0) nanoparticles onto zeolite-Y (TOF of 47 h^{-1} and 8600 TTO under otherwise identical conditions). Also reported is the interesting result that Cl⁻ (present as Proton Sponge H⁺Cl⁻) completely poisons benzene hydrogenation catalysis, but not the easier cyclohexene hydrogenation catalysis under otherwise the same conditions, results that suggest different active sites for these ostensibly related hydrogenation reaction. The results suggest that synthetic routes to "weakly ligated/labile ligand" nanoparticles exhibiting improved catalytic performance is an important goal worthy of additional effort.

Introduction

"Weakly ligated/labile ligand" nanoparticles^{1–8} are of interest to the nanoparticle catalysis community since their surfaces should be readily available for catalysis following only the dissociation of weakly coordinated ligands⁹ or solvent.^{3,10,11} In a previous publication,¹¹ we reported an easily prepared, highly active and selective "weakly ligated/labile ligand" nanoparticle catalyst system for neat-acetone hydrogenation consisting of iridium(0) plus dry-HCl formed in situ from the H₂ reduction of commercially available 1,5-cyclooctadienechloroiridium(I) dimer, [(1,5-COD)IrCl]₂. This Ir(0)/dry-HCl catalyst system is a superior catalyst for acetone hydrogenation at low temperature and pressure in terms of its activity (22 ± 0.1 °C and 40 ± 1 psig H₂

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^{(1) (}a) The nomenclature "nanoparticle" is used herein rather than "nanocluster". Although as Schmid and Fenske have noted there is at present no "sharp discrimination"^{1b} between these two terms, there is an evolving nomenclature where nanocluster is preferred when the composition and the structure of the species are precisely defined whereas nanoparticle is more appropriate when a size distribution is present.^{1b} However, reports exist where "nanoparticle" has been used to designate very precisely defined species.^{1c,d} (b) Schmid, G.; Fenske, D. *Philos. Trans. R. Soc. A* **2010**, *368*, 1207. (c) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *318*, 430. (d) Heaven, M. W; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc. **2008**, *130*, 3754.

⁽²⁾ Ott, L. S.; Finke, R. G. *Coord. Chem. Rev.* **2007**, *251*, 1075; see especially sections 4.1 and 4.2 and references therein to the work of others on what we have termed the "weakly ligated/labile ligand" nanoparticles problem.

⁽³⁾ Ott, L. S.; Finke, R. G. *Inorg. Chem.* 2006, 45, 8382; see the references therein to putatively "solvent-only stabilized nanoparticles". Also of interest is footnote 32 therein, reproduced here: "The "naked nanoparticle problem", perhaps more accurately called the "ligand-labile nanoparticle problem", is the need for efficient, high yield syntheses of metastable nanoparticles that have relatively easily removed ligands so that they can be used for low-temperature syntheses of novel heterogeneous catalysts or other applications of clean, ideally naked-surface nanoparticles."

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⁽⁵⁾ More recently, Evanoff and co-workers^{5a} reported "essentially naked" Ag nanoparticles with a large H_2O solvation cage which encapsulates the Ag nanoparticles. In a later paper,^{5b} the stability of the Ag nanoparticles were attributed to electrostatic repulsion afforded by the low ionic strength solution (Ag⁺ and OH⁻). (a) Chumanov, G.; Evanoff, D. D. J. Phys. Chem. B **2004**, 108, 13948. (b) Evanoff, D. D.; Chumanov, G. Chem. Phys. Chem. **2005**, 6, 1221.

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⁽⁷⁾ Mondloch, J. E.; Özkar, S.; Finke, R. G. Manuscript in preparation. As part of this mini-review, a fuller survey of the literature related to "naked nanoparticles", "solventonly stabilized nanoparticles",^{2,3} and "weakly ligated/labile ligand nanoparticles"³ is planned.

^{(8) (}a) Meisel and coworkers^{8b} find that a small amount of Ag⁺ is present on the surface of Ag nanoparticles, which in turn are negatively charged overall via adsorbed OH⁻ anions. (b) Merga, G.; Wilson, R.; Lynn, G.; Milosavljevic, B. H.; Meisel, D. J. Phys. Chem. C 2007, 111, 12220.

⁽⁹⁾ Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. Of interest here is the parallel between the development of the "weakly coordinating/labile ligand" nanocluster problem to the earlier "weakly coordinating anion" problem reviewed by S. H. Strauss.

⁽¹⁰⁾ Noteworthy here, however, is that even metal-alkane bond dissociation energies are $\sim 10 \pm 3$ kcal/mol, so that such putatively "naked" nanoparticles in even an alkane solvent would really be better labeled "weakly ligated/labile ligand" nanoparticles.^{10a-c} (a) Yang, G. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett.* **1986**, *125*, 566. (b) Simon, J. D.; Xie, X. J. *Phys. Chem.* **1989**, *93*, 291. (c) Morse, J. M., Jr.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471.

pressure with an estimated TOF of 1.9 s^{-1}), selectivity (95% 2-propanol, 5% diisopropyl ether), and total catalyst lifetime (16400 TTOs). These results suggested that it would be of interest to employ this easily formed, highly active Ir(0)/dry-HCl catalyst system for the solventless reduction of other challenging hydrogenations such as benzene hydrogenation.

The complete hydrogenation of aromatics is of interest^{12,13} for a number of reasons, including the growing demand for cleanerburning, low-aromatic-content diesel fuels (that thereby minimize powerful carcinogens¹⁴ in diesel exhaust particles that contribute to asthma or nasal allergies¹⁵). Benzene hydrogenation to cyclohexane is also important, cyclohexane being a key intermediate in the production of the nylon precursor adipic acid.¹⁶ However, benzene hydrogenation is notably difficult compared to simple olefin hydrogenation¹⁷ due to the loss of the resonance stabilization energy during benzene reduction and prior to the rate-determining transition state.¹⁸ Consequently, benzene hydrogenation has historically required higher temperatures and H₂ pressures (i.e., ≥ 100 °C and ~50 atm H₂).¹⁹ Confirming this, only 17 studies that we have been able to find report the complete hydrogenation of benzene to cyclohexane at temperatures ≤ 25 °C (*see* Table SI-1 in the Supporting Information).²⁰ Among those 17 studies, only 6 articles^{20b,c,f,j,o,q} report neat benzene hydrogenation, the conditions that will be employed herein. The reported neat-benzene hydrogenation catalyst systems also tend to involve multistep, sometime laborious catalyst preparation procedures.

