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Anisole Hydrogenation with Well-Characterized Polyoxoanion- and Tetrabutylammonium-Stabilized Rh(0) Nanoclusters: Effects of Added Water and Acid, Plus Enhanced Catalytic Rate, Lifetime, and Partial Hydrogenation Selectivity

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Following a comprehensive look at the arene hydrogenation literature by soluble nanocluster catalysts, six key, unfulfilled goals in nanocluster arene hydrogenation catalysis are identified. To begin to address those six goals, well-characterized polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters have been synthesized by the reduction of the precisely defined precatalyst $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ with H_2 in propylene carbonate solvent. These Rh(0) nanoclusters are characterized by their stoichiometry of formation, transmission electron microscopy, and the two rate constants which characterize their mechanism of formation; previous studies in our laboratories have provided additional characterization of polyoxoanion-stabilized Rh(0) nanoclusters. Propylene carbonate solutions of the Rh(0) nanoclusters catalyze the hydrogenation of anisole (methoxybenzene) under mild conditions (22–78 °C, 30–40 psig H_2). Proton donors such as water or $HBF_4\cdot Et_2O$ are discovered to affect both nanocluster formation and nanocluster arene hydrogenation catalysis. Under identical conditions, the Rh(0) nanoclusters are 10-fold more active than a commercially available, oxide-supported 5% Rh/Al_2O_3 catalyst of the same average metal-particle size. A series of lifetime experiments shows that the Rh(0) nanoclusters are capable of at least 2600 total turnovers (TTO), a lifetime significantly longer than the ∼100 TTO often seen for nanocluster arene hydrogenation catalysts, and a lifetime slightly better than the prior record of 2000 TTO for a literature nanocluster system. The present polyoxoanion-stabilized Rh(0) nanoclusters also display a record, albeit modest, 30% selectivity for the partial hydrogenation of anisole to 1-methoxycyclohexene with an overall yield of up to 8% at higher temperatures. In comparison to the 5% Rh/Al_2O_3 catalyst, the polyoxoanion-stabilized nanoclusters yield a 4.7-fold higher maximum yield of 1-methoxycyclohexene. Finally, the seven main findings of the present work are summarized, including how they address five of the aforementioned six main goals in nanocluster arene hydrogenation.

Introduction

Arene hydrogenation is an active area of modern research,[1−7] the origins of which can be traced back to the catalytic hydrogenation of benzene one century ago using finely divided nickel as the catalyst.[8,9] The production of substituted cyclohexanes from the corresponding substituted arenes is the goal of much of this research.[10−13] The hydrogenation of benzene to cyclohexane is probably the most important industrially practiced arene hydrogenation reaction, the resultant cyclohexane being used primarily in the production of the nylon precursor, adipic acid.[14,15] Partial arene hydro-

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genation to cyclohex*enes* is also an active area of research,[1,16,17] the industrially practiced partial hydrogenation of benzene to cyclohexene by Asahi Chemical Industry in Japan[18] being a noteworthy example.

Arene hydrogenation has also garnered current interest due to the demand for cleaner-burning, low-aromatic-content diesel fuels,[4] interest stimulated by the discovery that diesel exhaust particles contain powerful carcinogens,[19] particles which also contribute to the prevalence of asthma and nasal allergies.[20,21] The chemically demanding problem of hydrogenating aromatic polymers is also of current interest because the resultant polymers can have dramatically improved thermal and oxidative stability: for example, hydrogenation of aromatic rings in the biopolymer, lignin, has been suggested as a way to inhibit the yellowing of paper made from mechanical pulps.[22−25] Another example of the importance of aromatic polymer hydrogenation is the conversion of polystyrene to poly(cyclohexylethylene), a process which Dow Plastics is attempting to commercialize for use in optical media applications such as digital versatile disks (DVDs).[26] In short, arene hydrogenation remains an important area of research in catalysis.

Traditionally, most arene hydrogenation has been done with classical heterogeneous catalysts. However, the use of soluble transition-metal nanoclusters[27−42] for arene hydrogenation has increased dramatically in recent years[10−12,22,23,43−54] (see Table S1 of the Supporting Information for a complete list, plus a brief description, of each paper dealing with monocyclic arene hydrogenation by soluble nanocluster catalysts). Soluble nanocluster catalysts have some advantages over traditional heterogeneous catalysts: first, they are often more active under mild conditions than the corresponding traditional heterogeneous catalysts,[11,47] and the present work will quantify that reactivity in the case of our polyoxoanion-stabilized nanoclusters. This enhanced reactivity is important when the substrate is temperature sensitive, for example. Second, soluble nanocluster catalysts are also more selective than the corresponding traditional heterogeneous catalysts for some reactions;[28] for example, a larger cis/trans ratio for disubstituted benzene hydrogenation products is seen for nanoclusters.[47] Third, perhaps the most important advantage of soluble nanocluster catalysts is that they are easier to study because of their solubility and lack of a solid support; therefore, it is expected that they will be easier to optimize than traditional heterogeneous catalysts.

Disadvantages of soluble nanocluster catalysts exist as well, of course, in comparison to traditional heterogeneous catalysts: two of note are poorer stability toward bulk metal formation and the greater difficulty of catalyst/product separations over the simple filtration that is a hallmark advantage of traditional heterogeneous catalysts.

Much of the work using soluble nanocluster arene hydrogenation catalysts follows a seminal paper in 1983 by Januszkiewicz and Alper[43] which performed hydrogenations under biphasic, aqueous/organic reaction conditions using $[RhCl(1,5\text{-hexadiene})]_2$ as the precatalyst, and tetraalkylammonium hydrogen sulfate or tetraalkylammonium bromide as the phase transfer agent and nanocluster stabilizer (halide and tetraalkylammonium salts are well-known, widely used nanocluster stabilizers[28,29,34,36,37]). The colloidal nature of the catalyst was not known at the time, but these authors insightfully suggest a year later in 1984 that the actual

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catalyst is “a highly active form of colloidal rhodium”,[55] and subsequent studies by others on very similar systems identify colloidal Rh as the true arene hydrogenation catalyst in such systems.[23,49,51] Using mild reaction conditions (room temperature, 1 atm H_2), Januszkiewicz and Alper demonstrated up to 100 total turnovers for a variety of arenes (TTO, calculated by dividing the moles of hydrogenated arene by the moles of Rh present).[43] Unfortunately, no reaction times were given, so the catalytic activity (the turnover frequency, TOF) is unknown; providing a TOF for comparison to the literature and heterogeneous Rh catalysts is one of multiple goals, therefore, of the present work.

A perusal of the literature studies of soluble nanocluster arene hydrogenation catalysis in Table S1 of the Supporting Information demonstrates the following points. First, most studies use Rh(0) as the active metal, Rh also being the most active metal in the heterogeneous catalysis arene hydrogenation literature.[56] Second, Ru(0) nanoclusters are the second most common catalyst in this literature, again paralleling the extensive use of Ru in the heterogeneous catalysis of arene hydrogenation. Third, the three most commonly used nanocluster precursor compounds are $[RhCl(diene)]_2$, $RhCl_3\cdot 3H_2O$, and $RuCl_3\cdot 3H_2O$, and most soluble nanocluster arene hydrogenation catalysts use tetraalkylammonium salts to stabilize the nanoclusters against agglomeration. Fourth, the reaction conditions are typically mild (approximately room temperature and 1 atm H_2) and often biphasic (aqueous/organic). Fifth, the best soluble nanocluster arene hydrogenation catalyst in the previous literature, in terms of catalytic activity and lifetime, is the one developed in 1999−2000 by Roucoux and co-workers[52,53] involving water-soluble nanocluster catalysts formed by $NaBH_4$ reduction of $RhCl_3\cdot 3H_2O$ in aqueous solutions of hydroxyalkylammonium bromide salts. Using mild (room temperature, 1 atm H_2), aqueous/organic biphasic reaction conditions, they demonstrate a record 2000 TTO in 37 h for the hydrogenation of anisole (methoxybenzene).[53] It is not stated if their catalyst is still active after 2000 TTO.

More to the point of the present work, our comprehensive survey of the relevant literature (Table S1) reveals that the following are important, unfulfilled goals in the area of nanocluster arene hydrogenation: (i) the use of a nanocluster system in which the nanoclusters have been well characterized (so that one can use the relatively well-defined composition and nature of nanocluster metal-particle catalysts to understand better the observed catalysis); (ii) the use of nanoclusters stabilized by the anion which has a record stabilizing effect[57] and which yields nanoclusters with a record catalytic lifetime in solution for at least simple olefin hydrogenation,[58] the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion; (iii) the development of a nanocluster arene hydrogenation system that is not aqueous/organic biphasic so that the commonly observed effects of water in arene hydrogenation systems can be tested and better understood, an important component of the present work, vide infra; (iv) the extension of the catalytic lifetime beyond the normally observed ∼100 TTO in a well-defined system and, ideally, beyond the current record of 2000 TTO;[53] (v) the attainment of high yields of the valuable, partially hydrogenated, cyclohex*ene* products of arene hydrogenation, and with a better-defined, prototype nanocluster system; and (vi) the completion of a kinetic and mechanistic study.

Herein, we describe studies that address goals (i)−(vi). Specifically, in the present work, we describe the use of polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters,[58−60] for the hydrogenation of anisole. Polyoxoanion-stabilized Rh(0) nanoclusters have been prepared and well characterized in our prior work.[58−60] In addition, the Rh(0) nanoclusters made under the specific anisole hydrogenation conditions utilized herein have been independently characterized by (a) confirmation of the expected stoichiometry of nanocluster formation, (b) transmission electron microscopy (TEM), and (c) a determination of the two rate constants that have been shown to characterize unequivocally the kinetics and mechanism of nanocluster formation under H_2.[61,62] The Rh(0) nanoclusters are shown to hydrogenate anisole under mild conditions (22−78 °C, 30−40 psig H_2) in a single phase using propylene carbonate as the solvent; the results compare well with the best literature nanocluster catalysts in terms of activity and lifetime. The effects on catalytic performance of added water or $HBF_4\cdot Et_2O$ are also tested. Among soluble nanocluster catalysts in the literature, the polyoxoanion-stabilized Rh(0) nanoclusters display an unprecedented, albeit modest, selectivity for the partial hydrogenation of anisole to 1-methoxycyclohexene.

Results and Discussion

I. Synthesis and Characterization of Polyoxoanion-Stabilized Rh(0) Nanoclusters Formed under Anisole Hydrogenation Conditions.

