Article

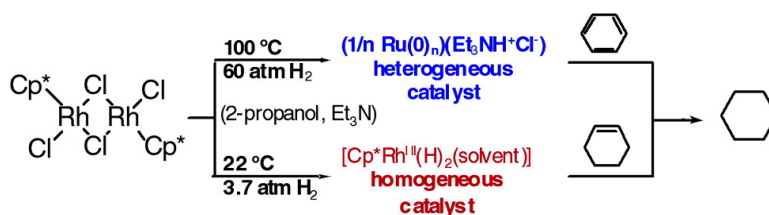# Is It Homogeneous or Heterogeneous Catalysis? Compelling Evidence for Both Types of Catalysts Derived from [Rh(□-CMe)Cl] as a Function of Temperature and Hydrogen Pressure

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Is It Homogeneous or Heterogeneous Catalysis? Compelling Evidence for Both Types of Catalysts Derived from [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ as a Function of Temperature and Hydrogen Pressure

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Abstract: Addressed herein is the 20+ year-old question of whether the true benzene and cyclohexene hydrogenation catalysts derived from the organometallic precursor [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$, **1**, are homogeneous or heterogeneous. The methodology employed is that developed earlier (Lin, Y.; Finke, R. G. *Inorg Chem.* **1994**, *33*, 4891, "A More General Approach to Distinguishing Homogeneous from Heterogeneous Catalysis..."). The kinetic evidence especially, but also the metal product (nanoclusters plus bulk metal), Hg(0) poisoning and other experiments, provide compelling evidence that Rh(0) nanoclusters are the true *benzene* hydrogenation *heterogeneous* catalyst derived from [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$, **1**, at the required more vigorous conditions of 50−100 °C and 50 atm H$_2$. However, the same methods reveal that the *cyclohexene* hydrogenation catalyst derived from **1** at the milder conditions of 22 °C and 3.7 atm H$_2$ is a nonnanocluster, *homogeneous* catalyst, most likely the previously identified complex, [Rh(η^5-C$_5$Me$_5$)(H)$_2$(solvent)] (Gill, D. S.; White, C.; Maitlis, P. M *J. C. S. Dalton Trans.* **1978**, 617). In short, the present results solve the two-decade-old problem of identifying the true benzene *and* cyclohexene hydrogenation catalysts derived from [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$. Perhaps most significant is the demonstration that the methodology employed has the ability to identify both heterogeneous and homogeneous catalysts from the same catalyst precursor.

Introduction

The question "Is it homogeneous or heterogeneous catalysis?" when beginning with monometallic, organometallic precatalysts under strongly reducing, often higher temperature conditions has proved to be a vexing one in organometallic chemistry and catalysis.[1] Identification of the true catalyst is important since all the key catalytic properties—activity, selectivity, stability, lifetime, poisoning phenomena, and catalyst recovery—are inherently different for monometallic homogeneous catalysts vs polymetallic, nanoparticle (or bulk metal or metal film) heterogeneous catalysts.[1] A recent review emphasizes the importance of this question by identifying >30 systems where further investigation is needed.[1] A second recent review by Dyson highlights the importance of addressing the homogeneous vs heterogeneous catalysis question in arene hydrogenations.[2]

One of the top systems identified[1] for reinvestigation is the hydrogenation catalyst which results when using [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$, **1**, vide infra, as the organometallic precursor.[3,4] Precatalyst **1** has been used for both arene and olefin hydrogenation; typical

reaction conditions from the literature[3,4,5,6] illustrate the well-known fact that benzene hydrogenation is considerably more difficult and therefore requires higher temperatures and pressures[6] than simple olefin hydrogenation. The true catalyst derived from **1** has been suggested to be heterogeneous at high temperatures but homogeneous at low temperatures.[3c] Can a

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(1) (a) See: Widegren, J. A.; Finke, R. G. A review of the problem of distinguishing true homogeneous catalysis from soluble or other metal-particle heterogeneous catalysis under reducing conditions. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317−341. That review covers prior work in the area (180 total references) including the early contributions by Maitlis, White-sides, Crabtree, Collman, Lewis, and our own group plus many other references. Table S1 of the Appendix of that review lists >30 catalyst systems for which metal−particle heterogeneous catalysts are suspected. (b) See also our 2003 review of soluble transition-metal nanoclusters as arene hydrogenation catalysts.[6]

(2) (a) Dyson, P. J. Arene Hydrogenation by Homogeneous Catalysts: Fact or Fiction? *Dalton Trans.* **2003**, 2964. As we discussed with Prof. Dyson, his valuable account requires, however, one important correction. Specifically, our 1998 paper[16] is misquoted in his review in a way that will cause confusion unless corrected. We concluded that the results in our 1998 paper[16] "call into question all previous claims of *benzene* hydrogenation—but not anthracene or naphthalene hydrogenation—by monometallic pre-catalysts". This deliberately carefully worded statement was misquoted elsewhere[2a] to claim that we were "question(ing) the whole concept of homogeneous *arene* hydrogenation catalysis [7]" (italics have been added to "*arene*"; ref 7 elsewhere[2] is the same as our 1998 paper cited herein[16]). In fact, and as our above-cited original quote makes clear, it is important to distinguish *the more difficult benzene reduction* from other, *easier to reduce*, polycyclic arenes.[6,16] This is the case since Halpern's kinetic and mechanistic work provides compelling evidence for homogeneous *anthracene and naphthalene* hydrogenation catalysts (see elsewhere for a discussion and references[6]). (b) Also emphasized elsewhere[1,6,14,16,17] is the importance of kinetic methods in addressing the "Is it homogeneous or heterogeneous catalysis?" question. Despite this clear lesson from the literature and our prior papers,[1,6,14,16,17] studies continue to appear which fail to be definitive due to the lack of kinetic data or its definitive analysis (e.g., studies which fail to fit sigmoidal-appearing kinetic curves by the A → B, A + B → 2B mechanism for nanocluster formation), easily done fits which would, if performed, provide strong kinetic evidence for nanocluster formation. Knowing what form the precatalyst mass is in, and then kinetic evidence revealing the relative activity of each form of that mass, are keys to a definitive resolution of the "Is it homogeneous or heterogeneous catalysis?" question. Recent work on Pd-catalyzed Heck couplings is also available,[2c,d] including work that does report the needed kinetic work.[2d] (c) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W. *J. Catal.* **2004**, *226*, 101−110. (d) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161.

change from heterogeneous to homogeneous catalysis be induced in this system by such subtle changes in the reaction conditions?[7] Can the methodology developed previously[8] unequivocally address the "Is it homogeneous or heterogeneous catalysis?" question in this system as a function of the reaction conditions?

The research group of one of us (P.M.M.) first prepared **1**, discovered its hydrogenation chemistry, and also first asked the question of "whether the reaction is wholly homogeneous or whether small amounts of metal of extremely high activity participate as well".[9a] A filtration test was published as a way to distinguish bulk-metal heterogeneous catalysts that could be removed by filtration from soluble homogeneous catalysts which are not retained by the filter.[9a] It was tentatively concluded in 1977 that the *benzene* hydrogenation catalyst derived from **1** is homogeneous based on light-scattering experiments and the lack of metal precipitate.[3] In hindsight, however, those experiments lacked the *kinetic data*[1] required to unequivocally identify the true catalyst, catalysis being a "wholly kinetic phenomena".[10,11] Thorough kinetic studies were, however, performed in the case of *cyclohexene* hydrogenation, evidence consistent with and interpreted in terms of a homogeneous, primarily [Rh(η^5-C$_5$-Me$_5$)(H)$_2$(solvent)] catalyst for cyclohexene hydrogenation.[3c] However, it was subsequently found (in 1980) that catalysts derived from the related but different precatalyst [Rh$_2$(η^5-C$_5$-Me$_5$)$_2$(OH)$_3$]Cl contained up to 42% of a heterogeneous component (based on the filtration test[9a]), formed from ≤12% of this precatalyst, again for the case of *cyclohexene* hydrogenation at 22 °C and 1 atm H$_2$. In short, the true nature of the catalyst(s) derived from **1** and related complexes, as a function of different substrates and reaction conditions,[9b,c] has remained uncertain until the present contribution.
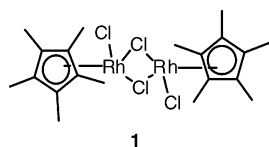
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In 1984 and while noting the "difficult and challenging problem" of distinguishing homogeneous from heterogeneous

catalysts, Collman and co-workers used polymer-bound substrates to obtain evidence that the true *benzene* hydrogenation catalyst derived from **1** "behaves like" a heterogeneous catalyst. They noted, however, that their evidence did not "definitively" establish the presence of a heterogeneous metal catalyst.[5,12] On the other hand, again using polymeric substrates and poisons, Collman's group tentatively concluded that the *cyclohexene* hydrogenation catalyst derived from **1** under mild conditions is *homogeneous*. Again, the nature of the true catalyst derived from **1** for hydrogenation reactions and as a function of the reaction conditions was not established unequivocally and remains a 20+ year-old challenge.

