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Surface Organometallic Chemistry: Chemisorption and Thermodecomposition of $Ru_3(CO)_{12}$ on Partially Hydroxylated Magnesia and Related Oxides

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The reaction between $Ru_3(CO)_{12}$ and the surface of fully or partially hydroxylated magnesia leads to the anionic cluster $[HRu_3(CO)_{11}]^-(Mg^{2+})_{1/2}$ ($[HRu_3(CO)_{11}]^-$ = [**1**]$^-$). The presence of [**1**]$^-$ at the surface has been deduced from in situ IR and mass balance experiments; finally [**1**]$^-$ has been extracted from the surface by [PPN]Cl. Formation of [**1**]$^-$ from $Ru_3(CO)_{12}$ occurs also on the surface of zinc and lanthanum oxides. During programmed thermal decomposition of [**1**]$^-$ on magnesia under vacuum or controlled atmosphere, various species have been evidenced depending on temperature and hydroxylation degree of the support: mononuclear $Ru^{II}(CO)_n(OMg{<})_2$ and metallic particles of ruthenium (10–15 Å) covered with undissociated carbon monoxide. Simultaneously, three types of reactions involving the cluster carbonyl ligands occur: water gas shift reaction (which transforms those ligands into CO_2 and H_2), CO dismutation to CO_2 and surface carbon, and methanation. The water gas shift reaction is tentatively attributed to the anionic cluster while the latter two are attributed to the metal particles.

The reactivity of transition-metal carbonyls, especially that of group VIII metal clusters, has been the subject of recent publications.[1-26] These studies have revealed a great variety of reactions between a metal carbonyl cluster and a support,[1] depending on the nature of the metal, the nature of the ligands, and the degree of dehydroxylation of the support. When adsorbed onto partially or fully hydroxylated basic oxides, $Fe_3(CO)_{12}$[17-19] reacts to give $[HFe_3(CO)_{11}]^-$, probably via a nucleophilic attack of surface OH groups at coordinated CO. Similarly, $Os_3(CO)_{12}$ reacts with magnesia[20] to give $[HOs_3(CO)_{11}]^-$ and $[Os_3(CO)_{11}]^{2-}$.

For $Ru_3(CO)_{12}$, the formation of $Ru_3(\mu\text{-}H)(\mu\text{-}OSi{<})(CO)_{10}$ that is observed on partially hydroxylated silica[21] parallels the behavior of $Os_3(CO)_{12}$.[3] On partially hydroxylated alumina, the surface organometallic chemistry of $Ru_3(CO)_{12}$ seems to be more complicated;[14,15] it depends on the pretreatment temperature of the alumina and on the experimental conditions. Studies related to $Ru_3(CO)_{12}$ on magnesia are much less numerous; Pierantozzi[27] recently reported formation of mixtures of anions $[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$.

We report here the behavior of $Ru_3(CO)_{12}$ at the surface of a fully or partially hydroxylated magnesia as part of our systematic study of the surface organometallic chemistry of group VIII metal carbonyl clusters.

Experimental Section

1. Materials. $Ru_3(CO)_{12}$ was purchased from Johnson-Mathey and used without further purification. The solvents (dichloromethane, pentane) were distilled prior to use over P_2O_5 and stored, under argon, over freshly activated zeolites. The magnesia support (200 m^2/g) was obtained by decomposition, under high vacuum, at 400 °C, of high-purity $Mg(OH)_2$. It was then submitted to several cycles of oxygen treatment (500 Torr, 0.5 h) and vacuum treatment (10^{-4} Torr, 2 h) at the same temperature. This procedure allowed the support to be degassed and dehydrated in a reproducible manner and reduced the amount of carbonate present. The supports obtained in this way could be rehydrated by introducing water vapor (22 Torr at 25 °C) for 16 h, and then a treatment under vacuum (10^{-4} Torr) at a given temperature (25, 200, or 500 °C) allowed the degree of hydroxylation to be varied in a controlled manner (MgO-25, MgO-200, or MgO-500). Under these conditions, MgO-25 represents a surface almost completely covered with a monolayer of OH groups and MgO-200 a partially hydroxylated magnesia whereas the hydroxylation degree of MgO-500 is much lower, so that some Mg^{2+} and O^{2-} ions become accessible.[28]

The zinc oxide (Texon) has a surface area of 43 m^2/g. Lanthanum oxide was purchased from Prolabo. These oxides have been submitted to the same pretreatment as that described for magnesia.