Because we have previously prepared and characterized polyoxoanion-stabilized 40 ± 6 Å Rh(0) nanoclusters under *cyclohexene* hydrogenation conditions,[58,59,60] all that is needed here is to detail our choice of anisole as a substrate, our standard conditions for its hydrogenation and to characterize the Rh(0) nanoclusters made under *anisole* hydrogenation conditions, so that, with our earlier work,[58,59,60] the resultant Rh(0) nanoclusters qualify as well-characterized nanoclusters.

a. Choice of Anisole and Standard Conditions for Its Hydrogenation. Anisole was chosen as the substrate for four main reasons: (i) it has a high boiling point (154 °C), which minimizes evaporative loss during the hydrogenation experiments and subsequent workup; (ii) the methyl group protons provide an excellent ^{1}H NMR handle; and (iii) the methoxy

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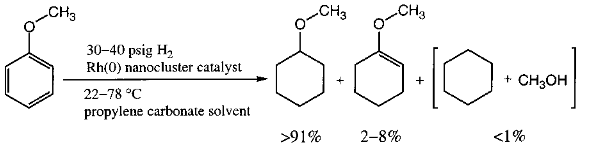
Scheme 1. Reaction Products Observed, Plus the Range of Conditions Used, for Anisole Hydrogenation[a]



[a] In every case, the fully hydrogenated compound, methoxycyclohexane, was the major product. Maximum yields of the partially hydrogenated intermediate, 1-methoxycyclohexene, were in the ∼2%−8% range (see Table 2). The hydrogenolysis products, cyclohexane and methanol, were observed in trace amounts (<1%). Most hydrogenations were done at 22 °C, but a few were run at temperatures as high as 78 °C, experiments which show that increasing the temperature leads to an increase in the maximum yield of 1-methoxycyclohexene.

substituent makes anisole relatively easy to partially hydrogenate, compared to benzene, and also allows determination of the selectivity for hydrogenation over hydrogenolysis ($Ph-OCH_3 + H_2 \rightarrow Ph-H + CH_3OH$). Also, significantly, (iv) most papers dealing with soluble nanocluster catalysts for arene hydrogenation have used anisole or a substituted anisole as a substrate (see Table S1); hence, comparisons of the literature with the work herein are greatly facilitated by the choice of anisole as the substrate.

The standard conditions for anisole hydrogenation developed and used herein are 2.9 mL of propylene carbonate, 0.14 mL of anisole (1.3×10^{-3} mol), 20 (±0.5) mg of precatalyst, $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, hereafter **A** ($3.6 \times 10^{-6}$ mol), 22 °C, and 40 (±1) psig initial H_2 pressure (∼3.7 atm), Scheme 1; these conditions allow for a maximum of 360 total turnovers at a maximum pressure loss at complete conversion of 11 psig in our apparatus, a value which will be used in the interpretation of several experiments which follow.

b. Formation of the Polyoxoanion-Stabilized Rh(0) Nanocluster Catalyst in Anisole. The in situ reduction of **A**, to form polyoxoanion-stabilized Rh(0) nanoclusters, was monitored as before[59] by measuring the H_2 pressure loss with a high-precision pressure transducer in an anisole hydrogenation under standard conditions; the resulting H_2 pressure versus time data are shown in Figure 1. At the end of the induction period, the solution begins to darken, giving the expected[59] clear, dark brown, completely soluble nanocluster solution after ∼1.0 h under standard conditions. Judging from the pressure loss, the anisole hydrogenation reaction is ∼20% complete after 22 h (∼70 TTO) with a maximum rate of hydrogen uptake of 0.16 psig/h (a TOF of 5.2 turnovers/h). The rate of hydrogen uptake has slowed considerably after 20 h, as Figure 1 shows, and even though the conversion was only ∼20%. A control experiment was done with the more easily reduced substrate cyclohexene to be sure that fully active Rh(0) nanoclusters were being formed; the observation of *H_2 mass-transfer-limited rates* of cyclohexene reduction (37.0 psig/h initial rate; Figure S1 of the Supporting Information) confirms (a) that very active nanoclusters are being formed, and therefore, (b) that anisole hydrogenation is just, as expected, a significantly more difficult reaction.

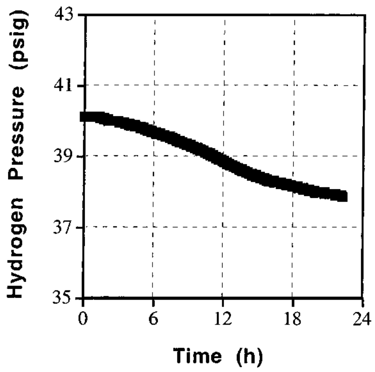


Figure 1. H_2 pressure vs time for a standard conditions anisole hydrogenation with $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **A**, as the precatalyst. The conditions for the hydrogenation include 2.9 mL of propylene carbonate, 0.14 mL of anisole (1.3×10^{-3} mol), 20 (±0.5) mg of **A** (3.6×10^{-6} mol), and 22 °C. The total change in H_2 pressure for this experiment (about 2 psig) indicates that the reaction is only about 20% complete after 22 h, yet the rate of hydrogen uptake has already slowed considerably because of deactivation of the Rh(0) nanocluster catalyst.

Scheme 2. Stoichiometry of Reduction for the Precatalyst $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **A**, under H_2.[a]

$$n\ \{\ [(1,5\text{-COD})Rh^{I}\bullet P_2W_{15}Nb_3O_{62}]^{8-} + 2.5\ H_2 \longrightarrow 1/n\ Rh(0)_n + \text{cyclooctane} + H^+ + P_2W_{15}Nb_3O_{62}{}^{9-}\ \} \quad (1)$$

$$n/2\ \{\ 2\ P_2W_{15}Nb_3O_{62}{}^{9-} + 2\ H^+ \longrightarrow P_2W_{15}O_{61}Nb_3\text{-}O\text{-}Nb_3O_{61}W_{15}P_2{}^{16-} + H_2O\ \} \quad (2)$$

[a] The evolution of 1.0 equiv of cyclooctane is a valuable GLC handle for monitoring the nanocluster formation reaction and its kinetics. Note also that the precedented[59,63] formation of the anhydride dimer of the polyoxoanion in the presence of acid produces 0.5 equiv of H_2O, eq 2 above.

c. Characterization of the Resultant Polyoxoanion-Stabilized Rh(0) Nanoclusters. The polyoxoanion-stabilized Rh(0) nanoclusters formed under anisole hydrogenation conditions were characterized by (i) their precedented[59] stoichiometry of formation, Scheme 2, (ii) TEM of the resultant unagglomerated nanoclusters, Figure 2, (iii) X-ray photoelectron spectroscopy (XPS) to confirm the expected[59,63] intimate presence of the polyoxoanion surrounding the Rh(0) nanocluster, and (iv) demonstration of the characteristic autocatalytic kinetics of formation, Figure 3, in a cyclooctane evolution experiment (described later). Briefly, quantitative GLC analysis confirms that the expected 1.0 (±0.1) equiv of cyclooctane evolves during the nanocluster formation reaction; the stoichiometry in Scheme 2 is further established by a hydrogen gas-uptake experiment reported elsewhere[59] showing that the precatalyst, **A**, dissolved in propylene carbonate and reduced by hydrogen in the absence of substrate, consumes the expected 2.5 equiv of H_2, plus 1.0 equiv of H_2 for the reduction of the polyoxoanion to its corresponding $W(V)^\bullet$ containing heteropoly blue (see the discussion provided elsewhere).[59] XPS on a sample of the polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters confirmed the presence of the polyoxoanion stabilizer (W, Nb, and O peaks) as well as the expected, but still interesting, *lack* of a Rh(0) signal, consistent with the Rh(0) nanoclusters being buried under a ≥15 Å sheath of the large (12 × 15 Å) $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion stabilizer (Figure S11a of the Supporting Information).

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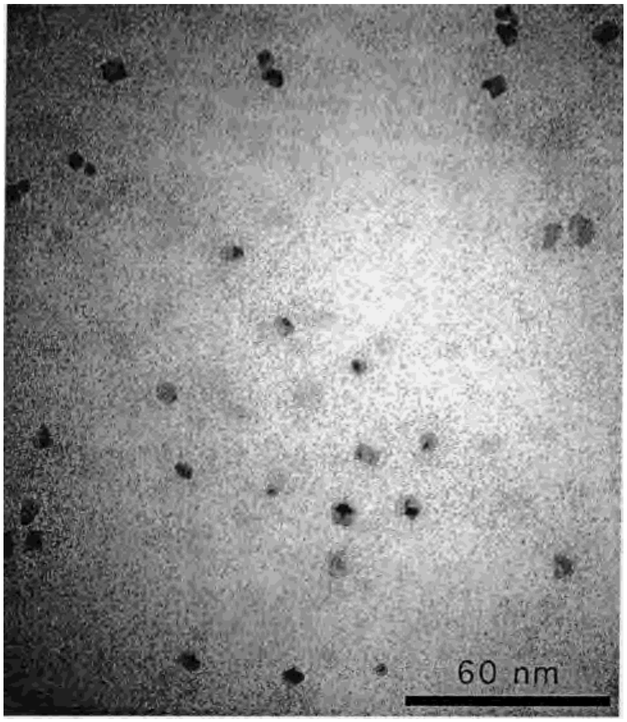

Figure 2. Transmission electron micrograph of polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters prepared under H_2 from $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ at 22 °C in 2.9 mL of propylene carbonate and 0.14 mL of anisole. Sample preparation involved removal of the propylene carbonate solvent via ether precipitation, as described in the Experimental Section. From 15 micrographs, including the one here, the size distribution of the resultant nanoclusters was found to be 5.3 (±1.0) nm (where the error bars are $\pm 1\sigma$ for a sample size of $n = 155$), corresponding to an average nanocluster size of $Rh_{\sim 5700}$.

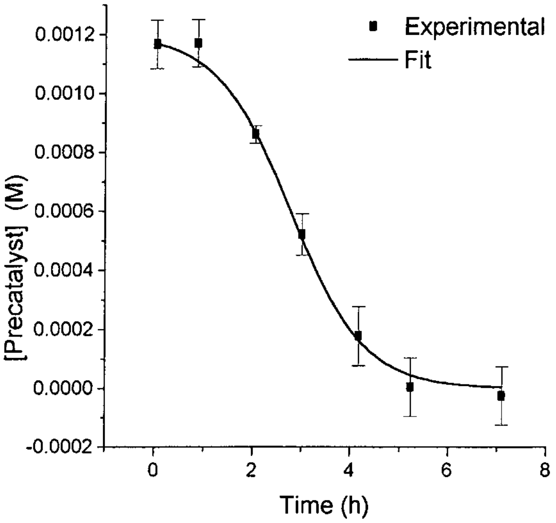

Figure 3. Loss of the Rh(0) nanocluster precatalyst $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **A**, as monitored by its GLC-determined evolution of 1.0 equiv of cyclooctane (according to eq 1 of Scheme 2). The expected[61,62] sigmoidal experimental data have been fit to the kinetic equations $\mathbf{A} \rightarrow \mathrm{B}$ (rate constant k_1) and $\mathbf{A} + \mathrm{B} \rightarrow 2\mathrm{B}$ (rate constant k_2), indicative of the nucleation and autocatalytic surface-growth mechanism.[61,62] The resulting, GLC-determined rate constants are $k_{1(\mathrm{GLC})} = 3.4 \times 10^{-2}$ h^{-1} and $k_{2(\mathrm{GLC})} = 1.1 \times 10^{3}$ M^{-1} h^{-1}.

