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Rh(0) Nanoclusters in Benzene Hydrogenation Catalysis: Kinetic and Mechanistic Evidence that a Putative $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$ Ion-Pair Catalyst Is Actually a Distribution of Cl^- and $[(C_8H_{17})_3NCH_3]^+$ Stabilized Rh(0) Nanoclusters

Katherine S. Weddle, John D. Aiken III, and Richard G. Finke*

Contribution from the Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523

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Abstract: A reinvestigation is reported of a prototype literature arene hydrogenation system, one previously believed to involve a $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$ ion-pair catalyst. The methodology employed to uncover the true catalyst, and to deal with the classic and difficult mechanistic problem of “is it homogeneous or heterogeneous catalysis?”, is the four-step mechanistic approach developed previously in our laboratories. The data obtained (i) provide unequivocal TEM evidence that Rh(0) nanoclusters are formed under the reaction conditions and (ii) provide kinetic evidence that the benzene catalytic hydrogenation reaction follows the nucleation ($A \rightarrow B$) and then autocatalytic surface-growth ($A + B \rightarrow 2B$) mechanism elucidated recently for metal(0) nanocluster growth. These latter results require that “A” (i.e., $[RhCl_4]^-$) is *not* the catalyst to within the error limits (5−15%) of the fits of the data to the autocatalytic surface-growth mechanism; the kinetic results also provide some of the strongest possible evidence that “B” is the true catalyst, “B” being the Rh(0) nanoclusters. In addition, (iii) H/D exchange and (iv) Hg(0) poisoning data confirm that the Rh(0) nanoclusters are the only active catalysts since added Hg(0) poisons the arene hydrogenation completely. The results reported herein are of fundamental significance in five ways: (i) they are only the second use each of two new and powerful methodologies that were required for the success of the studies reported, the (a) more general 4-step methodology for testing “is it homogeneous or heterogeneous catalysis”, and (b) the pseudoelementary, catalytic reporter methodology for following the nanocluster growth kinetics. In addition, (ii) they correct the claim that $[RhCl_4]^-$ is a benzene hydrogenation catalyst, and identify soluble Rh(0) nanoclusters as the true catalyst; (iii) they call into question *all* previous claims of *benzene* hydrogenation—but not anthracene or naphthalene arene hydrogenation—by monometallic precatalysts; and (iv) they re-emphasize that, prior to any claim of a homogeneous catalyst in a reaction (such as arene hydrogenation) where a facile heterogeneous M(0) catalyst is well established, one must first rule out catalysis by even trace amounts of possibly highly active nanocluster catalysts (e.g., by using the methods utilized herein and any other applicable method). Overall, the studies presented herein (v) provide a definitive answer, at least for the specific Rh system studied, to the 34-year-old question, one controversial for the past 17 years, of “is benzene hydrogenation homogeneous or heterogeneous?”.

Introduction

Selective arene hydrogenation[1] of, for example, benzene to cyclohexene[2] is a topic of considerable fundamental as well as commercial interest.[2o,p] One major impediment in this area is the lack of a well-defined, robust, and reproducible system that is also soluble, especially one in which the catalyst is also unequivocally identified. Such properties and information would, in turn, allow detailed catalyst composition and structure determination, plus kinetic, spectroscopic, and other mechanistic studies. Such key insights could then be employed to help in the rational design of better, more selective arene hydrogenation catalysts.

Exciting both in the above context, and for hybrid homogeneous/heterogeneous catalysis in general, is the realization that a few transition metal nanocluster systems have recently been found to be stable enough that they can behave as isolable and compositionally well-defined “soluble heterogeneous catalysts”—a little precedented situation[3] with exciting if not unparalleled possibilities for anyone interested in heterogeneous catalysis and in the rational development of mechanism-based, nanocluster catalysts. Such soluble analogues of heterogeneous catalysts are new enough, however, that isolable, high catalytic activity examples—ones proven to undergo tens of thousands of total turnovers of even less demanding reactions, such as olefin hydrogenation, in solution and without catalyst agglomeration into bulk metal—are presently restricted to one example.[3] That system is $[P_2W_{15}Nb_3O_{62}]^{9-}$ polyoxoanion- and $[Bu_4N^+]$-

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* E-mail: rfinke@lamar.colostate.edu.

(1) A literature search (Chemical Abstracts Service; CA file) of benzene(w)hydrogenation reveals 974 references, including 231 patents, while a literature search of selective(w)benzene(w)hydrogenation reveals only 50 references (an incomplete search, since we already have in our files more than 50 papers concerned with selectivity in benzene hydrogenation). Lead references follow: (a) Struijk, J.; d’Angremond, M.; Lucas-de Regt, W. J. M.; Scholten, J. J. F. *Appl. Catal. A: General* **1992**, *83*, 263. (b) Struijk, J.; Moene, R.; van der Kamp, T.; Scholten, J. J. F., *Appl. Catal. A: General* **1992**, *89*, 77. (c) Struijk, J.; Scholten, J. J. F. *Appl. Catal. A: General* **1992**, *82*, 277. (d) Odenbrand, C. U. I.; Lundin, S. T. *J. Chem. Technol. Biotechnol.* **1980**, *30*, 677. (e) Struijk, J.; Scholten, J. J. F. *Appl. Catal.* **1990**, *62*, 151. (f) Van der Steen, P. J.; Scholten, J. J. F. *Appl. Catal.* **1990**, *58*, 291. (g) Odenbrand, C. U. I.; Andersson, S. L. T. *J. Chem. Technol. Biotechnol.* **1982**, *32*, 691 (h) Don, J. A.; Scholten, J. J. F. *Faraday Discuss., Chem. Soc.* **1982**, *72*, 145. (i) Odenbrand, C. U. I.; Lundin, S. T. *J. Chem. Technol. Biotechnol.* **1981**, *31*, 660.

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stabilized $Ir(0)_{\sim 300}$ nanoclusters,[3,4] a system proven to undergo ≥18 000 turnovers of catalytic hydrogenation in solution.[11] Fundamental studies of nanocluster mechanisms of formation,[5] stabilization by polyoxoanions, by other anions,[6a] by various R_4N^+ cations,[6b] and by different solvents,[7] as well as the synthesis and characterization of other examples of polyoxoanion-stabilized nanoclusters (Rh_{xx}, Pd_{yy}, Pt_{zz}), are in progress and will be reported in due course. An overall goal of such studies is the development, application, and full kinetic and mechanistic understanding of nanocluster "soluble heterogeneous catalysts".[8]

Benzene hydrogenation is well established using traditional, oxide-supported metal particle heterogeneous catalysts.[1,2] Given this, and given that selective hydrogenation of benzene to cyclohexene is an important commercial goal, we reasoned that a perusal of the literature of benzene hydrogenations[1,2] was likely to reveal systems undergoing arene hydrogenation and claimed to be a monometallic, "homogeneous catalyst", but where the true catalyst could instead be the transition-metal nanoclusters formed from the monometallic *catalyst precursors.* Our key initial goal was to identify a prototype benzene hydrogenation system that we could, then, compare to our own efforts to develop polyoxoanion-stabilized Rh(0), Ru(0), and other nanocluster benzene hydrogenation catalysts.

Several systems arose from our literature search as possible—but undemonstrated and thus previously unrecognized—nanocluster benzene (or other substrate) hydrogenation catalysts.[9] The insightful review and analysis of reported benzene and other arene hydrogenation "homogeneous" catalysts in a chapter written by Collman available elsewhere[9a] is recommended as a first source of critically analyzed literature in this area. Note especially Collman's admonitions: (a) that the only kinetically demonstrated homogeneous arene hydrogenation catalysts are for the more easily reduced *polycyclic aromatics* (e.g., anthracene or naphthalene), but not from monocyclics such as benzene; (b) that these kinetically documented anthracene or naphthalene homogeneous catalysis systems do not, however, reduce benzene under conditions where they remain undecomposed and homogeneous; (c) that "a major question concerning these monocyclic arene hydrogenation catalysts is whether the active catalysts are metal "sols" in the 10−40 Å size range";[9a] and (d) that, "Previously we saw how difficult it is to determine the actual catalytically active species—even with well-defined homogeneous olefin hydrogenation catalysts. In the instance of monocyclic arene hydrogenation catalysts, this is more difficult".[9a] Of historical interest here is that the lore of catalysis once held that the observation of benzene reduction could be used as a *test* for heterogeneous catalysis—that is, that only heterogeneous catalysts could hydrogenate benzene. In one sense, then, this paper returns to attempt a more strenuous test of that issue. Note also that the first report of a "homogeneous" monocyclic arene (*o*-xylene) hydrogenation catalyst was in 1963 [Ni^{II}(2-ethylhexanoate) + Et_3Al; see ref 29 in Table 10.2 elsewhere[9a]], and that the first paper presenting a test for the "is it homogeneous or heterogeneous catalysis" question was Maitlis' 1990 paper (ref 55 cited elsewhere[9a]). The present paper returns, then, to this between 17- and 34-year-old issue and attempts to answer it definitively in the case of benzene hydrogenation and for the $RhCl_4^-$ precatalyst discussed below.

After a careful survey of the benzene and other arene hydrogenation literature, both of the claimed benzene homogeneous hydrogenation catalysts and also of the established heterogeneous catalysts, we chose to study a prototype literature benzene hydrogenation system (hereafter, the "literature system") shown in Scheme 1.[9c] This system is partially based on an earlier, important paper by a second group:[10]

Several features of the literature system[9c] caught our eye and are highly suggestive of the presence of stabilized nanocluster catalysts, at least in hindsight and with the advantage of recent

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(2) (a) The selective hydrogenation of benzene to cyclohexene is of synthetic and industrial interest[2b−l] since cyclohexene is a useful intermediate material in the synthesis of commercially important products,[2m] such as adipic acid.[2n,o] (b) Mitsui, O.; Fukuoka, Y. U.S. Patent 4,678,861, 1987, to Asahi Kasei Kogyo Kabushiki Kaisha. (c) Niwa, S.; Mizukami, F.; Kuno, M.; Takeshita, K.; Nakamura, H.; Tsuchiya, T.; Shimizu, K.; Imamura, J. *J. Mol. Catal*. **1986**, *34*, 247. (d) Niwa, S.; Mizukami, F.; Isoyama, S.; Tsuchiya, T.; Shimizu, K.; Imai, S.; Imamura, J. *J. Chem. Technol. Biotechnol*. **1986**, *36*, 236. (e) Ichihashi, H.; Yoshioka, H. U.S. Patent 4,575,572, 1986, to Sumitomo Chemical Company. (f) Niwa, S.; Immamura, J.; Mizukami, F.; Shimizu, K.; Orito, Y. U.S. Patent 4,495,373, 1985 to Director-General of the agency of Industrial Science and Technology. (g) Hideyuki, A.; Akio, K. U.S. Patent 4,197,415, 1980 to Toray Industries, Inc. (h) See ref 1c. (i) Drinkard, W. C. Patent 1,381,48, 1975 to du Pont de Nemours and Co. (j) Drinkard, W. C. U.S. Patent 3,767,720, 1973 to du Pont de Nemours and Co. (k) Hartog, F. Patent 1,094,911, 1965, to Stamicarbon N. V. (l) See ref 1g. (m) Hartog, F. U.S. Patent 3,391,206, 1968, to Stamicarbon N. V. (n) Nagahara, H.; Konishi, M. EP Patent 0220525, 1987, to Asahi Kasei Kogyo Kabushiki Kaisha. (o) G. W. Parshall notes: "The hydrogenation of benzene to cyclohexene has been a major target of industrial research because the oxidation of cyclohexene to adipic acid may proceed more cleanly than the current cyclohexane oxidation." Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, John Wiley & Sons: New York, 1992; pp 180−183. (p) We note that a plant for commercial, selective hydrogenation of benzene to cyclohexene was brought on line by Asahi in 1990: *Chem. Eng.* **1990**, *97(10)*, 25.

(3) Aiken, J. D., III; Lin, Y.; Finke, R. G. *J. Mol. Catal*. **1996**, *114*, 29.

(4) Yin, L.; Finke, R. G. *J. Am. Chem. Soc*. **1994**, *116*, 8335.

(5) (a) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382. (b) Watzky, M. A.; Aiken, J. D., III, Widegren, J.; Finke, R. G. *Chem. Mater*. Submitted ("A New Kinetic Method to Follow Transition-Metal Nanocluster Formation Based on Catalytic Activity and the Pseudoelementary Step Concept").

(6) (a) Aiken, J. D., III; Finke, R. G. Experiments in progress. (b) Aiken, J. D., III; Finke, R. G. Experiments in progress. (c) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.*, in press (Nanocluster Formation Synthetic, Kinetic and Mechanistic Studies. The Detection of, and Then Methods to Avoid, Hydrogen Mass-Transfer Limitations in the Synthesis of Polyoxoanion- and Tetrabutylammonium- Stabilized 40 ± 6 Å $Rh(0)_{\sim 1500}$ to $Rh(0)_{\sim 3700}$ Nanoclusters).

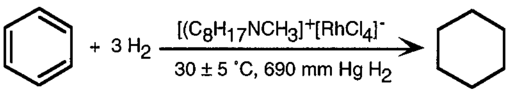
(7) Aiken, J. D., III; Finke, R. G. Unpublished results.

