Preparation of Ruthenium and Osmium Carbonyl Complexes Using Microwave Heating: Demonstrating the Use of a Gas-Loading Accessory and Real-Time Reaction Monitoring by Means of a Digital Camera

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Received October 31, 2007

By using a gas-loading accessory, we show that it is possible to perform reactions involving gases and prepare organometallic complexes easily in good yields using microwave heating. The complexes $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$ are prepared. Ligand substitution reactions of $Ru_3(CO)_{12}$ are also studied and, in the case of the reaction with triphenylphosphine, the reaction is monitored in real time by means of a digital camera interfaced with the microwave unit.

Introduction

Microwave heating offers a fast, easy way to perform chemical reactions that require heat. Synthetic organic chemists have taken advantage of microwave heating in their work and found that reaction times can often be reduced from hours to minutes and yields are improved. Microwave heating occurs on a molecular level, as opposed to relying on convection currents and thermal conductivity when using conventional heating methods. This offers an explanation as to why microwave reactions are so much faster. With microwave irradiation, since the energy is interacting with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be, for short times, much greater than the overall recorded temperature of the bulk reaction mixture. In essence, there will be sites of instantaneous localized superheating where reactions will take place much faster than in the bulk.

In the literature, there have been relatively few reports of the use of microwave heating in preparative organometallic chemistry. Green and co-workers have reported the microwave-assisted synthesis of group 6 zerovalent carbonyl compounds.[1] They prepared $M(CO)_4L$ complexes ($M = Cr, Mo, W$; $L =$ bidentate amine or phosphine ligand), finding that the reaction can be accelerated using microwave heating. Hogarth and co-workers have also investigated the use of microwave heating for the synthesis of group 6 carbonyl complexes.[2] This work was performed using open-vessel conditions in a domestic microwave, where accurate temperature monitoring is not possible. Building on this work, Chung and co-workers have used microwave heating to prepare (η^6-arene)tricarbonylchromium complexes.[3] Teflon autoclaves have been used by Mingos and co-workers, who have reported the synthesis of the rhodium and iridium(I) diolefin complexes $[Cp_2Rh]PF_6$, $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)]_2$, $[IrCl(CO)(PPh_3)]$, and $[RuCl(CO)(2,2'\text{-bipy})_2]Cl$.[4,5] The same group has performed the synthesis of a range of other transition-metal coordination compounds at atmospheric pressure under reflux conditions.[6] One reason why there have been only a few reports is that monitoring a reaction using microwave heating can be difficult. Generally it requires stopping the reaction, allowing the mixture to cool, and then using standard analysis techniques. This often makes optimization of reaction conditions such as time and temperature a matter of trial and error. This can be a particular problem when trying to prepare organometallic complexes. For example, in ligand exchange reactions, stopping a reaction after a desired number of substitutions is difficult if the reaction cannot be continually monitored. With conventional heating the reaction can be slow and aliquots removed and analyzed over time, but with microwave heating the reaction may be complete within a matter of minutes (or even seconds) and accessing a sealed vessel during a reaction is not possible. We have recently reported a way to overcome this by using in situ Raman spectroscopy as a tool. By studying some simple substitution reactions of $Mo(CO)_6$ with monodentate ligands, we have shown the potential applicability of this technique.[7] Although not as widely used as infrared, Raman spectroscopy is a useful tool for probing both molecular composition and structure in metal carbonyls. By focusing on the ν_{CO} stretching region of the Raman spectrum, it is possible to follow ligand substitution reactions as they occur.

Another limitation of microwave heating as a tool for the preparation of organometallic compounds is that often gaseous reagents are required. This is particularly the case when preparing metal carbonyl, hydride, and olefin complexes. We thought that, by overcoming this problem, it would be possible to open up more avenues for microwave-promoted synthesis of organometallics. Here we show how, by using a gas-loading accessory we developed for organic synthesis, we can now perform reactions involving gases and prepare organometallic complexes. We also extend our reaction monitoring work to

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10.1021/om701099p CCC: $40.75

include watching reactions as they take place by means of a digital camera interfaced with the microwave unit.

