

Mechanistic Studies of Single-Step Styrene Production Catalyzed by Rh Complexes with Diimine Ligands: An Evaluation of the Role of Ligands and Induction Period

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Supporting Information

ABSTRACT: Studies of catalytic benzene alkenylation using different diimine ligated Rh(I) acetate complexes and Cu(OAc)₂ as the oxidant revealed statistically identical results in terms of activity and product selectivity. Under ethylene pressure, two representative diimine ligated rhodium(I) acetate complexes were demonstrated to exchange the diimine ligand with ethylene rapidly to form [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ and free diimine. Thus, it was concluded that diimine ligands are not likely coordinated to the active Rh catalysts under catalytic conditions. At 150 °C under catalytic conditions using commercial Cu(OAc)₂ as the oxidant, [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ undergoes rapid decomposition to form catalytically inactive and insoluble Rh species, followed by gradual dissolution of the insoluble Rh to form the



soluble Rh, which is active for styrene production. Thus, the observed induction period under some conditions is likely due to the formation of insoluble Rh (rapid), followed by redissolution of the Rh (slow). The Rh decomposition process can be suppressed and the catalytically active Rh species maintained by using soluble Cu(II) oxidants or $Cu(OAc)_2$ that has been preheated. In such cases, an induction period is not observed.

KEYWORDS: rhodium, CH activation, diimine ligand, induction period, styrene, arene alkenylation

INTRODUCTION

Alkyl and alkenyl arenes serve as an important raw material for plastics, elastomers, pharmaceuticals, and fine chemicals.^{1–5} Alkyl and alkenyl arenes are currently produced by initial acidcatalyzed arene alkylation.^{1,2,5–8} For example, the current method for the industrial production of styrene involves Friedel–Crafts or zeolite-catalyzed benzene ethylation to generate ethylbenzene that is subsequently dehydrogenated.⁹ This method requires multiple steps, including a transalkylation reaction that converts poly ethylbenzene products to ethylbenzene, and it consumes substantial energy.^{6–8,10,11} The transition metal-mediated Heck reaction is able to accomplish arene alkenylation, but it usually incorporates an aryl halide or pseudohalide and a second organometallic reagent, which leads to the generation of a stoichiometric amount of metal-containing byproduct.^{12–15}

The development of transition metal-catalyzed single-stage oxidative alkenylation of arenes offers potential advantages. Although a variety of transition metal catalysts have been designed to achieve the net addition of an aromatic C–H bond across olefinic C=C bonds (i.e., olefin hydroarylation) to

synthesize alkyl aromatics,^{16–38} examples of the direct conversion of benzene (or related arenes such as toluene or xylenes) and unfunctionalized olefins to alkenyl arenes are rare.^{24,39–48} Reported catalysts are generally based on rhodium, ruthenium, platinum, or palladium, and they are often limited by low selectivity, low yield, poor catalyst longevity, and the use of non air-recyclable oxidants.^{19,49,50}

Previously, our group reported a Rh(I) complex (^{FI}DAB)-Rh(TFA)(η^2 -C₂H₄) (^{FI}DAB = *N*,*N'*-bis(pentafluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene; TFA = trifluoroacetate) that serves as a catalyst precursor for the direct oxidative conversion of benzene and ethylene to styrene with over 800 turnover number (TON) and quantitative yield relative to the air-recyclable Cu(II) oxidant (Scheme 1a).^{51,52} We also reported that the simple Rh(I) salt, [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂, can catalyze the oxidative reaction of α -olefins and arenes to produce alkenyl arenes using Cu(OAc)₂ as the

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Scheme 1. Catalytic Benzene Alkenylation by Rh(I) Catalyst Precursors

Previous work:





b) Benzene alkenylation to produce propenyl benzenes catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$



This work:

c) Mechanistic studies of styrene production process catalyzed by [(DAB)Rh(µ-OAc)]2 system





oxidant with up to 10:1 linear:branched product ratio and >1470 total catalytic turnovers (Scheme 1b).⁵³ Recently, we reported that an air-stable Rh catalyst, (5-FP)Rh(TFA)(η^2 -C₂H₄) (TFA = trifluoroacetate, 5-FP = 1,2-bis(*N*-7-azaindolyl)benzene), can catalyze aerobic oxidative arene alkenylation to selectively produce linear alkenyl arenes with in situ air as the terminal oxidant.⁵⁴ Previous mechanistic studies of styrene production using (^{FI}DAB)Rh(TFA)(η^2 -C₂H₄) as a catalyst precursor revealed complicated kinetics including observation of an induction period under some conditions.⁵² Microscopy and filtration experiments after the induction period suggested that Rh nanoparticles are not likely responsible for the observed catalytic arene alkenylation.

We report new findings regarding the catalytic oxidative vinylation of benzene to form styrene using several diimineligated rhodium acetate catalyst precursors (Scheme 1c). We have revealed that in the presence of ethylene, two representative diimine-based rhodium acetate complexes readily dissociate the diimine ligand and generate $[Rh(\mu - OAc)(\eta^2 - C_2H_4)_2]_2$. Under the catalytic conditions with commercial Cu(OAc)₂, $[Rh(\mu - OAc)(\eta^2 - C_2H_4)_2]_2$ undergoes rapid decomposition to form catalytically inactive and insoluble Rh species, from which soluble molecular Rh species gradually leach back into solution to form the soluble active catalyst. The process of Rh decomposition and redissolution is proposed to give rise to the observed induction period. Using either Cu(OAc)₂ treated to decrease particle size, either by heating or ball milling (herein, referred to as activated Cu(OAc)₂) or more soluble Cu(II) oxidants, such as copper(II) 2-ethylhexanoate [Cu(OHex)₂], the decomposition of $[Rh(\mu - OAc)(\eta^2 - C_2H_4)_2]_2$ to form insoluble rhodium

Scheme 2. General Synthetic Procedure for in Situ Generated Catalysts from Diimines and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2^a$



^{*a*}Complexes 3 and 6 have been isolated and fully characterized.



Figure 1. ORTEPs of complexes **3** (left) and **6** (right) (50% probability). H atoms and solvent molecules are omitted for clarity. For the structure of complex **6**, only the major position for the disordered atom in the phenyl ring is shown. Selected bond lengths (Å): for complex **3** Rh1–N1 1.957(5), Rh1–N2 1.964(5), Rh1–O3 2.061(5), Rh1–O1 2.066(4), O1–C1 1.259(8), O2–C1 1.232(7) C1–C2 1.524(9); for complex **6** Rh1–N2 1.945(3), Rh1–N1 1.968(3), Rh1–O1 2.057(3), Rh1–O4 2.086(2), O1–C41 1.251(5), O2–C41 1.259(5), C41–C42 1.515(5). Selected bond angles (deg): for complex **3** N1–Rh1–N2 77.6(2), N2–Rh1–O3 95.4(2), N1–Rh1–O1 93.5(2), O3–Rh1–O1 91.6(2), N1–Rh1–O3 168.7(2), N2–Rh1–O1 166.17(19), O2–C1–O1 127.4(6), C1–O1–Rh1 126.7(4), C1–O2–Rh2 122.9(4); for complex **6** N2–Rh1–N1 78.9(1), N1–Rh1–O1 95.9(1), N2–Rh1–O4 91.0(1), O1–Rh1–O4 92.9(1), N2–Rh1–O1 167.2(1), N1–Rh1–O4 168.59(12), O1–C41–O2 126.1(4), C41–O1–Rh1 124.7(3), C41–O2–Rh2 124.9(3).

species can be mitigated, and the induction period is not observed.

It is now well-established that some catalytic processes using molecular Rh,^{55–57} Pd,^{58–60} Ir,^{61–63} Ru,^{64,65} or Fe^{66–68} precursors occur through decomposition to form reduced nanoparticles, which serve as the actual catalysts. However, we are unaware of an example of an induction period attributed to degradation of molecular species to form an insoluble but inactive material followed by redissolution to provide the active and soluble catalyst.

RESULTS AND DISCUSSION

Effect of Diimine Ligand Identity on Reactivity and Selectivity for Benzene Alkenylation. Following the success of (^{FI}DAB)Rh(TFA/OAc)(C₂H₄) and [Rh(μ -OAc)-(η^2 -C₂H₄)₂]₂ complexes as catalyst precursors,^{51,52} we synthesized a series of new rhodium(I) acetate complexes (**1-6**) supported by different diimine ligands with varied electronic and steric properties (Scheme 2) and probed them for catalytic benzene alkenylation. The new N-supported Rh complexes were not isolated, but instead were utilized for catalysis after in situ generation by reaction of [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ with the diimine proligands in THF for 30 min at room temperature followed by removal of THF solvent. To test the viability of the synthetic procedure, the structures of two representative in situ generated diimine rhodium complexes (**3** and **6**) have been confirmed by X-ray diffraction (Figure 1), multinuclear NMR spectroscopy and elemental analysis. As depicted in Figure 1, both complexes 3 and 6 possess dimeric structures which are commonly observed in Rh(I) complexes.^{69–72} The N–Rh–N bond angles of complexes 3 and 6 are compressed from the ideal 90° bond angles of a four-coordinate square planar structure to less than 80°, which are typical for Rh(I) diimine complexes.^{73,74} The N–Rh–N and O–Rh–O bond angles are larger for complex 6 than complex 3.