TEM analysis of the final reaction solution of a standard conditions anisole hydrogenation, Figure 2, shows nanoclusters with an average diameter of 5.3 (±1.0) nm (these and all subsequent TEM error bars are one standard deviation ($\pm 1\sigma$) for >135 nanoclusters counted). Assuming that the nanoclusters are spherical and that they have the same density as bulk Rh metal, one can calculate (see footnote 29 elsewhere[63]) that the Rh(0) nanoclusters with a diameter of 5.3 nm contain *on average* ~5700 Rh atoms, $Rh(0)_{\sim 5700}$. The TEM in Figure 2 showing *unagglomerated* nanoclusters at the end of the anisole hydrogenation under standard conditions yields another important conclusion: the catalytic deactivation noted earlier is not due to nanocluster agglomeration or instability (consistent with this, the reaction solution remained clear, with no visible bulk metal or other precipitate throughout the anisole hydrogenation experiment). Hence, a surface deactivation phenomenon is most likely responsible for the observed loss of activity.[64-68]

d. Characterization of the Nanocluster Formation Kinetics via the Evolution of Cyclooctane. Previously, we developed novel methods[61,62] to follow the kinetics of nanocluster nucleation and growth using the concept of a pseudoelementary mechanistic step.[69-71] The mechanism we uncovered, and which is proving general for the formation of transition-metal nanoclusters by the reduction of metal salts under H_2,[61] consists of two pseudoelementary steps and their associated rate constants: slow continuous nucleation, $\mathbf{A} \rightarrow \mathrm{B}$ (rate constant k_1), followed by fast autocatalytic surface growth $\mathbf{A} + \mathrm{B} \rightarrow 2\mathrm{B}$ (rate constant k_2), where **A** is the nanocluster precursor $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ as before and B is the catalytically active surface Rh(0) metal. Characterization of the nanoclusters by showing this mechanism applies, plus measurement of the two rate constants k_1 and k_2, is actually one of the more important characterization tools for transition-metal nanoclusters. This is true since a high k_2/k_1 ratio correlates with increasing nanocluster size, an increasing tendency to near-monodispersity (≤15% size distribution[29]) and, in general, also reveals whether the nanoclusters are formed under a high degree of kinetic control.

The Rh(0) nanocluster formation reaction was monitored by removing aliquots of the reaction solution for GLC analysis to follow the evolution of the 1.0 equiv of cyclooctane that accompanies the conversion of the precursor, **A**, into Rh(0) nanoclusters under H_2, Scheme 2.[61,62] (The more precise and larger-data-set-generating method of monitoring the hydrogen uptake curve,[61,62] in this case for anisole hydrogenation, Figure 1, could not be used because of catalyst deactivation.) The cyclooctane evolution experiment

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(64) The formation of inactive spectator species, such as alkylidenes and alkylidynes, on the surface of metals is well-known from single-crystal surface science.[65,66] In addition, Bradley and co-workers have concluded that colloidal metals formed under mild conditions generally have highly defected surfaces on the basis of CO addition and then IR studies.[67] Hence, another possibility is that the observed deactivation is due to a slow surface rearrangement or "annealing" process which results in nanoclusters that are more thermodynamically stable, but less catalytically active.

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(70) Field, R. J.; Noyes, R. M. *Acc. Chem. Res.* **1977**, *10*, 214.

(71) Field, R. J.; Noyes, R. M. *Nature* **1972**, *237*, 390.

was carried out using the standard conditions described previously (except that the H_2 pressure was kept at a constant 40 (±1) psig, see the Experimental Section for further details). The loss of **A**, as measured by its 1:1 cyclooctane evolution stoichiometry (Scheme 2), has the expected, sigmoidal, autocatalytic[61,62] shape, Figure 3, with an induction period of about 1 h, followed by complete reduction of precatalyst in about 7 h. The experimental data are well fit by the slow continuous nucleation, then fast autocatalytic surface growth mechanism and associated kinetic equations, $\mathbf{A} \rightarrow \mathrm{B}$ (rate constant k_1) and $\mathbf{A} + \mathrm{B} \rightarrow 2\mathrm{B}$ (rate constant k_2).[61,62] The rate constants determined from the curve fit are $k_{1(\mathrm{GLC})} = 3.4 \times 10^{-2}\ \mathrm{h}^{-1}$ and $k_{2(\mathrm{GLC})} = 1.1 \times 10^{3}\ \mathrm{M}^{-1}\ \mathrm{h}^{-1}$ (no correction has been made to $k_{2(\mathrm{GLC})}$ for the "scaling factor",[61,62,72] that is, for the changing number of Rh atoms on the nanocluster surface). Significantly, the ratio of k_2 to k_1 is quite large ($>10^4$), a desirable feature indicating that the nanoclusters are formed in a kinetically controlled manner which generally leads to narrow size dispersion because nucleation (k_1) and growth (k_2) are well separated in time.[73] The sigmoidal shape of the curve in Figure 3 and the good curve fit to the $\mathbf{A} \rightarrow \mathrm{B}$ and $\mathbf{A} + \mathrm{B} \rightarrow 2\mathrm{B}$ kinetic scheme provide excellent evidence that nanocluster formation occurs with the same nucleation and then with the autocatalytic surface-growth mechanism that has been previously elucidated for transition-metal nanocluster formation under H_2.[61,62,72]

Significantly, the curve fit also shows that there is no detectable deactivation in the autocatalytic surface growth, at least for the time scale of nanocluster formation in this experiment (i.e., in the first ~7 h, compared to the 22 h of arene hydrogenation in the previous section and where deactivation is observed). These results are notable even for their simple proof of when the nanoclusters are completely formed (i.e., so that they are not harvested too early or late); most papers in the nanocluster area fail to follow their reactions in any manner that allows this simple but important insight. Also notable is the quantitative fit to an established mechanism of formation done here, an important measurement for well-characterized nanoclusters.

II. Effects of Added Water on Anisole Hydrogenation. Arene hydrogenation with soluble nanocluster catalysts has been performed in biphasic (aqueous/organic) solvent systems in 12 of 17 prior studies, Table S1. There are only five reports in the literature where "water-free" hydrogenations were attempted.[11,12,24,51,74,75] In every case, these "water-free" experiments exhibited either decreased hydrogenation activity or a complete lack of hydrogenation activity. Two studies report deuterium labeling experiments showing the incorporation of hydrogen from water into the hydrogenated product.[51,74] It was suggested that the rate enhancing effect of water "could involve a favored cleavage of a Rh−C bond [i.e., the Rh-arene bond] by protonation rather than reductive elimination of product from a hydrido−aryl species [H−Rh−Ar]".[51] In short, water is a key, but still ill-understood, component of arene hydrogenation with nanoclusters.

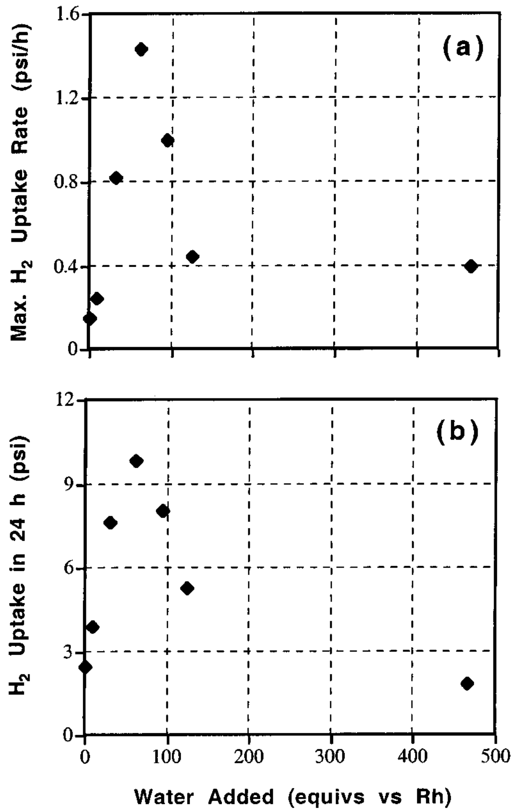

Figure 4. Effect of added H_2O on (a) the maximum rate of hydrogen uptake (i.e., the maximum rate of hydrogenation) and on (b) the total H_2 uptake (proportional to the total number of catalytic turnovers) observed over a 24 h period. Both graphs reach a maximum at 60 equiv added H_2O. In the experiments with ≥60 equiv of H_2O, a dark colored precipitate formed during the reaction, bulk metallic Rh(0) by XPS analysis.

By design, our system allowed us to study the effects of water on the catalytic activity and lifetime of polyoxoanion- and tetrabutylammonium-stabilized nanoclusters. Studying the effects of water necessitated that we control all sources, and the absolute amount, of water present; we accomplished this by using carefully dried glassware, solvents, and reagents (see the Experimental Section for details). Our accounting for the water present includes the 0.5 equiv of water per $P_2W_{15}Nb_3O_{62}^{9-}$ generated during the reaction by the well-documented formation of the anhydride of the polyoxoanion, $2P_2W_{15}Nb_3O_{62}^{9-} + 2H^+ \rightarrow [P_2W_{15}O_{61}Nb_3{-}O{-}Nb_3O_{61}W_{15}P_2]^{16-} + 1H_2O$, Scheme 2.[59,63]

The effects of H_2O on the Rh(0) nanoclusters were determined in a series of anisole hydrogenation experiments identical to the standard conditions anisole hydrogenation described earlier, except that 8−465 equiv of H_2O (vs Rh) was added. (A plot of the H_2 pressure vs time for each of these experiments is available as Figures S2−S7 in the Supporting Information.) Note that H_2O is present *during the formation of the nanoclusters*. Figure 4a shows a plot of maximum H_2 uptake rate versus the amount of H_2O added for this series of experiments. The maximum rate of H_2 uptake increases with added H_2O up to 60 equiv, Figure 4a.

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(73) Özkar, S.; Finke, R. G. Manuscript in preparation.

(74) Blum, J.; Amer, I.; Vollhardt, K. P. C.; Schwarz, H.; Hoehne, G. *J. Org. Chem.* **1987**, *52*, 2804.

(75) The true arene hydrogenation catalyst in the important system developed by Blum et al. was later found to be nanocolloidal: Weddle, K. S.; Aiken, J. D.; III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 5653.

With 60 equiv of H_2O added, the maximum rate of H_2 uptake was 1.4 psig/h, almost 10-fold faster than the standard conditions experiment described earlier (i.e., with no H_2O added). If >60 equiv of H_2O is added, the rate of hydrogenation begins to decrease, Figure 4a.

Figure 4b shows the same trend for the total H_2 uptake (which is proportional to the number of catalytic turnovers) in the first 24 h of each experiment: the total H_2 uptake reaches a peak for the experiment where 60 equiv of H_2O was added. Complete reduction of the precatalyst (i.e., complete nanocluster formation) was confirmed at the end of each of these experiments by quantitating the evolved cyclooctane with GLC. A black precipitate formed within the first 24 h for experiments with ≥60 equiv of H_2O added. The precipitate was unequivocally identified as bulk Rh(0) metal by XPS analysis (Figure S11b of the Supporting Information).[76]

These results are of fundamental importance as they show for the first time (i) a sharp maximum versus the amount of H_2O added and (ii) nanocluster destabilization and precipitation in the presence of H_2O; that is, these results show that excess H_2O beyond a critical maximum has deleterious effects, at least for $P_2W_{15}Nb_3O_{62}{}^{9-}$ -stabilized nanoclusters. Similar behavior is expected, but untested, for other anionic, Brønsted basic, nanocluster stabilizers.