A breakthrough in the ability to distinguish monometallic homogeneous catalysis from nanoparticle or other heterogeneous catalysis occurred in 1994 with the development of a more general methodology[8] to answer the "Is it homogeneous of heterogeneous catalysis?" question. That methodology (hereafter the 1994 methodology[8]) consists, broadly speaking, of (i) establishing metal products derived from the precatalyst (e.g., the use of transmission electron microscopy to look for metal nanocluster products); (ii) performing the required kinetic studies, especially searching for the *tell-tale sigmoidal kinetics indicative of nanocluster/metal particle formation*—the most important breakthrough provided by the 1994 work[8]; (iii) performing poisoning and other kinetic-based studies, (iv) using multiple physical methods or other techniques whenever possible, and (v) adhering strictly to the principle that the correct description of the catalyst (i.e., the correct mechanism) will of course be able to explain *all* the available data. Two figures further detailing the 1994 methodology are available for the interested reader (Figures 4 and 5 elsewhere[8]) as are the accounts of how the methodology was rigorously tested and refined by the discovery[8] of polyoxoanion-stabilized[13] Ir(0)[14] and Rh(0)[15] nanoclusters. The methodology developed in 1994 has since

(3) (a) Russell, M. J.; White, C.; Maitlis, P. M. Stereoselective Homogeneous Hydrogenation of Arenes to Cyclohexenes Catalyzed by [Rh(η^5-C$_5$Me$_5$)-Cl$_2$]$_2$. *J. Chem. Soc., Chem. Commun.* **1977**, 427. (b) Maitlis, P. M. *Adv. Chem. Ser.* **1979**, *173*, 31−42. (c) Prior kinetic evidence consistent with a homogeneous catalyst in the case of *cyclohexene* hydrogenation beginning [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$: Gill, D. S.; White, C.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 617. The situation for even cyclohexene hydrogenation was, however, previously unclear due to the subsequent report of a heterogeneous component for cyclohexene hydrogenation by a slightly different precatalyst.[9] (d) Details of the earlier light-scattering experiments and apparatus, aimed at explaining and understanding the results obtained at the time, are provided in the Supporting Information for the interested reader.

(4) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301.

(5) Collman, J. P.; Kosydar, K. M.; Bressan, M.; Lamanna, W.; Garrett, T. *J. Am. Chem. Soc.* **1984**, *106*, 2569. Briefly, the evidence for heterogeneity of benzene or polymer-bound benzene hydrogenation under conditions analogous to those used in the literature were (i) observation of dark-colored reaction solutions, (ii) routine observation of 1−2 h induction periods, an observation characteristic of the in situ formation of a metal-particle catalyst,[1] (iii) deposition of Rh metal on the reactor walls (in contrast to the reported lack of bulk metal[3a−b]), and (iv) primarily their polymer-bound substrate test (i.e., the observation that the catalyst is much more active for the hydrogenation of benzene than it is for the hydrogenation of polymeric-bound styrene).

(6) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *191*, 187−207.

(7) (a) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 1334. (b) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776.

(8) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891.

(9) (a) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543. (b) Later, during further exploration of olefin hydrogenation, it became clear that some of the Cp*Rh catalysts were strongly activated by oxidation, for example, by air.[9c] This took the form of a removal of some of the Cp* ligands by oxidation (to CO$_2$ and acetate), which in turn gives rise to unprotected and hence highly reactive rhodium species which, under hydrogenation conditions, readily give highly active Rh(0) metal. (c) Hamlin, J. E.; Hirai, K. V.; Gibson, C.; Maitlis, P. M. *J. Mol. Catal.* **1982**, *15*, 337.

(10) Halpern, J. *Inorg. Chim. Acta.* **1981**, *50*, 11.

(11) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1977**, *2*, 65.

(12) Collman and co-workers hypothesis was that homogeneous catalysts will be more active for the hydrogenation of polymer-bound substrates than heterogeneous catalysts, and they cite literature in support of this hypothesis in their paper.[5] However, the precedent for that statement appears to be largely from insoluble, oxide, or other supported heterogeneous metal-particle catalysts since well-defined nanoclusters were not available for control experiments when the 1984 studies were done, a point that Collman and co-workers specifically and insightfully noted.[5] Hence, it would be useful to test polymer-bound substrates with modern nanoclusters ≤50 Å in diameter (their original paper was also careful to note that they used only particles >80 Å in diameter to test the polymer-bound substrate method[5]). However, our feeling is that the polymer-bound substrate method will not receive much use now that the methods developed in 1994[8] are available and since the polymer-bound substrate method (i) requires the synthesis of polymer-bound substrates, (ii) is therefore a relatively slow and difficult method, (iii) provides results that are suggestive but which the authors note are equivocal, and (iv) since this approach changes the system to a *polymer-bound* substrate that is, in the final analysis, a new system so that the polymer-bound substrate method cannot address directly the original system of interest. The paper elsewhere[5] is, however, of current interest with respect to the topic of polymer hydrogenation by homogeneous, nanocluster heterogeneous, or other supported heterogeneous catalysts.

(13) (a) 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. (b) Aiken, J. D., III; Lin, Y.; Finke, R. G. *J. Mol. Catal. A: Chem.* **1996**, *114*, 29−51.

(14) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335.

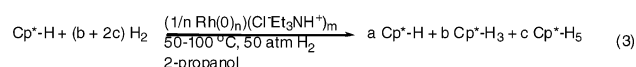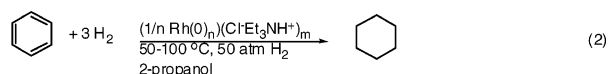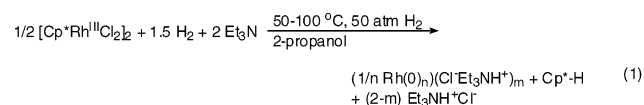(15) Aiken, J. D., III; Finke, R. G. *Chem. Mater.* **1999**, *11*, 1035.

proved successful in identifying two additional cases of heterogeneous metal-particle catalysis where mononuclear homogeneous catalysis was originally believed to be the case.[16,17] In addition, careful and thorough studies from I. Manners's group using the 1994 methodology have led to the identification of amine-borane and phosphine-borane dehydro-coupling catalysts which switch from heterogeneous to homogeneous catalysis.[7] The task remained, however, of seeing if the 1994 methodology could uncover the true catalyst or catalysts in both the benzene and the cyclohexene hydrogenation systems based on the precatalyst $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$, **1**.

Herein, we report compelling evidence that the *benzene* hydrogenation catalyst derived from **1** (and under the conditions depicted in eqs 1–3) is a soluble $Rh(0)_x$ nanoparticle heterogeneous catalyst while the *cyclohexene* hydrogenation catalyst derived from **1** (and under conditions of eqs 4 and 5) is a homogeneous metal complex. The results are significant in at least four ways: (i) they (and the most recent results from I. Manners's labs for a completely different system[7]) demonstrate the ability of the methods developed in 1994[8] to uncover *both* types of catalysis from the same precursor; (ii) they show unequivocally that going from milder to harsher conditions of temperature and pressure required for a more difficult substrate, benzene, can turn a homogeneous catalyst into a heterogeneous, nanoparticle catalyst; (iii) they show that the difficult reaction of *benzene* hydrogenation is typically indicative of well-precedented *heterogeneous*, not homogeneous, catalysis[6] as discussed in more detail in the summary section of the paper; and (iv) they provide a second example where control TEMs of the organometallic precursor are crucial due to the problem of TEM-induced nanocluster formation from monometallic precatalysts.[7]

Results and Discussion

Benzene Reduction at 50–100 °C and 50 atm H_2: Evidence for Rh(0) Formation at These More Vigorous Conditions. Precatalyst $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$, **1**, was used to hydrogenate benzene at 50–100 °C and 50 atm of H_2, eqs 1–3.

The Higher Pressure and Temperature Reactions

$$1/2\ [Cp^*Rh^{III}Cl_2]_2 + 1.5\ H_2 + 2\ Et_3N \xrightarrow[\text{2-propanol}]{50\text{-}100\ ^\circ C,\ 50\ atm\ H_2}$$
$$(1/n\ Rh(0)_n)(Cl^-Et_3NH^+)_m + Cp^*\text{-}H \quad (1)$$
$$+\ (2\text{-}m)\ Et_3NH^+Cl^-$$

$$\bigcirc + 3\ H_2 \xrightarrow[\substack{50\text{-}100\ ^\circ C,\ 50\ atm\ H_2 \\ \text{2-propanol}}]{(1/n\ Rh(0)_n)(Cl^-Et_3NH^+)_m} \bigcirc \quad (2)$$

$$Cp^*\text{-}H + (b + 2c)\ H_2 \xrightarrow[\substack{50\text{-}100\ ^\circ C,\ 50\ atm\ H_2 \\ \text{2-propanol}}]{(1/n\ Rh(0)_n)(Cl^-Et_3NH^+)_m} a\ Cp^*\text{-}H + b\ Cp^*\text{-}H_3 + c\ Cp^*\text{-}H_5 \quad (3)$$

Following a 50–100 °C benzene hydrogenation experiment with **1** as the precatalyst the reaction solution is *jet black* and a dark, metallic film coats the reactor parts in contact with the solution. Confirmation that the metallic film is in fact Rh(0) was obtained by XPS.[18] GC-MS experiments confirmed the

release of free Cp^*-H and its hydrogenation products, Cp^*-H_3 and Cp^*-H_5, eq 3, at a level of ~45% when the benzene hydrogenation is complete.