We first evaluated the reactivity of diimine ligated Rh complexes and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ for the single-step production of styrene from benzene and 40 psig ethylene (Figure 2). All reactions were performed under a standard set of conditions (10 mL benzene, 0.001 mol % Rh complex (relative to benzene) and 240 equiv of $Cu(OAc)_2$ (relative to the catalyst), 150 °C). As shown in Figure 2, overlap of the turnover (TO) versus time plots for all of the diimine-based Rh(I) catalyst precursors indicates that variation of the diimine ligand has a negligible effect on catalytic reactivity. The reactions with ethylene using diimine rhodium complexes show pronounced induction periods. Although the catalysis using diimine ligated Rh(I) catalyst precursors exhibit a shorter induction period compared with the catalysis using $[Rh(\mu OAc)(\eta^2 - C_2H_4)_2]_2$, the reaction using Rh(I) complexes with diimine ligands show a statistically identical apparent turnover frequency (TOF) after the induction period $(2.8 \times 10^{-3} \text{ s}^{-1})$ to $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (each TOF was calculated from



Figure 2. Plot of TO versus time for styrene production catalyzed by complexes 1-6 or $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$. Reaction conditions: 0.001 mol % of Rh (relative to benzene), 240 equiv of $Cu(OAc)_2$ (relative to Rh), 10 mL benzene, 40 psig ethylene, 150 °C. Each data point is the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

the linear portion of TO versus time plots, which are typically observed between 8 and 12 h). We also probed linear: branched selectivity for alkenvlation of benzene with the α olefin propylene. The catalytic conversion of benzene, propylene and Cu(OAc)₂ by diimine-based Rh(I) catalyst precursors and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ to propenyl benzenes was tested (Scheme 3). At 25 psig of propylene, all of the diimine Rh(I) catalyst precursors and $[Rh(\mu-OAc)(\eta^2 (C_2H_4)_2]_2$ selectively produce linear straight-chain alkenyl arenes (the anti-Markovnikov product) with identical 8:1 linear: branched ratios after 48 h (Scheme 3 and Table S1). The L: B ratio is determined based on the ratio of npropylbenzene to cumene that would result from hydrogenations of the alkenyl products (i.e., the ratio of allylbenzene and β -methylstyrenes to α -methylstyrene). Thus, the identity of diimine ligand has no demonstrable effect on linear:branched selectivity. Taken together, these results suggest that the diimine ligand is not likely coordinated to the active Rh catalyst.

Stability of Diimine Ligated Rh Complexes toward Ethylene Pressure. Given that no significant ligand effects on reactivity and selectivity are observed in the catalysis with ethylene and propylene, the diimine ligated Rh complexes 1-6and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ are likely converted to the same active Rh species under catalytic conditions. To test this hypothesis, we monitored the transformation of complexes 3 and 6 under ethylene pressure by in situ ¹H NMR spectroscopy. $Cu(OAc)_2$ was not used in those experiments as its paramagnetic properties result in broadened NMR spectra. As observed by ¹H NMR spectroscopy (Figure S1a), approximately 10 min after being treated with 10 psig of ethylene at room temperature, approximately 90% of $[(^{FI}DAB)Rh(\mu-OAc)]_2$ (3) in benzene- d_6 was converted to $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ accompanied by dissociation of the diimine ligand. The observations by ¹H NMR spectroscopy are consistent with the solution changing from purple $\{[(^{Fl}DAB) Rh(\mu-OAc)_{2}$ to yellow { $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ } immediately following the addition of ethylene to the vessel (Figure S2). Likewise, the addition of 10 psig of ethylene to a benzene solution of complex 6 results in the same observation by ¹H NMR spectroscopy (Figure S1b). Thus, in a standard catalytic reaction for all complexes 1-6, we believe that diimine dissociation occurs prior to catalysis.

Thermolysis of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ to Form Rh(0) Species. To study thermal decomposition, 0.0057 mmol of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ was dissolved with 0.5 mL of benzene- d_6 in a J-Young pressure NMR tube. The J-Young tube was heated at 150 $^\circ \mathrm{C}$ for 15 min, and a black solid and Rh mirror were observed, which is consistent with rapid reduction to elemental Rh (see next paragraph for discussion of analysis of the black solid). In addition, free HOAc and ethylene were observed by ¹H NMR spectroscopy (Figure S3). Kinetic studies were performed at 90, 100, 110, and 120 °C. The kinetic plots show a first order decay of $[Rh(\mu-OAc)(\eta^2 C_{2}H_{4}$, $C_{2}H_{4}$, the first-order rate constants from four different temperatures (Figure 3B), and the ΔH^{\ddagger} and ΔS^{\ddagger} were calculated to be 28(1) kcal/mol and -1(6) cal/(mol·K) respectively. The standard deviation for the ΔS^{\ddagger} value is too large to conclude if the actual ΔS^{\ddagger} is positive or negative. Additionally, when 20 psig ethylene was added, the decomposition of $[Rh(\mu OAc)(\eta^2-C_2H_4)_2]_2$ is much slower than in the absence of added ethylene with complete decomposition after 5 h of heating at 90 °C (Figure S4). Thus, the dissociation of ethylene is likely involved in the pathway for decomposition. In addition, the effect of the solvent was investigated. Benzene- d_{6} , protio-benzene, C_6F_6 , and *p*-xylene- d_{10} were compared. The Rh complex shows very similar decomposition rates in each of the four solvents (Figure S5), indicating that the solvent is likely not involved in the decomposition reaction.

We sought to characterize the black precipitate formed during the thermolysis of $[\rm Rh(\mu\text{-}OAc)(\eta^2\text{-}C_2H_4)_2]_2$ in the

Scheme 3. Oxidative Conversion of Benzene and Propylene to Propenylbenzenes Catalyzed by Complexes 1–6 or $[Rh(\mu - OAc)(\eta^2 - C_2H_4)_2]_2$





Figure 3. (A) Plot of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ concentration versus time for decomposition in benzene- d_6 at different temperatures. Each data point is the average of three separate experiments. Error bars represent the standard deviation based on a minimum of three independent experiments. (B) Eyring plot for $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ decomposition. Reaction conditions: 0.2 mol % of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (relative to benzene), 0.5 mL of benzene- d_6 , 20 psig N₂, 90–120 °C.

absence of Cu(OAc)₂ by transmission electron microscopy (TEM). A 10 mL benzene solution of $[Rh(\mu\text{-OAc})(\eta^2-C_2H_4)_2]_2$ (0.001 mol % Rh) under 40 psig of ethylene was heated to 150 °C for 1 h. The resulting mixture was centrifuged, and the supernatant was decanted to isolate the

insoluble black solid. Lattice parameter analysis, TEM-EDS measurement, and selected area diffraction were used to characterize the black solid (Figure 4). These data confirm that Rh nanoparticles are formed during the thermal decomposition. Rh(111) and Rh(200) planes are observed in the lattice constant analysis. The lattice parameters for Rh(111), Rh(200), and Rh(220) are found to be 0.22, 0.19, and 0.13 nm, respectively. Also, broad beam TEM-EDS measurement is consistent with the formation of Rh nanoparticles. In selected area diffraction measurement of the particles, three common planes of Rh nanoparticles, Rh(111), Rh(200), and Rh(220) were found.

Taken together, our experimental data indicate that the reductive decomposition of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ to form Rh(s) likely involves dissociation of ethylene and subsequent ethylene C–H activation to form a Rh-vinyl intermediate and acetic acid. Beyond these steps, our data do not allow additional elucidation about the details of the formation of Rh(s), but the similar rates of reductive decomposition in different arene solvents suggests that the solvent is not likely the reducing agent.

