

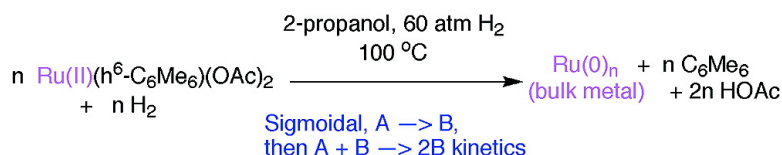
Article

Is It Homogeneous or Heterogeneous Catalysis? Identification of Bulk Ruthenium Metal as the True Catalyst in Benzene Hydrogenations Starting with the Monometallic Precursor, Ru(II)(η -CMe)(OAc), Plus Kinetic Characterization of the Heterogeneous Nucleation, Then Autocatalytic Surface-Growth Mechanism of Metal Film Formation

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Is It Homogeneous or Heterogeneous Catalysis? Identification of Bulk Ruthenium Metal as the True Catalyst in Benzene Hydrogenations Starting with the Monometallic Precursor, Ru(II)(η^6 -C₆Me₆)(OAc)₂, Plus Kinetic Characterization of the Heterogeneous Nucleation, Then Autocatalytic Surface-Growth Mechanism of Metal Film Formation

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Abstract: A reinvestigation of the true catalyst in a benzene hydrogenation system beginning with Ru(II)-(η^6 -C₆Me₆)(OAc)₂ as the precatalyst is reported. The key observations leading to the conclusion that the true catalyst is bulk ruthenium metal particles, and *not* a homogeneous metal complex or a soluble nanocluster, are as follows: (i) the catalytic benzene hydrogenation reaction follows the nucleation (A → B) and then autocatalytic surface-growth (A + B → 2B) sigmoidal kinetics and mechanism recently elucidated for metal(0) formation from homogeneous precatalysts; (ii) bulk ruthenium metal forms during the hydrogenation; (iii) the bulk ruthenium metal is shown to have sufficient activity to account for all the observed activity; (iv) the filtrate from the product solution is inactive until further bulk metal is formed; (v) the addition of Hg(0), a known heterogeneous catalyst poison, completely inhibits further catalysis; and (vi) transmission electron microscopy fails to detect nanoclusters under conditions where they are otherwise routinely detected. Overall, the studies presented herein call into question any claim of homogeneous benzene hydrogenation with a Ru(arene) precatalyst. An *additional, important finding* is that the A → B, then A + B → 2B kinetic scheme previously elucidated for soluble nanocluster homogeneous nucleation and autocatalytic surface growth (Widegren, J. A.; Aiken, J. D., III; Özkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312–324, and ref 8 therein) also quantitatively accounts for the formation of bulk metal via *heterogeneous* nucleation then autocatalytic surface growth. This is significant for three reasons: (i) quantitative kinetic studies of metal film formation from soluble precursors or chemical vapor deposition are rare; (ii) a clear demonstration of such A → B, then A + B → 2B kinetics, in which both the induction period and the autocatalysis are continuously monitored and then quantitatively accounted for, has not been previously demonstrated for metal thin-film formation; yet (iii) all the mechanistic insights from the soluble nanocluster system (op. cit.) should be applicable to metal thin-film formations which exhibit sigmoidal kinetics and, hence, the A → B, then A + B → 2B mechanism.

Introduction

The use of transition-metal complexes as precatalysts for reductive processes is widespread. The true catalyst may be a transition-metal complex, *but it can also be a metal film, a metal powder, or a metal nanocluster that forms from the precatalyst under reducing conditions.*¹ In fact, the in situ formation of nanoclusters or agglomerated-metal-particle catalysts appears to be common under reducing conditions.² However, distinguishing metal-complex homogeneous catalysis from metal-particle heterogeneous catalysis is not trivial; it can be especially

difficult to rule out the in situ formation of a completely soluble nanocluster catalyst.² Methods for distinguishing homogeneous versus heterogeneous catalysis began to be developed in about 1980 and include contributions from the groups of Maitlis,³ Whitesides,⁴ Crabtree,^{5–7} Collman,^{1,8} and Lewis,^{9,10} as well as our^{11,12} own group. As emphasized elsewhere,^{2,5,11} *no single*

[†] Research School of Chemistry, The Australian National University, Canberra, ACT, Australia, 0200.

(1) 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. The uncertainty about the identity of the true catalyst when beginning with several Ru organometallics, Table 10.2, entries F–I, p 550, is discussed on p 555 therein.

(2) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317–341. Table S1 of the Appendix lists about 30 catalyst systems for which metal-particle heterogeneous catalysts are suspected, including arene hydrogenation systems with Ru-based precatalysts.

(3) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543.

(4) 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.

(5) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

(6) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

(7) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738.

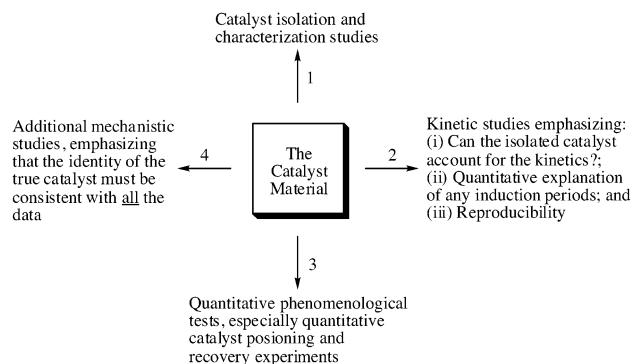


Figure 1. The most recent approach to distinguishing between a metal-particle “heterogeneous” catalyst and a metal-complex “homogeneous” catalyst. An expanded version of this approach is available as Figure 5 in ref 11.

experiment can convincingly determine if the true catalyst in such a system is homogeneous or heterogeneous; rather, it is necessary to perform a series of experiments, as illustrated in the more general protocol¹¹ shown in Figure 1, which is now known to be the most general, reliable approach for distinguishing homogeneous from heterogeneous catalysts.² The main features of this protocol are (1) catalyst isolation and characterization, especially by initial TEM studies; (2) kinetic studies—key experiments since catalysis is, as Halpern has noted, a “wholly kinetic phenomenon”;^{13,14} (3) quantitative catalyst poisoning experiments; and (4) the perhaps obvious, but still important, concept that the identity of the true catalyst must be consistent with all the data.

The hydrogenation of monocyclic arenes (e.g., benzene) is a difficult reaction to catalyze.^{15,16} Arene hydrogenation is typically accomplished with heterogeneous catalysts of group 8–10 metals, such as Rh/Al₂O₃ or Raney nickel,¹⁷ although the use of soluble transition-metal nanoclusters is increasing.¹⁹ The first ostensibly homogeneous benzene hydrogenation catalyst, a Ziegler-type system based on Et₃Al and Ni(II) 2-ethylhexanoate, was reported in 1963;¹⁸ in the intervening ~40 years there have been many more claims of homogeneous, transition-metal complexes capable of monocyclic arene hydrogenation catalysis.^{1,2,19,20} However, (i) there is usually little evidence to support the hypothesis that the true catalyst in these systems is homogeneous; (ii) one claimed “homogeneous” system^{21,22} based on RhCl₃ and [(C₈H₁₇)₃NCH₃]Cl has more recently been shown to be heterogeneous Rh(0)_n nanocluster catalysis;²³ and (iii) there is some evidence that several other monocyclic arene

hydrogenation systems are heterogeneous as well.² To our knowledge, the only examples of well-established,²⁴ monometallic,²⁵ homogeneous catalysts for the more difficult hydrogenation of benzene are those developed by Rothwell and co-workers based on Nb^V and Ta^V hydrido complexes.²⁶

Hence, the question of whether several Ru-complex-based benzene hydrogenation systems^{27–38} (see also Table 10.2 and Table S1 elsewhere^{1,2}) reported in the literature are truly homogeneous catalysts remains to be answered. The true catalyst in many of these systems may well be either a Ru nanocluster or bulk Ru metal, possibly present in only trace amounts and, therefore, hard to detect. Note here the point made elsewhere^{11,23} that metal-particle catalysis is the crucial alternative hypothesis,³⁹ one that must be carefully considered and ruled out before any claim of a homogeneously catalyzed reaction can be accepted for which metal-particle heterogeneous catalysis of that same reaction is well established.