Hence, still of interest is the complete hydrogenation of neat benzene (i.e., solventless, green conditions²¹) via a highly active, long-lived, readily available catalyst that operates under mild conditions, (≤ 25 °C and ≤ 10 atm H₂ pressure). Also desirable is clear documentation of the catalyst turnover frequency and total turnover number, as well as determination of the important, but too infrequently measured, percentage of active catalyst sites via catalyst poisoning studies (e.g., with CS₂).¹⁸

Herein, we report that in situ reduction of $[(1,5-COD)IrCl]_2$ under 40 ± 1 psig (~2.7 atm) initial H₂ pressure at 22 ± 0.1 °C

forms Ir(0)/dry-HCl as highly active catalyst for neat-benzene hydrogenation with 100% conversion to cyclohexane. The in situ coproduction of dry-HCl is relevant to the catalytic activity as demonstrated by multiple control experiments such as (i) scavenging in situ formed H⁺ via Proton Sponge, and (ii) comparing the catalytic activity of two other iridium precursors (i.e., [(1,5-COD)Ir(CH₃CN)₂]BF₄ and [(1,5-COD)Ir(CH₃CN)₂]PF₆) under otherwise identical conditions. A comparison to iridium black, employed as a benzene hydrogenation catalyst under otherwise identical conditions, reveals a 10-fold lower activity (TOF of 2.5 h^{-1} for iridium black²² vs 25 h^{-1} for Ir(0)/dry-HCl), but CS₂ poisoning studies indicate that ca. 2% of total iridium atoms are catalytically active when starting with [(1.5-COD)IrCl]₂, but only 0.2% when starting with iridium black (both assuming a 1:1 CS₂: Ir poisoning stoichiometry). Hence, the catalytic activity in each case is the same per exposed Ir(0)—results that also demonstrate the value of such active-site determination studies via quantitative poisoning experiments. The high activity and good lifetime, $25 \leq$ $TOF \le 1250 \text{ h}^{-1}$ and $5250 \le TTO \le 262500$, of the Ir(0)/dry-HCl catalyst system is consistent with the expected "weakly ligated/ labile ligand" nature of the Ir(0) nanoparticles and aggregates where only the possible ligands are benzene, H_2 (i.e., and hydrides), and the weak to nonligand HCl.

Experimental Section

Materials and General Considerations. All commercially obtained compounds were used as received unless indicated otherwise. Benzene (anhydrous, 99.8%), diethyl ether (≥99.9%), CH_2Cl_2 (anhydrous, $\geq 99.8\%$), Proton Sponge (1,8-bis(dimethylamino)naphthalene, 99%), and CS₂ (anhydrous, \geq 99%) were purchased from Aldrich Chemicals and transferred into a Vacuum Atmospheres nitrogen atmosphere drybox. CD₂Cl₂ (Cambridge Isotope Laboratories) was purchased in 1 mL glass ampules which were then transferred into the drybox where NMR sample preparations were performed. [(1,5-COD)IrCl]₂ and iridium black $(99.9\%, 30-60 \text{ m}^2/\text{gr})$ were purchased from Strem Chemicals. Sodium zeolite-Y (Na₅₆Y, Si/Al = 2.5) was purchased from Zeolyst Inc. and slurried with 0.1 M NaCl solution to remove cation defect sites, washed until free of chloride and calcined in dry oxygen at 500 °C for 12 h before use. Unless otherwise stated all studies were performed under oxygen- and moisture-free conditions using a Vacuum Atmospheres N_2 drybox (always < 5 ppm of O_2 , and typically <1 ppm of O_2 , as monitored by a Vacuum Atmospheres O₂ level monitor). ¹H NMR spectra were taken on a Varian INOVA-300 instrument with 300.115 MHz for ¹H. Gas Chromatography (GC) measurements were performed using a Hewlett-Packard 5890 series II GC with an MSD 5970 B. The GC was equipped with a 30 m (0.25 mm i.d., $0.25 \,\mu$ m film thickness) Supelco SPB-1 column and with an ionizing voltage of 70 eV. The GC parameters were as follows: initial temperature, 50 °C; initial time, 3 min; solvent delay, 2 min; temperature ramp, 10 °C/min; final temperature, 270 °C; final time, 5 min; injector port temperature, 280 °C; detector temperature, 290 °C; injection volume, 0.2 μ L. The iridium content of the Ir(0)/zeolite-Y sample was determined by ICP-OES analysis (Leeman-DRE) after each

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sample was completely dissolved in the mixture of HNO3:HCl with a 1:3 ratio (theoretical Ir: 1%, found Ir: 1%). Powder X-ray diffraction (XRD) patterns of Ir(0)/zeolite-Y samples were recorded with a Rigaku X-ray diffractometer (Model, Miniflex) with Cu K α (30 kV, 15 mA, $\lambda = 1.54051$ A) radiation at room temperature.

Hydrogenation Apparatus. All the hydrogenation reactions were carried out on the previously described, custom-built pressurized hydrogenation apparatus which allows monitoring the H₂ pressure decrease accompanying hydrogenations (± 0.01 psig) via a computer interface (LabView ver. 8.2) in real-time.^{23–25} A Fischer-Porter (F-P) bottle was connected via its Swagelock TFEsealed Quick Connects to a hydrogenation line and Omega D1512 10 V A/D converter with RS-232 connection to a computer. The hydrogen (>99.5) was purchased from Airgas and scrubbed via a Trigon moisture trap and a Trigon Technologies oxygen/moisture trap to remove O₂ and H₂O followed by a Trigon Technologies high capacity indicating oxygen trap.

Standard Conditions Procedure for the Complete Benzene Hydrogenation Experiments Starting with [(1,5-COD)IrCl]₂. To start, 17.5 mg (0.052 mmol in iridium) of the [(1,5-COD)IrCl]₂ precatalyst was weighed in a 2 dram glass vial and then dissolved in 1.0 mL (11.2 mmol) of benzene added via a 5.0 mL gastight syringe; a clear, orange solution 52 mM in iridium resulted. The solution was then transferred via a disposable polyethylene pipet into a new 22 \times 175 mm Pyrex culture tube containing a new $5/16 \times 5/8$ in. Teflon-coated stir bar. The culture tube was then sealed inside the F-P pressure bottle and brought outside the drybox. The F-P bottle was placed into a constant temperature circulating bath at 22 ± 0.1 °C, and attached via Swagelock TFEsealed Quick-Connects to the hydrogenation line (which had already been evacuated for at least 30 min to remove any trace oxygen and water present, then refilled with purified H₂ at 40 ± 1 psig). Stirring was started (at 600 rpm) and the F-P bottle was then purged 15 times with hydrogen (15 s per purge) and t = 0 was started. When the hydrogen uptake ceased, the F-P bottle was disconnected from the hydrogenation line, remaining H₂ pressure was released, and transferred back into the drybox, where a 9 in. glass Pasteur pipet was used to withdraw a ca. 0.05 mL aliquot from the culture tube. This aliquot was then added to 1 mL of CD_2Cl_2 in an individual glass ampule, mixed under agitation using the Pasteur pipet, and then transferred into an NMR sample tube which was subsequently brought out of the drybox after sealing for ¹H NMR investigation. The NMR analysis showed the complete reduction of benzene (7.26 ppm, m) to cyclohexane (1.44 ppm, s). None of the partially hydrogenated benzene reduction product, cyclohexene, was observed.