Removal of the Induction Period with Thermally Treated Cu(OAc)₂. As shown in Figure 2, for catalysis at 150 °C using $Cu(OAc)_2$ as the oxidant there is a pronounced induction period. We have discovered that this induction period is not observed in the catalysis when $Cu(OAc)_2$ is heated prior to the catalysis. Here, the $Cu(OAc)_2$ (48.8 mg) is heated in benzene (10 mL) for 12 h at 150 °C with subsequent introduction of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ using the standard catalytic conditions (Figure 5). For the reaction using preheated Cu(OAc)₂, the apparent TOF $(2.8 \times 10^{-3} \text{ s}^{-1})$ calculated after 8 h is statistically identical to that of the catalysis after the induction period without preheating $Cu(OAc)_2$. Additionally, catalysis using propylene with the same preheating treatment shows a statistically identical linear: branched ratio as compared to that observed under standard conditions (Table S1). These results indicate the same



Figure 4. TEM lattice analysis (left), TEM-EDS measurement (top right), and selected area diffraction analysis (bottom right) of Rh species from thermal decomposition of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ at 150 °C under 40 psig of ethylene in benzene in the absence of $Cu(OAc)_2$.



Figure 5. Plot of TO versus time for styrene production catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ after heating $Cu(OAc)_2$ (0.24 mol % relative to benzene) in benzene (10 mL) for 0 to 24 h at 150 °C. Reaction conditions: 0.001 mol % of Rh (relative to benzene), 40 psig ethylene, 150 °C. Each data point is the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

catalytically active species is likely formed in the catalytic reaction with or without preheating $Cu(OAc)_2$.

Having observed the removal of the induction period after preheating $Cu(OAc)_2$ at 150 °C for 12 h, we probed intermediate heating times for $Cu(OAc)_2$ pretreatment from 2 to 10 h. The induction period is reduced as the $Cu(OAc)_2$ heating time is increased (Figure 5). Again, regardless of length of induction period the apparent TOFs (calculated from 6 to 8 h when maximum apparent TOFs are achieved after the induction period) are nearly identical (Figure 5). The catalytic reactivity was not affected by increasing preheating time beyond 12 h of preheating (Figure 5).

We isolated solid materials by filtration from the mixture of $Cu(OAc)_2$ in benzene after heating for 12 h (Figure S6). The isolated solid $Cu(OAc)_2$ was used as the oxidant for standard catalytic reactions, and the induction period was not observed (Figure S6). Herein, we refer to the $Cu(OAc)_2$ solid which was treated to enable the removal of the induction period, either by heating or ball milling (see below), in the catalysis as activated $Cu(OAc)_2$. When the filtrate after heating $Cu(OAc)_2$ at 150 °C for 12 h was added to $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ along with untreated $Cu(OAc)_2$ and subjected to the standard catalytic conditions, there was a pronounced induction period (Figure S6). These results are consistent with some transformation of the solid $Cu(OAc)_2$ rather than generation of a soluble material that might reduce/remove the induction period. Catalysis using $Cu(OAc)_2$ solid isolated upon heating in hexanes (10 mL) for 12 h at 150 °C does not reveal a significant induction period, which implies benzene is not needed to make the activated $Cu(OAc)_2$ (Figure S7).

Powder-XRD and IR spectroscopy of the activated Cu-(OAc)₂ (i.e., Cu(OAc)₂ solid isolated after heating in benzene for 12 h) suggests negligible decomposition (Figures S8 and S9). Additionally, comparative TGA and IR analysis of commercial anhydrous Cu(OAc)₂ and copper(II) acetate hydrate provides evidence that the original anhydrous Cu(OAc)₂ sample is not contaminated by copper(II) acetate hydrate (Figures S9 and S10). Thus, the thermal treatment of the commercial anhydrous $Cu(OAc)_2$ is not likely decreasing the water content. Additionally, the induction period is observed in the reaction using anhydrous $Cu(OAc)_2$ prepared under dynamic vacuum at 150 °C for 18 h (Figure S11). Thus, it is unlikely that the induction period is due to the presence of water in the $Cu(OAc)_2$. Catalysis using untreated $Cu(OAc)_2$ with HOAc or other Cu species such as CuO, Cu_2O , Cu(OAc), or Cu powder, which might be formed during thermal treatment of $Cu(OAc)_2$. Thus, it is unlikely that these various Cu species are facilitating the generation of the actual Rh catalytic species or serving as cocatalyst.

We have observed the formation of Cu-based nanoparticles by TEM analysis after heating $Cu(OAc)_2$ in benzene for 12 h (Figure S12). To determine if these Cu-based nanoparticles play a role in the induction period, we ran the standard reaction using commercial Cu(OAc)₂ until it reached completion. At this stage, the resulting reaction mixture is expected to contain a variety of decomposed Cu species including the Cu-based nanoparticles and Cu(OAc) without $Cu(OAc)_2$. Then the mixture was charged with fresh [Rh(μ - $OAc)(\eta^2 - C_2 H_4)_2$ and commercial untreated $Cu(OAc)_2$, and the mixture was subjected to the standard catalytic conditions. The TO versus time plot shows an induction period and overlaps well with that of a standard catalytic reaction using commercial $Cu(OAc)_{2i}$ suggesting the decomposed Cu species do not contribute to the removal of the induction period (Figure S13).

Given the absence of evidence that chemical changes based on thermal treatment of $Cu(OAc)_2$ give rise to removal of the induction period, we evaluated possible physical changes. A saturated $Cu(OAc)_2$ mixture in benzene was prepared by adding a large excess of $Cu(OAc)_2$ in benzene. UV–vis spectroscopy of the resulting solution exhibited no absorption signal when scanning the wavelength range from 300 to 800 nm at 25 °C. This suggests the $Cu(OAc)_2$ is insoluble in benzene at room temperature. We preheated the $Cu(OAc)_2$ in benzene at 150 °C for 12 h, and the resulting $Cu(OAc)_2/$ benzene mixture was decanted after centrifuging to remove insoluble materials. The isolated filtrate showed no UV–vis absorption peaks within the 300–800 nm range, indicating that the thermally treated $Cu(OAc)_2$ is also insoluble in benzene at room temperature.

Maes and co-workers reported that controlling the structure (shape and size of the particles) of cesium carbonate base, which is almost completely insoluble in the reaction solvent toluene, can significantly increase the rate of aryl halide amination with a rate-limiting deprotonation step involved in the catalytic cycle.⁷⁵ To study the morphology of $Cu(OAc)_2$ solid materials under different conditions, we first used scanning electron microscopy (SEM) analysis. By comparing corresponding SEM images, although both samples showed irregularly shaped particles with a broad size distribution, we discovered that the solid materials isolated after heating Cu(OAc)₂ in benzene at 150 °C for 12 h possessed smaller particles than the untreated commercial $Cu(OAc)_2$ (Figure 6). We probed the specific surface area of both thermally treated and untreated commercial $Cu(OAc)_2$ using N₂ physisorption. However, the difference in the BET surface area between the commercial $Cu(OAc)_2$ (8.2 m²/g) and the activated Cu- $(OAc)_2$ (9.8 m²/g) is not significant. Notably, the particle size of commercial $Cu(OAc)_2$ observed in the SEM images is



Figure 6. SEM images of commercial $Cu(OAc)_2$ (A, B) and solid isolated by heating $Cu(OAc)_2$ in benzene at 150 °C for 12 h (C, D). Figure 7B and 7D was obtained by magnifying the area marked with red frame in Figure 7A and 7C, respectively.

considerably larger than that estimated from the BET surface area assuming spherical morphology. These results along with N₂ adsorption isotherm (Figure S14) indicate that indicate that the thermally treated $Cu(OAc)_2$ consists of small particles, whereas the commercial $Cu(OAc)_2$ mainly possesses large aggregates.

Catalytic styrene production using $Cu(OAc)_2$ ground by a ball mill reveals a shortened induction period (Figure 7).



Figure 7. Plot of TO versus time for styrene production catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ using ball-milled $Cu(OAc)_2$ and thermally treated ground $Cu(OAc)_2$ and its comparison to the standard reaction. Each data point is the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

Notably, heating ground $Cu(OAc)_2$ in benzene for 4 h at 150 °C prior to the catalysis resulted in the complete removal of the induction period in the catalysis (Figure 7). In contrast, preheating commercial $Cu(OAc)_2$ for the same amount of time (4 h) does not remove the induction period. These results support the hypothesis that reducing the size of $Cu(OAc)_2$ particles removes or reduces the induction period.

We performed catalyst fractional poisoning tests for catalysis with activated Cu(OAc)₂ using PPh₃, P(OCH₂)₃CEt, or 1,10phenanthroline as poisoning reagents. As detailed in the Experimental Section, the catalytic activities were tested as a function of the addition of 0.25, 0.5, and 1.0 equiv (per equivalent of Rh) of poisoning reagents and compared to the reaction without addition of the poison. The addition of PPh₃ or P(OCH₂)₃CEt leads to a slight reduction of reaction rate whereas the addition of 1,10-phenanthroline significantly slows the catalytic reaction. The key result from the poisoning reagent does not completely poison the catalyst, providing evidence against the formation of Rh nanoparticles as the active catalyst for the benzene alkenylation (Figure S15).

