Supramolecular Triruthenium Cluster-Based Benzene Hydrogenation Catalysis: Fact or Fiction?

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The question is addressed of whether the triruthenium cluster cation $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$, **1**, is a supramolecular, outer-sphere benzene hydrogenation catalyst or is **1** a precatalyst to well-known $Ru(0)_n$ catalysis of benzene hydrogenation. This question of "is it homogeneous or heterogeneous catalysis?" is especially important in the present case since if **1** is a supramolecular, homogeneous catalyst as postulated in the literature— that is, if **1** can in fact accomplish catalysis of reactions *as difficult as benzene reduction* with no inner-sphere, d-orbital-mediated ligand dissociation, oxidative addition, migratory insertion, or reductive elimination—then that finding holds promise of rewriting the rules of organometallic-based catalysis. The identity of the true catalyst derived from **1** is, therefore, addressed by a collaborative effort between research groups at the Université de Neuchâtel and Colorado State University. The methodology employed is that worked out previously for addressing the historically vexing question of "is it homogeneous or heterogeneous catalysis?" (Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891). A combination of the following classes of experiments have been employed: (i) Ru metal product studies; (ii) kinetic studies; (iii) Hg(0) and quantitative poisoning experiments, (iv) NMR studies of H/D exchange rates; (v) other data, plus (vi) the principle that the correct mechanism will explain all of the data. The results provide a compelling case that **1** is *not* the true benzene hydrogenation catalyst as previously believed; instead, all our evidence is consistent with, and supportive of, trace Ru(0) derived from **1** under the reaction conditions as the true, active catalyst. Nine additional conclusions are also presented as part of the summary and take-home messages, as well as a citation of "Halpern's rules" for catalysis.

Introduction

Supramolecular catalysis[1]—that is, catalysis by manmade macromolecular assemblies exhibiting the intermolecular, noncovalent complexation/recognition, lowered $\Delta G^{\ddagger}$, high selectivities and the other highly desirable aspects associated with, for example, enzymic catalysis— is a research topic of considerable interest that promises to flourish long into the 21st century. In 2002, one of us (G.S.F.) reported[2] that the novel cationic triruthe-

nium cluster $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$, **1**, added as tetrafluoroborate salt, [**1**][BF_4], at 0.10 mol % leads to the reduction of benzene to cyclohexane at 110 °C, 60 bar (∼60 atm) H_2, in water with a catalytic turnover frequency (TOF) of[2a] 289 h^{-1} and a total turnover (TTO) value of 740 after 2.5 h.[2b] Some, albeit nondefinitive, evidence[2a] suggested at the time that the observed catalysis was by intact **1**, surprisingly outer-sphere and, hence, "supramolecular".
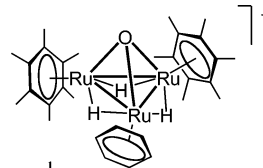
The notion of such supramolecular, outer-sphere catalysis by a transition metal complex—that is, putatively no inner-sphere, d-orbital-mediated ligand dissociation, oxidative addition, migratory insertion, or reductive elimination[3]—held the possibility of rewriting the rules of organometallic catalysis; hence, the first

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(1) Lehn, J. M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH Publishers: Weinheim, 1995. See pp 1−9 for Lehn's definitions and descriptions of supramolecular chemistry in which key notions are noncovalent, intermolecular interactions between molecules to achieve higher molecular assemblies capable of doing new chemistry.
(2) (a) Süss-Fink, G.; Faure, M.; Ward, T. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 99. (b) Süss-Fink, G.; Therrien, B.; Vieille-Petit, L.; Tschan, M.; Romakh, V. B.; Ward, T. R.; Dadras, M.; Laurenczy, G. *J. Organomet. Chem.* **2004**, *689*, 1362. Also reported in this second paper is an updated synthesis of the derivative of **1** in which an OH has replaced one of the bridging hydride ligands, namely, $[Ru_3(\mu_2\text{-}H)_2(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)(\mu_2\text{-}OH)]^+[BF_4]$, [**2**][BF_4]. (c) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G.; Ward, T. R. *J. Organomet. Chem.* **2003**, *684*, 117.

(3) 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.

paper[2a] attracted the interest of two *Chemical & Engineering News* articles.[4] Since then a second paper has been completed[2b] reporting (a) the relative rates of hydrogenation of methyl-substituted benzenes (toluene, xylenes, durene), (b) the slow exchange (for ethylbenzene) to no exchange (for d_6-benzene) of arenes with **1** on the time scale of benzene reduction catalysis, and (c) the high rates of ethylbenzene reduction due to the trace, autoxidation impurity $C_6H_5CH(OOH)CH_3$ and its reaction with **1**. The reported results also include (d) the X-ray structures for the novel host−guest complexes with benzene, $[C_6H_6\subset\textbf{3}][PF_6]$ and $[C_6H_6\subset\textbf{4}][BF_4]$, where **3** is $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_5(CH_2)_2OH)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$ and **4** is $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_5(CH_2)_3OH)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$.[2c] The two X-ray structure analyses provide unequivocal evidence for the previously proposed[2a] complexation of benzene to **1** and presumably also, therefore, to $[Ru_3(\mu_2\text{-}H)_2(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)(\mu_2\text{-}OH)]^+$, **2**.
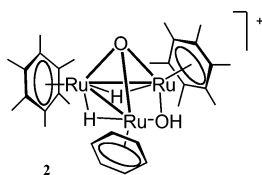
The research group of another of us (R.G.F.) has been interested in benzene hydrogenation for some time,[5−7] especially the intertwined, historically difficult, persistent problem[8] of distinguishing true, unprecedented *benzene* hydrogenation *homogeneous catalysis*[9] by a group 8−10 metal (e.g., by **1** or its intact Ru_3 derivatives) from well-precedented benzene hydrogenation *heterogeneous catalysis*[10,11] (i.e., $Ru(0)_n$ nanoclusters or bulk metal catalysis derived from **1**).[6,12−14] Our 2003 review[12] of 180 references from the literature on the "Is it homogeneous or heterogeneous catalysis?" question

identified 30 systems claiming homogeneous catalysis where the true catalyst may be heterogeneous. Significantly, and although polycyclic arene (e.g., naphthalene or anthracene) homogeneous hydrogenation is well established,[15] the more difficult *benzene* reduction using a homogeneous catalyst is compellingly demonstrated and thus precedented only for Ian Rothwell's Ta^V, Nb^V complexes[9] (see also Dyson's valuable review[16]). That is, group 8 metal *homogeneous* catalysis of benzene hydrogenation remains unprecedented, an important insight from the literature that must no longer be ignored.[17] The original report of homogeneous, supramolecular catalysis[2] by **1** is the most celebrated of the 30 systems identified in our review where homogeneous catalysis is claimed, but heterogeneous catalysis could not unequivocally be ruled out.[12] Hence, our Colorado State University (hereafter CSU) and Université de Neuchâtel (hereafter Neuchâtel University) research teams decided to collaborate to identify the true benzene hydrogenation catalyst derived from **1**: is it homogeneous (supramolecular) or heterogeneous (nanocluster or bulk metal)? It is this collaborative, productive, and we will argue definitive, effort that is the focus of the present paper.

A second topic highly relevant to the present paper is that of *outer-sphere* reactions for organotransition

(4) (a) Supramolecular Cluster Catalysis, Science and Technology Concentrates. *Chem. Eng. News* **2002**, *Jan 14*, 22. (b) *Chem. Eng. News* **2002**, *March 11*, 6, has a letter from one of the world's experts in hydrogenation chemistry,[4c] Prof. Brian James, a letter that makes it apparent that Prof. James did not quite believe the original report[2a] ("There can't be many more mechanistic surprises in catalytic hydrogenations!"). (c) A careful reading of Prof. James' letter makes it apparent that he is pointing out, ever so subtly, that nanocolloids or possible radical mechanisms (the latter as seen for $HCoCN_5^{3-}$)[18b] are the two alternative hypotheses he can see for the putative supramolecular chemistry.[2]

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

(6) Weddle, K. S.; Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653.

(7) For the closely related case of anisole reduction (by polyoxoanion- and Bu_4N^+-stabilized Rh nanocluster catalysts): Widegren, J. A.; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 1558.

(8) (a) Early contributions to the "Is it homogeneous or heterogeneous catalysis?" question by Maitlis, Whitesides, Crabtree, Collman, and Lewis are detailed elsewhere[12] for the interested reader. (b) Whether or not $Ru(0)_n$ colloids are the true catalysts derived from Ru-organometallic precatalysts is a current issue in interesting recent work aimed at finding a practical lignin hydrogenation catalyst: Wong, T. Y. H.; Pratt, R.; Leong, C. G.; James, B. R.; Hu, T. Q. *Chem. Ind.* **2001**, *82*, 255 and references therein.

(9) (a) The one case of bona fide benzene homogeneous hydrogenation catalysis is that from Rothwell's group. We are deeply saddened by Ian's untimely death.[9b] The present work provides additional evidence for the uniqueness of Ian's chemistry. (a) Rothwell, I. P. *Chem. Commun.* **1997**, 1331. (b) *Chem. Eng. News* **2004**, *June 7*, 44.

(10) Lead references to the extensive literature (see also ref 11) of benzene[10a] and other aromatic hydrocarbon[10b] heterogeneous hydrogenation are: (a) Weissermel, K.; Arpe, H. J. *Industrial Organic Chemistry*, 2nd ed.; VCH: New York, 1993. (b) Aromatic Hydrogenation Catalysis: A Review. Stanislaus, A.; Cooper, B. H. *Catal. Rev.− Sci. Eng.* **1994**, *36*, 75.

(11) Lead references to the more voluminous literature of the industrially important topic of the partial hydrogenation of benzene, with a focus on Ru heterogeneous catalysts, are: (a) Hu, S.-C.; Chen, Y.-W. *Ind. Eng. Chem. Res.* **2001**, *40*, 6099−6104. (b) Chen, Yu-Wen; Hu, Sung Cheng. *J. Chin. Inst. Chem. Eng.* **2000**, *31*, 529−532. (c) Hu, S.-C.; Chen, Y.-W. *J. Chin. Inst. Chem. Eng.* **1998**, *29*, 387−396. (d) Struijk, J.; Moene, R.; Van der Kamp, T.; Scholten, J. J. F. *Appl. Catal., A* **1992**, *89*, 77. (e) Struijk, J.; D'Angremond, M.; Lucas-De Regt, W. J. M.; Scholten, J. J. F. *Appl. Catal., A* **1992**, *83*, 263.