$Ru_3(^{13}CO)_{12}$ (100% enriched) has been synthesized by following the method described by Darensbourg.[29]

2. Infrared Measurements. All infrared measurements have been performed on a Nicolet MX 10 FT spectrometer. A special cell, previously described,[3] allowed in situ impregnation and in situ treatments of a disk of oxide.

3. Gas-Phase Analysis. The design of the reactor used for the analysis of evolved gases has already been described.[3] It allowed sampling of the gas phase while preventing contact with air. Qualitative and quantitative analysis of the gas phase was performed by GPC.[3]

4. Extraction of $[HRu_3(CO)_{11}]^-$ from the Surface. In a typical experiment, 44 mg (0.069 mmol) of $Ru_3(CO)_{12}$ in 20 mL of CH_2Cl_2 was adsorbed onto 2 g of pretreated MgO-25. The solid was then thoroughly washed with CH_2Cl_2, in order to remove unreacted $Ru_3(CO)_{12}$. A solution of [PPN]Cl (0.083 mmol) in 20 mL of CH_2Cl_2 was then introduced. After a few minutes of stirring at room temperature, the solid was decolorized and the solution turned red. After filtration and solvent evaporation, the extracted species was characterized by IR and ^{1}H NMR spectroscopies.

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Table I. Spectral Characteristics (IR, ^{1}H NMR) of $[HRu_3(CO)_{11}]^-$ Supported on (or Extracted from) Magnesia, Lanthanum Oxide, and Zinc Oxide

origin	ν(CO), cm^{-1} (in CH_2Cl_2)					δ
$Ru_3(CO)_{12}$/MgO-25	2078 m, sh	2026 s, br	1756 w			
$Ru_3(CO)_{12}$/MgO-200	2073 m	2020 s, br	1767 w			
$Ru_3(CO)_{12}$/MgO-500	2080 m, sh	2030 s, br				
$Ru_3(^{13}CO)_{12}$/MgO-200	2023 m, sh	1986 s, br	1956 s, br	1729 w		
extracted from MgO-200[a]	2075 w	2017 vs	1987 s	1953 sh	1780 w	−12.67[b]
extracted from La_2O_3-200[a]	2072 vw	2016 s	1987 s	1952 m		−12.56[b]
extracted from ZnO-200[a]	2072 w	2016 s	1987 s	1953 m		
$[HRu_3(CO)_{11}]^-[PPN]^+$	2072 w	2013 vs	1987 s	1902 m	1734 m[c]	−12.62[d]

[a] By [PPN]Cl in CH_2Cl_2. [b] In $CDCl_3$. [c] In THF; from ref 34. [d] In CD_3CN.

5. Electron Microscopy. For the characterization by transmission electron microscopy, the samples were prepared in the following manner: a small quantity of powder was sonicated in ethanol, and one drop of the resulting suspension was deposited on a copper grid (400 mesh) covered with a thin film of carbon. After evaporation of the solvent, the sample was transferred into a JEOL TEM-100CX transmission electron microscope.

Results

1. Chemisorption of $Ru_3(CO)_{12}$ onto a Partially Hydroxylated Magnesia. The reaction between a CH_2Cl_2 (or pentane) solution of $Ru_3(CO)_{12}$ and a partially hydroxylated magnesia (MgO-25, MgO-200, or MgO-500) is instantaneous at room temperature. Chemisorption is evidenced by the fact that the orange solution of the cluster is completely decolorized, while the solid becomes red. During the chemisorption process, only minor amounts of CO (0.06 mol/mol of cluster) and CO_2 (0.05 mol/mol of cluster) are detected in the gas phase. The infrared spectra (Table I) taken in situ suggest the formation, at the surface of magnesia, of the anionic hydrido cluster $[HRu_3(CO)_{11}]^-$. Electronic spectra (λ_{max} 235, 290, 370 nm) are in agreement with the existence of the Ru_3 frame and thus with the occurrence of this anion on the surface of magnesia. Moreover, this anion can be extracted from the surface by metathetical exchange with [PPN]Cl/CH_2Cl and has been characterized as $[HRu_3(CO)_{11}]^-$ by its IR and ^{1}H NMR spectra (Table I).

The high degree of similarity between the IR spectra of the chemisorbed and the extracted species constitutes a strong argument in favor of the formation of $[HRu_3(CO)_{11}]^-$ at the surface of magnesia. Observation of this similarity is a necessary requirement in view of the fact that $[HRu_3(CO)_{11}]^-$ can also be obtained by reaction between $Ru_3(CO)_{12}$ and surface OH^- catalyzed by [PPN]Cl.[30]

The initial degree of hydroxylation of magnesia has apparently no influence on the initial formation of $[HRu_3(CO)_{11}]^-$ on the surface, at least for temperatures of dehydroxylation up to 500 °C (MgO-25, MgO-200, MgO-500).