X-ray Photoelectron Spectroscopy (XPS) Analyses. At the end of the benzene hydrogenation reaction, the F-P bottle was vented and the solution was brought to dryness under vacuum to yield a gray solid. Some of that solid was then coated onto a XPS sample holder and subsequently sealed in a desiccator under the N₂ atmosphere of the drybox. The desiccator-enclosed sample was then removed from the drybox for analysis via a Physical Electronics (PHI) Model 5800 XPS system equipped with a monochromator (Al K α source, hv = 1486.8 eV; system pressure $\leq 5 \times$ 10^{-9} Torr) and a hemispherical analyzer to detect the ejected photons; XPS analysis was accomplished with the expert assistance of Pat McCurdy at the Central Instrument Facility of Colorado State University, Department of Chemistry. To minimize exposure of the sample to air, the desiccator was opened next to the instrument antechamber and the sample holder was mounted immediately followed by closing and evacuating the antechamber. The binding energies were compared to the literature values.²

Transmission Electron Microscopy (TEM) Analyses. i. Ir-(0)/Dry-HCl System. The final form of the hydrogenation reaction solution is not homogeneous; instead, a brown solution with black precipitate forms, so that the TEM images obtained as follows cannot be 100% representative of the whole medium. However, to obtain an idea about the particles present in solution, TEM samples were harvested after 4 h of a standard conditions benzene hydrogenation, and then at the end of this same reaction (i.e., after 8.7 ± 0.1 h). TEM samples were prepared as follows: the F-P bottle was detached from the hydrogenation line after 4 h of the reaction via its quick connects, vented, and brought back into the drybox. The solution was transferred with a disposable polyethylene pipet into a clean, 5 mL glass vial. TEM samples were prepared by dipping the SiO-TEM grid into the solution for 3 s. The F-P bottle was then resealed after transferring the solution back into the Pyrex culture tube in it, brought out of the drybox, reconnected to the line and pressurized to 40 ± 1 psig with H₂. At this point, collection of pressure versus time data was continued (ignoring the \sim 1 h gap required for the procedure). The same TEM preparation procedure was repeated at the end of the reaction, that is, after 8.7 ± 0.1 h. The resultant TEM grids were then placed separately in a screw-capped glass vials, were sealed and then were shipped to Clemson University for TEM analysis via the expert assistance of Dr. JoAn Hudson and her staff. TEM images were obtained with a Hitachi H7000 instrument operating at 120 keV.

ii. Ir(0)/Zeolite-Y System. When the otherwise standard conditions benzene hydrogenation reaction was complete (now after 4.7 \pm 0.1 h for this faster catalyst), the F-P bottle was detached from the hydrogenation line via its quick connects, vented, and brought back into the drybox. The Pyrex culture tube inside F-P bottle was transferred into a Schlenk tube and then brought to dryness under vacuum, yielding a gray solid. A small amount of the powdered sample was placed on a copper grid. Samples were examined at magnification between 100 and 400 K by using JEM-2010F microscope (JEOL) operating at 200 keV.

Control Experiments of Benzene Hydrogenation Starting with [(1,5-COD)IrCl]₂ Plus 1.0 or 0.02 equiv of Proton Sponge per equiv of Ir. Two separate control experiments were performed starting with 17.5 mg (0.052 mmol in iridium) [(1,5-COD)IrCl]₂ in 1.0 mL (11.2 mmol) of benzene, but now plus 1.0 or 0.02 equiv of Proton Sponge (0.052 or 1.04 \times 10^{-4} mmol, respectively) per equiv of iridium under the Standard Conditions of 22 ± 0.1 °C and 40 ± 1 psig initial H₂ pressure. The results are described in the Results and Discussion section.

Control Experiment of Cyclohexene Hydrogenation under Standard Conditions Starting with [(1,5-COD)IrCl]₂ in the presence of 1 equiv of Proton Sponge per equiv of Ir. A cyclohexene control hydrogenation experiment was performed starting with 17.5 mg (0.052 mmol in iridium) [(1,5-COD)IrCl]₂ in 1.0 mL (11.2 mmol) of benzene and 0.5 mL (4.9 mmol) cyclohexene plus 1 equiv of Proton Sponge (0.052 mmol) under the standard conditions of 22 ± 0.1 °C and 40 ± 1 psig initial H₂ pressure. The results are described in the Results and Discussion section.

Synthesis and Characterization of [(1,5-COD)Ir(CH₃-CN)₂][X] (X: BF₄ and PF₆). These complexes were synthesized and characterized according to the literature procedure.²⁷ 2.02 g of [(1,5-COD)IrCl]₂ (3.01 mmol) was dissolved in 42 mL of CH₂Cl₂. Upon the addition of 10 mL of CH₃CN, the dark red solution turned bright yellow. Then, 6.01 mmol of AgX (where X represents BF₄ for [(1,5-COD)Ir(CH₃CN)₂]BF₄ and PF₆ for [(1,5-COD)Ir(CH₃CN)₂]PF₆) was added to precipitate AgCl. The obtained solution was filtered into 200 mL of diethyl ether; yellow microcrystals resulted of [(1,5-COD)Ir(CH₃CN)₂][X], where X: BF₄ or PF₆. The resultant solution was then filtered, washed with

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 2×10 mL diethyl ether, and dried under vacuum for 12 h (80% yield of [(1,5-COD)Ir(CH₃CN)₂]BF₄ as a yellow solid; 81% yield of [(1,5-COD)Ir(CH₃CN)₂]PF₆ as a yellow solid). ¹H NMR data were compared to the literature²⁷ (in parentheses) to confirm the identity and purity of the complexes: 4.3 ppm, s (4.27 ppm, s); 2.5 ppm, s (2.53 ppm, s); 2.3 ppm, m (2.29 ppm, m); 1.8 ppm, m (1.78 ppm, m).

Control Experiments for Standard Conditions Benzene Hydrogenation Starting with $[(1,5-COD)Ir(CH_3CN)_2]BF_4$ and $[(1,5-COD)Ir(CH_3CN)_2]PF_6$. Two separate standard conditions benzene hydrogenation experiments were performed, but now using the two different iridium precursors $[(1,5-COD)Ir-(CH_3CN)_2]BF_4$ and $[(1,5-COD)Ir(CH_3CN)_2]PF_6$ in place of $[(1,5-COD)IrCI]_2$. The results are described in the Results and Discussion section.

Control Experiments with Commercial Iridium Black. Control experiments were performed by following the Standard Conditions, but now using commercial iridium black in place of $[(1,5-COD)IrCl]_2$. The results are described in the Results and Discussion section.

Catalyst Lifetime Experiments. Catalyst lifetime experiments were performed by following the Standard Conditions for the Ir(0)/dry-HCl and for Ir(0)/zeolite-Y catalyst, but with (i) 1.2 mg (3.6μ mol in iridium) of [(1,5-COD)IrCl]₂ precursor in 3.0 mL (33.6μ mol) of benzene corresponding to a maximum possible 9333 TTOs, and (ii) 1.75 mg (5.25μ mol in iridium) of [(1,5-COD)IrCl]₂ precursor and 48 mg zeolite-Y in 5.0 mL (56μ mol) of benzene corresponding to a maximum possible 10667 TTOs. The results are described in the Results and Discussion section.

CS₂ Poisoning Experiments. These experiments were each started as if they were a Standard Conditions benzene hydrogenation experiment. For each poisoning trial below (i.e., for each different equivs of CS₂ added), a fresh standard conditions benzene hydrogenation was started and allowed to proceed for 5 h while pressure versus time data were collected. The F-P bottle was then vented, taken into the drybox, and opened, and the desired amount of CS₂ was added. After the addition of CS₂, the F-P bottle was resealed, brought out of the drybox, reconnected to the line and pressurized to 40 ± 1 psig with H₂. At this point, collection of pressure versus time data was continued (ignoring the \sim 1 h gap required for the procedure). For example, for the Ir(0)/dry-HCl system, 0.1 equiv CS₂ with respect to the total iridium present was added and found to poison the previous catalytic activity completely. In the next experiment, the amount of CS₂ added was lowered to 0.01 equiv; this in turn did not poison the catalyst completely. The third experiment employed 0.03 equiv of CS₂, and that did completely cease the catalytic activity. Hence, ca. 0.02 equiv of CS2 was deemed sufficient to poison completely the catalytic activity.