Two possible rationalizations for the effect of activated $Cu(OAc)_2$ on the induction period are (1) the-Rh catalyzed arene alkenylation is a homogeneous process or (2) the Cu(II) oxidation step is a heterogeneous reaction. We believe that $Cu(OAc)_2$ becomes much more soluble in benzene as temperature increases from room temperature to 150 °C. On the basis of our previously proposed mechanism, at the reaction temperature (150 °C) soluble Cu(OAc)₂ can react with a Rh-H intermediate to regenerate a catalytically active Rh-OAc complex and complete the catalytic cycle.⁵⁰ We speculate that the activated $Cu(OAc)_2$ with a smaller particle size can dissolve in benzene more rapidly at the reaction temperature (150 °C) more rapidly than the untreated $Cu(OAc)_{2}$, which contains larger solid aggregates. This leads to the removal of the induction period since Rh intermediates react with $Cu(OAc)_2$ more rapidly than they undergo reductive decomposition. We cannot entirely rule out the possibility of the generation of amorphous Cu(OAc)₂ after preheating $Cu(OAc)_2$ in organic solvent. The amorphous $Cu(OAc)_2$ can dissolve in benzene at 150 °C more rapidly than untreated $Cu(OAc)_2$. However, we do not have evidence for the formation of the amorphous $Cu(OAc)_2$ since it is unobservable by powder-XRD and IR spectroscopy. Activated $Cu(OAc)_2$ containing smaller particles is more "accessible" in a heterogeneous reaction and thus reacts faster with Rh intermediates than untreated $Cu(OAc)_2$.

In addition to the catalysis with ethylene using activated $Cu(OAc)_2$, we have also performed the catalytic conversion of benzene and ethylene to styrene using 360 equiv of copper(II) 2-ethylhexanoate $(Cu(OHex)_2)$ as the oxidant. $Cu(OHex)_2$ is more soluble in benzene than $Cu(OAc)_2$. Using $Cu(OHex)_2$ as the oxidant, no apparent induction period was observed (Figure 8).

Removal of the Induction Period by the Addition of **Excess** ^{FI}DAB Ligand. We performed the standard reaction using 240 equiv of untreated $Cu(OAc)_2$ with the addition of 1 to 20 equiv of FlDAB ligand (relative to the quantity of Rh) at the start of the reaction (Figure 9). When excess ^{FI}DAB ligand is added, no pronounced induction period is observed. Notably, the introduction of additional ligand does not impact the rate of the catalysis with ethylene. Also, in the catalytic conversion of benzene and propylene to propenylbenzenes, the addition of 5 equiv of diimine ligand does not influence the linear: branched product ratio (Table S1). These results indicate the catalytic processes likely share the same active Rh catalyst. Monitoring the transformation of $[(^{Fl}DAB)Rh(\mu$ - $OAc)]_2$ under ethylene pressure at room temperature in the presence of 10 equiv of diimine (relative to Rh) by in situ ¹H NMR spectroscopy revealed that approximately 90% of



Figure 8. Plot of TO versus time for styrene production catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ using copper(II) 2-ethylshexanoate $[Cu-(OHex)_2]$ as the oxidant. Each data point is the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.



Figure 9. Plot of TO versus time for styrene production catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ with the addition of 0 to 20 equiv of ^{Fl}DAB ligand. Reaction conditions: 0.001 mol % of Rh (relative to benzene), 240 equiv of Cu(OAc)_2 (relative to Rh), 10 mL of benzene, 40 psig ethylene, 150 °C. Error bars represent the standard deviations based on a minimum of three independent experiments.

 $[({}^{FI}DAB)Rh(\mu-OAc)]_2$ is converted to $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ 10 min after being treated with 10 psig of ethylene (Figure S1c). This indicates that under the catalytic condition where a large excess of the diimine ligand is present, diimine ligand dissociation from $[({}^{FI}DAB)Rh(\mu-OAc)]_2$ is not inhibited and the catalyst precursor is likely $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$. After commercial Cu(OAc)₂ in benzene was heated in the presence of ${}^{FI}DAB$ ligand (a 48:1 Cu(OAc)₂ to ${}^{FI}DAB$ ratio was used) at 150 °C for 2 h, the resulting mixture was filtered to isolate the solid Cu materials. Catalysis using the isolated solid as the oxidant reveals no apparent induction

period (Figure S16). Powder-XRD and IR spectroscopy of the isolated $Cu(OAc)_2$ (before use in catalysis) shows similar features to $Cu(OAc)_2$ obtained by heating $Cu(OAc)_2$ in benzene at 150 °C for 12 h (Figures S8 and S9). This implies that the ^{FI}DAB ligand likely facilitates the conversion of commercial $Cu(OAc)_2$ to activated $Cu(OAc)_2$ through interaction of the diimine with $Cu(OAc)_2$.

As shown in Figure 2, catalysis using the diimine ligated Rh(I) catalyst precursor exhibits a reduced induction period compared with the catalysis using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$. This is likely due to dissociation of the diimine ligand from the diimine Rh(I) complex, followed by diimine interaction with Cu(OAc)₂ to facilitate the Cu(OAc)₂ activation process. To test this hypothesis, we have compared TO versus time plots for catalysis with 5-fold Rh loading (0.005 mol %) of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ and $[({}^{Fl}DAB)Rh(\mu-OAc)]_2$ (3) under the standard catalytic conditions. The reaction using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ shows an apparent induction period while the catalysis using ${}^{Fl}DAB$ ligated Rh complex does not (Figure 10). This result is consistent with the aforementioned



Figure 10. Comparison of TO versus time for styrene production catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ and $[({}^{Fl}DAB)Rh(\mu-OAc)]_2$ (3). Reaction conditions: 0.005 mol % of Rh (relative to benzene), 240 equiv of Cu(OAc)_2 (relative to Rh), 10 mL of benzene, 15 psig ethylene, 150 °C. Error bars represent the standard deviations based on a minimum of three independent experiments.

assumption that the dissociated diimine ligand from $[(^{Fl}DAB)$ - $Rh(\mu$ -OAc)]₂ helps activate $Cu(OAc)_2$ and thus removes the induction period. The addition of 100 equiv of FDAB compound (relative to the quantity of Rh) also shows no induction period, but the rate of catalysis is suppressed using 0.269 mmol of $Cu(OAc)_2$ (240 equiv relative to Rh) and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ containing 0.001 mol % Rh. In contrast, adding 100 equiv of FDAB does not have significant effects on the apparent TOF (calculated after 8 h) of the catalysis using 0.0001 mol % Rh and 0.269 mmol of Cu(OAc)₂ (2400 equiv relative to Rh) compared to that obtained in the standard catalytic run with no induction period observed (Figure 11). These results demonstrate that the addition of a large excess of FlDAB compound seemingly inhibits catalysis by its interaction with $Cu(OAc)_2$ instead of Rh species. This also implies that the activation of $Cu(OAc)_2$ is likely due to reversible coordination of diimine ligand to $Cu(OAc)_2$.



Figure 11. Comparison of TO versus time for styrene production using various loading of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ with the addition of 100 equiv of ^{FI}DAB ligand. Reaction conditions: 0.001 or 0.0001 mol % of Rh (relative to benzene), 100 equiv of ^{FI}DAB ligand (relative to Rh), 0.269 mmol Cu(OAc)₂ (240 equiv relative to 0.001 mol % Rh, 2400 equiv relative to 0.0001 mol % Rh), 10 mL of benzene, 40 psig ethylene, 150 °C. Each data point is the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

Analogous (diimine)Cu(Cl)₂ complexes have also been reported.^{76,77} Thus, the formation of activated Cu(OAc)₂ facilitated by diimine might be due to reversible coordination with Cu(OAc)₂ to generate a transient (^{FI}DAB)Cu(OAc)₂ adduct, and the dynamic equilibrium between soluble (^{FI}DAB)Cu(OAc)₂ and insoluble Cu(OAc)₂ solid leads to the activation of the Cu(OAc)₂. Cu(OAc)₂ is present in large excess relative to the diimine, thus complete conversion of Cu(OAc)₂ to (^{FI}DAB)Cu(OAc)₂ is not possible.