Our observation of Rh(0) metal confirms Collman and co-worker's report of dark solutions and bulk metal,[5] and it is now clear that the original report claiming that no bulk metal is formed is almost surely in error, an artifact of the reactor employed at the time.[3] Note that the presence of bulk Rh(0) implies, but does not by itself prove (since heterogeneous nucleation directly to bulk metal is also known[17]), that Rh(0) nanoclusters were formed in the reaction. However, the kinetics, Hg(0) poisoning, and activity of the soluble portion of the product solution—along with the observation of bulk metal (i.e., formed from the agglomeration of soluble nanoclusters)—together do provide good evidence for the formation of a nanocluster catalyst, vide infra. Those nanoclusters can be formulated as $[Rh(0)_n \cdot (Cl^-Et_3NH^+)_m]$, eq 1, by analogy to established systems.[6,15,16]

TEM Studies and Control Experiments Demonstrating Precatalyst Reduction in the TEM Beam and, Therefore, the Noninnocence of TEM in This Example. The 1994 methodology[8] makes use of early TEM studies whenever possible. However, in the present example TEM proved noninnocent, causing instead of accurately reporting the (TEM) observations. Our results below parallel the recent results of I. Manners's group[7] in which they found that even a 70 kV TEM beam will induce Rh(0) nanocluster formation from, in their case, a $[(1,5\text{-}COD)RhCl]_2$ precatalyst.[7] Schmid's[19] and our[20] reviews have both emphasized literature reports of TEM being noninnocent, although most of the previously documented cases are of "electron-beam induced nanocluster structural rearrangements, aggregation or decomposition", to quote our 1999 review (see p 8 elsewhere[20]). The results from I. Manners's group[7] are, therefore, significant.

We began as usual by obtaining a TEM of a sample of the black reaction solution deposited on a carbon-coated TEM grid. That TEM, Figure S1 of the Supporting Information, exhibits 1.9 ± 0.5 nm $Rh(0)_x$ particles (105 counted). Energy dispersive spectroscopy (EDS) confirms that Rh is in fact present on the

(16) Weddle, K. S.; Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653. This paper was the first to use the methodology employed herein to show that what was previously claimed to be a "$[(C_8H_{17})_3NCH_3]^+$[RhCl_4]$^-$" "ion-pair" benzene hydrogenation catalyst is actually a precatalyst to ca. 34 Å $Rh(0)_n$ nanoclusters stabilized by $[(C_8H_{17})_3NCH_3]^+Cl^-$ as the true catalyst.

(17) Widegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am Chem. Soc.* **2003**, *125*, 10301. This paper identifies bulk Ru(0) metal as the true catalyst in benzene hydrogenations starting with the monometallic precursor, Ru(II)-$(\eta^6\text{-}C_6Me_6)(OAc)_2$, a system previously believed to be homogeneous.

(18) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Physical Electronics, Inc.: Eden Prairie, MN, 1995.

(19) (a) The problem of TEM beam rearrangement is not a new one; Schmid published a review in the early 1990s showing that the TEM technique can cause metal-atom rearrangements, cluster growth and aggregation, and ligand desorption from the metal surface (Schmid, G. *Chem Rev.* **1992**, *92*, 1709), a review and conclusions cited in our 1999 review.[20] In addition, TEM damage of samples is a well-known problem addressed in textbooks on TEM.[19c] (b) Although we reported multiple TEM control experiments as part of our first 1994 Ir nanocluster paper[14] so as to avoid any TEM artifacts, in light of Manners' report of TEM-induced nanocluster formation we went back and reconfirmed that none of the following Ir precatalysts we have used in the past[8,14,23–25,27,33] yield detectable Ir(0) nanoclusters in a 120 kV TEM beam: $[(1,5\text{-}COD)Ir \cdot P_2W_{15}Nb_3O_{62}]^{9-}$, $[(1,5\text{-}COD)IrCl]_2$, or even the cationic and presumably more readily reduced $[(1,5\text{-}COD)Ir\text{-}(CH_3CN)_2]BF_4$. Note also that we have always made extensive use of the valuable 1,5-COD evolution handle in these precursors, namely, the detection by GLC of the 1,5-COD hydrogenation product, cyclooctane, to tell when the precatalyst has been completely converted to nanoclusters *before* a (therefore precursor-free) sample is submitted for TEM analysis. (c) It is well known that "Certain materials are more susceptible than others, but in the end, you can damage virtually anything you put into the TEM": Williams, D. B.; Carter, C. B. *Transmission Electron Microscopy*; Plenum Press: New York, 1996, Chapter 4.

(20) A review of modern transition-metal nanoclusters: Aiken, J. D., III; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1–44 and references therein.
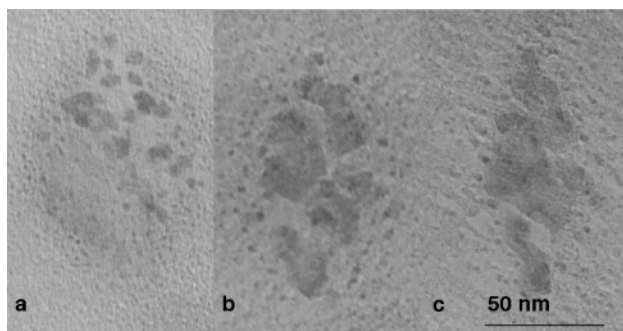
Figure 1. Control TEM experiment in which precatalyst, **1**, was diluted in 2-propanol, benzene, and triethylamine, placed on a TEM grid, and then examined as a function of time in the 120 kV TEM beam. The results show that the agglomerated nanoclusters increase in size the longer they are in the TEM beam (the scale bar is the same for all three micrographs). The micrographs also reveal smaller aggregates, results which require continual formation of nanoclusters in the TEM beam: (a) After $t = 5$ min in the TEM beam exhibiting 3.8−8.5 nm agglomerates; (b) Same sample area at $t = 25$ min exhibiting both smaller and larger aggregates, 2.3−22.3 nm; (c) Same sample area at $t = 45$ min exhibiting both small plus even larger aggregates, 3.1−34.6 nm.

TEM grid as judged by the $L_{\alpha 1}$ and $L_{\beta 1}$ lines of Rh at 2.70 and 2.83 keV, respectively.[21] However, *a key here is to know what amount of the precursor mass is in what form:* if precatalyst is still present, then a control TEM of precatalyst alone is in order, especially in light of the results from Manners' group.[7]

Recall that the GC-MS data cited above, on the release of Cp*−H and its hydrogenation products obtained after a benzene hydrogenation reaction is complete (eq 3), reveal that only ∼45% of the precatalyst has been converted to Rh(0) products. That is, when the TEM analysis is performed, it follows by mass balance that ∼55% of the Rh should still be present as the discrete organometallic precatalyst, $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$, **1**. This is actually a very typical situation in our experience, where very active nanoclusters are formed that accomplish 100% of the observed catalysis long before (slower) conversion of the (inactive) precatalyst to the catalyst can occur completely.[1,8,16,17] In an important control experiment, TEM of only precatalyst **1** (diluted in 2-propanol, benzene, and triethylamine) shows the presence of nanoclusters that, therefore, must have formed in the 120 kV TEM beam (Figure S2, Supporting Information). Their average size is the same within experimental error, 1.7 ± 0.3 nm (Figure S2), as the nanoclusters imaged at the end of the benzene hydrogenation reaction, 1.9 ± 0.5 nm (Figure S1). Hence, the true origin of the nanoclusters observed at the end of the benzene hydrogenation reaction is unclear from the above TEM experiments. Additional control experiments were also performed: Figure 1 shows that the nanoclusters clearly grow in size as a function of the time in the TEM beam; Figure S3 of the Supporting Information shows that nanoclusters are present but do not change their average size (1.7 ± 0.5 nm) in a TEM of precatalyst, **1**, in 2-propanol examined at −168 °C but still at 120 kV; and Figure S4 of the Supporting Information reveals that nanoclusters are still formed in the TEM beam at the mildest TEM conditions attainable with our instrumentation of 40 KV and −168 °C.

In short, the normally powerful TEM data are equivocal in this case regarding whether nanoclusters are formed as primary
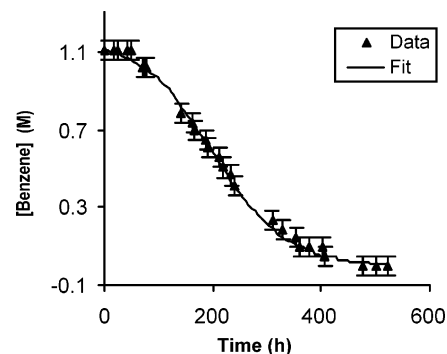
(21) Jones, I. P. *Chemical Microanalysis Using Electron Beams*; The Institute of Materials: London, 1992.

