energies of gold as a function of germanium cluster size.

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Registry No. Au$_2$, 12187-09-6; AuCu, 12006-51-8; AuGe, 12256-41-6; Au$_2$Ge, 67701-68-2; AuGe$_2$, 67701-72-8; Au$_2$Ge$_2$, 67701-69-3; AuGe$_3$, 67701-70-6; AuGe$_4$, 67701-71-7; Ge$_2$, 12596-05-3; Ge$_3$, 61349-37-9; Ge$_4$, 12184-87-1.

Supplementary Material Available: A table of the experimental ion currents (5 pages). Ordering information is given on any current masthead page.

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Surface-Supported Metal Cluster Carbonyls. Chemisorption Decomposition and Reactivity of Rh$_6$(CO)$_{16}$ Supported on Alumina, Silica–Alumina, and Magnesia

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The behavior of Rh$_6$(CO)$_{16}$ on the surface of inorganic oxides (alumina, magnesia, and silica–alumina) has been found to be strongly dependent on the mode of impregnation and on the water content of the support. On alumina it is possible to maintain the molecular nature of the cluster provided the water content of the alumina is low; otherwise the OH groups of the support are at the origin of a ready oxidation of the cluster resulting in a rhodium(I) carbonyl species. The rhodium(I) carbonyl species reacts with CO in the presence of excess water to give back the cluster Rh$_6$(CO)$_{16}$. (Rh(CO)$_2$Cl)$_2$ supported on alumina also reacts with CO in the presence of excess water to give Rh$_6$(CO)$_{16}$. A facile reduction of the rhodium(I) carbonyl species, obtained from oxidation of Rh$_6$(CO)$_{16}$, under hydrogen or excess water in the absence of CO leads to the formation of metallic rhodium together with an "intramolecular" rearrangement of a linear to a doubly bridged carbonyl ligand. It is possible to regenerate the rhodium(I) surface carbonyl species with oxygen followed by carbon monoxide. Infrared data for Rh$_6$(CO)$_{16}$ supported on alumina, magnesia, and silica–alumina indicate an electronic interaction between the support and the cluster, the rhodium(I) carbonyl species, or the metallic species obtained upon reduction of rhodium(I). A catalytic cycle is proposed which accounts for the water gas shift reaction carried out on the cluster frame and its oxidation products.

The analogies between very small particles of transition metals frequently used in heterogeneous catalysis[1] and molecular clusters, which are more seldom used in homogeneous catalysis,[2] have been recently examined.[3] Although these two classes of compounds belong to different fields of chemistry, namely, molecular and solid-state chemistry, many comparisons were made possible by the fast development of the synthesis and characterization of new molecular clusters of increasing nuclearity.[4] It appears that geometric as well as

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electronic analogies exist between very small particles and molecular clusters of high nuclearities having for example an internal "metallic" atom. Also, the analogy is even more obvious between the chemical behavior of ligands coordinated to a cluster frame and that of any substrate "chemisorbed" at the surface of a metallic particle.[6]

In order to determine if there is a gap in the properties or a kind of progressive change when one goes from the molecular state to the metallic state, we have undertaken a series of studies related to the thermal and chemical behavior of clusters of various nuclearity supported on various oxides. The main purpose of supporting the clusters on highly divided oxides is to prevent an easy aggregation in order to investigate the possible reversible ligand dissociation from the cluster framework. Previous preliminary studies in this field have already appeared.[7-11] Some data indicate that with $Ir_4(CO)_{12}$ or $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$ or $(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$,[7,8] a reversible CO ligand dissociation can occur on a surface while keeping the initial cluster frame. This reversibility of ligand dissociation was also advanced by Watters et al.[7] in the case of $Rh_6(CO)_{16}$ supported on alumina but we report here evidence to indicate that their conclusions may need to be reconsidered. We report here the results obtained by supporting $Rh_6(CO)_{16}$ on η-alumina. Results obtained on $Rh_6(CO)_{16}$ supported on magnesia and silica alumina are also briefly reported to provide some data on the influence of the support on the stability of the cluster. We report also some data related to the behavior under CO of $RhCl_3$ and $(Rh(CO)_2Cl)_2$ adsorbed on $\eta\text{-}Al_2O_3$. Preliminary work related to $Rh_6(CO)_{16}$ supported on silica has been reported in a previous paper.[12] The interesting catalytic properties of these supported cluster carbonyls in Fischer–Tropsch synthesis[13] and in the synthesis of ethanol[30] have also been recently reported.

Experimental Section

$Rh_6(CO)_{16}$ was prepared as described by James et al.[14] or purchased from Strem Chemicals. $RhCl_3\cdot nH_2O$ and $(Rh(CO)_2Cl)_2$ were purchased from Strem Chemicals. The various gases used (CO, O_2, H_2) were supplied by Air-Liquide. They had a purity of 99.99%. In all cases they were stored under activated 5-Å molecular sieves. Chloroform was purchased from Fluka; it was stored under argon and dehydrated on 5-Å molecular sieves.

The $\eta\text{-}Al_2O_3$ had a surface area of 315 m^2/g, and an average pore size of 30 Å.

The magnesia had a surface area of 245 m^2/g and the silica–alumina had a surface of 500 m^2/g (ketjen 13).