This hydrido–carbonyl anionic cluster is probably the result of the nucleophilic attack of the basic surface OH groups of magnesia at coordinated CO, a well-known reaction in solution in basic media:[31]

$$Ru_3(CO)_{12} + \text{H-O-Mg<} \rightarrow [HRu_3(CO)_{11}]^-(Mg^{2+})_{1/2} + CO_2(\text{ads}) \quad (1)$$

The expected CO_2 evolution (1 mol/mol of cluster) has not been observed due to the easy adsorption of CO_2 on magnesia as carbonates.[32] Moreover, the amount of carbonates expected under our experimental conditions is too small to be detected by IR spectroscopy.[17]

For $[HRu_3(CO)_{11}]^-$ on magnesia, we and others[27] have noticed a weak band at 1608 cm^{-1}, which had been ascribed to a possible tight ion-pair interaction. In order to check this hypothesis, we have studied the chemisorption of $Ru_3(^{13}CO)_{12}$ (100% enriched) onto magnesia-200. The whole spectrum (ν(CO) 2023 w, 1986 s, 1956 s, 1729 w cm^{-1}) is shifted to lower frequencies by ca. 40 cm^{-1}, as expected for ^{13}C substitution. However, the band at 1608 cm^{-1} was not shifted, indicating that this band is not due to a carbonyl but arises probably from reaction of CH_2Cl_2 with magnesia.

2. Chemisorption of $Ru_3(CO)_{12}$ onto Zinc Oxide and Lanthanum Oxide. Due to the high level of absorption of the infrared beam by zinc oxide and lanthanum oxide, the chemisorption process of $Ru_3(CO)_{12}$ onto these oxides cannot be followed by in situ IR spectroscopy.

In both cases, using the Schlenk tube technique, partial decolorization of the initial orange CH_2Cl_2 solution of $Ru_3(CO)_{12}$ occurs. The solid becomes pink, which suggests chemisorption of the cluster onto the support. In order to avoid any possible side reactions between nonchemisorbed $Ru_3(CO)_{12}$ and [PPN]Cl,[30] the solid is thoroughly washed with CH_2Cl_2. Then, the species extracted from the surface by [PPN]Cl/CH_2Cl_2 is characterized by its IR and ^{1}H NMR spectra (Table I) as $[PPN][HRu_3(CO)_{11}]$.

Apparently, the behaviors of zinc oxide and lanthanum oxide toward $Ru_3(CO)_{12}$ are very similar to what has been observed in the case of magnesia: the surface OH groups behave as nucleophiles toward coordinated CO. These results are analogous to those previously reported concerning the reactivity of $Fe_3(CO)_{12}$ toward these two supports.[17]

3. Thermodecomposition of $[HRu_3(CO)_{11}]^-$ ([1]$^-$) Adsorbed onto Magnesia. The thermodecomposition pattern of the supported anionic cluster [1]$^-$ is dependent on the degree of hydroxylation of the magnesia (MgO-25, MgO-200, and MgO-500). In each case, we have followed the reaction by in situ IR spectroscopy, quantitative analysis of the gases evolved in a closed vessel, and electron microscopy.

$[HRu_3(CO)_{11}]^-$ Adsorbed onto Magnesia-25. Anion [1]$^-$ is stable on the surface of MgO-25 between 25 and 50 °C, as evidenced by IR spectroscopy (Figure 1a,b). This is also in agreement with the fact that no significant amount of any gas (such as CO, CO_2, or H_2) is evolved (Figure 2).

At ca. 80 °C, [1]$^-$ is progressively transformed into two new species characterized respectively by a band at 2025 cm^{-1} and two other ones at 2065 and 1982 cm^{-1}. These two species do not show the same behavior under subsequent heat treatment. The band at 2025 cm^{-1} is shifted toward lower frequencies with increasing temperatures (to 1970 cm^{-1} at 200 °C) (Figure 1c–e). Under CO pressure (300 Torr) and at room temperature, this band is shifted back to its starting value (2025 cm^{-1}). This behavior is the one expected for CO adsorbed onto particles of ruthenium metal[33] (ν(CO) depends on coverage of the metallic particles). Simultaneously, the intensity of the bands at 2065 and 1985 cm^{-1} diminishes when the temperature is increased, but their frequency remains unchanged. They almost disappear at about 200 °C but are partially restored in the presence of 200 Torr of CO (Figure 1g); under these conditions, two new bands at 2138 and 2065 cm^{-1} appear. This behavior parallels the one already observed when $Os_3(CO)_{12}$ is chemisorbed on alumina[3] and thermally decomposed; the species thus formed have been shown to be Os(II) carbonyl