Control Experiment for Benzene Hydrogenation Showing That Transferring to the Drybox, Opening the F-P Bottle, and Then Restarting the Reaction Does Not Cause a Detectable Loss of Activity. This experiment was performed to ensure that the loss of activity seen in the CS2 poisoning experiment is due to the added CS_2 , and not some other aspect of the necessary manipulations cited above in the CS2 poisoning experiments. This control experiment was started as if it were a standard conditions benzene hydrogenation experiment. Pressure versus time data were collected for 5 h. Then the F-P bottle was vented, taken into the drybox, and opened. The F-P bottle was then resealed, brought out of the drybox, reconnected to the line and pressurized to 40 ± 1 psig with H₂. At this point, collection of pressure versus time data was continued (again ignoring the \sim 1 h gap required for the procedure). No detectable loss of activity due to the above transfer procedure was observed in this control experiment.

Catalyst Redispersibility Experiments. These experiments were each started as if they were a standard conditions benzene hydrogenation experiment. After complete hydrogenation of benzene, the F-P bottle was vented and the solution was brought to dryness under vacuum to yield a gray solid for both the Ir(0)/ dry-HCl and Ir(0)/zeolite-Y catalysts. In two separate experiments these gray residues were redispersed in 1.0 mL (11.2 mmol) of benzene, repressurized to 40 \pm 1 psig with H₂, and purged 15 times (15 s per purge), and the collection of pressure versus time data was restarted. The results are described in the Results and Discussion section.

Curve-Fitting Trials of the Hydrogen Uptake Data. Curve-fitting trials for concentration vs time data to the previously established 2-step²⁸ or 4-step²⁹ nanoparticle and agglomerated nanoparticle formation mechanisms were performed using nonlinear least-squares fitting in Origin ver. 7.0 or MacKinetics, respectively.

Procedure for the Complete Hydrogenation of Neat Benzene Starting with $[(1,5-COD)IrCl]_2$ plus Zeolite-Y (Na₅₆Y, Si/Al: 2.5). In a 2 dram glass vial, 17.5 mg (0.052 mmol in iridium) of the precatalyst $[(1,5-COD)IrCl]_2$ was weighed and then dissolved in 1.0 mL (11.2 mmol) of benzene added via a 5.0 mL gastight syringe to yield a clear, orange solution; this solution was then transferred via a disposable polyethylene pipet into a new 22×175 mm Pyrex culture tube containing a new $5/16 \times 5/8$ in. Teflon-coated stir bar. Next, 480 mg zeolite-Y (corresponding to 1.0% wt Ir on zeolite-Y) was added into this solution and mixed for half an hour. Then, the hydrogenation experiment was performed in the same way as described previously in the section Standard Conditions Procedure for the Complete Benzene Hydrogenation Experiments Starting with [(1,5-COD)IrCl]_2.

Results and Discussion

Product Characterization and Balanced Stoichiometry for the Complete Hydrogenation of Benzene Starting with [(1,5-COD)IrCl]₂ as Precatalyst under Standard Conditions. Figure 1 shows a typical benzene loss vs time plot for the complete hydrogenation of neat benzene (1.0 mL, 11.2 mmol) starting with the $[(1,5-COD)IrCl]_2$ (17.5 mg, 0.052 mmol Ir) precatalyst at 22 \pm 0.1 °C and 40 \pm 1 psig (~2.7 atm) initial H₂, which we will refer to as "standard conditions". The initial orange color of the solution due to the [(1,5-COD)IrCl]₂ precatalyst darkens within 30 min of the initiation of the reaction by the addition of H₂ pressure, and that dark color remains throughout the entire reaction. Complete hydrogenation of benzene was achieved after 8.7 ± 0.1 h as indicated by the cessation of H₂ uptake and the production of cyclohexane (100%) as the sole product and confirmed by ¹H NMR as detailed in the Experimental Section. This particular kinetic curve given in Figure 1 is not well fit by either our 2- or 4-step mechanisms of nanoparticle and agglomerated nanoparticle formation^{28,29} details of which are given in the Supporting Information for the interested reader (Figures SI-1 and SI-2).

The balanced stoichiometry of the formation of Ir(0)/dry-HCl from $[(1,5-COD)IrCl]_2$ and concomitant benzene hydrogenation under standard conditions is given in Scheme 1: the reduction of 1 equiv of $[(1,5-COD)IrCl]_2$ requires 5 equiv of H₂ and produces 2/n equiv of $Ir(0)_n$ plus 2 equiv of HCl by mass balance.^{24b} The evolution of 2 equiv of cyclooctane was confirmed by GC. The formation of Ir(0) was confirmed by XPS³⁰ on the vacuum-dried

^{(28) (}a) Watzky, M. A.; Finke, R. G. J. Am. Chem. Soc. 1997, 119, 10382 and references therein. (b) Watzky, M. A.; Finke, R. G. Chem. Mater. 1997, 9, 3083.
(c) Aiken, J. D., III; Finke, R. G. J. Am. Chem. Soc. 1998, 120, 9545 and references therein. (d) Widegren, J. A.; Aiken, J. D., III; Özkar, S.; Finke, R. G. Chem. Mater. 2001, 13, 312 and references therein.

^{(29) (}a) Besson, C.; Finney, E. E.; Finke, R. G. J. Am. Chem. Soc. 2005, 127, 8179.
(b) Besson, C.; Finney, E. E.; Finke, R. G. Chem. Mater. 2005, 17, 4925.
(c) Finney, E. E.; Finke, R. G. Chem. Mater. 2008, 20, 1956.

⁽³⁰⁾ The resultant XPS binding energies were compared to the literature²⁶ (in parentheses). The results confirm that the solid is Ir(0): 577 eV ($4p_{1/2}$, 578 eV), 494 eV ($4p_{3/2}$, 495 eV), 311 eV ($4d_{3/2}$, 312 eV), 298 eV ($4d_{5/2}$, 297 eV), 64 eV ($4_{f5/2}$, 64 eV), 61 eV ($4f_{7/2}$, 61 eV).



Figure 1. Typical benzene loss vs time plot for the catalytic hydrogenation of benzene starting with 17.5 mg of [(1,5-COD)-IrCl]₂ (0.052 mmol Ir) in 1.0 mL (11.2 mmol) benzene at $22 \pm 0.1 \,^{\circ}$ C with an initial H₂ pressure of 40 ± 1 psig (~2.7 atm). After an induction period of 0.7 ± 0.1 h, the hydrogenation starts with an initial rate of 2.0 ± 0.3 M benzene/h. Complete hydrogenation of benzene into cyclohexane was achieved in 8.7 ± 0.1 h as confirmed by ¹H NMR analysis.

solid gray catalyst residue collected after the hydrogenation of benzene was complete (i.e., after 8.7 ± 0.1 h). The darkening of the solution within 30 min following the addition of H₂ pressure is consistent with the formation of Ir(0) nanoparticles,³¹ and confirming evidence for those nanoparticles was obtained by ex situ TEM, Figure 2. The TEM images were taken at two different, key stages of the reaction: after 4 h of reaction, Figure 2a, and at the end of the reaction (after 8.7 ± 0.1 h), Figure 2b. The close inspection of these images reveals smaller, average diameter < 10 nm, nanoparticles present after 4 h of reaction but then larger, average diameter > 20 nm, nanoparticles present at the end of the reaction—that is, that agglomeration of the Ir(0) nanoparticles to larger particles occurs as the reaction proceeds.

