*Inorg. Chem.* **1994,** *33,* 4415−4417

# Surface-Mediated Synthesis of $[PtRh_5(CO)_{15}]^-$ on MgO

**Z. Xu,[†] S. Kawi,[†] A. L. Rheingold,[‡] and B. C. Gates[*,†,‡]**

Department of Chemical Engineering and Materials Science,
University of California, Davis, California 95616, and
Center for Catalytic Science and Technology, Department of
Chemical Engineering and Department of Chemistry and
Biochemistry, University of Delaware,
Newark, Delaware 19716

*Received November 30, 1993*

## Introduction

Some metal carbonyl clusters are synthesized more simply on surfaces of metal oxides than in solution.[1] Surface-mediated syntheses may take place in the absence of solvents, with the reactivity of the surface functional groups and the surrounding gas atmosphere determining the chemistry. For example, $[Os_5C(CO)_{15}]^{2-}$ has been prepared in high yield in one step from $[Os_3(CO)_{12}]$ on the surface of MgO in the presence of CO and in the absence of solvents, although there is no known synthesis that proceeds efficiently in solution.[2] $[Pt_{15}(CO)_{30}]^{2-}$ has been synthesized in one step on the surface of MgO from $Na_2PtCl_6$ in the presence of methanol and CO at room temperature.[3] The products of all the reported surface-mediated syntheses of metal carbonyl clusters are monometallic. Here we report the first surface-mediated synthesis of a bimetallic cluster, $[PtRh_5(CO)_{15}]^-$, on the surface of MgO. Supported mixed-metal carbonyl clusters are potentially valuable precursors of supported bimetallic catalysts.[4]

## Experimental Section

**Materials, Sample Preparation, and Handling.** All syntheses and sample transfers were performed with exclusion of air and moisture on a double-manifold Schlenk line and in a $N_2$-filled Braun MB150 drybox. Methanol (Aldrich) was deoxygenated by purging with $N_2$ (Matheson, 99.999%) for 30 min before use. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. CO (Matheson, UHP grade) was used without further treatment. Bis(triphenylphosphine)nitrogen(1+) chloride, [PPN][Cl], was dried overnight at 100 °C and stored in the drybox. $Na_2PtCl_6$ (Aesar) and $RhCl_3{\cdot}xH_2O$ (Rh content 40%) were used without purification.

The MgO powder (MX-65-1 powder, MCB reagents, surface area approximately 70 $m^2/g$) was evacuated at 25 °C for 2 h before use. The $\gamma$-$Al_2O_3$ (Degussa, aluminum oxide C, surface area roughly 100 $m^2/g$) was added to water to form a paste, which was dried in air at 120 °C overnight and ground to a powder.

$Na_2PtCl_6$ and $RhCl_3{\cdot}xH_2O$ were dissolved in undistilled methanol, giving a solution that was red-purple. The solution was degassed by purging with $N_2$ for 20 min and then transferred to a sealed flask containing MgO powder. The amounts of the precursors were chosen to give 1 wt % Pt in the final solid material; the Pt:Rh atomic ratio was 1:5. The mixture was stirred for 10 min, and CO was introduced into the flask, with the CO flow continuing for 4 h. CO was then added periodically as it was consumed; the sample was maintained in the presence of CO for 2 days. The solvent was then removed by evacuation for 24 h. The resultant solid was dark brown.

The equivalent procedure was used to prepare a $\gamma$-$Al_2O_3$-supported sample. The resultant solid was orange-yellow.

**Extraction and Purification.** Each MgO-supported sample in the presence of CO was brought into contact with a solution of [PPN][Cl] in methanol (or in THF) and allowed to equilibrate. The solid was isolated by filtration. Each resultant solid was white, indicating that the surface-bound organometallic species had been extracted. The solution containing the extracted species was evacuated to remove the solvent, giving a solid with a dark brown color. This was extracted with THF, and the extracted material was purified by removal of the THF by evacuation. The resultant solid was dark brown.

Each $\gamma$-$Al_2O_3$-supported sample was brought into contact with [PPN][Cl] in the same way. Each resultant solid was white, indicating that the surface-bound organometallic species had been extracted. The extract solution was yellow.

**Characterization by Physical Methods.** Infrared spectra were recorded with a Bruker IFS 66v spectrometer with a spectral resolution of 4 $cm^{-1}$. Solid samples were pressed into thin self-supporting wafers in the drybox and loaded into a controlled atmosphere infrared cell equipped with NaCl windows sealed with O rings. Liquid samples were transferred with an airtight syringe to a 0.1-mm NaCl cell equipped with a one-way Perfectum spring-clip stopcock (Aldrich) that prevented exposure of the sample to air. Each spectrum was obtained as the sample was scanned 64 or more times. The signal was averaged.