The goal of the present work is to answer the following question: what is the true catalyst in benzene hydrogenations beginning with Ru(arene) precatalysts such as Ru(II)(η⁶-C₆Me₆)-(OAc)₂?^{21,27,40,41} Herein we present compelling kinetic, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and catalyst poisoning studies indicating that the true benzene hydrogenation catalyst when starting with Ru(II)(η⁶-C₆Me₆)(OAc)₂ is bulk Ru metal; we also cite key data gleaned from the original catalytic studies^{27,40} supporting this

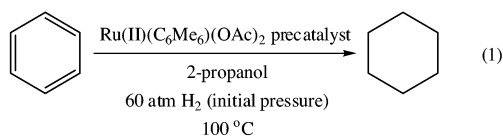
- (8) Collman, J. P.; Kosydar, K. M.; Bressan, M.; Lamanna, W.; Garrett, T. J. *Am. Chem. Soc.* **1984**, *106*, 2569.
 (9) Lewis, L. N.; Lewis, N. J. *Am. Chem. Soc.* **1986**, *108*, 7228.
 (10) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.
 (11) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891.
 (12) Lin, Y. Ph.D. Dissertation, Department of Chemistry, University of Oregon, March 1994.
 (13) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11.
 (14) Halpern, J.; Okamoto, T.; Zakhariiev, A. *J. Mol. Catal.* **1977**, *2*, 65.
 (15) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; Wiley-Interscience: New York, 1992; p 780.
 (16) Stanislaus, A.; Cooper, B. H. *Catal. Rev.—Sci. Eng.* **1994**, *36*, 75.
 (17) Augustine, R. L. *Heterogeneous Catalysis for the Synthetic Chemist*; Marcel Dekker: New York, 1996; Chapter 17.
 (18) Lapporte, S. J.; Schuett, W. R. *J. Org. Chem.* **1963**, *28*, 1947.
 (19) Widgren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *191*, 187.
 (20) Fish, R. H. *Aspects Homogeneous Catal.* **1990**, *7*, 65.
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 (23) Weddle, K. S.; Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653.

- (24) The Nb^V and Ta^V hydrido aryloxy complexes, such as [Ta{OC₆H₃-(C₆H₁₁)₂-2,6}₂(H)₂(PMe₃Ph)₂], developed by Rothwell and co-workers are well-established examples of monometallic catalysts capable of monocyclic arene hydrogenation based on the following evidence:²⁶ (i) the reduction of Nb^V or Ta^V by hydrogen to Nb(0) or Ta(0) metal particles is thermodynamically not possible under the reaction conditions; and (ii) the observed selectivity of the catalyst for the intramolecular hydrogenation of the aryloxy ligands is consistent with and strongly supportive of a homogeneous mononuclear catalyst, but difficult to explain if the true catalyst is heterogeneous (*ortho*-phenyl substituents on the aryloxy ligand are hydrogenated, while hydrogenation of phenyl rings *meta* or *para* to the aryloxy oxygen is not observed nor is hydrogenation of the phenoxide itself ever observed).
 (25) Although not soluble, Marks and co-workers’ supported (C₅Me₅)Th arene hydrogenation catalysts merit mention for their single-metal nature: Eisen, M. S.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10358.
 (26) Rothwell, I. P. *Chem. Commun.* **1997**, 1331.
 (27) Ennett, J. P. Ph.D. Dissertation, Research School of Chemistry, Australian National University, 1984.
 (28) Süß-Fink, G.; Faure, M.; Ward, T. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 99.
 (29) Johnson, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7395. These authors specifically state that they were unable to detect free hexamethylbenzene following catalytic reactions (their actual detection limits were, unfortunately and however, not stated). Even if their detection limits for free hexamethylbenzene were, say 3–5%, we commonly find^{11,23,57,58,60–63,91}—as also seen in the current study—that only a small amount of the precatalyst typically has to evolve before a highly active heterogeneous catalyst is formed, one often able to consume all of the substrate before the remaining precatalyst evolves to the heterogeneous catalyst. In addition, one of the main messages of this work, our prior work,²³ and a review of the literature of the “is it homogeneous or heterogeneous catalysis” problem² is that kinetic studies are essential to identification of the true catalyst.
 (30) Bennett, M. A.; Huang, T.-N.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 312.
 (31) Tocher, D. A.; Gould, R. O.; Stephenson, T. A.; Bennett, M. A.; Ennett, J. P.; Matheson, T. W.; Sawyer, L.; Shah, V. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1571.
 (32) Garcia Fidalgo, E.; Plasseraud, L.; Süß-Fink, G. *J. Mol. Catal. A: Chem.* **1998**, *132*, 5.
 (33) Plasseraud, L.; Süß-Fink, G. *J. Organomet. Chem.* **1997**, *539*, 163.
 (34) Dyson, P. J.; Ellis, D. J.; Welton, T.; Parker, D. G. *Chem. Commun.* **1999**, 25.
 (35) Bennett, M. A.; Ennett, J. P.; Gell, K. I. *J. Organomet. Chem.* **1982**, *233*, C17.
 (36) Bennett, M. A.; Ennett, J. P. *Organometallics* **1984**, *3*, 1365.
 (37) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2342.
 (38) Black, colloidal material is reported to form from several mononuclear Ru precatalysts used in lignin aromatic ring reduction in: James, B. R.; Wang, Y.; Alexander, C. S.; Hu, T. Q. *Chem. Ind.* **1998**, *75*, 233.
 (39) Platt, J. R. Strong Inference. *Science* **1964**, *146*, 347.

same conclusion. Our demonstration that the true catalyst is *not* a monometallic Ru complex is relevant to the broader, often vexing question in catalysis of “is the true catalyst homogeneous or heterogeneous?”^{2,42} The present studies are also of significance to organometallic chemistry,¹ nanocluster science,^{43–46} nanocluster catalysis,⁴⁷ and arene hydrogenations.¹⁹ Studies of arene hydrogenation are of broader current interest due to (i) the industrial importance of full⁴⁸ and partial^{49,50} benzene hydrogenation; (ii) the demand for cleaner burning, low-aromatic-content diesel fuels;⁵¹ and (iii) the chemically demanding problem of hydrogenating aromatic polymers^{52,53} such as polystyrene⁵³ to yield poly(cyclohexylethylene) for DVD disks and other applications.

Results

Benzene Hydrogenation Beginning with the Precatalyst Ru(II)(η^6 -C₆Me₆)(OAc)₂. The “standard conditions” for benzene hydrogenation with the precatalyst Ru(II)(η^6 -C₆Me₆)(OAc)₂, **1**,⁵⁴ in a Parr autoclave are (eq 1) 10.0 mL of benzene, 15.0 mL of 2-propanol, 40 (\pm 1) mg of **1**, 100 °C, and an initial H₂ pressure of 60 atm. These conditions are taken from the literature,^{27,40} except that the temperature is 100 °C and not the 50 °C used in the literature, for reasons that will become clear.



Catalyst Evolution Kinetic Studies. Figure 2 shows a plot of reaction progress versus time monitored by following the loss of hydrogen pressure versus time. Following a \sim 3 h

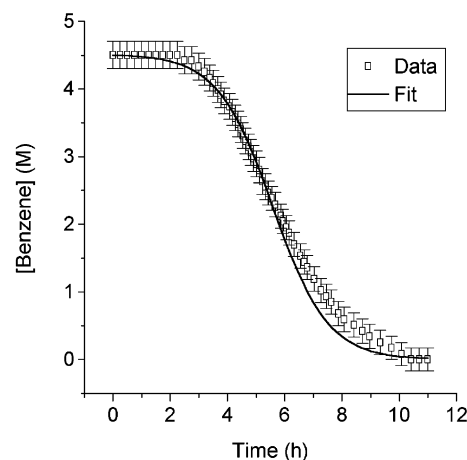


Figure 2. Data and curve-fit for a typical benzene hydrogenation experiment at 100 °C with 10 mL of benzene, 15 mL of 2-propanol, 39.8 mg of **1**, and an initial H₂ pressure of 60 atm. Following a \sim 3 h induction period, the reaction rate increases rapidly, and the reaction is complete after a total of \sim 11 h, that is, a sigmoidal curve typical of slow continuous nucleation, A \rightarrow B (rate constant k_1), then autocatalytic surface-growth, A + B \rightarrow 2B (rate constant k_2). The experimental data are well fit⁸⁹ to the analytic kinetic equations for these two processes.

induction period, the hydrogenation rate increases rapidly and is complete after a total of \sim 11 h. The experimental data are well fit to the analytic kinetic equations^{57,58} for the pseudo-elementary^{55–58} steps for *nucleation*, A \rightarrow B (rate constant k_1), and *autocatalytic surface growth*, A + B \rightarrow 2B (rate constant k_2).^{57,58} The rate constants determined from the nonlinear least-squares curve-fit in Figure 2 are $k_1 = 3.1 \times 10^{-3} \text{ h}^{-1}$ and $k_2 = 2.6 \times 10^2 \text{ M}^{-1} \text{ h}^{-1}$ (the mathematically required correction has been made to k_2 for the stoichiometry factor of 1100 as described elsewhere,^{57,58} but not for the “scaling factor”; that is, no correction has been made for the changing number of Ru atoms on the growing metal surface^{57–59}). The experiment shown in Figure 2 was performed a total of six times (by two different researchers), using three different batches of **1** (synthesized by two different researchers). In every case we observed *sigmoidal kinetics*, as seen in Figure 2. Such a sigmoidal, autocatalytic curve and curve-fit to A \rightarrow B and A + B \rightarrow 2B kinetics are very strong evidence for the in situ formation of metal(0) from a soluble transition-metal complex under H₂ given the prior work connecting such kinetics to metal(0) catalyst formation (previously metal(0) nanoclusters).^{2,11,23,57,58,60–63}

