

Surface-Mediated Organometallic Synthesis: Formation of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ on $\gamma\text{-Al}_2\text{O}_3$ and on MgO

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$[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ were prepared on MgO and on $\gamma\text{-Al}_2\text{O}_3$, each by surface-mediated synthesis from chemisorbed $[\text{Rh}(\text{CO})_2(\text{acac})]$ in the presence of CO. $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ was formed when the adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto either support was carried out in the presence of dehydrated hexane, whereas $[\text{Rh}_5(\text{CO})_{15}]^-$ was formed when the hexane contained water. Either cluster anion could be extracted into methanol solution by cation metathesis with $[\text{K}][\text{CH}_3\text{COO}]$; $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ was extracted under N_2 , and $[\text{Rh}_5(\text{CO})_{15}]^-$ was extracted under CO. The organometallic chemistry on the MgO and $\gamma\text{-Al}_2\text{O}_3$ surfaces is similar to that occurring in basic solution. The surface-mediated synthesis is an efficient method for the preparation of $[\text{Rh}_5(\text{CO})_{15}]^-$ (which was obtained in 47% yield); this anion in solution is easily converted into $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$.

Introduction

Clusters of rhodium metal on supports have been widely investigated, being prototypes of highly dispersed supported metal catalysts.¹ There is also an extensive literature of supported rhodium carbonyl clusters, with most of the attention having been devoted to $[\text{Rh}_6(\text{CO})_{16}]$, a relatively stable cluster that can be synthesized on $\gamma\text{-Al}_2\text{O}_3$ from various precursors by treatment in the presence of CO and traces of water.^{2,3} The literature also includes references to $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ on MgO,^{4–6} but the characterizations are less thorough than those reported for $[\text{Rh}_6(\text{CO})_{16}]$.

Rhodium metal clusters on amorphous metal oxide supports are catalytically active for CO hydrogenation, and rhodium is of interest because its catalytic activity and selectivity depend markedly on the support properties.⁷ The principal products of the catalytic reaction range from methanol when the support is rather strongly basic, to ethanol when it is weakly basic, to hydrocarbons when it is acidic. Rhodium carbonyl cluster anions are also potentially interesting catalysts, as some are stable at relatively high temperatures in the presence of CO and in basic media.⁸ $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ ⁸ and $[\text{Rh}_5(\text{CO})_{15}]^-$ ^{9,10} for example, have been implicated in the catalysis of CO hydrogenation in basic solutions to give ethylene glycol and methanol (although recent work indicates that the catalytically active species are mononuclear rhodium complexes¹¹). Rhodium carbonyl cluster anions have also been inferred to be formed in the cages of basic zeolites and suggested to play a role in CO hydrogenation catalysis to give

low-molecular-weight alcohols.¹² The salt $\text{K}_2[\text{Rh}_{12}(\text{CO})_{30}]$ has been deposited on SiO_2 and found to be a catalyst for alkene hydroformylation.¹³

The goal of the research reported here was to extend the chemistry of rhodium carbonyls on basic metal oxide surfaces. We report the synthesis of $[\text{Rh}_5(\text{CO})_{15}]^-$ ¹⁴ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ ^{15,16} on $\gamma\text{-Al}_2\text{O}_3$ and on MgO from $[\text{Rh}(\text{CO})_2(\text{acac})]$ and the characterization of the surface species by infrared spectroscopy and by extraction. The surface-mediated synthesis of $[\text{Rh}_5(\text{CO})_{15}]^-$ has been found to take place simply in high yields and is a recommended synthetic method.

Experimental Section

Materials, Sample Preparation, and Handling. All syntheses and sample transfers were conducted with exclusion of air and moisture on a double-manifold Schlenk line and in a Vacuum Atmospheres drybox. N_2 and He with purities of 99.999% (Matheson) were passed through traps containing particles of Cu_2O and molecular sieve zeolite to remove traces of oxygen and moisture, respectively. CO (Matheson, UHP grade) was passed through a trap containing particles of activated alumina at a temperature exceeding 200 °C to remove traces of iron carbonyl contaminants and through a trap containing particles of molecular sieve zeolite to remove moisture. Hexanes (Aldrich) were used without purification except for deoxygenation by purging with flowing N_2 for 2 h; alternatively, hexanes (Aldrich) were sometimes dried over sodium benzophenone ketyl. All solvents used in the extractions were deoxygenated prior to use; tetrahydrofuran (THF) was dried over sodium benzophenone ketyl, and methanol was dehydrated by distillation from Mg and sublimed I_2 . $[\text{Rh}(\text{CO})_2(\text{acac})]$ (Strem), $[\text{K}][\text{CH}_3\text{COO}]$ (Aldrich), and bis(triphenylphosphine)nitrogen(1+) chloride, $[\text{PPN}][\text{Cl}]$ (Aldrich), were used without purification.

The MgO support (MX-65-1 powder, MCB reagents, surface area approximately 70 m^2/g) was evacuated (pressure $<10^{-3}$ Torr) at 120 °C for 4 h. The $\gamma\text{-Al}_2\text{O}_3$ support (Degussa, aluminum oxide C) was made into a paste by adding deionized water, followed by drying at 120 °C overnight. It was then ground and evacuated (pressure $<10^{-3}$ Torr) at 120 °C for 4 h.

In a standard preparation of a supported 1 wt % Rh sample, 100 mg of $[\text{Rh}(\text{CO})_2(\text{acac})]$ was brought into contact with 4 g of pretreated MgO or $\gamma\text{-Al}_2\text{O}_3$ by slurring in either undried or dried hexanes (50 mL)

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in a Schlenk flask under a N_2 blanket. After the mixture was stirred at room temperature for 12 h, the solution was clear, indicating a complete uptake of the rhodium complex by the solid. The solvent was then pumped off and the solid dried in vacuo (pressure $<10^{-3}$ Torr) overnight. The resulting brownish-yellow solids were then stored in the drybox for future experiments.