Results and Discussion

Many of the approaches to binary metal carbonyl complexes involve using autoclaves, high pressures of CO, and long reaction times at elevated temperatures. A versatile starting material for the generation of ruthenium-containing compounds is $Ru_3(CO)_{12}$ (**1**). It has been prepared by several routes,[8–10] the most popular of which requires heating a methanol solution of ruthenium trichloride under a high pressure of carbon monoxide at 250 °C for several hours.[11] More recently, this and other ruthenium carbonyl clusters have been prepared under milder conditions by a two-step process involving carbonylation of $RuCl_3 \cdot nH_2O$ dissolved in ethylene glycol to give a mixture of ruthenium(II) tri- and dicarbonyl species followed by addition of specific amounts of alkali-metal carbonates and further reductive carbonylation.[12,13] A similar approach using potassium hydroxide has also been reported. In this case, the addition of 2 equiv of KOH per Ru under 1 atm of CO at 75 °C to a mixture of $[Ru(CO)_2Cl_2]_n$ and $[Ru(CO)_3Cl_2]_2$, generated in situ by carbonylation of $RuCl_3 \cdot nH_2O$ in 2-ethoxyethanol, triggers a reaction cascade producing **1** in good yields and with shorter reaction times.[14,15] We wanted to see if we could use microwave heating as a tool for the simple, rapid preparation of **1**. Our initial objective was to modify the original high-temperature, high-pressure synthesis so we could attempt this using microwave heating. To do this, we clearly needed to be able to load our reaction vessel with carbon monoxide. We have developed an apparatus for use with an 80 mL reaction vessel (Figure 1).[16,17] The gas is introduced directly into the vessel, and a pressure sensor is connected to the vessel in parallel. As a result, the exact loading pressure can be monitored in real time. Since the microwave apparatus is designed to contain the results of a vessel failure under pressure, the unit together with the gas-loading interface offers a very simple and safe way to perform chemistry using gaseous reagents at elevated pressures. Most commercially available microwave systems have a pressure limit of 20–30 bar. With the combination of a pressure of reactive gas and the autogenic pressure of solvents at elevated temperatures, there is a limit to the temperature to which reaction mixtures can be heated. We needed to take this into account when attempting to prepare **1**. In our first run, we placed a solution of $RuCl_3$ in methanol into the reaction vessel, closed it, and loaded it to an initial pressure of 50 psi of CO. Then, using an initial microwave power of 300 W, we heated the reaction mixture from room temperature to 110 °C, where we held it for 20 min. We could not heat to a higher temperature due to the pressure limits of the vessel. Upon cooling, analysis of the resultant solution showed only a trace of the desired product. This could be attributed to the fact that the reaction temperature and CO pressure are significantly lower than in the conventional procedure. We therefore turned our attention to the alternative, base-mediated routes to **1**. Using $RuCl_3$ as our ruthenium starting material, sodium carbonate as the base (Na_2CO_3:$RuCl_3$ molar ratio 3:2), methanol as the solvent, and an initial pressure of 50 psi of CO, we obtained a 40% yield of **1** after heating to 110 °C and holding until a total time of 15 min had elapsed. An observation we made was that, even at the end of the reaction, only a fraction of the sodium carbonate had dissolved in the methanolic solution. It occurred to us that this may be the contributing factor for the moderate yield of product. We therefore turned to cesium carbonate, which we knew was soluble in methanol. Using the same reaction conditions, we obtained a 90% yield of **1**. We were able to both shorten the reaction time to 10 min and reduce the Cs_2CO_3:$RuCl_3$ molar ratio from 3:2 to 1:1 without a deleterious effect on the product yield. This offers a very fast and easy route to **1** in one step (Scheme 1) and in yields comparable to or higher than those in previous literature reports.

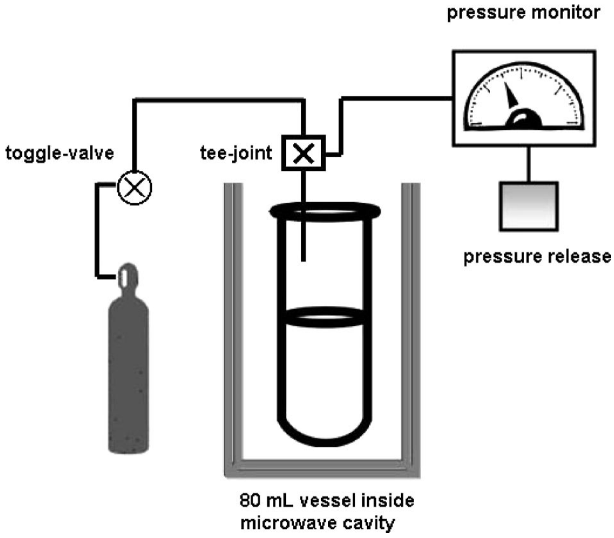

Figure 1. Schematic of the gas-loading interface.