(12) Widegren J. A.; Finke, R. G. *J. Mol. Catal.* **2003**, *198*, 317−341 ("A review of the problem of distinguishing true homogeneous catalysis from soluble or other metal-particle heterogeneous catalysis under reducing conditions"). Table S1 of the Appendix of that review lists >30 catalyst systems for which metal-particle heterogeneous catalysts are suspected to be the true catalysts.

(13) Widegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10301.

(14) Hagen, C.; Widegren J. A.; Maitlis, P. M.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, in press.

(15) It is important to distinguish *the more difficult benzene reduction* from other, *easier to reduce*, polycyclic arenes as we have made clear in our 1998 paper[16] and our review.[5] That this is true follows from Halpern's kinetic and mechanistic work which provides compelling evidence for homogeneous *anthracene and naphthalene* hydrogenation catalysts (see elsewhere for a discussion and references[35]). Note also the misquotation elsewhere[16] on this point as corrected in footnote 2 elsewhere.[14]

(16) Dyson, P. J. *Dalton Trans.* **2003**, 2964.

(17) Conclusion #8 from our recent paper[14] is worth repeating here: "A bit of history seems worth noting at this point. In *1957* (Smith, H. A. *Catalysis*; Emmet, P. H., Ed.; Reinhold: New York, 1975; p 175) it was noted that unactivated *benzene* reduction was taken as an indication of metal-particle catalysis. Since that time and beginning in 1963, 40+ years of studies have attempted to prepare monometallic benzene reduction catalysts (see Table A.1 elsewhere[12] and the 31 references therein from 1963 forward). 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-particles are the true benzene reduction catalysts. We are now in a position where five carefully reinvestigated systems that were previously claimed to be discrete, monometallic catalysts have been shown to be nanocluster[6,14,21] or bulk-metal[13] catalysts, the present study being counted as one of the five studies. After 40 years, only Rothwell's Nb^V and Ta^V hydrido complexes[9] appear to be an authentic case of homogeneous *benzene* hydrogenation catalysis (see footnotes 24−26 elsewhere[13] for further discussion). In short, future researchers would be wise to listen to the 1957 advice, and to test their catalysts by the methodology in Figure 1, before continuing the myth by claiming that they have invented a homogeneous *benzene*—not to be confused with the easier polycyclic arene[5,6] hydrogenation catalyst."

metal catalytic reactions[18,19] (i.e., reactions with no direct d-orbital-to-substrate participation), a relatively rare but now established phenomenon in, for example, hydrogenation reactions of carbonyl compounds.[18] However, outer-sphere, supramolecular hydrogenation of the difficult to reduce substrate benzene is not yet precedented. Note also that, as is well known[20a−d] and as Marcus−Hush theory explains,[20e,f] outer-sphere mechanisms are often slower than their inner-sphere counterparts due to the lower intrinsic barriers in the inner-sphere case as a result of simultaneous bond breaking and making.

Methodology Used to Address the "Is It Homogeneous or Heterogeneous Catalysis?" Question

The methodology used herein to uncover the true benzene hydrogenation catalyst derived from **1** is that reported in 1994 by one of our groups and illustrated schematically in Figure 1.[21] To date, this methodology has proven effective in distinguishing heterogeneous from homogeneous catalysis in four out of four systems that were originally claimed to be homogeneous catalysts[6,13,14,21] (three from the previously mentioned 30 suspect systems[12]). This includes distinguishing *both* heterogeneous catalysis (benzene reduction) from homogeneous catalysis (simple olefin reduction) derived from the same precursor, $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$, but under different conditions (heterogeneous catalysis at *higher temperatures and pressures*, but homogeneous catalysis at lower temperatures and pressures).[14] Important studies from I. Manners's group for a completely different class of catalytic reactions, amine-borane and phosphine-borane dehydrocouplings, have also been able to distinguish homogeneous from heterogeneous catalysis using the methodology in Figure 1.[22] Manners's interesting results lead to the intriguing and partially
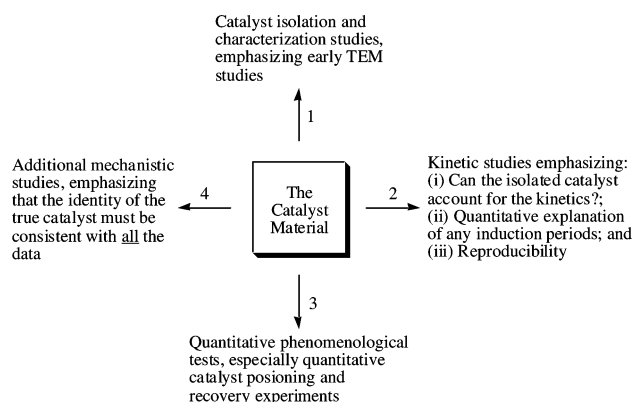

Figure 1. The most recent,[21] proving to be more general,[13,14,21,22] approach to distinguish between a metal-particle "heterogeneous" catalyst and a metal-complex "homogeneous" catalyst. The expanded, full (12 point) version of this approach is available in Figure 5 elsewhere.[21]

(but not yet completely) understood observation[22] that the heterogeneous catalysis corresponds in their system to the *lower* temperature conditions, the opposite of the above-noted case.[14] Obviously, the factors affecting homogeneous versus heterogeneous catalysis[12] can be system dependent. Others are now successfully adopting key aspects of the methodology in Figure 1 to address the true catalyst in solid-supported Mizoroki−Heck Pd-catalyzed chemistry as well.[23] Ultimately, the methods in Figure 1 emphasize several key principles: (i) that kinetic evidence is crucial, because catalysis is a wholly kinetic phenomenon;[24,25] (ii) that *no single* method can identify the true nature of the catalyst; and (iii) that the correct explanation/description of the catalyst must be able to explain *all* the available data.

Herein we determine the true benzene hydrogenation catalyst derived from **1** using the general methodology in Figure 1. Product, kinetic, Hg(0) poisoning, 1,10-phenanthroline poisoning, NMR, and other evidence[26] provide a compelling case that the true catalyst is not **1** but, instead, is a heterogeneous $Ru(0)_n$ catalyst derived from **1**. Most importantly, we have combined forces and have vigorously discussed and debated the experiments, interpretations, and conclusions in the present paper prior to this publication so as to be able to provide a jointly approved, definitive answer on the nature of the true benzene hydrogenation catalyst derived from **1**.

Results and Discussion

(i) Metal Product Studies. Pure $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+[BF_4]^-$, $[\mathbf{1}][BF_4]$, was used to

(18) (a) Radical pathways, notably the classic $HCoCN_5^{3-}$ and related hydrogenations,[18b] are known examples of outer-sphere hydrogenation pathways −"molecule assisted homolyses" in the language of organic chemistry.[18c−e] There are also the reports from Noyori's labs[18f−h] of ketone reductions occurring via an outer-sphere mechanism, a pathway that Casey's detailed mechanistic work[18i,j] helps document. Hence, there are already some, albeit infrequent, established cases of outer-sphere hydrogenation mechanisms in homogeneous catalysis. (b) James, B. R. In *Homogeneous Hydrogenation*; J. Wiley: New York, 1973; Chapter VIII, p 314. (c) Pryor, W. A. *ACS Symp. Ser.* **1978**, *69*, 33. (d) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 173. (e) Rüchardt, C.; Gerst, M.; Ebenhoch, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1406. (f) Noyori, R.; Masashi, Y.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (g) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40. Yamakawa, M. (h) Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466. (i) Casey, C. P.; Johnson, J. B. *J. Org. Chem.* **2003**, *68*, 1998. (j) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090.

(19) Relevant to non-d-orbital mechanisms of hydrogenation is, of course, the interesting example of nature's all-metal-free, organic-ligand-based hydrogenation system that, by definition, is free from any d-orbital influence: Reactions with Molecular Hydrogen in Microorganisms: Evidence for a Purely Organic Hydrogenation Catalyst: Thauer, R. K.; Klein, A. R.; Hartmann, G. C. *Chem. Rev.* **1996**, *96*, 3031.

(20) (a) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321. (b) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264. (c) Weaver, M. J. *Inorg. Chem.* **1979**, *18*, 402. (d) Rotzinger, F. P.; Kumar, K.; Endicott, J. F. *Inorg. Chem.* **1982**, *21*, 4111. (e) Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3465. (f) Reimers, J. R.; Hush, N. S. In *Electron and Ion Transfer in Condensed Media: Theoretical Physics for Reaction Kinetics*; Kornyshev, A. A., Tosi, M., Ulstrup, J., Eds.; World Scientific: Singapore, 1997; pp 326−346.

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

(22) (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.
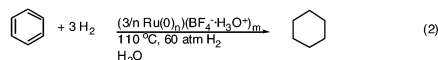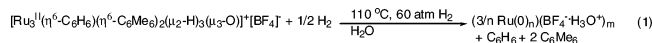
(23) (a) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W. *J. Catal.* **2004**, *226*, 101. (b) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161.

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

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

(26) The following results were obtained at Neuchâtel University: (i) the finding that complex **1** made at Neuchâtel University yields identical kinetic results when used at CSU; (ii) the finding that the same autocatalytic kinetics diagnostic of nanocluster formation are seen in experiments done at Neuchâtel University; (iii) the finding that bulk Ru(0) metal is also observed as a product in Neuchâtel University experiments; and (iv) the finding that such bulk metal is a kinetically competent catalyst. The H/D exchange NMR experiments for complex **1** were performed at the Ecole Polytechnique Fédérale de Lausanne.

hydrogenate benzene at 110 °C and 60 atm (880 psig) of H_2, eqs 1 and 2 (hereafter "Standard Conditions" as further detailed in the Experimental Section). As previously reported, the main metal "product" by ^{1}H NMR is ≥95% recovered [**1**][BF_4][2b] precatalyst which can be recycled for subsequent benzene hydrogenations (Figure S1 of the Supporting Information). However, a thin *metallic film*, confirmed to be Ru(0) by XPS,[27] is formed on the reactor components in contact with the solution. Note that bulk metal is the expected end product from any first-formed nanoclusters, "[(Ru(0)$_n$)($H_3O^+BF_4^-$)$_m$]",[28] as these nanoclusters have no effective stabilizer (BF_4^- is a weakly coordinating anion and thus a weak stabilizer at best; protonated $H_3O^+BF_4^-$ is expected to be a nonstabilizer[29-31]). The formation and activity of Ru(0) were also confirmed in experiments done at Neuchâtel University. In these experiments, a benzene hydrogenation was performed and the postreaction solution was removed by decanting. A transparent black film on the walls of the glass liner was able to convert benzene to cyclohexane with a TOF = 62 h^{-1} when fresh benzene and water were added (details are available in the Supporting Information).

$$[Ru_3^{II}(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+[BF_4]^- + 1/2\ H_2 \xrightarrow[H_2O]{110\ °C,\ 60\ atm\ H_2} (3/n\ Ru(0)_n)(BF_4^-\cdot H_3O^+)_m + C_6H_6 + 2\ C_6Me_6 \quad (1)$$

$$\bigcirc + 3\ H_2 \xrightarrow[\substack{110\ °C,\ 60\ atm\ H_2 \\ H_2O}]{(3/n\ Ru(0)_n)(BF_4^-\cdot H_3O^+)_m} \hexagon \quad (2)$$

Note that these metal product studies provide the first, crucial result key to the methodology shown in Figure 1: that catalytically active Ru(0) is present (≤5%), but the majority of precatalyst **1** (≥95%) remains unchanged.[2b] *This means that any physical method attempting to detect the true catalyst will be biased toward, and thus confused by, the presence of (mostly) **1***. The TEM studies and control done next illustrate the importance of these metal product experiments: knowing where the mass of one's precatalyst (**1** in this case) ends up at, the first step in the methodology in Figure 1.