Efforts to Understand the Transformation of Rh. To understand the nature of the induction period and how Rh evolves, we probed the reactivity of our Rh catalyst in solid and solution phases of reaction mixtures separately both during and after the induction period of the catalysis with ethylene, benzene and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$. In one case, a reaction was performed with untreated $Cu(OAc)_2$ under the standard conditions for 12 h (after the induction period). The reaction mixture was then filtered, and the filtrate was centrifuged in order to separate any remaining insoluble solid that passed through the filter. The insoluble materials collected from the filtration and centrifugation were combined. The solid material and the supernatant were then separately subjected to the same catalytic conditions (i.e., 0.269 mmol activated Cu(OAc)₂ (240 equiv. relative to 0.001 mol % Rh), 40 psig ethylene, 150 $^{\circ}C$) to compare their catalytic activity for styrene production (Figure 12A). The reaction using the supernatant achieved 90% yield of styrene after 12 h whereas the reaction using the solid material only produced 7% yield of styrene after 12 h. This suggests that after the induction period, the active Rh catalyst is soluble. This experiment is consistent with hypothesis of the active catalyst being a soluble molecular species. This result is also in agreement with the aforementioned catalyst fractional poisoning tests (see above). Notably, in the catalysis using the supernatant, the TO versus time plot

of the catalysis is linear without an induction period (Figure 12A) with no evidence of a second induction period (e.g., formation of Rh nanoparticle catalysts from molecular Rh). Also the catalysis with the supernatant showed a ~25% loss of reactivity relative to the catalysis with $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ and activated $Cu(OAc)_2$ according to the comparison of apparent TOF calculated after 8 h $[2.1 \times 10^{-3} \text{ s}^{-1}]$ (note that this apparent TOF is based on total starting amount of Rh) versus $2.8 \times 10^{-3} \text{ s}^{-1}$]. In contrast, catalysis using the insoluble material separated from the reaction mixture reveals an induction period.

Next, we performed a catalytic reaction with untreated $Cu(OAc)_2$ and stopped the reaction after 1 h (during the induction period). The sample preparation was performed as described immediately above to separate the insoluble and soluble materials. Using untreated $Cu(OAc)_2$ as the oxidant, the catalysis with the isolated solid materials gave 96 TOs of styrene after 20 h, while the soluble materials did not produce styrene after 20 h (Figure 12B). These results suggest that during the induction period most of the Rh is insoluble. It is also germane that the reaction using the solid materials shows an induction period and nearly identical apparent TOF following the induction period (calculated from 12 to 16 h) as was observed in the standard reaction using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ and untreated $Cu(OAc)_2$.

We used ICP-OES analysis to determine the amount of Rh in the reaction solution during and after the induction period. We performed standard catalytic reactions with $[Rh(\mu OAc)(\eta^2 - C_2H_4)_2]_2$ and untreated $Cu(OAc)_2$ and stopped the reaction after 1 h (during the induction period) or after 12 h (after the induction period). The soluble materials were then collected by filtration and centrifugation/decantation the reaction mixture. Analysis of the soluble materials at 1 h by ICP-OES reveals <1% of Rh relative to the total amount of starting Rh, which is in agreement with the negligible reactivity of the isolated soluble materials mentioned above (Figure 12B). However, 78% of starting Rh is found in the solution phase at the 12 h time point, which is consistent with $\sim 25\%$ loss of reactivity of the isolated solution phase described above (Figure 12A). These results indicate that most Rh materials are insoluble during the induction period, but after the induction period and during catalysis, most Rh is converted to soluble materials.

On the basis of these results, along with the observation that $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ undergoes rapid thermal decomposition to form Rh nanoparticles in the absence of Cu(II), we propose that at 150 °C under catalytic conditions with untreated Cu(OAc)₂, $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ thermally decomposes to catalytically inactive and insoluble Rh material.

Next, we sought evidence for reduction of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ in the presence of untreated $Cu(OAc)_2$. We studied the evolution of Rh species during the catalysis using X-ray photoelectron spectroscopy (XPS). To evaluate the binding energy of Rh(0), we obtained the photoemission spectrum of Rh metal foil and silica-supported Rh nanoparticles. As shown in Figure 13, the $3d_{5/2}$ binding energy for Rh(0) was measured to be 307.3 eV.

We then examined the black precipitate formed during the thermal decomposition of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ in benzene in the absence of $Cu(OAc)_2$. The Rh $3d_{5/2}$ binding energy of the Rh species in the precipitate is 307.3 eV (Figure S17), as was observed for Rh foil. Thus, we conclude that $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ decomposes to Rh(0) species upon



Figure 12. Comparison of TO versus time for styrene production using solid materials versus soluble material isolated from the reaction mixture after 12 h (A) or 1 h (B) of the catalysis with 40 psig ethylene using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ [0.001 mol % of Rh (relative to benzene)] at 150 °C. TOs of styrene were obtained by subtracting TO at 0 h (if any) from the raw TO data. Error bars represent the standard deviations based on a minimum of three independent experiments.



Figure 13. X-ray photoelectron spectra (Rh 3d region) of (top) Rh metal foil and (bottom) silica-supported Rh metal nanoparticles.

heating in benzene in the absence of $Cu(OAc)_2$, which is consistent with results from TEM studies that confirm the presence of Rh(0) nanoparticles.

Subsequently, we examined the recovered Rh species after 1 h (during the induction period) and 12 h (after the induction period) in the catalysis with ethylene and $[Rh(\mu-OAc)(\eta^2 (C_2H_4)_2$ using 240 equiv of untreated $Cu(OAc)_2$ (Figures 14A and 14B). XPS data revealed Rh 3d_{5/2} binding energies of 309.2 and 308.9 eV after 1 and 12 h, respectively (Figure 14A and 14B). Using activated Cu(OAc)₂ and analyzing the Rh material after 1 h reveals a Rh 3d_{5/2} binding energy of 308.9 eV (Figure 14C). From these data, we conclude that the catalyst resting state has a Rh 3d_{5/2} binding energy of 308.9 eV. We also acquired XPS data for three well-defined molecular Rh complexes with different formal oxidation states of Rh, [Rh(μ - $OAc)(\eta^2-C_2H_4)_2]_2$ (308.0 eV), $Rh_2(OAc)_4$ (308.7 eV), and RhCl₃·xH₂O (309.6 eV) (Figure S18 and Table S3). Figures 14B and 14C indicate that the recovered soluble catalytic active Rh species showed a Rh 3d_{5/2} binding energy at 308.9 eV, which is most consistent with XPS data of the well-defined Rh(II) complex $Rh_2(OAc)_4$. Although caution is needed when interpreting the XPS data, since different types of ligands may result in differences in observed binding energy, analysis of the XPS data are consistent with a Rh(II) catalyst resting state.

In a control experiment, $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ was heated together with mesoporous SiO₂ in benzene at 150 °C for 1 h in an attempt to capture the reduced Rh species on the SiO₂ support. The nonvolatile materials from this thermolysis



Figure 14. X-ray photoelectron spectra (region Rh 3d) of recovered Rh species formed (A and B) after 1 and 12 h of catalysis, respectively, with 40 psig ethylene and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (0.001 mol % Rh relative to benzene) using **untreated** Cu(OAc)₂ (240 equiv relative to Rh) and (C) after 1 h of catalysis with 40 psig ethylene and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (0.001 mol % Rh relative to benzene) using **activated** Cu(OAc)₂ (240 eq. relative to Rh).

reaction were analyzed by XPS and TEM-EDS. A $3d_{5/2}$ peak at 307.0 eV was observed by XPS, similar to metallic Rh (Figure S19). Indeed, TEM/EDS and lattice constant analysis confirmed that Rh(0) nanoparticles were captured by SiO₂ (Figure 15). These results verified that our sample recovery method enabled us to observe Rh(0) nanoparticles if they were formed during the catalytic reaction.

We also characterized the recovered Rh species formed after 1 h of catalysis using untreated $Cu(OAc)_2$ by scanning transmission electron microscopy (STEM). The STEM-EDS analysis of nonvolatile materials collected after the reaction



Figure 15. TEM/STEM images and EDS analysis of recovered Rh species from the thermal decomposition of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (0.001 mol % Rh relative to benzene) in benzene after 1 h in the presence of SiO₂. (A) Bright-field TEM images of SiO₂ captured Rh species, (B–D) dark-field STEM images of SiO₂ captured Rh species, and (E) EDS analysis of selected particle (circled in red in panel C).

indicated the presence of rhodium species present in the small bright spots in Figure 16. Although Rh nanoparticles formed during the thermal decomposition of $[Rh(\mu-OAc)(\eta^2-$

 $C_2H_4)_2]_2$ in benzene in the absence of $Cu(OAc)_2$, the nature of the Rh species in Figure 16 is ambiguous. Figure 17 shows compositional mapping in the vicinity of the features associated with Rh, confirming that Rh is present in a separate phase from the Cu component.