Figure 2. Data and curve fit for a benzene hydrogenation reaction with precatalyst **1** *at 50 °C* and an initial H_2 pressure of 50 atm. Following a ∼48 h induction period the reaction rate increases in a sigmoidial curve that is well fit by the slow continuous nucleation, A → B (rate constant k_1), then autocatalytic surface growth, A + B → 2B (rate constant k_2), mechanism diagnostic of nanoparticle and/or bulk metal formation. The rate constants determined from this curve fit are $k_1 = 0.0007$ h^{-1} and $k_2 = 0.013$ M^{-1} h^{-1}. This reaction is complete after a total time of ∼500 h (21 days). This means that the benzene reduction reaction at 50 °C takes ca. 80-fold longer to go to completion than the analogous 100 °C reaction, Figure 3. These results, in turn, clarify why the other benzene hydrogenation reactions reported herein were performed at the faster, and thus much more convenient, temperature of 100 °C.
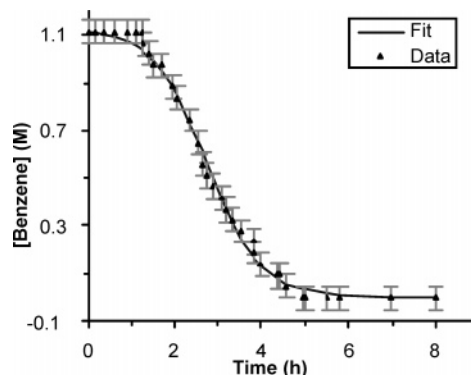

Figure 3. Data and curve fit for a typical benzene hydrogenation reaction with precatalyst **1** at 100 °C and an initial H_2 pressure of 50 atm. Following a ∼1.5 h induction period the reaction rate increases rapidly and the reaction is complete after a total of ∼6 h. A sigmoidal curve is observed, one that is well fit by the slow continuous nucleation, A → B (curve fit $k_1 = 0.019$ h^{-1}), then autocatalytic surface growth, A + B → 2B (curve fit $k_2 = 2.6 \times 10^2$ M^{-1} h^{-1}) mechanism for nanoparticle and/or bulk metal formation. Note that the relatively high k_2 value 260 M^{-1} h^{-1} is consistent with a highly active hydrogenation catalyst being formed (but note that this k_2 rate constant refers to the reduction of A (= **1**), not benzene).

reaction products. However, the observation of bulk metal and the kinetic, Hg(0) poisoning, and other data to be described will strongly support the conclusion that nanoclusters *are* formed as a primary metal reaction product (vide infra).

Kinetic Evidence for Nanocluster Formation. The first issue which must be addressed is that the reaction is too slow to be conveniently followed at the literature conditions of 50 °C.[3] Figure 2 shows the crucial kinetics of benzene hydrogenation at 50 °C and 50 atm of H_2, while Figure 3 shows the kinetics at 100 °C and 50 atm of H_2.[22] Note that each has the induction period and sigmoidal shape now known to be characteristic of nanocluster[8,16,23,24] (and/or bulk metal[17]) formation. Since both the 50 and 100 °C reactions show the same sigmoidal shape, dark reaction color, and bulk metal Rh(0) film product and since the 50 °C reactions require an unworkably inconvenient ∼21 days to go to completion (Figure 2), the remainder of the studies

reported herein employ the $\geq$80-fold faster and much more convenient ($\sim$6 h to completion) 100 °C reactions conditions.[22]

Returning to Figures 2 and 3, the observed induction period demands that **1** (=A) is not the catalyst; rather, **1** is a precatalyst that must be converted into the true catalyst (B) before catalysis is observed. (Recall that Collman's group also reported induction periods.[5]) Even more telling is that the sigmoidal kinetics observed in Figure 3 can be fit—and the fit is very good—to the A → B nucleation and A + B → 2B autocatalytic surface growth, kinetic scheme diagnostic of transition-metal nanocluster and/or bulk metal[17] formation under H_2.[1,6,8,15,16,23–26] Given that the metal product has been shown to be Rh(0) and that only Rh(0) but not precatalyst **1** is precedented as a benzene hydrogenation catalyst,[6] it follows that the A → B, A + B → 2B kinetic evidence is as compelling a single piece of evidence as exists for the *in situ* formation of a Rh(0) benzene hydrogenation catalyst, B, from the monometallic precatalyst **1**. Note also that due to the goodness of the fit A (= $[(\eta^5\text{-}C_5\text{-}Me_5)RhCl_2]_2$, **1**) cannot be the catalyst; instead, the kinetics demand that A must be converted to B (A → B, rate constant k_1) *before* any catalysis can occur.

Kinetic Competence of the Soluble Nanoclusters, Not the Metal-Coated Reactor. As noted previously, following a benzene hydrogenation reaction the reaction solution is jet black and the reactor parts in contact with the reaction solution are coated with metallic Rh(0). Two experiments were performed to determine which of the following is responsible for the observed catalysis: (i) the soluble $Rh(0)_x$ particles in the black reaction solution, (ii) the bulk Rh metal coating the reactor, or conceivably (iii) some combination of i and ii.

First, the black reaction solution was filtered through a 0.2 μm (i.e., 200 nm) nylon syringe filter in order to remove bulk metal (but not nanoclusters) into a clean glass liner (*without* cleaning the reactor components which come in contact with the solution). Then, the activity of the filtered solution was tested with fresh benzene. The filtered solution immediately catalyzed the hydrogenation of benzene without an induction period, Figure 4, and at a rate kinetically competent to account for the observed hydrogenations. Next, the catalytic activity of the metallic film was tested with fresh benzene and solvent. The
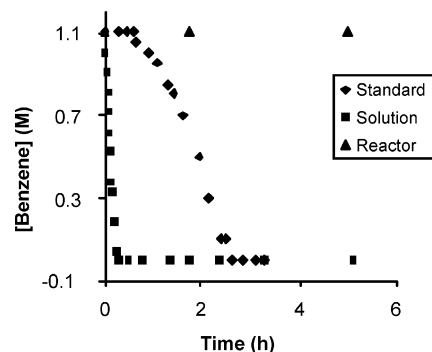

Figure 4. Plot of the benzene concentration vs time data for three separate benzene hydrogenation reactions. The diamonds (◆) show pressure vs time data for a Standard Conditions hydrogenation (see the Experimental Section) starting with **1**. After the hydrogenation reaction beginning with **1**, the final black reaction solution was separated from the metallic film, and in separate experiments each was used to catalyze a benzene hydrogenation reaction. The squares (■) show the data for the hydrogenation with what proved to be the highly active black filtrate, while the triangles (▲) show the data for the hydrogenation with the (inactive) bulk-metal film.

metallic film showed *no activity* within experimental error for the hydrogenation of benzene, Figure 4.

In a separate control experiment which illustrates issues in doing such controls, testing the black reaction solution but cleaning the reactor prior to the repeat benzene hydrogenation led to an induction period and a lower rate of hydrogenation (the latter due almost surely to the now lower amount of precatalyst **1** in the black solution), Figure S5 of the Supporting Information. Note that the problem with this control is that it unavoidably involves a 3-day, room-temperature storage of the black reaction solution in the drybox since the reactor activity had to be tested in a "blank" run and shown to be negligible (see the Experimental Section if further details are required). These results are consistent with the 3-day, room-temperature storage step causing deactivation of the soluble $Rh(0)_x$ nanoparticles.

The following sequence of reactions rationalizes the observed results: precatalyst + H_2 → active, high-surface-area $Rh(0)_x$ nanoparticle catalyst → less active agglomerated/poisoned nanoparticles → negligible activity, low-surface-area bulk metal upon extended (i.e., 3 day) storage. The implied instability of the $[Rh(0)_n \cdot (Cl^- Et_3NH^+)_m]$ nanoclusters is consistent with Cl^- and Et_3NH^+ providing (only) moderate nanocluster stabilization[25,26] in the also only weakly stabilizing,[25,26] low dielectric constant 2-propanol/benzene mixture. This example is prototypical in our experience: the formation of small amounts of highly active, but not well stabilized and thus metastable, nanocluster heterogeneous catalysts from organometallic precursors.[6,16]

Hg(0) Poisoning Evidence for Rh(0) Catalysis. As additional evidence for the identity of the true catalyst, we also performed a Hg(0) poisoning experiment.[27] Hg(0) poisons metal(0) catalysts by amalgamating the metal or adsorbing on the metal surface.[1,16] Relevant prior literature here for the interested reader is a review[6] and several prior papers[8,16,17] as well as I. Manners's recent results (e.g., where an oxide-supported heterogeneous catalyst is *not* poisoned by Hg(0) on at least shorter time scales[7]).

A Hg(0) poisoning experiment was started as if it were a Standard Conditions benzene hydrogenation experiment (i.e., 100 °C and an initial H_2 pressure of 50 atm). The benzene

(22) (a) The reader familiar with the original work[3] will know that 50 °C and 50 atm H_2 for 36 h were typical conditions employed there, not the 100 °C emphasized herein. It was crucial, therefore, that we performed benzene hydrogenation kinetics at 50 °C and showed that it, too, is sigmoidal. Figure 2 provides just such a 50 °C experiment, *one in which sigmoidal kinetics are observed* just as in the 100 °C experiments. Note that the time scale of the 50 °C experiment is a very inconvenient 500 h ($\sim$21 days), which is why our Standard Conditions herein (e.g., Figures 4–6) are all at 100 °C where the reaction times are much more convenient, 8–40 h. (b) Another subtlety here is that the original[3] 50 °C, 50 atm H_2 benzene hydrogenations were run for 36 h while our *scrupulously cleaned, glass lined*, PARR pressure reactor run in Figure 2 has an induction period of ca. 50 h and takes ca. 400 h to go to completion. The observation of much longer induction periods and slower reactions in cleaned reactors is unexplainable by the assumption of a homogeneous catalysis. *However*, slower reactions in reactors rigorously cleaned from adventitious metal (e.g., Rh(0) left over from prior reactions) in dirty reactors is another piece of evidence—precedented,[17,22c] excellent evidence—consistent with nanoparticle/bulk-metal formation. The underlying physical phenomenon is that *heterogeneous nucleation*[22c] is typically faster due to its lower $\Delta G^{\ddagger}$ in comparison to homogeneous nucleation; see elsewhere for more discussion of these points.[17,22c,23] Hence, the shorter induction periods in the earlier work[3] can now be safely interpreted as evidence for heterogeneous catalysis. (c) Strey, R.; Wagner, P. E.; Viisanen, Y. *J. Phys. Chem.* **1994**, *98*, 7748.
(23) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382.
(24) Widegren, J. A.; Aiken, J. D., III; Özkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312.
(25) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 5796.
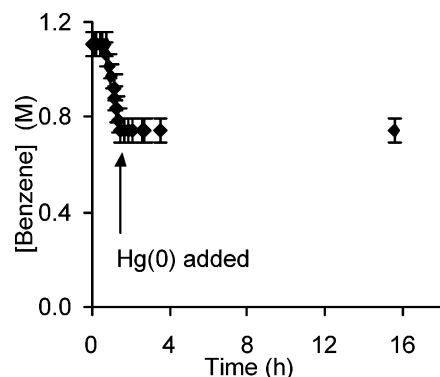(26) Özkar, S.; Finke, R. G. *Langmuir* **2003**, *19*, 6247.