(ii) Transmission Electron Microscopy (TEM) Studies. A control was done first to answer the question, does TEM "analysis" convert **1** to nanoclusters under the reductive conditions of the TEM beam? Since most of the mass is unreacted [**1**][BF_4], this is an important control. This control was performed by dissolving [**1**][BF_4] in water and benzene (1.5 M) and then placing 2−3 drops of this red-orange solution on a TEM grid, as detailed in the Experimental Section. The control TEM micrographs (120 kV) *showed the presence of 1.5 ± 0.5 nm Ru(0) particles from precatalyst [1][BF$_4$] alone*, Figure 2. Thus, in this case TEM is "causing" not reporting the news.[32] Manners's and co-workers have
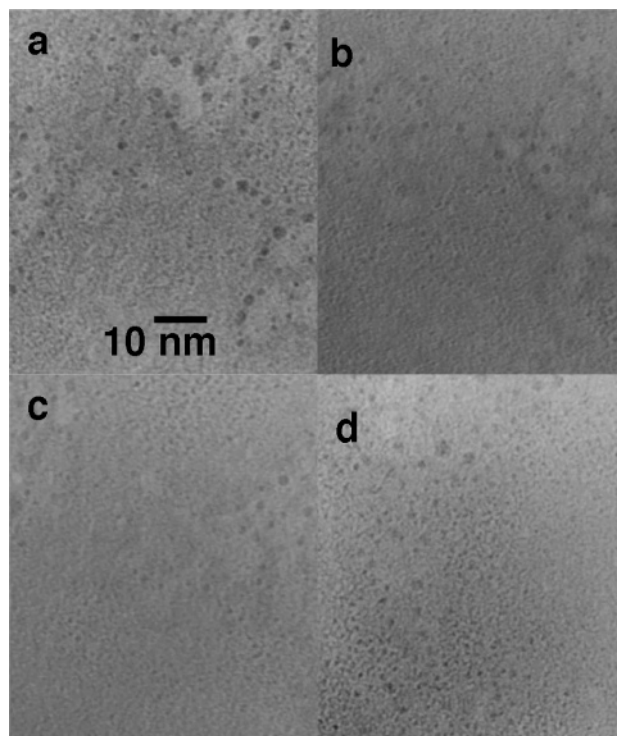

Figure 2. Control transmission electron micrograph (TEM) of 2−3 drops of the red-orange solution of [**1**][BF_4] in water and benzene (1.5 M). In this TEM control experiment precatalyst, [**1**][BF_4], was diluted in benzene and water, placed on a TEM grid, and then examined as a function of time in the 120 kV TEM beam. Nanoclusters ranging from 1.1 to 2.8 nm, with an average size of 1.5 ± 0.5 nm (110 nanoclusters counted) are observed. The nanoclusters formed in the TEM beam remain constant in size in the TEM beam (the scale bar is the same for all four micrographs). (a) The sample in the TEM beam after 5 min (1.1−2.8 nm nanoparticles); (b) the same sample area as in (a) but after 25 min (also exhibiting 1.1−2.8 nm nanoparticles); (c) the same sample area after 45 min (still exhibiting 1.1−2.8 nm nanoparticles); and (d) the same sample area after 65 min (but still exhibiting 1.1−2.8 nm nanoparticles). The results show that (i) TEM-beam-induced nanoclusters are formed, but (ii) that their size does not change as a function of time (under the specific TEM conditions employed).

recently reported similar TEM-beam-induced nanocluster formation from a [Rh(1,5-COD)Cl]$_2$ precatalyst,[22] and we have reported this also for a [Cp*RhCl$_2$]$_2$ precatalyst.[14] In Manners's system using less harsh TEM beam conditions (reducing the accelerating voltage to 30 kV) was found to eliminate the formation of nanoclusters from this precatalyst;[22b] however, at 40 kV TEM conditions we still observed the presence of nanoclusters derived from [Cp*RhCl$_2$]$_2$.[14,33] In further control

(27) 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.

(28) The formula "[(Ru(0))$_n$($H_3O^+ BF_4^-$)$_m$]" is written by analogy with other, established nanocluster systems.[13,28] This assignment should be considered tentative (the exact composition of the nanoclusters is nontrivial[21] and not a focus of, nor necessary for, the present work). (a) Aiken, J. D., III; Finke, R. G. *Chem. Mater.* **1999**, *11*, 1035. (b) Weddle, K. S.; Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653.

(29) Özkar, S.; Finke, R. G. *J. Organomet. Chem.* **2004**, *689*, 493.

(30) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 5796.

(31) Özkar, S.; Finke, R. G. *Langmuir* **2003**, *19*, 6247.

(32) TEM beam damage is not a new problem: (a) 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. (b) Our 1999 review also reminds readers of these problems with TEM: Aiken, J. D., III; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1. (c) See also ref 33.

(33) (a) "Certain materials are more susceptible than others, but in the end, you can damage virtually anything you put into the TEM".[33b] TEM-beam-derived radiolysis[33b] is a likely cause of the formation of nanoclusters from **1**. For a more in-depth discussion about conditions that may cause TEM beam damage in metals see Chapter 4 elsewhere.[33b] (b) Williams, D. B.; Carter, C. B. *Transmission Electron Microscopy*; Plenum Press: New York, 1996.
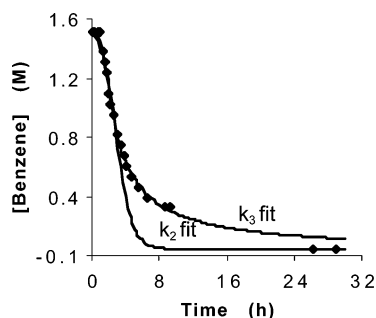
Figure 3. Data and two curve-fit lines for a benzene hydrogenation reaction with precatalyst [**1**][BF$_4$] at 110 °C and an initial H$_2$ pressure of 60 atm. Following a ~1.5 h induction period, the reaction rate increases rapidly and the reaction is complete after a total of ~24 h. A sigmoidal curve typical of the precedented nanocluster formation mechanism in Scheme 1 provides a good fit to the observed kinetic data. Note the line "k_2 fit", which does not include the k_3 agglomeration step (Scheme 1), provides a poor, inaccurate fit to the data. The kinetics provide excellent evidence for nanocluster formation, B, as the true catalyst then its aggregation (B + B → C) to larger nanoclusters and bulk metal, C.

experiments we attempted to inhibit TEM-beam-induced nanocluster formation from [**1**][BF$_4$] by monitoring the samples at 40 kV and under cryogenic conditions (−168 °C) at 120 and 40 kV, Figure S2 of the Supporting Information. However, Ru(0) nanoclusters derived from [**1**][BF$_4$] were still formed under these "milder" TEM conditions.

Consistent with the TEM-induced formation of nanoclusters from [**1**][BF$_4$], nanoclusters were also observed from the red-orange reaction solution following a benzene hydrogenation, most likely a result of unreacted [**1**][BF$_4$] (≥95%) in the reaction solution, Figure S3 of the Supporting Information.

The important conclusion here is that TEM is *not* a reliable indicator of nanocluster formation if any unreacted **1** remains in the sample. However, the visual and XPS evidence for Ru(0)$_x$ still demands[12] that a nanoparticle and/or bulk metal, heterogeneous catalyst be considered as the most likely, precedented[5,12,13,28b] catalyst for the observed benzene hydrogenation. Kinetic studies to be discussed next, along with visual and XPS evidence for bulk metal formation, proved to be more reliable in this case (vide infra) and perhaps in general[6,12−14] in providing evidence for the true catalyst.

(iii) CSU Kinetic Evidence for Nanocluster, then Bulk Metal, Formation. Figure 3 shows the crucial kinetics of benzene hydrogenation with [**1**][BF$_4$] at 110 °C and 60 atm H$_2$. Similar, CSU kinetic curves were obtained using complex **1** synthesized at Neuchâtel University, Figure S4 of the Supporting Information. The characteristic sigmoidal shape of the hydrogen-uptake curve, in which an approximately 2 h induction period in this case is followed by a rapid increase in catalytic activity, strongly suggests that **1** is not the true catalyst; if **1** were the true catalyst, then no induction period is expected. In fact, the sigmoidal kinetics in Figure 3 are well-fit by the A → B (slow nucleation), A + B → 2B (rapid autocatalytic surface growth), plus B + B → C (bimolecular aggregation)[34] kinetic model shown in Scheme 1, which is diagnostic of transition

Scheme 1

$$A \xrightarrow{k_1} B$$
$$A + B \xrightarrow{k_2} 2B$$
$$B + B \xrightarrow{k_3} C$$
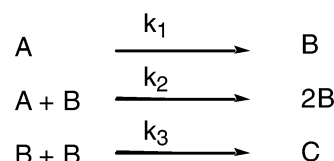
metal nanocluster[12,21,28,30,31,36,37] and/or bulk metal[13] formation under H$_2$. (The addition of an additional, autocatalytic agglomeration B + C → 1.5 C step to the kinetic model[35] is presented in Scheme S1 and Figure S5 of the Supporting Information for the interested reader, a detail that is, however, not crucial to the present work.) The kinetics are definitive[38] in ruling out **1** = A as the catalyst: *A must → B before catalysis can occur*. B is the true catalyst, not A (with some possible contribution by B's agglomerate, C).