(8) (a) However, it should be noted that other nanoclusters, such as the $Rh_{\sim 55}$ catalysts studied by Schmid[8b] were found of insufficient stability in solution to be able to catalyze even >10 turnovers of hydroformylation. Indeed, it is often stated that nanoclusters are insufficiently stable in solution to be able to support catalysis without aggregation to bulk metal or without supporting them on a solid-oxide support.[8c] (b) Schmid, G. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer: The Netherlands, 1990; Vol 7, p 31. (c) Schmid, G.; Maihack, V.; Lantermann, F.; Peschel, S. *J. Chem. Soc., Dalton Trans.* **1996**, 589.

(9) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. See pp 549−556, and Table 10.2, systems A−J and refs 29−38 therein, a section written by Professor Collman (who conducted research for several years in the "is it homogeneous or heterogeneous catalysis" area and specifically studying arene hydrogenation catalysts). (b) Jones, R. A.; Seeberger, M. H. *J. Chem. Soc., Chem. Commun*. **1985**, 373. Note the induction periods and dark catalyst colors described therein. (c) Blum, J.; Amer, I.; Vollhardt, K. P. C.; Schwarz, H.; Hohne, G. *J. Org. Chem*. **1987**, *52*, 2804. (d) We also found a couple of other systems[9e,f] that are ostensibly homogeneous Rh olefin or Ru aldehyde hydrogenation catalysts, but where it might be an interesting and rigorous test (perhaps of the method itself[11]), to see if these systems are actually homogeneous. (e) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1987**, *109*, 174. Note the effort by the authors to probe the "is it homogeneous or heterogeneous" catalysis question by the methods available at that time [e.g., their ^{31}P NMR (e.g., ≥ca. 90% catalyst recovery), ≥90% rate still after 18 catalyst recycles, Table 1), and use of Collman's three-phase test]. (f) Fache, E.; Senocq, F.; Santini, C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1990**, 1776. Note that this interesting water-soluble system shows little evidence for a nanocluster catalyst, save the induction period in Figure 1 therein, or the fact that the I^- effect seen could *possibly* be explained by I^- stabilization of Ru nanoclusters. As such, it would be of some interest to check the catalyst in this study too by especially the TEM method detailed elsewhere[11]—not an inappropriate suggestion, since one does not prove a mechanism, but only disproves alternative mechanisms.

Scheme 1. Summary of the Literature System[9c] under Study, Including Key Experimental Observations

The Literature System:[9c]



Selected, Key Observations from the Literature System:[a]

1. Formation of small dark particles which are soluble in hot DMSO or DMF. Precipitation is eliminated upon addition of trioctylamine.
2. Solid particles separated from reaction solutions were claimed to be inactive, whereas the filtrates showed the same rate as before filtration.
3. Characteristic induction periods for each substrate studied which disppear upon pretreatment of the $RhCl_4^-$ precatalyst with H_2.
4. d_3 - d_{12} deuterium incorporation into cyclohexane.
5. Up to a maximum of 86 total turnovers[32] observed.

[a] A careful reading of the paper these data were taken from[9c] led to a list of ca. 35 experimental observations bearing upon the nature of the system, its true catalyst, and other relevant issues. Hence, the above list is, as its title notes, *only selected, key observations*.

literature (vide infra).[11] These features are (i) the induction periods seen; (ii) the shortening or complete removal of the induction periods by pretreatment with H_2 (or H_2 plus arene substrate); (iii) the observation of "small amounts of dark particles (which dissolved in hot DMF or DMSO)"[9c] if both H_2 and arene substrate are present [this solubility property is characteristic of R_4N^+ X^- ($X^- = Cl^-$, Br^-) stabilized nanoclusters[12]]; and (iv) the "metallic rhodium" observed if the $[(C_8H_{17})_3NCH_3]^+$ $[RhCl_4]^-$ ion-pair precatalyst is prereduced with H_2 only (i.e., without arene present). Worth emphasizing here are two key points. The first is the correct logic of the observation of metallic Rh from a mononuclear precursor; this demands that Rh nanoclusters *must have been present in solution*, since there is no other way known, at least presently—nor is their any other easily imaginable way—to go from a *single metal* reactant to the *multi-metallic product* except via smaller metal(0) nanoclusters. The significance of this observation and its proper interpretation was not pointed out until 1994,[11] and is still under appreciated—but is a powerful way in and of itself to find literature systems claimed to be homogeneous, but which are strong candidates for nanoclusters as the true catalysts.

Second, any claim for a homogeneous catalyst, in a reaction where a very facile heterogeneous catalyst for that same reaction is well known, must consider and rule out any participation by even a trace amount of a possibly highly active nanocluster catalyst formed under the reaction conditions. This is first and foremost simply the scientific method restated—science is an exclusion process and thus is about disproof of all alternative hypotheses. Also noteworthy here is that Collman made this exact same point (about the possible contribution of trace amounts of highly active "sols") more than a decade ago and specifically for benzene hydrogenation.[9a] The new point here, then, is that we can now sharpen and amplify this key alternative hypothesis for claimed benzene (and possibly other) homogeneous catalysts in light of the rapidly evolving literature of nanocluster ("sol") catalysts, a literature that was largely unavailable even 5 years ago. The fundamental point to be appreciated here is that very high rates are possible for very small, high surface area, and thermodynamically higher energy and thus kinetically highly reactive nanoclusters (vs bulk metal, which is ca. 138 kcal/mol downhill vs the limit of a single unsolvated Rh(0) atom[13f]). This means that, even cases where, say, >99% of a homogeneous (pre)catalyst can be recovered from a catalytic reaction, the true catalyst may still be a highly active nanocluster formed from ≤1% of the precatalyst under the reaction conditions, and in this hypothetical example.

This brings us to one more important, but historically misinterpreted, property, that of the "highly reproducible" kinetic behavior seen, at least for prefiltered solutions,[9c] a property historically interpreted as compelling evidence that the true catalyst must be a discrete, generally monometallic, *homogeneous* catalyst. *This is a myth*; one that has now been disproved.[3,4] In fact, such ±≤15% reproducibility is another hallmark of nanocluster catalysts made under the hydrogen autocatalytic growth, narrow-size-distribution-producing, nanocluster formation mechanism that has been recently elucidated.[5] The observed effects of H_2O,[11] oxygen,[13] or common PR_3 impurities such as $O{=}PR_3$[14] are also understandable in terms of a nanocluster-based catalyst and the Rh nanocluster literature;[15] even the long-chain tertiary amine stabilization seen with the literature arene hydrogenation catalyst[9c] reexamined herein has good precedent within the nanocluster literature.[15a]

In short, then, a critical reanalysis of the literature system,[9c] in light of recent advances in the nanocluster literature[3−5] and

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[10] (a) Januszklewicz, K. R.; Alper, H. *Organometallics*, **1983**, *2*, 1055. (b) Note that these authors were aware that the actual catalyst had not been identified, specifically stating on p 1056 of their paper that, "Finally, we are not certain whether the phase-transfer process described herein involves a soluble or insoluble rhodium catalyst".

[11] Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891, and refs 16−27 therein to the earlier work of Maitlis, Whitesides, Laine, Crabtree, Collman, Lewis and Lewis, and others on the research problem "is it homogeneous or heterogeneous catalysis?".

[12] (a) Reetz, M. T.; Helbig, W.; Quaiser, S. A.; Stimming, U.; Breuer, N.; Vogel, R. *Science* **1995**, *267*, 367. (b) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Fretze, R.; Joussen, T.; Köpper, R.; Korall, B.; Neiteler, P.; Richter, J. *J. Mol. Catal.* **1994**, *86*, 129. (c) Bönnemann, H.; Brinkmann, R.; Neiteler, P. *Appl. Organomet. Chem.* **1994**, *8*, 361. (d) Reetz, M. T.; Helbig, W. *J. Am. Chem. Soc.* **1994**, *116*, 7401. (e) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Joussen, T.; Korall, B. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1312.

[13] (a) Reetz, M. T.; Quasier, S. A.; Winter, M.; Becker, J. A.; Schäfer, R.; Stimming, U.; Marmann, A.; Vogel, R.; Konno, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2092. (b) Kolb, U.; Quaiser, S. A.; Winter, M.; Reetz, M. T. *Chem. Mater.* **1996**, *8*, 1889. (c) Rothe, J.; Pollmann, J.; Franke, R.; Hormes, J.; Bönnemann, H.; Brijoux, W.; Siepen, K.; Richter, J. *Fresenius J. Anal. Chem.* **1996**, *355*, 372. (d) Harada, M.; Asakura, K.; Ueki, Y.; Toshima, N. *J. Phys. Chem.* **1992**, *96*, 9730. (e) Kiwi, J. *Isr. J. Chem.* **1979**, *18*, 369. (f) The ΔH(vaporization) for bulk $Rh(0)_n$ metal going to n Rh(0) atoms is 138 kcal/mol. For further discussion of the relationship of this to the intrinsic stability of different size nanoclusters, see elsewhere.[4−6,11]

[14] (a) A careful reading of the paper[9c] reexamined herein reveals that $O{=}PR_3$ is a likely culprit in the reported need[9c] to triply sublime $P(OMe)_3$ to make Mutterties' Co-based arene hydrogenation catalyst reproducible. (b) Schmid, G.; Maihack, V.; Lantermann, F.; Peschel, S. *J. Chem. Soc., Dalton Trans.* **1996**, 589. See the mention of $O{=}PPh_3$ formation on p 590. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, **1987**; pp 255, 264, 340, 365, 649.

[15] Other Rh nanoclusters: (a) Yonezawa, T.; Tominaga, T.; Richard, D. *J. Chem. Soc., Dalton Trans.* **1996**, 783. (b) Larpent, C. Brisse-Le Menn, F.; Patin, H. *New J. Chem.* **1991**, *15*, 361. This Rh nanocluster also shows facile H/D exchange with olefins and H_2 (D_2)/D_2O (H_2O). (c) Larpent, C.; Patin, H. *J. Mol Catal.* **1990**, *61*, 65. Noteworthy is that the Rh nanocluster shows H/D exchange with H_2/D_2O (or, alternatively, with D_2/H_2O). (d) See ref 6c. (e) Aiken, J. D., III; Finke, R. G. Polyoxoanion- and Tetrabutylammonium-Stabilized Near Monodisperse, 40 ± 6 Å $Rh(0)_{\sim 2400}$ Nanoclusters: Synthesis, Characterization and Hydrogenation Catalysis, submitted. (f) Edlund, D. J. Ph.D. Thesis, University of Oregon, 1987.

a knowledge that the modern methods to rule out nanocluster catalysis were not available previously, provides highly suggestive, *albeit not yet definitive*, evidence that Rh(0) nanoclusters may well be the true catalysts in the literature arene hydrogenation catalyst beginning with the $[(C_8H_{17})_3NCH_3]^+$ $[RhCl_4]^-$ ion-pair precatalyst.

Herein we report the following results: (i) demonstration by catalyst isolation and TEM that $[(C_8H_{17})_3NCH_3]^+$ $[RhCl_4]^-$ is a precatalyst, “A”, one converted under the reaction conditions to a polydisperse distribution of Rh(0) nanoclusters; (ii) demonstration that the isolated Rh(0) nanoclusters are kinetically competent catalysts;[16] (iii) demonstration that the benzene hydrogenation reaction follows the nucleation ($A \rightarrow B$) then autocatalytic surface growth ($A + B \rightarrow 2B$) mechanism for nanocluster growth that we recently reported elsewhere, results that require that A (i.e., $RhCl_4^-$) is not the catalyst to within the 5−15% error limits of the fits to the kinetic data; and (iv) demonstration that isolated Rh(0) nanoclusters hydrogenate benzene with D_2 to yield very similar H/D incorporation patterns to those seen when one begins with the $[(C_8H_{17})_3NCH_3]^+$ $[RhCl_4]^-$ precatalyst (and also H/D incorporation very similar to that previously reported in the literature), “fingerprint” results which argue strongly that all three reactions employ the same catalyst. We also (v) find that the catalyst becomes completely inactive when treated with Hg, the expected results for a Rh(0) metal nanocluster catalyst. In short, we present very strong if not compelling evidence that the true catalyst is the distribution of $[(C_8H_{17})_3NCH_3]^+$ and Cl^- stabilized Rh(0) nanoclusters which are formed under H_2 and the other, benzene hydrogenation reaction conditions.

We wish to emphasize up-front that the authors of the literature system reexamined herein were *well aware of*, and tested for, the question of “is it homogeneous or heterogeneous catalysis?”.[9c] They just did not have the advantages we now have of a 1998 knowledge of nanoclusters or the advantage of a new methodology for this “homogeneous or heterogeneous catalysis problem”, one developed and thus intrinsically tested on a nanocluster catalyst.[11] Stated another way, the paper describing the literature system reinvestigated herein is an important paper, literally a “treasure trove” of experimental data on arene hydrogenation.[9c] Hence, in no way do the studies which follow diminish the value of the earlier, original work which was focused toward the synthetic organic applications of the ion-pair precatalyst, $[(C_8H_{17})_3NCH_3]^+$ $[RhCl_4]^-$.