Characterization of Surface Species by Infrared Spectroscopy. Infrared spectra were recorded on a Nicolet 7199 spectrometer with a spectral resolution of 4 cm^{-1} . Samples of the initially prepared solid and those prepared by carbonylation were pressed into thin self-supporting wafers in the drybox and loaded into a controlled-atmosphere infrared cell. Flowing gas, CO, H_2 , and He could be brought into contact with the wafer for further treatment of the sample. Each spectrum was obtained as the sample was scanned 32 or more times; the signal was averaged.

Extraction of Rhodium Carbonyls from Supports. Surface-bound rhodium carbonyls were extracted from MgO and from $\gamma\text{-Al}_2\text{O}_3$ as the solid sample in the drybox was brought into contact with a solution of $[\text{PPN}][\text{Cl}]$ in THF or $[\text{K}][\text{CH}_3\text{COO}]$ in methanol. The liquid was transferred by pipet into a 0.2-mm CaF_2 solution infrared cell. The liquid sample was sealed in the cell, removed from the drybox, and scanned quickly. In some cases, extraction of rhodium carbonyls from MgO or from $\gamma\text{-Al}_2\text{O}_3$ was performed on a Schlenk line with a suspension of $[\text{K}][\text{CH}_3\text{COO}]$ in methanol or with $[\text{PPN}][\text{Cl}]$ in THF, either under N_2 or under CO; the liquid was transferred by cannula from the Schlenk flask to the solution infrared cell without air contamination, and the sample was scanned quickly. The infrared absorbances were ratioed to the background atmosphere in the spectrometer, and the infrared bands for THF or methanol were subtracted from the spectrum.

Characterization of Extracted Rhodium Carbonyls by Mass Spectrometry. Electrospray ionization was performed in the negative-ion mode by using a Quattro-BQ mass spectrometer (VG Biotech, Altrincham, U.K.). Samples ($10\ \mu\text{L}$) of liquid solutions were withdrawn by syringe from sealed containers and immediately introduced via loop injection. A $10\ \mu\text{L}/\text{min}$ flow of methanol provided by an Isco $\mu\text{L C-500}$ pump carried the sample into the mass spectrometer source. Ionization conditions were as follows: needle voltage = -3.00 kV ; counter electrode voltage = 0.50 kV ; nozzle-skimmer bias = 40 V .

Results

Chemisorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto MgO and onto $\gamma\text{-Al}_2\text{O}_3$. When $[\text{Rh}(\text{CO})_2(\text{acac})]$ was brought into contact with MgO or with $\gamma\text{-Al}_2\text{O}_3$ powder at room temperature in the presence of either dried or undried hexanes, it was adsorbed, with the solid becoming brownish-yellow. The uptake of the organometallic precursor from the solution was virtually complete, as evidenced by the color of the supernatant solution. The infrared spectra of the solid were characterized by two strong carbonyl bands (Figure 1B,C). A comparison with the spectrum of $[\text{Rh}(\text{CO})_2(\text{acac})]$ in hexanes (Figure 1A) shows that adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ either onto MgO or onto $\gamma\text{-Al}_2\text{O}_3$ from undried hexanes led to broadening and slight shifting of the carbonyl bands to lower wavenumbers. The band broadening is characteristic of adsorbed metal carbonyls, being consistent with the interaction of the metal complex with several chemically distinct surface sites. The shifting of carbonyl bands to lower wavenumbers indicates electron transfer from the MgO or the $\gamma\text{-Al}_2\text{O}_3$ to the rhodium. The infrared spectra are almost the same as those reported for rhodium subcarbonyls on $\gamma\text{-Al}_2\text{O}_3$ ¹ and for such complexes on MgO⁶ formed from $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{COO})]_2$ (Table 1).

Similar results were observed when dried hexanes were used in the adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto MgO or onto $\gamma\text{-Al}_2\text{O}_3$; the infrared spectra of the resulting brownish-yellow solids were almost the same as those of the samples prepared with undried hexanes.

The rhodium surface species could not be extracted from the MgO or from the $\gamma\text{-Al}_2\text{O}_3$ with THF alone, as shown by the lack of infrared absorptions characteristic of metal carbonyls in the THF solutions. However, when dilute aqueous HCl combined with $[\text{PPN}][\text{Cl}]$ in THF was added to the slurry, the solution

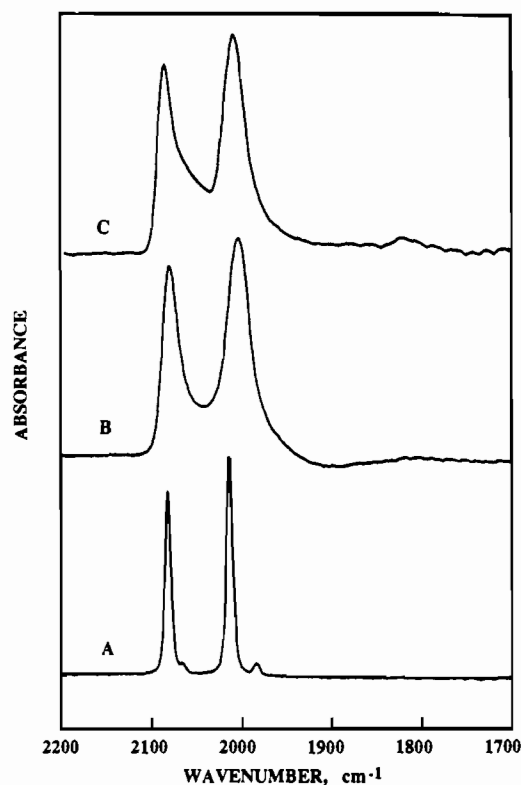


Figure 1. Infrared spectra of (A) $[\text{Rh}(\text{CO})_2(\text{acac})]$ dissolved in hexanes, (B) species formed by adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto MgO from undried hexanes, and (C) species formed by adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto $\gamma\text{-Al}_2\text{O}_3$ from undried hexanes.