The three measured rate constants, curve-fit k_1 = 0.0085 h^{-1}, k_2 = 2.2 M^{-1} h^{-1}, and k_3 = 7.6 M^{-1} s^{-1}, can be used, along with the numerical integration capabilities of MacKinetics,[34] to provide calculated concentration versus time profiles for A, B, and C, Figure 4. The nanoclusters, B, are only short-lived, whereas C (agglomerated nanoclusters plus bulk metal) is the main metal product, *consistent with the observed metal product studies*.

(iv) Analogous Neuchâtel University Kinetic Evidence for Nanocluster, then Bulk Metal, Formation. The kinetic data for a benzene hydrogenation reaction with [**1**][BF$_4$] was also performed at Neuchâtel University, Figure S6 of the Supporting Information. The kinetic data were necessarily obtained differently in this case since a sampling autoclave was not available: eight separate benzene hydrogenation reactions were set up and subsequently stopped at different times

(34) Hornstein, B. J.; Finke, R. G. *Chem. Mater.* **2004**, *16*, 139.

(35) (a) A recently discovered mechanism,[35b] which includes a fourth step of B + C → 1.5 C with rate constant k_4, also provides a good fit to the data, Figure S5 of the Supporting Information. Whether or not the three- or four-step mechanism is best is not crucial in the present case, the fourth step serving only to confirm that the nanoclusters are not stable (i.e., that B + C → 1.5 C agglomeration occurs, Scheme S1 of the Supporting Information). (b) Besson, C.; Finney, E. E.; Finke, R. G. Nanocluster Nucleation, Growth and Then Agglomeration Kinetic and Mechanistic Studies: A More General, Four-Step Mechanism Involving Double Autocatalysis, submitted for publication.

(36) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382.

(37) Widegren, J. A.; Aiken, J. D., III; Özkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312.

(38) (a) The Neuchâtel University group raised the issue of whether H$_2$(g) → H$_2$(solution) mass-transfer limitations (MTL) can be occurring and influencing the observed kinetics. The CSU group has studied MTL effects previously and specifically in nanocluster formation reactions;[38b] hence, we are well aware of MTL effects and the their diagnostics.[38b] Completely MTL-kinetics can unequivocally be ruled out in the present work as such kinetics would show zero-order kinetics (for rate-determining H$_2$(g) → H$_2$(solution)), a situation ruled out by the observed sigmoidal kinetics that are well-fit by the *chemical* mechanism A → B, A + B → 2B, and B + B → C diagnostic of nanocluster nucleation, growth, and agglomeration. Second, we employ a mechanically, 600 rpm propeller-(i.e., vigorously) stirred Parr bomb reactor in the present studies to mitigate against the effects of always present imperfect stirring. And third, since we have measured H$_2$ uptake rates of up to −d[H$_2$]/dt = 200 psig/h at 110 °C and 880 psig H$_2$ initial pressure in our 600 rpm stirred Parr reactor, we know that the H$_2$(g) → H$_2$-(solution) mass-transfer limit of our reactor (i.e., under the conditions we employ in the present studies) is ≥200 psigH$_2$/h. This, in turn, means that the maximum rates in the sigmoidal kinetic curves such as Figure 3 (−d[H$_2$]/dt = 40 psig/h), on which the main kinetic conclusions herein are based, have ≪20% MTL effects (if any) in those specific kinetics. In short, significant MTL effects are not complicating the kinetic-based conclusions reported herein. (b) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 9545.
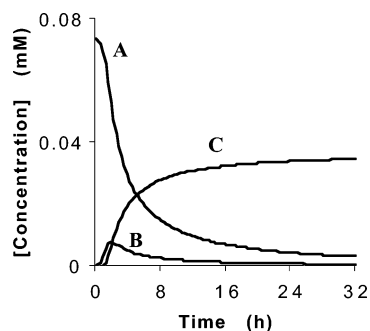
Figure 4. Calculated concentration versus time profiles of A, B, and C for the three-step mechanism in Scheme 1; generated using the measured k_1, k_2, and k_3 rate constants cited in the text and MacKinetics. Note the rapid disappearance of A, the relatively short-lived nanoclusters B, and the formation of agglomerated, less active nanoclusters plus bulk metal, C. Note that the A here refers to only the ~5% of A = **1** that is converted to B under the Standard Conditions experiment.

to obtain a point-by-point benzene conversion kinetic curve. The data in Figure S6 are again well-fit to the nanocluster nucleation (A → B, autocatalytic growth (A + B → 2B) and agglomeration (B + B → C) mechanism in Scheme 1. The Neuchâtel University kinetic data confirm the CSU kinetics: A (= **1**) must → B before catalysis can occur. A is not the catalyst; B is (along with some possible contribution by its agglomerate, C).

(v) Testing the Kinetic Competence of the Metallic Film versus the Red Reaction Solution. Following a Standard Conditions benzene hydrogenation, one observes that the glass liner and reactor components (thermocouple, impeller, dip tube, and cooling loop) are coated with a thin metallic film. Two experiments were performed in an attempt to determine if the observed catalysis is due to (i) the bulk Ru(0) metal coating the reactor; (ii) any nanometer-sized Ru(0)$_x$ particles that might be present, or (iii) conceivably some combination of (i) and (ii).

Immediately following a Standard Conditions benzene hydrogenation, the red-orange reaction solution was decanted from the glass liner into a scintillation vial and stored in the drybox for a subsequent experiment, vide infra. Fresh benzene and degassed water were added to the reactor. After a ~2 h induction period (due, apparently, to surface deactivation of the bulk-metal film), the bulk metal (~5% of precatalyst [**1**][BF$_4$]) coating the reactor components and glass liner were able to hydrogenate benzene, Figure 5, at a kinetic rate similar to a Standard Conditions benzene hydrogenation beginning with **1**.

Next, the catalytic activity of the previously stored red-orange reaction solution was tested as follows. First, a "blank" hydrogenation was performed in which a Standard Conditions benzene hydrogenation was run *without added catalyst* to verify that no catalytically active bulk metal remains on the cleaned reactor (the Experimental Section provides further details for how the reactor was cleaned and the "blank" experiments performed). Then, the red-orange reaction solution was filtered through a 0.2 μm (i.e., a 200 nm) nylon syringe filter into a clean glass liner to remove bulk metal. Finally, fresh benzene was added and the kinetic competence of the filtered solution was tested. An
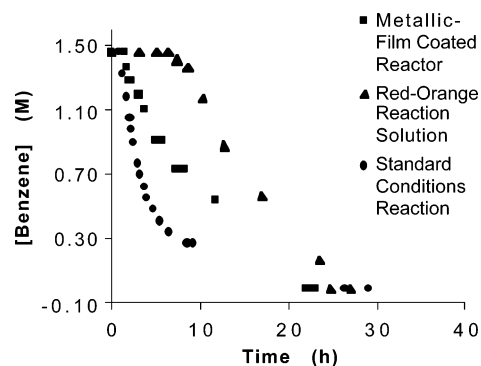

Figure 5. Plot of the benzene versus time data for three separate benzene hydrogenation experiments. The circles (●) show the benzene versus time data for a Standard Conditions hydrogenation starting with **1**. After the hydrogenation reaction with **1**, the final red-orange reaction solution was separated from the metallic film and, in separate experiments, each was used to catalyze a benzene hydrogenation reaction as described in the text. The squares (■) show the kinetic data for the active bulk metal film, while the triangles (▲) show the kinetic data for the red-orange solution. These experiments show that the product solution and metal-coated reactor contain the catalytically active species.

induction period of ~6 h was required before the red-orange reaction solution was able to hydrogenate benzene, Figure 5. Again A → B had to occur before catalysis could ensue.

(vi) Analogous Neuchâtel University Studies Showing That the Bulk Metal on the Reactor Components Is an Active Catalyst. Following a benzene hydrogenation experiment the reaction solution was removed by decanting, leaving a black metallic film coating the glass liner. Water and fresh benzene were added, and the kinetic competence of this metallic film was tested in a second benzene hydrogenation experiment. The metallic film was again able to hydrogenate benzene, revealing that the ~5% Ru(0) formed during the reaction is catalytically active (~5% Ru(0) based on mass balance plus the ~95% recovery of [**1**][BF$_4$][2b]).

(vii) Studies Beginning with RuO$_2$: Evidence for the Kinetic Competence of ≤15% of Heterogeneous Ru(0). The origin of these studies is the finding, at Neuchâtel University, that *ethylbenzene* hydrogenation is unusually fast (TOF of 3700 h^{-1}, ~1 order of magnitude faster than *benzene* reduction under identical conditions). Subsequent Neuchâtel University work uncovered the important insight that the autoxidation product of ethylbenzene, C$_6$H$_5$CH(OOH)CH$_3$ (present as an impurity in the ethylbenzene), is oxidizing the otherwise substitution-inert **1** to yield a faster catalyst,[2b,39] further evidence that **1** is not the catalyst.[2b] The finely dispersed metal product identified by energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) following these experiments proved to be RuO$_2$·nH$_2$O[2b] (the Ru^{IV}O$_2$ presumably forming by oxidation once the Ru(0) catalyst is exposed to air during the EDS and SEM analysis). Control

(39) The finding of an "autoxidation-initiated reduction catalyst" is important in its own right as an example of little appreciated autoxidation-product-initiated reactions: (a) Weiner, H.; Finke, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 9831. (b) Yin, X.; Finke, R. G. Autoxidation-initiated Vanadium Catechol Dioxygenases, manuscript in preparation.
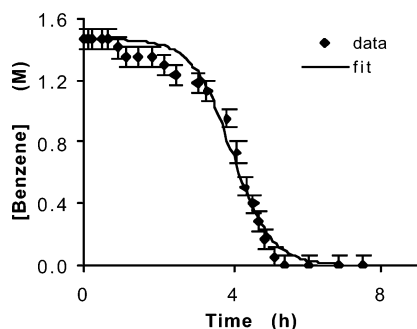
Figure 6. Data for a $RuO_2 \cdot nH_2O$ benzene hydrogenation reaction at 110 °C and an initial H_2 pressure of 60 atm. Following a ~2 h induction period, the reaction rate increases rapidly and the reaction is complete after a total of 8 h; that is, a sigmoidal curve typical of slow continuous nucleation, $A \rightarrow B$ ($k_1 = 0.0010$ (7) h^{-1}), then autocatalytic surface growth, $A + B \rightarrow 2B$ ($k_2 = 1.3$ (1) $M^{-1} h^{-1}$), is seen. The data reveal that ≤15 mol % Ru(0) is a competent benzene hydrogenation catalyst.

experiments done at Neuchâtel University showed that $RuO_2 \cdot nH_2O$ alone (catalyst/substrate ratio 1:1000, 110 °C, 60 atm H_2) has kinetic competence, that is, forms a sufficiently fast benzene reduction catalyst to account for the observed activity (TOF ≈ 3000 h^{-1}).[2b]

The high activity of ~15 mol % $RuO_2 \cdot nH_2O$ in a benzene hydrogenation (0.018 mmol RuO_2, 5.3 mL of benzene, 35 mL of water, 110 °C, 60 atm H_2) was also verified in experiments at CSU. Figure 6 shows that this small, ~15 mol % of RuO_2 is capable of hydrogenating benzene at a similar rate to a Standard Conditions reaction with **1**. Furthermore, sigmoidal kinetics diagnostic of nanocluster/bulk metal formation[12,13,21,34−37] under H_2 are seen, with an approximately 2 h induction period, Figure 6 (see the Supporting Information for an analogous experiment using anhydrous RuO_2, Figure S7). The RuO_2 experiments performed at CSU confirm that ≤15 mol % Ru(0) is capable of hydrogenating benzene at kinetically competent rates in comparison to the catalyst derived from **1**.