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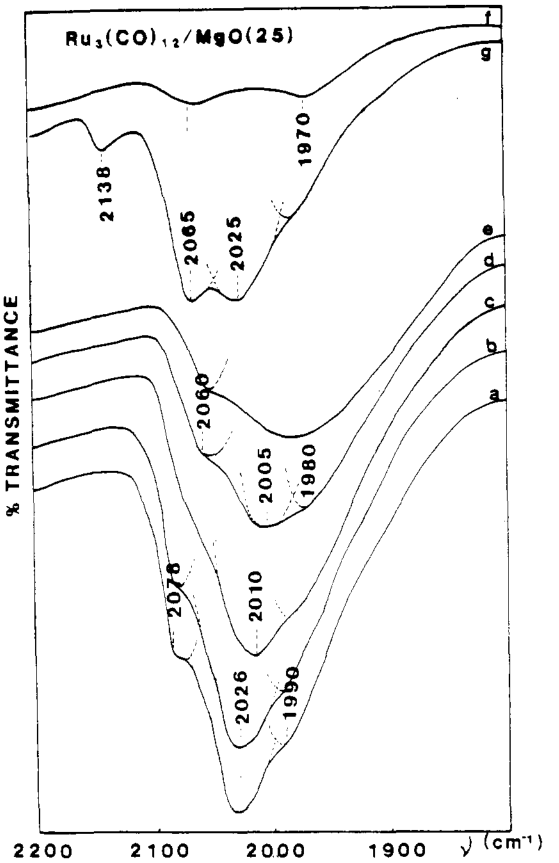


Figure 1. IR spectra in the ν(CO) region of $Ru_3(CO)_{12}$/MgO-25 after treatment under vacuum: (a) at 25 °C, 16 h; (b) at 50 °C, 5 h; (c) at 80 °C, 16 h; (d) at 105 °C, 5 h; (e) at 120 °C, 16 h; (f) at 200 °C, 4 h; (g) under 300 Torr CO, at 25 °C, 48 h.

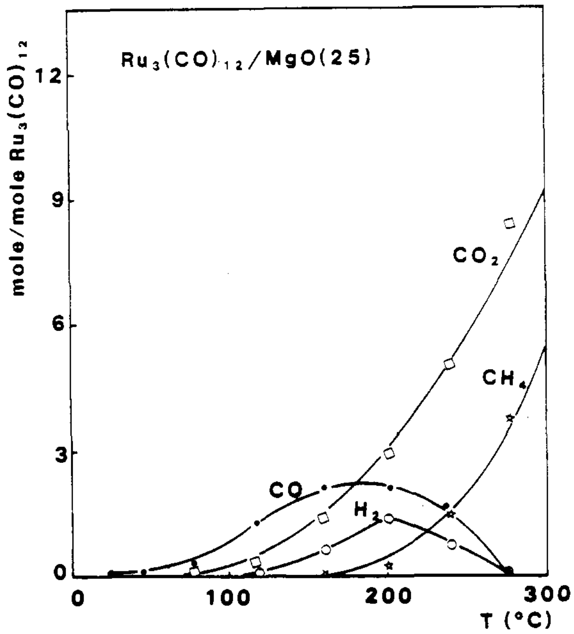


Figure 2. Gas evolution of $Ru_3(CO)_{12}$/MgO-25 during thermal treatment under vacuum.

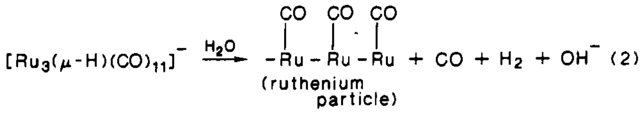
complexes of the type $Os^{II}(CO)_x(OAl<)_2$ ($x = 2, 3$). In our case, the observed frequencies (2138, 2085, and 1980 cm^{-1}) are in good agreement with the existence of $Ru^{II}(CO)_x(OMg<)_2$ ($x = 2, 3$) (Table II).[3,34-36]

