# Hydrogenation of Ru(1,5-cyclooctadiene)($\eta^3$-C$_3$H$_5$)$_2$ over Black Platinum. A Low-Temperature Reactive Deposition of Submonolayer Quantities of Ruthenium Atoms on Platinum with Real Time Control over Surface Stoichiometry

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**Abstract:** Black Pt effected the hydrogenation of Ru(COD)($\eta^3$-C$_3$H$_5$)$_2$ (**1**; COD is 1,5-cyclooctadiene) by dihydrogen gas (pressure ∼1 atm) at −10 °C in hexanes. The hydrogenation resulted in adsorption of Ru adatoms by the surface of Pt with concomitant formation of propane, cyclooctane, and small amounts of *cis*-bicyclo[3.3.0]octane and *n*-octane. Compound **1** did not react with dihydrogen gas under these conditions in the absence of Pt. The total amount of cyclooctane, bicyclo[3.3.0]octane, and *n*-octane in solution was equal to the amount of **1** consumed at all stages of the hydrogenation. The lifetimes of the organic fragments on the surface were short on the time scale of the hydrogenation. It was therefore possible to observe in *real time* both the stoichiometry and the activity of the evolving Ru−Pt surface by monitoring the concentrations of either **1** or the C$_8$ product hydrocarbons in solution. There was a kinetic burst during the initial stages of the hydrogenation that ended after deposition of 0.2−0.5 equiv of Ru versus Pt$_{surface}$ (Pt$_{surface}$ is an active site on black Pt). The rate decreased after the burst and then increased as more Ru was deposited on Pt to reach a maximum, constant rate after deposition of 1.5−1.8 equiv of Ru. Cyclic voltammograms recorded in 1.0 M H$_2$SO$_4$ of the bare surface, of the surface after adsorption of a monolayer of carbon monoxide, and of the surface in the presence of methanol showed that coverage of Pt by Ru was essentially complete after the maximum, constant rate was achieved during hydrogenation of **1**. The surface area of a Ru surface resulting from hydrogenation of 2.7 equiv of **1** was 67% that of the original Pt surface according to the charge associated with oxidation of an adsorbed monolayer of carbon monoxide. Anodic stripping of Ru showed that the total of C$_8$ hydrocarbon products in solution after hydrogenation of **1** equaled the amount of Ru deposited on Pt. A catalyst surface resulting from hydrogenation of 0.11 equiv of **1** was up to ∼14 times more active than bare Pt for the potentiodynamic oxidation of methanol ([MeOH] = 1.0 M, [H$_2$SO$_4$] = 0.5 M, 40 °C, sweep rate 5 mV/s). A catalyst surface resulting from hydrogenation of 0.33 equiv of **1** oxidized methanol potentiostatically at 0.158 V (vs SCE, [MeOH] = 0.5 M, [H$_2$SO$_4$] = 0.5 M, 25 °C) for 45 min with ∼13 times the activity of Pt under the same conditions. A catalyst surface resulting from deposition of 0.8 equiv of Ru oxidized methanol potentiostatically at 0.256 V (vs SCE) under the above conditions for a total of 1.5 h with negligible dissolution of Ru into the electrolyte.

## Introduction

This paper describes the hydrogenation of (COD)Ru($\eta^3$-C$_3$H$_5$)$_2$ (**1**; COD is 1,5-cyclooctadiene) by dihydrogen gas in hexanes solution over black Pt. The major objective of this work was to deposit controlled submonolayer or multilayer quantities of Ru adatoms on Pt metal using a chemical reaction between a dissolved ruthenium hydrocarbonyl compound and the Pt surface. Bimetallic clusters of Ru and Pt have been used to catalyze the hydrogenation of arenes,[1] the hydrogenolysis of propane,[1] the hydrogenation of carbon monoxide,[2] and the electrochemical oxidation of methanol in fuel cells.[3] Ru−Pt metallic clusters are typically prepared by chemical or electrochemical reduction of Ru and Pt compounds (e.g., chlorides, oxides, hydroxides, and amines) in the presence of a support.[3q−x,4] As is the case with most preparations of bimetallic clusters, the surface compositions and oxidation states of the resulting clusters are often ambiguous. Sources of ambiguity include variations in the rates of mass transport to the sites of cluster

growth, surface segregation during high-temperature stages of the synthesis (e.g., during reductions of precursors and during

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electrode pressing), interactions with the support, and dissolution of Ru during pretreatment by potential cycling.[3a,4a,f,h,p,5]  The method now used to synthesize bimetallic clusters that provides the most control over surface composition involves a two-step process in which a hydrocarbonyl compound of one of the metals is deposited on a support containing metal clusters of the other metal.[6]  The hydrocarbonyl compound is then reduced by dihydrogen gas at elevated temperatures.[1,7]  Control over the surface composition of several types of bimetallic clusters has been achieved by adjusting the ratio of the amount of hydrocarbonyl originally introduced to the system to the number of active sites on the clusters of the other metal (limiting-reagent control).  In contrast with limiting-reagent control, our approach was to develop a clean deposition reaction that allowed for monitoring the extent of deposition *in situ*, and that could be interrupted when the desired surface stoichiometry was achieved (reaction-rate control).