(viii) Hg(0) Poisoning Evidence for Heterogeneous Catalysis. We employed, as before,[13,14,40] the commonly used Hg(0) poisoning test[12,13,40] for metal(0) catalysts. The Hg(0) poisons metal(0) catalysts by amalgamating the metal or adsorbing on the metal surface.[12,28b]

The Hg(0) poisoning experiment was started as if it were a Standard Conditions benzene hydrogenation experiment (i.e., at 110 °C and an initial H_2 pressure of 60 atm). The benzene hydrogenation was allowed to proceed until it was about one-third complete (as judged by H_2 pressure loss and as subsequently verified by ^1H NMR). Then, ~300 equiv of Hg(0) (versus Ru) was added with good stirring since both are known to be crucial to performing this test properly.[12,13,28b] *Consistent with heterogeneous metal-particle catalysis, the addition of*
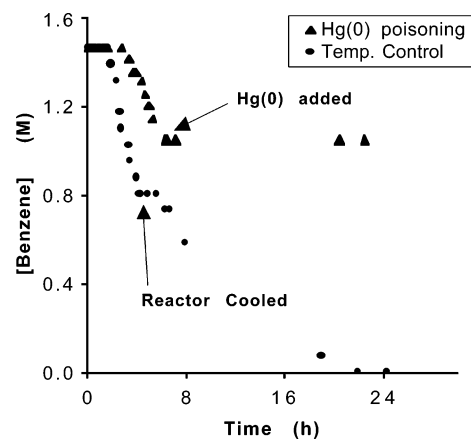
(40) (a) Hornstein, B. J.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 1625. (b) We have recommended[12] the use of quantitative poisons such as CS_2[12,40a] rather than Hg(0), since CS_2 can be studied quantitatively. However, we have also shown[13] that CS_2-poisoned catalysts become reactivated at higher temperatures (due to the exothermicity of CS_2 binding),[13] making the otherwise preferred CS_2 poison inapplicable for the current 110 °C benzene hydrogenation studies. This is why we developed the 1,10-phenanthroline and N-heterocyclic carbene poisons as part of the present work.

Figure 7. Plot of benzene concentration versus time in the Hg(0) poisoning experiment and a temperature control experiment. A Standard Conditions benzene hydrogenation with **1** was run to ~30% completion. The H_2 pressure was then released, and, in the case of Hg(0) poisoning (▲), 2.69 g of Hg(0) was added (~300 equiv versus Ru). 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) with the catalyst. Following addition of the Hg(0), no further benzene hydrogenation is observed, a result confirmed by ^1H NMR on an aliquot of the post-Hg(0) addition solution. For the temperature control experiment (●), a Standard Conditions benzene hydrogenation with **1** was run to ca. 50% completion. The H_2 pressure was then released, an aliquot removed for NMR, the reactor repressurized with H_2, and the reaction allowed to continue with vigorous stirring. After a ~2 h induction period during which the catalyst is reactivated, the benzene hydrogenation went to completion. This control experiment shows that the loss of activity in the Hg(0) poisoning experiment (▲) is due to the addition of Hg(0), not the necessary cooling and then rewarming of the reactor involved in performing the Hg(0) poisoning experiment.

Hg(0) halted the catalytic activity completely, Figure 7 (the ▲ data points). A control experiment was performed to confirm that the necessary cooling, then rewarming, of the reactor involved in the Hg(0) poisoning experiment did not irreversibly halt the catalytic activity, Figure 7, the ● data points. The crucial finding, then, is that the addition of Hg(0) to the active catalyst completely inhibits benzene hydrogenation, further evidence for a Ru(0) benzene hydrogenation catalyst.

(ix) Other Poisoning Evidence Unequivocally Ruling Out 1 As the True Catalyst and Providing Additional Strong Evidence for Heterogeneous Catalysis. Quantitative poisoning experiments in which <1.0 equiv of poison inhibits catalysis can provide strong evidence for heterogeneous catalysis, in which ≪100% (and often ≤50%)[12,40] of the metal atoms are on the metal particle surface and thus ≤50% are available to added poisons. On the other hand, the outer-sphere supramolecular catalysis mechanism predicts that complex **1** will be totally insensitive to added ligand, as long as the added ligand cannot compete with the benzene binding pocket in **1**. Hence, a fractional poisoning experiment offers a clear way to distinguish between the proposed outer-sphere homogeneous and inner-sphere heterogeneous catalysis mechanisms.

A fractional poisoning experiment employing 1,10-phenanthroline was started as if it were a Standard
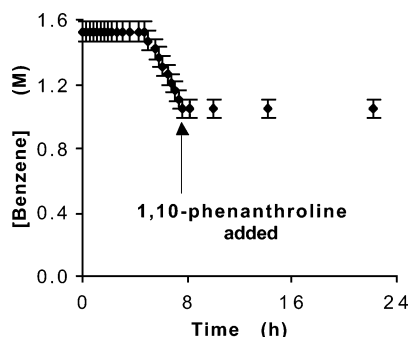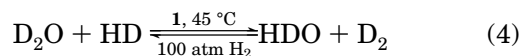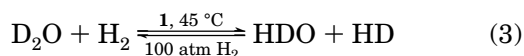
Figure 8. Plot of benzene concentration versus time in the 0.5 equiv 1,10-phenanthroline poisoning experiment. Following addition of the 1,10-phenanthroline, complete inhibition of benzene hydrogenation is observed, a result confirmed by ^{1}H NMR on an aliquot of the solution.
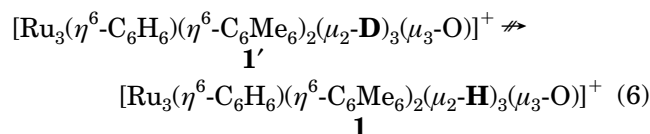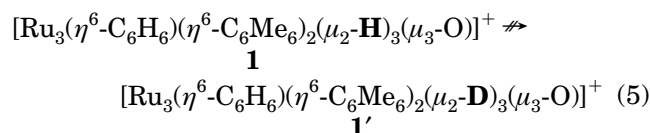
Conditions benzene hydrogenation experiment (i.e., 110 °C and an initial H_2 pressure of 60 atm). As in the Hg(0) poisoning experiment, the benzene hydrogenation was allowed to proceed to ca. one-third completion. At that point, ∼0.5 equiv of 1,10-phenathroline (versus Ru present in **1**) was added with good stirring. *A complete loss of catalytic activity is observed*, Figure 8. Control experiments show (a) that the opening/cooling/rewarming of the autoclave involved in this experiment are not responsible for the observed inhibition and (b) that the weakly coordinating base, Proton Sponge (1,8-bis(dimethylamino)naphthalene), did not cause any inhibition (Figure S8 of the Supporting Information); that is, 1,10-phenanthroline is not just acting as a H^+-scavenger.

In a separate experiment the N-heterocyclic carbene (generated in situ from 1,3-bis(2,4,6-trimethyl)-4,5-dihydroimidazolium tetrafluoroborate and potassium *tert*-butoxide, ∼0.5 equiv versus Ru) with its strong metal−carbon bond,[41] was able to halt the catalytic activity for ∼8 h, Figure S9 of the Supporting Information. Overall, the 1,10-phenanthroline and N-heterocyclic carbene fractional poisoning experiments rule out **1** as the catalyst and provide further evidence consistent with a Ru(0) metal-particle catalyst.

(x) Demonstration by in Situ High-Pressure NMR Study That the H/D Exchange Process between H_2 and D_2O Is Not Catalyzed by [Ru$_3(\mu_2$-H)$_3$-(η^6-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2(\mu_3$-O)]$^+$, [1], or [Ru$_3(\mu_2$-D)$_3(\eta^6$-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2(\mu_3$-O)]$^+$, [1′]. If the organometallic cation **1** is the hydrogenation catalyst, then it is likely that it will activate and exchange H_2 (D_2) as fast (or faster) than the observed reduction of benzene. Experiments designed at Neuchâtel University and performed at the Ecole Polytechnique Fédérale de Lausanne studied the H/D exchange reaction of H_2 and D_2O in the presence of [Ru$_3(\mu_2$-H)$_3(\eta^6$-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2(\mu_3$-O)]$^+$, **1**, by high-pressure in situ NMR spectroscopy. The H/D exchange reactions, eq 3 and 4, are known to occur between 20 and 50 °C.[42]

$$D_2O + H_2 \underset{100\ \text{atm}\ H_2}{\overset{1,\ 45\ °C}{\rightleftharpoons}} HDO + HD \qquad (3)$$

(41) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
(42) Kovács, G.; Nádasdi, L.; Joó, F.; Laurenczy, G. *C. R. Acad. Sci. Paris, Chim.* **2000**, *3*, 601.

$$D_2O + HD \underset{100\ \text{atm}\ H_2}{\overset{1,\ 45\ °C}{\rightleftharpoons}} HDO + D_2 \qquad (4)$$