Table II. Infrared Spectra (ν(CO)) of Ruthenium(II) and Osmium(II) Complexes

complex	ν(CO), cm^{-1}			ref
$Ru(CO)_3Cl_2]_2$	2143 s	2082 s	2015 m[a]	34, 35
$[Ru(CO)_3Br_2]_2$	2137 s	2073 s	2010 w[a]	34, 35
$[Ru(CO)_3I_2]_2$	2128 s	2069 s	2012 w[b]	35
$[Ru(CO)_2Cl_2]_n$	2066 m	1988 m[a]		35
$[Ru(CO)_2Br_2]_n$	2059 s	1990 m[a]		35
$[Ru(CO)_2I_2]_n$	2053 s	1995 s[b]		35, 36
$Ru(CO)_3(OMg<)_2$	2138 m	2065 s		this work
$Ru(CO)_2(OMg<)_2$	2065 s	1970 s[c]		this work
$[Os(CO)_3Cl_2]_2$	2134 m	2059 s		36
$[Os(CO)_2I_2]_n$	2112 w	2039 s	1980 s[b]	36
$[Os(CO)_3(OAl<)_2]_2$	2127 m	2034 s		3
$[Os(CO)_2(OAl<)_2]_n$	2127 m	2034 s, br	1970 mbr	3

[a] In CH_2Cl_2. [b] Nujol mull. [c] In CCl_4.

These observations suggest the simultaneous formation of metal particles covered with CO and oxidized Ru(II) carbonyl complexes, according to



$$[Ru_3(\mu\text{-}H)(CO)_{11}]^- \xrightarrow{H_2O} \overset{CO}{\overset{|}{-Ru}}-\overset{CO}{\overset{|}{Ru}}-\overset{CO}{\overset{|}{Ru}} + CO + H_2 + OH^- \quad (2)$$

(ruthenium particle)

$$[Ru_3(\mu\text{-}H)(CO)_{11}]^- \xrightarrow{H_2O} Ru^{II}(CO)_n(OMg<)_2 + H_2 + CO + OH^- \quad (n = 2, 3) \quad (3)$$

These reactions are accompanied by the progressive evolution of CO, H_2, CO_2, and CH_4 (Figure 2). The simultaneous formation of H_2 and CO_2 at low temperature can be ascribed to the occurrence of a water gas shift reaction between evolved CO and surface H_2O. This reaction is probably catalyzed by the anionic cluster $[1]^-$, which is known to catalyze the water gas shift reaction in basic medium.[37,38] At temperatures above 200 °C, besides CO_2, methane is the second major component in the gas phase. It results, probably, from CO methanation over Ru metal particles since CH_4 formation parallels CO disappearance.

These metal particles seem to be highly sensitive to oxidation by surface water since one does not further detect their presence by IR spectroscopy after 16-h evacuation under vacuum at 200 °C (Figure 2):

$$Ru(0) + HO\text{-}Mg< \rightarrow Ru^{II}(OMg<)_2 + H_2 \quad (4)$$

Indeed one expects this redox equilibrium to be strongly displaced toward the right in IR experiments that are carried out under vacuum, whereas it is less pronounced in a closed vessel, where the gas phase is in equilibrium with the products (the study of gas evolution is performed in a closed vessel).

$HRu_3(CO)_{11}^-$ Adsorbed onto Magnesia-200. The anionic cluster $[1]^-$ is progressively decomposed between 25 and 100 °C. This phenomenon is evidenced mainly by the progressive decrease of the intensity of the band at 1756 cm^{-1} (Figure 3). Simultaneously, the evolution of about 1 mol of CO/mol of cluster (Figure 4) is detected in the gas phase.

Above 130 °C, the major species observed on the surface of magnesia is Ru metal covered with CO, characterized by a broad band at 2000 cm^{-1} that is shifted to 1990 cm^{-1} at 180 °C (Figure 3d,e); these metal particles of ruthenium are well dispersed on the support, and their average diameter is 10–15 Å, as detected by electron microscopy. These metal particles are probably responsible for the reaction of CO methanation. This reaction occurs between CO arising from ligand dissociation and H_2 resulting from the water gas shift reaction.

$HRu_3(CO)_{11}^-$ Adsorbed onto Magnesia-500. Thermodecomposition of the anion $[1]^-$ on a more dehydroxylated magnesia such as MgO-500 leads to its decomposition already above ca. 85 °C