Figure 17. STEM-EDS maps of recovered Rh species formed after 1 h in the catalysis with 40 psig ethylene and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (0.001 mol % Rh relative to benzene) using untreated $Cu(OAc)_2$ (240 equiv relative to Rh). (A) Overall dark-field STEM image, (B) EDS map of Rh, (C) EDS maps of Cu, and (D) EDS maps of O. Rh, Cu, and O are shown in yellow, orange, and red, respectively. EDS maps were obtained from the area marked with the orange frame in Figure 17A.

In an effort to study the catalytically active Rh species under catalytic conditions, where an induction period is not observed (i.e., using activated $Cu(OAc)_2$ as the oxidant or using 5 equiv of ^{Fl}DAB ligand), catalytic reactions were stopped after 1 h and



Figure 16. A STEM image of recovered Rh species formed after 1 h of catalysis with 40 psig ethylene and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (0.001 mol % Rh relative to benzene) using untreated Cu(OAc)₂ (240 equiv relative to Rh) (left) and EDS analysis of selected single particle circled in red on the left STEM image (right).



Figure 18. Plot of TO versus time for styrene production using the solution phase of the reaction mixture after 1 h of the catalysis with 40 psig ethylene using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ under the conditions where activated $Cu(OAc)_2$ oxidant is used (A) or 5 equiv of ^{FI}DAB ligand is added (B) and its comparison to the catalysis with 40 psig ethylene using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ with the use of activated $Cu(OAc)_2$ (a) or addition of 5 equiv of ^{FI}DAB ligand (b). TO of styrene was obtained by subtracting TO at 0 h (if any) from the raw TO data. Error bars represent the standard deviations based on a minimum of three independent experiments.

filtered. The filtrates were subsequently centrifuged, and the supernatants were decanted. The reactivity of the resulting soluble Rh species with ethylene was studied by subjecting the soluble Rh species to catalytic conditions where an induction period is not observed (i.e., using activated Cu(OAc)₂ as the oxidant or using 5 equiv of ^{Fl}DAB ligand) (Figure 18). As expected, no apparent induction period is observed for either of these reactions. For both types of soluble materials, a 20–30% loss of reactivity is observed when compared to the catalysis using [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ precursor.

In addition, ICP-OES analysis has been conducted to quantify the amount of Rh content in the solution phase after 1 h of catalysis with $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ where induction period is not observed (i.e., using activated Cu(OAc)₂ or an addition of 5 equiv of ^{Fl}DAB ligand). The analysis shows that, with activated Cu(OAc)₂, soluble materials contains 68% of Rh relative to the total amount of Rh added before the catalysis, and with 5 equiv of added ^{Fl}DAB ligand, 75% of Rh is in the solution (Figure 18). This result indicates that in either case, at 1 h most of the molecular Rh species have not decomposed to insoluble Rh material but remain in the solution instead. In

contrast, as mentioned above, ICP studies of the catalysis using untreated $Cu(OAc)_2$ found that <1% of starting Rh is in solution after 1 h.

The results of reactivity tests and ICP-OES analysis indicate that the addition of activated $Cu(OAc)_2$ or diimine ligand helps stabilize soluble molecular Rh species in the reaction solution, and thus the decomposition of $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ precursor to form insoluble Rh species is suppressed. However, the ICP analysis shows a rhodium loss of approximately 20–30%, indicating that part of the soluble Rh is converted to a presumably inactive Rh precipitate. This loss in rhodium is consistent with the observed 20–30% loss of reactivity of the soluble Rh species (Figure 18).

Given that the induction period is not observed in the catalysis using soluble copper oxidants $(Cu(OHex)_2)$, we expected, in contrast to the catalysis using untreated $Cu(OAc)_2$, no significant change in the amount of soluble Rh during catalysis. We performed reactions with ethylene and 240 equiv of $Cu(OHex)_2$ under standard catalytic conditions and performed filtration/centrifugation and decantation after 15 and 45 min of reaction (the reaction reaches completion at 1 h). We found that 82% and 84% of starting Rh remained (as detected by ICP-OES) at 15 and 45 min, respectively (Table 1). In contrast, in the catalysis using untreated $Cu(OAc)_2 < 1\%$

Table 1. Comparison of Amount of Soluble Rh Material at Different Time Points in the Catalysis with 40 psig $Ethylene^{a}$

catalytic conditions	untreated Cu(OAc) ₂ , 1 h	untreated Cu(OAc) ₂ , 12 h	Cu(OHex) ₂ , 15 min	Cu(OHex) ₂ , 45 min
amount of soluble Rh material ^b	<1%	78%	82%	84%

^{*a*}Conditions: 10 mL of benzene, 0.001 mol % Rh complex (relative to benzene), and 240 equiv of Cu(II) (relative to Rh), 150 °C. ^{*b*}Determined by ICP-OES and calculated relative to the total amount of starting Rh.

and 78% of starting Rh is found in the solution phase at the 1 h (during the induction period) and 12 h (after the induction period) time point, respectively (Table 1). These results are consistent with our hypothesis that Cu(II) oxidants mitigate the conversion of soluble Rh materials to insoluble Rh. Notably, based on the amount of soluble Rh material in Table 1 (soluble Rh is considered to be catalytically active species whereas insoluble Rh material is considered to be inactive), the actual TOF of the catalysis using $Cu(OAc)_2$ (after the induction period) and Cu(OHex)₂ are $\sim 3.7 \times 10^{-3} \text{ s}^{-1}$ (calculated from 8 to 16 h) and $\sim 3.7 \times 10^{-2} \text{ s}^{-1}$ (calculated after 1 h) respectively. To eliminate the possibility that the decomposition process may occur before 1 h of catalysis, we ran the standard reaction using activated $Cu(OAc)_2$ at 125 °C to slow down the reaction rate so that we could monitor the reaction at earlier stages (Figure S20). At 125 °C, an induction period was not observed within 8 h of reaction. In addition, we performed catalysis using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ and untreated $Cu(OAc)_2$ under standard conditions until 1 h at which time it is anticipated that most of the Rh would be insoluble. The reaction mixture was subsequently treated with activated $Cu(OAc)_2$ or 5 equiv of ^{Fl}DAB ligand and then subjected to the standard catalytic conditions (Figures S21 and S22). The new catalysis with either treatment exhibited an induction

period. Thus, activated $Cu(OAc)_2$ or diimine ligand does not likely remove the induction period by facilitating the leaching process of insoluble decomposed Rh species. It is of interest to note that when a benzene solution of $[Rh(\mu-OAc)(\eta^2 (C_2H_4)_2]_2$ and 5 equiv of ^{Fl}DAB was heated under ethylene in the absence of $Cu(OAc)_2$ for 1 h and subsequently added to untreated $Cu(OAc)_2$ and tested under the standard reaction conditions, a significant induction period was observed (Figure S23). This indicates that excess diimine ligand cannot directly mitigate the degradation of molecular Rh materials. Instead, ^{Fl}DAB ligand likely suppresses the formation of insoluble Rh species by rapidly transforming commercial $Cu(OAc)_2$ to activated $Cu(OAc)_{2}$, which possesses significantly minimized particle size. In addition, $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ was heated in benzene under ethylene in the absence of $Cu(OAc)_2$ for 1 h to form insoluble Rh decomposition product. In separate experiments, the resulting reaction mixture was added to activated $Cu(OAc)_2$ and treated with the standard reaction conditions. Unlike the catalysis using $[Rh(\mu-OAc)(\eta^2 C_2H_4)_2$ precursor (Figure 5), the catalysis using the insoluble decomposed Rh materials showed no reactivity for the first 2 h under this conditions (Figure S24), indicating the reduced Rh species formed during thermal decomposition of $[Rh(\eta^2 C_2H_4)_2(\mu$ -OAc)]₂ is catalytically inactive, but after a pronounced induction period catalytic activity was observed. This is consistent with our hypothesis that upon continued heating reduced Rh species are reoxidized by $Cu(OAc)_2$ and Rh leaches back into solution to form soluble molecular Rh species that catalyze styrene production.

SUMMARY AND CONCLUSIONS

Similar catalytic reactivity and product selectivity have been observed in catalysis with ethylene and propylene using a variety of diimine ligated rhodium(I) acetate complexes and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$. This observation along with the in situ NMR studies of two representative diimine rhodium(I) acetate complexes with diimine ligands indicate that the ligated Rh complexes release diimine ligand and are likely converted into the same catalytically active Rh species under catalytic conditions. In the absence of Cu(II) oxidant, $[Rh(\mu-OAc)(\eta^2 (C_2H_4)_2]_2$ initiates ethylene C-H activation and undergoes thermal decomposition to form Rh(0) species as evidenced by ¹H NMR spectroscopy, TEM/EDS, and XPS analysis. ICP-OES analysis and reactivity comparison experiments indicate that the generation of catalytically inactive and insoluble Rh from $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]$, occurs in the early stage of catalysis (i.e., during the induction period) when commercial $Cu(OAc)_2$ is used as the oxidant. However, TEM analysis of the insoluble Rh species showed no evidence of the existence of Rh nanoparticles, and XPS studies indicate that the formed insoluble Rh species are in a higher oxidation state than Rh(0). Yet, when $Cu(OAc)_2$ is omitted, evidence for the formation of Rh nanoparticles has been obtained either in the absence or presence of silica. We hypothesize that the untreated $Cu(OAc)_2$ serves to capture the reduced Rh, as either single atoms or small clusters (which cannot be observed with current data), and this results in insoluble Rh in a higher oxidation state than Rh(0). With continued heating, the Rh trapped by $Cu(OAc)_2$ can leach back into solution to catalyze arene alkenylation.