Experiments Demonstrating the Requirement for the in situ Formation of Dry-HCl for the Observed Catalytic Activity. As mass balance requires and the balanced stoichiometry in Scheme 1 indicated, one equiv of HCl is produced in situ per one equiv of Ir(I) reduced by H_2 .^{24b} Control experiments were done (vide infra) and reveal that the in situ formation of dry-HCl is a required component of the observed, high catalytic activity reported herein. Specifically, 1.0 equiv of Proton Sponge (1,8-bis-(dimethylamino)naphthalene)³² per equiv of iridium was added to an otherwise standard conditions benzene hydrogenation to learn the effects of removing the H⁺ (Proton Sponge is a strongly basic, conjugate acid aqueous $pK_a = 12.3$, weakly coordinating, scavenger of H⁺ that has been shown to be valuable in nanoparticle syntheses^{24b}). No detectable hydrogen uptake was observed in the presence of 1.0 equiv of Proton Sponge, even after more than 10 h. Immediate darkening of the initially orange reaction solution upon the application of hydrogen pressure indicates that $\mathrm{Ir}(0)$ nanoparticles were still formed,³¹ albeit ones significantly less catalytically active in the presence of the resultant 1.0 equiv of Proton Sponge•H⁺Cl⁻ that can serve as an iridium nanoparticle ligand, Scheme 2. As a further control to confirm that a (less active, more stable) nanoparticle catalyst is formed when 1.0 equiv of Proton Sponge is added, the same experiment was repeated, except now with just one change: the much more easily reduced substrate, cyclohexene (0.5 mL), also added. H₂ uptake now occurred, but ceased right after the required stoichiometric

Scheme 1. Balanced Stoichiometry for the Formation of Ir(0)/Dry-HCl from the Precursor [1,5-COD)IrCl]₂ and Subsequent Benzene Hydrogenation under Standard Conditions

Catalyst Formation

$$[(1,5-\text{COD})\text{IrCl}]_2 + 5 \text{ H}_2 \xrightarrow{22 \pm 0.1 \text{ °C}} 2 \longrightarrow 2 + 2/n \text{ Ir}(0)_n + 2 \text{ H}^+\text{Cl}^-$$

Neat Benzene Hydrogenation Catalysis

$$3 H_2 + \bigcirc \frac{2/n Ir(0)_n + 2 H^+CI^-}{22 \pm 0.1 \ ^{\circ}C, 40 \pm 1 \text{ psig } H_2} \bigcirc$$

amount of H_2 needed (~14 psig H_2) to convert (only) the cyclohexene into cyclohexane. No benzene hydrogenation was observed (¹H NMR was used to confirm that the initial amount of benzene still remained while the complete conversion of cyclohexene into cyclohexane had occurred). This cyclohexene (only) hydrogenation curve is fit roughly ($R^2 = 0.997$) to the 2-step mechanism of nanoparticle nucleation and autocatalytic growth,²⁸ Figure 3. TEM investigation of the resultant product once the cyclohexene hydrogenation was complete reveals Ir(0)nanoparticles with >10 nm in diameter, Figure 4. The finding that Proton Sponge•H⁺Cl⁻ poisons room temperature benzene reduction catalysis, but not cyclohexene hydrogenation catalysis, is of some interest in its own right and is suggestive of either a different requirement for HCl in these two ostensibly related hydrogenation reactions or possible different active sites for these two reactions.

In an attempt to see if more stable, yet still active iridium nanoparticles could be formed via the addition of <1.0 equiv Proton Sponge, the addition of 0.02 equiv was tried (the 0.02 equiv being picked since it matches the number of active iridium atoms found by CS₂ poisoning experiments, vide infra). Interestingly, even just 0.02 equiv of Proton Sponge poisons the activity, Figure 5.

Very interestingly, however, replacing Cl⁻ by PF₆⁻ or BF₄⁻ does not yield a better catalyst as one might have guessed. Instead, these salts yield inferior, totally inactive systems. When the iridium precursors [(1,5-COD)Ir(CH₃CN)₂]PF₆ (that should yield HPF₆ under H₂) and [(1,5-COD)Ir(CH₃CN)₂]BF₄ (that should yield HBF₄ under H₂) were employed separately in an otherwise standard conditions benzene hydrogenation experiments (i.e., 0.052 mmol iridium concentration in 1.0 mL benzene at 22 ± 0.1 °C and initial H₂ pressure of 40 ± 1 psig), neither of the non-Cl⁻ containing, non-HCl generating precatalysts yielded any catalytic activity whatsoever, Figure 6. Both [(1,5-COD)Ir-(CH₃CN)₂]PF₆ and [(1,5-COD)Ir(CH₃CN)₂]BF₄ do, however, yield black precipitates of bulk iridium metal after ~ 9 h along with a clear (and thus largely Ir(0) nanoparticle-plus aggregatefree) solution. The inactivity of catalysts formed from the PF_6^- or BF_4^- salts of the iridium precursors is, however, not completely unexpected since we have previously seen that even these traditionally weakly coordinating anions PF_6^- and BF_4^- can coordinate well to at least Ir(0) nanoparticle surfaces.³ The implication is that Cl binds H^+ in preference to the Ir(0) surface, while the opposite is true for BF_4 and $PF_6^{-.33}$ Restated, the Cl precursor is superior in yielding weakly ligated/labile ligand nanoparticles plus aggregates as benzene hydrogenation catalysts than are the $PF_6^$ and BF_4^- precatalysts.

Catalyst Lifetime Demonstration for Ir(0)/Dry-HCl System in the Complete Hydrogenation of Benzene. A catalyst lifetime experiment reveals 5250 TTOs of complete benzene hydrogenation over 320 h. The initial clear-yellow solution darkens as the

 ⁽³¹⁾ Widegren, J. A.; Finke, R. G. J. Mol. Cat. A: Chem. 2003, 198, 317.
 (32) Brzezinski, B.; Schroeder, G.; Grech, E.; Malarski, Z.; Sobczyk, L. J. Mol. Soc., Perkin Trans. 1991, 2, 1643.



Figure 2. TEM images of the solution fraction of the heterogeneous reaction at different key stages of the reaction confirming the agglomeration of the Ir(0) nanoparticles in the solution fraction: (a) TEM image after 4 h of reaction exhibiting an average diameter < 10 nm, and (b) TEM image of the resultant, final solution once benzene hydrogenation is complete (after 8.7 ± 0.1 h) showing an increased average diameter of > 20 nm.