In 1988, Whitesides *et al.* reported that (diolefin)dialkylplatinum(II) complexes were reduced by dihydrogen gas over Pt black to generate the corresponding alkanes and Pt(0) that was incorporated onto the surface of Pt black.[8]  We now disclose that hydrogenation of **1** in hexanes by dihydrogen gas was also effected by black Pt, and that the hydrogenation resulted in adsorption of Ru adatoms by the surface of Pt (eq 1).
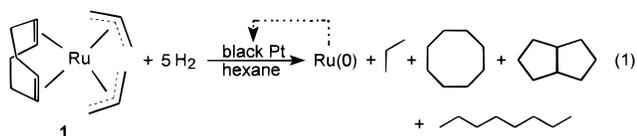


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(6) Either the hydrocarbonyl compound of the second metal is physisorbed on the support and migrates to the metal clusters of the first metal during the reduction by dihydrogen,[1] or the hydrocarbonyl is grafted onto the surface of the first metal before reduction by dihydrogen. The latter process is called surface organometallic chemistry.[7]

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## Results and Discussion

**General Methods.**  Compound **1** was prepared as described in the literature[9] and sublimed immediately before use.  This compound has the attractive features that it can be prepared in pure form and that it contains no components (halide ions, phosphines, carbonyls, heteroatoms) that might act as catalyst poisons.  We used a blacked Pt gauze as substrate.[10]  The surface area of the black Pt was determined from the Coulombic charge in the cathodic hydride region of cyclic voltammograms recorded in a 1.0 M aqueous solution of $H_2SO_4$ under argon.[11]  We then used the following procedure to transfer the gauze from the aqueous acid electrolyte to the vessel in which the hydrogenation was carried out.  First, the surface of the gauze was protected as oxides by holding the potential at 1.2 V (all potentials in this paper are reported relative to the saturated calomel electrode (SCE)) for 2 min.  Second, the gauze was raised above the electrolyte and rinsed with purified water under argon.  Third, while protected by drops of purified water,[12] the gauze was quickly transferred through air to the hydrogenation vessel.  Fourth, the gauze was dried under a stream of argon and then placed under an atmosphere of dihydrogen gas to reduce the surface oxides to hydrides.  The gauze was then immersed in dihydrogen-saturated hexanes at the desired reaction temperature.  The reaction mixture was rapidly stirred (800 rpm), and a continuous stream of dihydrogen gas (~10 mL/min) was bubbled through the solution during the hydrogenation to ensure that mass transfer of dihydrogen to the surface of the gauze was not rate limiting (reaction-rate-limiting conditions rather than mass-transport-limiting conditions).[8]  To determine if significant changes in surface area occurred during these manipulations, a control experiment was performed in which the above procedure was repeated in the absence of **1**.  After being immersed in a blank hexanes solution under dihydrogen gas for a typical time of reaction, the Pt gauze was lifted above the hexanes under dihydrogen gas in the hydrogenation vessel, the hexanes were removed by cannula from the vessel, and the gauze was dried under a stream of dihydrogen gas.  Protected under several drops of purified water, the gauze was quickly transferred through air to an electrochemical cell containing a 1.0 M solution of $H_2SO_4$ in water under argon, and the surface area was determined again using cyclic voltammetry.  Little change (a decrease by ~6%) in the surface area of the black Pt had occurred during these manipulations.

**Hydrogenation of 1.**  To begin a hydrogenation, a solution of **1** and a decane internal standard dissolved in hexanes were quickly and quantitatively transferred to the reactor under dihydrogen.  Aliquots were removed at timed intervals.  The aliquots were analyzed by gas chromatography (GC) and the concentrations of product hydrocarbons were determined, and by the UV−vis absorbance of the solution and the decrease in concentration of **1** was determined.  Since the products of the hydrogenation were alkanes and Ru(0) adsorbed on the surface of Pt, the only component of the hydrogenation mixture with a significant UV−vis absorbance was **1**.  Control experiments[13] showed that reaction between **1** and dihydrogen gas did not occur under these conditions in the absence of Pt.

(9) Albert, M. O.; Singleton, E.; Yates, J. E. *Inorg. Synth.* **1989**, *26*, 249.

(10) A shiny 52 mesh platinum gauze was connected to a platinum wire that was sealed to a uranium glass tube. The gauze was blacked as described in DiCosimo, R.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 768.

(11) Woods, R. *Electroanal. Chem. Interfacial. Electrochem.* **1974**, *49*, 217.

(12) Use of prepurified water to protect platinum surfaces during transfer in air is an established technique often used in electrochemistry with platinum electrodes. See: Clavilier, J.; Faure, R.; Guinet, G. Durand, R. *J. Electroanal. Chem.* **1980**, *107*, 205.

(13) Monitored by GC and by ^{1}H NMR spectroscopy.
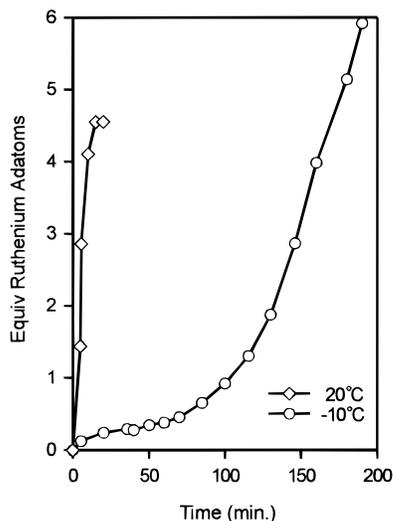
**Figure 1.** Number of equivalents of Ru adatoms deposited on Pt by hydrogenation of **1** versus time for reactions carried out at 20 and −10 °C. The number of equivalents of Ru was determined from the total amount of C8 product hydrocarbons in solution.