Table 1. Infrared Data for the Carbonyl Stretching Region of Soluble Rhodium Carbonyls and of Supported Species Formed from Adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto MgO or onto $\gamma\text{-Al}_2\text{O}_3$

sample	ν_{CO} , cm^{-1}	ref
$[\text{Rh}(\text{CO})_2(\text{acac})]$ in hexanes	2084 vs, 2066 vw, 2014 vs, 1984 vw	this work
sample formed by adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto MgO	2080 vs, 2003 vs	this work
sample formed by adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto $\gamma\text{-Al}_2\text{O}_3$	2083 vs, 2008 vs	this work
sample formed by adsorption of $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{COO})]$ onto MgO	2083 s, 2004 s	6
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ in THF	2053 s, 1976 s	17

became light yellow, with an infrared spectrum (ν_{CO} : 2053 s and 1976 s cm^{-1}) similar to that of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ ¹⁷ (Table 1).

Carbonylation of Samples Prepared with Dried Hexanes. The sample prepared on MgO from $[\text{Rh}(\text{CO})_2(\text{acac})]$ dissolved in dried hexanes was loaded into a Schlenk flask and treated with CO at 1 atm and room temperature. After 4 days under CO, the sample was violet-purple. The infrared spectrum changed from that characteristic of a rhodium subcarbonyl to a spectrum that is markedly different, simple, and suggestive of a single surface species (ν_{CO} : 2086 sh, 2070 sh, 2047 vs, 2034 sh, 2012 sh, 1815 w, 1797 w cm^{-1}) (Figure 2A). When the resultant rhodium carbonyl was exposed to air for 2 min, the ν_{CO} spectrum changed to two strong bands, at 2081 and 2004 cm^{-1} , similar to the spectrum of the original supported rhodium dicarbonyl species shown in Figure 1B.

The sample prepared from $[\text{Rh}(\text{CO})_2(\text{acac})]$ adsorbed on $\gamma\text{-Al}_2\text{O}_3$ from dried hexanes was similarly treated in CO in a Schlenk flask at room temperature for 4 days. The infrared spectrum of the resulting violet-purple $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium species (Figure 2B) is almost the same as that of the species supported on MgO; the results suggest the formation of the same rhodium species on each surface. Like the ν_{CO} infrared spectrum

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Table 2. Infrared Data Characterizing the Carbonyl Stretching Region of the Supported Species Formed from Adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ Dissolved in Dried Hexanes onto MgO or onto $\gamma\text{-Al}_2\text{O}_3$

sample ^a	ν_{CO} , cm^{-1}
carbonylated rhodium/MgO (1A) ^b	2086 sh, 2070 sh, 2047 vs, 2034 sh, 2012 sh, 1815 w, 1797 w
1A following air exposure	2081 vs, 2004 vs
extract of 1A/[K][CH ₃ COO]/CH ₃ OH/N ₂	2067 sh, 2045 vs, 2008 sh, 1761 w
extract of 1A/[PPN][Cl]/THF/N ₂ /1 min	2087 vw, 2046 vs, 2017 vw, 1760 w
extract of 1A/[PPN][Cl]/THF/N ₂ /30 min	2054 ms, 1976 vs, 1823 mw, 1766 m
carbonylated rhodium/ $\gamma\text{-Al}_2\text{O}_3$ (1B) ^b	2086 sh, 2050 vs, 2035 sh, 2010 sh, 1825 w, 1797 s
1B following air exposure	2083 vs, 2009 vs
extract of 1B/[K][CH ₃ COO]/CH ₃ OH/N ₂	2068 vw, 2046 vs, 2010 vw, 1757 w
extract of 1B/[PPN][Cl]/THF/N ₂ /30 min	2055 ms, 2040 w, 2010 vw, 1976 vs, 1825 w, 1767 mw
[N(CH ₃) ₃ (C ₆ H ₆)] ₂ [Rh ₁₂ (CO) ₃₀] in THF	2070 w, 2053 s, 2040 s, 2007 w, 1823 w, 1807 w, 1771 s

^a The notation denotes the conditions of treatment of each sample during extraction of the rhodium carbonyl species from the surface by cation exchange metathesis; for example, extract formed from 1A denoted by 1A/[K][CH₃COO]/CH₃OH/N₂ was prepared by treatment of sample 1A with [K][CH₃COO] in methanol solution under N₂. ^b Carbonylated rhodium/MgO or carbonylated rhodium/ $\gamma\text{-Al}_2\text{O}_3$ denotes the MgO- or $\gamma\text{-Al}_2\text{O}_3$ -supported sample, respectively, prepared from the $[\text{Rh}(\text{CO})_2(\text{acac})]$ sample that had been carbonylated in CO at 1 atm and room temperature for 4–5 days.

