Polyoxoanion- and Tetrabutylammonium-Stabilized Rh(0)$_n$ Nanoclusters: Unprecedented Nanocluster Catalytic Lifetime in Solution

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Abstract: The solution catalytic lifetimes of polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters have been investigated, including comparison to the lifetimes of [RhCl(PPh$_3$)$_3$] (Wilkinson's catalyst), [(1,5-COD)Rh(CH$_3$CN)$_2$]BF$_4$, and 5% Rh/Al$_2$O$_3$ under identical conditions. These Rh(0) nanoclusters, derived from the polyoxoanion-supported organometallic precursor [(n-C$_4$H$_9$)$_4$N]$_5$Na$_3$[(1,5-COD)Rh·P$_2$W$_{15}$-Nb$_3$O$_{62}$], exhibit catalytic lifetimes that are the longest lifetimes reported for a transition metal nanocluster catalyst *in solution*, $\geq$193 000 turnovers for olefin hydrogenation. The Rh(0) nanocluster catalytic lifetimes approach those of a solid-oxide-supported heterogeneous Rh(0) catalyst and are an order of magnitude higher than any previously reported for an unsupported nanocluster in solution. The results are of significance in that they provide the catalytic lifetime evidence needed to support the concept of highly stabilized nanocluster catalysts, such as the present polyoxoanion- and tetrabutylammonium-stabilized nanoclusters, serving as "soluble heterogeneous catalysts".

Introduction

One exciting application of transition-metal nanoclusters[1] (particles which have diameters of $\leq$100 Å (10 nm)[2,3]) is in chemical catalysis, where nanoclusters offer the potential to serve as "soluble analogues of heterogeneous catalysts".[2] Such nanocluster catalysts are expected to be highly active, in part due to the high percentage of metal atoms present on the surface of nanoclusters,[4] ca. 50% for a M(0)$_{\sim300}$ nanocluster, for example.

The key issues in catalysis, and hence that any attempt to develop a new class of catalysts must consider, include catalytic activity, stability and total lifetime (total numbers of turnovers possible), selectivity (often a crucial issue once sufficient activity and lifetime are in hand), and important practical issues such as the ease or difficulty of separation of the catalyst from the products or the regeneration of the catalyst. The current major stumbling block, among the above list of issues, in the quest to develop nanoclusters as "soluble heterogeneous catalysts" has been achieving sufficiently long catalyst lifetimes (i.e., tens- or even hundreds-of-thousands of turnovers) using transition-metal nanoclusters *in solution*. Indeed, the nanocluster literature teaches a clear belief that one must first immobilize (i.e., insolubilize and thereby heterogenize) nanoclusters on a solid support to prevent nanocluster deactivation via agglomeration.[5] This belief is well founded, in that nearly all previous transition-

metal nanoclusters lack sufficient stability to serve as long-lived catalysts in solution. For example, early solution catalytic lifetime experiments, typically performed using tetraalkylammonium halide (R$_4$N$^+$X$^-$)-stabilized nanoparticles (for example, the reported attempts to use (Octyl)$_4$N$^+$X$^-$-stabilized Pd clusters as liquid-phase hydrogenation catalysts in solution[6]), resulted in agglomeration of the nanoclusters after only 6−7 min of catalysis.[6] Similarly, Pt colloids precipitate out of solution when H$_2$ pressure is applied,[7] and Rh$_{55}$[P(t-Bu)$_3$]$_{12}$Cl$_{20}$ nanoclusters are unstable under catalytic hydrogenation conditions, forming bulk Rh(0) metal within a few hours. This latter report caused the authors to conclude, at that time and correctly given the literature available then, that "the future of large clusters in homogeneous catalysis is doubtful" and that "the application of larger clusters [in catalysis] can only be done via the formation of heterogeneous catalysts".[8] For this reason, the majority of nanocluster catalytic activity studies available to date involve transition-metal nanoclusters pre-immobilized onto a solid support (Table A, Supporting Information).[9]

(1) (a) *Clusters and Colloids; From Theory to Applications*; Schmid, G., Ed.; VCH: New York, 1994. (b) *Active Metals: Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH: Weinheim, 1996. (c) *Physics and Chemistry of Metal Cluster Compounds*; de Jongh, L. J., Ed.; Kluwer Academic Publishers: Dordrecht, 1994; Vol. 18. (d) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709−1727.

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

(3) Aiken, J. D., III; Finke, R. G. A Review of Modern Transition-Metal Nanoclusters: Their Synthesis, Characterization, and Applications in Catalysis. *J. Mol. Catal. A: Chem.* **1999**. In press.

(4) Pool, R. *Science* **1990**, *248*, 1186−1188.

(5) Examples of high turnover numbers obtained using transition-metal nanocluster-derived *heterogeneous* catalysts (i.e., nanoclusters immobilized on a solid support) include: (i) Rh$_{55}$ clusters supported on TiO$_2$, which show as many as 430 000 turnovers for the hydroformylation of ethene and propene;[5a] and (ii) Pd nanoclusters on charcoal, which show 96 000 turnovers in the hydrogenation of cyclooctadiene (compared to commercial Pd/C, which show only 36 000 turnovers).[5b] Additionally, Schmid reports that the activity of bimetallic Au(core)/Pt and Pd(core)/Pt nanoclusters supported on Al$_2$O$_3$ "remains the same over six cycles of reuse at 60 °C" in the hydrosilylation of 1-octene.[5c] (a) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709−1727. (b) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Fretzen, R.; Joussen, T.; Koppler, R.; Korall, B.; Neiteler, P.; Richter, J. *J. Mol. Catal.* **1994**, *86*, 129. (c) Schmid, G.; West, H.; Mehles, H.; Lehnert, A. *Inorg. Chem.* **1997**, *36*, 891−895.

(6) Bönnemann, H.; Brinkmann, R.; Neiteler, P. *App. Organomet. Chem.* **1994**, *8*, 361.

(7) Bönnemann, H.; Braun, G.; Brijoux, W.; Brinkmann, R.; Schulze Tilling, A.; Seevogel, K.; Siepen, K. *J. Organomet. Chem.* **1996**, *520*, 143.

(8) Schmid, G. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Publishers: Dordrecht, 1990; Vol. 7.

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More recently, however, demonstrations of transition metal nanoclusters as catalysts *in solution* have appeared[10−13] (Table B, Supporting Information, provides further details on these systems), but the majority of these reports are only qualitative demonstrations of catalysis, often lacking quantitative data on catalyst lifetime or even activity in some cases. In addition, the data provided in Table B of the Supporting Information show that the highest, previously demonstrated lifetime of any nonpolyoxoanion-stabilized[14] nanocluster catalyst in solution is only ca. 2300−10000 turnovers;[15] more commonly the total number of turnovers demonstrated is ≤50. Moreover, turnover frequencies and catalyst lifetimes are typically not corrected for the number of exposed metal atoms, and only in a few cases are nanocluster catalysts compared directly to their respective heterogeneous counterparts under identical reaction conditions. Such comparisons are important if one is to evaluate the potential of soluble nanocluster catalysts in comparison to available heterogeneous catalysts of the same metal.

The previous record catalytic lifetime for a nonpolymer-protected nanocluster catalyst is our own 18 000 total turnovers (TTOs) for our polyoxoanion-stabilized $Ir(0)_{\sim 300}$ nanoclusters[14] and for the common test reaction, cyclohexene hydrogenation.[2,3]

(9) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709−1727.

(10) Olefin hydrogenation or acetoxylation reactions: Vargaftik, M. N.; Zargorodnikov, V. P.; Stolarov, I. P.; Moiseev, I. I.; Kochubey, D. I.; Likholobov, V. A.; Chuvilin, A. L.; Zamaraev, K. I. *J. Mol. Catal.* **1989**, *53*, 315−348.

(11) Heck, Suzuki, or McMurry coupling reactions: (a) Reetz, M. T.; Lohmer, G. *J. C. S. Chem. Commun.* **1996**, 1921−1922. (b) Reetz, M. T.; Breinbauer, R.; Wanninger, K. *Tetrahedron Lett.* **1996**, *37*, 4499−4502. (c) Beller, M.; Fischer, H.; Kuhlein, K.; Reisinger, C.-P.; Herrmann, W. A. *J. Organomet. Chem.* **1996**, *520*, 257−259. (d) Reetz, M. T.; Quaiser, S. A.; Merk, C. *Chem. Ber.* **1996**, *129*, 741−743.