An interesting, telling observation from the six experiments about whether the catalyst is homogeneous or heterogeneous is that the experimentally determined k_1 varies by 3 orders of magnitude, from $4.8 \times 10^{-1} \text{ h}^{-1}$ to $5.4 \times 10^{-4} \text{ h}^{-1}$. The observation of irreproducible kinetics in the nucleation rate constant, k_1 , is consistent with and highly supportive of the presence of *heterogeneous*^{64,65} nucleation en route to the formation of a *heterogeneous* catalyst.² This follows since the nucleation step is typically the energetically most difficult part in nanocluster formation reactions. Heterogeneous nucleation

- (40) Bennett, M. A.; Ennett, J. P. *Inorg. Chim. Acta* **1992**, 198–200, 583.
 (41) One of us (M.A.B.) has been aware of and concerned with the “is it homogeneous or heterogeneous catalysis” issue since the original^{27,40} catalytic studies with Ru(II)(η^6 -C₆Me₆)(OAc)₂. A telling quote from our earlier work²⁷ is “The reduction of benzene to cyclohexane using arene ruthenium(II) catalysts occurs at high hydrogen pressure under a variety of conditions. The homogeneity of these catalytic reactions could not be established unequivocally, and in some cases decomposition to give a heterogeneous component was observed.” However, at the time that work was being performed, reliable methods for answering the “homogeneous or heterogeneous” question were not yet available. Since others of us (R.G.F. and co-workers) developed a more general approach to the “is it homogeneous or heterogeneous catalysis” question in 1994,¹¹ we decided to combine forces and see if that methodology could discover the true catalyst in benzene hydrogenations beginning with the precatalyst Ru(II)(η^6 -C₆Me₆)(OAc)₂.
 (42) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, 31, 485.
 (43) Schmid, G. *Chem. Rev.* **1992**, 92, 1709.
 (44) Lewis, L. N. *Chem. Rev.* **1993**, 93, 2693.
 (45) Bradley, J. S. In *Clusters and Colloids. From Theory to Applications*; Schmid, G., Ed.; VCH: New York, 1994; pp 459–544.
 (46) Finke, R. G. In *Metal Nanoparticles: Synthesis, Characterization, and Applications*; Feldheim, D. L., Foss, C. A., Jr., Eds.; Marcel Dekker: New York, 2001; Chapter 2.
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 (48) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis, 2nd ed.; The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1992.
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 (50) Hu, S.-C.; Chen, Y.-W. *J. Chin. Inst. Chem. Eng.* **1998**, 29, 387.
 (51) Stanislaus, A.; Cooper, B. H. *Catal. Rev.—Sci. Eng.* **1994**, 36, 75.
 (52) Hu, T. Q.; James, B. R. *J. Pulp Pap. Sci.* **2000**, 26, 173.
 (53) Tullo, A. New DVDs Provide Opportunities for Polymers. In *Chem. Eng. News* **1999**, 77, 14.
 (54) Unlike the literature,³¹ we formulate **1** as the anhydrous complex. The justification for this is that **1** is synthesized and stored in a drybox and because we have no evidence for waters of hydration. Further comments are provided in the Materials section.

- (55) Noyes, R. M.; Field, R. J. *Acc. Chem. Res.* **1977**, 10, 273.
 (56) Field, R. J.; Noyes, R. M. *Acc. Chem. Res.* **1977**, 10, 214.
 (57) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, 119, 10382.
 (58) Widegren, J. A.; Aiken, J. D., III; Özkar, S.; Finke, R. G. *Chem. Mater.* **2001**, 13, 312.
 (59) Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, 9, 3083.
 (60) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, 116, 8335.
 (61) Aiken, J. D., III; Finke, R. G. *Chem. Mater.* **1999**, 11, 1035.
 (62) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, 124, 5796.
 (63) Özkar, S.; Finke, R. G. *Langmuir* **2003**, 19, 6247.

is the typically lower ΔG^\ddagger , and hence faster, nucleation that occurs from heterogeneous—and thus variable—surfaces such as metal autoclave parts, trace metal deposited on reactor surfaces, glass surfaces, and other, nonhomogeneous, non-solution-based sources of nucleation.^{64,65} By comparison, the k_1 for homogeneous nucleation of the formation of $\text{Ir}(0)_n$ nanoclusters prepared from the well-characterized, compositionally precise, precursor $[\text{Bu}_4\text{N}]_5\text{Na}_3[(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{11,58,59,60}$ has never varied by more than about an order of magnitude ($\pm 10^{1.2}$),⁶⁶ even over a 7 year period and in multiple researchers' hands. In addition, that variability of k_1 there is understood: variations in the trace water, acetone impurities, and precursor purity are the origins of the $\pm 10^{1.2}$ variations in k_1 .^{11,57,58,60} Since the variables of water and solvent purity are controlled in the present case of arene hydrogenation beginning with the precatalyst $\text{Ru}(\text{II})(\eta^6\text{-C}_6\text{Me}_6)(\text{OAc})_2$, **1**, the 10^3 variability in k_1 is strong evidence for the in situ formation of a heterogeneous catalyst involving heterogeneous nucleation.⁶⁷

The value of k_2 varies nearly 3-fold, from 1.3×10^2 to $3.7 \times 10^2 \text{ M}^{-1} \text{ h}^{-1}$, and thus more than the $\pm 15\%$ we typically see for discrete nanocluster catalysts.^{57–63} This result is consistent with the formation of insoluble bulk metal as catalyst (vide infra) with its *variable surface area* and, hence, variable catalytic activity. Noteworthy here is Epstein's warning that imperfect mixing often has large effects on autocatalytic reactions,⁶⁸ a prediction we have documented in the nanocluster area;⁶⁹ accordingly, our autoclave is well stirred at 600 rpm to minimize any mixing problems in the present studies.

Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS) Data. As expected,^{27,40} the reaction solution from the standard conditions benzene hydrogenation experiment with **1** had changed from yellow-orange to a dark red-brown, and a dark film coated the glass liner, impeller, and the other parts of the reactor in contact with the reaction solution. Analysis of the red reaction solution by TEM failed to show any soluble nanoclusters; only micrometer-size particles were observed (see Figure S1 of the Supporting Information for an example micrograph).⁷⁰ The dark film coating the glass liner, etc., was confirmed to be $\text{Ru}(0)$ metal by XPS (see Figure S2 of the Supporting Information).

- (64) Strey, R.; Wagner, P. E.; Viisanen, Y. *J. Phys. Chem.* **1994**, *98*, 7748.
 (65) A very nice example showing how *soluble* metal particle, seeded growth gives kinetically faster, well-controlled nanocluster formation is: Yu, H.; Gibbons, P. C.; Kelton, K. F.; Buhro, W. E. *J. Am. Chem. Soc.* **2001**, *123*, 9198. Note, however, that these authors use the term “heterogeneous” in their title (“Heterogeneous Seeded Growth...”) to mean *different metal* nucleation, an unfortunate usage as it will get confused with the earlier, well-defined term heterogeneous nucleation.⁶⁴
 (66) For example, the independently determined values of k_1 in refs 57 and 58 are 5.6×10^{-4} and $1.0 \times 10^{-2} \text{ h}^{-1}$, respectively, different by $\pm 10^{1.2}$, as large a difference in k_1 as we have seen.
 (67) Of interest here is that the *experimental* $\pm 10^3$ variability is the same as the *reliability of current nucleation theory*, Oxtoby having noted “Nucleation theory is one of the few areas of science where agreement between predicted and measured rates to within several orders of magnitude is considered a major success”: Oxtoby, D. W. *Acc. Chem. Res.* **1998**, *31*, 91.
 (68) Epstein, I. R. *Nature* **1995**, *374*, 321 (The Consequences of Imperfect Mixing in Autocatalytic Chemical and Biological Systems).
 (69) Slow H_2 (gas) to H_2 (solution) mass transfer results in very poorly formed, broad dispersions of nanoclusters in a system that otherwise produces near-monodisperse nanoclusters: Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 9545.
 (70) Rigorously, TEM cannot be used to rule out the presence of a nanocluster catalyst; however, the absence of nanometer-size particles in these micrographs, under conditions where we have never failed to see nanoclusters when we expected them, plus the enormous sensitivity of the TEM to see even individual nanoclusters, is strong evidence that nanocluster catalysis is not important in the present, $\text{Ru}(\text{II})(\eta^6\text{-C}_6\text{Me}_6)(\text{OAc})_2$ -derived system.