We also tested the effect of H_2O on the activity of Rh(0) nanoclusters that were *formed in the absence of H_2O*. First, the nanoclusters were formed in the absence of substrate under what are otherwise essentially standard conditions (20 mg of **A** in 3.0 mL of propylene carbonate, 22 °C, and 40 psig constant H_2 pressure). After 16 h under hydrogen, ample time for the complete reduction of the precatalyst **A**, 360 equiv of anisole (vs Rh) was added. The subsequent H_2 uptake rate is similar to the maximum H_2 uptake rate observed under standard conditions (0.094 psig/h and 0.16 psig/h, respectively), but TEM analysis of the resultant nanoclusters shows they are 6.2 (±1.5) nm in diameter, corresponding to $\sim$Rh(0)$_{\sim 9100}$, and hence a bit larger on average than the 5.3 nm nanoclusters formed in the presence of substrate, a precedented, largely understood observation.[77]

After 5 h of anisole hydrogenation, at which point the anisole hydrogenation was about 4% complete, 60 equiv of H_2O (vs Rh) was added to the reaction solution, 60 equiv being chosen because it corresponds to the maximum in Figure 4a,b. (A plot of the hydrogen uptake curve for this experiment is available as Figure S8 of the Supporting Information.) After adding H_2O, the H_2 uptake rate was about twice as fast as before the H_2O was added (0.22 psig/h vs 0.094 psig/h). This experiment shows that H_2O increases the rate of hydrogenation, even for fully formed Rh(0) nanoclusters, *but only by 20% of the rate enhancement observed if H_2O is present while the nanoclusters are forming*. TEM measurements show no change beyond experimental error in average nanocluster diameter with added H_2O,[78] certainly nothing like the 10-fold change seen in the H_2 uptake rates with 60 equiv of H_2O present. Therefore, the effect of H_2O on nanocluster formation must be more subtle than simply a change in total surface area.[79−81] These results, too, are of *fundamental significance as they suggest a previously missed effect of H_2O on the nanocluster formation reaction* in addition to its effect on arene hydrogenation catalysis.

The remaining hypotheses here are that the rate enhancing effect of H_2O is caused by water acting as an acid, either protonating the basic polyoxoanion, $P_4W_{30}Nb_6O_{123}{}^{16-} + H_2O \rightarrow HP_4W_{30}Nb_6O_{123}{}^{15-} + OH^-$ (which would effectively replace the $P_4W_{30}Nb_6O_{123}{}^{16-}$ with OH^-, a ligand that we previously demonstrated to be less stabilizing than the polyoxoanion[63]), or cleaving of the Rh−Ar bond by protonation to form the product, as suggested in the literature discussed earlier.[51] If it is the acidity of H_2O that is important for the rate enhancement, as the last two hypotheses suggest, then the addition of a different, stronger acid should have even larger effects than H_2O. Just such an experiment is described in the next section.

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(76) Because it is important for the interpretation of the data, we verified that the black precipitate from one of the hydrogenations is actually bulk Rh metal. Because it was coated with the black precipitate, the stir bar from the experiment with 60 equiv of added water was used as the XPS sample (see the Experimental Section for details). The XPS survey spectrum shows the expected Rh(0) peaks (see Figure S11b of the Supporting Information) and, importantly, shows the absence of polyoxoanion stabilizer (compare to Figure S11a of the Supporting Information).

(77) The same trend has been observed before with polyoxoanion- and tetrabutylammonium-stabilized Ir(0) nanoclusters: those formed in the absence of cyclohexene substrate are 3.0 (±0.4) nm, while those formed in the presence of cyclohexene are smaller, 2.0 (±0.3) nm.[63] This effect is readily explained by cyclohexene either increasing k_1 or slowing k_2 in the mechanism of formation of the nanoclusters (i.e., decreasing the k_2/k_1 ratio, thereby decreasing the nanocluster size).[62,72]

(78) The presence of nanoclusters was confirmed by TEM for all of the "water-added" experiments, but size distributions were only determined for solutions with no visible precipitate. Of course, it is difficult to get a representative sample from an inhomogeneous reaction mixture; a reliable size distribution by TEM is generally not possible from a solution that also contains a precipitate.

(79) Teo, B. K.; Sloane, N. J. A. *Inorg. Chem.* **1985**, *24*, 4545.

(80) The hypothesis that the rate enhancing effect of H_2O is in part due to an effect of H_2O on nanocluster formation was tested by determining the nanocluster size distribution by TEM for the experiments with 8 and 30 equiv of water added. The experiment with 8 equiv of H_2O added gives a size distribution of 5.3 (±0.9) nm, while the experiment with 30 equiv of H_2O added gives a size distribution of 4.6 (±0.7) nm. It is conceivable, but perhaps unlikely, that the rate-enhancing effect of H_2O changes dramatically as a function of nanocluster size, with the rate enhancement being greater for the smaller, developing nanoclusters than it is for the larger, preformed nanoclusters. This is a difficult hypothesis to test because it requires that one have access to preformed nanoclusters of a wide range of sizes.

(81) Rather dramatic changes in catalytic rate are observed when small amounts of water are added to the anisole hydrogenation experiments, as demonstrated in Figure 4. The change in the maximum hydrogen uptake rate (see Figure 4a) in going from the experiment with no water added to the experiment with 30 equiv of water added is about a factor of 5. The change in total hydrogen uptake in 24 h (see Figure 4b) in going from the experiment with no water added to the experiment with 30 equiv of water added is about a factor of 3. The following argument details why these rate changes cannot be entirely explained by a change in nanocluster surface area. A "magic number" (i.e., full shell) nanocluster with 12 complete shells has 6525 atoms[79] with 22% of the atoms on the surface of the nanocluster. A "magic number" nanocluster with 9 complete shells has 2869 atoms[79] with 28% of the atoms on the surface of the nanocluster. Note that the change in surface area between these full shell clusters is *less than a factor of 1.5*, even though the size difference between them is *greater* than the experimentally determined size difference in question (i.e., the size difference between the nanoclusters with no water added and the nanoclusters with 30 equiv of water added). Therefore, nanocluster surface area alone cannot account for the 3-fold to 5-fold difference in catalytic rate between the two experiments with and without added water.

III. Effects of Added $HBF_4 \cdot Et_2O$ on Anisole Hydrogenation. The hypothesis that H_2O is acting as a Brønsted acid was tested by seeing if a different acid, $HBF_4 \cdot Et_2O$, had any effect. $HBF_4 \cdot Et_2O$ was chosen because (i) it can be purchased anhydrous, which eliminates any interfering effects of water, (ii) it is a very strong acid, so any effect due to Brønsted acidity should be magnified, and (iii) the weakly coordinating anion BF_4^- has been shown not ligate or otherwise interfere with the stabilization of the nanoclusters by the much more basic, coordinating $P_2W_{15}Nb_3O_{62}^{9-}$.[57]

Given the issue of the *timing* of H_2O or other H^+ addition (before or after nanocluster formation), an experiment was performed in which fully *preformed* Rh(0) nanoclusters were prepared (as detailed in the Experimental Section). Then, 360 equiv of anisole (vs Rh) was added, and the H_2 uptake rate was measured. Finally, 10 equiv of $HBF_4 \cdot Et_2O$ (vs Rh) was added, and the H_2 uptake rate was measured again. The H_2 uptake rate was *about 6-fold faster* after the $HBF_4 \cdot Et_2O$ was added (0.63 psig/h; see Figure S9 of the Supporting Information for the hydrogen uptake curve). This experiment shows that $HBF_4 \cdot Et_2O$ increases the catalytic activity of fully formed Rh(0) nanoclusters.

The effects of acid or water are consistent with either (or a combination of both) of the hypotheses noted previously: an H^+-assisted cleavage of the Rh−Ar bond (we are accumulating evidence that H^+-assisted reductive elimination of nanocluster M−C bonds is a more general phenomenon[82]) and/or protonation of the polyoxoanion, thereby removing it from the surface of the nanocluster and yielding both a more active, and a less stable, nanocluster. The observation of a metal precipitate when excess H^+ or H_2O is added requires that some of the observed effects must be due to the interaction of H^+ or H_2O with the basic $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion (conjugate acid p$K_a \sim 12$; see the Supporting Materials elsewhere[83]).

IV. Comparison of the Surface-Area-Corrected TOF for the Rh(0) Nanocluster Catalysts and 5% Rh/Al_2O_3. By definition, TOF [(moles product) × (moles active site)$^{-1}$ × (time)$^{-1}$] should include corrections for the true number of active sites.[84] A first approximation way to estimate the number of active sites is to correct the TOF for the calculated number of surface atoms on an average nanocluster.[85] For example, in Roucoux's 2.1 nm average diameter nanoclusters,[53] about 50% of the Rh(0) atoms are on the surface of the nanocluster.[79] Hence, dividing the uncorrected average TOF for Roucoux's catalyst of 54 turnovers/h (i.e., 2000 TTO/37 h reaction time) by 0.5 gives a corrected TOF of about 110 turnovers/(h·mol exposed Rh).

Table 1. Total Turnover Experiments with Rh(0) Nanoclusters or 5% Rh/Al_2O_3

experimental detail	TTO demonstrated	reaction time
standard TTO Conditions[a]	1500 ± 100	120 h[e]
30 equiv of H_2O added	2600[b]	215 h[e]
60 equiv of H_2O added	1500 ± 100	120 h[e]
10 equiv of $HBF_4 \cdot Et_2O$ added	2600[b]	144 h[e]
acetone solvent[c]	130 ± 10	95 h[f]
7.4 mg of 5% Rh/Al_2O_3[d]	55 ± 4	48 h

[a] The standard conditions for TTO experiments included 20.0 (±0.5) mg $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh \cdot P_2W_{15}Nb_3O_{62}]$ (3.6×10^{-6} mol), 2.0 mL propylene carbonate, 1.0 mL anisole (9.2×10^{-3} mol; 2600 equiv vs the total Rh present), constant 40 psig H_2, and 22 °C. Changes or additions to the standard conditions are noted in the experimental detail column in the table. [b] Complete conversion of the substrate was observed in this experiment. [c] The acetone used for this experiment is fairly "wet", containing 0.26% H_2O (compared to <0.005% H_2O for the propylene carbonate); for this experiment, the acetone solvent contains 64 equiv of H_2O vs Rh. [d] This amount of catalyst was chosen because 7.4 mg of 5% Rh/Al_2O_3 contains 3.6×10^{-6} mol of Rh, the same as the other TTO experiments. [e] A small amount of black precipitate was visible at the end of the reaction. [f] A large amount of precipitate was visible at the end of the reaction.

A TEM of the polyoxoanion-stabilized Rh(0) nanoclusters taken after 24 h in an experiment using standard TTO conditions (see Table 1) reveals 3.7 (±0.6) nm diameter nanoclusters, corresponding to an average size of $Rh(0)_{\sim 1900}$ in which ∼30% of the Rh(0) atoms are on the surface of the nanocluster.[79] Using the data in Table 1 for the standard TTO conditions experiment and dividing the apparent TOF by 0.3, one calculates a corrected TOF of 42 turnovers/(h·mol exposed Rh), *about half that of Roucoux's catalyst*.