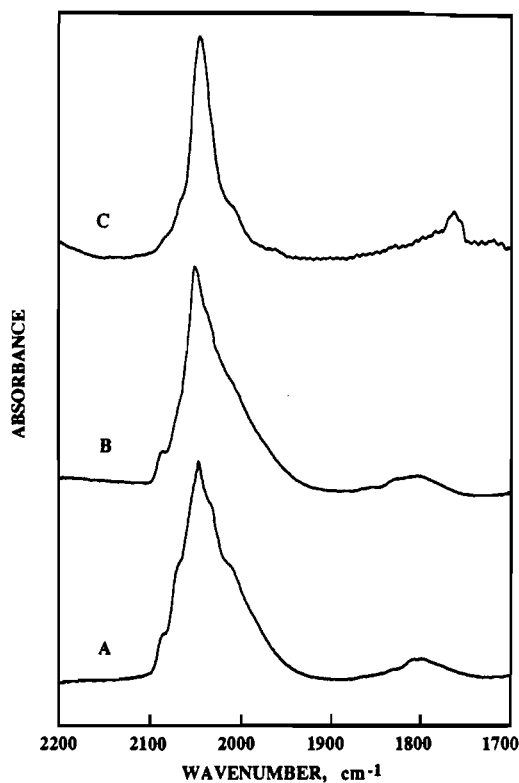


Figure 2. Infrared spectra characterizing treatment in CO at 1 atm and room temperature for 4 days of the samples prepared by adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ in dried hexanes onto (A) MgO and (B) $\gamma\text{-Al}_2\text{O}_3$. Spectrum C represents an extract solution formed by treating the sample of spectrum A with [K][CH₃COO] in methanol under a N₂ blanket.

of the MgO-supported rhodium species, that of the $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium species became two strong bands, at 2083 and 2009 cm^{-1} , upon short exposure of the sample to air; this result suggests the formation of rhodium dicarbonyls.

Attempts to extract the surface species from the MgO surface were carried out in the drybox as follows: About half of the carbonylated sample (about 1 g) was transferred into a Schlenk flask and brought into contact with [K][CH₃COO] in methanol solution under N₂; the solution immediately became violet and the solid white. Evidently, the supported species had been extracted. The solution in the drybox was transferred to an infrared cell, which was then sealed, and the spectrum of the violet solution was recorded (ν_{CO} : 2067 sh, 2045 vs, 2008 sh, 1761 w cm^{-1}) (Figure 2C). This spectrum is similar to that of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ in THF¹⁵ (Table 2). The extract solution, after being in the drybox for 2 h, remained violet, and the infrared spectrum recorded 2 h later was the same as that of Figure 2C.

Another 1-g sample in another Schlenk flask was used in an

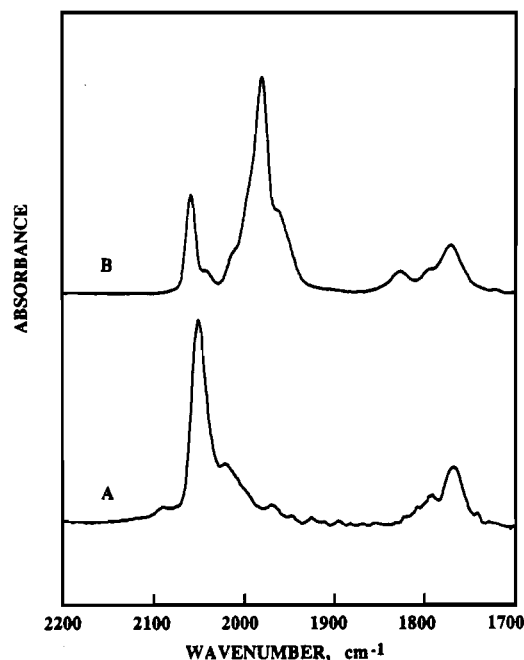


Figure 3. Infrared spectra of the extract solution formed by treatment of the sample of spectrum 2A with [PPN][Cl] in THF: (A) spectrum taken within 1 min; (B) spectrum taken after 30 min.

attempt to extract the surface species. No extraction was observed with THF alone; the solid remained violet-purple and the THF solution clear. However, when [PPN][Cl] was added to the THF slurry, the solution immediately became violet and the solid white. The immediately recorded infrared spectrum of the violet solution includes ν_{CO} bands (Figure 3A) similar to those characterizing the solution resulting from the extraction described above with [K][CH₃COO] in methanol (Figure 2C); these results indicate that $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ had been extracted with [PPN][Cl] in THF. However, the extract solution changed color; after 30 min in the drybox, the color changed from violet to greenish brown. The infrared spectrum of the resultant solution showed that the carbonyl bands corresponding to $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ had decreased in intensity, and a new, strong peak at 1766 cm^{-1} was observed (Figure 3B). These results indicate that $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ was not stable in THF solution in the presence of [PPN][Cl].

When the equivalent extraction experiments were carried out with samples of the carbonylated rhodium species supported on $\gamma\text{-Al}_2\text{O}_3$, the same results were observed (Table 2).