Scheme 1

$$RuCl_3.3H_2O \quad + \quad CO \xrightarrow[Cs_2CO_3,\ MeOH]{MW} \underset{\mathbf{1}}{Ru_3(CO)_{12}}$$

50 psi CO, heat to 110 °C and hold until a total time of 15 min has elapsed

Having prepared **1**, we next wanted to assess the use of microwave heating as a tool for some ligand substitution reactions.[18] As a starting point, we wanted to prepare phosphine-substituted derivatives. It is possible to replace up to three of the carbonyl groups on **1** with phosphine ligands by simple thermolysis in a hydrocarbon solvent.[19] Since **1** and hydrocarbons are nonpolar, they do not heat efficiently under microwave irradiation. Therefore, we decided to perform the chemistry using 1,2-dichloroethane as solvent. We focused attention on preparing the triphenylphosphine-substituted complexes

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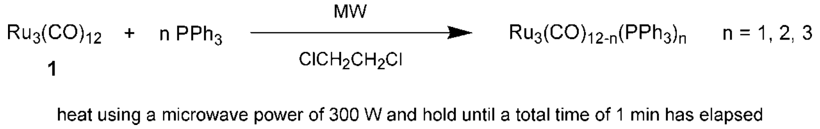
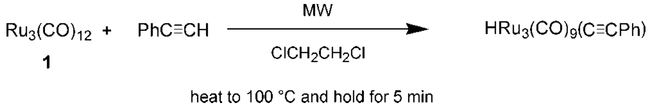
Scheme 2



$$\underset{\mathbf{1}}{Ru_3(CO)_{12}} + n\,PPh_3 \xrightarrow[ClCH_2CH_2Cl]{MW} Ru_3(CO)_{12-n}(PPh_3)_n \quad n = 1, 2, 3$$

heat using a microwave power of 300 W and hold until a total time of 1 min has elapsed

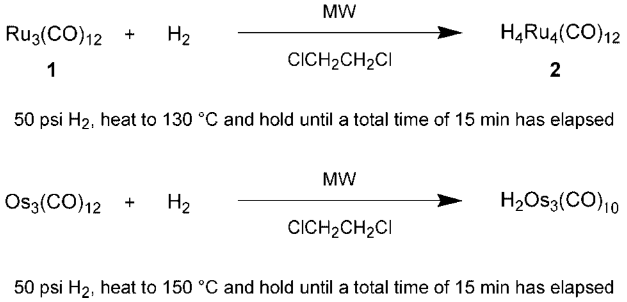
Scheme 3



$$\underset{\mathbf{1}}{Ru_3(CO)_{12}} + PhC{\equiv}CH \xrightarrow[ClCH_2CH_2Cl]{MW} HRu_3(CO)_9(C{\equiv}CPh)$$

heat to 100 °C and hold for 5 min

Scheme 4



$$\underset{\mathbf{1}}{Ru_3(CO)_{12}} + H_2 \xrightarrow[ClCH_2CH_2Cl]{MW} \underset{\mathbf{2}}{H_4Ru_4(CO)_{12}}$$

50 psi H_2, heat to 130 °C and hold until a total time of 15 min has elapsed

$$Os_3(CO)_{12} + H_2 \xrightarrow[ClCH_2CH_2Cl]{MW} H_2Os_3(CO)_{10}$$

50 psi H_2, heat to 150 °C and hold until a total time of 15 min has elapsed

$Ru_3(CO)_{12-n}(PPh_3)_n$ ($n = 1-3$). Heating a solution of **1** and PPh_3 in the correct molar ratio led to the formation of the desired phosphine complexes within 1 min of microwave irradiation (Scheme 2). Product purity was checked by performing ^{31}P NMR on the entire product mixture. In the case of the synthesis of $Ru_3(CO)_{11}(PPh_3)$, some evidence for over-reaction to generate $Ru_3(CO)_{10}(PPh_3)_2$ was observed (approximately 5%). A similar observation was made when preparing $Ru_3(CO)_{10}(PPh_3)_2$: $Ru_3(CO)_9(PPh_3)_3$ was present in the product mixture (~10%). This is as much, if not more, of an issue in the conventionally heated protocol.