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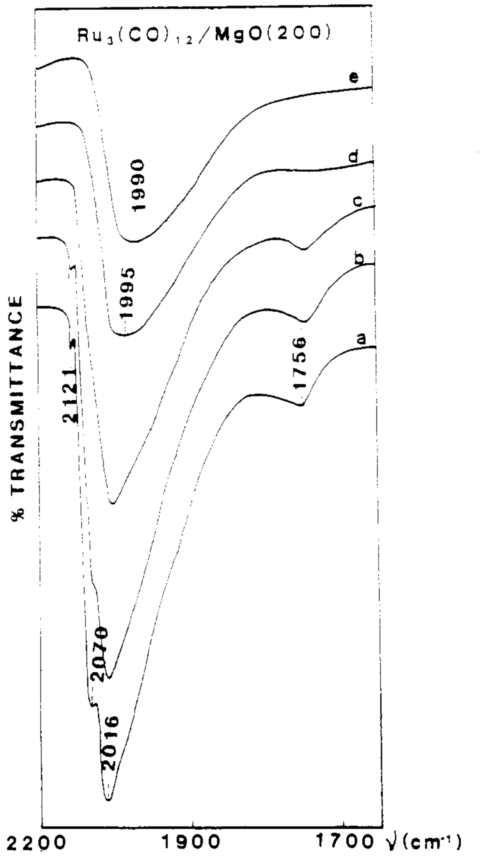

Figure 3. IR spectra in the ν(CO) region of $Ru_3(CO)_{12}$/MgO-200 after treatment under vacuum: (a) at 25 °C, 16 h; (b) at 50 °C, 5 h; (c) at 88 °C, 5 h; (d) at 127 °C, 16 h; (e) at 179 °C, 16 h.

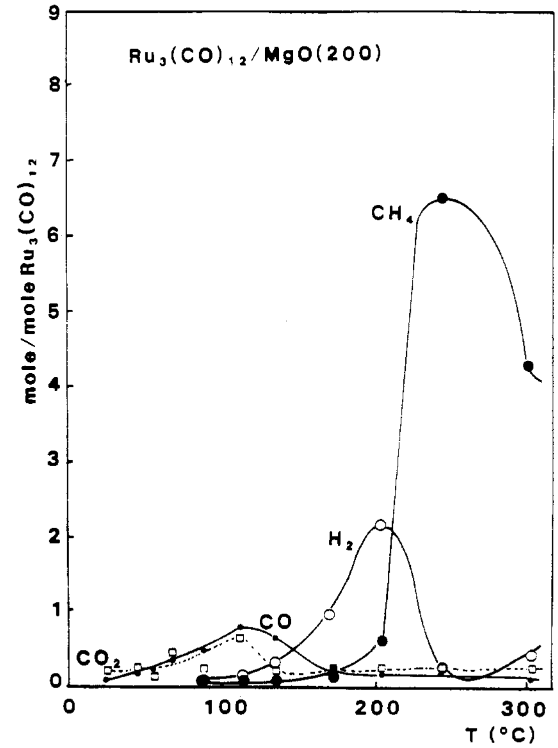

Figure 4. Gas evolution of $Ru_3(CO)_{12}$/MgO-200 during thermal treatment under vacuum.

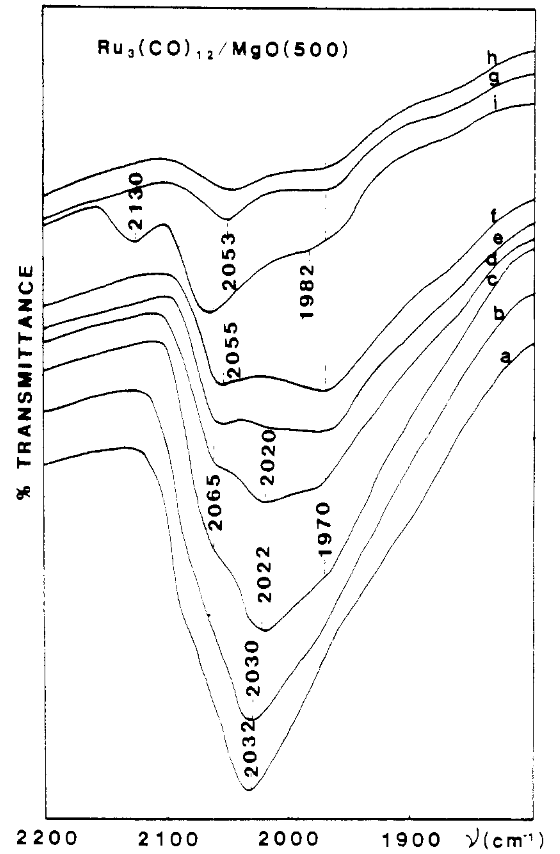

Figure 5. IR spectra in the ν(CO) region of $Ru_3(CO)_{12}$/MgO-500 after treatment under vacuum: (a) at 25 °C, 16 h; (b) at 50 °C, 5 h; (c) at 80 °C, 16 h; (d) at 105 °C, 5 h; (e) at 120 °C, 16 h; (f) at 150 °C, 3 h; (g) at 150 °C, 16 h; (h) at 170 °C, 4 h; (i) under 300 Torr, at 25 °C, 48 h.