**Figure 2.** Number of equivalents of **1** consumed and total number of equivalents C$_8$ hydrocarbon products produced in solution versus time for a hydrogenation of **1** carried out at −10 °C.

The nature of the hydrocarbon products (as determined by gas chromatography−mass spectrometry) from the hydrogenation of **1** depended on the reaction temperature. Propane,[14] cyclooctane (89% of C$_8$ products), *cis*-bicyclo[3.3.0]octane (8% of C$_8$ products), and *n*-octane (3% of C$_8$ products) were produced at room temperature. Free COD in solution was not detected. Propane, cyclooctane (95% of C$_8$ products), and *cis*-bicyclo[3.3.0]octane (5% of C$_8$ products) were produced at −10 °C. The ratio of C$_8$ products did not change within experimental error over the course of the hydrogenation. The absence of *n*-octane at −10 °C indicated that its formation proceeded via a higher energy pathway than hydrogenation of **1**.

Figure 1 shows plots of the number of equivalents of Ru adatoms (based on hydrocarbon products in solution) adsorbed by Pt versus time for hydrogenations carried out at 20 °C and −10 °C. The number of equivalents of Ru is relative to the initial number of sites on black Pt, and it was assumed to equal the total number of equivalents of cyclooctane, *cis*-bicyclo[3.3.0]-octane, and *n*-octane in each aliquot as determined by GC.

There was a kinetic burst during the initial stages of the hydrogenations carried out at −10 °C that ended after deposition of 0.2−0.5 equiv of Ru. The size of the burst varied among Pt samples. The rate of hydrogenation slowed after the burst, and then increased as more Ru was deposited on Pt to reach a maximum, constant rate after deposition of 1.5−1.8 equiv of Ru. This rate remained constant until **1** was depleted from solution.

Figure 2 shows a plot of consumption of **1** and total production of all C$_8$ product hydrocarbons (cyclooctane and *cis*-bicyclo[3.3.0]octane) in solution between hydrogenation of 0 and ∼1.8 equiv **1** at −10 °C, when submonolayer quantities of Ru adatoms were adsorbed by the surface of Pt. The rates of consumption of **1** and of formation of C$_8$ hydrocarbons were the same within experimental certainty. The decrease in **1** and the increase in C$_8$ hydrocarbons in solution were also the same within experimental certainty at all stages of the hydrogenation. Since there was no observable time lag between consumption of **1** and the formation of C$_8$ hydrocarbons in solution, we conclude that the lifetimes of the surface hydrocarbonyls were short on the time scale of the hydrogenation. It was therefore possible to observe in *real time* the number of Ru adatoms
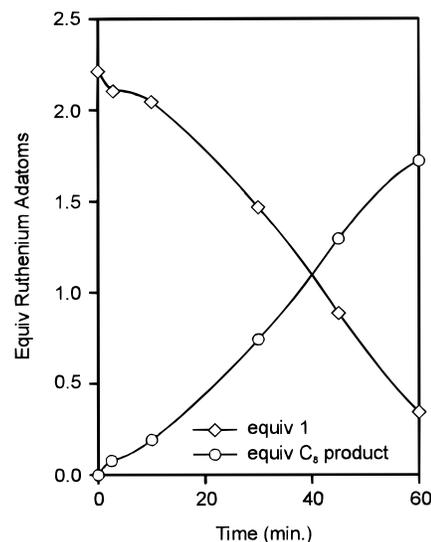
adsorbed by the Pt surface by monitoring either the concentration of **1** or the total concentration of C$_8$ hydrocarbon products in solution.

As the lifetimes of the surface hydrocarbonyls appear short on the time scale of the hydrogenation, the curves in Figures 1 and 2 show the actual evolution of the surface's activity toward hydrogenation of **1** as the coverage of Pt by Ru increased. Kinetic bursts similar to those observed during low-temperature hydrogenations of **1** (Figures 1 and 2) were also observed by Whitesides *et al.* during low-temperature hydrogenations of (COD)Pt(Me)$_2$ over Pt black carried out under reaction-rate-limiting conditions.[8] We believe the bursts during hydrogenation of **1** resulted from a proportion of the active sites on Pt being substantially more active than the others, and that these highly active sites reacted quickly during the initial stages of the hydrogenation. An alternative interpretation is that the initial burst was caused by the surface being saturated with dihydrogen at the beginning of the hydrogenation, and that the decrease in rate after the burst resulted from limitations in mass transport of dihydrogen to the surface. We do not feel that mass transport of dihydrogen limited the rate of hydrogenation after the initial burst because the rate of reaction increased as more Ru was deposited on Pt.

The increase in rate after the burst indicated that Ru was more active than Pt toward hydrogenation of **1**. We believe that the rate increased until all the active sites on Pt were covered by Ru. To investigate this possibility, we interrupted hydrogenations after the maximum, constant rate was achieved and analyzed the resulting surfaces using cyclic voltammetry.