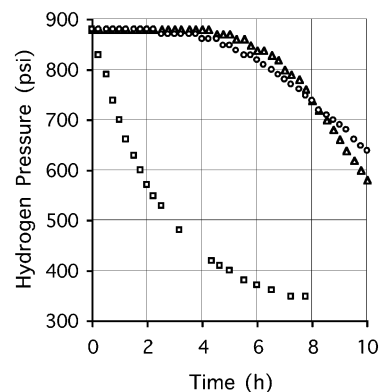


Figure 3. Plot of the hydrogen pressure vs time data for three separate benzene hydrogenation reactions. The triangles (Δ) show pressure vs time data for a standard conditions hydrogenation starting with **1**; that reaction was stopped after 10 h, at which point it was 55% complete. After the hydrogenation reaction with **1**, the final dark red reaction solution was separated from the metallic film, and in separate experiments, each was used to catalyze a benzene hydrogenation reaction. The squares (\square) show the data for the hydrogenation with the metallic film, while the circles (\circ) show the data for the hydrogenation with the dark red filtrate. With the metallic film as catalyst, the hydrogenation starts without an induction period and proceeds at a kinetically competent rate. With the dark red filtrate as catalyst, the hydrogenation begins after an hours-long induction period. These experiments show that, within experimental error, *all* of the hydrogenation activity observed for this system is accounted for by the bulk metal film.

Testing the Kinetic Competence of the Metallic Film and the Red Reaction Solution. A standard conditions benzene hydrogenation experiment was started and was allowed to proceed to 55% completion (Figure 3, the triangles); the rate of H_2 uptake was 80 psi/h at that point. Next, a benzene hydrogenation experiment was performed using only the dark red metallic film as catalyst. The hydrogen uptake proceeded rapidly and without a detectable induction period (Figure 3, the squares), showing that the metallic film is indeed an active catalyst for benzene hydrogenation. Additionally, the rate of hydrogen uptake immediately following 55% completion was the same as before, 80 psi/h, *showing that the metallic film is a kinetically competent catalyst in the present case*. Similar experiments were performed following two other benzene hydrogenations with **1**, and comparable results were obtained for those experiments as well (i.e., the metallic film hydrogenated benzene rapidly with no detectable induction period).

After the removal of any traces of *bulk* metal with a micropore filter, the catalytic activity of the dark red reaction solution was also tested. Hydrogenation activity was observed *only after an induction period of several hours* (Figure 3, the circles), similar to the hydrogenation reaction in which **1** was used as the precatalyst. A dark film coated the glass liner and the wetted reactor parts at the end of this reaction. In short, the solution exhibited no catalytic activity until and unless a metal film was remade. The soluble Ru complexes detectable by ^1H NMR in the red reaction solution (see the Supporting Information as well as elsewhere²⁷) are, then, just precursors to the heterogeneous catalyst.

Mercury-Poisoning Experiment. The ability of added $\text{Hg}(0)$ to poison metal(0) heterogeneous catalysts^{4,71,72} by amalgamating the metal catalyst or adsorbing on its surface has been known for >80 years;⁷³ this is the single most widely used test of homogeneous versus heterogeneous catalysis.² The suppression of catalysis by $\text{Hg}(0)$ is evidence for a heterogeneous catalyst;

if Hg(0) does not suppress catalysis, the implication is that the catalysis is homogeneous. The Hg(0)-poisoning experiment is easy to perform, *but is not definitive by itself, and not universally applicable* because Hg(0) reacts with some single-metal complexes.^{4,74–77} Also, this test inherently provides negative evidence (no poisoning) in cases where the catalyst is homogeneous; this is a problem, since experience shows that one must ensure intimate contact of the Hg(0) bead with the entire reactor—by using a large excess of Hg(0) in a well-stirred solution^{11,23}—to avoid erroneous conclusions.⁷¹ Hence, controls with authentic nanoclusters of the metal in question are crucial in the event that no change in catalytic activity is seen upon adding Hg(0).²

A standard conditions benzene hydrogenation experiment with **1** was started as described above. After about 30% conversion, the reaction was stopped, ~320 equiv of Hg(0) (vs Ru) was added, and the reaction was then restarted, as shown in Figure 4. The addition of Hg(0) *completely eliminated further catalysis* (i.e., for the next 13 h over which it was monitored). This result is consistent with and strongly supportive of heterogeneous metal(0) catalysis.^{2,4,11,23} Since the activity was completely poisoned, this result also requires that the heterogeneous metal(0) catalyst is the only active species present. A control experiment⁷⁷ showed that Hg(0) does not react with the precatalyst (see the Supporting Information for details).

Quantitating the Amount of Precatalyst Decomposition by ¹H NMR. To estimate the amount of Ru metal that forms from **1** during benzene hydrogenation, we used ¹H NMR to estimate the amount of free hexamethylbenzene in the reaction solutions. Typically we find that only a small amount of the precatalyst evolves to the true, highly active heterogeneous catalyst.^{23,57,58,60–62}

At the end of the experiment shown in Figure 2 about 40% of the precatalyst has been reduced to Ru(0) metal (see the

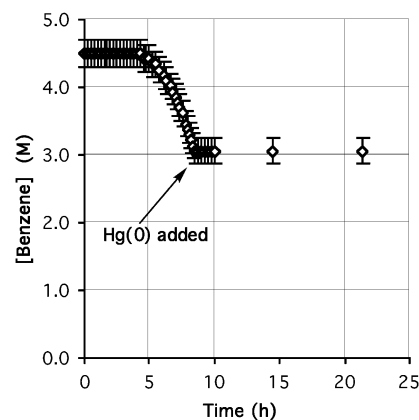


Figure 4. Plot of the benzene concentration vs time for a mercury-poisoning experiment.

Supporting Information for further details). At the end of the initial benzene hydrogenation reaction shown in Figure 3 (i.e., a benzene hydrogenation at 55% completion beginning with **1**), <15% of the precatalyst has been reduced to Ru(0) metal. This result is, again, consistent with Ru(0) metal as the true catalyst.

The above result illustrates an important logic point: the ability to isolate a large percentage of the precatalyst complex (or some other soluble metal complex) following catalysis is *not* good evidence for homogeneous catalysis. Such a result *does not* rule out the possibility that a small percentage of highly active nanoclusters or bulk metal is responsible for the observed catalysis (see elsewhere^{3,11} for further discussion of this point). The failure to recognize this point in several literature reports^{28,29,78–80} suggests that misidentification of the true catalyst in those systems may have occurred.

Benzene Hydrogenation at $\ll 100$ °C. For benzene hydrogenations at $\ll 100$ °C we observe very long induction periods (i.e., there is no significant nucleation at $\ll 100$ °C). For example, under the exact literature conditions^{27,40} of 50 °C there was no observable activity during 17 h of reaction (as monitored by H₂ pressure and GLC); the reaction solution became dark red, but, significantly, no visible metallic film formed and no catalytic activity was seen. An experiment at 75 °C also failed to give significant activity during the first 22 h of reaction. However, *after raising the temperature to 100 °C*, both of these benzene hydrogenation reactions went to completion in <12 additional hours and both formed metallic films. The exact difference(s) between our work and the earlier work^{27,40} is readily explainable and, again, evidence for Ru(0) catalysis: the *expected* variability here is due to the variable source and amount of heterogeneous nucleation in the crucial k_1 step.^{57,58} We clean and test the reactor for background benzene hydrogenation catalytic activity (see the Experimental Section) to minimize the more facile, lower ΔG^\ddagger , heterogeneous nucleation from trace Ru(0) metal,^{64,65} for example. We also use Monel metal parts and a glass liner in the present studies with the intent of minimizing the amount of heterogeneous nucleation in our autoclave reactor. Hence, the most likely explanation for the 50 °C versus 100 °C nucleation and growth pathways in the literature versus the present study, respectively, is that larger

- (71) The Hg(0)-poisoning experiment is occasionally performed improperly and with a lack of understanding of what this experiment is designed to test. In one literature example,²⁸ a solution of *precatalyst* was stirred with Hg(0) for 1 h, the solution was filtered *removing the Hg(0)*, and a catalytic hydrogenation reaction was then started. The hydrogenation proceeded with the same catalytic activity as an experiment in which Hg(0) was never present. This was then used—erroneously!—to rule out the presence of a nanocluster catalyst. The obvious problem with this experiment is that the Hg(0) was removed by filtration *before the catalytic reaction was allowed to start*, that is, *before any metal-particle heterogeneous catalyst was allowed to be formed*. As performed, this experiment shows only that the *precatalyst* does not react with Hg(0). One needs to add Hg(0) to a solution that already has been shown to be active. In the above example, the Hg(0) should have remained in the reaction solution for the duration of the catalytic reaction or have been added after the catalytic reaction had already begun, as done elsewhere.^{11,23}
- (72) For a hydrogenation reaction, the following protocol is recommended. Allow the catalytic hydrogenation reaction to proceed to ~50% completion, release the H₂ pressure, add the (excess of) Hg(0) to the reaction solution, let the reaction solution stir so that the Hg(0) has a chance to contact any and all metal particles that may be present, repressurize the reactor with H₂, and then check for catalytic activity.^{11,23}
- (73) Paal, C.; Hartmann, W. *Chem. Ber.* **1918**, *51*, 711.
- (74) van Asselt, R.; Elsevier, C. J. *J. Mol. Catal.* **1991**, *65*, L13.
- (75) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 126.
- (76) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 3693.
- (77) Hg(0) is probably most effective in poisoning metals that form an amalgam, such as Pt, Pd, and Ni; metals that do not form amalgams with Hg(0), such as Ir, Rh, and Ru, may be more difficult to poison with Hg(0).⁴ Hence, if the addition of Hg(0) to the reaction solution suppresses the catalytic activity, one should perform a control experiment showing that the precatalyst complex does not react with Hg(0); if Hg(0) does react with the precatalyst, then this test becomes ambiguous. Similarly, if the addition of Hg(0) to the reaction solution has little effect on the catalytic activity, one should perform a control experiment showing that an authentic heterogeneous catalyst of the same metal is poisoned under the identical conditions.