Electronic spectra were recorded with a Perkin-Elmer Lambda 2 ultraviolet−visible spectrometer. Solution spectra were recorded as follows: A quartz cell with a circular opening was sealed with a septum cap, evacuated, and filled with CO. The liquid sample was transferred to the cell with an airtight syringe and diluted with THF. The solution was shaken and the spectrum recorded within 2 min. The spectrum of THF was removed by background subtraction.

Electrospray ionization mass spectrometry was performed with a Quattro-BQ quadrupole mass spectrometer in the negative-ion mode (Fisons Instruments VG Biotech Division, Manchester, U.K.). Samples of liquid solutions (10 μL) containing the species extracted from MgO as described above were withdrawn from sealed containers and immediately introduced by syringe. The scan range was 100−2500 and the scan rate one per 15 s. The sample was scanned 20 times, and the data were averaged.

## Results

The slurry of the MgO-supported sample containing adsorbed Pt and Rh with an atomic ratio of 1:5 was treated with CO at 25 °C. After 6−8 h, the color of the sample changed from orange-red to yellow-green, the color of $[Pt_{15}(CO)_{30}]^{2-}$;[3] after the sample had been treated in CO for 15 h, the color changed to blue-green, the color of $[Pt_{12}(CO)_{24}]^{2-}$.[5] The color did not change noticeably during an additional 10 h of treatment in CO, but thereafter a brown color started to appear, becoming gradually more intense. The sample was stirred under CO for another 24 h to allow the reaction to proceed to completion. The solvent was removed by evacuation, giving a product that was dark brown. The infrared spectrum of the solid includes four bands in the $\nu_{CO}$ region: 2076 (m), 2041 (s), 2008 (sh), 1791 (m) $cm^{-1}$ (Figure 1A).

The infrared spectrum of the liquid extracted from MgO includes four bands in the $\nu_{CO}$ region: 2082 (vw), 2040 (s), 2009 (m), 1789 (m) $cm^{-1}$ (Figure 1B). This spectrum closely matches that reported for $[PtRh_5(CO)_{15}]^-$ in THF [2080 (vw), 2038 (s), 2010 (m), 1785 (m) $cm^{-1}$].[6,7]

---

[†] University of California.

[‡] University of Delaware.

(1) Lamb, H. H.; Fung, A. S.; Tooley, P. A.; Puga, J.; Krause, T. R.; Kelley, M. J.; Gates, B. C. *J. Am. Chem. Soc.* **1989**, *111*, 8367.

(2) Johnson, B. G. F.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; Schroder, M.; Vargas, M. D. *J. Chem. Soc., Dalton Trans.* **1983**, 2447.

(3) Chang, J.-R.; Koningsberger, D. C.; Gates, B. C. *J. Am. Chem. Soc.* **1992**, *114*, 6460.

(4) Braunstein, P.; Rose, J. *Stereochem. Organomet. Inorg. Compd.* **1989**, 3.

(5) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225.

(6) Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Bruckner, S.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1978**, 195.

(7) Fumagalli, A.; Martinengo, S.; Chini, P.; Galli, D.; Heaton, B. T.; Pergola, R. D. *Inorg. Chem.* **1984**, *23*, 2947.

0020-1669/94/1333-4415$04.50/0

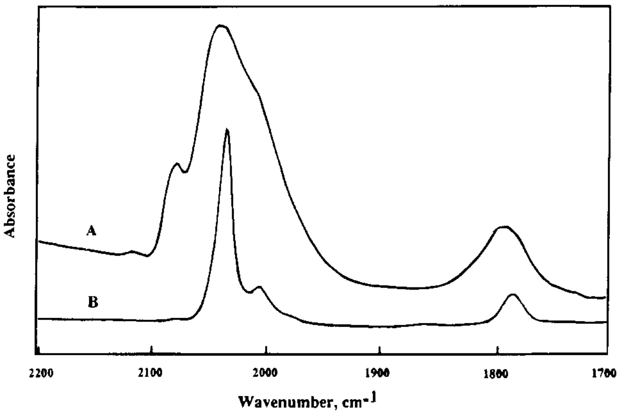

**Figure 1.** Infrared spectra characterizing (A) the sample formed by treatment in CO at 1 atm and room temperature for 2 days from a mixture of $Na_2PtCl_6$ and $RhCl_3 \cdot xH_2O$ with MgO powder in methanol and (B) the extract solution formed by treatment of the sample referred to in (A) with [PPN][Cl] in THF.