The H/D exchange was monitored by the decrease of the H_2 signal ($\delta = 4.73$ ppm, singlet), the transient appearance of the HD signal ($\delta = 4.69$ ppm, triplet), and the increase of the HDO signal ($\delta = 4.71$ ppm, singlet).[42] During this time (12 h), the water-soluble cluster cation **1** can be observed by its intense C$_6$Me$_6$ signal ($\delta = 2.40$ ppm, singlet) and its characteristic hydride resonances at −19.13 ppm (doublet) and −19.81 ppm (triplet), Figure 9. *The signals of **1** remain unchanged during time scale of H/D exchange,* eqs 3 and 4. The 2:1 ratio and multiplicities of the hydride signals remain unperturbed, even though the H/D exchange is proceeding, as evidenced by the simultaneous changes in the H_2, HD, and HDO signals. Clearly, **1** does not take part in the H/D exchange process; its hydride ligands are unchanged during this catalytic reaction as eq 5 summarizes.

$$[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{Me}_6)_2(\mu_2\text{-}\mathbf{H})_3(\mu_3\text{-O})]^+ \nleftrightarrow$$
$$\mathbf{1}$$
$$[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{Me}_6)_2(\mu_2\text{-}\mathbf{D})_3(\mu_3\text{-O})]^+ \quad (5)$$
$$\mathbf{1'}$$

$$[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{Me}_6)_2(\mu_2\text{-}\mathbf{D})_3(\mu_3\text{-O})]^+ \nleftrightarrow$$
$$\mathbf{1'}$$
$$[\text{Ru}_3(\eta^6\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{Me}_6)_2(\mu_2\text{-}\mathbf{H})_3(\mu_3\text{-O})]^+ \quad (6)$$
$$\mathbf{1}$$

To exclude the alternative explanation of a rapid H/H exchange between H_2 and **1** prior to the H/D exchange with D_2O, we studied the same reaction conditions using the fully deuterated cluster cation [Ru$_3(\mu_2$-D)$_3(\eta^6$-C$_6$H$_6$)(η^6-C$_6$Me$_6$)$_2(\mu_3$-O)]$^+$, **1′**, as its BF$_4^-$ salt, [**1′**][BF$_4$] (Figure S10 of the Supporting Information). Indeed, the H/D exchange process mirrors the results with **1** (no signals appear in the region between δ −18 and −20 ppm), revealing that **1′** also does not exchange its deuteride ligands with H_2 to form hydride ligands, eq 6, at least at 45 °C. Therefore, the participation of the cluster cation **1** or **1′** in the catalytic H/D exchange between H_2 and D_2O can be ruled out unequivocally at 45 °C. Overall, these experiments require that some other catalyst is formed from **1** that is the true H/D exchange catalyst at 45 °C. However, since the hydride signals of **1** are affected by the H/D exchange at 90 °C, possible catalysis by **1** at higher temperatures (>90 °C) cannot completely be excluded on the basis of these NMR experiments alone.

After the H/D exchange reaction, a thin metallic film is observed on the walls of the NMR tube. No paramagnetic species or other decomposition products can be detected in the NMR spectra, and the solid recovered from the solution is mainly (> 95%) unchanged [**1**][BF$_4$] or [**1′**][BF$_4$]. Given the high stability of the cluster cation and its inertness to the H/D (or arene[2]) exchange reaction, the small quantities of Ru(0) detected by the product, kinetic, and poisoning studies are, again, strongly implicated as the true catalyst at 110 °C.

(xi) Additional Data: Adherence to the Principle That the Correct Mechanism Will Explain *All* the Data. A final part of the methodology in Figure 1
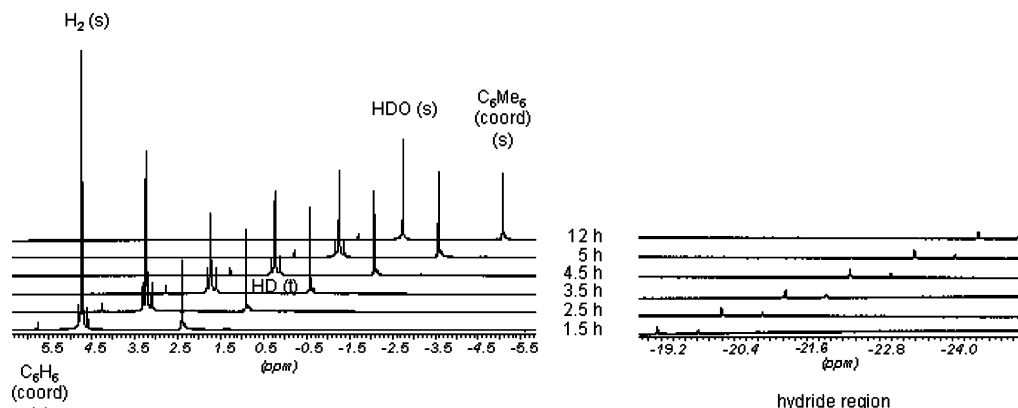
Figure 9. NMR spectra showing the simultaneous changes in the H_2, HD, and HDO signals plus the unchanged signals for the precatalyst, **1**, at 45 °C.

is to be sure that the proposed identification of the true catalyst will explain *all* the available data. A reanalysis of the data interpreted previously in terms of **1** as a homogeneous catalyst is provided in the Supporting Information. That analysis confirms that a Ru(0) heterogeneous catalyst is consistent with, and supported by, all of the available data.[2]

(xii) One Final Alternative Hypothesis: Is 1%, or Even Just 0.1%, of Catalysis by Intact 1 Consistent with the Kinetic Data? While the evidence is compelling that $Ru(0)_n$ nanoclusters formed from **1** are the dominant catalyst, an alternative hypothesis[43] is that 1%, 0.1%, or 0.001% (or even lower levels of) catalysis by **1** could still be occurring. This type of alternative hypothesis, that **1** still has some, small percentage of activity, is a type of "increasingly quantitative" alternative hypothesis that is always present in science and often nearly impossible to disprove. Arguing against such more complex explanations typically comes down to the use of Ockham's razor:[44] we conditionally[44] exclude these alternative hypotheses since there is no evidence for them, there is evidence that they are not needed (i.e., in the present example compelling evidence for $Ru(0)_n$ catalysis of benzene hydrogenation exists), and the simplest explanation is thus chosen (again *conditionally*, via the use the logic rule[44] we call Ockham's razor) as the best explanation until and unless a new experiment can be designed to test such alternative hypotheses.

However, in the present case we can use the available kinetic data to provide a rather small upper limit on the maximum possible contribution by intact **1** to the observed benzene reduction catalysis. Via the further, detailed analysis of the kinetic data provided in the Supporting Information, it can be shown that *at least* $\geq 99.97\%$ of the observed catalysis is due to $Ru(0)_n$ metal, so that $\leq 0.03\%$ *at most* could conceivably be due to intact **1**. And, there is still no evidence requiring any contribution by intact **1**.

Conclusions

The main take-home messages from the present work can be summarized as follows:

(1) The true benzene hydrogenation catalyst derived from $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$, **1**, is a heterogeneous, $Ru(0)_n$ catalyst according to all our data (i.e., since there is no other alternative hypothesis, at least that we can think of, that remains to be disproved[43] and that can explain the available data). In addition, the data require that $Ru(0)_n$ is responsible for at least $\geq 99.97\%$ of the observed catalysis.

(2) Supramolecular, host–guest complexation of benzene by the novel complex **1** is unequivocally demonstrated by X-ray crystallography, ES-MS, and molecular mechanics data. However, supramolecular-mediated reduction of the difficult to reduce substrate benzene (i.e., noncovalent, weak-force-directed, outer-sphere, non-d-orbital-mediated benzene reduction) remains undemonstrated.

(3) Extremely well-precedented,[3] inner-sphere pathways for organometallic-derived catalysts involving ligand substitution, oxidative addition, attack on coordinated ligands, migratory insertion, and reductive elimination are still the norm despite the now established outer-sphere reduction mechanisms observed in a few cases.[18]

(4) The general methodology shown in Figure 1 for distinguishing homogeneous catalysis from heterogeneous catalysis has now been successfully used in six of six cases if one includes the present case along with our four prior examples,[6,13,14,21] plus I. Manners's recent success.[22]

(5) The key evidence for or against homogeneous versus heterogeneous catalysis is—as predicted[6,12–14,21]—*kinetic in origin along with an identification of where the mass of the precatalyst lies*.

(6) One of "Halpern's rules", that "if you can isolate it, it is probably not the catalyst", is again obeyed in this case, despite well-known exceptions to this useful heuristic device.[24,25,45]

(7) One should no longer use the following experiments *alone* to try to provide evidence for or against heterogeneous versus homogeneous catalysis: precatalyst reisolation; product selectivities; Hg(0) poisoning (especially without controls as detailed elsewhere[12]); TEM studies; or any of the other, single experiments cautioned against elsewhere.[12] Especially noteworthy here are I. Manners[22] and our[14] recent findings—plus those herein—that TEMs obtained when organometallic precursors are present can be very misleading. TEM-induced nanocluster formation from organometallic

(43) Platt, J. R. *Science* **1964**, *146*, 347. This classic paper emphasizes the importance of multiple alternative hypotheses and disproof in science.

(44) Hoffmann, R.; Minkin, V. I.; Carpenter, B. K. *Bull. Soc. Chim. Fr.* **1996**, *133*, 117.

precursors has now been well documented in three cases.[14,22] Hereby added to the methodology in Figure 1 are the must-do controls of verifying, by an independent method before the TEM analysis, that all the precursor has been converted to nanoclusters, or the control of obtaining the TEM of the precursor: are nanoclsuters formed in the TEM beam?

(8) A very interesting finding emanating from the prior work[2b] is that of an autoxidation-product-initiated reaction, in this case, an autoxidation-product-induced reduction reaction.[39]

(9) And most importantly the power and significance of Platt's scientific method emphasizing *disproof of multiple alternative hypotheses*—the basic method underlying the present studies—is again emphasized as necessary, especially for difficult cases with misleading initial observations ("for exploring the unknown, there is no faster method"[43]).

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. Nanoclusters hold considerable promise to serve as discrete, compositionally well-defined systems that can do the more difficult reactions exhibited by heterogeneous catalysts. Yet they have the distinct advantage that they can be studied by powerful solution spectroscopic and kinetic methods en route to their detailed understanding and, therefore, rational improvement as soluble analogues of the commercially available important heterogeneous catalysts.[46]

Experimental Section

The experimental details that follow refer to work done at CSU by one of us (C.M.H.); experiments performed at Neuchâtel University necessarily used different equipment and, hence, are marked as such in what follows.