(12) Cyclizations of hydroxymethylamines: van Benthem, R. A. T. M.; Heimstra, H.; van Leeuwen, P. W. N. M.; Geus, J. W.; Speckamp, W. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 547.

(13) Enantioselective hydrogenations: Bönnemann, H.; Braun, G. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1992−1995.

(14) The near-monodisperse 20 ± 3 Å $Ir(0)_{\sim 300}$ polyoxoanion- and tetrabutylammonium-stabilized Ir(0) nanoclusters[14a−d] are synthesized in acetone, under H_2, from the polyoxoanion-supported organometallic complex[14e−h] $[(n-C_4H_9)_4N]_5Na_3[(1,5-COD)Ir \cdot P_2W_{15}Nb_3O_{62}]$. The Ir(0) nanoclusters are active, long-lived cyclohexene hydrogenation catalysts, ones which give turnover frequencies per active-Ir(0) atom of 3200 ± 1000 turnovers per hour.[14b] Furthermore, preliminary experiments show that the Ir(0) nanoclusters are active in solution for up to 18 000 turnovers, and over a 10 day period.[14b] Such lifetimes were previously without precedent for a nonpolymer protected,[14i] nanocluster-catalyzed reaction in solution, and have recently been recognized in the literature as such by others.[14j,k] Another important feature of these as well as other nanoclusters (see Table B of the Supporting Information) is that they can be isolated as a powder and then redissolved in solution while retaining nearly all of their original catalytic activity.[2,14b] (a) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335−8353. (b) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891−4910. (c) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382−10400. (d) Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, *9*, 3083−3095. $(1,5-COD)M \cdot P_2W_{15}Nb_3O_{62}^{8-}$: (e) Nomiya, K.; Pohl, M.; Mizuno, N.; Lyon, D. K.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 186−201. (f) Pohl, M.; Lyon, D. K.; Mizuno, N.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 1413. (g) Pohl, M.; Finke, R. G. *Organometallics* **1993**, *12*, 1453−1457. (h) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1784−1787. (i) For an excellent review on colloid and cluster catalysis, containing catalytic data for many colloids protected by polymers, see: Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693−2730. (j) Schmid, G. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 2, p 641. (k) Schmid, G.; Maihack, V.; Lantermann, F.; Peschel, S. *J. Chem. Soc., Dalton Trans.* **1996**, 589.

(15) One of the better-studied nanocluster catalysts in solution is Mosieev and co-workers' $Pd(0)_{\sim 570}(phen)_{\sim 60}(OAc)_{\sim 180}$ nanoclusters.[10] Moiseev and co-workers' $Pd(0)_{\sim 570}$ nanoclusters, one of the first examples of a well-characterized nanocluster catalyst in solution, are active hydrogenation and Wacker-type oxidation catalysts in $EtOH/CH_3CN$.[10] The kinetic reproducibility using these clusters is reported to be ca. 10%, with turnover frequencies ranging from 0.3 to 15 h^{-1} and catalyst lifetimes of about 10 000 turnovers. However, no direct comparison of these Pd nanoclusters to a heterogeneous Pd catalyst has been reported.
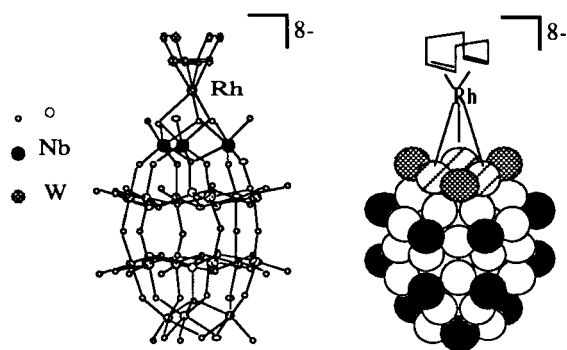

Figure 1. (A) Ball-and-stick representation and (B) space-filling representation of the $[(1,5-COD)Rh \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ polyoxoanion-supported Rh(I) nanocluster precatalyst, **1**. The Bu_4N^+ and Na^+ counterions have been omitted for clarity. In the space-filling representation the black circles represent terminal oxygens, the white circles represent bridging oxygens, the gray circles represent terminal Nb−O oxygens, and the three hatched circles atop the polyoxoanion to which the Rh is bonded represent the three Nb−O−Nb bridge oxygens.

That study also includes a quantitative comparison of the polyoxoanion-stabilized $Ir(0)_{\sim 300}$ nanoclusters to 80% dispersed Ir(0) on η-Al_2O_3,[14b] results which show, for such a highly dispersed heterogeneous catalyst, that the $Ir(0)_{\sim 300}$ nanoclusters were ~1.8 time more reactive and as long-lived within experimental error (the above noted 18 000 TTOs versus 20 000 for the 80% dispersed Ir(0) on η-Al_2O_3).[14b]

Recently we reported the synthesis and characterization of the second example of polyoxoanion- and tetrabutylammonium-stabilized, near-monodisperse[2] nanoclusters,[16] 40 ± 6 Å Rh(0) nanoclusters synthesized under hydrogen from the Rh polyoxoanion precursor complex,[14e−h] $[(n-C_4H_9)_4N]_5Na_3[(1,5-COD)-Rh \cdot P_2W_{15}Nb_3O_{62}]$, **1**, Figure 1.[17] Initial experiments revealed, as expected for the second row Rh(0) versus our previous, third row $Ir(0)_{\sim 300}$ nanoclusters, that the Rh(0) nanoclusters were the more active hydrogenation catalysts.

Several questions remained, however, specifically: (a) Just how long-lived is the catalytic activity of low concentrations of small, highly active Rh(0) nanoclusters? Also, (b) how do the Rh(0) nanocluster catalytic lifetimes compare to other homogeneous and heterogeneous Rh catalysts? More importantly, (c) does a test of the catalytic lifetime of polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanocluster catalysts support the emerging concept[2,3] of such highly stabilized nanoclusters as "soluble heterogeneous catalysts", or are nanocluster catalysts incapable of doing hundreds of thousands of catalytic turnovers in solution without agglomeration to the thermodynamic sink[2,3] of bulk metal?

Herein we report catalyst lifetime studies in solution for polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters demonstrating lifetimes that are the longest reported for transition metal nanocluster catalysts in solution, ≥193 000 turnovers. These lifetimes are then compared to those for three other Rh catalysts, two homogeneous Rh catalysts (or precatalysts), specifically Wilkinson's catalyst, $RhCl(PPh_3)_3$, and the precatalyst $[(1,5-COD)Rh(CH_3CN)_2]BF_4$, and then to the heterogeneous Rh catalyst, 5% Rh/Al_2O_3. All catalysts were tested under reaction conditions as identical as experimentally possible

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

(17) We have also reported a second route to 10−40 Å $Rh(0)_n$ nanoclusters, grown by the photolysis of $[(n-C_4H_9)_4N]_8[Rh(CO)_2 \cdot P_2W_{15}-Nb_3O_{62}] \cdot (n-C_4H_9)_4NBF_4$ under H_2. See: Nagata, T.; Pohl, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1997**, *36*, 1366.

(18) Gates, B. C. *Catalytic Chemistry*; John Wiley: New York, 1992; p 387.
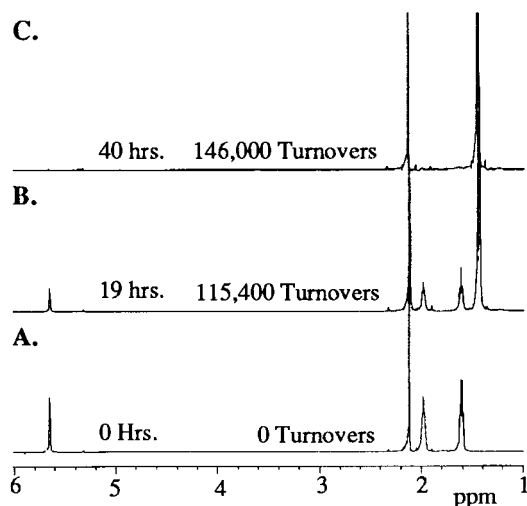
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Figure 2. Three ^{1}H NMR spectra, taken during the course of a typical catalyst lifetime experiment beginning with **1**, and directly monitoring the conversion of cyclohexene ($\delta = 1.6, 1.9, 5.6$) to cyclohexane ($\delta = 1.4$); the fifth peak (at $\delta = 2.1$) is from the solvent, acetone. The observed number of turnovers for this particular experiment was the maximum number possible (146 000). Spectrum A (bottom), 0 h, 0 turnovers. Spectrum B (middle), 19 h, 115 400 turnovers. Spectrum C (top), 40 h, 146 000 turnovers.

and using a prototypical structure-insensitive reaction,[18] cyclohexene hydrogenation. These studies continue our efforts to establish the strengths, and also the limitations, of polyoxoanion- and tetrabutylammonium-stabilized transition-metal nanoclusters. Overall, the long lifetimes observed offer additional support for the concept that highly stabilized nanoclusters can, in fact, operate as "soluble analogues of heterogeneous catalysts",[2,3] at least at mild temperatures.