Since the phosphine-substituted complexes are deep orange or red, we decided to follow the reaction in real time using a digital camera interfaced with our microwave unit. We have used this before to monitor macroscopic effects as organic reactions proceed, including color and viscosity changes, evolution of gases, and metal-mediated couplings.[20] We decided to monitor the formation of $Ru_3(CO)_9(PPh_3)_3$. The video is presented in the Supporting Information. It shows that the reaction occurs very rapidly upon starting the microwave irradiation and the characteristic color of the product is clearly seen growing in intensity. By monitoring reactions in real time, we can watch for deposition of metal particles on the surface of the glass reaction vessels as starting materials or products decompose. These particles, if allowed to form, can superheat in the microwave field, melt the glass, and lead to failure of the reaction vessel. They can, to a great extent, be avoided by ensuring that the reaction mixture is stirred efficiently throughout the microwave heating process.

We next turned our attention to the reaction of **1** with phenylacetylene. The interaction of trinuclear ruthenium complexes with unsaturated hydrocarbons has been the subject of considerable research interest for some years, but few general patterns of reactivity have been uncovered.[21] Terminal alkynes react with **1** to give the hydrido complexes $HRu_3(CO)_3(C{\equiv}CR)$, in which the acetylide residue interacts with all three ruthenium atoms. Using a 1:1 molar ratio of **1** to phenylacetylene and using 1,2-dichloroethane as solvent, we obtained a quantitative conversion of **1** to $HRu_3(CO)_3(C{\equiv}CPh)$ in 5 min at 100 °C (Scheme 3). No mononuclear or dinuclear biproducts were formed in the reaction, unlike the case of conventional heating, where this can be an issue.

Having shown that ligand exchange reactions can be efficiently effected using microwave heating and can be monitored in real time, we turned back to our gas-loading accessory with the objective of converting **1** into the tetranuclear hydrido complex $H_4Ru_4(CO)_{12}$ (**2**). This compound finds uses as a catalyst for a range of synthetic organic transformations.[22] Conventionally, **2** is prepared either by passing hydrogen through a refluxing octane solution of $Ru_3(CO)_{12}$[23] or in an autoclave (25 atm of H_2, 120 °C, 2 h).[24] We performed a series of test reactions using our microwave apparatus. Our attention focused mainly on the effects of time and temperature on the outcome of the reaction. We placed a solution of $Ru_3(CO)_{12}$ in 1,2-dichloroethane into our reaction vessel and, after sealing, loaded it with 50 psi of hydrogen. When the mixture was heated to 130 °C, we found that the reaction reached completion after a total time of 15 min and we obtained a good yield of the desired tetranuclear product (Scheme 4). Running for shorter times resulted in incomplete conversion. Of added interest was the observation that, in all of the reactions we performed, while **2** was the predominant product, ^1H NMR studies showed the presence of a second hydride-containing compound. The chemical shift correlated with the minor product being the previously reported dihydrido complex $H_2Ru_3(CO)_{10}$.[25] Since this is a very reactive species, it was not possible to isolate it from the reaction mixture. Decreasing the reaction temperature to 80 °C gave almost exclusively **2** after a reaction time of 15 min, but starting material remained. Prolonging the reaction time to 30 min led to better conversion.

Staying with the theme of preparing hydrido-containing complexes, we turned our attention to the reaction of $Os_3(CO)_{12}$ with dihydrogen. Conventionally, passing hydrogen through a refluxing octane solution of $Os_3(CO)_{12}$ results in the formation of the unsaturated complex $H_2Os_3(CO)_{10}$.[23,26] Prolonged heating in the presence of hydrogen leads to moderate yields of $H_2Os_4(CO)_{12}$. Using our approach, we converted $Os_3(CO)_{12}$ into $H_2Os_3(CO)_{10}$ nearly quantitatively after 15 min at 150 °C using an initial hydrogen loading of 50 psi (Scheme 4). No $H_2Os_4(CO)_{12}$ was observed.