**Characterization of the Ru Surface.** We interrupted hydrogenations after the desired number of equivalents of Ru was deposited on Pt (as determined by GC or by UV−vis absorbance) by quickly lifting the gauze above the reaction mixture, rinsing the gauze in the reactor with cooled (−10 °C) dihydrogen-saturated hexanes, removing the hexanes from the reactor, and drying the gauze under a stream of dihydrogen gas. The reactor was transferred to a glovebox, and the gauze, protected by surface hydrides, was transferred through the atmosphere of argon in the glovebox to an electrochemical cell. An argon-saturated 1.0 M aqueous solution of H$_2$SO$_4$ was transferred to the cell while the gauze was held above the level of the solution, and according to procedures developed by

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(14) Identified using GC but not quantified.
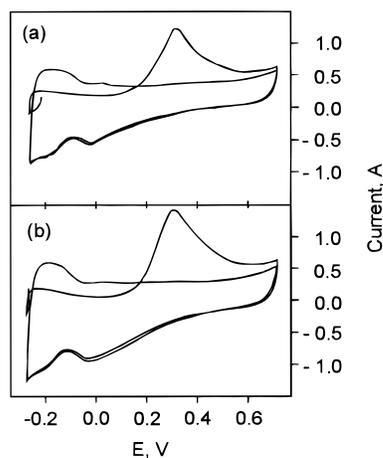
**Figure 3.** (a) Cyclic voltammograms (sweep rate 5 mV·s$^{-1}$ in 1.0 M H$_2$SO$_4$) of a catalyst surface resulting from hydrogenation of 2.7 equiv of **1** recorded before and after adsorption of a monolayer of carbon monoxide at $-0.19$ V. (b) Cyclic voltammograms of a black Ru electrode recorded under conditions identical with those in (a). The voltammograms in (a) and (b) are not normalized for surface area.
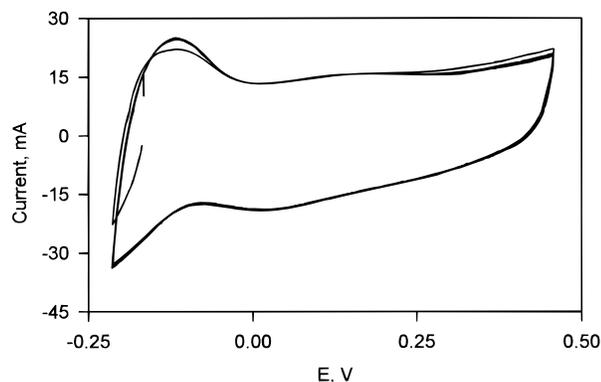


**Figure 4.** Cyclic voltammograms (sweep rate 5 mV·s$^{-1}$, [H$_2$SO$_4$] = 0.5 M, [MeOH] = 0.5 M, 25 °C) of a catalyst surface generated by hydrogenation of 3.5 equiv of **1**.

Gasteiger *et al.*,[3g] the potential of the gauze was set to $-0.19$ V concurrent with immersion of the gauze into the electrolyte.

We analyzed a surface resulting from hydrogenation of 2.7 equiv of **1** by recording voltammograms before and after adsorption of a monolayer of carbon monoxide. The voltammograms were compared to those of a control black Ru surface prepared by electrochemical deposition of excess Ru on a black Pt gauze. As described by other workers, the carbon monoxide was adsorbed at $-0.19$ V before initiating the potential sweeps.[15] These workers showed using bulk Ru—Pt alloys that the potential of the anodic wave for oxidation of adsorbed carbon monoxide depended on the ratio of Ru and Pt atoms at the surface.[15] Figure 3 shows the cyclic voltammograms. The voltammograms of the control black Ru surface and the surface resulting from hydrogenation of 2.7 equiv of **1** were quite similar both in shape and in peak positions before and after adsorption of the carbon monoxide. To further characterize the surface after the maximum, constant rate was achieved during hydrogenation of **1**, voltammograms were recorded in an aqueous solution of H$_2$SO$_4$ and MeOH of a surface resulting from hydrogenation of 3.5 equiv of **1**. Figure 4 shows the resulting voltammograms. Neither was there adsorption of methanol, nor were there appreciable oxidation currents below 0.46 V. This

behavior is identical to that observed by Gasteiger et al. using a pure Ru surface.[3g]

We believe that, first, the nearly identical electrochemical behaviors of the control black Ru surface and of the surfaces resulting from hydrogenation of 2.7 and 3.5 equiv **1** and that, second, the maximum, constant activity of the surface toward hydrogenation of **1** indicated that the coverage of Pt by Ru was essentially complete after adsorption of 1.5−1.8 equiv of Ru by the surface of Pt. That more than 1 equiv of Ru was required to cover the active sites on Pt was likely due to a combination of factors. These factors include uncertainties in the measured surface area of black Pt, hydrogenation occurring on the adsorbed Ru as well as on Pt, the mobility of the Ru atoms on the surface, the relative affinities of Ru adatoms for Ru and for Pt, and the fact that more than 1 equiv of Ru adatoms was likely required to cover the rough atomic morphology of black Pt. We also note that the radius of Ru is ∼96% that of Pt.[16] We therefore use the number of equivalents of Ru in Figures 1 and 2 as an approximate measure of surface composition.