Figure 5. Plot of benzene concentration vs time in a Hg(0)-poisoning experiment. A Standard Conditions benzene hydrogenation with **1** was allowed to proceed for ∼2.5 h, at which point the benzene hydrogenation was ∼30% complete. Then the H$_2$ pressure was released and 6.05 g of Hg(0) was added (∼300 equiv vs Rh). The reactor was repressurized with H$_2$, and the reaction was allowed to continue with vigorous stirring to ensure good mixing of the Hg(0) and catalyst. Following addition of Hg(0), no further benzene hydrogenation is observed.
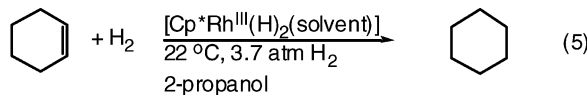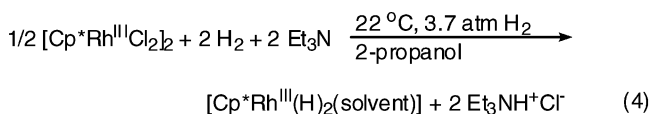
hydrogenation was allowed to proceed until it was about one-third complete, as judged by the H$_2$ pressure loss plus verification by ^{1}H NMR. At that point ∼300 equiv of Hg(0) was added with good stirring (an excess of Hg(0) plus good stirring are known to be crucial to perform this test properly[1,16,17]). The addition of Hg(0) halted catalytic activity *completely*, Figure 5, consistent with heterogeneous metal-particle catalysis. A control experiment was performed which showed that the necessary cooling, then rewarming, of the reactor during the Hg(0) poisoning experiment did not change the catalytic activity and thus cannot be responsible for the loss of activity seen when adding Hg(0) (Figure S6, Supporting Information).

As discussed above, we know from our kinetic experiments that A → B, A + B → 2B and, therefore, that A (=[(η^5-C$_5$-Me$_5$)RhCl$_2$]$_2$, **1**) cannot be the catalyst; instead, B is the catalyst. We also know that Rh(0) is the postcatalysis metal product and that the soluble Rh(0) nanoclusters have the dominant fraction of the catalytic activity. In addition, Hg(0) poisons *all* the catalytic activity, and Hg(0) is known to poison M(0) nano-cluster catalysts (M = transition metals). It follows, therefore,[28] that the Hg(0) poisoning experiment is another piece of evidence consistent with and strongly supportive of Rh(0) nanoclusters, B, as the true catalyst.

Cyclohexene **Hydrogenation: Evidence for a Homogeneous Catalyst.** All of the cyclohexene hydrogenation experiments were performed at 22 °C and 3.7 atm H$_2$, eqs 4 and 5. These conditions are considerably milder than the 100 °C and

50 atm H$_2$ required for the facile hydrogenation of the more difficult to reduce substrate, benzene.

The Lower Pressure and Temperature Reactions

$$\text{1/2 [Cp*Rh}^{\text{III}}\text{Cl}_2]_2 + 2\,\text{H}_2 + 2\,\text{Et}_3\text{N} \xrightarrow[\text{2-propanol}]{22\ ^\circ\text{C, 3.7 atm H}_2}$$

$$[\text{Cp*Rh}^{\text{III}}(\text{H})_2(\text{solvent})] + 2\,\text{Et}_3\text{NH}^+\text{Cl}^- \qquad (4)$$

$$\bigcirc + \text{H}_2 \xrightarrow[\substack{22\ ^\circ\text{C, 3.7 atm H}_2 \\ \text{2-propanol}}]{[\text{Cp*Rh}^{\text{III}}(\text{H})_2(\text{solvent})]} \bigcirc \qquad (5)$$

There is literature precedent for such a change in conditions causing a change in the nature of the true catalyst.[7,29,30] Especially relevant are the kinetics obtained by one of us for simple olefin hydrogenation[3c] and the results obtained by Collman's group using polymer-bound substrates and poisons.[5] The tentative conclusion from those studies is that precatalyst **1** yields a homogeneous catalyst under the mild conditions used for olefin hydrogenation (20 °C and 1 atm).[5] Hence, it was of special interest to see whether the 1994 methodology[8] is able to definitively identify the true cyclohexene hydrogenation catalyst derived from **1** at 22 °C and 3.7 atm H$_2$.

Six lines of evidence lead us to conclude that the true catalyst when starting with precatalyst **1** is in fact *homogeneous* under the mild conditions where cyclohexene hydrogenation occurs.[31] First, unlike the benzene hydrogenation experiments, the cy-clohexene hydrogenation reaction solution remains dark red and does not turn black (black reaction solution being indicative of the formation of large amounts of Rh(0)); there is also no visual evidence for the formation of metallic precipitates.

Second, we examined the kinetics of cyclohexene hydrogenation. As shown in Figure 6, the hydrogen loss vs time occurs *without* an observable induction period and is *not* sigmoidal. Since we also know that most of the Rh is in its red, homogeneous, non-Rh(0) form, it follows that the kinetics argue strongly for a homogeneous catalyst. Either the homogeneous hydrides known to form[3b,c,4] are the faster catalysts for the more easily hydrogenated cyclohexene or there are just too few nanoclusters to perform the bulk of the catalysis. In either case, the important result is that the kinetic evidence strongly supports the postulate of a *homogeneous* cyclohexene hydrogenation catalyst.

(27) (a) Hornstein, B. J.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 1625. Note that, all else being equal, we recommend[1] the use of poisons such as CS$_2$ rather than Hg since CS$_2$ and related S-poisons can be studied *quantitatively*. For example, the Rh(0) nanoclusters in the above cited 2002 paper are fully poisoned by 0.018 equiv of CS$_2$/equiv of the Rh(I) precatalyst used to synthesize the nanoclusters. Such complete poisoning by ≪1 equiv of poison/equiv of metal is strong evidence for a nanocluster and against a homogeneous catalyst (a ≥2 equiv of CS$_2$/equiv of Rh(I) precatalyst is expected for a single metal, homogeneous catalyst in the case of the Rh(I) precatalyst employed[27a]). *However*, we have shown that CS$_2$-poisoned nanoclusters are reactivated at 100 °C for the specific case of Ru(0).[17] This is as expected due to the catalyst + CS$_2$ ⇌ poisoned catalyst·CS$_2$ + heat equilibrium being shifted to the left at higher temperatures. This fact makes the otherwise preferred, quantifiable CS$_2$ poison inapplicable for the current, 100 °C benzene hydrogenation studies. (b) We have recent evidence that 1,10-phenthroline and N-heterocyclic carbenes can be used as nanocluster poisons as higher temperatures of 100 °C. Hagen, C. M.; Finke, R. G. Unpublished results.

(28) Normally, we would also do the control of showing whether the Hg(0) reacts with the precatalyst at the reaction conditions (the side reaction of Hg(0) with at least some organometallic complexes is an undesirable feature of the Hg(0) test[1]). The technical difficulty and safety issues of using Hg(0) at 100 °C inside the NMR probe caused us to reflect on whether we really needed to perform this test in the present case. Reflection revealed that we did not: the kinetic evidence requires that A is not the catalyst, so that any reaction of A with Hg(0) is not relevant and could actually be misleading. In addition, the Hg(0) result (nonpoisoning) in the 22 °C cyclohexene experiment in Figure 7 requires that Hg(0) does not interfere with the discrete, homogeneous catalyst formed under those milder conditions. However, we do recommend the control of Hg(0) plus the precatalyst, and do it ourselves,[17] whenever required.

(29) van Asselt, R.; Elsevier, C. J. *J. Mol. Catal.* **1991**, *65*, L13.

(30) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743.