(78) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324.

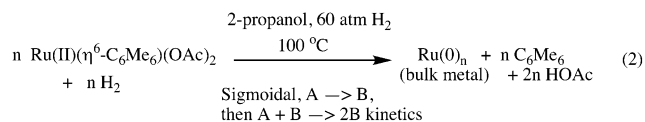
(79) Bennett, M. A.; Huang, T.-N.; Smith, A. K.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1978**, 582.

(80) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1987**, *109*, 174.

amounts of metallic Ru or other nucleation sites are present in the literature reactor, resulting in even more facile heterogeneous nucleation in that case.

Another probable source of heterogeneous nucleation also exists with the Ru(II)(η^6 -C₆Me₆)(OAc)₂ precatalyst: traces of a black precipitate, possibly Ru(0), are formed during one stage of its preparation. Hence, a benzene hydrogenation with a low-purity batch of precatalyst (which visibly contained some of the black precipitate and which was only 74% pure by ¹H NMR) was deliberately performed in anticipation that it would show a higher *k*₁ value due to the additional heterogeneous nucleation present. Indeed, a standard conditions hydrogenation at 100 °C yielded a rate constant for nucleation of *k*₁ = 4.8 × 10⁻¹ h⁻¹, >30 times higher than any of the values of *k*₁ obtained with 96–97% pure precatalyst. A lengthy induction period of >24 h was still seen with this impure precatalyst at 50 °C, however. These experiments show just how crucial the nucleation process is, and how hard it is to control, when it is primarily heterogeneous. In summary, the shorter induction periods (larger *k*₁ values) for the literature, in comparison to our longer induction periods (smaller *k*₁ values) under conditions that strive to keep the heterogeneous nucleation to a minimum (i.e., so as to allow any homogeneous catalyst every opportunity to form), is another strong piece of evidence for heterogeneous nucleation en route to a heterogeneous catalyst.

A very interesting, novel part of the present studies is the demonstration that the A → B, then A + B → 2B kinetic scheme quantitatively fits the observed sigmoidal kinetic curves for the metal deposition reaction, eq 2. This *quantitative accounting for the full kinetic curve*, in solution precursor decomposition routes or CVD (chemical vapor deposition) routes to metal(0) thin films, has not been previously reported in any study we can find, despite the common occurrence of autocatalysis.^{81–83} In fact, and despite their significance, kinetic studies of metal film formation are relatively rare,^{82–84} perhaps due to the problems in monitoring such CVD or solution deposition reactions in real time.⁸⁵ Another novel observation is that the kinetic curves for *heterogeneous nucleation* and the *formation of bulk Ru(0)* metal have the same sigmoidal shape and are well fit by the A → B, then A + B → 2B kinetics that are observed for *homogeneous* nucleation to form *soluble transition-metal nanocluster catalysts*.⁵⁷



Discussion

The more general approach for distinguishing homogeneous and heterogeneous catalysts, Figure 1, is a useful guide for the following discussion. The experiments in the first “prong” of Figure 1, which involve catalyst isolation and characterization and emphasize early use of TEM, are not intended to unequivocally identify the true catalyst; rather, they are intended as scouting experiments to determine if metal particles form under the catalytic conditions. There is a key point regarding the observation of bulk metal when starting with a single-metal precatalyst: this demands *either* that nanoclusters were formed en route to the bulk metal *or* that heterogeneous nucleation has occurred, since there are no other known ways to go from a monometallic complex to bulk metal.¹¹ Hence, in such cases highly active,⁸⁶ completely soluble, and to the eye apparently “homogeneous”^{11,60,61} nanoclusters are the highest priority hypotheses for the true catalyst demanding testing.²

In benzene hydrogenations with **1** as the precatalyst, the in situ formation of bulk metal is seen as a dark film on the glass liner and the other, wetted reactor parts; verification that the film is indeed bulk Ru(0) metal was accomplished using XPS. TEM, the single most powerful and broadly applicable method to test for the presence of nanoclusters,² failed to detect nanometer-size particles in the evaporated reaction solution in the present case. *This is the expected result* due to the complete lack of any nanocluster stabilizer in this system. Note that the potential, but weak, stabilizer acetate becomes protonated (yielding HOAc) during the reduction of the precatalyst (eq 2).⁸⁷ Consequently, only the conjugate acid, acetic acid, is present, and it is neither known nor expected to be a nanocluster stabilizer.⁸⁸

To determine which of the species present (soluble Ru complexes, bulk Ru(0), or possibly unstable, transient Ru(0) nanoclusters) is responsible for the observed catalysis, one must turn to kinetic experiments (the second prong of the method shown in Figure 1), the source of the most compelling evidence for the identity of the true catalyst. Three observables containing kinetic information help identify the present case as heterogeneous rather than homogeneous: (i) the observation of induction periods and sigmoidal kinetics, the kinetic fingerprints for metal(0) formation from homogeneous precursors; (ii) the ±10³ kinetic irreproducibility in *k*₁ indicative of heterogeneous nucleation; and (iii) the testing of the resultant solutions and metal-coated reactor parts for their kinetic competence. Note here that if an induction period is observed, then the complex added to the reaction must actually be a *precatalyst*. That is, if the overall kinetics are sigmoidal, and if the kinetics can be fit to the A → B nucleation, and A + B → 2B autocatalytic surface-

- (81) Lead papers citing autocatalysis in metal film growth: (a) Lee, T. R.; Whitesides, G. M. *Acc. Chem. Res.* **1992**, *25*, 266. (b) Lee, T. R.; Laibinis, P. E.; Folkers, J. P.; Whitesides, G. M. *Pure Appl. Chem.* **1991**, *63*, 821. (c) Chae, Y. K.; Komiyama, H. *J. Appl. Phys.* **2001**, *90*, 3610. (d) Kellerman, B. K.; Chason, E.; Adams, D. P.; Mayer, T. M.; White, J. M. *Surf. Sci.* **1997**, *375*, 331. (e) Adams, D. P.; Mayer, T. M.; Chason, E.; Kellerman, B. K.; Swartzentruber, B. S. *Surf. Sci.* **1997**, *371*, 445. (f) Crane, E. L.; You, Y.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **2000**, *122*, 3422.
- (82) Kinetic studies of autocatalytic metal film growth: (a) Xue, Z.; Thridandam, H.; Kaesz, H. D.; Hicks, R. F. *Chem. Mater.* **1992**, *4*, 162. (b) See also their short review: Zinn, A.; Niemer, B.; Kaesz, H. D. *Adv. Mater.* **1992**, *4*, 375.
- (83) Kinetics of the related topic of autocatalytic *electrochemical* metal film growth: (a) Lyamina, L. I.; Tarasova, N. I.; Gorbunova, K. M. *Elektrokhimiya* **1979**, *15*, 1615. (b) Schreiber, R.; Basaez, L.; Gardiazabal, I.; Gomez, H.; Cordova, R.; Quierolo, F. *Boletín de la Sociedad Chilena de Química* **1991**, *36*, 65.
- (84) Two superb papers on the kinetic and mechanistic details of redox transmetalation reactions in metal thin-film formation, specifically Pd(hfac)₂ + Cu(0) → Pd(0) + Cu(hfac)₂, are: (a) Lin, W.; Wiegand, B. C.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1996**, *118*, 5977. (b) Lin, W.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1996**, *118*, 5988.
- (85) The growth of Mo(0)_n on Au(111) deposited from Mo(CO)₆ has been monitored at selected times by STM: Song, Z.; Cai, T.; Rodriguez, J. A.; Hrbek, J.; Chan, A. S. Y.; Friend, C. M. *J. Phys. Chem. B* **2003**, *107*, 1036.

(86) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8803.