We estimated the surface area of the catalyst surface after hydrogenation of 2.7 equiv of **1** using the charge associated with oxidation of a monolayer of adsorbed carbon monoxide. The measured surface area was 67% that of the black Pt before hydrogenation of **1**. Oxidation of carbon monoxide can only be used to approximate the surface area of Ru.[15,17] We therefore propose only that major changes in surface area did not occur during hydrogenation of **1**.

**Composition of the Ru Deposit.** We determined the amount of Ru deposited on Pt after several hydrogenations by anodic stripping of Ru from the resulting surfaces. Anodic stripping was carried out in 1.0 M aqueous solution of NaOH at room temperature using a 9 V battery as power source.[18] UV−vis spectroscopy showed that Ru in the resulting electrolyte was mainly in the form of sodium ruthenate. The amount of Ru in solution was determined by inductively coupled plasma spectrophotometry (ICP) and was found to equal the total of cyclooctane, *cis*-bicyclo[3.3.0]octane, and *n*-octane in the hydrogenation mixture as determined by GC. All the Ru atoms generated by hydrogenation of **1** were therefore adsorbed by the surface of Pt. These results, taken together with the results of the GC−UV−vis studies shown in Figure 2 indicate that little, if any, carbon from COD was trapped by the Ru deposit.

The chemical composition of the Ru deposit was further investigated by hydrogenating at room temperature ∼30 equiv of **1** over Pt black powder with an approximate dispersion of 8%.[19] The molar ratio of Ru to Pt in the resulting particles was 2.9:1 according to neutron activation analysis.

**Oxidation of Methanol by Ru−Pt Surfaces.** Figure 5 shows the potentiodynamic activity for oxidation of methanol by black Pt and by a black Ru−Pt catalyst resulting from interrupting a hydrogenation of **1** after deposition of 0.11 equiv of Ru. The onset of oxidation was ∼100 mV lower for Ru−Pt than for Pt, and the current remained higher (by up to a factor of ∼14) until the potential reached ∼0.65 V. This behavior is similar to those of the bulk alloys of Ru−Pt studied by Gasteiger et al. for which the surface compositions were precisely known.[3g] The activity of the Ru−Pt surface noticeably de-

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(16) The metallic radii of platium and ruthenium are 139 and 134 pm, respectively. See: *Tables of Physical and Chemical Constants*, 15th ed.; Kaye, G. W. C., Laby, T. H., Eds.; Longman Inc: New York, 1986.

(17) (a) Kinoshita, K.; Ross, P. N. *J. Electroanal. Chem.* **1977**, *78*, 313. (b) Bett, J.; Kinoshita, K.; Routis, K.; Stonehart, P. *J. Catal.* **1973**, *29*, 160.

(18) For a related procedure see: Connick, R. E.; Hurley, R. *J. Am. Chem. Soc.* **1952**, *74*, 5012.

(19) We used Johnson Matthey, fuel-cell grade Pt black as substrate for these experiments. The surface area is reported to be 25 m$^2$/g.

**Figure 5.** Potentiodynamic oxidation of methanol ([MeOH] = 1.0 M, [H₂SO₄] = 0.5 M, 40 °C, sweep rate 5 mV·s⁻¹) by black Pt and by a Ru−Pt catalyst surface resulting from hydrogenation of 0.11 equiv of **1**. The currents are normalized to 4.1 $\mu$mol of surface atoms.
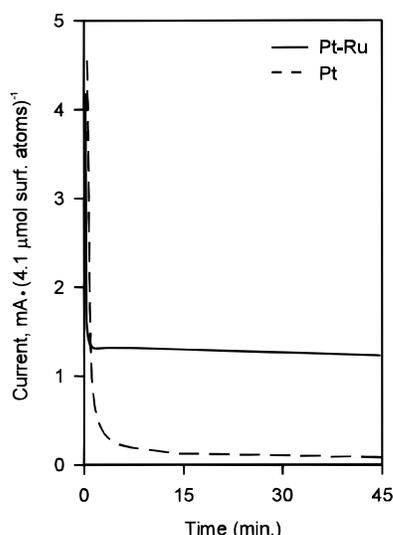


**Figure 6.** Potentiostatic oxidation of methanol ([MeOH] = 0.5 M, [H₂SO₄] = 0.5 M, 25 °C) by black Pt and by a Ru−Pt catalyst surface resulting from hydrogenation of 0.33 equiv of **1**. The currents are normalized to 4.1 $\mu$mol of surface atoms.

creased after four sweeps up to 1.0 V. Ru dissolves in sulfuric acid solutions at potentials above ∼0.65 V,[5a−c] and we believe that this decrease in activity was caused by dissolution of Ru above this potential. Analysis (ICP) of the electrolyte for Ru ions after six sweeps showed that ∼54% of the Ru originally on the surface had dissolved.

To study the stability of these surfaces near the upper operating potentials of an anode in a methanol fuel cell, we carried out a potentiostatic oxidation of methanol at 0.158 V for 45 min using a Ru−Pt catalyst surface resulting from interrupting a hydrogenation of **1** after deposition of 0.33 equiv of Ru. Figure 6 shows the variation of current with time for the potentiostatic oxidation of methanol using both the Ru−Pt catalyst and black Pt in aqueous solutions of H₂SO₄ and MeOH. A high initial current followed by a rapid decrease to a lower, more steady value is typical behavior for the electrochemical oxidation of methanol using catalysts that contain Pt. It is believed that the high initial current results from the rapid dehydrogenation of methanol and oxidation of the resulting surface hydrides. The loss in initial current is proposed to result

from poisoning of the catalyst surface by carbon monoxide or COH.[3g,20−22] For both the Ru−Pt and the Pt catalysts, the current generated by the poisoned surfaces decreased slightly over the course of the oxidations. The current generated by the poisoned Ru−Pt surface remained higher than that of the Pt surface by a factor of ∼13, indicating that surfaces resulting from deposition of submonolayer quantities of Ru on Pt by hydrogenation of **1** are appreciably durable under these conditions.