The leaching of active soluble Rh species from the insoluble Rh materials results in observed induction periods when using commercial Cu(OAc)₂. Heating Cu(OAc)₂ in benzene prior to catalysis or the addition of extra ^{FI}DAB ligand at the beginning of catalysis is believed to mitigate the decomposition of $[Rh(\mu - OAc)(\eta^2 - C_2H_4)_2]_2$ to the insoluble Rh species. In that case, the induction period is not observed or it is shortened. Although in situ reduction of soluble Rh to form catalytically active Rh nanoparticles is precedented, to our knowledge, this is the first example of Rh catalyzed reactions attributing the origin of an induction period to a transformation of the initial molecular catalyst precursor into insoluble but catalytically inactive material followed by redissolution to form the active and soluble catalyst.

With activated $Cu(OAc)_2$ or soluble $Cu(OHex)_2$, the Rh complex $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ does not undergo initial decomposition to form insoluble Rh. While we have no direct evidence to determine how activated $Cu(OAc)_2$ or soluble $Cu(OHex)_2$ prevent the Rh decomposition, we hypothesize that Rh–H intermediates are likely involved in the reductive decomposition from $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ to Rh(0). Perhaps CuX_2 (X = OAc or OHex) with a smaller particle size or enhanced solubility in benzene serves as a more "accessible" oxidant source and thus results in a rapid reaction to convert Rh–H intermediates to Rh–X thus kinetically suppressing Rh decomposition.

These new studies allow us to speculate on the nature of the Rh species responsible for arene alkenylation. Since previous DFT calculations involved ^{FI}DAB coordinated Rh,⁵² these modeled intermediates are not likely relevant to the actual catalytic process. However, the details of the previous kinetic studies remain valid, including order in Rh, ethylene, oxidant and benzene under different conditions. The previously published kinetic data are consistent with an active catalyst that is a soluble mononuclear Rh species, although a binuclear Rh species can form as an intermediate, giving half-order kinetics in Rh, under some conditions.⁵² Our previous kinetic studies, including kinetic isotope effects $(C_6H_6 \text{ vs } C_6D_6)$ under different conditions are consistent with benzene C-H activation preceding rate limiting ethylene insertion, and new data reported herein do not contradict these conclusions. Thus, we suggest a similar catalytic cycle to our previous report, without coordination of diimine, is likely,⁵² and the XPS data are consistent with a Rh(II) catalyst resting state. More detailed characterization of possible catalytic intermediates will require additional experimental and computational studies.

EXPERIMENTAL SECTION

General Considerations. Reactions were performed under anaerobic conditions employing standard Schlenk techniques or in a nitrogen-filled glovebox unless specified otherwise. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer $(O_2 \text{ concentration was <15 ppm for all reactions})$. Tetrahydrofuran (THF) was dried over potassium benzophenone ketyl under N2. Benzene was dried by passage through columns of activated alumina. Pentane was dried over sodium benzophenone ketyl. Benzene- d_6 , was used as received and stored under a N2 atmosphere over 4 Å molecular sieves. Ethylene and propylene were purchased in gas cylinders from GTS-Welco and used as received. Copper(II) acetate and copper(II) 2ethylhexanoate were purchased from Alfa Aesar and used as received. Rhodium(II) acetate dimer was purchased from Strem Chemicals and used as received. Rhodium(III) chloride

hydrate was purchased from Pressure Chemical and used as received. All other reagents were purchased from commercial sources and used as received. $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ was prepared according to literature procedures.⁷⁸ All of the diimine ligands (diazbutadienes, or DABs) were synthesized according to literature procedures.^{79,80} $[(^{Fl}DAB)Rh(\mu-OAc)]_2$ (3) was synthesized according to literature procedures.⁵² Measurement of the ¹H, ¹³C, and ¹⁹F NMR spectra were

performed on a Varian Mercury 600 MHz spectrometer. All ¹H and ¹³C spectra are referenced against residual proton signals (¹H NMR) or ¹³C resonances (¹³C NMR) of deuterated solvents. GC/FID was performed using a Shimadzu GC-2014 system with a 30 m \times 90.25 mm HP5 column with 0.25 μ m film thickness. Infrared spectra were collected on a Shimadzu IRAffinity-1 FT-IR instrument using KBr pellets. UV-vis spectra were collected on a PerkinElmer Lambda 25 UV/vis Spectrometer. SEM images were captured using a FEI Quanta 650 Scanning Electron Microscope (SEM). Phase identification was performed using X-ray diffraction on a PANalytical X'Pert Pro MPD with a Cu source operating at 45 kV and 40 mA. The single-crystal X-ray diffraction details are given in the Supporting Information. Specific surface area was obtained by N₂ physisorption at 77 K based on the Brunauer-Emmett-Teller (BET) method on a Micromeritics ASAP 2020 analyzer.

To sample the reaction mixtures in the Fisher-Porter reactors, the reactors were cooled to room temperature, sampled under N2, recharged with olefin, and reheated. Aliquots of the reaction mixture (<100 μ L) were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene). Styrene, allylbenzene, α methylstyrene, trans- β -methylstyrene, and cis- β -methylstyrene production was quantified using linear regression analysis of gas chromatograms of standard samples of authentic product. A plot of peak area ratios versus molar ratios gave a regression line using hexamethylbenzene (HMB) as the internal standard. The slope and correlation coefficient of the regression lines were 1.67 and 0.99 (styrene), 0.87 and 0.99 (trans-stilbene), 1.40 and 0.99 (allylbenzene), 1.23 and 0.99 (α -methylstyrene), 1.47 and 0.99 (cis- β -methylstyrene), and 1.38 and 0.99 (trans- β -methylstyrene), respectively.

Procedure for TEM/EDS Experiments for TEM/EDS Experiments. Samples analyzed by transmission electron microscopy (TEM) were prepared by dispersing the powders in cyclohexane (99.5%, anhydrous, Sigma-Aldrich) and sonicating for 1 min before mounting on Au-supported holey carbon grids. The catalyst samples were imaged using a FEI Titan 80-300 operating at 300 kV. The sample was also characterized by an energy dispersive spectrometer (EDS) system in the scanning mode of TEM for single-nanoparticle composition analyses and elemental mapping. Lattice spacings were determined from selected-area electron diffraction and Fourier transforms of high resolution TEM images.

Procedure for XPS Experiments. X-ray photoelectron spectroscopy (XPS) was performed using a Phi VersaProbe III with a monochromatic Al K α X-ray source (1486.7 eV) and a hemispherical analyzer; instrument base pressure was ~10⁻⁷ Pa. Because of the air sensitivity of Rh catalysts, a PHI vacuum transfer vessel (Model 04–111) was used to protect the sample from exposure to ambient atmosphere during transfer from the glovebox to the XPS analysis chamber. An X-ray beam of 100 μ m was utilized and was rastered over 1.4 mm to reduce the X-ray flux on the target. The electron-energy analyzer was operated with a pass energy of 55 eV for high-

resolution scans with a 50 ms per step dwell time. Dual-charge compensation, using a low-energy flood gun with a bias of 1 eV and a low-energy Ar^+ beam, was utilized during data acquisition. The Si $2p_{3/2}$ peak for SiO₂ (103.5 eV) and the C 1s (284.6 eV) peak were used as a binding energy references for the spectra.