For comparison, using the data in Table 1 for the 5% Rh/Al_2O_3 and dividing by a correction factor of[86] 0.3, one calculates a corrected TOF of 4 turnovers/(h·mol exposed Rh). These simple calculations yield another important insight, one fortified by an analogous finding in our catalyst poisoning work:[84] *the Rh(0) nanoclusters are at least 10-fold more active per exposed metal atom than their oxide-supported analogues.*

V. Anisole Hydrogenation Catalytic Lifetime Experiments with Polyoxoanion-Stabilized Rh(0) Nanoclusters and Their Comparison to Known Literature Catalysts. Practical catalytic applications, as well as mechanistic studies of meaningful catalysts, both require a reasonable catalyst lifetime. To date, most of the literature systems using soluble (i.e., unsupported) nanoclusters as arene hydrogenation

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(82) Hornstein, B. J.; Lyon, D. K.; Aiken, J. D., III; Finke, R. G. Unpublished results.

(83) Weiner, H.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 7905.

(84) A paper developing the CS_2 poisoning method to determine the number of nanocluster active sites, and thus nanocluster TOFs, has been accepted for publication: Hornstein, B. J.; Aiken, J. D., III; Finke, R. G. Nanoclusters in Catalysis: A Comparison of CS_2 Catalyst Poisoning of Polyoxoanion- and Tetrabutylammonium-Stabilized Rh(0) Nanoclusters to 5% Rh/Al_2O_3, Including an Analysis of the Literature Related to the CS_2 to Metal Stoichiometry Issue. *Inorg. Chem.*, in press. As noted in this paper, the 3.6 (±≥1.8) nm particle size for the 5% Rh/Al_2O_3 catalyst carries ±≥1.8 nm error bars due to the heterogeneity of, and thus sampling error with, the 5% Rh/Al_2O_3 catalyst.

(85) When correcting the TTO and the TOF values for the number of surface atoms, one of the assumptions is that the number of metal atoms on the surface does not change during the course of the reaction. This assumption cannot hold true for our *lifetime experiments* because the observed agglomeration (i.e., bulk metal formation) at long reaction times *in the lifetime experiments* means that the total surface area is decreasing during the course of the reaction. Nevertheless, by taking a TEM sample early in the reaction, an upper limit on the surface area can be established.

(86) TEM analysis of the 5% Rh/Al_2O_3 catalyst shows the Rh(0) particles are 3.6 (±≥1.8) nm in diameter,[84] almost exactly the same average size as the Rh(0) nanoclusters in the TTO experiment. Additionally, H_2 and CO chemisorption studies of the 5% Rh/Al_2O_3 show that about 33% of the Rh atoms are exposed, which is in good agreement with the TEM data.[84] Consequently, the TOF for the 5% Rh/Al_2O_3 was divided by 0.3 to correct for the average number of surface Rh(0) atoms in this heterogeneous catalyst.

catalysts have had modest lifetimes at best, generally in the range $\leq$100 TTO, as Table S1 of the Supporting Information documents. The longest catalytic lifetime reported in the literature for such a system is the recent work by Roucoux and co-workers mentioned in the Introduction: under biphasic conditions, and using an aqueous solution Rh(0) nanoclusters stabilized by *N*-alkyl-*N*-(2-hydroxyethyl)ammonium bromide salts, they demonstrated 2000 TTO for anisole hydrogenation in 37 h at 20 °C and 1 atm of H_2.[53]

We tested the catalytic lifetime of our polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters for anisole hydrogenation in propylene carbonate, Table 1, first without, and then with, added H_2O or $HBF_4{\cdot}Et_2O$, and under conditions which allow for a maximum of 2600 TTO. We also tested the 5% Rh/Al_2O_3 catalyst under the same conditions as a valuable comparison point.

The essence of the results, as summarized in Table 1, is that (i) under standard TTO conditions, 1500 TTO are seen, but they require a rather long time, 120 h, and yield a small amount of black precipitate at the end of the reaction; (ii) with 30 equiv of H_2O added, 2600 TTO are observed, a value higher than any reported in the literature (cf. Table S1 of the Supporting Information), but a long time of 215 h is required, and again, a small amount of black precipitate is visible at the end of the reaction; (iii) 60 equiv of H_2O (the amount of water corresponding to the maximum in rate in Figure 4) does not improve the TTO beyond 1500 TTO because of the effects of water destabilizing the nanoclusters, more black precipitate being visible at the end of this experiment than for either of the previous two experiments (the reaction was stopped at 120 h); and (iv) 10 equiv of $HBF_4{\cdot}Et_2O$ is more effective in that it gives 2600 TTO in a shorter, 144 h time. (An interesting organic side product, dodecahydrotriphenylene, precipitated from solution during the reaction with $HBF_4{\cdot}Et_2O$; see the Supporting Information for the unequivocal characterization, as well as two possible mechanisms of formation, of this product from acid-catalyzed condensation of the partial hydrogenation product 1-methoxycyclohexene.) Other key findings from the data in Table 1 are (v) acetone is clearly an inferior solvent to propylene carbonate,[87] giving only 130 TTO plus more precipitate after only 95 h (when the reaction was stopped) than in any of the experiments in propylene carbonate; and (vi) the commercial 5% Rh/Al_2O_3 catalyst is very inferior compared to the Rh(0) nanoclusters at the same level of Rh loading and same general particle size,[86] giving only 34 (±2) TTO after 25 h, and (in the same experiment) only 55 (±4) TTO after 48 hours. This result is consistent with literature reports of relatively low activities of supported Rh catalysts for arene hydrogenation under similar conditions.[47,53,88]

These lifetime experiments show that the polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters are reasonably long-lived catalysts for anisole hydrogenation, at least in comparison to the present state-of-the-art. In fact, the catalytic lifetime of ∼2600 TTO (*in 144 h* with 10 equiv $HBF_4{\cdot}Et_2O$ added) is the longest demonstrated lifetime for any soluble nanocluster arene hydrogenation catalyst in the literature. However, recall that the Rh nanocluster catalyst developed by Roucoux and co-workers is capable of 2000 TTO *in 37 h*,[53] and we suspect that it may be capable of even greater TTO values. The additional suggestion here, which is unproven but quite plausible, is that the weakly basic and nonchelating Br^- stabilizer used in the Roucoux catalyst binds less strongly to the nanocluster surface, affording a higher TOF (vide supra), but a shorter lifetime, versus the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion. Obviously, additional studies of the rate and lifetime (and selectivity, vide infra) of arene hydrogenation versus the X^- stabilizer[57] are warranted.

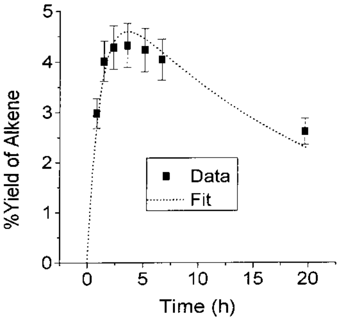

Figure 5. Percent yield of 1-methoxycyclohexene (determined by GLC) vs time for an anisole hydrogenation with polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters. The conditions were 2.9 mL of propylene carbonate, 0.14 mL of anisole, 20 mg of $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh{\cdot}P_2W_{15}Nb_3O_{62}]$, 40 °C, and 40 psig H_2 pressure. The maximum yield of 1-methoxycyclohexene for this experiment was 4.3%, which occurred at 65% conversion of anisole. The data are fit to an A → B → C kinetic scheme[93] (the dotted line), where B is the intermediate, 1-methoxycyclohexene.

VI. Observation of Partial Hydrogenation Products in the Hydrogenation of Anisole. Despite the widespread use of anisole as a substrate in arene hydrogenation studies with many types of catalysts (i.e., not just soluble nanocluster catalysts), its partial hydrogenation has been observed in only four cases.[89−92] The highest yield of 1-methoxycyclohexene with any of these catalysts is 20% using a heterogeneous 5% Ru/charcoal catalyst.[89] Even though anisole or some other aryl ether is used as a substrate in fourteen of the references in Table S1, the partial hydrogenation of an aryl ether has never been observed with a soluble nanocluster catalyst (see the documentation of this claim in the Supporting Information). Consequently, the yields of 1-methoxycyclohexene as high as 8% observed in the present anisole hydrogenation experiments are noteworthy.

Figure 5 shows the percent yield of 1-methoxycyclohexene for an anisole hydrogenation experiment done at 40 °C; the identity of 1-methoxycyclohexene was unequivocally established by gas chromatography-mass spectrometry (GC-MS)

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Table 2. GLC-Determined Selectivity for the Catalytic Hydrogenation of Anisole to 1-Methoxycyclohexene under Various Conditions

experimental detail	initial selectivity (%)[b]	max yield[c] (%)	% conversion at max yield[d]
standard conditions (22 °C)[a]	30 ± 2	2.1 ± 0.2	70 ± 14
40 °C	31 ± 2	4.2 ± 0.4	64 ± 7
78 °C	33 ± 2	8.1 ± 0.8[e]	41 ± 2[e]
1.05 equiv of $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ added	30 ± 2	2.8 ± 0.3	39 ± 9
2.01 equiv of $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ added	27 ± 2	1.8 ± 0.2	29 ± 3
60 equiv of H_2O added	31 ± 2	2.6 ± 0.3	62 ± 12
acetone solvent	32 ± 2	1.7 ± 0.2	21 ± 8
7.4 mg of 5% Rh/Al_2O_3[f] at 22 °C	38 ± 3	1.7 ± 0.2[e]	8 ± 1[e]
7.4 mg of 5% Rh/Al_2O_3[f] at 78 °C	22 ± 2	1.4 ± 0.1[e]	6 ± 1[e]

[a] The standard conditions for these experiments included 20.0 (±0.5) mg of $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$ (3.6×10^{-6} mol), 2.9 mL of propylene carbonate, 0.14 mL of anisole (1.3×10^{-3} mol), constant 40 psig H_2, and 22 °C. Changes or additions to the standard conditions are noted in the experimental detail column above. [b] The initial selectivity is defined as [mol alkene/(mol alkene + mol alkane)] × 100. The initial selectivity was determined at $\leq\sim$10 TTO. Error bars of ±7% have been assigned, which encompass the maximum variation in nine repeat experiments under various conditions. [c] The yield is defined as [mol alkene/(mol alkene + mol alkane + mol arene)] × 100. Error bars of ±10% have been assigned, ±10% being twice the maximum variation in three repeat experiments at 40 °C. [d] The % conversion is defined as [(mol alkene + mol alkane)/(mol alkene + mole alkane + mol arene)] × 100. The error bars were determined by the frequency of sampling relative to the reaction progress. [e] Deactivation stopped the hydrogenation at this point. [f] This amount of catalyst was chosen because 7.4 mg of 5% Rh/Al_2O_3 contains 3.6×10^{-6} mol of Rh, the same as the other experiments.

and verified by the GLC retention time versus authentic 1-methoxycyclohexene. Quantitation of the amount of 1-methoxycyclohexene was accomplished by GLC using the established concept of "effective carbon number", and the accuracy of the quantitation was verified by ^{1}H NMR (see the Supporting Information for details). The concentration of 1-methoxycyclohexene versus time, Figure 5, is typical of, and quite well fit by, a classic A → B → C kinetic scheme,[93] the intermediate 1-methoxycyclohex*ene*, B, growing in and then being completely converted to the final product, methoxycyclohex*ane*, C, in hydrogenations that were allowed to go to completion.