To determine if dissolution of Ru into the electrolyte occurred under these conditions, we carried out a potentiostatic oxidation of methanol at 0.256 V (a higher potential than the previous potentiostatic oxidation) first for 0.5 h, and then for an additional 1 h using a Ru−Pt catalyst surface generated by hydrogenation of 0.8 equiv of **1**. Analysis using ICP showed only traces of Ru ions in the electrolyte after the first 0.5 h. The signal was too small to accurately quantify, but roughly corresponded to 0.06% of the Ru originally on the surface. ICP analysis of the same electrolyte after oxidation of methanol for a further 1 h showed no change in the amount of Ru ions in solution.

**Conclusions.** Hydrogenation of **1** by dihydrogen gas over Pt at −10 °C is among the lowest energy processes we are aware of for deposition of adatoms of a foreign metal on the surface of another metal.[23] It appears to allow for the first time generation of a prototypic kinetic bimetallic surface with real time control over the stoichiometry and activity of the evolving surface. We believe this system offers certain advantages over conventional methods of deposition of metal adatoms (e.g., metal atom evaporation and chemical vapor deposition), namely, providing uniform coverage over all exposed sides of a rough, blacked metal surface after adsorption of less than 2 equiv of adatoms, allowing for deposition of submonolayer equivalents of adatoms under reaction-rate control at low temperatures, allowing for use of simple, bench-top equipment and techniques, and use of a Ru precursor (**1**) containing no components that may poison the resulting catalyst surface. Further, the resulting Ru−Pt surfaces had appreciable activities and durability toward both the potentiodynamic and the potentiostatic oxidation of methanol under conditions that are typical for an operating fuel cell. Since this deposition proceeded via a reaction with a metal surface, it will in principle allow for self-directed depositions on Pt clusters dispersed on an inert support. Finally, we propose that the combination of Pt and Ru is not unique, and that this methodology can be applied to a number of metal systems provided the appropriate precursors are employed.

## Experimental Section

**General Procedures.** Argon (Linde, prepurified) was passed through molecular sieves (Anachemia, activated type 4 Å) prior to use. Dihydrogen (Linde, prepurified) and carbon monoxide (Matheson, ultrahigh purity) were used as received. Water was deionized, distilled from alkaline permanganate under nitrogen, and purged with argon for

(20) Watanabe, M.; Motoo, S. *Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 267.

(21) Franaszczuk, K.; Sobkowski, J. *J. Electroanal. Chem.* **1992**, *327*, 235. Wang, S.; Fedkiw, P. S. *J. Electrochem. Soc.* **1992**, *139*, 2519.

(22) Iwasita, T.; Nart, F. C.; Vielstich *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1030. Kunimatsu, K. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1025. Wasmus, S.; Vielstich, W. *J. Appl. Electrochem.* **1993**, *23*, 120.

(23) A low-energy deposition related to hydrogenation of **1** is electroless deposition. For examples, see: Lamouche, D.; Clechet, P.; Martin, J. R.; Haroutiounian, E.; Sandino, J. P. I. *J. Electrochem. Soc.: Solid-State Sci. Technol.* **1987**, *134*, 692. Baum, T. H. *J. Electrochem. Soc.* **1990**, *137*, 252. Stremsdoerfer, G.; Martin, J. R.; Clechet, P.; Nguyen-Du. *J. Electrochem. Soc.* **1990**, *137*, 256. Murphy, M. M.; Van herle, J.; McEvoy, A. J.; Thampi, K. R. *J. Electrochem. Soc.* **1994**, *141*, L94. Wang, Y. F.; Pollard, R. *J. Electrochem. Soc.* **1995**, *142*, 1712 and references cited therein. As far as we are aware, control over submonolayer quantities of adatoms has not been achieved with electroless deposition.

30 min prior to use. Hexanes (BDH, HPLC grade) were stirred over concentrated $H_2SO_4$ for 24 h, passed through aluminum oxide (grade 1), hydrogenated (pressure of dihydrogen 1 atm) over platinum black for 24 h, and distilled under argon. Heptane and decane were purified similarly. Methanol (BDH, HPLC grade) was distilled from Mg-(OCH$_3$)$_2$ under argon. Diethyl ether (Calendon) was distilled from potassium/benzophenone under argon. Cyclohexane-$d_{12}$ was flash distilled from potassium/benzophenone under argon and degassed by three freeze−pump−thaw cycles. $H_2SO_4$ (ACS grade, BDH) was used as received. Rubber septa were extracted for 24 h with HPLC grade hexane in a Soxhlet extractor, and dried under vacuum. All glassware was rinsed with a 1:5 mixture of 30% aqueous hydrogen peroxide/concentrated $H_2SO_4$, water, a 5% mixture of ammonium hydroxide in absolute ethanol, and ethanol and dried in an oven. ($\eta^4$-1, 5-Cyclooctadiene)Ru($\eta^3$-C$_3$H$_5$)$_2$ (**1**) was prepared by a literature method[9] and twice sublimed under vacuum.