Results and Discussion

Methodology Employed to Address the Question “Is It Homogeneous or Heterogeneous Catalysis?”. First, we need to remind the reader of the four main components of the methodology used herein to address the central question “is it homogeneous or heterogeneous catalysis?” The methodology is that which we developed in 1994;[11] it is an improved, more general methodology especially for testing for nanocluster catalysis in that it was developed, and thereby intrinsically tested, on what proved in the end to be a previously unidentified, high activity and catalytically long-lived[3] $Ir(0)_{\sim 300}$ nanocluster catalyst. The four key steps to this method are shown in Figure 1: (i) catalyst isolation and then characterization by transmission electron microscopy (TEM); (ii) kinetic studies testing the kinetic competence or noncompetence of the isolated catalyst (e.g., of any nanoclusters identified by TEM); (iii) quantitative phenomenological tests (such as the classic Hg poisoning test known to poison “heterogeneous” M(0) transition metal catalysts); and (iv) then additional mechanistic studies as needed, for example, in the present case of arene hydrogenation linking the observed selectivities for H/D incorporation or exchange to those independently observed for the isolated nanoclusters. That is, a final but crucial step of the new approach to answering the question “is it homogeneous or heterogeneous catalysis?” is the strict adherence to the principle that the correct mechanism and true catalysts will explain all of the data. A more complete figure, showing the actual 12 specific experiments performed in the four subcategories in Figure 1, is available as Figure 5 elsewhere.[11] Of note is that the present study is just the second use of the methodology in Figure 1 to uncover otherwise hidden nanocluster catalysts, and the first time that the Figure 1 methodology has been combined with a new kinetic method for following nanocluster growth kinetics.[5a]

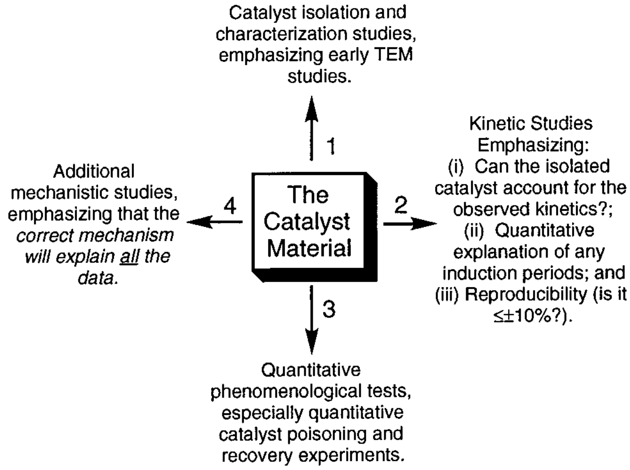

Figure 1. A more general approach to distinguishing between a “heterogeneous” colloid-nanocluster catalyst and a discrete, homogeneous catalyst as developed elsewhere.[11]

Benzene Hydrogenation. Hydrogenation Apparatus and “Standard Conditions”. The hydrogenation of benzene was carried out using the two sets of conditions originally described in the literature[9c] as Method A and Method B. Methods A and B differ in that A is performed using a biphasic dichloroethane/H_2O solution whereas B is done in a monophasic THF solution. The two methods were both carried out using a set of standard conditions which include $RhCl_3{\cdot}3H_2O$, trioctylamine, Aliquat 336 (i.e., $[(C_8H_{17})_3NCH_3]^+Cl^-$), benzene, and H_2O at 31 ± 1 °C and under 687 ± 7 Torr hydrogen. The reaction was followed via GLC to monitor the loss of benzene. The hydrogenation apparatus used herein (Figure A, Supporting Information) consists of a 25 mL side-armed Schlenk flask and two hydrogen reservoirs (500 mL side-armed round-bottomed, and a 100-mL round-bottomed flask) connected to a standard Schlenk line equipped with a Hg manometer. Not surprisingly, we found Method B to be easier to work with because of the homogeneous nature of the reaction solution. But, as needed to reinvestigate the reported system,[9c] we have reexamined *both* of the reported methods, A and B.

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[16] The literature system does not explain how the rates were determined, nor does it define the term “rate”. (The failure to define “rate” in terms of a specific differential equation that refers to a specific reaction is one of the most common, yet most easily preventable, mistakes in reporting kinetic data.) We were unable to calculate the cited maximum rate (p 2805, column 1, line 62, $k = (3.51 \pm 0.15) \times 10^{-3}$ mmol L^{-1} min^{-1}) given the data. Using data taken from the benzene conversion graph (p 2805, Figure 1) we calculated $k = 3.98$ mmol L^{-1} min^{-1} from a first-order plot (as the literature study describes their system as following first-order kinetics). We found that the data had a better fit to an autocatalytic growth curve, Figure 4, and expect, therefore, that the rate reported in the literature study has no rigorous meaning because the data were fit to the wrong mechanism.

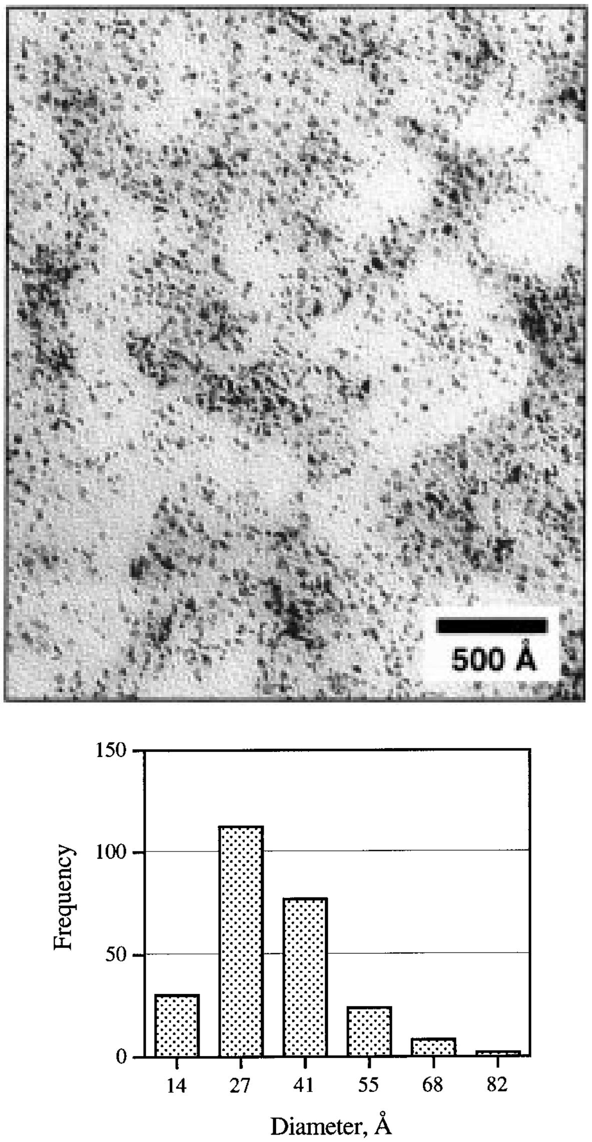

Figure 2. (a) Top: TEM *after reuse* of isolated Rh(0) nanoclusters (prepared from the monophasic reaction of $RhCl_3{\cdot}3H_2O$ with H_2 in the presence of THF/Aliquat 336/H_2O/trioctylamine/benzene). (b) Bottom: Histogram of the Rh(0) nanocluster diameters. The mean diameter is 34 Å, with a standard deviation of 13 Å, from a sample population of 252.

Our two earlier publications on the use of pseudo-elementary catalytic reporter reactions (benzene hydrogenation in the present case) to follow nanocluster growth will allow the reader to readily understand how we can (i) follow benzene hydrogenation but (ii) still learn about the kinetics of nanocluster formation; otherwise, this point will probably be obscure.[5]

Catalyst Isolation and Characterization. (1) Formation and Isolation of Rh(0) Nanoclusters from $RhCl_4^-$. The hydrogenation reaction was allowed to run ca. 4 h using the standard conditions established in the literature[9c] for each method (see the Experimental Section). The reaction flask was removed from the hydrogenation apparatus and taken back into a Vacuum Atmospheres drybox where it was evacuated to dryness overnight to yield a black solid.

(2) Catalyst Characterization by TEM. To obtain TEM images, a small amount of the isolated black solid was dissolved in DMSO. The TEMs taken of isolated and then reused Rh(0) nanoclusters from benzene hydrogenations in dichloroethane (Figure D, Supporting Information) and THF (Figure 2) *both* show the presence of somewhat polydisperse, irregular-shaped Rh(0) nanoclusters. Restated, TEMs confirm that *Rh(0) nanoclusters are indeed formed* from $RhCl_4^-$ in this system. The clusters made in dichloroethane are 48 ± 18 Å, whereas the clusters made in THF are 34 ± 13 Å, that is, of ca. ±40% size dispersion. These values correspond to the range of $Rh_{\sim 1000}$ (30 Å) to $Rh_{\sim 11000}$ (66 Å) in dichloroethane, and the range $Rh_{\sim 350}$ (21 Å) to $Rh_{\sim 3900}$ (47 Å) in THF[17]—an order of magnitude spread in the number of Rh(0) atoms in the smallest to the largest nanoclusters.

Kinetic Evidence That $RhCl_4^-$ Is Not the Active Catalyst, but That Rh(0) Nanoclusters Are the True Catalysts. Four key experimental observations provide very strong evidence that the observed Rh(0) nanoclusters are the true catalysts in the literature system. First, a hydrogenation performed in THF using $RhCl_3{\cdot}3H_2O$ as the precatalyst began only after an ca. 20−30 min induction period, Figure 3a. At the end of this period, the color of the reaction solution changed from clear orange-red to an opaque, deep red/black. Such changes in color are indicative of the formation of soluble metal particles.[18] Second, hydrogenations performed using isolated Rh(0) nanoclusters proceed immediately with no observable induction periods, Figure 3b.

Third, and most significantly, essentially all the kinetic curves observed that start with $[RhCl_4^-]$, including a kinetic reanalysis of the data reported in Figure 1 of the literature study[9c] (vide infra, Figure 4), reveal induction periods plus a sigmoidal-shaped curve that can be quantitatively curve fit, to within ±5−15% error bars, to the nucleation ($A \rightarrow B$; rate constant, k_1) then autocatalytic surface-growth ($A + B \rightarrow 2B$; rate constant, k_2) mechanism elucidated recently. Note that such a fit is the *kinetic signature* for nanocluster formation from monometallic precursors (A) and using H_2 as the reductant.[5] Specifically, Figure 3a shows the excellent curve fit according to this mechanism for a reaction beginning with $[RhCl_4^-]$. Note that in Figure 3b, in which the isolated Rh(0) nanoclusters are employed as the catalyst, *no induction period is seen* and the sigmoidal-shaped curve has been replaced by the expected exponential decay curve. Fourth, Figure 4 reveals that the kinetic data taken directly out of the literature study[9c] (and which began with $[RhCl_4^-]$ in dichloroethane/H_2O) reveals an induction period (which was previously reported as a general observation)[9c] and a sigmoidally shaped kinetic curve. This kinetic curve is also closely fit by the $A \rightarrow B$, then $A + B \rightarrow 2B$ nucleation plus autocatalytic surface-growth mechanism.[5a] Moreover, Figure F(a) of the Supporting Information shows a similarly shaped kinetic curve, one also closely fit (to within ±5−15% error bars) by this mechanism. As noted in our earlier work, the ability of the two-step nucleation plus autocatalysis mechanism to account for a multistep nanocluster self-assembly reaction [one of ≥3900 steps (i.e., to ≥47 Å $Rh(0)_{\sim 3900}$ nanoclusters, Figure 2)] is remarkable.[5a] It is also completely understandable, however,

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(17) (a) The number (*N*) of Rh atoms in a Rh nanocluster within a given diameter can be approximated using the following equation: $N = (N_0 \rho V)/102.9$, where $N_0 = 6.022 \times 10^{23}$, $\rho = 12.4$ g/cm^3, and $V = (4/3)\pi(D/2)^3$. In dichloroethane, the nanoclusters with average diameter of 46 ± 17 Å can be approximated as Rh_{3700} which is near the magic-number size cluster of Rh_{3871}. Similarly, 63 Å (i.e., 46 + 17) and 29 Å (i.e., 46 − 17) nanoclusters can be approximated as Rh_{9500} and Rh_{930}, respectively. In THF, the nanoclusters with average diameter of 34 ± 13 Å can be approximated as Rh_{1770} (the next magic-number size cluster is Rh_{2057}). Similarly, 49 Å (i.e., 36 + 13) and 23 Å (i.e., 36 − 13) nanoclusters can be approximated as Rh_{4470} and Rh_{460}, respectively. (b) See also elsewhere[5b] and references therein.

(18) (a) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Fretzen, R.; Joussen, T.; Korall, B. *J. Mol. Catal.* **1992**, *74*, 323. (b) See also ref 16a. (c) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543.