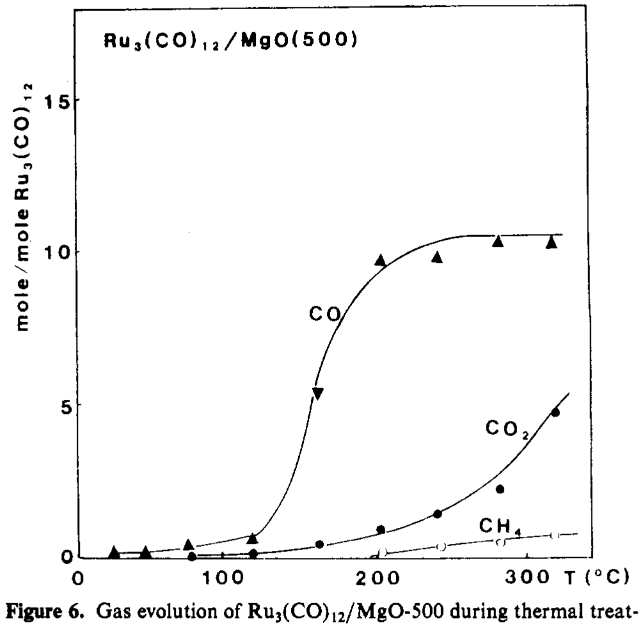

Figure 6. Gas evolution of $Ru_3(CO)_{12}$/MgO-500 during thermal treatment under vacuum.

(Figure 5); simultaneous formation of metal particles and oxidation of zerovalent Ru to $Ru^{II}(CO)_n$ (n = 2, 3; ν(CO) 2065, 1970 cm^{-1}) are observed. Complete decarbonylation is achieved at ca. 200 °C. Analysis of the gas-phase composition during thermal activation is in agreement with the IR results: about 10 mol of CO/mol of cluster is detected in the gas phase at 200 °C (Figure 6). Some CO ligands are likely disproportionated to carbon and CO_2 (at 300 °C); methane formation occurs next, probably by the reaction $C + 2H_2 \rightarrow CH_4$, the H_2 resulting from a partial oxidation of Ru(0) by the support (eq 4).[39] These transformations

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certainly happen on Ru metal particles.

Conclusion

The first step of the reaction between $\mathrm{Ru_3(CO)_{12}}$ and partially or fully hydroxylated magnesia is the formation of the hydrido anionic cluster $\mathrm{[HRu_3(CO)_{11}]^-}$. In solution, this anionic cluster has been obtained by reaction of $\mathrm{Ru_3(CO)_{12}}$ with a methanolic solution of KOH.[31] On the surfaces of magnesia and zinc and lanthanum oxides, $\mathrm{[HRu_3(CO)_{11}]^-}$ probably results from the nucleophilic attack at coordinated CO by the basic OH groups of the surface; concomitant $\mathrm{CO_2}$ evolution could not be observed due to adsorption of $\mathrm{CO_2}$ as carbonates onto magnesia.

This behavior compares with the one observed in the case of $\mathrm{Fe_3(CO)_{12}}$ on the surface of alumina or magnesia, for which the formation of $\mathrm{[HFe_3(CO)_{11}]^-}$ had been evidenced.[17] Nevertheless, some differences deserve to be noticed. On alumina, $\mathrm{[HFe_3(CO)_{11}]^-}$ is in strong interaction with the surface Lewis acid sites $\mathrm{Al^{3+}}$, through a kind of tight ion pairing, as evidenced by the large shift of the bridging ν(CO) band to lower frequency. In the case of $\mathrm{[HRu_3(CO)_{11}]^-}$ on magnesia, such an interaction does not seem to occur: the ν(CO) frequency in the bridging region is close to the values observed in solution with $\mathrm{[PPN]^+}$ as counterion (Table I), where no tight ion pairing is existing, and far from the values reported for $\mathrm{[HRu_3(CO)_{11}]^-Li^+}$ (ν(CO) 1653 $\mathrm{cm^{-1}}$).[40] The reason that such a type of interaction is not observed is not yet clear. However, the surface $\mathrm{Mg^{2+}}$ sites of magnesia are weaker Lewis acids[32] than the $\mathrm{Al^{3+}}$ of alumina.