We next attempted to prepare the hexanuclear cluster $Ru_6C(CO)_{17}$ from **1**. Traditionally, this was prepared by thermolysis[27,28] or pyrolysis[29] of **1**. More recently, reaction of a heptane solution of **1** with ethene under conditions of moderate

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temperature and pressure (150 °C; 30 atm) has been shown to generate $Ru_6C(CO)_{17}$ in substantially higher yields.[30] Mechanistic studies have shown that this reaction involves the formation of "$Ru(CO)_3$" type intermediates.[31] Using our microwave apparatus, **1** as starting material, and dichloroethane as solvent and loading the reaction vessel with ethene, we screened a range of reaction conditions for the formation of $Ru_6C(CO)_{17}$, but without success. In the majority of cases, **1** was recovered quantitatively, indicating that no reaction was taking place. With the combination of a pressure of ethene and the autogenic pressure of the solvent at elevated temperatures, there is a limit to the initial loading pressure and the temperature to which reaction mixtures can be heated. At lower loading pressures we can reach higher reaction temperatures, and conversely, at higher loading pressures we are limited by the temperature to which we can heat the reaction mixture. We believe that these limitations are preventing us from reaching conditions under which reaction to generate the mononuclear fragments necessary for formation of $Ru_6C(CO)_{17}$ will occur.

Conclusion

In summary, we have shown here how microwave heating is a useful tool for the preparation of ruthenium and osmium complexes. By using our gas-loading accessory, we have developed a fast and easy route to $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$. We have studied the ligand substitution reactions of $Ru_3(CO)_{12}$ with triphenylphosphine and phenylacetylene. In the case of the former, we followed the reaction in real time using a digital camera interfaced with our microwave unit. These initial results build on the limited reports in the literature using microwave heating for the preparation of organometallics and show the potential for the technique. Work is now underway to prepare other important classes of organometallic complexes as well as develop routes to complexes previously inaccessible using conventional heating.

Experimental Section

General Experimental Conditions. All reagents were obtained from commercial suppliers and used without further purification. ^1H NMR spectra were recorded at 293 K on a 300 or 400 MHz spectrometer. IR spectra were recorded on a Jasco FT-IR-4000 spectrophotometer. Reactions were performed using a CEM Discover microwave unit. This consists of a continuous focused microwave power delivery system with operator-selectable power output from 0 to 300 W. Reactions were performed in either 10 or 80 mL capacity sealed tubes. The temperature of the contents of the vessel was monitored using an IR sensor located underneath the reaction vessel or a fiber-optic temperature probe inserted directly into the reaction mixture. Pressure was controlled by a load cell connected directly to the vessel. The contents of the reaction vessel were stirred by means of an electromagnet located below the floor of the microwave cavity and a Teflon-coated magnetic stirbar in the vessel. Temperature, pressure, and power profiles were monitored using commercially available software provided by the microwave manufacturer. For real-time reaction monitoring, a CEM Discover S-class microwave unit was used. A 1.3 megapixel camera was interfaced with the microwave unit by means of an access port in the side of the microwave cavity. The face of the lens was positioned outside the cavity wall and protected with a plastic cover. Three white light LEDs were placed in the bottom of the microwave cavity in order to illuminate the reaction vessel. The camera was connected to a PC via a USB 2.0 interface and controlled using computer software. Using this, it was possible to record temperature, pressure, and microwave power profiles at the same time as the video images.

Preparation of $Ru_3(CO)_{12}$ (1). In a dry 80 mL glass vessel equipped with a magnetic stirbar were added $RuCl_3$ (30 mg, 0.13 mmol), Cs_2CO_3 (47 mg, 0.14 mmol), and methanol (15.0 mL). The vessel was sealed in the microwave apparatus, with a septum containing ports for pressure and temperature measurement devices. A pressure of 50 psi of carbon monoxide was introduced into the vessel, the pressure sensor being kept closed. The line to the carbon monoxide regulator was then closed and the pressure vented to the atmosphere through the pressure sensor. This process was repeated two more times, and then the vessel was loaded to 50 psi and sealed. With stirring, the reaction mixture was heated to 110 °C using an initial microwave power of 300 W and was held at this temperature until a total reaction time of 10 min had elapsed. The reaction mixture was then cooled to 50 °C, at which time the remaining pressure was carefully vented. The contents of the reaction vessel were transferred into a round-bottom flask, and the methanol was removed on a rotary evaporator. Hexane (30 mL) was added to the flask and heated to extract $Ru_3(CO)_{12}$. This was repeated three times, and the combined hexane washings were collected. Removal of the solvent left pure $Ru_3(CO)_{12}$ in 90% yield.