Methoxycyclohexane and 1-methoxycyclohexene are the only *major* products detected by GLC in these experiments, Scheme 1. For example, see Figure S10b of the Supporting Information for the GLC trace for the reaction solution of an anisole hydrogenation run at 78 °C. Hydrogenolysis of the ether linkage to yield cyclohexane and methanol, Scheme 1, was detected, but occurred at trace levels (<1% yield).

Table 2 shows a list of experiments for which the selectivity to 1-methoxycyclohexene was quantitated. Using standard conditions, the initial selectivity to 1-methoxycyclohexene was 30 (±2)%, and the maximum yield of 1-methoxycyclohexene was 2.1 (±0.2)%, which occurred at about 70% conversion. Increasing the temperature of the reaction to 78 °C does not significantly change the initial selectivity, but it has a fairly dramatic effect on the maximum yield of 1-methoxycyclohexene: the maximum yield doubles on going from 22 to 40 °C, and doubles again on going from 40 to 78 °C. The 78 °C experiment had a maximum yield of 8.1 (±0.8)% at 41% conversion, at which point the catalyst had lost all activity (although no precipitate was visible to the eye at this point). Complete deactivation occurred within about 1 h in the 78 °C experiment. By TEM, these deactivated nanoclusters were found to be 5.7 (±1.0) nm in diameter, the same size within experimental error as the 5.3 (±1.0) nm nanoclusters formed at 22 °C. It follows that a surface deactivation, and not an agglomeration, process must have inactivated the nanoclusters.

The most obvious explanation for the relatively high selectivity in our system and for the partially hydrogenated product, 1-methoxycyclohexene, is the presence of the surface-attached[59,62,63] $P_2W_{15}Nb_3O_{62}{}^{9-}$; hence, we undertook experiments designed to probe the effect of the presence of the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion. The addition of 1.0 equiv of the parent polyoxoanion, $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$, to an otherwise standard conditions experiment (i.e., in which 1.0 equiv $P_2W_{15}Nb_3O_{62}{}^{9-}$ per Rh atom is already present) gave no change in the initial selectivity but did lead to a small, probably significant increase in the maximum yield of alkene (compared to the standard conditions experiment). Interestingly, the reaction profile changed with added $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$: the maximum yield of alkene occurred at about 39% conversion, sooner than for the standard conditions experiment. When 2.05 equiv of $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ was added to an otherwise standard conditions experiment, the rate of catalytic hydrogenation was severely depressed, and the maximum yield of alkene actually went back down to the level of the standard conditions experiment. Control experiments were also done which rule out the possible effects of H_2O[94] or solvent[95] on the observed, high selectivities; control experiments with the 5% Rh/Al_2O_3 catalyst were also performed.[96] The important implication is *that the $P_2W_{15}Nb_3O_{62}{}^{9-}$ is at least partially, and perhaps predominantly, responsible for the observed, and desired, selectivity.* Such demonstrations that nanocluster surface ligands can alter selectivity[97] are quite important, pointing to future directions of nanocluster research that promise to be productive. Figure S12 in the Supporting Information shows how, in a general way, surface adsorbed polyoxoanions or other ligands can alter selectivity to the monoene by increasing the *K*(desorption) equilibrium constant for the monoene intermediate and

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(93) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981.

(94) A control experiment was done to rule out possible effects of H_2O as the explanation for the relatively high selectivity in our system for the partially hydrogenated 1-methoxycyclohexene. The addition of 60 equiv (4 μL) of H_2O to an otherwise standard conditions experiment had no effect on the selectivity to alkene within experimental error, Table 2. Therefore, the presence (or absence) of H_2O does not seem to be responsible for the observed selectivity, at least for our current system.

(95) To determine if the solvent is responsible for the observed selectivity, a hydrogenation experiment was done using acetone as the solvent instead of propylene carbonate. However, the initial selectivity in acetone is the same as it is in propylene carbonate, so there is no evidence for a solvent effect. (The nanoclusters are not as soluble in acetone as they are in propylene carbonate, which leads to their precipitation from the acetone solution and causes the rate of catalytic hydrogenation to be severely depressed. Consequently, only the initial selectivity can be safely compared with that in the standard conditions experiment.)

in the classic Horiuti−Polanyi mechanism for catalytic hydrogenation on metal surfaces.

The important points, then, are (i) partial hydrogenation of an aryl ether to the substituted cyclohexene using a nanocluster catalyst has been observed for the first time; (ii) a similar average particle size,[86] and thus surface area, 5% Rh/Al_2O_3 catalyst has a similar selectivity at low temperature, but poorer selectivity at higher temperature, than the nanoclusters, and (iii) hence, the nanocluster catalyst provides the highest yield of 1-methoxycyclohexene. Overall, then, an important finding is that the polyoxoanion-stabilized nanoclusters (iv) behave as soluble analogues of heterogeneous catalysts,[29] but ones with improved selectivity, at least in this one particular reaction and under the conditions employed. This discovery also makes the present catalyst system an intriguing one for the further study of the many important variables in the partial hydrogenation of arenes with metal particle catalysts;[1,17,98] studies of the deactivation processes in those catalysts are also warranted. Looking at the effects of polyoxoanions on functioning arene hydrogenation heterogeneous catalysts is also an important avenue of research suggested by our experiments.

Summary and Conclusions

Six key goals in the area of nanocluster arene hydrogenation were delineated in the Introduction from our analysis of the prior literature, namely the goals of (i) the use of a nanocluster system in which the nanoclusters have been well characterized; (ii) the use of nanoclusters stabilized by the most effective anionic stabilizer currently known,[57] $P_2W_{15}Nb_3O_{62}^{9-}$; (iii) the development of a nanocluster arene hydrogenation system that is not aqueous/organic biphasic so that the effects of water can be tested, and so that kinetic and mechanistic studies can be more easily performed and interpreted; (iv) the extension of the catalytic lifetime beyond the normally observed ∼100 TTO, and ideally even beyond the current record lifetime of 2000 TTO;[53] (v) the attainment of high yields of the valuable, partially hydrogenated, cyclohex*ene* products of arene hydrogenation; and ideally also (vi) the completion of a kinetic and mechanistic study of the best, prototype nanocluster arene hydrogenation system. The following list summarizes our efforts in achieving the first five of these six goals:

(1) The Rh(0) nanoclusters used in this study are well characterized and well understood, especially if one considers our previous work with such nanoclusters.[58−60] Herein, the nanoclusters are characterized by confirmation of their expected stoichiometry formation, by TEM, and via a determination of their nanocluster formation rate constants.

(2) In situ reduction of the well-defined precatalyst, $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, with H_2 ensures that the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion is the only anionic stabilizer present.

(3) The Rh(0) nanoclusters are soluble and active in monophasic propylene carbonate (or other polar aprotic organic solvents). This allowed us to discover that proton donors such as water and $HBF_4\cdot Et_2O$ affect both the nanocluster formation reaction and the nanocluster arene hydrogenation catalytic reaction. As Figure 4 shows, the plot of activity versus added water has a sharp, heretofore unappreciated, maximum at ∼60 equiv of water per Rh present, at least for polyoxoanion-stabilized nanoclusters.

(4) A series of lifetime experiments showed that the Rh(0) nanoclusters are 10-fold more active than their traditional oxide-supported analogue, 5% Rh/Al_2O_3. The lifetime experiments also show that the Rh(0) nanoclusters are capable of at least 2600 TTO, the longest demonstrated lifetime for any soluble nanocluster arene hydrogenation catalyst reported in the literature, albeit over a relatively long 144 h. Hence, the development of even more active, *longer-lived* nanocluster catalysts remains an important goal in this area.

(5) The polyoxoanion-stabilized Rh(0) nanoclusters display a modest, albeit a record, selectivity for nanocluster partial hydrogenation of anisole to 1-methoxycyclohexene with yields up to 8% at the relatively mild, maximum temperature examined of 78 °C. Obviously, higher yields of the alkene product are desirable; however, polyoxoanion-stabilized nanoclusters display sufficient selectivity to make them of interest as a model system for further studies of the many important variables in the partial hydrogenation of arenes using metal particle catalysts.

(6) The polyoxoanion-stabilized nanoclusters provide both a higher yield of 1-methoxycyclohexene, and a longer lifetime prior to deactivation, than does a traditional 5% Rh/Al_2O_3 heterogeneous catalyst. This improved performance appears to be due to the presence of the polyoxoanion, results which suggest that the polyoxoanion is an interesting additive to study with other arene hydrogenation catalysts.

(7) A mechanistic study of nanocluster-catalyzed arene hydrogenation was only touched upon in this study, but even here we have an interesting result. We uncovered further evidence that H^+-assisted reductive elimination of nanocluster M−C bonds is a general phenomenon.[82]

Experimental Section

Materials. Propylene carbonate (Aldrich, 99.7%, anhydrous, packaged under N_2) was transferred into the drybox, evacuated for ≥1 h, and stored over 5 Å molecular sieves activated in the drybox by heating at 105 °C under vacuum for 8 h. Anisole (Aldrich, 99.7%, anhydrous, packaged under N_2) was transferred into the

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(96) Control experiments examining the selectivity of the 5% Rh/Al_2O_3 catalyst at 22 and 78 °C were also performed and proved interesting. Using 7.4 mg of 5% Rh/Al_2O_3 (3.6×10^{-6} mol of Rh) instead of 3.6×10^{-6} mol of **A** yielded the following results: at 22 °C, this typical heterogeneous catalyst displays a comparable (to slightly better) initial selectivity for the alkene intermediate, 38 (±3)% vs 30 (±2)% for the nanoclusters, Table 2, but this selectivity is *not* increased at the higher, 78 °C, temperature. These results, as well as the product vs time curves at both temperatures (not shown), reveal deactivation of the 5% Rh/Al_2O_3 catalyst is occurring: complete deactivation occurs after only 1 h at 78 °C, similar to the polyoxoanion-stabilized nanoclusters (vide supra). Nevertheless, the polyoxoanion-stabilized nanoclusters win the test of the maximum yield of alkene: 8.1 (±0.8)% for the nanocluster vs 1.7 (±0.2)% for the 5% Rh/Al_2O_3 catalyst.

(97) For an important paper showing the dramatic effects that ligands can have on nanocluster catalytic selectivities, see: Schmid, G.; Maihack, V.; Lantermann, F.; Peschel, S. *J. Chem. Soc., Dalton Trans.* **1996**, 589.