This extract solution was characterized by mass spectrometry. A 10-mL round-bottom flask containing 0.5 g of the MgO-supported sample was purged with CO for 10 min, and then 5 mL of [PPN][Cl] in THF was transferred into the flask with an airtight syringe. The mixture was stirred for 5 min, whereupon the solution became dark brown and the solid became white. The solution was injected into the mass spectrometer. The negative-ion electrospray mass spectrum of the sample showed peaks for the negative anions from the sample. The *m/z* value of the most abundant species (1129) exactly matches the value for $[PtRh_5(CO)_{15}]^-$. A group of peaks was observed at $m/z$ = 1128, 1129, 1130, and 1132. These correspond to $[PtRh_5(CO)_{15}]^-$ containing the four isotopes of Pt (Rh only has one isotope). The ratio of the peak intensities is similar to the ratio of isotope abundances of Pt. There were also groups of peaks at $m/z$ = 1100, 1101, and 1102 and at $m/z$ = 1072, 1073, and 1074, and these were much less intense than the major peak characterizing $[PtRh_5(CO)_{15}]^-$ itself. They indicate the species derived from $[PtRh_5(CO)_{15}]^-$ by removal of one and two CO ligands, respectively.

The extract solution obtained from the MgO-supported sample was also characterized by ultraviolet–visible spectroscopy. The solution was transferred to the cell, which was evacuated and then filled with CO. The solution was diluted with THF to obtain the optimum spectrum. The absorption spectrum (not shown) includes no prominent peak; the absorbance declines markedly between 300 and 400 nm and gradually between 400 and 700 nm.

Another sample supported on MgO (or, equivalently, on $\gamma$-$Al_2O_3$) was prepared as described above, except that it contained no Pt. This sample was initially purple, and after it had been treated in CO at 25 °C for 2 days under the same conditions as stated above, the color changed to orange-red. The infrared spectrum of the extract solution includes six peaks in the $\nu_{CO}$ region: 2085 (w), 2046 (s), 2014 (s), 1872 (m), 1842 (m), 1788 (m) cm$^{-1}$ (Figure 2A); these peaks closely match the reported spectrum of $[Rh_5(CO)_{15}]^-$ [8] and confirm the reported synthesis of the cluster anion on the MgO surface.[9]

The solution extracted from the $\gamma$-$Al_2O_3$-supported sample made from the combination of $Na_2PtCl_6$ and $RhCl_3 \cdot xH_2O$ was also characterized by infrared spectroscopy. The spectrum (Figure 2B) closely matches that reported[10] for $[Rh(CO)_2Cl_2]^-$ in methanol solution and that reported for rhodium subcarbonyls bonded to the surface of $\gamma$-$Al_2O_3$.[11]

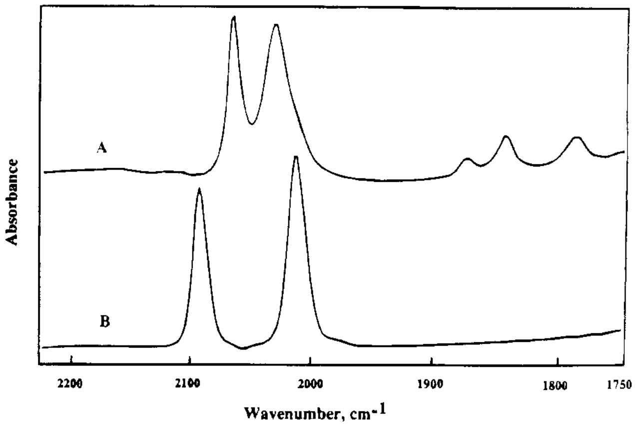

**Figure 2.** Infrared spectra of (A) the extract solution formed by treatment of the sample formed from $RhCl_3 \cdot xH_2O$ and $\gamma$-$Al_2O_3$ powder in methanol after treatment in CO at 1 atm and room temperature for 2 days (the extraction was done with [PPN][Cl]) and (B) the extract solution formed by treatment of the sample prepared by mixing $Na_2PtCl_6$ and $RhCl_3 \cdot xH_2O$ with $\gamma$-$Al_2O_3$ powder in methanol after treatment in CO at 1 atm and room temperature for 2 days (the extraction was done with [PPN][Cl]).