The reactor used for the hydrogenations was a 2.3 × 10.3 cm Pyrex tube containing a 4 × 14 mm Teflon-coated magnetic stir bar and fitted with a rubber septum pierced with a disposable pipet (used as a dihydrogen gas inlet) and a glass tube supporting the blacked platinum gauze.

Electrochemical experiments were performed using a Pine Bipotentiostat Model AFCBP1 controlled with Pinechem 2.00 software or using a homemade potentiostat equipped with a Hewlett-Packard 7004 chart recorder. Inductively coupled plasma spectroscopy (ICP) was performed using a Perkin-Elmer Optima equipped with an atomic emission detector. Gas chromatography−mass spectrometry was performed using a VG-7070E with a Varian 6000 GC fitted with a 30 m J&B DB5 column using a MSS data system. Electrolytes were purged with argon for at least 10 min prior to use, and electrochemical experiments were performed under argon unless stated otherwise. The reference electrode was an anodized silver wire behind a D-porosity glass frit, but potentials are referred to a standard calomel electrode in the same electrolyte. The counter electrode was a blacked platinum wire behind a D-porosity glass frit. Gas chromatography (GC) was performed on a Hewlett-Packard series 530 $\mu$m × 10 m methyl silicone column, model no. 19057-121, fitted to a Hewlett-Packard 5980A gas chromatograph with a Hewlett-Packard 3392A integrator. $^1$H NMR spectra were measured on a Bruker AM-400 NMR spectrometer operating at 400.13 MHz.

**Blacked Platinum.** Platinum gauze (52 mesh, 99.9%, 25 × 25 mm, Aldrich) was threaded with platinum wire (∼200 mm in length, 0.127 mm in diameter, 99.9%, Aldrich) and supported by flame sealing the wire leads through 3 mm uranium glass tubing. The gauze was blacked[10] and its surface area determined from the coulometric charge of the hydrogen adsorption region in cyclic voltammograms recorded in 1.0 M $H_2SO_4$ according to literature procedures.[11] The blacked platinum was then held at 1.2 V for 2 min, rinsed with four 2 mL portions of purified water under argon, and quickly transferred wet through air to the hydrogenation reactor. The blacked platinum was dried with a stream of argon for 3 h, and exposed to a stream of dihydrogen gas for a further 1 h to reduce the surface oxides and to remove the resulting water.

**Hydrogenation of 1 over Blacked Platinum.** Dihydrogen-purged hexanes (15 mL) were transferred via cannula to the reactor containing the hydrogen-saturated blacked platinum, and the reactor was immersed into the cooling bath. The blacked Pt was kept above the hexanes until the hydrogenation was begun. A slow stream (∼10 mL/min) of dihydrogen was passed through the solution throughout the reaction. Freshly sublimed **1** (10−12 mg) was weighed into a small vial in a drybox, and the vial was capped with a rubber septum. A weighed amount of decane was added to the vial containing **1** using a 5 $\mu$L syringe to act as an internal standard for GC analysis. The contents of the vial were dissolved in hexanes and then quantitatively transferred to the reactor with a cannula and with several rinses with hexanes, and the volume of solution in the reactor was brought up 20 mL. The stir rate was set at 800 rpm,[24] the platinum was immersed into the reaction mixture, and timed aliquots (100−300 $\mu$L) were cannulated from the reaction mixture. The aliquots were analyzed using GC and UV spectrophotometry. To interrupt the hydrogenation at a desired

coverage, the platinum was raised above the solution, and the solution was cannulated out of the reactor. The catalyst surface and the reactor walls were rinsed with four 5 mL portions of hexanes, and the catalyst was dried under a stream of dihydrogen gas for 30 min.

**Control Experiments.** The entire hydrogenation procedure was repeated in the absence of **1**. The surface area of the platinum as determined using cyclic voltammetry had decreased by 6% during the treatment by dihydrogen.

Dihydrogen (pressure ∼1 atm) was bubbled through a hexane (40 mL) solution of **1** (25 mg) for 30 min at room temperature. Analysis of the solution by GC showed no reaction occurred. This experiment was repeated in cyclohexane-$d_{12}$ at a higher concentration (39.6 mg of **1** in 2.5 mL of solvent). Analysis by $^1$H NMR spectroscopy also showed that no reaction occurred after 30 min.

**Anodic Stripping of Ruthenium.** The ruthenium−platinum surface obtained by hydrogenation of **1** was transferred in air to an electrochemical cell that contained a Teflon-coated stirbar and a 1.0 M solution of NaOH in argon-purged water (80 mL). The black platinum counter electrode was fitted behind a D-porosity glass frit. The cathode ("+" terminal) of a 9 V battery was connected to the ruthenium−platinum electrode, and the anode ("−" terminal) was connected to the counter electrode. The solution was stirred under argon for 10−30 min as the color of the solution turned orange. The solution was quantitatively transferred to a 100 mL volumetric flask and diluted to volume with 1.0 M NaOH. The amount of ruthenium in solution was determined using ICP analysis. UV−vis spectra of the solutions indicated that the product of the anodic stripping was sodium ruthenate.[25] Further anodic stripping in fresh electrolyte showed that all the ruthenium was stripped from the electrode by this treatment.