(31) Note that TEM is useless (if not potentially very misleading) in addressing if the cyclohexene hydrogenation catalyst derived from **1** is homogeneous or heterogeneous since the controls cited earlier (Figures S4) showed that even the mildest, 40 kV and −168 °C, conditions induced nanocluster formation from **1**. Hence, TEM studies of the cyclohexene hydrogenation reaction were deliberately avoided other than to satisfy our curiosity and show that, as expected, TEM of the product solution from a cyclohexene hydrogenation reaction did show nanoclusters (Figure S7), as expected due to TEM-beam-induced nanocluster formation from **1**.
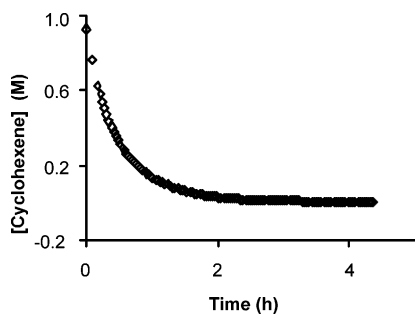
Figure 6. Data for a typical cyclohexene hydrogenation reaction with precatalyst **1** at 22 °C and an initial H_2 pressure of 3.7 atm. The reaction proceeds without an observable induction period and is complete after a total of ~3 h. Cyclohexane is the sole product by ¹H NMR spectroscopy.
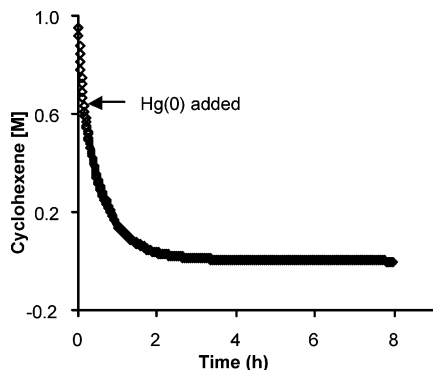

Figure 7. Plot of cyclohexene concentration vs time for a mercury-poisoning experiment. A cyclohexene hydrogenation with **1** was allowed to proceed until 8 psi pressure loss, at which point the cyclohexene hydrogenation was ~30% complete. Then the H_2 pressure was released and 1.65 g of Hg(0) (~300 equiv vs Rh) was added. The reactor was repressurized with H_2, and the reaction was allowed to continue with vigorous stirring to ensure good mixing. No loss of catalytic activity is observed as revealed by the smooth progression of the curve even after the addition of excess Hg(0).

The third piece of evidence is that the dark-red reaction solution obtained following a cyclohexene hydrogenation reaction is a kinetically competent catalyst without any significant induction period (see Figure S8a of the Supporting Information). A fourth piece of evidence is that the addition of a large excess of Hg(0) to an active solution had no detectable effect on the catalytic activity, Figure 7. A fifth line of evidence is from the literature, namely, the experiments performed by Collman's group using polymer-bound substrates and poisons which point to a homogeneous olefin hydrogenation catalyst under mild conditions.[5] Sixth, the rate law for cyclohexene hydrogenation provided previously by one of us[3c] is consistent with, and when combined with the evidence presented herein very strongly supportive of, a homogeneous catalyst.[3c]

In short, the evidence is compelling that the *cyclohexene* catalyst derived from **1** at 22 °C and 3.7 atm H_2 is homogeneous under the room temperature, 3.7 atm H_2 conditions. The monometallic (η^5-C_5Me_5)Rh(III)(H)$_2$(solvent) previously identified by one of us[3,4] is the most probable candidate for that homogeneous catalyst.

Conclusions

The main conclusions from this work are as follows.

(1) The true *benzene* hydrogenation catalyst derived from [Rh-(η^5-C_5Me_5)Cl$_2$]$_2$, **1**, is a nanoparticle heterogeneous catalyst. This answers a 20+ year-old question and corrects the previous

belief[3] that the *benzene* hydrogenation catalyst derived from **1** is a monometallic, homogeneous catalyst.

(2) The true *cyclohexene* hydrogenation catalyst derived from **1** is a homogeneous catalyst, at least under the mild conditions employed herein, as originally postulated by one of us[3b,c,4] and as Collman and co-workers also tentatively concluded.[5]

(3) The 1994 methodology[8] for distinguishing homogeneous catalysis from heterogeneous catalysis has now been successfully used in five of five cases if one includes the present case along with our three prior examples[8,16,17] and the important recent study from I. Manners's group.[7] Significantly, the present example as well as the example from the Manners group[7] shows that both heterogeneous and homogeneous catalysts can be successfully identified using the 1994 methodology, at least in favorable cases. It is important to note that the sigmoidal kinetic signature of many (but not all) nanocluster/metal particle formation reactions[8] is a key component behind the success of the 1994 methodology.

(4) The present results and those of the Manners's group echo the early warning made by Halpern:[32] it is unwise to extrapolate mechanisms of one transition-metal system to another, even a very closely related system, without kinetic and other mechanistic data. Seemingly small changes often change dramatically the pathway and, now, even the primary state of the transition metal (i.e., from single metal organometallic to multimetallic nanoclusters, quite different species).

(5) The present results suggest that the polymer-bound substrate test is probably best replaced by the 1994 methodology[8] (and for the reasons detailed in ref 12). The filtration test as it stands can probably also be abandoned in favor of the 1994 methodology, although now that well-defined nanoclusters are available[13,20] it would be of interest to re-perform the original filtration tests[9] with those authentic nanoclusters. The filtration test remains valuable for distinguishing filterable bulk metal precipitate from catalysis by soluble species, however.

(6) The following three examples allow insights into when nanoparticles are and are not formed: a soluble nanocluster catalyst forms in the present case beginning with [Rh(η^5-C_5-Me_5)Cl$_2$]$_2$, **1**, as it also does when [R$_3$NMe]$^+$[RhCl$_4$]$^-$ is used as the precatalyst.[16] In contrast, a thin-film, bulk-metal catalyst is formed in the case beginning with[17] Ru(II)(η^6-C_6Me_6)(OAc)$_2$. The difference between these cases is very likely due to the presence of base in the former two cases, so that the stabilizer formed is [R$_3$NR′]$^+$Cl$^-$ (R′ = H or Me), a much better stabilizer than the (nonstabilizing) HOAc formed in the latter case (e.g., from Ru(II)(η^6-C_6Me_6)(OAc)$_2$ + H_2 → Ru(0) + 2HOAc + C$_6$-Me$_6$). A recent paper provides evidence for the importance of scavenging the acid formed by added base when metal halide precursors are reduced with H_2 to form nanoclusters (plus HX), Base·H$^+$X$^-$ being a far superior nanocluster stabilizer compared to (the poorly stabilizing) HX.[25,33] The case of the dehydrocoupling catalysts derived from [(1,5-COD)RhCl]$_2$ is more complex: a heterogeneous Rh(0) nanoparticle catalyst is seen for R$_2$NH·BH$_3$ at 25 °C in toluene, but a homogeneous catalyst

(32) (a) Halpern, J. *Acc. Chem. Res*. **1982**, *15*, 332. (b) Many other examples document the assertion that organometallic pathways and mechanisms are sensitive to seemingly small changes in conditions,[32c] see for example, eq 4.25 and chapter 5 elsewhere.[32d] (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, 1987.
(33) Özkar, S.; Finke, R. G *Langmuir* **2002**, *18*, 7653.

is seen for $Ph_2PH \cdot BH_3$ at the higher temperature of 90 °C, also in toluene. Factors determining the homogeneous vs heterogeneous catalysis in this case which were identified from very careful studies include the following:[7] (i) greater reducing ability of the $R_2NH \cdot BH_3$ vs $Ph_2PH \cdot BH_3$; (ii) the lower B−P bond energy and thus increased ease of dissociation of $Ph_2PH \cdot BH_3$ vs $R_2NH \cdot BH_3$; and (iii) the apparent Ph_2PH poisoning of nanocluster active sites. Other factors that one suspects are involved but remain to be identified and, if present, quantified include the following: (iv) the little understood $M_n + (x \cdot m)L \rightleftharpoons M_{n-m} + mML_x$ equilibrium, L = a general ligand, and its temperature dependence (as discussed on p 334 elsewhere[6]); (v) the related issue of the $M_n \cdot L$ bond energies (i.e., for L = Ph_2PH vs R_2NH); and (vi) the apparent preference of the Ph_2-$PH \cdot BH_3$, 90 °C system for a single-metal mechanism of dehydrocoupling. Obviously, the factors which favor heterogeneous over homogeneous catalysis can be multiple, varied, and complex.

(7) Next, a bit of history merits noting at this point. In 1957 it was noted that unactivated *benzene* reduction was taken as an indication of metal particle catalysis.[34] Since that time and beginning in 1963, 40+ years of studies have attempted to prepare monometallic benzene reduction catalysts (see Table A.1 elsewhere and the 31 references therein beginning in 1963[1]). During the past 40 years homogeneous benzene hydrogenation catalysts were often claimed without sufficient attempts—and often no attempt whatsoever—at *disproof* of the leading, well-precedented, must-be-considered alternative hypothesis: that metal(0) particles are the true benzene reduction catalysts. We are now in a position where four carefully reinvestigated systems that were previously claimed to be discrete monometallic catalysts have been shown to be nanocluster[8,16] or bulk metal[17] catalysts, the present study being counted as one of the four studies. After 40 years only Rothwell's Nb^V and Ta^V hydrido complexes[35] appear to be authentic cases of homogeneous *benzene* hydrogenation catalysis (see refs 24−26 in ref 17 for further discussion). In short, in the future it would be wise to heed the approaching 50-year-old 1957 advice and test catalysts by the 1994 methodology before continuing the myth by claiming that one has invented a homogeneous *benzene*—not to be confused with the easier polycyclic arene[2,6,16]—hydrogenation catalyst. Noteworthy here is that a SciFinder search of "benzene *homogeneous* hydrogenation" reveals 56 papers,[36] 15 of which merit reinvestigation in our opinion for their claims of a homogeneous benzene hydrogenation catalyst.