Figure 3. Cyclohexene hydrogenation curve (\diamond) and approximate fit to 2-step mechanism of nanoparticle formation²⁸ (-) obtained after the addition of 1.0 equiv of Proton Sponge plus 0.5 mL of cyclohexene under otherwise standard conditions. The fit is only approximate in this case ($R^2 = 0.997$), not unexpectedly since agglomerated nanoparticles and bulk metal are among the products. The resultant rate constants are $k_1 = 0.352 \text{ h}^{-1}$ and $k_{2corr} = 249 \text{ M}^{-1} \text{ h}^{-1}$ (k_2 being corrected as is proper by the stoichiometric factor of \sim 95; see elsewhere for the reasons for, and details of, this mathematically required correction factor when the evolution of the catalyst is being followed by the cyclohexene hydrogenation reporter reaction method²⁸).

iridium(0) nanoparticles are first generated, followed by the formation of a precipitate of bulk iridium(0) metal (via XPS^{30}) which



Figure 4. TEM image of the resultant nanoparticles after cyclohexene hydrogenation was completed. The presence of large Ir(0) nanoparticles with > 10 nm in diameter indicates agglomerated nanoparticles and bulk metal are among the products.

becomes visible after a few hours, eventually yielding a clear, colorless (i.e., Ir(0) nanoparticle free) solution. The average TOF during



Figure 5. Standard conditions complete benzene hydrogenation (i) without (\diamond), (ii) with 0.02 equiv (\Box), and (iii) with 1.0 equiv (Δ) of Proton Sponge addition. Even just 0.02 equiv of Proton Sponge (\sim 1.0 equiv per *active* iridium, vide infra) yields negligible activity in comparison to the experiment without Proton Sponge.

the 320 h total catalyst lifetime, and 5250 TTOs, is 16.4 h^{-1} , before complete deactivation by aggregation into bulk metal occurs. The bulk Ir(0) metal product is of course the thermodynamic sink of the system, one readily formed here since there is little DLVO (Derjaugin–Landau–Verwey–Overbeek)³⁴ or other stabilization present for the initially formed Ir(0) nanoparticles, especially with Cl⁻ largely tied up as weakly to noncoordinating HCl.

Redispersibility of the Ir(0)/Dry-HCl Catalyst System under Standard Conditions. Since aggregated Ir(0) is formed as catalysis proceeds, one would expect less than 100% catalytic activity in a second cycle/reuse of the in situ formed Ir(0)/dry-HCl catalyst system. In addition, the volatile HCl should be lost in isolating the catalyst. As expected, only some (60%) of the previous initial catalytic activity is retained in a second, Stardard Conditions benzene hydrogenation.

Control Experiments with Iridium Black and CS₂ Poisoning Experiments Allowing the Comparison of the Activity per Exposed Ir(0) of the In Situ Ir(0)/Dry-HCl System. Iridium black was examined as a neat-benzene hydrogenation catalyst and in the absence of HCl;²² an average TOF of 2.5 $h^$ under otherwise Standard Conditions was seen, that is, 10-fold lower than the TOF of 25 h^{-1} for the in situ Ir(0)/dry-HCl system, Table 1. CS₂ poisoning experiments³⁵ uncovered the primary source of the difference, ca. 0.02 equiv of CS₂ per iridium is sufficient to completely poison the benzene hydrogenation for the in situ Ir(0)/dry-HCl system whereas only ca. 0.002 equiv of CS2 is necessary for the Ir black/no-HCl system. Hence, the in situ formation of the Ir(0)/dry-HCl system produced a 10-fold more dispersed catalyst, Table 1. As a simple control to check the CS₂ poisoning work, a standard conditions benzene hydrogenation with 10 times more iridium black (i.e., using 0.520 mmol iridium



Figure 6. Comparison of hydrogenation activities of three different iridium precursors for complete benzene hydrogenation: $[(1,5-COD)IrCl]_2(\Box), [(1,5-COD)Ir(CH_3CN)_2]BF_4(\bigcirc), and [(1,5-COD)Ir(CH_3CN)_2]PF_6(\diamondsuit)$. Each experiment was performed under otherwise identical following conditions: 0.052 mmol iridium in 1.0 mL benzene (11.2 mmol) at 22 ± 0.1 °C and 40 ± 1 psig initial H₂ pressure. In the cases of the [(1,5-COD)Ir(CH_3CN)_2]BF_4 and [(1,5-COD)Ir(CH_3CN)_2]PF_6 precursors, catalytically inactive, poisoned bulk Ir(0) are observed.

Table 1. Comparison of Iridium Catalysts' Activity and Percentage of Active Iridium Atoms Determined by CS₂ Poisoning Experiments under Otherwise Standard Conditions

catalyst system	iridium (mmol)	average activity (TOF, h ⁻¹)	active iridium atom percentage (%) via CS ₂ poisoning	average activity per active iridium atom (h ⁻¹ Ir ⁻¹)
Ir(0)/dry-HCl	0.052	25	2	12.5
iridium black	0.052	2.5	0.2	12.5
iridium black	0.520	25	0.2	12.5

vs 0.052 mmol iridium for Standard Conditions) was performed. As the above poisoning results predict, that experiment exhibited the same overall catalytic activity as the 0.052 mmol Ir(0)/dry-HCl system, showing an average turnover frequency of 25 h⁻¹, Table 1.

The CS₂ poisoning experiments, along with those using Proton Sponge and those with the HCl, HPF₆ and HBF₄ generating precatalyst salts above, reveal that the Ir(0)/dry-HCl catalyst system (i) provides a 10-fold more highly dispersed, weakly ligated/labile ligand nanoparticle plus aggregates catalyst, one where Cl⁻ is largely unavailable as a ligand for Ir(0) since it is tied up as HCl and where the only other ligands are benzene, H₂ and hydrides formed from H₂.

Two important findings here, then, are that: (a) Cl^- containing precursor systems that generate HCl in situ are preferred, weakly ligated/labile ligand nanoparticle and aggregate catalyst systems; and (b) that the active catalyst that results is indistinguishable from surface Ir(0) of commercial iridium black, except that it is formed in situ in a 10-fold higher dispersion.

Catalyst Activity Comparison of Ir(0)/dry-HCl System with the Prior Highest Activity Catalysts. The CS₂ poisoning experiments allow a comparison of the catalytic activity to the prior best catalysts. Employing 1:1 CS₂:Ir poisoning stoichiometry assumption yields an estimated per-active site TOF of 1250 h⁻¹ and TTOs of 262 500 for the Ir(0)/dry-HCl catalyst system (The use of a 1:1 CS₂:Ir poisoning stoichiometry provides the most conservative, least favorable estimate as CS₂ is known to poison 7 or more active sites in some cases³¹). The highest TOF values previously reported for the complete hydrogenation of neat benzene at ≤ 25 °C and ≤ 10 atm are intrazeolite

⁽³³⁾ To determine any effect of CH₃CN (present in the other two iridium precursors along with BF₄ or PF₆) a control experiment was performed. Specifically, the addition of even 5 equiv (per iridium) of CH₃CN to a standard conditions benzene hydrogenation with [(1,5-COD)IrCl]₂ yielded the same catalytic activity within the experimental error as standard conditions benzene hydrogenation with [(1,5-COD)IrCl]₂. The implication is that it is not the CH₃CN, but rather the PF₆⁻ or BF₄⁻, that is the catalyst poison. (34) DLVO theory^{34a} was developed to describe the stabilization of colloids in

⁽³⁴⁾ DLVO theory^{34a} was developed to describe the stabilization of colloids in 1940s and relies on the Coulombic repulsion between anions and coordinatively unsaturated electrophilic surface of colloids. Further details of the theory, its application to transition metal nanoparticles stability, and implications of DLVO stabilization of nanoparticles are well reviewed for the interested reader.^{2,3,34} (a) Verwey, E. J. W.; Overbeek, J. T. G. *Theory of the Stability of Lyophilic Colloids*, 2nd ed; Dover Publications: Mineola, NY, 1999; (b) Ott, L. S.; Cline, M. L.; Finke, R. G. J. Nanosci. Nanotech. **2007**, *7*, 2400.