**Hydrogenation of 1 Over Platinum Black.** In air, platinum black (10−11 mg, Johnson Matthey, fuel cell grade) was weighed into a 3 dram, 21 × 50 mm vial containing a 4 × 14 mm Teflon-coated magnetic stir bar and capped with a rubber septum pierced with two steel needles used as a gas inlet and outlet. The reactor was flushed with argon for 10 min and then placed under an atmosphere of dihydrogen gas. Hexanes (∼3 mL) were added via cannula to a 3 dram vial that was capped with a rubber septum and that contained freshly sublimed **1** (42−48 mg, weighed in a drybox). The solution of **1** in hexanes was flushed with a stream of dihydrogen gas (∼20 mL/min) for 2 min. Hexanes (∼1 mL) were added via cannula to the reactor containing the hydrogen-saturated platinum black, and a stream of dihydrogen gas (∼20 mL/min) was passed through the hexanes for 1 min while the mixture was stirred at ∼400 rpm. The solution of **1** in hexanes was transferred to the reactor with a cannula using an additional ∼2 mL of hexanes for rinses. The total volume of the solution in the reactor was brought up 6 mL. A stream of dihydrogen (∼10 mL/min) was passed through the reaction for the duration of the reaction. After 24 h at room temperature, the solution was drained using a cannula and the contents of the reactor were rinsed with hexanes (three ∼5 mL portions). The contents of the reactor were then dried at room temperature under vacuum (∼0.01 Torr) for 2 h.

**Neutron Activation Analysis.** Samples and standards, packed in HNO$_3$-washed polyethylene 100 mL tubes, were individually irradiated for 300 s at a neutron flux of 1 × 10$^{11}$ n cm$^{-2}$ s$^{-1}$ in an inner site of the University of Alberta SLOWPOKE II Nuclear Reactor. Following a decay period of 18 min, each sample was counted for 300 s at a sample-to-detector distance of 3 cm using a 34% hyperpure Ge detector attached to an 8k channel PC-based multichannel analyzer. Analysis was performed by the comparator method of INAA using RuCl$_3$·3H$_2$O and K$_2$PtCl$_6$ (98%) as standards. Platinum was quantified using the 542.96 and 185.76 keV $\gamma$-ray emissions of $^{199}$Pt ($T_{1/2}$ = 30.8 min) produced *via* the reaction $^{198}$Pt(n, g) → $^{199}$Pt while Ru was determined using the 724.27 keV $\gamma$-ray emission of $^{105}$Ru ($T_{1/2}$ = 4.44 h) produced *via* the thermal neutron reaction $^{104}$Ru(n, g) → $^{105}$Ru.

**Adsorption and Oxidation of Carbon Monoxide.** A ruthenium−platinum surface was prepared by hydrogenation of 2.7 equiv of **1**. The reaction vessel containing the rinsed and dried electrode was transferred to a glovebox, and the electrode was transferred to the electrochemical cell under argon. The cell was removed from the glovebox, flushed with argon, and fitted with two disposable pipets

(24) With the aid of a calibrated strobe light.-

(25) Connick, R. E.; Hurley, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 5012.

(to be used as gas inlets), with a reference electrode, and with a counter electrode. An argon-purged solution of $H_2SO_4$ (1.0 M in water) was transferred to the cell via a polyethylene cannula. The potential of the ruthenium−platinum working electrode was set to −0.19 V concurrent with immersion into the electrolyte. With stirring (700 rpm) at room temperature, carbon monoxide was bubbled through the solution for 30 min followed by bubbling argon through the solution for 2 min. The stirring was stopped, and the potential of the working electrode was swept at 5 mV/s up to 0.723 V and then down to −0.262 V.

A control black ruthenium electrode was prepared by potentiostatic deposition of ruthenium on a black platinum electrode at −0.267 V for 15 min from a stirred solution of $RuCl_3\cdot3H_2O$ (0.005 M) and $H_2$-$SO_4$ (1.0 M) in water. Using the Coulombic charge passed during the deposition, we calculate that 15 equiv of Ru was deposited on the electrode surface. The electrode was rinsed with $H_2SO_4$ and transferred quickly in air to the electrochemical cell, and the oxidation of adsorbed carbon monoxide was repeated as described above.

**Oxidations of Methanol.** A hydrogenation of **1** was interrupted as described above after deposition of 0.11 equiv of ruthenium. The rinsed and dried catalyst surface was transferred in a glovebox to an electrochemical cell. An argon-purged aqueous solution (90 mL) of $H_2SO_4$ (0.5 M) and methanol (1.0 M) at 40 °C was transferred via cannula to the cell. The potential of the ruthenium−platinum surface was set to −0.200 V concurrent with immersion into the electrolyte and then swept to 1.0 V at 5 mV/s while the temperature of the electrolyte was maintained at 40 °C using a heated oil bath.

The potentiostatic oxidations of methanol were carried out similarly at 25 °C, [$H_2SO_4$] = 0.5 M, and [MeOH] = 0.5 M. The potentials of the catalyst surfaces were set to −0.17 V concurrent with immersion into the electrolyte, and then set to the desired potential to begin the oxidation.