Finally, we conclude by noting that it is not unfortunate, *but instead quite exciting*, when nanoclusters are found to be the true catalysts in important reactions such as in the present case. The partially coordinatively unsaturated, multimetallic surfaces of nanoclusters can perform reactions that single-metal organometallics cannot but that the more widely industrially used heterogeneous catalysts can. Nanoclusters hold considerable potential to be "soluble analogues of heterogeneous catalysts",[13] that is, soluble metal particles whose composition, surface composition, mechanisms, selectivity, deactivated forms, and other properties can be interrogated by powerful solution spectroscopic and kinetic methods. Of course, to have any hope of rationally developing a catalyst, one must know whether it is a soluble nanocluster catalyst or a conceptually quite different single-metal homogeneous catalyst. That has now been accomplished for the precatalyst, $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$, **1,** and as a function of the two limits of temperature and pressure where this precatalyst is commonly employed.

Experimental Section

Materials. Benzene (Aldrich, 99.8%, anhydrous, packaged under N_2) and 2-propanol (Aldrich, 99.5%, anhydrous, packaged under N_2) were transferred into the drybox and used as received. Hg(0) (Aldrich, 99.9995%) was brought into the drybox just before it was needed and then removed after that since Hg(0) will poison the oxygen-scavenging Cu catalyst of the drybox. Triethylamine (Aldrich, 99.5%) was stored in a refrigerator under argon and used as received. Cyclohexene (Aldrich, 99%) was purified by distillation from Na^0 under argon and stored in the drybox. Hydrogen gas (General Air, 99.5%) was used as received. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. The rhodium precatalyst complex $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (Strem, 99%), **1,** was stored in the drybox and used as received.

Analytical Procedures. Nuclear magnetic resonance (NMR) spectra were obtained at 25 °C on a Varian Inova 300 MHz instrument. Chemical shifts were referenced to the residual proton resonance of CD_2Cl_2 at 5.32 ppm. Spectral parameters for ^1H NMR (300 MHz) include the following: tip angle, 30°; acquisition time, 2.67 s; relaxation delay, 0.0 s; sweep width, 6000 Hz. TEM micrographs were collected using a Philips CM-12 TEM with a 70 μm lens operating at 120 kV and, where noted in subsequent control experiments, 40 KV. X-ray photoelectron spectra (XPS) were collected using a Physical Electronics (PHI) model 5800 XPS system equipped with a monochromator with an Al Kα source ($h\nu$ = 1486.8 eV). A hemispherical analyzer detected ejected photoelectrons; the pressure in the spectrometer was $\leq 5 \times 10^{-9}$ Torr. Calibration was accomplished by setting the carbon 1s binding energy to 284.8 eV.

General Procedures for Benzene Hydrogenations. All benzene hydrogenations were performed in a Parr pressure reactor (model 4561) made of Monel 400 alloy. The reactor is equipped with a pressure gauge marked at intervals of 20 psi and an automatic temperature controller (±2.5 °C). Additionally, the inside of the reactor contains a *stainless steel* (i.e., non-Monel) impeller, thermocouple, cooling loop, and dip tube for sampling during reactions; all these components are in contact with 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. The precatalyst was stored, and all reaction solutions prepared, under oxygen- and moisture-free conditions in a Vacuum Atmosphere glovebox (<2 ppm of O_2 as continuously monitored by a Vacuum Atmosphere O_2-level monitor). All of the benzene hydrogenations were performed with an initial H_2 pressure of 740 psig (~50 atm) H_2. Pressurizing the reactor took about 2 min, and t = 0 was set once the reactor was fully pressurized. Pressure gauge readings vs time data were then collected and recorded.

Cleaning the Reactor between Benzene Hydrogenation Reactions, and Testing the Residual Hydrogenation Activity of the Reactor Itself. During benzene hydrogenation reactions with precatalyst **1**, deposits of metallic Rh form on the parts of the reactor that contact the reaction solution (i.e., the thermocouple, dip tube, cooling loop, and impeller). Consequently, it is possible for the reactor itself to have

(34) Smith, H. A. In *Catalysis*; Emmet, P. H., Ed.; Reinhold: New York, 1957; p 175.

(35) Rothwell, I. P. *Chem. Commun.* **1997**, 1331.

(36) Of the 56 papers found containing the concept "benzene homogeneous hydrogenation" from SciFinder Scholar (July 21, 2004), 25 of these papers have complexes that contain benzene. Seven of the papers involve systems investigated[12,14,17] or currently under investigation by our group.[3] Three of the papers are reviews on homogeneous hydrogenation. The remainder of the papers discuss homogeneous hydrogenation of arenes: (i) four for rhodium; (ii) three for nickel; (iii) two for ruthenium; and (iv) seven for cobalt. In light of the present and our past[6,16,17] work in this area, each of these systems merits at least some level of reanalysis and, where warranted, experimental reinvestigation.

nonnegligible hydrogenation activity if not carefully cleaned and then checked for activity with a blank (i.e., no added precatalyst **1**) control reaction prior to the next catalytic run. Hence, following a benzene hydrogenation reaction any Rh film was carefully removed by scrubbing with a steel wool pad and then rinsing with water, nitric acid, and more water. This was followed by further scrubbing with the steel wool pad and finally rinsing with water and acetone (Certified ACS, 99.7%). After each cleaning the reactor was taken into the drybox along with an oven-dried glass liner for the following control experiment. A "blank" hydrogenation experiment, in which no precatalyst was added to the reactor, was then performed in the following manner to test the reactivity level of the cleaned reactor: in the drybox 4.0 mL (44.8 mmol) of benzene, 36 mL of 2-propanol, and 0.41 mL (2.94 mmol) of Et_3N were placed in the glass liner. The glass liner was sealed in the reactor, the reactor was then removed from the drybox and temperature equilibrated at 100 °C (while stirring at 600 rpm), and then the reactor was pressurized to 740 psig with H_2. In the present work, this cleaning procedure always gave no H_2 loss (0 psi) overnight. However, in our other earlier work we have occasionally seen >20 psi H_2 lost overnight, and anytime this level of loss is observed (i.e., ≥20/740 which is ≥2.7%) we cleaned the reactor again and performed another "blank" hydrogenation until a ≤20 psi overnight pressure loss was observed.[17]

Standard Conditions, 100 °C Benzene Hydrogenation with [Rh-(η^5-C_5Me_5)$Cl_2]_2$, 1. In the glovebox 62.5 (±1) mg (0.101 mmol) of **1** was quantitatively transferred into an oven-dried glass liner with 4.0 mL (44.8 mmol) of benzene and 36 mL of 2-propanol, yielding a clear, orange solution with some undissolved precatalyst. Then 0.41 mL (2.94 mmol) of triethylamine was added with a syringe, and the glass liner was sealed in the reactor. The reactor was removed from the drybox, equilibrated at 100 °C (while stirring at 600 rpm), and pressurized to 740 psig with H_2. Under these conditions complete conversion of benzene to cyclohexane corresponds to a pressure loss of about 240 psi. At the end of each hydrogenation reaction the percent conversion was verified directly by ^1H NMR analysis as a control to avoid attributing possible reactor leaks to hydrogenation activity (the NMR sample was prepared by dissolving a drop of the final reaction solution in CD_2Cl_2). Nine repeats of this Standard Conditions experiment were performed, all of which showed sigmoidal hydrogen-uptake curves. The data for one such experiment is shown in Figure 3.

The pressure data were converted to benzene concentration data by a simple proportional relationship: [benzene] = [benzene]$_{initial}$ × (pressure − pressure$_{final}$)/(pressure$_{initial}$ − pressure$_{final}$). This treatment assumes that pressure$_{final}$ corresponds to complete conversion of benzene to cyclohexane; this assumption was verified experimentally by ^1H NMR as noted above (i.e., ≥95% conversion was observed by ^1H NMR at the end of the reaction). The error bars shown for the H_2 pressure (or benzene concentration) assume an error of ±10 psi in the pressure gauge reading and ±2.5 °C in the temperature control. Curve fitting the benzene concentration vs time data was performed as before[24] using the analytic equations for the A → B then A + B → 2B mechanism and the commercial software package Microcal Origin 3.5.

GC-MS Experiment Showing Cp* Ligand Loss from 1 by Observation of the Resultant Cp*−H and Its Hydrogenation Products Cp*−H_3 and Cp*−H_5. These experiments are detailed in the Supporting Information.

Hydrogenations at 50 °C. The exact literature 50 °C hydrogenation conditions[3] were tested in our pressure reactor in three experiments identical to the above experiments except that the temperature was 50 °C instead of 100 °C. At the end of these hydrogenation reactions the percent conversion was verified directly by ^1H NMR analysis of the reaction solution. Three experiments at the original conditions of 50 °C were performed, all of which showed a long induction period, followed by slow hydrogen uptake, Figure 2.