(87) We cannot rule out the possibility that hydrogen transfer from 2-propanol is involved in precatalyst reduction even though a high pressure of H₂ is present. If that is indeed the case, then the relevant equation is (CH₃)₂CHOH + Ru(II)(η^6 -C₆Me₆)(CH₃COO)₂ → Ru(0) + C₆Me₆ + 2CH₃COOH + acetone. We thank a referee for pointing out this possibility.

(88) Consistent with this argument, the simple addition of a noncoordinating base such as Proton Sponge produces a much better nanocluster stabilizer: Özkar, S.; Finke, R. G. *Langmuir* **2002**, *18*, 7653.

growth, kinetic scheme that has been previously elucidated for transition-metal nanocluster formation under H_2 ,^{2,11,19,23,57,58,60–63} then that is as compelling a single piece of evidence as exists for the in situ formation of a heterogeneous catalyst, at least for hydrogenation catalysis.² The kinetics are telling us that the precatalyst, “A”, $Ru(II)(\eta^6-C_6Me_6)(OAc)_2$, is *not* the catalyst, but must, instead, be converted to the catalyst, “B”, before catalysis is observed! Note that the curve-fit in Figure 2 is excellent until late in the reaction, where the loss of catalyst surface area due to bulk metal formation, for example, would account for the slower-than-predicted rate.^{89,90}

The experiment shown in Figure 3 demonstrates that the isolated metallic film is a kinetically competent catalyst for the hydrogenation of benzene. On the other hand, the dark red reaction solution catalyzed benzene hydrogenation only after another induction period (leading to the observation of fresh $Ru(0)$); therefore, any soluble species that form during the reaction are simply precursors to the true, in this case heterogeneous, catalyst. *Note how the single kinetic experiment shown in Figure 3 compellingly identifies bulk Ru metal as the true catalyst*; hence, such kinetic studies must be performed in any catalytic hydrogenation system in which a metallic precipitate forms.

The third prong of the method shown in Figure 1 emphasizes quantitative poisoning studies with CS_2 or other ligand-based poisons.⁹¹ As discussed elsewhere,² if one can show that $\ll 1$ equiv of CS_2 per metal present completely poisons catalysis, that is compelling evidence for a heterogeneous catalyst in which only a fraction of the metal is on the surface of the metal particle.⁹² Note that a homogeneous catalyst typically must have ≥ 1 site of coordinative unsaturation for catalytic activity, so that a much different, readily distinguished CS_2 /metal poisoning ratio of ≥ 1 is expected. One serious limitation of the quantitative CS_2 -poisoning experiment, however, is that exothermically binding ligands will dissociate from a metal-particle heterogeneous catalyst at higher temperatures.^{93–95} Indeed, a control experiment showed that active $Rh(0)_n$ nanoclusters, which were completely poisoned by 0.05 equiv of CS_2 (vs Rh) at 25 °C, were not poisoned at 100 °C (see the Supporting Information for the details of that experiment). Hence, we were forced to turn to the more commonly used, but unfortunately *nonquantitative*, $Hg(0)$ -poisoning experiment where an excess of $Hg(0)$

must be used so that the useful poison/metal ratio cannot be obtained. Consistent with a heterogeneous catalyst, a previously active catalyst was poisoned completely following the addition of ~ 320 equiv of $Hg(0)$ with rapid stirring to ensure good mixing (Figure 4).

The fourth prong of the method shown in Figure 1 emphasizes the perhaps obvious, but crucial, concept that the identity of the true catalyst must be consistent with all the data.⁹⁶ The hypothesis that the true catalyst is bulk $Ru(0)$ metal is consistent with all the data presented herein. Moreover, it (and only it) explains a key observation in the prior literature^{27,30,40,79} of arene hydrogenation beginning with $Ru(\text{arene})$ complexes: *visible precatalyst decomposition (to form metallic precipitates, presumably) is commonly observed in the more active systems.*^{27,79} Only heterogeneous catalysis can account for all the observed data.

Summary and Conclusions

Compelling product, kinetic, $Hg(0)$ poisoning, and other evidence have been presented showing that bulk Ru metal is the true catalyst in the benzene hydrogenation system formed from $Ru(II)(\eta^6-C_6Me_6)(OAc)_2$ as the precatalyst. It is likely that other benzene hydrogenation catalysts derived from $Ru(\text{arene})$ precatalysts are also heterogeneous (see the listing of these catalysts in the Introduction);² we are testing some of these in separate experiments.⁹⁷ Significantly, the paradigm in Figure 1 continues to be the currently most reliable and generally applicable method to dissecting the “is it homogeneous or heterogeneous catalysis” problem.^{2,23}

Conditions Favoring Metal-Particle Heterogeneous Catalysis and Telltale Indicators. The formation of a metal-particle heterogeneous catalyst from a monometallic precatalyst is more likely under certain circumstances. As discussed in greater detail elsewhere,² the conditions under which a heterogeneous catalyst is likely to form include (i) when easily reduced transition-metal complexes are used as precatalysts; (ii) when forcing reaction conditions are employed [higher temperatures in particular appear to be thermodynamically conducive to metal-particle formation since the $nM(0)L_x \rightleftharpoons M(0)_n + n \cdot xL$ equilibrium is probably often endothermic and thus driven to the right (i.e., toward nanoclusters) at higher temperatures²]; (iii) when nanocluster stabilizers are present;⁶² and (iv) when *monocyclic* arene hydrogenation is observed, due to the typically more forcing conditions required. Other telltale signs of heterogeneous catalysis include² (iv) the formation of dark reaction solutions and metallic precipitates;⁹⁸ and especially (v)

(89) The curve-fit is easily within experimental error of the data for at least the first half of the benzene hydrogenation reaction. However, at longer times the hydrogenation is slower than predicted by the curve-fit. Deviations between the curve-fit and the data near the end of the reaction can occur for a variety of understood reasons. For example, the pseudoelementary step method^{57,58} used herein assumes that the catalytic reaction is zero order in substrate. Obviously, at some point later in the reaction, when the substrate concentration approaches zero, this assumption is no longer true. Also, any deactivation process that occurs to a significant extent on the time scale of the experiment will cause deviations such as those seen in Figure 2. For example, a loss of catalyst surface area due to (observed) bulk metal formation will cause the reaction to be slower than predicted.⁹⁰ For these reasons, only the first half of the data in Figure 2 was used to generate the curve-fit, a precaution we typically employ.^{57,58}

(90) Hornstein, B. J.; Finke, R. G. Submitted for publication.

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

(92) For example, 3.5 mol % CS_2 completely poisons a commercial Rh/Al_2O_3 catalyst with an average metal-particle diameter of about 3.6 nm.⁹¹ Geometry is one reason that so little poison is needed: only about 1/3 of the metal atoms are on the surface of a metal particle this size; another reason is that ≥ 5 adjacent surface atoms can be poisoned by a single molecule of even the relatively small poison CS_2 .⁹¹

(93) Gonzalez-Tejuca, L.; Aika, K.; Namba, S.; Turkevich, J. *J. Phys. Chem.* **1977**, *81*, 1399.

(94) Frety, R.; Da Silva, P. N.; Guenin, M. *Catal. Lett.* **1989**, *3*, 9.

(95) Butt, J. B. *Catal. Sci. Technol.* **1987**, *6*, 1.

(96) In the past, the absence of H–D scrambling and the formation of all-*cis*- $C_6H_6D_6$ from $C_6H_6D_2$ or $C_6D_6H_2$ have been taken as strong supporting evidence for a homogeneous process.⁷⁸ For example, the formation of all-*cis*- $C_6H_6D_6$ with **1** as the precatalyst was reported previously,²⁷ but H–D scrambling does occur using $[Ru(\eta^6-C_6Me_6)(\eta^4-C_6Me_6)]$, a catalyst previously believed to be homogeneous.²⁹ The bottom line here is that these criteria are *not* reliable indicators of whether the catalyst is homogeneous or heterogeneous and, hence, are *not recommended*, especially now that the now proven methodology in Figure 1 is available. Note also that it is unlikely that further studies of these criteria will ever make them easy to use or reliable (i.e., in comparison to the methods in Figure 1). This follows since one would need, for each system at hand, to have authentic homogeneous and heterogeneous (i.e., both nanocluster and bulk metal) catalysts of the same metal, ligands, and nanocluster stabilizers available for the needed control studies; that is, one would have to have *resolved* the “is it homogeneous or heterogeneous catalysis?” question *before* such criteria could be reliably used! The conceptual significance of, and the “Catch 22” situation present by, such up-front control experiments with authentic catalysts is presented and discussed as the topmost part of Figure 5 elsewhere.¹¹

(97) Hagen, C.; Finke, R. G. Experiments in progress.

the observation of induction periods and sigmoidal kinetics, the kinetic fingerprint of metal(0) formation from monometallic precatalysts under H_2 .^{57,58}