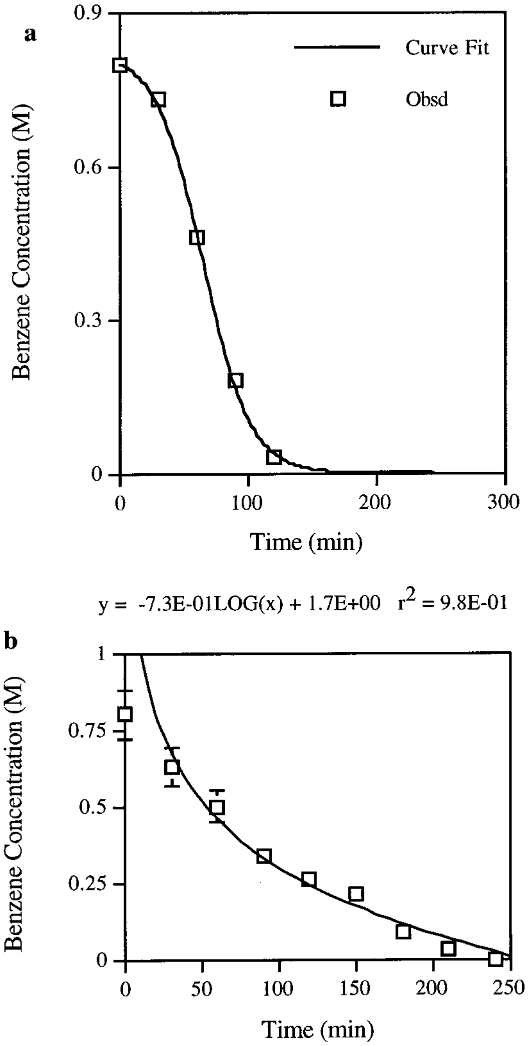

Figure 3. (a). The percent benzene conversion vs time from the reaction of $RhCl_3{\cdot}3H_2O$ with 693 Torr of D_2 in the presence of THF/Aliquat 336/H_2O/trioctylamine/benzene at 31 ± 0.5 °C and its curve fit (solid line) to the A → B nucleation plus A + B → 2B autocatalytic surface growth nanocluster formation mechanism and analytic integrated kinetic equations detailed elsewhere.[5] The resultant rate constants from the fit described in the text to the A → B (rate constant, k_1), then A + B → 2B (rate constant, k_2) kinetic fits are: $k_1 = 1.5\ (\pm\ 0.2) \times 10^{-3}$ min^{-1}, $k_2 = 6.7\ (\pm\ 0.4) \times 10^{-2}\ \text{M}^{-1}\ \text{min}^{-1}$. (b) The percent benzene conversion vs time from the reaction of isolated Rh(0) nanoclusters with 693 Torr of D_2 in the presence of THF/H_2O/benzene at 31 ± 1 °C and its approximate fit to an exponential decay. Note the absence in (b) of the nucleation period seen in (a).

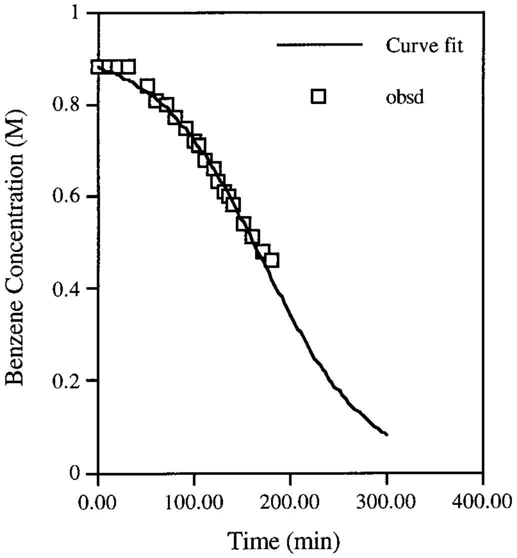

Figure 4. Literature data[9c] for the hydrogenation of benzene from the reaction of $RhCl_3{\cdot}3H_2O$ in the presence of dichloroethane/Aliquat 336/H_2O/trioctylamine/benzene. Also shown is a curve fit of the data according to the A → B and A + B → 2B nucleation, then autocatalytic surface-growth mechanism developed elsewhere.[5] The resultant $k_1 = 7.9\ (\pm 0.6) \times 10^{-4}\ \text{min}^{-1}$ and $k_2 = 2.0\ (\pm 0.1) \times 10^{-4}\ \text{M}^{-1}\ \text{min}^{-1}$.

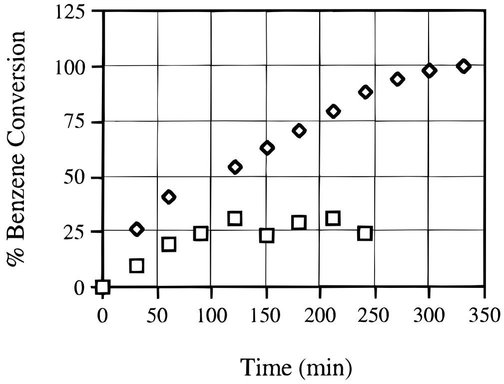

Figure 5. The percent benzene conversion vs time from the reaction of isolated then reused Rh(0) nanoclusters in the monophasic solution of THF/H_2O/benzene. The solution was divided in two, with one-half of the reaction solution being filtered (□) and the other half not (◇). Note that the nonfiltered solution (◇) proceeds to 100% conversion while the filtered solution (□) only shows activity to ca. 25% conversion. [A data point for the filtered solution at longer reaction times (1070 min) shows 24% (and thus no additional) conversion of benzene, but was omitted from the graph for clarity.]

since it is the A + B → 2B autocatalytic surface-growth step which is the key, repetitive mechanistic step.[5a] *In short, these benzene-loss kinetic data, plus the direct TEM observation that Rh(0) nanoclusters are the product ("B") formed from* $[RhCl_4]^-$ *precatalyst, provide compelling evidence that Rh(0) nanoclusters are the true catalysts for benzene hydrogenation.* Recall also that polymetallic Rh(0) particles, but not $RhCl_4^-$, are well-precedented arene hydrogenation catalysts.[1,2]

One issue that comes up here is whether any agglomerated Rh(0) nanoclusters or bulk, filterable Rh(0) metal, are contributing to the observed catalytic activity. To test this, two hydrogenations were performed using a single sample of a solution of Rh(0) nanoclusters, but with one-half of the *black* solution being filtered through Whatman #1 paper while the other half was not. The results (Figure 5) show, not unexpectedly, that the filtered solution exhibits a lower reactivity in comparison to the nonfiltered solution. This result requires that the black solid filtered from the solution is also catalytically active. As a control, a TEM image of the filtered solution reveals that the nanoclusters in solution are still present and, as expected, have not been detectably disturbed by this bulk metal filtration process (Figure B, Supporting Materials). Note that the black color of the solution makes it impossible to detect by eye any black solid composed of agglomerated nanoclusters plus bulk metal in the (black) solutions. Note also how this result ties in to the point made elsewhere[11] and cited in the Introduction: the observation of insoluble M(0) transition metal in a reaction beginning with a monometallic precursor *demands* that nanoclusters have been formed in solution.

The converse to the above observation is also generally true, in that if nanoclusters are present in solution, then sufficiently high temperatures and long enough times will cause them to precipitate bulk metal. This latter observation provides a simple experimental test for the presence of soluble nanocluster catalysts: heat the solution; if metal precipitate is formed, then obtain a TEM of the *unheated* reaction solution to see if nanoclusters are present (and also do the control, as done herein, to show that the TEM electron beam does not induce the formation of nanoclusters from the monometallic precursor).

Testing the Kinetic Reproducibility of the Literature System. The presence of agglomerated, insoluble Rh(0) nanoclusters detected above made us retest the literature study's report[9c] of "highly reproducible" kinetics, at least when using their prefiltered solutions (which their experimental section says they did "if some precipitate was formed"[9c]). The results presented in the previous section make it clear that the experimental protocol of prefiltering the (black) reaction solutions can now be seen to be a problematic, nonreproducible experimental procedure; the black color of the solutions precludes any *reproducible* visual determination of the (black) Rh(0) precipitate. Based on results with Ir(0) nanoclusters and when bulk metal is formed, a variability of at least 70% in rate is expected due to the precedented variable surface area of bulk metal precipitates.[19,20] In addition, the TEM results reported herein, and which show a ±40% size distribution of nanoclusters, predict that that the rates should vary by at least 2-fold since the percentage of catalytically active Rh(0) surface atoms decreases by 2-fold, from ca. 52% to ca. 26%, on going from the smaller 21 Å to the larger 47 Å Rh(0) nanoclusters seen by TEM. In short, the predicted kinetic (ir)reproducibility for unfiltered or even filtered solutions is predicted to be ≥200%.

In five otherwise identical experiments (Method B, unfiltered solutions), the kinetic (ir)reproducibility was ca. ±210% for k_1 and ca. ±340% for k_2. Moreover, a comparison of the k_1 and k_2 values from the literature data in Figure 4 ($k_1 = 7.9\ (\pm 0.6) \times 10^{-4}\ \mathrm{min}^{-1}$; $k_2 = 2.0\ (\pm 0.1) \times 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{min}^{-1}$) to those of two experiments done herein and under nearly identical conditions ($k_1 = 4.28\ (\pm 1.54) \times 10^{-3}\ \mathrm{min}^{-1}$; $k_2 = 1.63\ (\pm\ 0.84) \times 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{min}^{-1}$) shows that the k_2 values from both this work and from our kinetic analysis of the literature data (Figure 5 herein) *are the same* within the large error bars observed. [Our k_1 value is ca. 325% faster than that reported for the literature system,[9c] but, again, the k_1 values are the same within the large error bars observed (±210% for k_1, at 1σ). Note that the Method A conditions detailed in the literature system's[9c] experimental section were used in these experiments, not those provided in the figure caption for Figure 1 elsewhere.[9c]] In short, these tests of the kinetic (ir)reproducibility of the present arene hydrogenation system both (a) confirm, by the irreproducibility seen, the predicted kinetic behavior for the range in size of nanoclusters plus bulk metal present, and (b) show that the literature system has the same kinetic k_1 and k_2 rate constants within the large error bars seen.[19c] This provides another significant piece of kinetic evidence in support of the conclusion that the literature system's catalyst, and the Rh(0) nanoclusters characterized herein, are one and the same.

Two other conclusions are worth noting here. First, the observations of such ≥± ca. 100−200% variable rates in unfiltered solutions is another semiquantitative test that can now be used to distinguish soluble nanocluster vs agglomerated nanocluster plus bulk metal catalysis—one can now add a kinetic reproducibility of ≤15% or ≥100−2300% as semiquantitative guidance to Maitlis' classic filtration tests for distinguishing "homogeneous" from "heterogeneous" catalysts[18c] (where, for this filtration test, "heterogeneous" means agglomerated, bulk metal catalysts). Note also here that this finding fortifies the conceptual point made previously:[11] it is crucial, in the third step of the four-step method (Figure 1),[11] to apply *quantitatively* any phenomenological tests used to distinguish homogeneous from heterogeneous catalysis. Second, the present Rh(0) nanocluster system is *not*, because of its kinetic irreproducibility, a useful one for studying the kinetics and mechanism of arene hydrogenation in a soluble nanocluster system. However, nanoclusters which show near-monodisperse[3] distributions, and hence which give rise to ≤15% reproducible rates,[3−5] should be of significant interest in this regard and are, therefore, under separate investigation.

Phenomenological Tests for Heterogeneous vs Homogeneous Catalysis. (1) D Incorporation and H/D Exchange Studies. The literature system[9c] reports multiple deuterium incorporation into cyclohexane (d_3-d_{12}), but found no incorporation of deuterium into unreacted benzene at 50% conversion. This exchange pattern can be used as a "fingerprint", one characteristic of the true catalyst functioning in the literature system.

Two experiments, one using the precatalyst and the second using isolated Rh(0) nanoclusters, were done to determine the deuterium incorporation both into the product and the H/D exchange into the unreacted benzene starting material. The hydrogenation reaction using the precatalyst under D_2 was sampled by GC-MS along the way to 100% conversion of the benzene. GC-MS analysis at, for example, 44% conversion showed multiple deuterium incorporation (d_3-d_9) into cyclohexane, Figure 6, and when the electron impact mass spectra were obtained at an ionizing voltage of 17 eV. No deuterium incorporation into unreacted benzene is seen, consistent with the literature system's findings.[9c] In what proved to be a telling experiment, we repeated the deuterium incorporation "fingerprint" experiment using isolated Rh(0) nanocluster catalyst, D_2 and at 66% conversion and 17 eV ionizing voltage. The results

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(19) (a) Clusters of 47 Å (34 +13 Å) correspond to Rh_{3945} which is close to the magic number cluster size of Rh_{3871} (where the shell number[19b] is $n = 10$). To determine the number of Rh atoms on the surface of the cluster, one needs to calculate how many atoms were added to the cluster from the $n - 1$ cluster. Using the equation for calculating magic number clusters, $n = 9$ corresponds to Rh_{2869}. Using this value one can calculate that 1002 (3871 − 2869) Rh atoms were added to the surface on going from the $n = 9$ to $n = 10$ cluster. This means approximately 26% [(1002/3871) × 100)] of the total Rh atoms are on the surface of the cluster. The same calculation can be done for the 21 Å (34 − 13 Å) clusters which correspond to Rh_{352} which is close to the magic cluster size of Rh_{309} ($n = 4$), where it can be shown that 52% of the Rh atoms are on the surface of a Rh_{561} cluster. Therefore, the surface number of Rh atoms decreases from ca. 52% to ca. 26% (i.e., a 2-fold drop in the number of surface Rh atoms) on going from a 47 Å to a 21 Å cluster. (b) Teo, B. K.; Sloane, N. J. A. *Inorg. Chem.* **1985**, *24*, 4545. (c) Of course, and since kinetic studies were not a focus of the earlier work, it is not even clear how the claim of "highly reproducible" (p 2805, top left-hand column)[9c] was evaluated (no kinetic data were actually reported to support the claim of reproducible kinetics, nor were any experimental details provided for how the kinetics were performed[9c]). Since the curves show an induction period and are sigmoidal (i.e., as shown by the fit of the literature data in Figure 4 herein), but since their autocatalytic nature was not appreciated previously, they could not have been properly analyzed previously and, hence, any focus attempting to further analyze the prior claim of highly reproducible kinetics is probably a misguided effort.