Results and Discussion

Catalyst Lifetime Experiments Beginning With [(1,5-COD)Rh·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$, 1. Catalytic lifetime experiments for the Rh(0) nanoclusters were carried out under the same conditions used previously for their Ir(0) nanocluster congeners.[14b] Briefly, the nanocluster-forming polyoxoanion-supported pre-catalyst complex[19] [(1,5-COD)Rh·P$_2$W$_{15}$Nb$_3$O$_{62}$],[8-] **1**, is dissolved in acetone, cyclohexene is added, and the solution is placed under a constant pressure of 40 psig of H$_2$ in a Fischer−Porter bottle at room temperature. The conversion of cyclohexene to cyclohexane is followed *directly* by ^{1}H NMR by periodically removing aliquots of the reaction solution.

Figure 2 shows three ^{1}H NMR spectra taken at 0, 19.5, and 40 h during the course of a typical catalyst lifetime experiment beginning with [(1,5-COD)Rh·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$, **1**. In this

(19) (a) Our choice to start with the nanocluster *precatalyst* **1**, and not with previously isolated 40 ± 6 Å Rh(0)$_{\sim2400}$ nanoclusters,[16] is deliberate. Specifically, it is based on the following observations which suggested to us that generation of the Rh(0) nanoclusters in situ would result in the highest-activity, longest-lived nanoclusters: (i) our earlier demonstration that polyoxoanion- and tetrabutylammonium-stabilized Ir(0) nanoclusters, generated in situ from [(1,5-COD)Ir·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$, performed up to 18 000 turnovers for cyclohexene hydrogenation;[14b] (ii) our recent demonstration that a low concentration of Rh(0) nanoclusters are active cyclohexene hydrogenation catalysts;[16,19b] (iii) and our mechanistic studies of nanocluster formation[14a,c,19c] and agglomeration[19c] which reveal the simple insight that low concentrations of nanoclusters will be stabilized kinetically towards bimolecular agglomeration. (b) Recently we have reported kinetic and mechanistic studies of [(C$_8$H$_{17}$)$_3$NCH$_3$]$^+$- and Cl$^-$-stabilized Rh(0) nanoclusters, grown from RhCl$_3$, which are active for benzene hydrogenation: Weddle, K. S.; Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653−5666. (c) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 9545−9554.
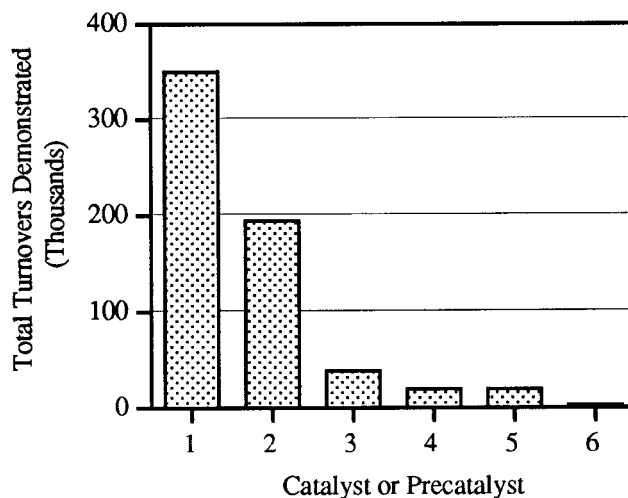
1. 5% Rh/Al$_2$O$_3$
2. (COD)Rh·P$_2$W$_{15}$Nb$_3$O$_{62}$$^{8-}$ (**1**)
3. (COD)Ir·P$_2$W$_{15}$Nb$_3$O$_{62}$$^{8-}$ (This Study)
4. (COD)Ir·P$_2$W$_{15}$Nb$_3$O$_{62}$$^{8-}$ (Prior Study[14b])
5. Rh(PPh$_3$)$_3$Cl (Wilkinson's Catalyst)
6. [(COD)Rh(CH$_3$CN)$_2$]BF$_4$

Figure 3. Total number of cyclohexene hydrogenation turnovers demonstrated beginning with five different catalysts or precatalysts.

experiment, the reaction reached 100% conversion (146 000 turnovers) by 40 h.

In a separate experiment, designed to reach higher turnovers with additional cyclohexene present, the Rh(0) nanoclusters derived from **1** proved capable of performing *at least* 193 000 total turnovers, Figure 3. Note that 100% conversion of cyclohexene is obtained in this experiment, results which suggest that even longer catalytic lifetimes may be possible (vide infra). An important observation in this catalytic lifetime experiment is that, upon standing, a light brown precipitate of the Rh(0) nanoclusters settled out of the solution as conversion of the cyclohexene to the slightly less polar cyclohexane approaches 100%, resulting in a decrease in the solution's polarity, a result we have seen previously for Ir(0)[14b] [and Rh(0)[16]] nanoclusters. Even with this limitation, the 193 000 turnovers are the highest reported catalyst lifetime for a transition-metal nanocluster in solution, an order of magnitude increase over the old record.

Further experimental evidence for solubility being the turnover-limiting issue for the Rh(0) nanoclusters under the reaction conditions employed is shown in Figure 4. As the ratio of cyclohexene (substrate) to acetone (solvent) was increased in order to increase the maximum possible number of turnovers, the percent conversion and, hence, the catalyst lifetime dropped significantly. Specifically, when a catalyst lifetime experiment was initiated beginning with a cyclohexene:acetone volume ratio of 3:1 (6.0 mL of cyclohexene, 2.0 mL of acetone) plus a mere 1.4 mg **1**, *fewer turnovers* (98 500 $\pm$ 200) out of a possible 237 000 turnovers were observed after 68 h. Additionally, when the cyclohexene:acetone volume ratio was increased to 4:1 (10.0 mL cyclohexene, 2.5 mL acetone, 1.4 mg **1**), the percent conversion dropped to only ca. 4% after 68 h (17 600 $\pm$ 200 turnovers, out of a possible 393 000), Figure 4. Solubility control experiments confirm that neither the nanocluster precursor **1**, nor the resulting polyoxoanion-stabilized Rh(0) nanoclusters, are soluble in cyclohexene alone. Hence, it is clear that the decrease in catalytic lifetime with increasing cyclohexene, Figure
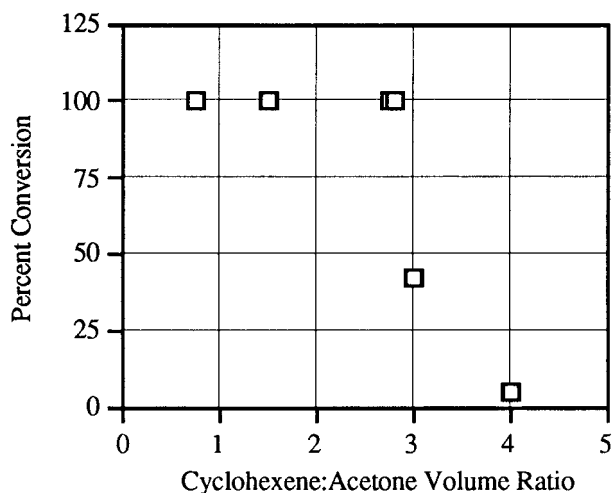
Figure 4. Plot of percent conversion obtained versus the ratio of cyclohexene volume to acetone volume in catalyst lifetime experiments beginning with **1**. A 100% conversion of cyclohexene is obtained when the ratio of cyclohexene to acetone is less than three; however, when this ratio is ≥ 3, <100% conversion is obtained. This is due to the insolubility of both the precatalyst, and the catalyst, in the cyclohexene reactant as well as in the product solution (cyclohexane/acetone), as demonstrated via independent control experiments with the precatalyst and, separately, the isolated catalyst.