Reaction of $Ru_3(CO)_{12}$ with Phenylacetylene. In a dry 10 mL glass vessel equipped with a magnetic stirbar were added $Ru_3(CO)_{12}$ (19.4 mg, 0.03 mmol), phenylacetylene (3.1 mg, 0.03 mmol), and 1,2-dichloroethane (2 mL). The vessel was sealed with a septum and placed in the microwave apparatus. With stirring, the reaction mixture was heated to 100 °C using an initial microwave power of 300 W and was held at this temperature for 5 min. The reaction mixture was then cooled to 50 °C, the contents were transferred into a round-bottom flask, and the solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane (30 mL) and silica gel (9.5 g) added. The solvent was then removed, leaving the product adsorbed on the silica. The silica was washed with hexane to remove unreacted starting materials and then with dichloromethane to elute the product which, upon removal of the solvent, was obtained in 98% yield.

Reaction of $Ru_3(CO)_{12}$ with Triphenylphosphine. In a dry 10 mL glass vessel equipped with a magnetic stirbar were added $Ru_3(CO)_{12}$ (30 mg, 0.05 mmol), triphenylphosphine (36 mg, 0.15 mmol), and 1,2-dichloroethane (2 mL). The vessel was sealed with a septum and placed in the microwave apparatus. With stirring, the reaction mixture was heated using an initial microwave power of 300 W for 1 min, at which point the reaction mixture had reached 110 °C. The reaction mixture was then cooled to 50 °C, the contents were transferred into a round-bottom flask, and the solvent was removed on a rotary evaporator. The product was isolated using the same procedure as in the case of the reaction of $Ru_3(CO)_{12}$ with phenylacetylene to give $Ru_3(CO)_9(PPh_3)_3$ in 92% yield.

Preparation of $H_4Ru_4(CO)_{12}$ (2). In a dry 80 mL glass vessel equipped with a magnetic stirbar were added $Ru_3(CO)_{12}$ (30 mg, 0.05 mmol) and 1,2-dichloroethane (15.0 mL). The vessel was sealed in the microwave apparatus, with a septum containing ports for pressure and temperature measurement devices. A pressure of 50 psi of hydrogen was introduced into the vessel, the pressure sensor being kept closed. The line to the hydrogen regulator was then closed and the pressure vented to the atmosphere through the pressure sensor. This process was repeated two more times, and then the vessel was loaded to 50 psi and sealed. With stirring, the reaction mixture was heated to 130 °C using an initial microwave

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power of 300 W and held at this temperature until a total reaction time of 15 min had elapsed. The reaction mixture was then cooled to 50 °C, at which point the remaining pressure was carefully vented. The contents of the reaction vessel were transferred into a round-bottom flask, and the solvent was removed on a rotary evaporator. Analysis by ^{1}H NMR spectroscopy relative to an internal standard showed a near-quantitative conversion to the desired product.

Preparation of $H_2Os_3(CO)_{10}$. In a dry 80 mL glass vessel equipped with a magnetic stirbar were added $Os_3(CO)_{12}$ (30 mg, 0.03 mmol) and 1,2-dichloroethane (15.0 mL). The vessel was sealed and loaded with hydrogen in the same way as in the case of the reaction with $Ru_3(CO)_{12}$. With stirring, the reaction mixture was heated to 150 °C using an initial microwave power of 300 W and held at this temperature until a total reaction time of 15 min had elapsed. After cooling and removal of the solvent, analysis by IR and ^{1}H NMR spectroscopy showed a near-quantitative conversion to the desired product.

Acknowledgment. Pfizer, the Connecticut Business & Industry Association (CBIA), and the Petroleum Research Foundation, administered by the American Chemical Society, are thanked for funding and CEM Corp. is thanked for equipment support. Input from T. Michael Barnard is gratefully acknowledged.

Supporting Information Available: Video file for the reaction of $Ru_3(CO)_{12}$ with PPh_3 to form $Ru_3(CO)_9(PPh_3)_3$ and instructions on how to view it. This material is available free of charge on the Internet at http://pubs.acs.org.

OM701099P