Materials. Benzene (Aldrich, 99.8%, anhydrous, packaged under N_2) was transferred into the drybox and used as received. All water used in reaction solutions was doubly deionized and underwent three cycles of freeze, pump, thaw degassing. Hg(0) (Aldrich, 99.999%) and water were brought into the drybox just before they were needed, and then immediately removed (as Hg(0) will poison the drybox oxygen scavenging Cu catalyst). Hydrogen gas (General Air, 99.5%) was used as received. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. and used as received. The ruthenium precatalyst $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+[BF4]^-$, [1][$BF_4$],[47] was synthesized according to the literature[47a] with important modifications.[47a] $RuO_2 \cdot nH_2O$ and anhydrous RuO_2 (99.9+%) were purchased from Strem Chemicals, Inc., 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 d_6-acetone at 2.05 ppm. Spectral parameters for ^{1}H NMR (300 MHz) include tip angle, 30°; acquisition time, 2.67 s; relaxation delay, 0.0 s; sweep width, 6000 Hz. 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, and the pressure in the spectrometer was below 5×10^{-9} Torr. For energy calibration, the carbon 1s binding energy was set to 284.8 eV. TEM micrographs were collected using a Philips CM-12 TEM with a 70 μm lens operating at 120 kV, except for those obtained more recently at 40 kV.

General Procedures of Benzene Hydrogenations. All benzene hydrogenations were preformed in a Parr pressure reactor (Model No. 4561) made of Monel 400 alloy. The reactor is equipped with a pressure gauge marked at intervals of 20 psig and an automatic temperature controller (±2.5 °C). The inside of the reactor contains a stainless steel impeller, a thermocouple, a cooling loop, and a dip tube for sampling during reactions; all these components are in contact with the solution during reactions and, hence, must be cleaned between reactions (see "Cleaning the Reactor between Benzene Hydrogenation Reactions, and Testing the Residual Hydrogenation Activity of the Reactor Itself", vide infra). A glass liner is used to avoid contacting the reaction solution with the interior of the reactor. The glass liner was dried overnight in a 160 °C

(45) (a) The useful heuristic device of Halpern's rules[45b] (or, really, "guidelines" as formulated by Professor R. G. Bergman[45c]—somewhat tongue-in-cheek, he notes!) is now well known to mechanistic chemists in the organometallic and catalysis community and derives from Professor Halpern's seminal work, perhaps most notably on Wilkinson's hydrogenation catalyst and the Monsanto L-Dopa asymmetric hydrogenation catalyst.[45d] In the Wilkinson catalyst case, for example, the five species detectable by nonkinetic methods are all not only not the catalyst, they instead are "anticatalysts" in that they slow the rate by removing Rh from the catalytically active cycle involving the 14-electron intermediate, $RhClL_2$, and instead store that Rh in the five detectable, nonproductive species. (b) Halpern's "rules" (or really "guidelines", vide infra, as Bergman emphasizes) go something like the following:[45c] if you can isolate it, it is probably not the catalyst; if it is metastable and you can detect it, it *could* be the catalyst; and if it is highly unstable and undetectable, then it probably *is* the catalyst! Again, it is important to realize that these "rules" are, of course, intended only as heuristic "guidelines" or "cautions" since counterexamples exist, as both we and Professor Bergman recognize, for example metallocene olefin polymerization catalysts[45e] or metathesis catalysts[45f–g] (even the latter are still a ligand dissociation away from the active catalyst in most cases)[45h–k] (c) Professor R. G. Bergman, private communication, cited with permission. (d) See Chapter 6, pp 531–541, and references therein, in: 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. (e) Yang, X.; Stern, C.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (f) Landis, C. R.; Rosaaen, K. A.; Kimberly, A.; Sillars, D. R. *J. Am. Chem. Soc.* **2003**, *125*, 1710. (g) Sillars, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **2003**, *125*, 9894. (h) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459. (i) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. (j) Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975. (k) Tallarico, J. A.; Bonitatebus, P. J., Jr.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157.

(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.

(47) Work at CSU began ca. 1 year prior to our collaboration, but much of that time was spent trying to obtain sufficient quantities of pure [1][BF_4] by the initially reported route[48a] to do the required experiments. Problems encountered in the prior[48a] synthesis were (i) the unreported air-sensitivity of the preparation prior to addition of $NaBF_4$; (ii) the color change during $NaBH_4$ addition (reported yellow to red, but yellow to black in CSU hands); (iii) the unspecified method and length of $NaBH_4$ addition; and (iv) the low isolated yields of water-soluble [1][BF_4] due to the use of water washings. Fortunately, work at Neuchâtel University on just these issues was in progress at the time, so that communication of our separate results, followed by joint efforts, quickly led to an improved, reliable synthesis of 1.[48b] That synthesis involves the following improvements: (i) performing all steps up through the addition of $NaBF_4$ under air-free conditions; (ii) cooling the yellow solution containing $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ in an ice-bath for 30 min prior to the slow addition of aqueous $NaBH_4$ via cannula; (iii) heating the solution in a 60 °C oil bath (rather than a 50 °C) for 3 days; (iv) initially centrifuging the final product and removing the aqueous layer, but then taking the solid up in methylene chloride and filtering through Celite prior to purifying by preparative thin-layer chromatography (TLC, 2:1 acetone/methylene chloride); and finally (v) isolation of the red band from acetone and solvent removal in vacuo, yielding the red solid 1 (50–55%). The purity of [1][BF_4] is verified by CHN and NMR analysis from syntheses done both at U. Neuchâtel and CSU.[48b] The improved synthesis is being written up separately and in detail so as to make the improved synthesis available to, and reliable in, the hands of others.[48b] (a) Faure, M.; Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *Polyhedron* **1999**, *18*, 2679. (b) Vieille-Petit, L.; Hagen, C. M.; Finke, R. G.; Süss-Fink, G.; Laurenczy, G.; Geneste, F.; Moinet, C. Improved Synthesis, Electrochemistry and High-Pressure NMR Study of the Cluster Cation $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$, manuscript in preparation.

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 880 psig (~60 atm). Pressurizing the reactor took about 4 min, and $t = 0$ was set once the reactor was fully pressurized. Pressure versus time data were recorded at selected time intervals.

Standard Conditions, 110 °C Benzene Hydrogenation with [Ru₃($η^6$-C₆H₆)($η^6$-C₆Me₆)₂($μ_2$-H)₃($μ_3$-O)][BF₄], [1][BF₄]. In the glovebox 30 (±5) mg (0.0362 mmol) of [**1**][BF₄] was quantitatively transferred with 5.3 mL (59.3 mmol) of benzene and 35 mL of Nanopure water into an oven-dried glass liner, yielding a clear, red-orange solution. Next, the glass liner was placed into the Parr bomb reactor and the reactor sealed shut. The reactor was then removed from the drybox, equilibrated at 110 °C (while stirring at 600 rpm), and pressurized to 880 psi with H_2. Under these conditions complete conversion of benzene to cyclohexane corresponds to a pressure loss of about 280 psig. At the end of each hydrogenation reaction the percent conversion (benzene to cyclohexane) was verified directly by ^{1}H NMR analysis (the NMR sample was prepared by dissolving a drop of the final organic layer reaction solution in d_6-acetone). Seven repeats of this Standard Conditions experiment were performed, all of which showed sigmoidal hydrogen-uptake curves. The data for one such representative experiment are 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, verified experimentally by ^{1}H NMR (i.e., ≥95% conversion was observed by ^{1}H NMR at the end of each reaction). The error bars shown for H_2 pressure (or benzene concentration) assume an error of ±10 psig in the pressure gauge reading and ±2.5 °C in the temperature control. Curve-fitting the benzene concentration versus time data was performed as before[34,37] using the commercial software package Microcal Origin 3.5 (and the analytic equation for the A → B, then A + B → 2B mechanism[49]) or MacKinetics v. 0.9 numerical integration (for the A → B, A + B → 2B, plus B + B → C three-step mechanism).[34]

Catalyst Isolation Following a Standard Conditions 110 °C Benzene Hydrogenation with [1][BF₄]. The details of this experiment are presented in the Supporting Information.

Analogous 110 °C Benzene Hydrogenation Kinetic Experiments Performed at Neuchâtel University. The details of this experiment are presented in the Supporting Information.

Transmission Electron Microscopy (TEM). Twenty samples for TEM were prepared on 300 mesh copper TEM grids with a carbon support film and Formvar backing purchased from Ted Pella, Inc. The Formvar backing was removed prior to use according to the supplier's instructions by gently dipping the grids in acetone for 5 s, chloroform for 20 s, and then acetone for 5 s, followed by drying in air. After a benzene hydrogenation reaction with precatalyst **[1][BF₄]**, the reactor was immediately brought into the drybox and opened. The reaction solution was transferred to a glass scintillation vial that was then taken out of the drybox. The TEM samples were prepared by placing 2−3 drops of reaction solution on the grid, blotting the excess liquid with a piece of filter paper, and allowing the solvent to evaporate. The TEM grids were packaged in glass vials and sent to the University of Oregon, where TEM analyses were performed as before[36] with the expert assistance of Dr. JoAn Hudson and Dr. Eric Schabtach. Note that neither this preparation method nor the

TEMs themselves are an O_2-free procedure, so some surface oxide coating of the nanoclusters is expected. This does not hinder the present work, however, as only the presence or absence of nanoclusters, and not their precise size as prepared, is the main question of interest.

X-ray Photoelectron Spectroscopy (XPS). Following a Standard Conditions benzene hydrogenation 110 °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 primarily Ru(0) with binding energy peaks at 280.78 (3d$_{5/2}$), 283.27 (3d$_{3/2}$), 463.00 (3p$_{3/2}$), and 484.62 (3p$_{1/2}$) eV, in good agreement with the literature.[27] The same procedure was used following a RuO_2 hydrogenation (vide infra). Note that upon more extended time in O_2 or for higher surface area material, oxidized Ru (i.e., RuO_2) is seen by XPS as in experiments done at Neuchâtel University and reported in the Results and Discussion.

Cleaning the Reactor between Benzene Hydrogenation Reactions and Testing the Residual Hydrogenation Activity of the Reactor Itself. During benzene hydrogenation reactions with **1**, deposits of metallic Ru(0) form on the parts of the reactor that contact the reaction solution (i.e., on the stainless steel thermocouple, dip tube, cooling loop, and impeller). Consequently, it is possible for the reactor itself to have non-negligible hydrogenation activity if not carefully cleaned after each reaction. Hence, the Ru film formed after a given reaction was carefully removed by scrubbing with a steel wool pad, 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. A "blank" hydrogenation experiment was then performed as follows *without* precatalyst to test for any residual catalytic activity of the (cleaned) reactor.