4, is due to a decrease in solubility of either the precatalyst **1**, or the polyoxoanion- and tetrabutylammonium-stabilized Rh-(0) nanoclusters, (or both) in solutions containing $\geq 75\%$ cyclohexene by volume.

However, the data in Figure 4 suggest that longer lifetimes may be achieved by simple changes such as the use of more polar solvents, larger reaction vessels that allow the use of more solvent, or the use of the longer chain R_4N^+ countercations already well-known in the nanocluster area.[6,7,11,20] Since the use of larger volumes is a simple "engineering" change that should work, but adds no new fundamental understanding, we chose to investigate, instead, the use of a more polar solvent, for example propylene carbonate.[11a,21] As documented in the Experimental Section, up to 188 000 total turnovers for cyclohexene hydrogenation by the Rh(0) nanoclusters are observed using propylene carbonate. The use of proplyene carbonate results in a biphasic reaction solution, with a top, cyclohexene layer, and a bottom, propylene carbonate layer. As expected, the Rh(0) nanoclusters do not precipitate out of the propylene carbonate layer by the end of the reaction, and the propylene cabonate-based, two-phase reaction system has the added advantage of ease of product separation by decanting the top, product-containing layer. But, the biphasic nature of this system does, however, lead to some added complications, particularly somewhat variable turnover numbers (as detailed further in the Experimental Section); the total lifetime was not enhanced beyond the now 10-fold greater, 193 000 TTOs record. Hence, it is likely that a combination of longer-chain R_4N^+ and polar solvents will be needed to break this new record by a soluble nanocluster catalyst, and work toward this goal, and toward a fundamental understanding of the effects of different R_4N^+

(20) Wilcoxon, J. P.; Williamson, R. L.; Baughman, R. *J. Phys. Chem.* **1993**, *98*, 9933.

(21) One of the keys to scaling up our Ir(0) and Rh(0) nanocluster syntheses was the choice of propylene carbonate as the solvent: Aiken, J. D., III; Müller, F.; Finke, R. G. Manuscript in preparation ("Synthesis, Characterization and Catalytic Stability of Polyoxoanion- and Tetrabutyl-ammonium-Stabilized Transition-Metal 'Soluble Analogs of Heterogeneous Catalysts'. Scaled-up Synthesis and Effect of Solvent on the Catalytic Activity and Thermal Stability of Ir(0) Nanoclusters").

countercations on other nanocluster physical properties besides catalysis, is in progress.

Five Lines of Evidence That the Active Catalyst Is Rh(0) Nanoclusters. Five lines of evidence provide strong support for the postulate that polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters, not bulk Rh(0) metal or a homogeneous monometallic Rh complex, are the active catalysts in this system. First, and most convincingly, the precipitate present at the end of a catalyst lifetime experiment beginning with **1** can be collected and redissolved in the more polar solvent, acetonitrile, indicating that the material is *not* bulk Rh(0) metal (which is insoluble in acetonitrile[22] and tends to have a low surface area and low catalytic rate[14b]). In addition, TEM images of this clear, light amber solution of the isolated catalyst after 146 000 turnovers *confirm the presence of 26 ± 6 Å Rh(0) nanoclusters*. Second, detailed TEM and kinetic and mechanistic studies[16] have been published showing that the precursor **1** forms polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters when placed under closely related reaction conditions (i.e., our previously described Standard Conditions[14b,16] for cyclohexene hydrogenation: 40 psig of H_2, 22 °C, 1.65 M cyclohexene, and acetone as solvent). Third, the kinetic and Hg(0) poisoning data published elsewhere[16] demonstrate (a) that **1** *cannot* be the catalyst and (b) that Rh(0) nanoclusters account for *all* of the observed catalytic activity with ± 5% error.[16] Fourth, GLC of the reaction mixture at the end of a catalyst lifetime experiment shows that free cyclooctane evolves from the bound 1,5-cyclooctadiene ligand present in **1**, consistent with the conversion of **1** into Rh(0) nanoclusters.[16] Fifth, control experiments reported below show that Rh(0) bulk metal, made by the reduction of [(COD)Rh(CH_3CN)_2]BF_4 under identical reaction conditions, gives a maximum of only ca. 2100 total turnovers (vide infra); hence, bulk, lower-surface-area Rh(0) *metal* cannot account for the long lifetimes achieved beginning with **1**.

Taken together, the above five lines of evidence provide strong—if not compelling—support for the thesis that the Rh(0) nanoclusters are the true, highly active, and long-lived catalysts in this system.

Catalyst Lifetime Comparison to Other Homogeneous and Heterogeneous Catalysts. The catalytic lifetime of the poly-oxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclus-ters was compared to three other rhodium-containing catalysts, Figure 3, under reaction conditions as nearly identical as experimentally possible. The three catalysts studied are Wilkin-son's catalyst, RhCl(PPh_3)_3, the Rh(I) precatalyst [(1,5-COD)-Rh(CH_3CN)_2]BF_4, and a commercially available 5% Rh/Al_2O_3 heterogeneous catalyst.

The two soluble rhodium complexes, [(1,5-COD)Rh(CH_3-CN)_2]BF_4 and RhCl(PPh_3)_3, Wilkinson's catalyst,[23] showed significantly lower catalyst lifetimes compared to the poly-oxoanion-stabilized Rh(0) nanoclusters. In the case of [(1,5-COD)Rh(CH_3CN)_2]BF_4, a clear, pale-yellow solution of this precatalyst complex rapidly changes color under H_2 as it is reduced to low-surface-area,[14b] bulk Rh(0) metal within 10 min, producing a maximum lifetime of only ca. 2100 turnovers,[24] Figure 3. Even the well-known homogeneous hydrogenation catalyst, Wilkinson's catalyst,[23] yielded only ca. 19 000 total turnovers before deactivation, Figure 3. A small amount of black material deposited on the stir bar and in the bottom of the

(22) Rhodium metal is not attacked by acids and reacts with aqua regia only when finely divided. See: *The Merck Index*, 9th ed.; Merck & Co: Rahway, NJ, 1976; p 1062.

(23) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; John Wiley: New York, 1992.

reaction vessel once the reaction solution was allowed to sit undisturbed at the end of the experiment. Deactivation pathways such as phosphorous–carbon bond cleavage are well-known for Wilkinson's catalyst.[25] Note that such ligand deactivation pathways are avoided by the thermally robust, all-inorganic nature of the polyoxoanion ligand that stabilizes the Rh(0) nanoclusters. The nanocluster-stabilizing polyoxoanion[26] is stable at temperatures as high as 250–450 °C[27] and hence does not degrade, and then poison, the nanocluster's metal surface at even 150–200 °C temperatures as do, for example, the less-stable phosphine ligands present in Wilkinson's and other homogeneous, organic-ligand-stabilized catalysts. Relevant here is that phosphine-stabilized $Pd_{\sim570}$ nanoclusters[28] have already been reported to suffer these same, PR_3 ligand, phosphorus–carbon bond-cleavage reactions and associated problems.

We also carried out a lifetime experiment beginning with a commercially available, 5% Rh/Al_2O_3 heterogeneous catalyst. This catalyst proved to be the longest-lived catalyst among those we tested, exhibiting a total of 350 100 ± 1700 turnovers (per mol Rh total) over the course of 4 days before, however, *it too became deactivated*. Note that the larger number of turnovers for 5% Rh/Al_2O_3 in comparison to the Rh(0) nanoclusters is somewhat of an "artifact" of the ability to use larger volumes of cyclohexene with the (insoluble) 5% Rh/Al_2O_3 catalyst compared to what was—but not what could be (i.e., by increasing the size of the reaction)—used for the Rh(0) nanoclusters. [In the case of the Rh(0) nanoclusters, one must use some of the volume available for solvent (i.e., and not just mostly cyclohexene) in order to keep the Rh(0) nanoclusters soluble, so that there are advantages of lower volume and less of a need for solvent in the case of the 5% Rh/Al_2O_3 catalyst.[29]] Hence, one perhaps obvious limitation of polyoxoanion-stabilized nanocluster "soluble analogues of heterogeneous catalysts" is hereby identified, namely that they retain their high activity only if kept in solution[30] (or perhaps if supported; studies of supported nanoclusters are in progress[30a]). The present results make it conceivable, however, that under optimized conditions the

nanoclusters may be able to out-perform the lifetime of even the 5% Rh/Al_2O_3, and additional studies in larger volume pressure vessels and with longer-chain R_4N^+ countercations are planned. (See the Experimental Section for initial experiments using $[(n\text{-}C_{18}H_{17})_4N]^+$ counterions which, however, did not lead to active catalysts, perhaps due to the presence of Br^-.)