Carbonylation of Samples Prepared with Undried Hexanes. About 3 g of the sample prepared from $[\text{Rh}(\text{CO})_2(\text{acac})]$ adsorbed on MgO from undried hexanes was placed in a Schlenk flask and treated with CO at 1 atm and room temperature. After 5 days under CO, the sample was reddish orange. The infrared spectrum

Table 3. Infrared Data Characterizing the Carbonyl Stretching Region of the Supported Species Formed from Adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ Dissolved in Undried Hexanes onto MgO or onto $\gamma\text{-Al}_2\text{O}_3$

sample ^a	ν_{CO} , cm^{-1}
carbonylated rhodium/MgO (1A) ^b	2085 w, 2046 vs, 2012 vs, 1818 m, br
1A following air exposure	2081 vs, 2004 vs
extract of 1A/[K][CH ₃ COO]/CH ₃ OH/CO (2A)	2046 vs, 2014 vs, 1871 mw, 1841 m, 1788 m
2A following N ₂ purge	2087 vw, 2046 vs, 2017 vw, 1760 w
extract of 1A/[PPN][Cl]/THF/CO/1 min	2047 vs, 2015 vs, 1845 m, 1787 m
extract of 1A/[PPN][Cl]/THF/CO/30 min	2043 ms, 2014 s, 1976 s, 1840 w, 1826 mw, 1787 w
extract of 1A/[K][CH ₃ COO]/CH ₃ OH/N ₂	2082 sh, 2045 vs, 2010 sh, 1758 w
carbonylated rhodium/ $\gamma\text{-Al}_2\text{O}_3$ (1B) ^b	2087 w, 2050 s, 2014 s, 1820 br, m
1B following air exposure	2084 vs, 2009 vs
extract of 1B/[K][CH ₃ COO]/CH ₃ OH/CO	2045 vs, 2012 vs, 1869 w, 1840 mw, 1787 mw
[PPN][Rh ₅ (CO) ₁₅] in THF ¹⁷	2045 s, 2010 vs, 1868 m, 1838 ms, 1785 m

^a See footnote a, Table 2. ^b See footnote b, Table 2.

changed from that characteristic of a rhodium subcarbonyl to a markedly different spectrum that is simple and suggestive of a single surface species (ν_{CO} : 2085 w, 2046 vs, 2012 vs, 1818 br, m cm^{-1}) (Figure 4A). After exposure of the resultant sample to air for 2 min, the spectrum included only two ν_{CO} bands, at 2081 and 2004 cm^{-1} , similar to the spectrum of the original supported rhodium dicarbonyl (Figure 1B). When the $\gamma\text{-Al}_2\text{O}_3$ -supported $[\text{Rh}(\text{CO})_2(\text{acac})]$ was treated in the same way, the sample also became reddish orange and had an infrared spectrum (Figure 4B) very similar to that of the MgO-supported rhodium species (Figure 4A).

The sample of the carbonylated rhodium species on MgO was separated into three 1-g portions in the drybox; each flask was removed from the drybox and connected to a Schlenk line. The sample in flask A was purged with CO and then brought into contact with $[\text{K}][\text{CH}_3\text{COO}]$ in methanol solution; the solution immediately became reddish orange and the solid white. Evidently, the supported species had been extracted. The infrared spectrum of the reddish orange solution was recorded (ν_{CO} : 2046 vs, 2014 vs, 1871 mw, 1841 m, 1788 m cm^{-1}) (Figure 4C). This spectrum is virtually the same as that reported for $[\text{Rh}_5(\text{CO})_{15}]^-$ in THF,¹⁴ which also is reddish orange (Table 3). The ultraviolet-visible spectrum was also recorded: strong absorptions were observed at 210 and 291 nm. The extract solution remained reddish orange under CO for 2 h, and the infrared spectrum recorded 2 h later was unchanged from that of Figure 4C. However, when the Schlenk flask containing the soluble rhodium carbonyl was purged with N₂ to remove CO, the solution turned violet. The infrared spectrum of the violet solution is characterized by ν_{CO} bands similar to those of Figure 2C, indicative of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$. The solution color changed back from violet to the original reddish orange when the Schlenk flask was purged with CO, and the infrared spectrum of the resultant reddish-orange solution was again similar to that of the spectrum recorded before the N₂ purge. These observations are consistent with the well-known reversible transformation of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ in solution.^{14,15}

A similar experiment was performed to investigate the effect of [PPN][Cl] in THF solution on the extraction. When the sample in flask B was brought into contact with THF under CO, the solid remained reddish orange and the solution clear. After addition of [PPN][Cl] to the slurry, the solution immediately became reddish orange. The immediately recorded infrared spectrum (Figure 5A) is the same as that in Figure 4C. However, the solution changed color from reddish orange to greenish brown in 30 min, and the infrared spectrum recorded after this time indicated the appearance of a peak at 1976 cm^{-1} (Figure 5B), similar to that observed in the extraction of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ with [PPN][Cl] in THF solution.

Another experiment was performed to investigate the extraction in the absence of CO; N₂ was present instead. The reddish-orange sample in flask C was brought into contact with methanol under N₂; the solution was clear, but the solid changed color to violet-purple. When $[\text{K}][\text{CH}_3\text{COO}]$ was added to the slurry,

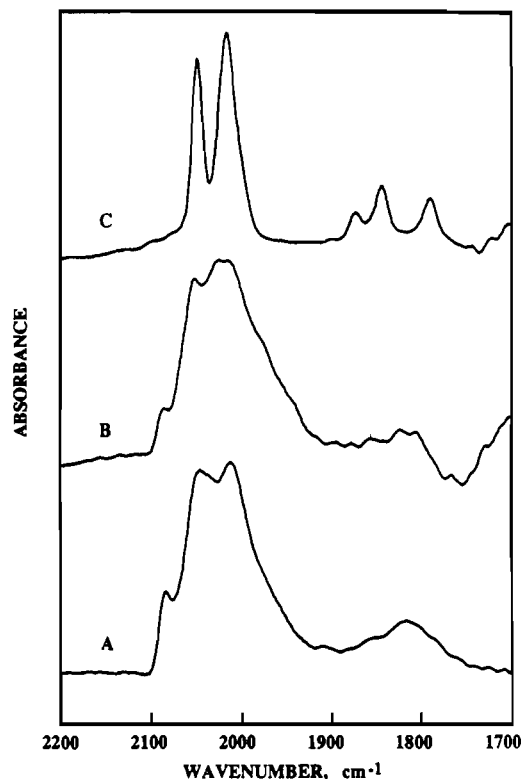


Figure 4. Infrared spectra characterizing treatment in CO at 1 atm and room temperature for 4 days of the samples prepared by adsorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ in undried hexanes onto (A) MgO and (B) $\gamma\text{-Al}_2\text{O}_3$. Spectrum C is for an extract solution formed by treating the sample of spectrum A with $[\text{K}][\text{CH}_3\text{COO}]$ in methanol under a CO blanket.

the solution became violet, and the infrared spectrum was similar to that of Figure 4C, indicating the presence of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, not $[\text{Rh}_5(\text{CO})_{15}]^-$.