The solution formed by extraction with [PPN][Cl] of a sample prepared as stated above from 5 g of MgO and the platinum and rhodium salts was filtered through a medium-porosity glass frit in the presence of CO, and the powder was washed with 10 mL of methanol, followed by filtration through the frit. The resultant solution was evacuated, and the solid, which was dark brown, was added to 20 mL of THF. A precipitate formed, which was washed with 5 mL of THF, giving a solution that was evacuated to give the final solid product $[PPN][PtRh_5(CO)_{15}]$, which was dark brown. The yield found by weighing was 84%.

## Discussion

**Surface-Mediated Synthesis of $[PtRh_5(CO)_{15}]^-$ on MgO.** The results indicate that $[PtRh_5(CO)_{15}]^-$ has been synthesized on the surface of MgO powder with high yield by treatment of $Na_2PtCl_6$ and $RhCl_3 \cdot xH_2O$ in CO at room temperature. The evidence includes (1) the infrared spectrum of the supported carbonylated species which is similar to that of $[PtRh_5(CO)_{15}]^-$ reported in literature, (2) the infrared spectrum of the extracted species, which is consistent with the identification of $[PtRh_5(CO)_{15}]^-$, (3) the mass spectrum of the extract solution that has *m/z* equal to that of $[PtRh_5(CO)_{15}]^-$, and (4) the colors of the solid sample and the extracted solution, which match that of $[PtRh_5(CO)_{15}]^-$.

This is the first report of a surface-mediated synthesis of a bimetallic cluster. The synthesis is simple and efficient, with a product yield of 84%.

**Comparisons between Reactions in Basic Solution and on the Basic MgO Surface.** $[PtRh_5(CO)_{15}]^-$ was first synthesized by reaction of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$ in THF in the presence of CO at 25 °C.[6] $[PtRh_5(CO)_{15}]^-$ was the only reported product, but the yield was not stated. $[PtRh_5(CO)_{15}]^-$ has also been synthesized more simply by reductive carbonylation of mixtures of $Na_2PtCl_6$ and $RhCl_3 \cdot xH_2O$ in methanol under 1 atm

---

(8) Fumagalli, A.; Koetzle, T. F.; Takusagawa; F.; Chini, P.; Martinengo, S.; Heaton, B. T. *J. Am. Chem. Soc.* **1980**, *102*, 1740.

(9) Kawi, S.; Xu, Z.; Gates, B. C. *Inorg. Chem.* **1994**, *33*, 503.

(10) Browing, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.

(11) Dossi, C.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1989**, *359*, 105.

of CO at room temperature;[7] NaOH was added at regular intervals. The yield was reported to be 85%.

The results of this work indicate clearly that $[PtRh_5(CO)_{15}]^-$ was formed in high yield from $Na_2PtCl_6$ and $RhCl_3{\cdot}xH_2O$ on the surface of MgO powder. The reaction conditions for the surface-mediated reaction closely resemble those reported by Fumagalli et al.[7] for the synthesis in solution. The precursors, temperature, and CO pressure are all the same. However, in the surface-mediated synthesis there are no reagents other than the precursor salts, methanol, and the MgO providing the surface, whereas in the solution synthesis NaOH is a reagent. We infer that the basic surface of MgO plays a role analogous to that of NaOH in solution. This inference is consistent with the observation that the synthesis does not proceed on the less strongly basic $\gamma$-$Al_2O_3$ surface.

The basic groups on the surface of MgO are $O^{2-}$ and $OH^-$ groups. These are inferred to participate in the syntheses of a number of binary metal carbonyl anions. For example, the Longoni–Chini clusters $[Pt_n(CO)_{2n}]^{2-}$ ($n = 2-5$) have been synthesized from mononuclear platinum precursors on MgO,[3,12,13] and $[Rh_5(CO)_{15}]^-$ and $[Rh_{12}(CO)_{30}]^{2-}$ have been synthesized from $[Rh(CO)_2(acac)]$ on MgO.[9] In these examples, the surface-mediated syntheses take place by chemistry similar to that of the solution syntheses, with the basic character of the MgO surface being crucial. However, MgO that has been treated at high temperatures is a strong reducing agent, and MgO may also play the role of a reducing agent in the synthesis of platinum clusters.[12]

**Chemistry of Formation of $[PtRh_5(CO)_{15}]^-$ in Solution and on MgO.** The crystal structure of $[PtRh_5(CO)_{15}]^-$ is similar to that of $[Rh_6(CO)_{16}]$,[14] with one Rh atom replaced by a Pt atom. The synthesis in solution has been proposed to take place by the following sequence:[7]

$$\begin{aligned}&[PtCl_6]^{2-} + [RhCl_3] \rightarrow [Pt(CO)Cl_3]^- \rightarrow\\ &\qquad [Pt_3(CO)_6]^{2-}_{5\text{ or }6} + [Rh(CO)Cl_2]^- \rightarrow\\ &\quad [Pt_3(CO)_6]^{2-}_{4\text{ or }5} + [Rh(CO)_2Cl_2]^- \rightarrow [PtRh_5(CO)_{15}]^- \quad (1)\end{aligned}$$