In any event, the 193 000 total turnovers exhibited here for soluble, polyoxoanion- and tetrabutylammonium-stabilized Rh-(0) nanoclusters is a milestone in the quest[31] to develop soluble analogues of heterogeneous catalysts.

Summary

In summary, we have demonstrated that soluble, high-activity Rh(0) metal nanocluster catalysts evolve from the polyoxoanion-supported complex **1**, a catalyst capable of performing ≥193 000 turnovers in the hydrogenation of cyclohexene. Five lines of evidence were reported which provide strong support that the active catalyst is, indeed, the polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters that were identified directly by TEM following 146 000 turnovers. One simple, but key, aspect of the present invention is to use the nanocluster

(24) This experiment with the $[(1,5\text{-}COD)Rh(CH_3CN)_2]BF_4$ complex, chosen because it contains the same $(1,5\text{-}COD)Rh^+$ moiety present in the nanocluster precursor, **1**, but lacks the polyoxoanion and tetrabutylammonium components, provides compelling evidence that the polyoxoanion-stabilizing component is crucial in preventing nanocluster aggregation and, hence, in keeping the Rh(0) nanoclusters in a high-surface-area, high catalytic activity form. This nanocluster stabilization is achieved by the large size (ca. 12 × 15 Å) and high charge (9−) of the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion, which provides both steric and electronic stabilization of the nanoclusters in solution.[2] Importantly, the polyoxoanion is able to impart sufficient stability to the individual metal particles to prevent aggregation, but without acting as a catalyst poison, at least in solution. (Excess amounts of polyoxoanion do suppress the catalytic activity, however.[14c,30])

(25) (a) Phosphorous–carbon bond cleavage: Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171−185. (b) The nonactive forms of Wilkinson's catalyst are well-established, see: 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; p 532.

(26) (a) As described elsewhere,[2] the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion has several features which are thought to lead to the apparent special nature of this complex as a nanocluster-stabilizing anion. These include the following: (i) the six basic and chelating Nb−O$^-$ and Nb−O−Nb surface oxygens; (ii) the fact that the 3− surface charge is localized largely in the Nb-containing end of the polyoxoanion; and (iii) the otherwise overall low and dispersed surface charge, in combination with the large size, leads to a low charge density and thus a less compacted, more extended, and therefore greater thickness (and thus greater stabilizing[1a]) double or "multi"layer around the nanoclusters.

(27) (a) Comuzzi, C.; Dolcetti, G.; Trovarelli, A.; Cavani, F.; Trifirò, F.; Llorca, J.; Finke, R. G. *Catal. Lett.* **1996**, *36*, 75−79. (b) Cavani, F.; Comuzzi, C.; Dolcetti, G.; Etienne, E.; Finke, R. G.; Selleri, G.; Trifirò, F.; Trovarelli, A. *J. Catal.* **1996**, *160*, 317−321 and references therein.

(28) Moiseev, I. I.; Vargaftik, M. N. *New. J. Chem.* **1998**.

(29) (a) In addition, a further issue hindering a direct comparison between the Rh/Al_2O_3 and the Rh(0) nanocluster catalysts is that the number of exposed Rh atoms in the two catalysts is potentially different. Carbon disulfide poisoning experiments of the Rh/Al_2O_3 and the Rh(0) nanoclusters, in combination with CO and H_2 chemisorption analysis on Rh/Al_2O_3, can be used to estimate the number of exposed Rh atoms in the Rh(0) nanoclusters. Preliminary CS_2 poisoning experiments for these experiments show that 15 ± 5% of the Rh atoms in the Rh(0) nanoclusters are predicted to be "exposed surface atoms" by CO and H_2 chemisorption analysis, results which will be reported in due course.[29b] (b) Aiken, J. D., III, Finke, R. G. Manuscript in preparation.

(30) (a) Note that these results imply that the polyoxoanion- and tetrabutylammonium-stabilizing components, not surprisingly, block the metal surface of the materials once simply taken to dryness. It remains to be tested whether polyoxoanion- and tetrabutylammonium-stabilized nanoclusters supported on solid oxides will lead to high activity, long lifetime catalysts. The concept of supported nanoclusters has been explored by others (see Table A of the Supporting Information), albeit with mixed success.[30b] (b) There are at least two examples in the literature where immobilization of transition-metal nanoclusters on a solid support leads to a *decrease* in catalytic activity or lifetime. For example, 25 Å $R_4N^+Br^-$-stabilized Ni clusters show lifetimes of ca. 39 turnovers in the [3 + 2] cycloaddition of methylenecyclopropane to methyl acrylate. However, when these Ni clusters are immobilized on Al_2O_3 or charcoal their lifetime *drops* to between 1 and 7 turnovers.[30c] Likewise, 80 Å "propylene carbonate"-stabilized Pd clusters have been shown to catalyze the Heck reaction with yields ranging between 8 and 100%. When the same clusters are deposited on Al_2O_3, the yield drops, with only 1% of product obtained after 17 h at 155 °C.[11a] A probable reason for this is that any $R_4N^+X^-$ that is not washed away covers and deactivates (or otherwise prevents access to) the more reactive, "naked" supported metal particle's surface. (c) The same deactivation effect[30b] appears to occur with the polyoxoanion- and tetrabutylammonium-stabilized nanoclusters studied herein, that is when they precipitate out of a low-polarity cyclohexane/acetone solution toward the end of the high turnover cyclohexene hydrogenation lifetime experiments. (d) Reetz, M. T.; Breinbauer, R.; Wedemann, P.; Binger, P. *Tetrahedron* **1998**, *54*, 1233−1240.

(31) The development of soluble analogues of multimetallic, heterogeneous catalysts has long been of a goal of inorganic, organometallic, and catalytic chemists, a goal popularized by, for example, Mutterties' writings on the cluster-catalysis hypothesis (i.e., that metal carbonyl clusters might fulfill this goal) nearly 20 years ago.[31a–g] The CO-poisoned nature of metal carbonyl clusters led, however, to limits to the activities, or range of catalytic reactions, observed for carbonyl clusters. Carbonyl clusters have, however, served as impressive, X-ray crystallographically characterizable models of the possible bonding modes of a wide range of ligand types to multimetallic complexes; see for example the work of R. Adams for lead references to an extensive series of papers. [31g] Lead references: (a) Mutterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959. (b) Mutterties, E. L. *Science* **1997**, *196*, 839. (c) Mutterties, E. L. *Chem. Eng. News Special Rep.* **1982**, Aug. 30, 28−41. (d) Smith, A. K.; Basset, J. M. *J. Mol. Catal.* **1977**, *2*, 229. (e) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1980**, *19*, 896, and all of the later papers in the series from the Union Carbide group. (f) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. (g) *Catalysis by Di- and Polynuclear Metal Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley: New York, 1998.

precursor (**1**) at ca. 10^{-7} M (see the Experimental Section and Table C of the Supporting Materials) thereby[19] (i) generating low concentrations of small (ca. 26 Å), high surface area and highly active Rh(0) nanoclusters; and (ii) using their low concentrations to stabilize the Rh(0) nanoclusters kinetically against bimolecular agglomeration.

The finding that the catalytic lifetime demonstrated by the Rh(0) nanoclusters exceeds the lifetimes measured for all other *soluble* Rh catalysts tested under identical conditions is significant; the nanocluster catalysis lifetimes reported herein extends by an order of magnitude the longest reported catalytic lifetime for any transition metal nanocluster *in solution*. The present work is also important in that it allows identification of the resultant, highly active and long-lived Rh(0) nanoclusters as *only the fifth class of hydrogenation catalysts*,[23,24b] an important result since new, more active, longer-lived and especially functional-group-selective hydrogenation catalysts are still needed (see p 4892 and footnote 12 elsewhere[14b]), despite hydrogenations being one of the oldest known catalytic reactions.