(98) Struijk, J.; Scholten, J. J. F. *Appl. Catal., A* **1992**, *82*, 277.

drybox and evacuated for ≥1 h before use. Cyclohexene (Aldrich, 99%) was distilled from Na under argon and stored in the drybox. Acetone (Burdick and Jackson, 0.26% H_2O) was purged with Ar for 30 min before being transferred into the drybox. Methoxycyclohexane (Sigma-Aldrich Library of Rare Chemicals, about 80% pure by GLC) was used as received. A sample of 1-methoxycyclohexene (about 60% pure by GLC) was generously given to us by Professor Yian Shi's research group here at Colorado State University (the synthetic procedure for 1-methoxycyclohexene is available elsewhere[99]). Sealed ampules (1 g) of CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, Inc. "Nanopure" water (distilled water filtered through a Barnstead filtration system) was used for the hydrogenation experiments where water was added. Tetrafluoroboric acid (Aldrich, 54 wt % solution in diethyl ether) was transferred into the drybox and used as received.

The 5% Rh/Al_2O_3 (preactivated under H_2 by the manufacturer) was purchased from Strem. H_2 and CO chemisorption analysis shows that about 33% of the Rh atoms in this catalyst are exposed.[84] TEM analysis of this catalyst shows the Rh(0) particles are 3.6 (±1.8) nm in diameter, and thus in the same general size range as our Rh(0) nanoclusters.[84] A control experiment described in the Supporting Information shows that this 5% Rh/Al_2O_3, after being evacuated at room temperature overnight and transferred into the drybox, has a high activity and long lifetime for the hydrogenation of cyclohexene, as we have found previously.[58] Nevertheless, we found that reactivating the catalyst under hydrogen had a beneficial effect on the anisole hydrogenation activity. Before reactivation, the 5% Rh/Al_2O_3 gave only 13 (±1) TTO in 24 h, compared to 34 (±2) TTO in 25 h following reactivation. The 5% Rh/Al_2O_3 was reactivated by heating it to 130 °C for 1.5 h in a constant flow of H_2.[89] All of the anisole hydrogenation experiments with 5% Rh/Al_2O_3 reported herein were performed using the reactivated material.

The rhodium nanocluster precursor complex $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **A**, was prepared by literature methods[100] from $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ made by our most recent method[83] (using $K_7HNb_6O_{19}$ as the Nb source) and stored in the drybox. ^{31}P NMR showed **A** to be 94% pure. Analysis for **A**, calcd (found): C 18.93 (18.73); H 3.47 (3.61); N 1.25 (1.28). ^{19}F NMR showed that 98% of the $[Bu_4N]BF_4$ generated during the support reaction, in which $[(1,5\text{-COD})Rh(CH_3CN)_2]BF_4$ is added to $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$, had been removed by the ethyl acetate/acetonitrile precipitations (the 2% $[Bu_4N]BF_4$ which remained is 0.08 equiv vs Rh).

General Procedures. All glassware, except for the syringes, was dried for at least overnight in a 160 °C drying oven before being transferred into the drybox while still hot. The syringes used to measure and transfer propylene carbonate and anisole were dried overnight at 100 °C in a vacuum oven before being transferred into the drybox while still hot. All catalyst reaction solutions were prepared under oxygen- and moisture-free conditions in a Vacuum Atmospheres drybox (<2 ppm of O_2 as continuously monitored by a Vacuum Atmospheres O_2-level monitor).

Analytical Procedures. Gas−liquid chromatography (GLC) was performed using a Hewlett-Packard 5890 series II instrument with a FID detector. The instrument was equipped with a 30 m × 0.25 mm Supelcowax-10 column and was coupled to a Hewlett-Packard 3395 integrator. Parameters were as follows: initial temperature, 50 °C; initial time, 3 min; ramp, 10 °C/min; final temperature, 250 °C; final time, 1 min; injector port temperature, 250 °C; detector temperature, 250 °C; injection volume, 4 μL.

Nuclear magnetic resonance (NMR) spectra were obtained as CD_2Cl_2 solutions in Spectra Tech NMR tubes (5 mm o.d.) at 25 °C on a Varian Inova 300 MHz instrument. Chemical shifts were referenced to the residual solvent impurity at 5.32 ppm. Spectral parameters for ^1H NMR (300 MHz) include tip angle, 30° (pulse width, 2.9 μs); acquisition time, 2.667 s; relaxation delay, 0.0 s; sweep width, 6000 Hz. An integration error of 5% was assumed in the error propagation for lifetime experiments followed by ^1H NMR.

Gas chromatography-mass spectrometry (GC-MS) was performed using a Hewlett-Packard 5890 series II GC with an MSD 5970 B. The GC was equipped with a 30 m (0.25 mm i.d., 0.25 μm film thickness) Supelco SPB-1 column. The ionizing voltage was 70 eV. The GC parameters were as follows: initial temperature, 50 °C; initial time, 3 min; solvent delay, 2 min; temperature ramp, 10 °C/min; final temperature, 270 °C; final time, 5 min; injector port temperature, 280 °C; detector temperature, 290 °C; injection volume, 0.1 μL. The mass marker calibration of the GC-MS was performed using perfluorotributylamine.

X-ray photoelectron spectroscopy (XPS) was performed using a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al Kα radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W) and a pass energy of 23.5 eV. Peaks were referenced to the C 1s line at 284.8 eV to account for sample charging. Good quality survey spectra were obtained with a single scan. High-resolution spectra were integrated over 5−20 scans, depending of the intensity of the spectral region of interest. Two XPS samples were prepared. The sample for nanoclusters generated in a standard conditions anisole hydrogenation was prepared exactly as described later for TEM samples (i.e., the nanoclusters were twice precipitated with diethyl ether and then dried under vacuum; a piece of glass coated with the residue was used as the XPS sample). The sample of the black precipitate (i.e., the precipitate that formed in hydrogenations with ≥60 equiv of water added) was prepared from the stir bar used in the experiment in which 60 equiv of water was added. In the drybox, the stir bar, which was coated with a film of the black precipitate, was removed from the reaction solution. The stir bar was thoroughly rinsed, first with acetonitrile and then with acetone, neither of which noticeably dissolved the precipitate. The stir bar was then dried under vacuum while still in the drybox. Both samples were briefly exposed to air when they were introduced into the spectrometer.

Transmission electron microscopy analysis was performed as before[62,63] at the University of Oregon with the expert assistance of Dr. Eric Schabtach. As described previously, micrographs of the nanoclusters were obtained with a Philips CM-12 microscope (with a 2.0 Å point-to-point resolution) operating at 100 keV.[62,63] Size measurements were obtained from micrographs with magnifications of 430 K. Each size distribution was determined by measuring 136−165 nanoclusters. A control experiment published elsewhere[60] shows that Rh(0) nanoclusters do not form from the nanocluster precursor **A** under the electron beam.

We have experienced problems when using propylene carbonate solutions of nanoclusters to prepare TEM grids. The samples tend to charge in the electron beam, with consequent instability and destruction of the support films. This is probably due the presence of substantial amounts of (nonconducting) propylene carbonate, even on "dry" TEM grids (propylene carbonate has a high boiling point and is difficult to remove by evaporation). Additionally, the nanoclusters on TEM grids prepared from propylene carbonate solutions tend to be in large clumps. Because of our difficulties preparing good TEM samples in the presence of propylene

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(99) Crivello, J. V.; Yoo, T. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 717.

(100) Nomiya, K.; Pohl, M.; Mizuno, N.; Lyon, D. K.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 186.

carbonate, we first isolated the nanoclusters from propylene carbonate by precipitating them twice in the following manner. In the drybox, 0.25 mL of reaction solution was measured into a glass scintillation vial with a 1-mL plastic syringe. Then, 10 mL of ethyl ether was added with a polyethylene pipet while swirling the contents of the vial. The solution turned cloudy after the addition of about 2 mL of ether. Following the addition of ether, the cloudy solution was agitated for a few seconds with the polyethylene pipet. Then the vial was capped and sealed with Parafilm. The sealed vial was brought out of the drybox, and the fine precipitate was separated by centrifugation (1 h at 1200 rpm in a swinging-bucket centrifuge with a radius of 20 cm). The vial was transferred back into the drybox where the clear, colorless supernatant was decanted, leaving a small amount of dark colored oily solid in the bottom of the vial. This solid readily dissolved when 0.5 mL of acetonitrile was added with a 1-mL plastic syringe. Then, 12 mL of ethyl ether was added with a polyethylene pipet while swirling the contents of the vial. The solution turned cloudy after the addition of about 4 mL of ether. Following the addition of ether, the cloudy solution was agitated for a few seconds with the polyethylene pipet. Then, the vial was once again capped and sealed with Parafilm. The sealed vial was brought out of the drybox and centrifuged again. The vial was transferred back into the drybox where the clear, colorless supernatant was decanted, leaving a small amount of dark colored oily solid in the bottom of the vial. The vial was evacuated for 30 min, leaving a dark colored residue on the bottom of the vial. This TEM sample was sealed with Parafilm, double-bottled, and sent as a solid to Dr. Eric Schabtach at the University of Oregon. Dr. Schabtach dissolved the TEM samples in 0.5 mL of acetonitrile, placed a drop of the solution onto a carbon-coated copper TEM grid, and blotted off the excess liquid with a piece of filter paper.

A control experiment was performed to see if isolating the nanoclusters from propylene carbonate affects the nanocluster size distributions in the TEM samples. This experiment was performed using the reaction solution from an experiment in which the Rh(0) nanoclusters were formed in the absence of substrate. A small amount of the reaction solution was diluted 60:1 with acetonitrile; the TEM grid was prepared from the diluted solution. Electron micrographs of that grid showed a size distribution of 6.0 (±1.2) nm (only 62 nanoclusters were measured because of the difficulties described previously), compared to a size distribution of 6.2 (±1.5) nm for such nanoclusters after being isolated from propylene carbonate using the precipitations described previously. Hence, the precipitations do not affect the nanocluster size within experimental error.

Standard Conditions Anisole Hydrogenation Experiment. This experiment was done in a manner analogous to the cyclohexene hydrogenation experiments that we have been performing for some time now.[59,62,63] A schematic of the hydrogenation apparatus used is available in Figure 6 elsewhere.[101] In the drybox, 20 (±0.5) mg of $[Bu_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **A**, ($3.6 \times 10^{-6}$ mol) was weighed into a 2-dram glass vial. Then, 2.9 mL of propylene carbonate was added to the vial with a 5-mL gastight syringe, followed by the addition of 0.14 mL of anisole (1.3×10^{-3} mol) with a 1-mL gastight syringe. This mixture was briefly agitated with a disposable polyethylene pipet until **A** dissolved completely. Using the same pipet, the bright yellow solution of **A** was then transferred into a new 22 × 175 mm Pyrex culture tube containing a $^5/_8 \times ^5/_{16}$ in. Teflon-coated stir bar. The culture tube was placed in a Fischer−Porter (hereafter, F−P) pressure bottle modified with Swagelock TFE-sealed Quick-Connects. The F−P bottle was then sealed, brought out of the drybox, placed in a 22.0 (±0.1) °C temperature-controlled water bath, and connected to a H_2 line via the Quick-Connects. Using the top (purge) valve, the F−P bottle was then purged 15 times (waiting 15 s between purges) with 40 psig H_2. Following the purges, the F−P bottle was pressurized to 40 (± 1) psig H_2 and then isolated (by closing the valve to the H_2 line). During the purging (and during the hydrogenation reaction), the reaction solution was vortex-stirred (at >600 rpm). Five minutes after the beginning of the purges was designated $t = 0$, and at this time, data collection (H_2 pressure vs time) was initiated using an Omega PX-621 pressure transducer (manufacturer specifications for the transducer include ±0.005 psig precision and ±0.15 psig accuracy) interfaced to a PC. The final reaction solution (after 24 h under H_2) was clear and dark brown with no visible precipitate.