Conditions that favor *homogeneous*, monometallic catalysts are becoming apparent² and also deserve mention: (a) lower temperatures; (b) higher concentration of good ligands (e.g., CO, PR_3 , bidentate phosphines, etc.); and (c) reactions that require oxidation states of the metal ≥ 1 (i.e., when other ligands that stabilize colloids in higher oxidation state metals, such as O^{2-} , OH^- , and so on, are not present). A good example here is a study testing PVP (i.e., poly(vinylpyrrolidone))-stabilized Rh nanoclusters as a precatalyst for MeOH + CO to give CH_3CO_2H in the presence of I^- (i.e., for the Monsanto acetic acid process). Not unexpectedly, the true catalyst in this system is the well-established Rh(I) complex $Rh^I(CO)_2I_2^-$, produced by MeI oxidation of the Rh(0) nanoclusters under CO pressure.⁹⁹ Kinetic data are again the key: the PVP-stabilized Rh(0) nanoclusters are considerably less reactive than is $Rh^I(CO)_2I_2^-$; the rate upon recycling the Rh(0) nanocluster precatalyst increases concomitant with the increase in the concentration of $Rh^I(CO)_2I_2^-$, which builds to $\sim 29\%$ of the total Rh, and the activation energy, E_a , for the reaction beginning with the Rh(0) nanoclusters is the same within experimental error as the E_a for $Rh^I(CO)_2I_2^-$.

The More General Problem of “Is It Homogeneous or Heterogeneous Catalysis?” The work herein and a recent review² indicate that it is important to use the paradigm in Figure 1 to test a variety of other systems where the in situ formation of a heterogeneous catalyst from a homogeneous precatalyst is suspected. A list and brief description of about 30 such systems are available as Table S1 of the Appendix elsewhere.²

Also, although the focus of the present paper was hydrogenation catalysis, the problem of distinguishing homogeneous and heterogeneous catalysis is not limited to hydrogenation reactions. In situ formation of metal-particle heterogeneous catalysts has also been identified as an issue in hydrosilylation reactions,^{9,10,76} ring-opening polymerization catalysis,¹⁰⁰ alkane activation,¹⁰¹ and C–C coupling reactions.¹⁰² The pervasiveness of the “homogeneous or heterogeneous” problem in catalytic science is further illustrated by the identification of *homogeneous species* as the true catalysts for initially *heterogeneous* oxidation catalysts based on molecular sieves,^{103,104} and for carbonylation and Heck coupling catalysts where Pd/C and Pd/ Al_2O_3 are the *precatalysts*.¹⁰⁵ Hence, the present work addressing the “is it homogeneous or heterogeneous catalysis” problem is just one component of a mechanistic issue of much broader significance.

The $A \rightarrow B$, then $A + B \rightarrow 2B$ Mechanism Also Fits Bulk Metal Formation via Heterogeneous Nucleation. An important finding herein is that the $A \rightarrow B$, then $A + B \rightarrow 2B$,

nucleation then autocatalytic surface-growth mechanism accounts quantitatively for the heterogeneous nucleation and autocatalytic kinetics of formation of the bulk metal film produced in the present studies. Hence, both nanocluster formation from homogeneous precatalysts via homogeneous nucleation^{57,58} and heterogeneous nucleation to bulk metal film now fall under the umbrella of this mechanism. One can ask if soluble nanoclusters are not intermediates in the formation of the metal film as well? Soluble nanoclusters as intermediates were considered, but conditionally ruled out in the present case since none could be detected by TEM, even though nanoclusters are readily and routinely detected in our hands by this method^{11,23,57–63,86,91} and at concentrations we estimate as low as 10^{-12} M.² The significance of this finding is that the detailed mechanism elucidated previously for the $A \rightarrow B$, then $A + B \rightarrow 2B$ kinetic scheme^{57,58}—with its implications for nucleating and growing desired metal films and deposits, including multimetallic films,⁵⁹ as well as its kinetic methods^{57,58}—should, therefore, be applicable to any other metal thin-film formation system^{81–83} that exhibits such kinetics.

Experimental Section

Materials. Benzene (Aldrich, 99.8%, anhydrous, packaged under N_2), 2-propanol (Aldrich, 99.5%, anhydrous, packaged under N_2), and Hg(0) (Aldrich, 99.9995%) were transferred into the glovebox and used as received. Hydrogen gas (General Air, 99.5%) was used as received. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. “Nanopure” water (distilled water filtered through a Barnstead filtration system) was used to wash the reactor between reactions (vide infra).

The ruthenium precatalyst complex $Ru(II)(\eta^6-C_6Me_6)(OAc)_2$, **1**, was prepared (and, unlike the literature, stored) in a nitrogen-atmosphere drybox from $[Ru(\eta-C_6Me_6)Cl_2]_2$ and silver acetate (Aldrich, 99%) following literature methods.³¹ The $[Ru(\eta-C_6Me_6)Cl_2]_2$ was prepared according to the literature procedure¹⁰⁶ from hexamethylbenzene (Aldrich, 99+%, sublimed) and the *p*-cymene complex $[Ru(\eta-C_{10}H_{14})Cl_2]_2$ (Strem, 98%). Three batches of **1** were used for the present study. 1H NMR showed the batches of **1** to be 97% pure, 96% pure, and 74% pure (see Figure S3 of the Supporting Information for the 1H NMR of the 97% pure batch). The 74% pure batch was used only for a repeat benzene hydrogenation experiment; this experiment showed that the presence of impurities from the preparation of **1** has an effect on the kinetics of catalyst formation.¹⁰⁷ The decomposition point of the 97% pure batch of **1** was 163–165 °C, compared to a literature value of 162–165 °C.³¹ The literature³¹ formulates compound **1** as the monohydrate, $[Ru(II)(\eta^6-C_6Me_6)(OAc)_2] \cdot H_2O$, based on IR spectra, complete elemental analysis, and 1H NMR. In this paper we have written **1** as the anhydrous compound because we do not observe water by 1H NMR. The absence of a resonance for water in the 1H NMR does not definitively rule out a hydrate since the water peak is broad and easy to miss,²⁷ but it is consistent with our strict use of anhydrous conditions for the preparation, handling, and storage of **1**. In any case, the presence or absence of one water of hydration introduces an acceptable weighing error of only $\sim 5\%$, and the solvent itself contains about 1 equiv of water versus Ru in a standard benzene hydrogenation reaction.

Analytical Procedures. Nuclear magnetic resonance (NMR) spectra were obtained at 25 °C on a Varian Inova 300 MHz instrument.

- (98) One should suspect heterogeneous catalysis even if the metallic precipitate is inactive because the following process may be occurring: monometallic precursor (inactive) \rightarrow high-surface-area, less negative $\Delta H_{formation}$ (i.e., high intrinsic energy, and thus reactive) nanocluster (very active) \rightarrow low-surface-area, more negative $\Delta H_{formation}$ bulk metal (low activity to inactive).
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- (107) The rate constants for nucleation, k_1 , and autocatalytic surface growth, k_2 , for this less-pure batch of precatalyst were $k_1 = 4.8 \times 10^{-1} h^{-1}$ and $k_2 = 3.7 \times 10^2 M^{-1} h^{-1}$. For comparison, in five experiments with 96–97% pure precatalyst the values of k_1 ranged from 1.6×10^{-2} to $5.4 \times 10^{-4} h^{-1}$ and the values of k_2 ranged from 1.3×10^2 to $2.6 \times 10^2 M^{-1} h^{-1}$.

Chemical shifts were referenced to the residual proton resonance of the solvent. Spectral parameters for ^1H NMR (300 MHz): tip angle, 30° ; acquisition time, 2.667 s; relaxation delay, 0.0 s; sweep width, 6000 Hz.

X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al $K\alpha$ radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W) and a pass energy of 23.5 eV. An XPS sample was prepared in the following manner. A glass liner that had been used in a benzene hydrogenation reaction was broken with a hammer. A flat piece of the glass liner that was coated with the black film was selected. It was rinsed with acetone and allowed to dry on the bench before being introduced into the instrument.