The results also provide further evidence that the Rh(0) nanoclusters are properly designated as "soluble analogues of heterogeneous catalysts", analogues which exhibit catalytic rates[14b] and lifetimes approaching those of "naked" solid-oxide-supported heterogeneous catalysts, yet catalysts which are soluble and thus can be studied in solution where one can employ powerful solution kinetic and spectroscopic probes. Important issues remain, however, in developing such "soluble heterogeneous catalysts", notably the present limitations to the range of the temperature stability and demonstrated types of catalytic reactions of nanoclusters in comparison to the much better studied heterogeneous catalysts. Studies addressing those, and other goals, are continuing.

Experimental Section

Materials and Analytical Procedures. All catalyst reaction solutions were prepared under oxygen- and moisture-free conditions in a Vacuum Atmospheres drybox (<5 ppm of O_2 as continuously monitored by a Vacuum Atmospheres O_2-level monitor). Cyclohexene (Aldrich, 99+%, stabilized with 0.01% 2,6-di-*tert*-butyl-4-methylphenol) was distilled from Na under argon (≥99% purity by GLC) and stored in a drybox. Acetone (Burdick and Jackson, 0.26% H_2O) was transferred into a drybox and purged for 30 min using a glass bubbler. Wilkinson's catalyst, $RhCl(PPh_3)_3$, (Strem Chemicals) was opened and stored in a drybox and used as received. $[(1,5\text{-COD})Rh(CH_3CN)_2]BF_4$ was prepared according to the literature[32] and characterized by ^1H NMR (CD_2-Cl_2, $\delta = 2.01, 2.37, 2.55, 4.51$). 5% Rh/Al_2O_3 was obtained from Strem Chemicals and came preactivated under H_2 by the manufacturer. The percent active metal dispersion of 5% Rh/Al_2O_3 was obtained by H_2 and CO chemisorption performed by Micromeritics (Norcross, GA) using a Micromeritics 2010C instrument.[33] The $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}$-$Nb_3O_{62}$ polyoxoanion used in the synthesis of **1** was synthesized according to our more recent procedure[34] and its purity checked by ^{31}P NMR. (As a further check of the purity of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$, the ^{31}P NMR titration with $(1,5\text{-COD})M(CH_3CN)_2{}^+BF_4{}^-$ (M = Rh, Ir)

shown elsewhere[34a] is recommended, and a break point of 1.0 ± 0.1 should be seen.) The polyoxoanion nanocluster precatalysts, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **1**, and $[(n\text{-}C_4H_9)_4N]_5Na_3\text{-}[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ were prepared as previously described;[14e-h] their purity was confirmed by ^{31}P NMR and by C, H, N analysis. Analysis for the Rh complex, (calc) found: C (18.93) 18.88; H (3.47) 3.54; N (1.25) 1.27. Analysis for the Ir complex, (calc) found: C (18.63) 18.59; H (3.41) 3.42; N (1.23) 1.29. As noted elsewhere,[16] it is crucial to follow the synthesis of the $P_2W_{15}Nb_3O_{62}{}^{9-}$ and complex **1** *exactly* as described.[14e-h,34]

^1H NMR were performed on a Varian Mercury 300. Spectra were obtained in methylene-d_2 chloride in 5 mm o.d. Spectra Tech NMR tubes at room temperature and were referenced to the residual solvent impurity. Spectral parameters include the following: pulse width, 6.7 μs; tip angle, 51.7°; acquisition time, 2.67 s; repetition time, 2.67 s; no relaxation delay; sweep width, 6000 Hz.

Gas−liquid chromatography (GLC) was performed using a Hewlett-Packard 5890 Series II GC with a FID detector equipped with a Supelcowax 10 column coupled to a Hewlett-Packard 3395 integrator. Unless otherwise stated, parameters were as follows: $T_1 = 50$ °C, $t_1 = 3$ min, ramp $= 10$ °C, $T_2 = 250$ °C, $t_2 = 1$ min, injection volume $= 2$ μL.

Transmission electron microscopy (TEM) was performed as previously described[16,19c] using a JEOL TEM 2000 EX-II operating with an accelerating voltage of 100 keV. Several types of control experiments have also been done and are reported elsewhere.[16,19c]

General Procedure for Catalyst Lifetime Experiments. A summary of all catalyst lifetime experiments is provided in Table C of the Supporting Information. All catalyst lifetime experiments were performed on the previously described,[16] custom-built pressurized hydrogenation apparatus consisting of a pressurized Fischer−Porter bottle attached via Swagelock quick-connects to both a hydrogen supply (passed through water- and oxygen-scavengers) and to a pressure transducer. Unless otherwise stated, all reactions were carried out in the following manner and are based on our previously established[14b] reaction conditions for catalyst lifetime experiments. In a drybox, the catalyst or precatalyst material was weighed into a disposable 2-dram glass vial. Acetone was added via a gastight syringe (the exact amount is indicated in the specific catalytic experiments provided, vide infra) and the catalyst or precatalyst metarial was dissolved under agitation using a disposible polyethylene pipet. Cyclohexene was then added to the solution by gastight syringe, and the solution was mixed further by agitation using a disposable polyethylene pipet. Next, the solution was transferred into a new, previously unused 22 × 175 mm culture tube containing a new, previously unused $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. (The use of a new culture tube and a new stir bar is a caution we have long employed[14b] to avoid heterogeneous nucleation of the nanocluster formation reaction.[14c]) The culture tube was then placed inside of the Fischer−Porter bottle, sealed, brought from the drybox, and attached to the hydrogenation apparatus via the quick-connects. Stirring was started (at >600 rpm) and the Fischer−Porter bottle was then purged 15 times with 40 psig of H_2 (15 s/purge). A timer was started and the pressure in the Fischer−Porter bottle was then set at a constant 40 ± 1 psig H_2 for the entire course of the reaction by leaving the Fischer−Porter bottle open to the hydrogen supply. (Reactions were carried out at ambient temperature, 22 ± 2 °C; an asbestos pad was placed between the stir plate and the Fischer−Porter bottle to minimize warming of the solution by the stir plate.)

The reaction was monitored by periodically withdrawing aliquots of the reaction solution for ^1H NMR spectroscopy. Aliquots were removed by stopping the timer, sealing the Fischer−Porter bottle, disconnecting it from the hydrogenation line, transferring it into a drybox, releasing the H_2 pressure, and using a 9 in. glass pasteur pipet

(32) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345−2355.

(33) (a) Note that stoichiometric factors of 2 for H/Rh and 1 for CO/Rh were assumed in the chemisorption analysis, an assumption justified *ex post facto* by the good agreement (33% exposed Rh metal) using these assumptions. However, we note that there are reports in the literature of higher stoichiometric factors of CO/Rh = 1.94 for 1% Rh/SiO₂ (the H/Rh value was 1.84, that is close to 2.0). Ichikawa, S. *J. Chem. Soc., Chem. Commun.* **1989**, 403. (b) In addition, others show that in the H₂ and CO chemisorption analysis of Ir/Al₂O₃, the H/Ir ratio varies from 1.14 to 2.10 and the CO/Ir ratio varies from 0.84 to 1.78, a variation that is dependent upon the percent metal loading in the sample. McVicker, G. B.; Baker, R. T. K.; Garten, R. L.; Kugler, E. L. *J. Catal.* **1980**, *65*, 207.

(34) P₂W₁₅Nb₃O₆₂⁹⁻ synthesis and characterization papers: (a) Weiner, H.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 7905−7913 and references therein {note that this paper has two typographical errors: p 7910, righthand column, 12th line, "84% excess" should read "2% excess"; p 7910, footnote 20, 4th line, "5%" should read "0.5%"}. (b) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Weakley, T. J. *Acta Crystallogr., Sect. C* **1990**, *46*, 1592. (c) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692−1704.

inserted into the reaction solution to draw out a ca. 0.2 mL aliquot. This reaction solution aliquot was then placed in an NMR tube and further dissolved in 1 g of CD_2Cl_2 (from individual glass ampules of CD_2Cl_2). The Fischer—Porter bottle was then resealed, transferred back out of the drybox, reattached to the hydrogenation apparatus (which had been evacuated and repressurized with H_2 in the meantime), and purged again 10 times (15 s per purge); the pressure was reestablished at a continuous 40 ± 1 psig of H_2 and the timer was restarted. This whole procedure takes ≤ 30 min and, therefore, does not introduce significant error in the stated reaction times.