In the drybox 5.3 mL (59.3 mmol) of benzene and 35 mL of degassed water (only) were placed in the glass liner. The glass liner was sealed in the Parr bomb reactor; the reactor was then removed from the drybox, temperature-equilibrated at 110 °C, stirred at 600 rpm, and pressurized to 880 psig with H_2. If the pressure in the reactor decreased by >20 psig overnight, the reactor was deemed "dirty" and, therefore, cleaned again followed by another blank hydrogenation experiment. This cycle of cleaning, then blank, experiments was repeated until a ≤20 psig H_2 overnight pressure loss (corresponding to ≤20/280 = ≤7% reaction) was observed.[13]

Testing the Kinetic Competence of the Metallic Film and of the Red-Orange Reaction Solution from a Benzene Hydrogenation Experiment. A Standard Conditions benzene hydrogenation experiment was started and was allowed to proceed to completion, as verified by ^{1}H NMR. At that point the reactor was cooled quickly to room temperature in an ice bath, vented, taken into the drybox, and opened. The orange-red reaction solution was decanted and stored in a glass scintillation vial in the drybox. To the glass liner containing the metallic film were added 5.3 mL (59.3 mmol) of fresh benzene and 35 mL degassed water. The reactor was immediately sealed (i.e., deliberately *without* cleaning the Ru-coated thermocouple, dip tube, cooling loop, and impeller in this particular experiment), brought out of the drybox, equilibrated at 110 °C, stirred at 600 rpm, and pressurized to 880 psig with H_2. Three repeats of this experiment were performed with equivalent results; the data for one such representative experiment are shown in Figure 5.

After cleaning the reactor the normal way (vide supra), the catalytic activity of the red-orange reaction solution was also tested. In the drybox, the reaction solution was filtered through a disposable nylon syringe filter (0.2 μm pore size) into a clean, oven-dried glass liner. Filtration did not noticeably change the appearance of the red-orange solution. Then, 5.3 mL (59.3 mmol) of benzene was added with a gastight syringe before

sealing the glass liner in the reactor. After removing the reactor from the drybox, it was equilibrated at 110 °C, stirred at 600 rpm, and pressurized to 880 psig with H_2. Three repeats of this experiment were performed with equivalent results; data for one such representative experiment are shown in Figure 5.

Analogous Bulk Metal Benzene Hydrogenation Experiments Performed at Neuchâtel University. The details of this experiment are presented in the Supporting Information.

Control Experiment for Benzene Hydrogenation Showing That Cooling, Transferring to the Drybox, and Opening the Parr Reactor, and Then Preceding to Reheat and Restart the Reaction Does Not Cause a Detectable Loss of Activity. This experiment was performed to ensure that the loss of activity seen in the Hg(0) poisoning experiment, in which the reactor needs to be cooled so that it can be opened and the Hg(0) added, is due to the Hg(0) addition and not the unavoidable cooling, opening, resealing, and then reheating of the reactor. This experiment was started as if it were a Standard Conditions benzene hydrogenation experiment (i.e., 30 mg (0.0362 mmol) of **[4][BF₄]**, 5.3 mL (59.3 mmol) of benzene, 35 mL of degassed water, 110 °C, and an initial pressure of 880 psig H_2). Pressure versus time data were collected until the pressure had decreased to 800 psi, that is, until ca. 30% completion. Then the reactor was cooled to room temperature, vented, taken into the drybox, and opened. The reactor was then resealed, brought out of the drybox, equilibrated at 110 °C, and pressurized to 800 psig with H_2. At this point, collection of pressure versus time data was restarted (ignoring the ~1 h gap required for the control procedure). The experiment was performed twice, giving identical results; data for one such representative experiment are shown in Figure 7.

Control Experiment using RuO₂·nH₂O as the Catalyst, Showing That ≤0.15 Equiv of Ru is Capable of Hydrogenating Benzene Under Identical Conditions As Used for Precatalyst [1][BF₄]. In the drybox 2.4 (±0.2) mg (0.018 mmol) of RuO_2 was quantitatively transferred into an oven-dried glass liner with 5.3 mL (59.3 mmol) of benzene and 35 mL of degassed water, yielding a clear solution with some undissolved RuO_2. The glass liner was sealed in the reactor and the reactor removed from the drybox, equilibrated at 110 °C, stirred at 600 rpm, and pressurized to 880 psig with H_2. At the end of the hydrogenation reaction the reaction solution was clear, with a small amount of metallic Ru(0) (verified by XPS, vide infra) on the glass liner and reactor parts in contact with the solution. Percent conversion was verified directly by ^{1}H NMR analysis. The Ru(0) nature of the metallic film was confirmed by XPS (peaks at 278.86 ($3d_{5/2}$), 284.19 ($3d_{3/2}$), 464.05 ($3p_{3/2}$), 485.68 ($3p_{1/2}$) eV). Three repeats of this reaction were performed with equivalent results; data for one such representative experiment are shown in Figure 6.

Control Experiment Using Anhydrous RuO₂ As the Catalyst, Showing That ≤0.15 Equiv of Ru Is Capable of Hydrogenating Benzene under Identical Conditions As Used for Precatalyst [1][BF₄]. The details of this experiment are presented in the Supporting Information.

Mercury Poisoning Experiment for Benzene Hydrogenation. This experiment was started as if it were a Standard Conditions benzene hydrogenation experiment (i.e., 30 (±5) mg (0.0362 mmol) of **1**, 5.3 mL (59.3 mmol) of benzene, 35 mL of Nanopure water, and an initial pressure of 880 psig H_2). Pressure versus time data were collected until the pressure had decreased to 800 psi, that is, ca. 30% (complete conversion corresponds to a pressure change of ~280 psig). Then the reactor was cooled to room temperature, vented, taken into the drybox, and opened. Next, 2.69 g (13.4 mmol) of Hg(0) was added to the red-orange reaction solution (~300 equiv versus Ru precatalyst). The uncleaned reactor was then resealed, brought out of the drybox, equilibrated at 110 °C,

and pressurized to 800 psig with H_2. At this point, the collection of pressure versus time data was restarted (ignoring the ~1 h gap required for the poisoning procedure). The experiment was repeated twice with identical results, and the data for one such representative experiment are shown in Figure 7.

1,10-Phenanothroline Poisoning Experiment for Benzene Hydrogenation. The experiment was started as if it were a Standard Conditions benzene hydrogenation experiment (i.e., 30 (±5) mg (0.362 mmol) of **1**, 5.3 mL (59.3 mmol) of benzene, 35 mL of degassed water, 110 °C, and an initial pressure of 880 psi). Pressure versus time data were collected until the pressure had decreased to 800 psig, that is, until ca. 30% completion. Then the reactor was cooled to room temperature, vented, taken into the drybox, and opened. Next, 10.0 (±0.2) mg (0.056 mmol, ~50 mol % versus Ru) of 1,10-phenanthroline (Aldrich, 99+%) was added to the red-orange reaction solution. The reactor was then resealed, brought out of the drybox, equilibrated at 110 °C, and pressurized to 800 psig with H_2. At this point, the collection of pressure versus time data was restarted (ignoring the ~1 h gap required for the poisoning procedure). The experiment was performed twice, giving identical results; data for one such representative experiment are shown in Figure 8.

Testing Whether or Not 1,10-Phenanthroline Is Halting Catalytic Activity via Proton Scavenging or Direct Metal Coordination Using the Sterically Bulky Base Proton Sponge. The details of this control experiment are presented in the Supporting Information.

N-Heterocyclic Carbene Poisoning Experiment for Benzene Hydrogenation. The details of this experiment are presented in the Supporting Information.

Deuterated NMR Studies, Showing Precatalyst [1][BF₄] Is Not Responsible for the H/D Exchange Catalysis. These experiments were performed at Ecole Polytechnique Fédérale de Lausanne. The high-pressure NMR spectra were recorded with a Bruker DRX-400 instrument using a sapphire tube assembly according to published methods.[48] The NMR studies were carried out in a sapphire tube with H_2 pressure equipment[50] at 45 °C over a period of 12 h, the initial hydrogen pressure being 100 atm H_2 (D_2O 559 mg, [**1**][BF₄] 8.0 mg, H_2 52 mg). Every 30 min a ^{1}H NMR spectrum was recorded over the region $6 > \delta > -6$ ppm. This method allows the direct observation of all species involved in the catalytic process, provided they are present at >2% abundance.

Supporting Information Available: Figure S1, Isolation and catalyst recycling following a 110 °C benzene hydrogenation; Standard Conditions 110 °C benzene hydrogenation for reactions performed at Neuchâtel University with **1**; Testing the kinetic competence of the metallic film at Neuchâtel University; Figure S2, Control TEM micrographs at 40 kV and under −168 °C cryogenic conditions at 40 and 120 kV; Figure

(48) (a) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (b) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.

S3, TEM micrograph from the red-orange reaction solution following a Standard Conditions hydrogenation; Figure S4, Benzene versus time graph using complex **1**, synthesized at Neuchâtel University, but employed in a kinetic run at CSU; Figure S5, Data and curve-fit for a Standard Conditions benzene hydrogenation using the four-step mechanism; Figure S6, Kinetic study for the benzene hydrogenation under biphasic conditions with precatalyst **1** at Neuchâtel University; Figure S7, Control experiment using anhydrous RuO_2 as the catalyst, showing that ≤ 0.15 equiv of Ru is capable of hydrogenating benzene under conditions identical to those used for precatalyst **1**; Figure S8, Control experiment, employing the sterically bulky base Proton Sponge (1,$-$8-bis(di-methylamino)naphthalene), testing whether 1,10-phenanthroline is halting catalytic activity via proton scavenging or direct metal coordination; Figure S9, N-Heterocyclic carbene poisoning experiment for benzene hydrogenation with **1**; Figure S10, NMR studies for deuterated cluster cation $[Ru_3(\mu_2\text{-}D)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$; a critical re-examination of the prior data interpreted in terms of homogeneous catalysis by complex $[Ru_3(\mu_2\text{-}H)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$, **1**; and an analysis of the kinetic data showing that $\geq 99.97\%$ of the observed catalysis is due to $Ru(0)_n$ metal. This material is available free of charge via the Internet at http://pubs.acs.org.