The anionic cluster $\mathrm{[HRu_3(CO)_{11}]^-}$ is stable under vacuum on the surface of magnesia up to temperatures of ca. 100 °C. Above this temperature, the trinuclear anion is mainly transformed into small metal particles and to a smaller extent into oxidized ruthenium (Ru(II)).

A kind of equilibrium seems to exist between ruthenium(0) and ruthenium(II) due to a redox process involving surface protons and gaseous hydrogen (eq 4 above). Under vacuum this equilibrium is shifted to the right whereas in static experiments this equilibrium is in favor of zerovalent ruthenium.

Various kinds of reactions are observed with the carbon monoxide issued from the carbonyl ligands of the cluster:

(i) A water gas shift reaction that is probably catalyzed by the cluster itself is observed although we have no proof in favor of such a conclusion. The fact that $\mathrm{[1]^-}$ and $\mathrm{Ru(CO)_2(OMg<)_2}$, as well as ruthenium metal, coexist at not too different temperatures on the surface makes a clear conclusion difficult.

(ii) A CO methanation reaction is observed on the three types of magnesia. It should be noticed that on magnesia-200 a very high percentage of the carbonyls of the cluster (ca. 6 among 12) are transformed into methane. The hydrogen is obviously coming from the water of the support (and therefore from the water gas shift reaction) since on magnesia-500 almost no methane is formed.

(iii) A CO disproportionation to gaseous $\mathrm{CO_2}$ and surface C is also evidenced clearly from mass balance studies, especially on magnesia-500. It is very likely that a methanation reaction as well as CO disproportionation is occurring on the small metal particles of ruthenium that have been detected by electron microscopy.

All these observations indicate that great care must be taken before any conclusion is made regarding catalytic properties of supported molecular clusters. We have shown that at least three types of different species can coexist at the surface of magnesia after and/or during thermal decomposition of $\mathrm{[HRu_3(CO)_{11}]^-(Mg^{2+})_{1/2}}$: the anion $\mathrm{[1]^-}$ itself, mononuclear $\mathrm{Ru^{II}(CO)_2(OMg<)_2}$, and ruthenium metal particles.

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Registry No. $\mathrm{Ru_3(CO)_{12}}$, 15243-33-1; $\mathrm{HRu_3(CO)_{11}^-}$, 60496-59-5; MgO, 1309-48-4; ZnO, 1314-13-2; $\mathrm{La_2O_3}$, 1312-81-8.

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Synthesis and Characterization of Hexadentate Cobalt(III) Complexes with Novel edta-Type Ligands. 1. Circular Dichroism of a Cobalt(III) Complex of Ethylenediamine-*N*-acetic-*N*,*N'*,*N'*-tri-3-propionic Acid

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The trans($\mathrm{O_5O_6}$) geometrical isomer of the cobalt(III) complex of ethylenediamine-*N*-acetic-*N*,*N'*,*N'*-tri-3-propionic acid ($\mathrm{H_4eda3p}$) has been prepared and resolved. More complete resolution of the previously reported $\mathrm{[Co(edtp)]^-}$ complex (edtp = ethylenediaminetetra-3-propionate) has been achieved. The ^{1}H NMR, electronic absorption, and circular dichroism (CD) spectra were used to characterize the Co(III) complexes. The $(+)_{546}$-*trans*($\mathrm{O_5O_6}$)-$\mathrm{[Co(eda3p)]^-}$ complex with a positive CD peak at lowest energy in the first spin-allowed d–d absorption band region is tentatively assigned the Λ absolute configuration.

Introduction

The spectral data and structural parameters of the $\mathrm{[Co(edta)]^-}$ complex (edta = ethylenediaminetetraacetate) are available.[2,3] This system, having a five-membered diamine backbone ring (E ring) and two different pairs of glycinate rings (G rings in equatorial positions and R rings in axial positions), was found to be strained.[3] This strain is manifested more in the girdle plane (the plane of two G rings) than in the glycinate rings lying outside of this plane (R rings). Similar structural data should be expected in the directly related $\mathrm{[Co(}S\text{-pdta)]^-}$ and $\mathrm{[Co(}S,S\text{-cydta)]^-}$ complexes[4,5] containing only five-membered rings (*S*-pdta = (*S*)-1,2-propanediaminetetraacetate; *S*,*S*-cydta = (1*S*,2*S*)-1,2-*trans*-cyclohexanediaminetetraacetate). Model complexes that are less strained than $\mathrm{[Co(edta)]^-}$ contain ligands that are structurally similar to edta but have longer diamine backbone or carboxylate chains. Complexes such as $\mathrm{[Co(1,3\text{-pdta})]^-}$[6,7] and

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