The extracted rhodium carbonyl species were further characterized by mass spectrometry, as follows. In a Schlenk flask 2 g of the MgO-supported $[\text{Rh}_5(\text{CO})_{15}]^-$, formed in the surface-mediated synthesis from $[\text{Rh}(\text{CO})_2(\text{acac})]$ as described above, was purged with CO and slurried with acetone added with an airtight syringe. The slurry was stirred for 5 min, and the solution became reddish orange, indicating the extraction of $[\text{Rh}_5(\text{CO})_{15}]^-$ into the solution. About 10 μL of the solution was immediately injected with an airtight syringe into the mass spectrometer. The negative-ion electrospray mass spectrum of the solution exhibits a prominent peak at m/z 1051; this product is attributed to an adduct formed from the cluster anion and two acetone molecules, namely, $[\text{Rh}_5(\text{CO})_{15}(\text{acetone})_2]^-$ (calculated m/z : 1050.5). This product was not observed when methanol was used instead of acetone as the solvent; rather, only cluster fragments were observed.

In another mass spectrometry experiment, $[\text{Rh}_5(\text{CO})_{15}]^-$ was extracted with methanol from the similarly prepared sample under

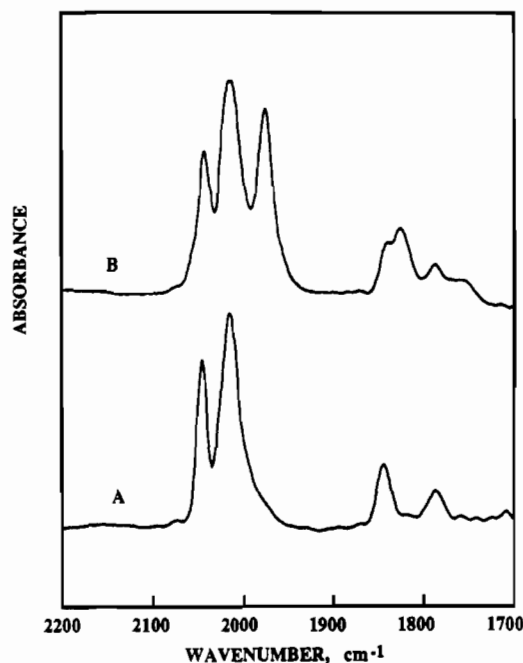


Figure 5. Infrared spectra of the extract solution formed by treatment of the sample of spectrum 4A with [PPN][Cl] in THF under a CO blanket: (A) spectrum taken within 1 min; (B) spectrum taken after 30 min.

CO and then converted into the dimeric $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ by replacing the CO with N_2 , as indicated by the color change from reddish orange to violet. The negative-ion electrospray mass spectrum of the violet solution exhibits a prominent peak at m/z 1038.4, which is in good agreement with the monoisotopic mass of $[\text{HRh}_6(\text{CO})_{15}]^-$ (calculated m/z : 1038.4), a known cluster that is converted facily into the dimeric $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$.¹⁸ The spectrum also included a peak of the expected size at m/z 1039.4, identified as the above cluster anion with one ^{13}C atom and confirming the identification as a singly charged species (dianions would give peaks separated by only 0.5 m/z unit). The observation of $[\text{HRh}_6(\text{CO})_{15}]^-$ rather than the parent $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ dimer indicates the instability of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ under the conditions used to effect electrospray ionization. The lack of infrared bands corresponding to the presence of hydrogen in the dianion in solution supports the contention that the incorporation of hydrogen takes place during the ionization and nebulization process.

To estimate the yield of $[\text{K}][\text{Rh}_5(\text{CO})_{15}]$ in the surface-mediated synthesis from $[\text{Rh}(\text{CO})_2(\text{acac})]$, a MgO-supported sample containing the former and prepared as described above was transferred to the drybox. A 50-mL round-bottom Schlenk flask was connected to a frit, a 2.0-g sample containing 1 wt % Rh was placed on top of the frit, and the flask was sealed with a septum. The sample color changed from orange-red to light orange during the sample transfer. After the sample had been removed from the drybox, CO was introduced at 1 atm. The sample was kept under CO for 20 h, and its color changed back to orange-red. A degassed solution of a large excess of $[\text{K}][\text{CH}_3\text{COO}]$ in methanol was introduced into the space above the frit by an airtight syringe, and an orange-purple liquid inferred to be $[\text{K}][\text{Rh}_5(\text{CO})_{15}]$ formed immediately and flowed down through the frit and into the flask. During this extraction, CO flow was maintained through the sample to stabilize the $[\text{K}][\text{Rh}_5(\text{CO})_{15}]$. In a period of 4 h, 25 mL of $[\text{K}][\text{CH}_3\text{COO}]$ solution was used, and a significant fraction of the rhodium cluster was extracted, as indicated by the observation that the solid had become almost white. The liquid extract was evacuated for 5 h to remove the methanol solvent, and the color changed to purple, indicative of

$[\text{K}]_2[\text{Rh}_{12}(\text{CO})_{30}]$; 0.017 g of solid sample was obtained, indicating that about 47% of the rhodium was recovered. This is a rough estimate and is considered to be a lower limit of the attainable yield, since some of the rhodium remained on the surface of the metal oxide; no attempt was made to maximize the yield.