(20) Elsewhere we have recently shown that H_2 gas-to-solution mass-transfer limitations (MTL) can occur in nanocluster formation reactions for transition metals that are among the faster hydrogenation catalysts; in fact, the specific case we demonstrated this for is Rh.[6c] We also showed that variable rates and polydisperse nanoclusters are the result of such mass-transfer limitations.[6c] Hence, we tested whether the literature conditions are actually H_2 mass-transfer limitation conditions or not. The results described in the Experimental Section indicate that the system is not influenced by the stirring rate in the region under study (Figure G, Supporting Information). Fortunately, then, H_2 mass-transfer limitations are not a problem in the literature,[9c] nor the present, study.

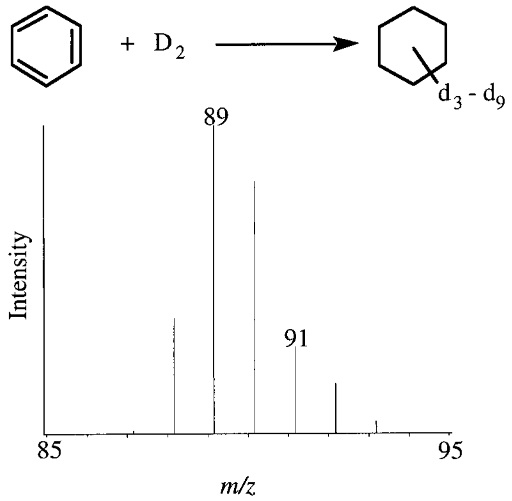

Figure 6. Deuterium incorporation into cyclohexane taken at 44% benzene conversion from the reaction of $RhCl_3{\cdot}3H_2O$ with 657 Torr of D_2 in the presence of dichloroethane/Aliquat 336/H_2O/trioctylamine/benzene at 31 ± 0.5 °C. The MS shown are at 17 eV rather than 70 eV, since the former conditions avoid D fragmentation from the $R^{+\bullet}$ produced by electron impact. The $m/z = 89$ corresponds, for example, to $C_6H_7D_5$.

again showed multiple deuterium incorporation into cyclohexane (d_1-d_{11}) but no deuterium incorporation into unreacted benzene, again quite consistent with the literature system's results.[9c] Noteworthy here is the fact that D-incorporation into benzene is known in the benzene hydrogenation literature,[21] indicating that a different mechanism or active site may be responsible for this process.

A comparison of our incorporation data to that reported in the literature system,[9c] Table 1, entries 1−3, shows that our data exhibit a quite similar but not identical pattern, at least at a 17 eV ionizing voltage. This caused us to wonder what the effects of the ionizing voltage might be, so we repeated our experiments at 70 eV. Entries 4 and 5 in Table 1 provide the second, and most telling, D-incorporation experiment in terms of identifying the true catalyst. The results with either the $[RhCl_4]^-$ precatalyst (entry 4) or isolated Rh(0) nanoclusters (entry 5) *are identical within experimental error* over the full range of observed d_1-d_{11} deuterium incorporation. These results offer excellent, confirming, "fingerprint" mass spectral evidence that (i) the Rh(0) nanoclusters are the active catalysts, and (ii) that the literature catalyst formed from $RhCl_4^-$, and the authentic Rh(0) nanoclusters characterized herein, are one and the same.

A bit more comment is required here about the different D-incorporation observed by mass spectroscopy at the 17 vs the 70 eV ionizing voltages. It helps to realize first that the literature mass spectroscopy work[9c] was done in the labs of Professor H. Schwarz and thus under the guidance of a mass spectroscopy expert.[9c] His choice of a low, 17 eV ionizing voltage was obviously deliberate and clever, chosen to avoid "hydrogen elimination from the molecular ion" (see Table 1, footnote b elsewhere[9c]). This both predicts and explains the observed 1−2 amu lower peaks we see at the higher, 70 eV ionizing voltage; they are due to D loss from the $R^{+\bullet}$ formed following (too energetic) electron impact. Rather clearly, then, the higher amu pattern of D-incorporation peaks reflects the true D-incorporation. On the other hand, the mass spectra at 70 eV are likely to be more sensitive and repeatable, especially from lab to lab, and this is borne out in our results in entries 4 and 5, Table 1. Overall, these experiments serve as a useful experimental reminder of a well-established[22a−c] (but perhaps still under appreciated) point for anyone doing D-incorporation analyses by mass spectroscopy: they should be done as a function of ionizing voltage if electron impact methods are employed.

(2) Mercury Poisoning Experiments. Mercury is a well known and accepted heterogeneous catalyst poison, due to its adsorption onto the catalyst surface or amalgam formation.[23] The literature system[9c] reported that the addition of mercury (an unreported and perhaps too small amount, vide infra) had no effect on the observed reaction. However, we find that sufficient Hg to contact all the catalyst reproducibly causes a complete loss of catalytic activity. Literature precedent also shows that large equivalents of Hg/equiv of metal catalyst have generally been used in such Hg(0) poisoning studies,[11,23b,c] and our results below strengthen the recommendation to examine variable ratios of Hg(0) to catalyst in Hg(0) poisoning experiments (from ca. 1.0 equiv to large, ≥300 equiv, excesses of Hg(0)).

Three types of experiments were done to determine the effect of Hg on the precatalyst as well as the isolated Rh(0) nanocluster catalyst. First, a dark red/black reaction solution, made from precatalyst, was stopped after 80% conversion and ca. *320 equiv* of mercury was added. After stirring for 1 h, the reaction solution had changed color from dark red/black to yellow-orange. The solution was reconnected to the hydrogenation apparatus and, after 5 h, no further loss (≤±10%) of benzene was detected (Figure 7), indicating that Hg had completely poisoned a previously functioning catalyst. (Solution color changes following Hg reaction with either monometallic precatalysts or nanoclusters are well established; in some cases, reactions with the precatalyst ruins the applicability of the Hg test. The interested reader is directed to the results and literature summarized in Table A elsewhere.[11])

Second, excess Hg completely poisoned a fully active catalytic solution of isolated Rh(0) nanoclusters. A fresh reaction solution beginning with isolated Rh(0) nanocluster catalyst was allowed to go to 46% conversion, after which time ca. *310 equiv* of Hg was added and allowed to stir for 1 h. The color of the solution changed from dark red/black to clear and colorless (such color changes of transition M(0) nanocluster

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[21] We surmise that the observation of D-incorporation into the unreacted benzene seen in the following literature is indicating another mechanism, and possibly a different active site, one perhaps able to undergo a C−H oxidative-addition mechanism (i.e., to form $Rh(D)_2(H)(Ph)$ surface intermediates) which can then lead to D-incorporation into the unreacted benzene. (a) Moyes, R. B.; Wells, P. B. *Adv. Catal.* **1973**, *23*, 121. (b) Van Hardeveld, R.; Hartog, F. *Adv. Catal.* **1972**, *22*, 75. (c) Siegel, S. *Adv. Catal.* **1966**, *16*, 123. (d) Rooney, J. J.; Webb, G. *J. Catal.* **1964**, *3*, 488. (e) Bond, G. C. *Catalysis by Metals*; Academic Press: New York, 1962; pp 316−319.

[22] (a) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*; Holden-Day, Inc.: San Francisco, CA, 1967; pp 49−93. (b) McLafferty, F. W. *Interpretation of Mass Spectra*; 3rd ed.; University Science Books: Mill Valley, CA, 1980; pp 138−189. (c) Biemann, K. *Mass Spectrometry-Organic Chemical Applications*; McGraw-Hill: New York, 1962. (d) We also observed reverse fractionation on the GLC column in our GC-MS studies, the well-established phenomenon[22e−g] in which the more deuterated species elutes from the mass spectrum before the least deuterated species (i.e., $C_6D_{11}H_1$ comes out before C_6H_{12}). (e) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713. (f) Possanzini, M.; Pela, A.; Liberti, A.; Cartoni, G. P. *J. Chromatog.* **1968**, *38*. 492. (g) See, for example, pp 216 and 217 elsewhere.[22c]

[23] (a) Georgiades, G. C.; Sermon, P. A. *J. Chem. Soc., Chem. Commun.* **1985**, 975. (b) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819. (c) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

Table 1. Comparison of Deuterium Incorporation into Cyclohexane from the Reaction of $RhCl_3 \cdot 3H_2O$ with D_2 in the Presence of Dichloroethane/Aliquat 336/H_2O/Trioctylamine/Benzene[a]

system	% deuterium incorporation into cyclohexane											
system *m/z*	d_1 85	d_2 86	d_3 87	d_4 88	d_5 89	d_6 90	d_7 91	d_8 92	d_9 93	d_{10} 94	d_{11} 95	d_{12} 96
lit. study[9c*b*]			1	4.5	17	30	17	11	9	6	3	1.5
present study (precatalyst)[c] 17 eV			1	15	38	30	9	6	1			
present study [Rh(0)][d] 17 eV		1	8	17	25	20	10	8	7	3	1	
present study (precatalyst)[c] 70 eV	1	1	5	15	24	23	10	7	6	5	3	
present study [Rh(0)][d] 70 eV	1	2	9	17	22	17	11	9	6	4	2	

[a] The values have been corrected for the natural ^{13}C abundance in each M + 1 peak. [b] Data taken at 50% benzene conversion using $RhCl_3 \cdot 3H_2O$/dichloroethane/H_2O/trioctylamine/benzene/Aliquat 336 (Method A); note that a very low 17 eV ionizing voltage was deliberately used in this literature study so that "hydrogen elimination from the molecular ions does not take place".[9c] [c] Data taken at 44% benzene conversion using Method A. [d] Data taken at 63% benzene conversion using isolated Rh(0) nanoclusters/dichloroethane/H_2O/benzene.

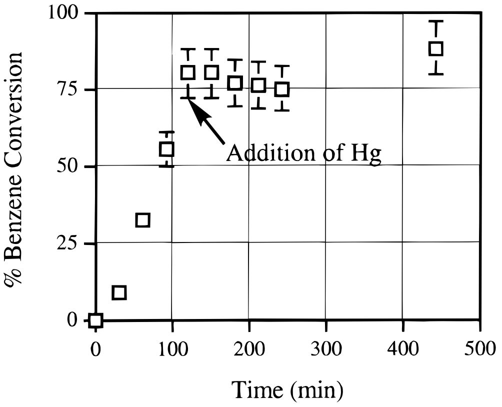

Figure 7. Hg poisoning of the catalyst in the reaction of $RhCl_3 \cdot 3H_2O$ with 686 Torr of H_2 in the presence of THF/Aliquat 336/H_2O/trioctylamine/benzene at 30.5 ± 0.5 °C. After the reaction had gone to 88% conversion, 321 equiv of Hg was added and allowed to stir for 1 h. No further loss of benzene (±10%) was observed even after 5 h.

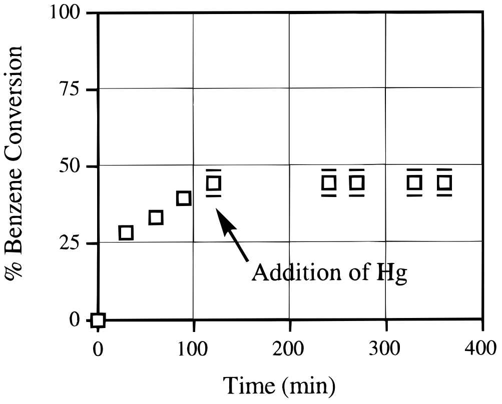

Figure 8. Hg poisoning of isolated Rh(0) nanoclusters with 687 Torr of H_2 in the presence of THF/Aliquat 336/H_2O/trioctylamine/benzene at 30 ± 0.5 °C. After the reaction had gone to 46% conversion, 312 equiv of Hg was added and allowed to stir for 1 h. No further loss of benzene (±10%) was observed even after 2 h.

catalysts upon contact and reaction with Hg have precedent in our earlier work[4]). No further catalytic activity (≤±10%) was seen after 2 h, Figure 8.