Catalyst Lifetime Beginning with [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)-Rh·P_2W_{15}Nb_3O_{62}]$, 1, in Acetone. A total of eight catalyst lifetime experiments beginning with **1** in acetone were performed. The amount of **1** used was varied between 1.4 and 2.9 mg (2.5×10^{-7} to 5.2×10^{-7} mol) at concentrations of between 2×10^{-5} and 7×10^{-5} M. The maximum number of turnovers *possible* per experiment ranged between 57 000 and 393 000. Complete experimental details for each lifetime experiment are provided in the Supporting Information. A table summarizing all reaction conditions and results is also provided as Table C of the Supporting Information.

A typical experiment is as follows: a catalyst lifetime experiment was carried out beginning with [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)Rh·P_2W_{15}-Nb_3O_{62}]$, **1**, (1.7 mg, 3.0×10^{-7} mol) dissolved in 3.0 mL of acetone and 4.5 mL of cyclohexene (4.4×10^{-2} mol; 146 000 turnovers maximum), all prepared in the drybox. As described in the section titled the General Procedure for Catalyst Lifetime Experiments, the resultant colorless reaction solution was then transferred into a 22 × 175 mm culture tube containing a $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. (A small, 0.2 mL aliquot of the reaction solution was removed at this point via disposable pipet for a time = 0 analysis by ^1H NMR spectroscopy and GLC.) The culture tube was sealed in the Fischer—Porter bottle, removed for the drybox, and attached to the hydrogenation line via the Swagelock quick-connects; a catalyst lifetime experiment was then carried out with vigorous stirring under a constant 40 ± 1 psig H_2 pressure. At prechosen times, the Fischer—Porter bottle was disconnected from the hydrogenation line, returned to the drybox, and a ca. 0.2 mL aliquot of the light-blue reaction solution was removed (the solution was blue due to the presence of heteropolyblue, a reduced form of the polyoxoanion[14a]). ^1H NMR of the removed aliquot showed that 115 400 ± 400 turnovers had occurred after 19 h. After a total of 40 h, ^1H NMR analysis of another aliquot of the reaction solution (still slightly blue in color) showed that all of the cyclohexene had been converted to cyclohexane, indicating that the maximum of 146 000 turnovers had occurred.

At the end of the experiment (40 h), the Fischer—Porter bottle was returned to the drybox and the reaction solution was decanted into a 2-dram vial, capped, and allowed to stand undisturbed for 2 h, during which a fluffy, light-brown precipitate had settled to the bottom of the vial. This precipitate (and some of the mother liquor) was removed by polyethylene pipet and transferred into a clean one-dram vial. Solvent (CH_3CN, 1.5 mL) was added, which dissolved the fluffy precipitate to yield a clear, light-amber solution. TEM images of this solution show nanoclusters that are 26 ± 6 Å in diameter (for the 42 particles counted).

Catalyst Lifetime Beginning with [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)-Rh·P_2W_{15}Nb_3O_{62}]$, 1, in Propylene Carbonate. A catalyst lifetime experiment beginning with **1** in propylene carbonate was performed beginning with [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)Rh·P_2W_{15}-Nb_3O_{62}]$, **1**, (2.1 mg, 3.8×10^{-7} mol) dissolved in 2.5 mL of propylene carbonate and 7.0 mL of cyclohexene (6.9×10^{-2} mol; 188 000 turnovers maximum), all prepared in the drybox. The resulting solution was biphasic. The top (cyclohexene) layer was clear and colorless; the bottom (propylene carbonate) layer was clear and light yellow. The reaction solution was then transferred into a 22 × 175 mm culture tube containing a $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was sealed in the Fischer—Porter bottle, removed for the drybox, and attached to the hydrogenation line via the Swagelock quick-connects; a catalyst lifetime experiment was then carried out with vigorous stirring under a constant 40 ± 1 psig of H_2 pressure. After 17 h, the reaction was ended by stopping the stirring and releasing the H_2 pressure. Within 2 min, the reaction solution had settled into two layers. The top layer was clear and colorless, and the bottom layer was light brown. No

precipitate was visible in either layer. ^1H NMR of an aliquot of the top layer (dissolved in 1 g of CD_2Cl_2) showed only cyclohexane. ^1H NMR of an aliquot of the bottom layer (dissolved in 1 g of CD_2Cl_2) showed only propylene carbonate and a trace of cyclohexane. No cyclohexene was observed in either layer, indicating that 188 000 total turnovers had occurred after 17 h. This reaction was repeated two times with different amounts of **1** and cyclohexene. Again, in all cases the reaction solution was biphasic. The results for the two additional experiments are the following: first experiment, 1.4 mg of **1**, 2.5 mL propylene carbonate, 12.5 mL cyclohexene, 17 h 88000 ± 1000 turnovers, 36 h 150000 ± 1000 turnovers, 60 h 168000 ± 1000 turnovers, 92 h 168000 ± 1000 turnovers; second experiment, 2.0 mg of **1**, 2.5 mL of propylene carbonate, 9.0 mL of cyclohexene, 21.5 h 30500 ± 200 turnovers, 43.5 h 41200 ± 100 turnovers.

Catalyst Lifetime Beginnning with [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)-Rh·P_2W_{15}Nb_3O_{62}]$ in Propylene Carbonate and in the Presence of Added ($C_8H_{17})_4N^+Br^-$. In a drybox, [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)Rh·P_2W_{15}Nb_3O_{62}]$, **1**, (2.0 mg, 3.6×10^{-7} mol) was dissolved in 2.5 mL of propylene carbonate and 9.0 mL of cyclohexene (6.9×10^{-2} mol; 247 000 turnovers maximum). Next, ($C_8H_{17})_4N^+Br^-$ (60 μL of a 1.8 × 10^{-2} M stock solution in propylene carbonate, 3 equiv) was added to the reaction solution using a gastight syringe. The reaction solution was then transferred into a 22 mm × 175 mm culture tube containing a $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was sealed in the Fischer—Porter bottle, removed for the drybox, and attached to the hydrogenation line via the Swagelock quick-connects; a catalyst lifetime experiment was then carried out with vigorous stirring under a constant 40 ± 1 psig of H_2 pressure. After 24 h, the reaction was ended by stopping the stirring and releasing the H_2 pressure. ^1H NMR analysis showed that no catalytic turnovers had occurred.

Catalyst Lifetime Experiment Beginning with "[(n-$C_4H_9)_4N]_5-[($n$-$C_8H_{17})_4N]_3[(1,5-COD)Rh·P_2W_{15}Nb_3O_{62}]$" in Propylene Carbonate. In a drybox, [(n-$C_4H_9)_4N]_5Na_3[(1,5-COD)Rh·P_2W_{15}Nb_3O_{62}]$, **1**, (51 mg, 9.14×10^{-6} mol) was dissolved in 2.0 mL of acetone in a 2-dram borosilicate glass vial containing a $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. In a separate but otherwise identical 2-dram vial, ($C_8H_{17})_4N^+Br^-$ (15.0 mg, 2.7×10^{-5} mol, 3 equiv per mol **1**) was dissolved in 2 mL of acetone to yield a clear, colorless solution. Next, the clear, colorless ($C_8H_{17})_4N^+Br^-$ solution was added dropwise using a disposable polyethylene pipet to the stirred acetone solution of **1**. The resulting bright-yellow reaction solution was stirred for an additional 30 min, by which time a white crystalline precipitate became visible. The bright-yellow reaction mixture was filtered twice through Whatmann no. 2 filter paper to remove the white precipitate, and then dried under vacuum at room-temperature overnight to yield a light-brown [(n-$C_4H_9)_4N]_5[($n$-$C_8H_{17})_4N]_3[(1,5-COD)Rh·P_2W_{15}Nb_3O_{62}]$ product.