⁽³⁵⁾ Hornstein, B. J.; Aiken, J. D.; Finke, R. G. Inorg. Chem. 2002, 41, 1625.

Table 2. Comparison of the Catalytic Activity, Lifetime, and Catalyst Preparation Steps for the Present Ir(0)/Dry-HCl Catalyst System with the
Prior Two Best Catalyst Systems Identified from an Extensive Literature Search of Benzene Hydrogenation at Room Temperature or Lower
Conditions ($\leq 25 \text{ °C}$ and $\leq 10 \text{ atm H}_2 \text{ pressure})^a$

authors	catalyst system	activity (TOF, h^{-1})	lifetime (TTO)	catalyst preparation steps	ref
Özkar and co-workers ^b	neat benzene at 22 °C and 2.7 atm H ₂	1040	2420	ion exchange followed by borohydride reduction of Ru(III) to Ru(0) within the cages of zeolite	200
Wai and co-workers	neat benzene at 20 °C and 10 atm H ₂	$1038 \le \text{TOF} \le 2414^c$	not reported	sonochemical, synthesis of Rh nanoparticles on carbon nanotubes	20q
Finke and co-workers	neat benzene at 22 °C and 40 psig (~2.7 atm) H ₂	$25 \le \text{TOF} \le 1250^d$	$5250 \leq \text{TTO} \leq 262\ 500^d$	one-pot use of [(1,5-COD)IrCl] ₂ as a precatalyst	this study

^{*a*} The complete table of the 17 prior, most relevant literature studies is provided in the Supporting Information for the interested reader, Table SI-1³⁶. ^{*b*} The activity and lifetime values in this report is not corrected for the number of exposed surface atoms; that is, the values given are lower limits. ^{*c*} The lower limit TOF (of 1038 h⁻¹) was defined as the number of molecules reacted per unit weight of catalyst per unit time. The upper limit TOF of 2414 h⁻¹ was calculated from dispersion values evaluated from the mean size of Rh nanoparticles via TEM images.^{37 d} The TOF and TTO values reported herein are the lowest limit (i.e., considering all the iridum atoms are active catalysts) and then the estimated upper limit calculated from the CS₂ poisoning experiments and assuming a 1:1 CS₂:Ir poisoning stoichiometry; see the main text for details.



Figure 7. TEM image of zeolite-supported iridium(0) nanoparticles taken at the end of the hydrogenation of 1.0 mL neat benzene starting with 17.5 mg of $[(1,5-COD)IrCl]_2$ precatalyst (0.052 mmol Ir) plus 480 mg of zeolite-Y at 22 ± 0.1 °C with an initial H₂ pressure of 40 ± 1 psig (~2.7 atm). Scale bar corresponds to 25 nm.

ruthenium(0) nanoparticles with a TOF (uncorrected for active sites) of 1040 h⁻¹ and TTOs (also uncorrected) of 2420.²⁰⁰ The second most active catalyst system is that reported by Wai and coworkers with 1038 \leq TOF \leq 2414 h⁻¹,^{20q} Table 2. Hence and overall, the Ir(0)/dry-HCl catalyst system has comparable TOF and superior TTO values, without any need for laborious catalyst preparation steps, in comparison to the prior best two catalyst systems, Table 2.³⁶

Supporting Ir(0) Nanoparticles on Zeolite-Y to Obtain More Stable and More Active Catalyst. The observed agglomerated Ir(0) nanoparticles and resultant bulk metal after extensive catalytic cycles make apparent the relatively low level of nanoparticle stabilization in these weakly ligated/labile ligand nanoparticles and aggregates. Restated, the weakness of weakly ligated/labile ligand nanoparticles in *solution-based* catalysis is just this, the lack of stabilization in solution of the nanoparticles. However, supporting the Ir(0) nanoparticles on microporous and macroporous materials (e.g., zeolite, Al_2O_3 , TiO_2 , etc.), then testing their activity and lifetime for benzene hydrogenation under the same mild temperature conditions, is expected to yield an improved catalyst lifetime.

To test this hypothesis, $[(1,5\text{-COD})\text{IrCl}]_2$ plus zeolite-Y (Na₅₆Y, Si/Al: 2.5) was prepared in situ as described in the Experimental Section. This precatalyst was then used for in situ generation of the Ir(0)/HCl catalyst during neat-benzene hydrogenation to cyclohexane at 22 ± 0.1 °C and 40 ± 1 psig (~2.7 atm) initial H₂ pressure. The initial orange color of the suspension ([(1,5-COD)IrCl]₂ plus zeolite-Y powders) darkens within 30 min of the initiation of the reaction with H₂ pressure; TEM analysis confirms the implied and expected formation of zeolite-supported Ir(0) nanoparticles, Figure 7. After an induction period of 0.3 ± 0.1 h, hydrogenation starts with an initial rate of 2.6 ± 0.3 M benzene/h and the complete hydrogenation of benzene into cyclohexane (100%) is achieved after 4.7 ± 0.1 h as confirmed by ¹H NMR analysis. Significantly, a smooth sigmoidal curve for the evolution of the catalyst and catalytic activity is now observed, along with an excellent ($R^2 = 0.999$) fit to the 2-step mechanism of nanoparticle formation, ²⁸ Figure 8, with rate

^{(36) (}a) S.Ö. wishes to point out that in a recent publication^{36b} some wording and information in Table S-1 of that publication^{36b} was adapted, inadvertently without proper referencing^{36b} to the present paper, from the literature search first done in 2007 as part of the present work and as summarized in Table SI-1 herein (i.e., and not the other way around, as it might appear since that *J. Am. Chem. Soc.* paper^{36b} appeared first). (b) Zahmakıran, M.; Tonbul, Y.; Özkar, S. *J. Am. Chem. Soc.* **2010**, *132*, 6541.



Figure 8. Data (O) and fit (—) for the catalytic hydrogenation of benzene starting with 17.5 mg [(1,5-COD)IrCl]₂ (0.052 mmol Ir) plus 480 mg zeolite-Y (Ir theoretical, 1%; Ir found, 1%) in 1.0 mL benzene at 22 ± 0.1 °C and 40 ± 1 psig (~2.7 atm) initial H₂ pressure. Following 0.3 ± 0.1 h of induction period, the hydrogenation rate increases in sigmoidal curve, which is well fit by the slow, continuous nucleation Ir(I) → Ir(0) (rate constant, k_1), then autocatalytic surface growth, Ir(I) + Ir(0) → 2 Ir(0) (rate constant, k_2). This observed sigmoidal curve fits well ($R^2 = 0.999$) to a 2-step nanoparticle formation mechanism²⁸ with rate constants $k_1 = 0.081 \pm 0.002$ h⁻¹ and $k_{2corr} = 22.8 \pm 0.5$ M⁻¹ h⁻¹.