Third, a Hg poisoning (control) experiment was performed to see the effect that a *reduced amount* of added Hg had on catalytic activity of solutions starting with both $RhCl_3 \cdot 3H_2O$ and isolated Rh(0) nanoclusters. The reactions were run just as in the experiments above except for in the reaction beginning with isolated Rh(0) nanoclusters, where no Aliquat 336 or trioctylamine was added to the isolated black solid. The reactions were allowed to run to ca. 50% conversion, but now *only 2.0* (19.0 mg, 9.47×10^{-2} mmol) *and 3.0 equiv of Hg* (27.9 mg, 13.9×10^{-2} mmol), respectively, were added to the reaction solutions. After stirring for 1 h, the solutions had *not* changed color. After reconnection to the hydrogenation line, the reactions proceeded until ca. 80% and 65% conversion, respectively, then stopped (Figures H and I, Supporting Information). Rather clearly, it seems that excess Hg(0) is needed to be sure that the mercury physically makes full contact with all the active Rh(0) catalyst.

These Hg poisoning experiments—the complete stoppage to within ≤±10% of the reaction by sufficient Hg to contact the surface of the catalyst—provide confirming evidence that the true catalyst in this system is the range of Rh(0) nanoclusters present, a statement that is true quantitatively to within the ≤±10% error limits of the complete poisoning observed.[24] These experiments also warn against using small amounts of Hg in attempts to do definitive Hg poisoning studies.

Can Rh(0) Nanoclusters as the True Catalysts Explain All the Available Data? As noted in the Introduction and Figure 1, one final key to the approach employed,[11] and to reliable mechanistic studies in general, is to ask the question shown in part 4 of Figure 1, "Can the proposed mechanistic hypothesis, in this case that nanoclusters are the true catalysts, explain all the available data?" We reexamined the literature paper[9c] with this question in mind, and specifically with our list of the 35 observations or other pieces of data (citations of previous literature, etc.) from the literature paper in mind (i.e., the list that we had collected and which is alluded to in footnote *a* of Scheme 1). Actually, all but a couple of the *key* observations have been dealt with already in the paper.

However, two interesting pieces of data from the literature study merit discussion. First is the report[9c] that styrene pretreatment leads to a 1.4 times faster catalyst. This observation, one unexplained in the literature report,[9c] has many plausible explanations in the case of a Rh(0) nanocluster. A couple of possible nanocluster-based explanations are: an effect of styrene on the size or distribution of nanoclusters; an effect of some polystyrene produced under the reaction conditions on the size, stability, or activity of the Rh(0) nanoclusters (since polymer stabilized nanoclusters are very well known; see the references listed elsewhere[3,4]); or perhaps the effect of styrene

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(24) (a) In principle, we would have liked to have repeated the literature system's use of a *homogeneous* catalyst poison (in this case, dibenzocyclooctatetraene, or dct) to support or refute their report that catalytic activity is stopped when dct is added to the reaction solutions. However, upon further reflection this was not attempted, since (i) the synthesis is known to be unreliable and proceeds with unreasonably low yields,[18b] (ii) dct is no longer commercially available, and, most importantly (iii) in light of the strong evidence uncovered for Rh(0) nanocluster catalysis, the testing of a "homogeneous" catalyst poison such as dct on Rh(0) nanoclusters is no longer sensible or cost-effective. (b) Crabtree, R. H. Private communication.

coordinating to an adjacent, surface Rh(0) (something only possible in a multimetallic Rh(0) catalyst). On the other hand, it is much harder to see any precedented explanation for the styrene or other olefin and acetylene effects reported[9c] in the $RhCl_4^-$ catalysis hypothesis.

A second observation is, in the case of *naphthalene hydrogenation* done in a NMR pressure tube, the literature study which reported[9c] three *triplets* and one unresolved multiplet that are ascribed to Rh−H intermediates; that is, presumably a Rh_2−H intermediate *in naphthalene hydrogenation* [−22.35 ppm ($J_{Rh-H} = -7.6$ Hz), −23.12 ppm ($J_{Rh-H} = 9.1$ Hz), −24.29 ppm ($J_{Rh-H} = -7.6$ Hz)] and a rather different signal at +22.78 ppm (unresolved multiplet, $J_{Rh-H} = -7.6$ Hz, one that was presented without further discussion in the literature study).[9c] Unfortunately, no experimental details were provided for these NMR experiments, so that they are not rigorously repeatable.[9c] The well-resolved triplets with detectable coupling in the range expected for Rh^I-H (i.e., smaller than 15−30 Hz)[25] does indeed seem to require the presence of discrete, presumably Rh_2−H hydrides and *possibly* a homogeneous hydrogenation system *for naphthalene (only)*, assuming that these hydride signals can be connected to kinetically competent catalysis in a future study. However, note that any eventual demonstration of such kinetic data and thus homogeneous catalysis for this *naphthalene* system *does not apply logically to benzene hydrogenation*. The differences between benzene, naphthalene, and anthracene hydrogenations were pointed out by Collman back in 1987.[9a] Moreover, the unresolved multiplet at +22.78 ppm may be a nanocluster-bound Rh_n-H species, one with a Knight-shift[26] contribution to its unusual chemical shift, an observation therefore meriting further attention. Bradley's excellent review is recommended for anyone interested in the issues surrounding the detection by NMR of nanocluster surface-bound intermediates,[26] an important area for future nanocluster studies.

A closer look at Halpern's kinetic and mechanistic studies of, for example, anthracene hydrogenation merits mention here.[27] Halpern has provided good evidence for homogeneous anthracene hydrogenation by, for example, a cationic[27a] Rh−H or[27b] a Ru−H_x complex. Note, however, that the stated rate of benzene hydrogenation is "*negligible*" (see p 841, right-hand column[27a]) under mild conditions (≤60 °C, 1 atm H_2) where the anthracene hydrogenation is, however, facile. Halpern points out that the ease of (and thus greater rates of) reduction anthracene > naphthalene ≫ benzene reduction parallel the Hückel approximation β localization energies of 1.16β, 1.21β, and 1.53β, respectively (i.e., in the anthracene case for its localization into the "diene + naphthalene", higher energy electronic configuration). In short, one needs to be cautious in transition metal chemistry in extrapolating mechanisms from one system to even seemingly closely analogous systems, a point that is also made by Halpern in an earlier, classic study of metal hydride reactivity.[27] In short, we see no observable in the literature study that is not best—if not only—explained by Rh(0) nanoclusters as the true catalysts for *benzene* hydrogenation.

Summary and Conclusions

The major findings of the present study can be summarized as follows.

(1) First, an up-front reanalysis of the data published for a prototype arene hydrogenation literature system,[9c] and in light of recent advances in nanocluster chemistry and in distinguishing "heterogeneous from homogeneous catalysts",[3,4,5,11] allows the recognition of several key experimental observations indicative of nanocluster formation and catalysis [specifically, the literature reports of (i) induction periods, (ii) disappearance of the induction periods following pretreatment of the $RhCl_4^-$ precatalyst with H_2, (iii) the observation of a dark, black color as the reaction proceeds, and (iv) the formation of both soluble and insoluble black (i.e., Rh(0)) metal)—all prima facie evidence for the formation of Rh(0) nanoclusters in solution]. As such, the present work may serve as a good example of what can now be identified as "tell-tale" observables to look for in up-front analyses of other systems in the literature, catalytic systems presently believed to be mononuclear homogeneous catalysts but which may, instead, be polymetallic, soluble nanoparticle catalysts.[28]

(2) Second, the use of the most recent, more powerful four-step methodology to distinguish "homogeneous" from "heterogeneous" catalysis worked effectively and efficiently in the present case of a benzene hydrogenation catalyst. This is only the second time this methodology has been applied.

(3) Third, very strong, if not compelling, evidence has been gathered indicating that the true benzene hydrogenation catalyst is a distribution of Rh(0) nanoclusters—a statement that is quantitatively true to within the 5−15% error limits of the kinetic fits or the complete deactivation within experimental error (±10%) of the catalyst by added Hg(0). The key evidence is (i) the direct TEM demonstration that the black reaction solution consists of ±40% polydisperse Rh(0) nanoclusters; (ii) the sigmoidal-shape kinetic curves and their induction periods; and especially (iii) the quantitative fit of the observed kinetic curves to the nucleation plus autocatalytic surface-growth ($A \rightarrow B$, $A + B \rightarrow 2B$) kinetic signature and mechanism first elucidated elsewhere,[5] kinetic evidence which requires that $RhCl_4^-$ ("A") is not kinetically active, but that the product "B" is the true catalyst (where B is the TEM-identified Rh(0) nanoclusters plus insoluble agglomerated Rh(0) nanoclusters and

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[25] (a) Mason, J. *Multinuclear NMR*; Plenium Press: New York, 1987; p 552. The reported ^1J ($^{103}Rh^1H$) of Rh(I) ($RhHL_4$) is between 0 and 8 Hz. (b) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; pp 248, 249. These authors also note that the ^1J ($^{103}Rh^1H$) for Rh(I) ($RhHL_4$) are much less than those observed for Rh(III) hydrides, the latter usually falling in the range of 15−30 Hz.

[26] Bradley, J. In *Colloids and Clusters: From Theory to Applications*; Schmid, G., Ed.; VCH Publishers: New York, 1994; see pp 515−522.

[27] (a) Landis, C. R.; Halpern, J. *Organometallics* **1983**, *2*, 840. (b) Wilczynski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* **1983**, *105*, 2066. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics,* **1985**, *4*, 34.

[28] (a) Also of some interest, as the literature study notes, is the "close similarity between the rhodium- and (Muetterties') cobalt-catalyzed arene hydrogenation".[9c] Although the task remains of applying the methods and techniques[11] used herein to the Co system (which we do not have plans to do), the expectation based on the available evidence is that it, too, may well be a nanocluster-based system, as there are certainly numerous examples of Co nanoclusters. However, an important difference between Co and Rh is that Co is not reducible, thermodynamically speaking, to Co(0) atoms, at least not by only 1 atm of H_2.[28b−i] In this regard, it is interesting that the literature[9c] reports that the Muetterties (allyl)Co[$POMe_3$]$_3$ precatalyst system is "difficult to reproduce, ...extremely sensitive to the quality of the reducing agent as well as the purity of the trimethyl phosphite" (the latter an effect of O=PMe_3 impurities?);[14] it is also reported that one has to raise the "temperatures to 60−80 °C" and the "hydrogen pressure to 3−6 atm" to get the reported yields of benzene or toluene reduction. A cobalt nanocluster catalyst needs to be carefully looked for in this system as well and by the methods employed herein.[11] (b) Osuna, J.; de Caro, D.; Amiens, C.; Chaudret, B.; Snoeck, E.; Respaud, M.; Broto, J.-M.; Fert, A. *J. Phys. Chem.* **1996**, *35*, 14571. (c) Hayashi, T.; Hirono, S.; Tomita, M.; Umemura, S. *Nature* **1996**, *381*, 772. (d) Becker, J. A.; Schäfer, R.; Festag, J. R.; Wendorff, J. H.; Hensel, F.; Pebler, J.; Quaiser, S. A.; Helbig, W.; Reetz, M. T. *Surf. Rev. Lett.* **1996**, *3*, 1121. (e) Billas, I. M. L.; Châtelain, A.; de Heer, W. A. *Science* **1994**, *265*, 1682. (f) Gong, W.; Li, H.; Zhao, A.; Chen, J. *J. Appl. Phys.* **1991**, *69*, 5119. (g) Chidress, J. R.; Chien, C. L. *J. Appl. Phys.* **1991**, *70*, 5885. (h) Sapieszko, R. S.; Matijevic, E. *Corrosion* **1980**, *36*, 522. (i) Hess, P. H.; Parker, P. H., Jr. *J. Appl. Polym. Sci.* **1966**, *10*, 1913.

bulk metal). Confirming evidence includes (iv) the "fingerprint" D-incorporation that is the same for either the isolated Rh(0) nanoclusters or when beginning with the $RhCl_4^-$ precatalyst; (v) the lack of D-incorporation into the unreacted benzene, consistent with what the literature system also reported; (vi) the demonstration that the well-known heterogeneous catalyst poison[23] elemental mercury shuts down completely the catalytic activity of previously active benzene hydrogenation catalyst solutions; and (vii) the similar kinetic curves, curve-fits (i.e., and k_1 and k_2 rate constants), and similar fingerprint D-incorporation patterns seen in the data taken from literature system.[9c] One other, very important piece of data is (viii) that Rh(0) metal is a well-established arene hydrogenation catalyst,[1,2] while monometallic $Rh^{I/III}$ will *not* hydrogenate benzene under conditions where it reduces homogeneously the more easily reduced anthracene.[27c] We have also considered (ix) whether the Rh(0) nanocluster hypothesis can explain all of the available data, and believe that it can, although a few issues remain which will require their own, independent study (the effect of styrene, the $Rh_2{-}H$ intermediates seen and whether they are catalysts, and the possibility of a homogeneous Rh−H naphthalene hydrogenation system). To our knowledge, no other hypothesis for the nature of the catalyst is presently available which can also explain all the available data.[26]

The present results have broader implications as well; specifically they (4) verify the prediction that the use of the pseudo-elementary reporter-reaction method[5b] is a more generally useful, powerful new method for following nanocluster formation; (5) provide evidence fortifying the expectation[5a] that the new mechanism uncovered recently of A → B nucleation followed by A + B → 2B autocatalytic surface growth might well be a more general, new mechanistic paradigm for transition metal nanocluster formation under hydrogen; and (6) call into question *all* previous claims of *benzene* hydrogenation—but not anthracene or naphthalene arene hydrogenation—by monometallic precatalysts. The studies presented herein also (7) reemphasize that, prior to any claim of a homogeneous catalyst in a reaction (such as arene hydrogenation) where a facile heterogeneous M(0) catalyst is well established, one must first rule out catalysis by even trace amounts of possibly highly active nanocluster catalysts (e.g., by using the methods utilized herein and any other applicable method), and (8) call for a reinterpretation of all of the other papers in the literature[29] which used what was previously believed to be a $RhCl_4^-$ ion-paired catalyst under hydrogen for catalytic reductions. This work also (9) offers a reminder that electron impact mass spectroscopy studies of D-incorporation need to be done at both high and low ionizing voltages.