The mechanism of the formation of $[PtRh_5(CO)_{15}]^-$ in solution has not been reported. Fumagalli et al.[7] found that $[Pt_{12}(CO)_{24}]^{2-}$ was formed prior to the formation of $[PtRh_5(CO)_{15}]^-$; and $[Rh_{12}(CO)_{30}]^{2-}$ has been shown to react cleanly with $[Pt_{12}(CO)_{24}]^{2-}$ to form $[PtRh_5(CO)_{15}]^-$. Furthermore, it has been found that, in the presence of CO, $[PtRh_5(CO)_{15}]^-$ is in equilibrium with $[Rh_{12}(CO)_{30}]^{2-}$.[7] Because it has also been shown[7] that $[Rh_{12}(CO)_{30}]^{2-}$ equilibrates with $[Rh_5(CO)_{15}]^-$, we suggest that it is likely that either $[Rh_5(CO)_{15}]^-$ or $[Rh_{12}(CO)_{30}]^{2-}$ is a precursor in the formation of $[PtRh_5(CO)_{15}]^-$. This possibility is consistent with the observations that the following clusters are formed on the surface of MgO: $[Pt_{12}(CO)_{24}]^{2-}$,[13] $[Rh_5(CO)_{15}]^-$,[9] and $[Rh_{12}(CO)_{30}]^{2-}$.[9] However, $[Pt_{12}(CO)_{24}]^{2-}$ is not the cluster that was formed from platinum precursors in the absence of rhodium under the conditions used here for the synthesis of the bimetallic cluster. Rather, it has been reported that $[Pt_{15}(CO)_{30}]^{2-}$ was formed when $Na_2PtCl_6$ and MgO were treated in methanol under CO at 25 °C for 5 h.[3] The synthesis of $[Rh_5(CO)_{15}]^-$ from $RhCl_3$ on MgO took place in the presence of methanol under CO at 25 °C, and the reaction required 2 days, about the same time required for the synthesis of $[PtRh_5(CO)_{15}]^-$. However, when $Na_2PtCl_6$ and $RhCl_3$ were mixed with MgO and methanol under CO at 25 °C, neither $[Pt_{15}(CO)_{30}]^{2-}$ nor $[Rh_5(CO)_{15}]^-$ was observed; instead, $[PtRh_5(CO)_{15}]^-$ was the product.

Previous attempts to synthesize bimetallic clusters by surface-mediated reactions have not been successful. For example, salts and organometallic precursors of Pt and Re were supported on the surface of MgO and treated under various conditions in attempts to make bimetallic clusters.[12] The products were binary metal carbonyls, including $[Pt_6(CO)_{12}]^{2-}$ and $[Re_2(CO)_{10}]$, but no bimetallic clusters.[12] Similarly, mononuclear precursors of Pt and Ir were supported on the surfaces of MgO and $\gamma$-$Al_2O_3$ and treated under various conditions in attempts to form bimetallic clusters.[15] In these and numerous other preparations, mixtures of monometallic clusters of Pt and Ir were formed.

Because there is little understanding of the nature of surface species which may be involved in surface-mediated synthesis, there is little basis for inference of reaction mechanisms and for prediction of when surface-mediated synthesis of bimetallic clusters may be successful. The best strategy for synthesis of bimetallic clusters on surfaces appears to be to take advantage of presumed analogies with better-understood solution chemistry.

**Acknowledgment.** We thank A. D. Jones of the University of California at Davis for the mass spectrometry experiments and K. E. Garrett of the University of Delaware for contributing to the preliminary experimentation. This work was supported by the National Science Foundation (Grant CTS-9300754) and the University of Delaware Research Foundation.

---

(12) Xu, Z.; Rheingold, A. L.; Gates, B. C. *J. Phys. Chem.* **1993**, *97*, 9465.

(13) Puga, J.; Patrini, R.; Sanchez, K. M.; Gates, B. C. *Inorg. Chem.* **1991**, *30*, 2479.

(14) Hieber, W.; Lagally, H. *Z. Anorg. Allg. Chem.* **1943**, *251*, 96.

(15) Garrett, K. E.; Xu, Z.; Rheingold, A. L.; Gates, B. C. Unpublished results.