Scheme 3. Minimalistic, 2-Step Nanoparticle Nucleation Then Autocatalytic Surface Growth Mechanism and Its Implied More Detailed Steps (Right) for [(1,5-COD)IrCl]₂ Precatalyst plus Zeolite-Y (i.e., A Below) System en Route to the Zeolite-Y Supported Ir(0) Nanoparticles (i.e., B Below) under H₂

$$A \xrightarrow{k_1} B \qquad n \operatorname{Ir}^{I} \xrightarrow{H_2} \operatorname{Ir}(0)_n$$
$$A + B \xrightarrow{k_2} 2B \qquad \operatorname{Ir}^{I} + \operatorname{Ir}(0)_n \xrightarrow{H_2} \operatorname{Ir}(0)_{n+1}$$

constants $k_1 = 0.081 \pm 0.002 \text{ h}^{-1}$ and $k_{2\text{corr}} = 22.8 \pm 0.5 \text{ M}^{-1} \text{ h}^{-1}$. The minimalistic nanoparticle formation kinetic scheme and the correspondent iridium/zeolite species are given in Scheme 3. The ability to follow in real time, even if indirectly, the formation of a supported heterogeneous catalyst in contact with solution is not trivial and of considerable interest by itself; hence such kinetics and mechanism of the formation of supported heterogeneous catalysts is being vigorously pursued in separate studies in our laboratories.³⁸

The catalytic activity of the zeolite supported iridium(0) nanoparticles is increased almost 2-fold to a TOF of 47 h⁻¹ (vs 25 h⁻¹ for the unsupported Ir(0)/dry-HCl catalyst system), while the TTO also increased some to 8600 TTOs over 232 h before deactivation (vs 5250 over 320 h for the unsupported Ir(0)/dry-HCl catalyst).

In a separate experiment, it was also shown that the vacuumdried gray powder form of the resultant Ir(0)/zeolite-Y exhibited 89% of its initial activity in a second run of benzene hydrogenation.

Conclusions

The primary findings of the present work are:

- (i) That the "weakly ligated/labile ligand" nanoparticle plus aggregates concept has been explored in benzene hydrogenation starting with a [(1,5-COD)IrCl]₂ that evolves under H₂ to a Ir(0)/dry-HCl system that is quite active for the 100% reduction of neat benzene to cyclohexane at 22 \pm 0.1 °C and 40 \pm 1 psig (~2.7 atm) of initial H₂ pressure;
- (ii) That the CS₂-active site corrected, per Ir(0) benzene hydrogenation catalytic activity (TOF) and lifetime (TTOs) are at the high end of what has been observed at room temperature and mild pressures in comparison to the prior literature, $25 \le \text{TOF} \le 1250 \text{ h}^{-1}$ and $5250 \le \text{TTO} \le 262500$;
- (iii) That the 10-fold higher activity of the [(1,5-COD)-IrCl]₂ plus H₂ system compared to Ir black/no-HCl catalyst is due to the 10-fold higher dispersion of the in situ formed Ir(0)/HCl catalyst. The number of active sites in this more highly dispersed catalyst is still just 0.02 equiv (2%) out of the total Ir present (and if one uses a 1:1 CS₂:Ir stoichiometry for the poisoning; the real number of active sites is possibly \geq 7 fold higher³¹);
- (iv) That, significantly, what one can properly call weakly ligated/labile ligand Ir(0) nanoparticles and aggregates have been made in situ as demonstrated by the fact that they have identical, per exposed Ir(0)activity within experimental error to Ir(0) black and that they have no possible ligands other than those desired for the catalysis plus the at best poor ligand HCl. Further consistent with the weakly ligated/ labile ligand nanoparticle concept is that the iridium complexes [(1,5-COD)Ir(CH₃CN)₂]BF₄ and [(1,5-COD)Ir(CH₃CN)₂]PF₆, employed as precatalysts under otherwise identical conditions yield negligible benzene hydrogenation activity compared to the Cl⁻ containing, [(1,5-COD)IrCl]₂ precatalyst. The implication is that BF_4^- and PF_6^- prefer the Ir(0) surface rather than H^+ , where as $Cl^$ prefers H^+ leading to a more active Ir(0) catalyst. That is, Cl^- is a preferred ligand over BF_4^- and PF_6^{-} in the presence of H⁺ for at least the present weakly ligated/labile ligand nanoparticle and aggregates catalysts.
- (v) That even 0.02 equiv of Cl⁻ (Cl⁻ formed from the HCl plus Proton Sponge to give Proton Sponge• H⁺Cl⁻) poisons the room temperature benzene hydrogenation catalysis by the weakly ligated/labile ligand nanoparticles and their aggregates. Restated, H⁺ is a key component of the present, weakly ligated/ labile ligand nanoparticle plus aggregates system.
- (vi) That the weakness of the weakly ligated/labile ligand nanoparticles, however, is their expected poor stabilization due to the lack of stabilizing ligands. Hence, aggregation and the formation of bulk metal yields only 60% of the initial activity in a second cycle of benzene hydrogenation.
- (vii) That one can, however, generate the Ir(0)/dry-HCl catalyst in situ from supported [(1,5-COD)IrCl]₂ on zeolite-Y. The resultant Ir(0) nanoparticles are more stable and exhibit modest improvements in the catalyst activity (2-fold increase) and

⁽³⁷⁾ Boudart, M. Chem. Rev. 1995, 95, 661.

^{(38) (}a) Mondloch, J. E.; Yan, X.; Finke, R. G. *J. Am. Chem. Soc.* **2009**, *131*, 6389. (b) Mondloch, J. E.; Wang, Q.; Frenkel, A. I.; Finke, R. G. Development Plus Kinetic and Mechanistic Studies of a Prototype Supported-Nanoparticle Heterogeneous Catalyst Formation System in Contact with Solution: Ir(1,5-COD)Cl/ γ -Al₂O₃ and Its Reduction by H₂ to Ir(0)_n/ γ -Al₂O₃. *J. Am. Chem. Soc.*, **2010**, in press.

lifetime (1.6 fold increase) under otherwise identical conditions.

- (viii) That both Ir(0)/dry-HCl and Ir(0)/zeolite-Y catalyst systems are also relatively "green" in that they satisfy 9 out of 12 proposed principles of green chemistry.²¹ The Ir(0)/zeolite-Y heterogeneous catalyst is of course isolable, bottleable and reusable as is the case with other supported-nanoparticle heterogeneous catalysts, and finally
- (ix) That Proton Sponge•H⁺Cl⁻ poisons room temperature benzene, but not cyclohexene, catalysis is of interest and implies either a different requirement for H⁺ in these two, otherwise ostensibly related, types of hydrogenation reactions or, possibly, different active sites for these two hydrogenations.

This paper is our third exploring the weakly ligated/labile ligand nanoparticle catalysts hypothesis.^{3,11} Additional studies

of this hypothesis are in progress and will be reported in due course. 7,38

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Supporting Information Available: Literature table of 17 studies reporting the complete hydrogenation of benzene under room temperature conditions and mild pressures (≤ 25 °C and ≤ 10 atm H₂ pressure) and attempted fits of the kinetic data in Figure 1 to either a 2- or 4-step mechanism of nanoparticle and agglomerated nanoparticle formation, plus brief discussion of the results. This material is available free of charge via the Internet at http://pubs.acs. org.