Discussion

Formation of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ on MgO and on $\gamma\text{-Al}_2\text{O}_3$ Surfaces. The results are consistent with the inference that the rhodium carbonyl species initially formed from $[\text{Rh}(\text{CO})_2(\text{acac})]$ on MgO and on $\gamma\text{-Al}_2\text{O}_3$ were converted in high yield to give either supported $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ or supported $[\text{Rh}_5(\text{CO})_{15}]^-$, depending on the conditions of the adsorption of the rhodium precursor. The evidence includes (1) the infrared spectra of the supported rhodium carbonyls, which clearly demonstrate the conversion of the initially formed species, (2) the colors of the solid samples, which respectively match those of rhodium carbonyls in solution, (3) the infrared spectra of the extracted species, which (depending on the conditions) are consistent with the identification of either $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ or $[\text{Rh}_5(\text{CO})_{15}]^-$ as the predominant extracted species and suggest that one of these clusters or the other was the predominant surface species, and (4) the mass spectra of the corresponding extracted rhodium carbonyl clusters.

This is the first report of the syntheses of these clusters on surfaces. The surface-mediated syntheses of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ are simple and effective. The best reported syntheses of these anions involve multistep procedures starting with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ^{14,15} or $[\text{Rh}_4(\text{CO})_{12}]$.¹⁹ The surface-mediated syntheses described here are among the few to have been reported.²⁰⁻²²

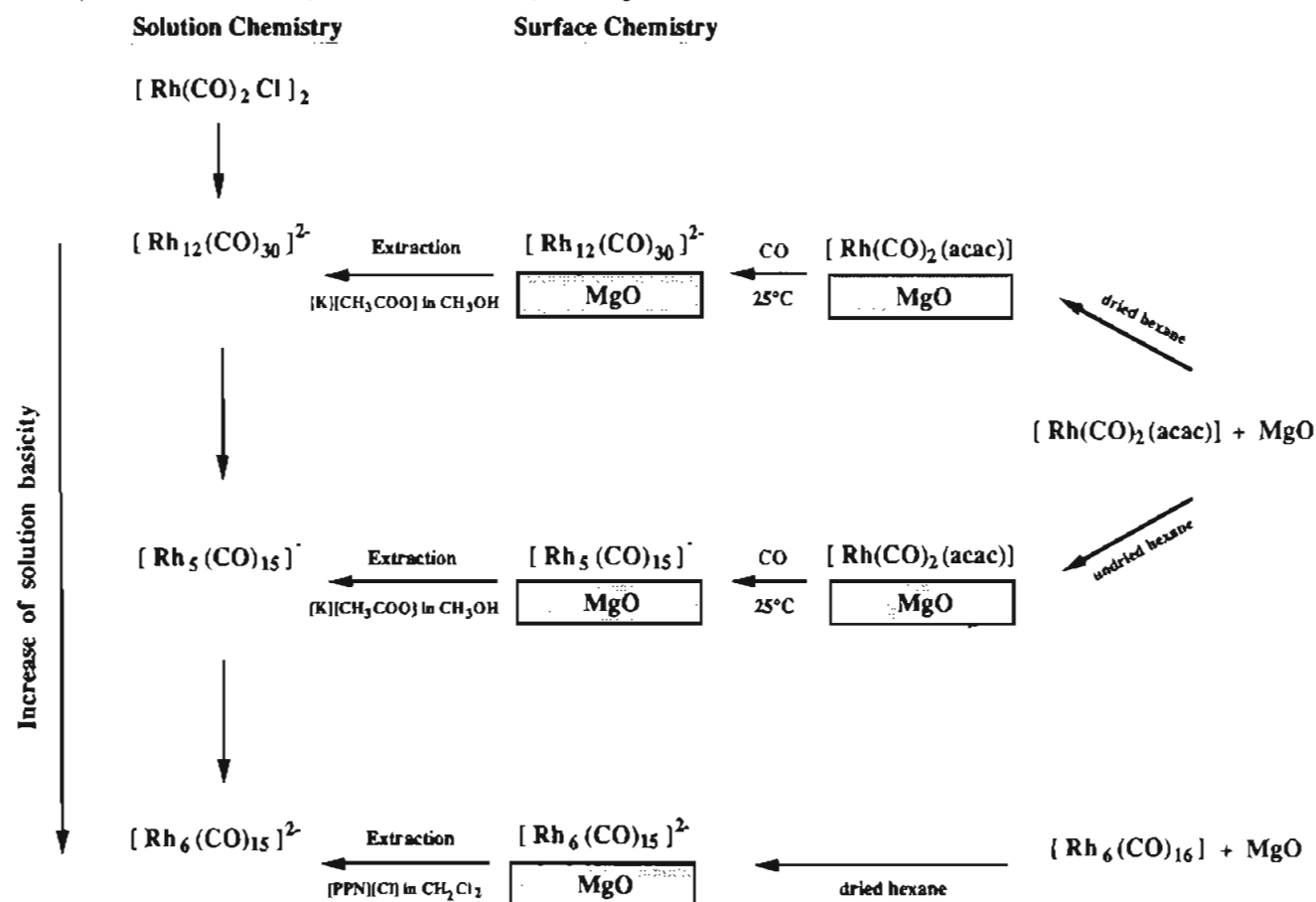
The basic surface of MgO is known to be an efficient medium for the synthesis of anionic metal carbonyl clusters^{22,23} from mononuclear metal carbonyl precursors. The reported results show that the chemistry of osmium and iridium carbonyls on the surface of partially hydroxylated MgO parallels the chemistry of the osmium and iridium carbonyls in basic solutions.^{20,22} The experiments reported here with a mononuclear rhodium carbonyl precursor on MgO and on $\gamma\text{-Al}_2\text{O}_3$ extend the surface organometallic chemistry, as discussed in the following paragraphs.