Generation of Diimine Rhodium Complexes. To a stirring solution of $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ (200 mg, 0.368 mmol) in THF (25 mL), the dimine ligand (0.735 mmol) was added, and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the solid was washed with pentane (ca., 100 mL) and dried to yield the corresponding in situ rhodium catalyst. X-ray quality crystals of representative complex 6 were grown by the vapor diffusion method using benzene and *n*-pentane. X-ray quality crystals of representative $[(^{Fl}DAB)Rh(\mu-OAc)]_2$ (3) were grown by vapor diffusion using THF and *n*-pentane. The characterization data for the representative complex 6 are as follows. ¹H NMR (600 MHz, denzene- d_6): δ 7.27 (t, J = 7.5 Hz, 2H, p-Ar-H), 7.17 (d, J = 7.6 Hz, 4H, *m*-Ar-H), 2.41 (s, 12H, *o*-CH₃), 1.47 (s, 3H, N = C- CH_3), -0.80 (s, 6H, N = C-CH₃). ¹³C NMR (151 MHz, benzene- d_6): δ 186.60 (N = C-CH₃), 156.09 (COOCH₃), 154.66 (ipso-Ar-C), 130.77 (o-Ar-C), 127.82 (m-Ar-C), 125.47 (p-Ar-C), 23.15 (COOCH₃), 19.45 (o-CH₃), 18.73 $(N = C-CH_3)$. Anal. Calcd for $C_{22}H_{27}N_2O_2Rh$: C, 58.15; H, 5.99; N, 6.17. Found: C, 58.18; H, 5.99; N, 6.17. The ¹H, ¹³C, and ¹⁹F NMR data for the representative [(^{Fl}DAB)Rh(μ - $OAc)]_2$ (3) have been reported.⁵² The elemental analysis data for $[(^{Fl}DAB)Rh(\mu-OAc)]_2$ are as follows. Anal. Calcd for C₁₈H₉F₁₀N₂O₂Rh: C, 37.39; H, 1.57; N, 4.85. Found: C, 37.69; H, 2.33; N, 5.20.

Synthesis of Silica-Supported Rh Nanoparticles. Silica-supported Rh nanoparticle catalysts were prepared via an ion exchange of the Rh precursor using Davisil 636 silica (Sigma-Aldrich) as a support.^{81,82} For example, the rhodium-(III) chloride hydrate precursor (0.250 g, 99%, Sigma-Aldrich) was dissolved in a solution of aqueous ammonia (5.428 cm³ ammonium hydroxide, ACS plus, Fisher Scientific, in 282 cm³ distilled deionized water). The metal solution was added dropwise over 10 min to 4.75 g of acid-washed Davisil 636 silica in 114 cm³ of distilled deionized water at 343 K. The metal salt and silica slurry was stirred for 60 min at 343 K and, then, cooled to room temperature. The mixture was washed with water and vacuum-dried overnight. After calcination in flowing air (medical grade, GTS-Welco) at 673 K for 2 h, the sample was prereduced in flowing H₂ (99.999%, GTS-Welco) at 523 K for 2 h.

Catalytic Alkenylation of Benzene with Ethylene and Propylene Using Cu(OAc)₂ (Untreated Cu(OAc)₂, Dried Cu(OAc)₂, Ball-Milled Cu(OAc)₂), or Cu(OHex)₂ with or without the Addition of Additives (i.e., Excess FDAB Ligand, Cu₂O, CuO, CuOAc, or HOAc). Representative catalytic reactions are described here. A stock solution containing an diimine rhodium complex or $[Rh(\eta^2 (C_2H_4)_2(\mu$ -OAc)]₂ (0.011 mmol, 0.001 mol % of Rh relative to benzene), hexamethylbenzene (0.073 g, 0.46 mmol), and benzene (200 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with stock solution (10 mL), copper(II) acetate (240 equiv relative to Rh, 0.049 g, 0.27 mmol), and additives (if any). The vessels were sealed, pressurized with ethylene (40 psig) or propylene (25 psig), and subsequently, stirred and heated to 150 °C. For the catalysis with ethylene, the reactions were sampled every 4 h

until 24 h. For the catalysis with propylene, the reactions were sampled until 48 h, when the solution turned yellowish brown and Cu oxidant is consumed.

Kinetics of Thermal Decomposition of $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ in the Absence of Cu(OAc)_2. The experiment at 100 °C in benzene- d_6 is used here as an example: 0.0075 g (0.017 mmol) of $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ was dissolved with 1.5 mL of benzene- d_6 in a volumetric flask. The solution was then equally distributed into three J-Young pressure NMR tubes. Each NMR tubes was pressurized with 35 psig N₂ to prevent the solvent from boiling. The J-Young tubes were heated in a 100 °C oil bath. Every 20 min, the J. Young tubes were taken out of the oil bath and cooled to room temperature with water. After ¹H NMR spectra were acquired, the J-Young tubes were put back into the oil bath. The experiment was stopped when the resonances from the Rh complex were no longer observed in the ¹H NMR spectra.

Isolation of Black Precipitates Formed during Thermal Decomposition of $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ in the Absence of Cu(OAc)₂. A stock solution containing $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ (0.011 mmol, 0.001 mol % of Rh relative to benzene) and benzene (200 mL) was prepared in a volumetric flask. Fisher–Porter reactors were charged with stock solution (10 mL). The vessels were sealed, pressurized with ethylene (40 psig), and subsequently, stirred and heated to 150 °C for 1 h. The resulting reaction mixtures were decanted after centrifuging to leave only black precipitates and remove any soluble materials. The solid was subsequently sonicated in cyclohexane, decanted, and the remaining solid was deposited on the grid for TEM/EDS analysis or collected for XPS analysis.

Catalytic Alkenylation of Benzene with Ethylene and Propylene after Cu(OAc)₂ Preheating Treatment in Benzene. A stock solution containing hexamethylbenzene (0.073 g, 0.46 mmol), and benzene (200 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with stock solution (10 mL) and copper(II) acetate (0.050 g, 0.28 mmol). The vessels were sealed, pressurized with N_2 (70 psig), and subsequently stirred and heated to 150 °C for 2, 4, 6, 8, 10, 12, or 24 h. A stock solution containing $[Rh(\eta^2-C_2H_4)_2(\mu OAc)_{2}$ (0.0049 g, 0.022 mmol),= and benzene (2 mL) was prepared in a volumetric flask. After preheating, the reactors were cooled to room temperature, brought into the glovebox, and charged with 0.1 mL of stock solution containing [Rh(η^2 - $(C_2H_4)_2(\mu$ -OAc)]₂. The vessels were sealed, pressurized with ethylene (40 psig) or propylene (25 psig) and, subsequently, stirred and heated to 150 or 125 °C. For the catalysis with ethylene, the reactions were sampled every 2 h until 12 h. For the catalysis with propylene, the reactions were sampled until 48 h, when the solution turned yellowish brown and Cu oxidant is consumed.

Procedure for Ball Mill. Five grams of $Cu(OAc)_2$ powder and tungsten carbide grinding balls with a weight ratio of 1:5 were added to a high density polyethylene bottle sealed in a glovebox under Argon atmosphere. The well-sealed jar was then loaded in SPEX 8000 apparatus and vibrationally ball milled for 10 min. The resulting powder was used for catalysis.

Catalytic Alkenylation of Benzene with Ethylene Using Insoluble Solid Materials or Supernatant Isolated from the Reaction Mixture after the Catalytic Styrene Production. A representative catalytic reaction is described here. A stock solution containing $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ (0.011 mmol, 0.001 mol % of Rh relative to benzene), hexamethylbenzene (0.073 g, 0.46 mmol), and benzene (200 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with stock solution (10 mL) and copper(II) acetate (240 equiv relative to per Rh, 0.049 g, 0.27 mmol). The vessels were sealed, pressurized with ethylene (40 psig) or propylene (25 psig), and subsequently stirred and heated to 150 °C for 1 h. The reactors were cooled to room temperature and brought into the glovebox. Each reaction mixture was filtered through a frit. The filtrate was centrifuged to separate any remaining insoluble solid that passed through the frits. The insoluble solid materials collected from the filtration and centrifugation were combined. For the use of ICP-OES measurement, volatile species from the supernatant were removed under vacuum and the remaining solid was sent for analysis. For the catalysis using the supernatant, new Fisher-Porter reactors were charged with copper(II) acetate (0.049 g, 0.27 mmol) and the supernatant. For the catalysis using the insoluble solid material, new Fisher-Porter reactors were charged with hexamethylbenzene (0.018 g, 0.11 mmol) and the solid material. The vessels were sealed, pressurized with ethylene (40 psig), and subsequently, stirred and heated to 150 °C. The reactions were sampled every 2 h until 12 h.

Isolation of Recovered Rh Species from Catalytic Reactions for the Use of TEM/EDS and XPS Analysis. After catalytic reactions, the reactors were cooled to room temperature and brought into the glovebox. Volatile species from the reaction mixture were removed under vacuum and the remaining solid was collected for analysis. For the use of XPS analysis, the samples were sealed in a vacuum transfer vessel in the glovebox prior to analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b01480.

Representative kinetic data, experimental procedures, and characterization data (PDF)

Crystallographic data for complex 3 (CIF)

Crystallographic data for complex 6 (CIF)

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Notes

The authors declare no competing financial interest.

CCDC 1903971-1903972 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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