Overall, the studies presented herein provide a definitive answer, at least for the specific Rh system studied, to the 34-year-old question, one controversial for 17 years, of "is benzene hydrogenation homogeneous or heterogeneous?". The present study is, however, just one of the early steps toward our broader goal of developing nanocluster "soluble heterogeneous catalysts", including selective arene hydrogenation catalysts. Further work toward this goal is continuing and will be reported in due course.

Experimental Section

Materials. Rhodium(III) chloride hydrate (obtained from Strem Chemicals), trioctylamine (98%), benzene (anhydrous, 99.8%), cyclooctane (99+%), dichloroethane (99.8%, HPLC grade), and tetrahydrofuran (anhydrous, 99.8%, inhibitor free) were obtained from Aldrich and opened and then stored in a Vacuum Atmospheres drybox. Alumina oxide (Aldrich, activated, acidic, Brockmann I), Aliquat 336 (i.e., $[(C_8H_{17})_3NCH_3]^+Cl^-$, Aldrich), mercury (D. F. Goldsmith Chemical & Metal Corp., elemental grade, triply distilled), hydrogen (General Air, 99.5%), and dichloromethane (Fisher Scientific, HPLC grade) were used as received.

Analytical Procedures. Unless otherwise reported, all reaction solutions were prepared under oxygen- and moisture-free conditions using a Vacuum Atmospheres nitrogen atmosphere drybox. O_2 levels were maintained at less than 3 ppm as continuously monitored by a Vacuum Atmospheres O_2-level monitor.

Gas−liquid chromatography (GLC) was performed using a Hewlett-Packard 5890 series II GLC with a FID detector equipped with a 30 m (0.25 mm i.d.) Econo-cap Carbowax column (Alltech) and coupled to a Hewlett-Packard 3395 integrator. Parameters were as follows: initial temperature, 35 °C; initial time, 4.0 min; ramp, 15 °C/min; final temperature, 200 °C; final time, 5 min; injector port temperature, 180 °C; detector temperature, 200 °C; injection volume, 2 μL.

Gas chromatography mass spectrometry (GC-MS) was preformed using a Hewlett-Packard 5890 series II GC with a VG AutoSpec equipped with a 30m DB-5 column (J&W Scientific). The ionizing voltages of 17 eV and 70 eV were both employed for reasons discussed in the main text. The GC parameters were as follows: initial temperature, 0 °C (via dry ice); initial time, 6 min; solvent delay, 4 min; first ramp, 5 °C/min until 20 °C; second ramp, 25 °C/min until 100 °C; injector port temperature, 180 °C; detector temperature, 200 °C; injection volume, 1 mL. Mass marker calibration of the GC-MS was performed using heptacosafluorotributylamine. The percent D-incorporation was calculated according to the reaction $C_6H_6 = nD_2 \rightarrow aC_6H_5D_1 + bC_6H_5D_2 + cC_6H_5D_3$ (and so on); that is, the sum of $a + b + c$ (etc.) relative to the total original concentration of C_6H_6 gives the fraction (and thus percent) of D-incorporation.

Transmission electron microscopy (TEM) was performed on a JEOL 2000 EX-II operating at an accelerating voltage of 100 keV. Samples were examined at magnifications between 100 and 400K, and in at least three different places on the sample grid to ensure that the images were representative of the sample as a whole. Samples were prepared using type A (300 mesh) Formvar and carbon coated copper grids (Ted Pella, supplier). Grids were suspended in chloroform for about 30 s immediately prior to use to remove the Formvar coating and to expose a fresh carbon surface. One drop of the solution (in DMSO) was placed on the carbon-coated grid using a gas-tight syringe and allowed to air dry. Particle size distributions were determined once the original negative had been digitally scanned into Adobe Photoshop and expanded to > 20 in. × 25 in. for more accurate resolution and measurement.

A control experiment was done using a precatalyst solution in THF (Method B) to show that deposition of the ion-pair precatalyst on a TEM grid, followed by its subsequent TEM examination under the conditions used to visualize the Rh(0) nanoclusters, did *not* yield any (TEM-beam induced) Rh(0) nanoclusters. This control, which was repeated, did not yield a clear image (as expected since no nanoclusters are present) but is definitive in showing that the TEM beam does not produce images characteristic of the nanoclusters seen in, for example, Figure 2.

Hydrogenation Apparatus and "Standard Conditions". The hydrogenation apparatus used herein was modeled after a standard catalytic hydrogenation apparatus for hydrogenations at atmospheric pressure.[30] This apparatus (Figure A, Supporting Information) consists of a 25-mL side-armed Schlenk flask, a 500-mL side-armed round-

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(29) (a) Blum, J.; Amer, I.; Zoran, A.; Sasson, Y. *Tetrahedron Lett.* **1983**, *24*, 4139 (hydrogenation of a variety of aromatics). (b) Amer, I.; Amer, H.; Blum, J. *J. Mol. Catal.* **1986**, *34*, 221 (hydrogenation of naphthalene). (c) Azram, J.; Buchman, O.; Amer, I.; Blum, J. *J. Mol. Catal.* **1986**, *34*, 229 (selective hydrogenation of α, β-unsaturated ketones and esters). (d) Amer, J.; Bravdo, T.; Blum, J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1987**, *28*, 1321 (selective hydrogenation of unsaturated nitro compounds). (e) Amer, I.; Amer, H.; Ascher, R.; Blum, J.; Vollhardt, K. P. C. *J. Mol. Catal.* **1987**, *39*, 185 (selective hydrogenation of polycyclic compounds). (f) Blum, J. *Russ. Chem. Bull.* **1993**, *42*, 1619 (hydrogenation of aromatics).

(30) Augustine, R. L. *Catalytic Hydrogenation*; Marcel Dekker: New York, 1965.

bottomed, and a 100-mL round-bottomed flask (the latter two were used as H_2 reservoirs) connected to a standard Schlenk line equipped with a Hg-manometer.

Unless otherwise reported, all hydrogenation experiments were performed using the following “standard conditions”. Two general reaction conditions taken from the previous literature[9c] were used: a biphasic system (H_2O/dichloroethane), Method A,[9c] and a monophasic system (THF), Method B.[9c] Amounts of reagents identical with those used in the literature[9c] were employed for both Method A and Method B (for details see the sections which follow). The reaction solutions were mixed in the drybox and placed into a 25-mL side-armed flask containing a $^5/_{16}$ in. × $^1/_2$ in. Teflon-coated magnetic stir bar. The flask was capped and sealed, taken out of the drybox, and connected to the hydrogenation apparatus. The reaction solution was frozen at ca. −40 °C using a CO_2/ethanol bath. Once frozen, the entire apparatus was placed under ca. 10^{-3} Torr vacuum for ca. 2−3 min. The low-temperature bath was removed and replaced by a silicone oil bath thermostated at 31 ± 1 °C causing the reaction solution to thaw. The entire apparatus was placed under 687 ± 7 Torr of hydrogen pressure. Stirring of the reaction solution at 770 ± 30 rpm was started and the time was set equal to zero at this point. [The literature reports stirring at 400 rpm[9c] so control experiments were done at 350 ± 75 and 1100 ± 100 rpm, reported in a section below, to test for possible H_2 mass-transfer limitations. The results show that there is no effect beyond experimental error in the rate of arene hydrogenation due to the stirring rate difference between 375, 770, and 1100 rpm (Figure G, Supporting Information).]

Note also, and as discussed in the text, we deliberately did not use the step used previously of filtering the catalyst through a fluoropore filter “if some precipitate was formed”,[9c] since this step both depends on the irreproducible identification of a black precipitate in a black solution (i.e., it was neither used uniformly before, nor can it be reproducibly applied by us or others) and since it would then remove the catalytic contribution of agglomerated plus bulk Rh(0) that we have shown is present in unfiltered solutions.

To monitor the loss of benzene, aliquots of the reaction solution (1−2 drops, ca. 50 μL) were withdrawn via the septum-capped side arm using a 9 in. long, 12-gauge metal needle attached to a 5-mL glass syringe. For GLC analysis, 5 μL of this sample was added to 1 mL of fresh solvent (either dichloroethane or THF) and (as described in the literature, vide infra) filtered through ca. 200 mg (1.96 mmol) acidic alumina (i.e., to remove water and filter out Rh(0) nanoclusters that were present). This filtration step, which is based on the literature procedure,[9c] proved necessary, as without it irreproducible GLC results were obtained, probably due to the inhomogeneous (biphasic) nature of the product mixture.

One ambiguity regarding the literature system[9c] is whether Aliquat 336 and trioctylamine were readded when the activity of the reported, isolated black solid catalyst was studied. Because of this, when we performed arene hydrogenations with the catalyst isolated under the literature conditions, we did so both with and without added Aliquat 336 and trioctylamine. Fortunately, we find that the presence of this additional aliquot of stabilizers has no effect on the activity of the isolated catalyst; hence, no ambiguity is raised between the conditions used in the literature and our need to repeat those literature conditions as exactly as possible.

Hydrogenation of Benzene in Dichloroethane Using $RhCl_3 \cdot 3H_2O$ as a Precatalyst and TEM Sample Preparation. Method A. This reaction was carried out under the “standard conditions” described above and is based on Method A described elsewhere.[9c] In a drybox Aliquat 336 (23.4 mg, 5.8 × 10^{-2} mmol) was weighed into a 1-dram vial and dissolved in 0.5 mL (6.35 mmol) of dichloroethane, 50 μL (0.11 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, and 64 μL (0.47 mmol) of cyclooctane. In a separate dram vial $RhCl_3 \cdot 3H_2O$ (10.4 mg, 5.0 × 10^{-2} mmol) was weighed and the colorless dichloroethane solution was added using a disposable polyethylene pipet. While still in a drybox, 0.5 mL (28 mmol) of H_2O was added using a 1-mL gastight syringe and the mixture was stirred until the $RhCl_3 \cdot 3H_2O$ had dissolved. The percent benzene conversion vs time is summarized in Figure F(a), Supporting Information. As the reaction proceeded, the solution changed from a clear orange-red to an opaque, deep red/black. After 4 h the flask was brought back into the drybox. The solution was evacuated overnight at room temperature to yield a black solid. A TEM sample was prepared by dissolving ca. 2 mg of the black solid in ca. 3.5 mL of DMSO at room temperature to yield a clear brown solution. A TEM image of this sample is shown in Figure C, Supporting Information.

Formation, Isolation, and Reuse of Rh(0) Nanoclusters Plus Aliquat 336 in Dichloroethane. A “standard conditions”, Method A hydrogenation was performed using Aliquat 336 (20.9 mg, 5.79 × 10^{-2} mmol), 0.5 mL (6.35 mmol) of dichloroethane, 50 μL (0.11 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3 \cdot 3H_2O$ (10.3 mg, 4.92 × 10^{-2} mmol), and 0.5 mL (28 mmol) of H_2O. After 4 h, the reaction flask was disconnected from the hydrogenation line and brought back into the drybox. The reaction mixture was evacuated to dryness under vacuum overnight at room temperature yielding a black solid. The black solid was redissolved in 0.5 mL of dichloroethane, 50 μL of trioctylamine, 89 μL of benzene, 64 μL of cyclooctane, Aliquat 336 (21.7 mg, 5.37 × 10^{-2} mmol), and 0.5 mL of H_2O, and a second hydrogenation run was begun with 682 Torr of hydrogen. Hydrogenation of benzene proceeded *without* a detectable induction period and was allowed to continue for 4 h. The percent benzene conversion vs time is summarized in Figure F(b), Supporting Information. A TEM of the reaction mixture is shown in Figure D, Supporting Information.