Two samples for transmission electron microscopy (TEM) were prepared on 300-mesh copper TEM grids with a carbon support film. Following a hydrogenation reaction with precatalyst **1**, the reactor was immediately brought into the glovebox and opened. The samples were prepared by diluting an aliquot of the dark red-brown reaction solution 30:1 or 180:1 with 2-propanol. A small drop of the diluted solution was placed on a TEM grid, and the excess liquid was blotted with a piece of filter paper. The TEM grids were packaged in glass vials and sent to the University of Oregon, where TEM analysis was performed as before^{57,60} with the expert assistance of Dr. Eric Schabtach. As described previously, micrographs of the nanoclusters were obtained with a Philips CM-12 microscope (with a 2.0 Å point-to-point resolution) operating at 100 keV.^{57,60}

General Procedures for Hydrogenations. All hydrogenation reactions were performed in a Parr pressure reactor (model No. 4561) made of Monel 400 alloy. The reactor is equipped with an automatic temperature controller ($\pm 5^\circ\text{C}$) and a pressure gauge marked in intervals of 20 psi. Additionally, the bomb head assembly includes a turbine type impeller, a thermocouple, a dip tube for taking liquid samples, and a cooling loop, all four of which contact the reaction solution. A glass liner was used to avoid contacting the reaction solution with the rest of the reactor. The glass liner was dried overnight in a 160°C drying oven before being transferred into the glovebox while still hot. All catalyst reaction solutions were prepared under oxygen- and moisture-free conditions in a Vacuum Atmospheres glovebox (< 2 ppm of O_2 as continuously monitored by a Vacuum Atmospheres O_2 -level monitor). During all of the hydrogenation experiments the reaction solution was stirred at 600 rpm with a turbine type impeller. Unless otherwise noted, the reactor was pressurized with H_2 to an initial value of 880 psi (~ 60 atm). Pressurizing the reactor took about 2 min, and $t = 0$ was set once the reactor was fully pressurized. Pressure versus time data were collected by reading the pressure gauge at selected time intervals.

Cleaning the Reactor between Hydrogenation Reactions, and Testing the Residual Hydrogenation Activity of the Reactor Itself. During hydrogenation reactions with precatalyst **1**, deposits of metallic Ru form on the parts of the reactor that contact the reaction solution (i.e., on the impeller, the thermocouple, the dip tube, and the cooling loop). Because of this, the reactor had to be carefully cleaned between hydrogenation reactions. After each hydrogenation, the metallic film was removed by polishing the reactor with a steel wool pad and soapy water. After polishing, the reactor was rinsed with water, nitric acid, water, and finally acetone (Burdick and Jackson).

Since parts of the reactor become coated with metallic Ru, the reactor itself can have significant hydrogenation activity if not carefully cleaned. Therefore, a control experiment was done each time the reactor was cleaned to ensure that any residual activity of the reactor itself was negligible. Specifically, a “blank” hydrogenation, in which no precatalyst was added to the reactor, was performed in the following manner. In the drybox 10.0 mL of benzene and 15.0 mL of 2-propanol were placed in an oven-dried glass liner. The glass liner was sealed in the reactor, and the reactor was then removed from the glovebox, equilibrated at 100°C (with stirring), and pressurized with H_2 . If the

pressure in the reactor decreased by > 20 psi within the first 2 h, the reactor was cleaned again and another “blank” hydrogenation performed. To keep the residual hydrogenation activity of the reactor at a negligible level, we replaced the impeller following each hydrogenation with **1**.

Standard Conditions Benzene Hydrogenation Beginning with the Precatalyst $\text{Ru(II)}(\eta^6\text{-C}_6\text{Me}_6)(\text{OAc})_2$. In the glovebox 40 (± 1) mg of **1** was transferred into an oven-dried glass liner and dissolved in 10.0 mL of benzene and 15.0 mL of 2-propanol, yielding a clear, yellow-orange solution. The glass liner was sealed in the reactor, and the reactor was then removed from the glovebox, equilibrated at 100°C (with stirring), and pressurized with H_2 . Under these conditions complete conversion of benzene to cyclohexane corresponds to a pressure loss of about 550 psi. At the end of each hydrogenation reaction the percent conversion was verified directly by ^1H NMR analysis (the NMR sample was prepared by dissolving a drop of the final reaction solution in CD_2Cl_2).

The pressure data were converted to benzene concentration data by a simple proportional relationship: $[\text{benzene}] = [\text{benzene}]_{\text{initial}} \times (\text{pressure} - \text{pressure}_{\text{final}}) / (\text{pressure}_{\text{initial}} - \text{pressure}_{\text{final}})$. This treatment assumes that $\text{pressure}_{\text{final}}$ corresponds to complete conversion of benzene to cyclohexane; this assumption was verified experimentally by ^1H NMR (i.e., $\geq 95\%$ conversion was observed by ^1H NMR at the end of the reaction). The error bars shown for the H_2 pressure (or the benzene concentration) assume an error of ± 20 psi in the pressure gauge reading and $\pm 5^\circ\text{C}$ in the temperature control and probably correspond to the maximum error for this system. Curve-fitting the benzene concentration versus time data was performed as before⁵⁸ using the commercial software package Microcal Origin.

Testing the Kinetic Competence of the Metallic Film and of the Red Reaction Solution. A standard conditions benzene hydrogenation experiment was started and was allowed to proceed until the hydrogenation was 55% complete by pressure loss (verified by ^1H NMR). At that point the reactor was cooled to room temperature, vented, brought into the glovebox, and opened. The dark red reaction solution was removed with a pipet, taking care not to remove any of the dark film that adheres to the glass liner and the wetted reactor parts; the dark red solution was stored in a screw-capped glass vial. Next, 10 mL of benzene and 15 mL of 2-propanol were placed in the precipitate-containing liner. The reactor was resealed, brought out of the glovebox, equilibrated at 100°C (with stirring), and pressurized with H_2 .

After cleaning the reactor in the normal way (vide supra), the catalytic activity of the dark red reaction solution was also tested. In the glovebox, 15 mL of the reaction solution was filtered through a disposable nylon syringe filter (0.2 μm pore size) into a clean, oven-dried, glass liner. Then 7 mL of benzene and 6 mL of 2-propanol were added¹⁰⁸ before sealing the glass liner in the reactor. After removing the reactor from the glovebox, it was equilibrated at 100°C (with stirring) and pressurized with H_2 .

Mercury-Poisoning Experiment. This experiment was started as if it were a standard conditions benzene hydrogenation experiment. Pressure versus time data were collected until the pressure had decreased to 700 psi, at which point the reaction was about one-third complete (complete conversion corresponds to a pressure change of ~ 550 psi). Then the reactor was cooled to room temperature, vented, taken into the glovebox, and opened. Next, 6.61 g of $\text{Hg}(0)$ was added to the dark red reaction solution (~ 320 equiv vs Ru). The reactor was then resealed, brought out of the glovebox, equilibrated at 100°C , and stirred for 1.0 h at that temperature to ensure that the $\text{Hg}(0)$ had fully contacted the reaction solution and the reactor. Finally, the reactor was pressurized to 700 psi with H_2 . At this point, the collection of pressure versus time data was recommenced (ignoring the ~ 2 h gap required for the poisoning procedure).

Quantitating the Amount of Precatalyst Decomposition by ^1H NMR. See the Supporting Information for details.

Control Experiment Showing that Ru(II)(η^6 -C₆Me₆)(OAc)₂ Does Not React with Hg(0). See the Supporting Information for details.

CS₂-Poisoning Experiment. See the Supporting Information for details.

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sample of **1**. We also thank Mr. Collin Hagen for repeating the standard conditions benzene hydrogenation experiment and Dr. James Ennett for carrying out preliminary hydrogenation experiments on benzene hydrogenation with **1** as a catalyst precursor at the Australian National University.²⁷ Financial support was provided by the Department of Energy, Chemical Sciences Division, Office of Basic Energy, grant DOE FG06-089ER13998, and by NSF grant CHE-0078436.

Supporting Information Available: Figure S1, transmission electron micrograph of the evaporated reaction solution following a benzene hydrogenation with the precatalyst Ru(II)(η^6 -C₆Me₆)(OAc)₂; Figure S2, XPS of the dark film formed during a benzene hydrogenation with the precatalyst Ru(II)(η^6 -C₆Me₆)(OAc)₂; Figure S3, ¹H NMR of the Ru(II)(η^6 -C₆Me₆)(OAc)₂ precatalyst in CDCl₃; details regarding the determination of the extent of precatalyst decomposition during a benzene hydrogenation experiment with Ru(II)(η^6 -C₆Me₆)(OAc)₂; details regarding the control experiment showing that Ru(II)(η^6 -C₆Me₆)(OAc)₂ does not react with Hg(0); and description of the CS₂-poisoning experiment with Rh(0)_x nanoclusters at 25 and 100 °C (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(108) We chose to add 7 mL of benzene and 6 mL of 2-propanol because this gives a reaction solution that closely approximates the initial reaction solution in a standard conditions benzene hydrogenation experiment. Specifically, the reaction solution for this experiment contains ~15 mL of 2-propanol, ~10 mL of benzene, and ~3 mL of cyclohexane (i.e., the same as a standard conditions benzene hydrogenation experiment, except for the presence of ~3 mL of cyclohexane). The volumes are approximate because, among other things, they assume exactly 50% conversion in the benzene hydrogenation reaction with **1**, and they assume that there is no volume change associated with the conversion of benzene to cyclohexane. The volume of the initial reaction solution for this experiment is 28 mL, instead of the normal 25 mL. This changes the headspace in the (300 mL) reactor only by ~1%, so no correction was made to the H₂ pressure uptake curve shown in Figure 3.