Control Experiment Comparing the Rate of Anisole Hydrogenation with the Rate of Cyclohexene Hydrogenation. This experiment is described in the Supporting Information.

Monitoring Nanocluster Formation via the Evolution of Cyclooctane. This experiment was started in exactly the same way as the standard conditions anisole hydrogenation, except that the F−P bottle was left open to the H_2 line, which maintains the H_2 pressure at 40 (±1) psig (this was done because the pressure must be released each time a sample is removed for GLC analysis). At regular intervals, the purge valve on the F−P bottle was opened and a GLC sample removed. The GLC sample was obtained by threading an oven-dried, H_2-purged, 12-in., stainless steel needle through the purge valve into the culture tube. A 0.05-mL aliquot of the reaction solution was removed with a disposable 1-mL syringe (which was attached to the needle). The purge valve was then closed so that the F−P bottle could repressurize to 40 psig. During the sampling procedure, the constant flow of H_2 out of the F−P bottle protects the atmosphere inside it. The evolved equivalents of cyclooctane were determined by directly injecting the reaction solution into a calibrated gas chromatograph using a 10 μL gastight syringe.

Addition of Water to Anisole Hydrogenation Experiments. Water was added to many of the reaction solutions. Unless otherwise noted, the water was added immediately after **A** had been dissolved in propylene carbonate and anisole (i.e., before the reaction solution was transferred to the culture tube and while still in the inert atmosphere glovebox). The water was added to the solution with a syringe. For volumes <1.0 μL, a Hamilton 1.0 μL syringe with a Cheney adapter was used. For volumes from 1 to 10 μL, a Hamilton gastight 10 μL syringe was used. For volumes >10 μL, a Hamilton 50 μL syringe was used. The addition of water to the reaction solution did not cause a visible change in appearance.

Effect of Water on the Anisole Hydrogenation Activity of Rh(0) Nanoclusters Preformed in the Absence of Substrate. For this experiment, the nanoclusters were formed in exactly the same way as in the section titled "Control Experiment Comparing the Rate of Anisole Hydrogenation with the Rate of Cyclohexene Hydrogenation". Briefly, the nanoclusters were formed from 20 mg of **A** in 3.0 mL of propylene carbonate at 22 °C and 40 psig constant H_2 pressure. After 16 h under hydrogen, the F−P bottle was sealed, removed from the H_2 line, and brought into the drybox. Then, 0.14 mL of anisole (1.3×10^{-3} mol) was added to the culture tube with a 1-mL gastight syringe. The F−P bottle was then sealed, brought out of the drybox, placed in a 22.0 (±0.1) °C temperature-controlled water bath, and connected to a H_2 line via the Quick-Connects. Using the top (purge) valve, the F−P bottle was then purged 15 times (waiting 15 s between purges) with 40 psig H_2. Following the purges, the F−P bottle was pressurized to 40 (±1) psig H_2 and then isolated (by closing the valve to the H_2 line).

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

During the purging (and during the hydrogenation reaction), the reaction solution was vortex-stirred. Immediately after the F−P bottle was pressurized to 40 (±1) psig H_2, data collection (H_2 pressure vs time) was initiated using an Omega PX-621 pressure transducer interfaced to a PC. After about 5 h of anisole hydrogenation, the F−P bottle was once again sealed and brought into the drybox. Then, 4.0 μL of H_2O (60 equiv vs Rh) was added to the culture tube with a 10 μL gastight syringe. The F−P bottle was then attached to the H_2 line in the same way it was done after the anisole had been added. For a plot of the hydrogen uptake curve for this experiment, see Figure S8 of the Supporting Information. The reported H_2 uptake rates for anisole hydrogenation in this experiment were determined in exactly the same way as in the section titled “Control Experiment Comparing the Rate of Anisole Hydrogenation with the Rate of Cyclohexene Hydrogenation”.

Effect of $HBF_4 \cdot Et_2O$ on the Anisole Hydrogenation Activity of Rh(0) Nanoclusters Preformed in the Absence of Substrate. This experiment was performed exactly like the experiment described in the section titled “Effect of Water on the Anisole Hydrogenation Activity of Rh(0) Nanoclusters Preformed in the Absence of Substrate”, except that the initial anisole hydrogenation was only allowed to proceed for about 3 h (instead of 5 h) and 5.0 μL of $HBF_4 \cdot Et_2O$ (10 equiv vs Rh) was added (instead of 4.0 μL H_2O). Following the addition of $HBF_4 \cdot Et_2O$, the clear brown reaction solution turned deep blue immediately after the F−P bottle was pressurized with H_2. For a plot of the hydrogen uptake curve for this experiment, see Figure S9 of the Supporting Information.

Anisole Hydrogenation Catalytic Lifetime Experiments. Lifetime experiments with precatalyst **A** were set up in a manner analogous to standard conditions anisole hydrogenations (vide supra), except as follows: 2.0 mL of propylene carbonate and 1.0 mL of anisole (9.2×10^{-3} mol) were used to dissolve the 20 (±0.5) mg of precatalyst (this allows for a maximum of 2600 TTO); the F−P bottle was left open to the H_2 line, which maintained the H_2 pressure at 40 (±1) psig; and the reaction was monitored by periodically withdrawing aliquots of the reaction solution for ^{1}H NMR spectroscopy.

Aliquots were removed for ^{1}H NMR analysis as follows. First, the F−P pressure bottle was sealed, removed from the hydrogenation line, and brought into the drybox. In the drybox, the F−P bottle was opened, and a couple drops of the reaction solution were removed with a polyethylene pipet. The F−P bottle was then resealed, brought back out of the drybox, attached to the hydrogenation line, and purged 15 times with H_2 in the normal manner and the reaction allowed to continue at 40 (±1) psig H_2. (This sampling procedure takes about 30 min, which is insignificant on the time scale of the lifetime experiments.) The aliquot removed for ^{1}H NMR was placed in an NMR tube and dissolved in 1 g of CD_2Cl_2. The TTO values were determined using the integrals of the peaks for the methyl group protons of anisole and methoxycyclohexane (the peaks are at δ 3.8 and 3.3, respectively). The intermediate, 1-methoxycyclohexene, was ignored in the determination of TTO by ^{1}H NMR because it was present in quantities $\leq$5%.

The lifetime experiment with $HBF_4 \cdot Et_2O$ added was started in the manner described above. After 16 h under hydrogen, the F−P bottle was sealed and brought into the drybox. In the drybox, 5.0 μL of $HBF_4 \cdot Et_2O$ (10 equiv vs Rh) was added using a 10-μL gastight syringe. The F−P bottle was then resealed, brought out of the drybox, attached to the hydrogenation line, purged with H_2 in the normal manner, and re-pressurized to 40 (±1) psig H_2.

The lifetime experiment with 5% Rh/Al_2O_3 as the catalyst was performed just like lifetime experiments with **A**, except that 7.4 mg of 5% Rh/Al_2O_3 (3.6×10^{-6} mol Rh) was used instead of 20 mg of **A** (3.6×10^{-6} mol Rh). A total of 2600 TTO are possible in this experiment.

Control Experiment Showing the Activity and Lifetime of the 5% Rh/Al_2O_3 for Cyclohexene Hydrogenation. This experiment is described in the Supporting Information.

Observation of Partial Hydrogenation Products in the Hydrogenation of Anisole. These experiments were performed in the same general manner as the experiment described in the section titled “Monitoring Nanocluster Formation via the Evolution of Cyclooctane”. The F−P bottle was left open to the H_2 line, which maintains the H_2 pressure at 40 (±1) psig. At regular intervals, the purge valve on the F−P bottle was opened, and a GLC sample was removed using the procedure described in the section titled “Monitoring Nanocluster Formation via the Evolution of Cyclooctane”. No GLC samples were removed until after the end of the induction period, as judged by a noticeable darkening in the reaction solution. This precautionary measure ensures that the sampling procedure will have as little effect as possible on the nanocluster nucleation process. For each GLC data point, the relative amounts of anisole, 1-methoxycyclohexene, and methoxycyclohexane were quantified. The identities of the analyte peaks in the GLC traces were established by the retention times of authentic compounds. Additionally, the identities of anisole, 1-methoxycyclohexene, and methoxycyclohexane were verified by GC-MS.

Table 2 shows a list of experiments for which the amount of 1-methoxycyclohexene was quantified. The experiment in Table 2 described as standard conditions was performed exactly like the experiment described in the section titled “Monitoring Nanocluster Formation via the Evolution of Cyclooctane”. The experiment with 60 equiv of H_2O added (Table 2) only differed in that 4.0 μL of H_2O was added to the reaction solution with a 10-μL gastight syringe while still in the drybox. The experiments with 1.05 and 2.01 equiv of $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ added (Table 2) were performed exactly like the standard conditions experiment, except that 24.1 and 45.4 mg of $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$, respectively, were weighed into the same vial as the precatalyst **A** while in the drybox. The experiments at 40 and 78 °C (Table 2) were performed exactly like the standard conditions experiment, except that the temperature of the water bath was adjusted to 40 and 78 °C, respectively. The experiment with acetone solvent (Table 2) was performed exactly like the standard conditions experiment, except that 2.9 mL of acetone was used instead of 2.9 mL of propylene carbonate. The experiments using 7.4 mg of 5% Rh/Al_2O_3 (Table 2) were performed exactly like the experiments with **A**, except that 7.4 mg of 5% Rh/Al_2O_3 was used instead of 20 mg of **A**.

The “initial selectivity” (i.e., the initial ratio of 1-methoxycyclohexene to methoxycyclohexane) was determined from direct injection of the first GLC sample. It was calculated by dividing the area of the 1-methoxycyclohexene peak by the sum of the areas for the 1-methoxycyclohexene and methoxycyclohexane peaks. This calculation makes use of the concept of “effective carbon number” (see the Supporting Information). To determine the percent yield of 1-methoxycyclohexene, the GLC sample was diluted 20:1 with propylene carbonate. This dilution was necessary to keep the concentrations of anisole, 1-methoxycyclohexene, and methoxycyclohexane in the range of linear FID response. The percent yield of 1-methoxycyclohexene was calculated by dividing the area of the 1-methoxycyclohexene peak by the sum of the areas for the 1-methoxycyclohexene, methoxycyclohexane and anisole peaks.

The curve fit shown in Figure 5 was generated by Microcal Origin, a commercial software package that we have previously validated for generating nonlinear curve fits.[61] The data in Figure

5 were fit to the analytic kinetic equation for the concentration of "B" in an A → B → C kinetic scheme (see eqs 4–6 elsewhere[93]).

Use of Effective Carbon Number (ECN) for GLC Quantitation. See the Supporting Information for details.

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Note Added in Proof. A review of nanoclusters as arene hydrogenation catalysts has been written and is in press.[102]

Supporting Information Available: Literature survey and additional figures, tables, and text. This material is available free of charge via the Internet at http://pubs.acs.org.

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