X-ray Photoelectron Spectroscopy (XPS). After a Standard Conditions benzene hydrogenation at 100 °C the glass liner was broken with a hammer and a sample of the metallic-film-coated glass liner analyzed

by XPS. The metallic film proved to be Rh(0), with binding energy peaks at 48.41 (4p), 307.72 (3d$_{5/2}$), 312.65 (3d$_{3/2}$), 496.34 (3p$_{3/2}$), 522.06 (3p$_{1/2}$), and 630.49 (3s) eV, in good agreement with the literature.[18]

Transmission Electron Microscopy (TEM). Samples for TEM were prepared on 300-mesh copper TEM grids with a 1.5−2.5 nm carbon support film and Formvar backing, purchased from Ted Pella, Inc. Prior to their use the Formvar backing was removed following the supplier's instructions by gently dipping the grids in acetone for 5 s, chloroform for 20 s, and acetone for 5 s. Following a hydrogenation reaction with precatalyst **1** the reactor was immediately brought into the drybox and opened. The reaction solution was transferred to a glass scintillation vial and taken out of the drybox. An aliquot of the black reaction solution was diluted 1:30 with 2-propanol. The TEM samples were prepared by placing 2−3 drops of the diluted solution on a TEM grid, blotting the excess liquid with a piece of filter paper, and allowing the solvent to evaporate. The nanoclusters observed were confirmed to be Rh(0) by EDS, showing peaks at 2.65 and 2.79 keV from a 100 °C reaction sample and 2.67 and 2.81 keV from a 22 °C reaction sample, both in good agreement with the literature.[21]

For the TEM control experiments, 62.5 (±1) mg (0.101 mmol) of **1** was quantitatively transferred into an oven-dried glass liner with 4.0 mL (44.8 mmol) of benzene and 36 mL of 2-propanol, yielding a clear, orange solution with some undissolved precatalyst, in the glovebox. Then 0.41 mL (2.94 mmol) of triethylamine was added with a syringe, yielding a dark-red solution which was stirred for ~1 h. An aliquot of the red reaction solution was diluted 1:30 with 2-propanol. The TEM samples were prepared by placing 2−3 drops of the diluted solution on a TEM grid, blotting the excess liquid with a piece of filter paper, and allowing the solvent to evaporate. TEMs at 120 kV were obtained: (i) at room temperature and 5, 25, and 45 min of TEM beam exposure and (ii) at −168 °C and 5, 25, 45, and 65 min of beam exposure. TEMs at 40 kV were obtained with 5 min of TEM beam exposure.

The above TEM grids were packaged in glass vials and sent to the University of Oregon, where TEM and EDS analysis was performed as before[23] with the expert assistance of Dr. JoAn Hudson, Dr. Eric Schabtach, and their staff. Note that neither this sample preparation procedure nor the TEMs themselves are O_2-free, so that some surface oxide coating of the nanoclusters is expected. This does not hinder the present work, however, where only the presence of the nanoclusters, and not their precise size as prepared, is the main question of interest.

Testing the Kinetic Competence of the Metallic Film and of the Black Reaction Solution from a Benzene Hydrogenation Experiment. A Standard Conditions benzene hydrogenation experiment was started and allowed to proceed to completion, as verified by ^1H NMR. At that point the reactor was cooled quickly to room temperature via the cooling loop, vented, taken into the drybox, and opened. The black reaction solution was filtered through a disposable nylon syringe filter (0.2 μm pore size) into a clean, oven-dried glass liner (the reactor components in contact with the reaction solution were not cleaned). Filtration did not noticeably change the appearance of the black solution. Then, 4.0 mL (44.8 mmol) of benzene was syringed into the solution with a gas-tight syringe before sealing the glass liner in the reactor. After removing the reactor from the drybox, it was equilibrated at 100 °C (while stirring at 600 rpm) and pressurized to 740 psig with H_2.

In a separate experiment, to the glass liner containing the metallic film, 4.0 mL (44.8 mmol) of benzene, 36 mL of 2-propanol, and 0.41 mL (2.94 mmol) of triethylamine were added. The reactor was sealed (i.e., without cleaning the Rh-coated thermocouple, dip tube, cooling loop, and impeller), brought out of the drybox, equilibrated at 100 °C (while stirring at 600 rpm), and pressurized to 740 psig with H_2. These experiments were repeated 3 times with equivalent results; see Figure 4 for the data from one such representative set of experiments.

Mercury-Poisoning Experiment for Benzene Hydrogenation. This experiment was started as if it were a Standard Conditions benzene hydrogenation experiment [i.e., 62.5 mg (0.101 mmol) of **1**, 4.0 mL (44.8 mmol) of benzene, 36 mL of 2-propanol, 0.41 mL (2.94 mmol)

of Et$_3$N, 100 °C, and an initial pressure of 740 psig]. Pressure vs time data were collected until the pressure had decreased to 660 psi, that is, until ca. one-third completion (complete conversion corresponds to a pressure change of ~240 psi). Then the reactor was cooled to room temperature, vented, taken into the drybox, and opened. Next, 6.05 g of Hg(0) (30.2 mmol, ~300 equiv vs Rh precatalyst) was added to the black reaction solution. The reactor was then resealed, brought out of the drybox, equilibrated at 100 °C, and pressurized to 660 psi with H$_2$. At this point the collection of pressure vs time data was restarted (the ~2 h gap required for the poisoning procedure was ignored as the data in Figure 5 show is justified). The experiment was repeated twice with identical results within experimental error; the data for one experiment are shown in Figure 5.

Control Experiment for Benzene Hydrogenation Showing That Cooling, Transferring to the Drybox, and Opening the Parr Reactor and then Reheating and Restarting the Reaction Does Not Cause a Detectable Loss of Activity. The details of this control are presented in the Supporting Information.

Cyclohexene Hydrogenation with the Precatalyst 1, 22 °C. The setup for this experiment has been described in detail previously.[8,23] Briefly, in the drybox 16 ($\pm$1) mg (0.026 mmol) of **1** was dissolved in 1.0 mL (9.87 mmol) of cyclohexene, 9.0 mL of 2-propanol, and 0.11 mL (0.789 mmol) of triethylamine. This orange solution was transferred into a new 22 × 175 mm Pyrex culture tube containing a 5/8 × 5/16 in. Teflon-coated stir bar. The culture tube was placed in a Fischer–Porter (F–P) pressure bottle modified with Swagelock TFE-sealed Quick-Connects.[8,23] The F–P bottle was then sealed, removed from the drybox, attached to a H$_2$ line via the Quick-Connects, and purged every 15 s for 15 repetitions (for a total time of 195 s) with 40 psig H$_2$ (in order to replace the nitrogen atmosphere with hydrogen). Following the purges the F–P bottle was filled to an initial pressure of 40 ($\pm$1) psig H$_2$. During the purging (and during the hydrogenation reaction) the reaction solution was vortex stirred. Five minutes after beginning the purging cycle the time was designated as $t = 0$ (as detailed previously[8,23]), and data collection was initiated using an Omega PX-621 pressure transducer interfaced to a PC. Ten repeats of the cyclohexene hydrogenation were performed; the data for one representative experiment are shown in Figure 6.

Experiment Testing the Kinetic Competence of the Red Reaction Solution from a Low-Temperature Cyclohexene Hydrogenation Experiment. The details of this experiment are presented in the Supporting Information.

Mercury-(Non)Poisoning Experiment for Cyclohexene Hydrogenation. This experiment was started as if it were a normal cyclohexene hydrogenation experiment [i.e., 16 mg (0.026 mmol) of **1**, 1.0 mL (9.87 mmol) cyclohexene, 9.0 mL of 2-propanol, 0.11 mL (0.789 mmol) of Et$_3$N, 22 °C, and an initial H$_2$ pressure of 40 psig]. Pressure vs time data were collected until the pressure had decreased to 32 psig, at which point the reaction was about one-third complete (complete conversion corresponds to a pressure change of about 24

psig). Then the F–P bottle was taken into the drybox and opened. Next, 1.65 g of Hg(0) (8.23 mmol; ~300 equiv vs Rh precatalyst) was added to the red reaction solution. The F–P bottle was then resealed, brought out of the drybox, and repressurized to 32 psig of H$_2$. At this point the collection of pressure vs time data was recommenced (ignoring the ~1 h gap required for the poisoning procedure). The experiment was repeated three times with equivalent results. The data for one representative experiment are shown in Figure 7.

Supporting Information Available: GC/MS detection of Cp*–H and its hydrogenation products (Table S1); transmission electron micrograph following a Standard Conditions benzene hydrogenation with precatalyst **1** at 100 °C (Figure S1); control experiment testing if TEM can induce the formation of Rh(0) nanoclusters from **1** alone (Figure S2); time vs size control TEM experiment performed using low-temperature (−168 °C) TEM (Figure S3); control experiment testing if TEM can induce formation of Rh(0) nanoclusters from **1** alone at 40 kV (Figure S4); alternative procedure for testing the kinetic competence of soluble species vs the metal-coated reactor (Figure S5); control experiment for benzene hydrogenation showing that cooling, transferring to the drybox, opening the Parr reactor, and then reheating and restarting the reaction does not cause a detectable loss of activity (Figure S6); experiment testing the kinetic competence of the red reaction solution from a low-temperature cyclohexene hydrogenation experiment; TEM at 120 kV following a Standard Conditions cyclohexene hydrogenation with precatalyst, **1**, at 22 °C (Figure S7); kinetic competence test of the cyclohexene hydrogenation product solution (Figure S8a); mercury poisoning experiment at 22 °C and an initial H$_2$ pressure of 3.7 atm when using as the catalyst the final dark-red solution produced from a prior cyclohexene hydrogenation that began with **1** (Figure S8b); details regarding the early light-scattering experiments and apparatus. This material is available free of charge via the Internet at http://pubs.acs.org.

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