Hydrogenation of Benzene in THF Using $RhCl_3 \cdot 3H_2O$ as a Precatalyst and TEM Sample Preparation. Method B. This reaction was carried out under the “standard conditions” described above and is based on Method B described elsewhere.[9c] Aliquat 336 (21.8 mg, 5.39 × 10^{-2} mmol) was weighed into a 1-dram vial and dissolved in 1.0 mL (12.3 mmol) of THF, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene and 64 μL (0.47 mmol) of cyclooctane. $RhCl_3 \cdot 3H_2O$ (10.3 mg, 4.92 × 10^{-2} mmol) was then dissolved in the above THF solution and 50 μL (2.8 mmol) of H_2O was added. The resulting *monophasic* solution was placed into the reaction flask, sealed, removed from the drybox, and connected to the hydrogenation apparatus as detailed above. After 4 h, the flask was brought back into the drybox. The solution was evacuated overnight at room temperature to yield a black solid. A TEM sample was prepared by dissolving ca. 2 mg of the black solid in ca. 3.5 mL of DMSO at room temperature to yield a clear brown solution. A TEM image of the reaction mixture is shown in Figure E, Supporting Information.

Formation, Isolation, and Reuse of Rh(0) Nanoclusters Plus Aliquat 336 in THF. A “standard conditions”, Method B hydrogenation was performed using Aliquat 336 (21.5 mg, 5.31 × 10^{-2} mmol), 1.0 mL (12.3 mmol) of THF, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3 \cdot 3H_2O$ (10.0 mg, 4.78 × 10^{-2} mmol), and 50 μL (2.8 mmol) of H_2O. After 4 h, the reaction flask was disconnected from the hydrogenation line and brought back into the drybox. The reaction mixture was evacuated to dryness under vacuum overnight at room temperature yielding a black solid. The black solid was redissolved in 1.0 mL of THF, 100 μL of trioctylamine, 89 μL of benzene, 64 μL of cyclooctane, Aliquat 336 (22.0 mg, 5.44 × 10^{-2} mmol), and 50 μL of H_2O, and another hydrogenation run was performed under 685 Torr of hydrogen. The reaction proceeded *without* a detectable induction period and was allowed to run 4 h. A TEM image of the reaction mixture is shown in Figure 2.

Filtration Experiments on Isolated and Then Reused Rh(0) Nanoclusters in THF. These are detailed in the Supporting Information.

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(31) (a) See Figure 13 and pp 114 and 115 of Che, M.; Bennett, C. O. *Adv. Catal.* **1989**, *36*, 55. (b) Milone, C.; Neri, G.; Donato, A.; Musolino, M. G.; Mercadante, L. *J. Catal.* **1996**, *159*, 253.

(32) The literature[9c] did not provide this number. The total turnover number calculated is the maximum predicted. This number is calculated assuming 100% conversion of benzene to cyclohexane and from a single batch of material under standard conditions (see Experimental Section) in THF. The total turnover number was corrected for the number of active available Rh(0) atoms, assuming that, at a *maximum*, 31% of the Rh(0) atoms were available and active for the average Rh(0) nanocluster size of 36 Å ± 13 [2057 Rh atoms].[19]

Curve-Fitting of the Literature Data for Benzene Concentration *vs* Time. Curve-fitting of the benzene concentration vs time data given in Figure 4 herein (of the data taken from Figure 1 of the literature paper[9c]) and also of the data in Figures 3a and F(a) of the Supporting Information was performed using the program and kinetic equations described elsewhere, basically, the analytical integrated equations corresponding to the kinetic steps of nucleation ($A \rightarrow B$; rate constant, k_1), and then autocatalytic surface growth ($A + B \rightarrow 2B$, rate constant, k_2).[5] The resultant k_2 values are *not* corrected for the "stoichiometry" or "scaling" factors detailed elsewhere;[5] that is, the values are $k_{2(\text{curve}-\text{fit; uncorrected})}$. Note also that, as in our earlier work,[5] no possible particle size effects were deconvoluted from the kinetic fits, an important future research goal since the particle size effect (the "structure sensitivity or insensitivity") of benzene hydrogenation is an unsettled issue.[31]

IR Spectroscopy on the Product Solutions Attempting to Show That All the $RhCl_4^-$ Precursor Has Been Converted to Rh(0) Nanoclusters. This experiment is detailed in the Supporting Information.

Probing for H_2 Gas-to-Solution Mass-Transfer Limitations[6c] under the 770 Rpm Stirring Rates Employed. These experiments are detailed in the Supporting Information. These controls make it clear that (i) there are no discernible differences between data obtained at the 350, 770, and 1100 rpm stirring rates; and thus (ii) H_2 mass-transfer limitations are not an issue at the 770 stirring rate used in the present system (although we have shown elsewhere that they can be for very fast hydrogenation catalysts and at higher catalyst concentrations[6c]).

Hydrogenation of Benzene under D_2 in Dichloroethane Using $RhCl_3{\cdot}3H_2O$ as the Precatalyst. A "standard conditions" hydrogenation was performed using Aliquat 336 (21.5 mg, 5.32×10^{-2} mmol), 0.5 mL (6.35 mmol) of dichloroethane, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (9.8 mg, 4.68×10^{-2} mmol), and 1.0 mL (56 mmol) of H_2O. A hydrogenation run was begun under 657 Torr of D_2. The reaction was allowed to proceed until completion, 3 h. Every 30 min, samples were removed for GLC analysis. A plot of loss of benzene vs time is shown in Figure F(a), Supporting Information.

Hydrogenation of Benzene under D_2 in Dichloroethane Using Isolated Rh(0) Nanoclusters. A "standard conditions" hydrogenation was performed using Aliquat 336 (21.6 mg, 5.34×10^{-2} mmol), 1.0 mL (12.7 mmol) of dichloroethane, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (10.1 mg, 4.83×10^{-2} mmol), and 1.0 mL (55.5 mmol) of H_2O. A hydrogenation run was performed under 695 Torr of hydrogen. After 4 h, the reaction flask was disconnected from the hydrogenation line and taken back into the drybox. The solution was evaporated to dryness overnight under vacuum at room temperature yielding a black solid. The black solid was dissolved in 0.5 mL (6.35 mmol) of dichloroethane, 89 μL of benzene, 64 μL of cyclooctane, and 1.0 mL of H_2O. A second hydrogenation run was begun under 662 Torr of D_2. The reaction was allowed to run until completion, 4 h. Every 30 min, samples were removed for GLC analysis. A plot of the percent benzene conversion vs time is shown as Figure F(b), Supporting Information,

Hydrogenation of Benzene under D_2 in THF using $RhCl_3{\cdot}3H_2O$ as the Precatalyst. A "standard conditions" hydrogenation was performed using Aliquat 336 (21.0 mg, 5.20×10^{-2} mmol), 1.0 mL (12.3 mmol) of THF, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (10.6 mg, 5.06×10^{-2} mmol), and 50 μL (2.8 mmol) of H_2O. A hydrogenation run was begun under 693 Torr of D_2. The reaction was allowed to run to completion, 4 h. Every 30 min, samples were removed for GLC analysis. A plot of loss of benzene vs time is shown in Figure 3a.

Hydrogenation of Benzene under D_2 in THF Using Isolated Rh(0) Nanoclusters under D_2. A "standard conditions" hydrogenation was performed using Aliquat 336 (22.7 mg, 5.62×10^{-2} mmol), 1.0 mL (12.3 mmol) of THF, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (10.0 mg, 4.78×10^{-2} mmol), and 50 μL (2.8 mmol) of H_2O. A hydrogenation run was performed under 693 Torr of hydrogen. After 4 h the reaction flask was disconnected from the hydrogenation line and taken back into the drybox. The solution was evaporated to dryness overnight under vacuum at room temperature yielding a black solid. The black solid was dissolved in 1.0 mL of THF, 89 μL of benzene, 64 μL of cyclooctane, and 50 μL of H_2O. A second hydrogenation run was begun under 645 Torr of D_2. The reaction was allowed to run until completion, 4 h. Every 30 min, samples were removed for GLC analysis. A plot of loss of benzene vs time is shown in Figure 3b.

D Incorporation and H/D Exchange Studies under D_2 Using $RhCl_3{\cdot}3H_2O$ as the Precatalyst in the Presence of Benzene-d_0 and Dichloroethane. A "standard conditions" hydrogenation was performed using Aliquat 336 (20.5 mg, 5.07×10^{-2} mmol), 0.5 mL (6.35 mmol) of dichloroethane, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (9.6 mg, 4.59×10^{-2} mmol), and 1.0 mL (56 mmol) of H_2O. A hydrogenation run was begun under 686 Torr of D_2. The reaction was allowed to proceed until 44% conversion, approximately 90 min. Every 30 min, samples were removed for GLC analysis. At 90 min, a sample was removed for GC-MS analysis; specifically, 25 μL of the red/black solution was added to 0.5 mL (7.8 mmol) of dichloromethane, and this sample was analyzed at ionizing potentials of 17 *and* 70 eV. The data for deuterium incorporation into cyclohexane are summarized in Table 1 and Figure 6. Reverse fractionation is observed on the GLC column in the GLC-MS experiments.[22d]

D Incorporation and H/D Exchange Studies under D_2 Using Isolated Rh(0) Nanoclusters and in the Presence of Benzene-d_0 and Dichloroethane. A "standard conditions" hydrogenation was performed using Aliquat 336 (20.0 mg, 4.95×10^{-2} mmol), 0.5 mL (6.35 mmol) of dichloroethane, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (10.0 mg, 4.78×10^{-2} mmol), and 1.0 mL (55.5 mmol) of H_2O. A hydrogenation was performed under 693 Torr of hydrogen. After 4 h, the reaction flask was disconnected from the hydrogenation line and taken back into the drybox. The solution was evaporated to dryness overnight under vacuum at room temperature yielding a black solid. The black solid was dissolved in 0.5 mL of dichloroethane, 89 μL of benzene, 64 μL of cyclooctane, and 1 mL of H_2O. A second hydrogenation was begun under 690 Torr of D_2. The reaction was allowed to run to 63% conversion, approximately 2 h. Every 30 min samples were removed for GLC analysis. At 120 min, a sample was removed for GC-MS analysis; specifically 25 μL of the red/black solution was added to 0.5 mL (7.8 mmol) of dichloromethane, and this sample was analyzed at ionizing potentials of 17 *and* 70 eV. The data for deuterium incorporation into cyclohexane are summarized in Table 1. Reverse fractionation is observed on the GLC column in the GLC-MS experiments.[22d]

Hg Poisoning Tests Using $RhCl_3{\cdot}3H_2O$ as the Precatalyst in the Presence of Hg(0) and Benzene. A "standard conditions" hydrogenation was performed using Aliquat 336 (21.7 mg, 5.37×10^{-2} mmol), 1.0 mL (12.3 mmol) of THF, 100 μL (0.23 mmol) of trioctylamine, 89 μL (1.0 mmol) of benzene, 64 μL (0.47 mmol) of cyclooctane, $RhCl_3{\cdot}3H_2O$ (10.0 mg, 4.78×10^{-2} mmol), and 50 μL (2.8 mmol) of H_2O. After 2 h (80% conversion) the reaction was stopped. The reaction flask was disconnected from the hydrogenation line and taken back into the drybox. The red/black solution was placed into a 2 dram vial and stirred with Hg (3.0905 g, 15.4 mmol, 321 equiv) for 1 h. The resulting clear yellow-orange solution was filtered through a Whatman #1 paper to remove the excess elemental Hg and placed into a clean reaction flask. The filter paper was then washed with ca. 0.5 mL (6.2 mmol) of THF and the washings were added to the reaction solution. To compensate for any benzene lost during filtration, 40 μL (0.44 mmol) of benzene was added to the reaction flask. A second hydrogenation reaction was then started by placing the system under 689 Torr of hydrogen. The previously fully active catalyst was completely inactivated by Hg. Even 5 h 30 min after the Hg treatment, the catalyst was still inactive. The percent benzene conversion vs time data is shown in Figure 7.

A second Hg poisoning (control) experiment was performed to see the effect that a reduced amount of added Hg had on catalytic activity.

The reaction was run just as above, the reaction was stopped at ca. 50% conversion, and only 2.0 equiv of Hg (19.0 mg, 9.47×10^{-2} mmol) was added to the reaction solution. After stirring for 1 h, the black solution had not changed color. After reconnection to the hydrogenation line, the reaction proceeded until ca. 80% conversion, then stopped, Figure H, Supporting Information. This control experiment warns against using small amounts of Hg in poisoning studies.

Hg Poisoning Tests Using Isolated Rh(0) Nanoclusters Plus Aliquat 336 in the Presence of Hg(0) and Benzene. These experiments are detailed in the Supporting Information.

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Supporting Information Available: Figure A, hydrogenation apparatus; Figures B–E, transmission electron micrographs of Rh(0) nanoclusters; Figure F, curve fits for isolated, and isolated then reused, Rh(0) nanoclusters in dichloroethane; Figure G, stirring rate controls; Figures H and I, Hg(0) poisoning using reduced amounts of Hg(0); experimental details for filtration experiments on isolated and then reused Rh(0) nanoclusters in THF; experimental details for IR spectroscopy on the product solutions (attempting to show that all the $RhCl_4^-$ precursor had been converted to Rh(0) nanoclusters); experimental probing for H_2 gas-to-solution mass-transfer limitations under the 770 rpm stirring rates employed; experimental details for Hg poisoning tests using isolated Rh(0) nanoclusters plus Aliquat 336 in the presence of Hg(0) and benzene (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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