Chemisorption of $[\text{Rh}(\text{CO})_2(\text{acac})]$ onto MgO and onto $\gamma\text{-Al}_2\text{O}_3$. $[\text{Rh}(\text{CO})_2(\text{acac})]$ is a convenient precursor for the synthesis of rhodium carbonyl clusters because it is readily available and because the acac ligand (in contrast to chloride, for example) is not expected to affect substantially the properties of MgO or $\gamma\text{-Al}_2\text{O}_3$, which are important in regulating the surface organometallic chemistry.²³ After contacting of the support under N_2 with a hexane solution of $[\text{Rh}(\text{CO})_2(\text{acac})]$, a fast chemisorption took place, as evidenced by the color change of the solution and by a shifting to slightly lower energy of the carbonyl bands in the infrared spectrum. By analogy to what has been suggested for the reaction of $[\text{Ir}(\text{CO})_2(\text{acac})]$ with the MgO surface,²² the primary surface reaction of $[\text{Rh}(\text{CO})_2(\text{acac})]$ with MgO or with $\gamma\text{-Al}_2\text{O}_3$ is suggested to take place through the protolysis of the acac ligand by the hydroxyl groups of the MgO or the $\gamma\text{-Al}_2\text{O}_3$ surface to form $[\text{Rh}(\text{CO})_2\{\text{OM}\}_2]$ (where M denotes Mg or Al and the braces denote groups terminating the solid metal oxide). A similar interpretation has been suggested by Dossi et al.⁶ for the formation of $\text{Rh}(\text{CO})_2\{\text{OMg}\}_2$ as a result of adsorption of $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{COO})]_2$ on MgO. The basic O^{2-} sites of the MgO

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Scheme 1. Surface Chemistry of Rhodium Carbonyls on MgO



surfaces, and the chemistry of MgO is complicated by the significant reducing character of the highly dehydroxylated MgO surface.²³

We postulate that the surface chemistry of formation of the rhodium cluster anions is roughly analogous to the solution chemistry summarized above, but in view of the complexity of the surface chemistry, it would seem to be imprudent to attempt to unravel the possible influences of base strength, reducing properties, and concentration of surface hydroxyl groups in interpreting the surface reactivity.

The formation of these rhodium carbonyls on MgO and on γ -Al₂O₃ has not been observed before. Dufour et al.⁴ observed the formation of the green [Rh₆(CO)₁₅]²⁻ upon adsorption of [Rh₆(CO)₁₆] onto a partially hydroxylated MgO.⁴ When the MgO was dehydroxylated at high temperature, simple physisorption of [Rh₆(CO)₁₆] was observed. However, Dossi et al.⁵ observed the formation of green species upon adsorption of [Rh₆(CO)₁₆] onto dehydroxylated MgO; it was inferred to be [Rh₆(CO)₁₅]²⁻. When the MgO surface was treated in vacuo at room temperature, simple physisorption of [Rh₆(CO)₁₆] was observed.

The contrasting observations of the reactivity of [Rh₆(CO)₁₆] on MgO by these two groups might be reconciled with each other by the suggestion that surface hydroxyl group content plays a role in the chemistry. We suggest that the reason that these authors observed the formation of [Rh₆(CO)₁₅]²⁻, and not [Rh₅(CO)₁₅]⁻ or [Rh₁₂(CO)₃₀]²⁻, may be related to their use of highly dehydroxylated MgO, which is a strong reducing agent.²³ Reduction of [Rh₆(CO)₁₆] on the surface may have formed [Rh₆(CO)₁₅]²⁻ directly.

When MgO- and γ -Al₂O₃-supported [Rh(CO)₂Cl]₂ were reductively carbonylated, [Rh₆(CO)₁₆] was formed.²⁶ The formation of the neutral, not an anionic, rhodium carbonyl cluster was suggested to be caused by the presence of chloride species on the surface, making the surface acidic.⁶

The surface chemistry of rhodium carbonyls on MgO is summarized in Scheme 1.

Conclusions

Reductive carbonylation at 25 °C and 1 atm of CO of the rhodium species formed from adsorbed [Rh(CO)₂(acac)] on MgO and on γ -Al₂O₃ gives supported [Rh₁₂(CO)₃₀]²⁻ or supported [Rh₅(CO)₁₅]⁻, depending on the degree of hydroxylation of the surface. [Rh₁₂(CO)₃₀]²⁻ is formed on both MgO and γ -Al₂O₃ surfaces when the adsorption is carried out in the presence of dried hexanes; this anion can be extracted efficiently with [K][CH₃COO] in methanol solution under N₂. [Rh₅(CO)₁₅]⁻ is formed when undried hexanes are used in the adsorption of the rhodium precursor; this anion can be extracted efficiently with [K][CH₃COO] in methanol solution under CO. There is at least a rough parallel between the organometallic surface chemistry and that occurring in basic solutions. The surface-mediated synthesis is recommended as an efficient method for preparation of [Rh₅(CO)₁₅]⁻, which can easily be converted to [Rh₁₂(CO)₃₀]²⁻.

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