A catalyst lifetime experiment was then carried out beginning with [(n-$C_4H_9)_4N]_5[($n$-$C_8H_{17})_4N]_3[(1,5-COD)Rh·P_2W_{15}Nb_3O_{62}]$ in propylene carbonate. In a drybox, [(n-$C_4H_9)_4N]_5[($n$-$C_8H_{17})_4N]_3[(1,5-COD)Rh·P_2W_{15}Nb_3O_{62}]$ (2.5 mg) was dissolved in 2.5 mL of propylene carbonate and 9.0 mL of cyclohexene (6.9×10^{-2} mol). The reaction solution was then transferred into a 22 mm × 175 mm culture tube containing a $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was sealed in the Fischer—Porter bottle, removed for the drybox, and attached to the hydrogenation line via the Swagelock quick-connects; a catalyst lifetime experiment was then carried out with vigorous stirring under a constant 40 ± 1 psig of H_2 pressure. After 24 h, the experiment was ended by stopping the stirring and releasing the H_2 pressure. ^1H NMR analysis showed that no catalytic turnovers had occurred.

Catalyst Lifetime Beginning with Wilkinson's Catalyst, [RhCl-($PPh_3)_3$]. In a drybox, a 1.1×10^{-3} M stock solution of [RhCl($PPh_3)_3$] was made by dissolving [RhCl($PPh_3)_3$] (2.1 mg, 2.3×10^{-6} mol) in 2.0 mL of acetone (added by gastight syringe) in a 2-dram vial. Next, 400 μL (4.5×10^{-7} mol Rh) of this clear, copper-orange stock solution was added using a 500 μL gastight syringe to 3.00 mL of acetone and 4.5 mL of cyclohexene (4.4×10^{-2} mol cyclohexene, 98 000 turnovers maximum) to yield a clear, slightly orange solution. This solution was then used for a catalyst lifetime experiment. ^1H NMR analysis of an aliquot after 18 h showed that 8000 ± 100 turnovers had occurred. After 39.5 h, ^1H NMR analysis of another aliquot revealed that 12 100

± 100 turnovers had occurred. The reaction was terminated after 90 h by returning the Fischer−Porter bottle to the drybox and then releasing the hydrogen pressure. ^{1}H NMR analysis of a third aliquot showed that 19 000 ± 200 turnovers had occurred. The reaction solution was light yellow, but a small amount of black material was visible on the stir bar and on the bottom of the flask.

Catalyst Lifetime Beginning with [(1,5-COD)Rh(CH₃CN)₂]BF₄. A 1.3×10^{-3} M stock solution of [(1,5-COD)Rh(CH₃CN)₂]BF₄ was made by dissolving 2.0 mg of solid, yellow [(1,5-COD)Rh(CH₃CN)₂]-BF₄ in 4.0 mL of acetone in the drybox, resulting in a clear, pale-yellow solution. This solution was further diluted by transferring 260 μL (3.60×10^{-7} mol Rh) of the stock solution via a 1000 μL syringe into 3.75 mL of acetone (total solution volume, ca. 4.0 mL). Cyclohexene (3.0 mL, 3.0×10^{-2} mol; 83 000 maximum possible turnovers) was added to yield a clear, colorless solution. A catalyst lifetime experiment was then started. ^{1}H NMR showed that 1100 ± 100 turnovers had occurred after 19 h. ^{1}H NMR showed that, after an additional 53 h (72 h total), 2100 ± 100 total turnovers had occurred. This experiment was performed a second time using a 2.6×10^{-3} M stock solution of [(1,5-COD)Rh(CH₃CN)₂]BF₄, made by dissolving 2.0 mg of solid, yellow [(1,5-COD)Rh(CH₃CN)₂]BF₄ in 2.0 mL of acetone in the drybox resulting in a clear, pale-yellow solution. Using a 250 μL syringe, 170 μL of the stock of [(1,5-COD)Rh(CH₃CN)₂]BF₄ was drawn and added to a one-dram vial containing 4.0 mL of acetone and 3.0 mL of cyclohexene yeilding a clear, colorless solution. After 4 days, ^{1}H NMR showed that 1100 ± 100 turnovers had occurred. No additional catalytic activity was observed, even after a total of 8 days.

An additional control experiment showed that bulk low-surface-area[14b] Rh(0) is formed within minutes when a solution of 1.9 mg of [(1,5-COD)Rh(CH₃CN)₂]BF₄ (5.0×10^{-3} mmol) dissolved in 2.5 mL of acetone and 0.5 mL of cyclohexene was placed under 40 psig of H₂.

Control: Catalyst Lifetime Beginning with [(n-C₄H₉)₄N]₅Na₃[(1,5-COD)Ir·P₂W₁₅Nb₃O₆₂]. [(n-C₄H₉)₄N]₅Na₃[(1,5-COD)Ir·P₂W₁₅Nb₃O₆₂] (2.3 mg, 4.1×10^{-7} mol) was dissolved in 4.0 mL of acetone and 3.0 mL of cyclohexene (3.0×10^{-2} mol; 73 000 maximum turnovers possible) to give a clear, yellow solution. The Fischer−Porter bottle was removed from the drybox, coupled via the Quick-Connects to the hydrogenation line, and a catalyst lifetime experiment was started as described above. After 42 h, the Fischer−Porter bottle was transferred into a drybox and an aliquot of the slightly blue solution was drawn. ^{1}H NMR analysis showed that 14 700 ± 100 turnovers had occurred. The Fischer−Porter bottle was removed from the drybox, reattached to the hydrogenation apparatus, repressurized to 40 psig, and the hydrogenation was allowed to continue. After a total of 7 days the reaction was stopped. ^{1}H NMR analysis showed that a total of 36 700 ± 400 turnovers had occurred. (Previously, 18 000 turnovers over 10 days were observed in an analogous, but not identical, lifetime experiment.[14b]) The reaction solution was exposed to air, after which the blue color disappeared within seconds to give a cloudy brown solution. This cloudy solution was transferred into a screw-cap vial and allowed to settle on the bench overnight. By morning, a fine brown precipitate of CH₃CN soluble[14b] Ir(0) nanoclusters had settled to the bottom of the vial beneath a clear, colorless solution.

Catalyst Lifetime Beginning with 5% Rh on Al₂O₃. A catalyst lifetime experiment was started beginning with 5% Rh/Al₂O₃ (1.5 mg, 7.3×10^{-7} mol Rh) in 20.0 mL of cyclohexene (1.97×10^{-1} mol). ^{1}H NMR analysis after 24 h showed a 94% conversion of cyclohexene to cyclohexane had occurred (254 900 ± 900 turnovers). At this point, an additional 6.0 mL of cyclohexene (5.9×10^{-2} mol) was added to the reaction mixture, which was then repressurized under 40 psig of H₂. ^{1}H NMR spectra were obtained after a total of 46, 55, and 68 h, respectively; the results revealed that 305200 ± 2400 turnovers, 324300 ± 1500 turnovers, and 340100 ± 2000 turnovers had occurred. At this point (i.e., after 68 h total), an additional 6.0 mL of cyclohexene (5.9×10^{-2} mol) was added, so that the total amount of cyclohexene used was 32.0 mL (433 000 maximum turnovers possible); the reaction solution was then repressurized under 40 psig of H₂. After an additional 10 h (78 h total), ^{1}H NMR analysis showed that no additional turnovers had occurred (313100 ± 1700 turnovers were indicated from the ^{1}H NMR data). After 97.5 h total, ^{1}H NMR analysis confirmed that only 350100 ± 1700 turnovers (ca. 81% conversion) had occurred versus the 340100 ± 2000 seen after 68 h. The reaction was terminated at this point. A black film was visible on both the stir bar and sides and bottom of the culture tube. Small black pieces of a black material were also visible in the reaction solution, suggesting that the 5% Rh/Al₂O₃ had become deactivated by forming low surface area, bulk Rh(0) metal.

Supporting Information Available: Summary of key literature reporting catalysis via transition-metal nanoclusters immobilized on a heterogeneous support (Table A), summary of key literature reporting catalysis by transition-metal nanoclusters *in solution* (Table B), summary of catalyst lifetime experiments (Table C), complete experimental details for additional catalyst lifetime experiments performed beginning with **1**, and complete experimental details for two additional catalyst lifetime experiments performed with 5% Rh(0)/Al₂O₃. This material is available free of charge via the Internet at http://pubs.acs.org.

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