Infrared spectra were obtained on a 225 Perkin-Elmer spectrophotometer. The techniques used to carry out infrared spectra of solids under well-controlled atmosphere have been widely reported.[15] When the impregnation of the alumina disk by the cluster was carried out in situ, under high vacuum, a degassed chloroform solution of $Rh_6(CO)_{16}$ was introduced onto the alumina disk through a break-seal. In most cases the support was degassed under a 10^{-5} torr vacuum, overnight, at a given temperature, before impregnation in situ. The rhodium content on the disk was determined after the experiment. In most cases it ranged between 0.4 and 2 wt % Rh. $(Rh(CO)_2Cl)_2$ was adsorbed on alumina in the same way as $Rh_6(CO)_{16}$: A degassed chloroform solution of $(Rh(CO)_2Cl)_2$ was introduced onto the alumina disk through a break-seal. The rhodium content of the alumina ranged between 1 and 2 wt % Rh.

In some cases the impregnation of $Rh_6(CO)_{16}$ was carried out in THF solution. The results were identical with those obtained in chloroform solution indicating that the chlorination of the alumina surface by $CHCl_3$ did not change the reactivity of $Rh_6(CO)_{16}$ toward the alumina surface. As a matter of fact surface reaction between chlorinated solvent and hydroxyl groups of alumina usually does not occur below 200 °C.[31]

Results

I. Behavior of $Rh_6(CO)_{16}$ on an Alumina Surface. A characteristic feature of the adsorption and grafting of $Rh_6(CO)_{16}$ onto an alumina surface is that the nature of the surface species obtained depends on whether the impregnation is carried out in the presence of absence of air.

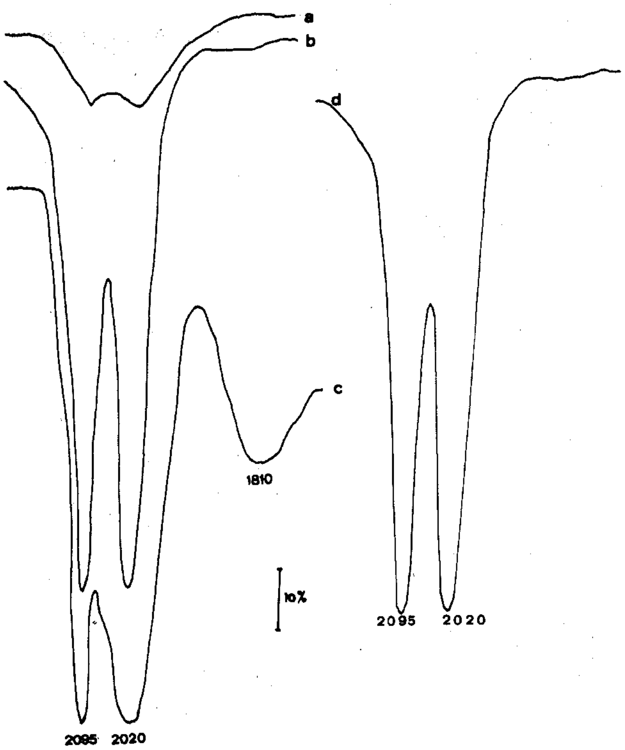


Figure 1. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina after impregnation in air; (b) sample exposed to 30 torr of CO for 5 min at 25 °C; (c) sample exposed to 600 torr of CO for 15 min at 25 °C; (d) sample subsequently treated with O_2 (100 torr) for 5 min at 25 °C.

Ia. Impregnation in Air. When impregnation is carried out by using a chloroform solution in air, in a manner similar to that used by Watters et al.,[7] the resulting solid does not exhibit any significant carbonyl band in the ν(CO) region (Figure 1a). This indicates that chemisorption onto the surface, easily detected by the color change observed during impregnation, produces a fast decarbonylation. Introduction of 30 torr of CO to this decarbonylated species produces two intense ν(CO) vibrations of almost equal intensity at 2020 and 2095 cm^{-1}, probably corresponding to the symmetric and asymmetric stretching vibrational modes of two carbonyl ligands coordinated to an "oxidized" rhodium atom[16] (Figure 1b). Upon increasing the CO pressure up to 600 torr or upon increasing the temperature up to 70 °C, we observe that the band at 2020 cm^{-1} broadens and a broad band appears at about 1810 cm^{-1} (Figure 1c). Upon treatment under O_2 (100 torr) for 5 min at 25 °C the band at 1810 cm^{-1} and a contributing peak of the broad band at 2020 cm^{-1} disappear instantaneously and give back the original two bands at 2020 and 2095 cm^{-1} (Figure 1d).

In order to assign the various bands observed, we carried out three sets of experiments on the species characterized by the strong doublet at 2020 and 2095 cm^{-1}.

Upon treatment under hydrogen at increasing temperature the two symmetric bands are progressively replaced by broad bands centered at 2020 and 1850 cm^{-1} which are characteristic of CO adsorbed on dispersed metallic rhodium (linear and bridged forms[17]). These two bands are easily removed under oxygen (160 torr) at room temperature, with formation of carbon dioxide. Upon CO admission on the surface "oxidized" species, the doublet at 2020 and 2095 cm^{-1} is reobtained at low pressure of carbon monoxide; when the temperature is raised to 200 °C, the spectrum of CO adsorbed on metallic rhodium appears together with that of the doublet (Figure 2).

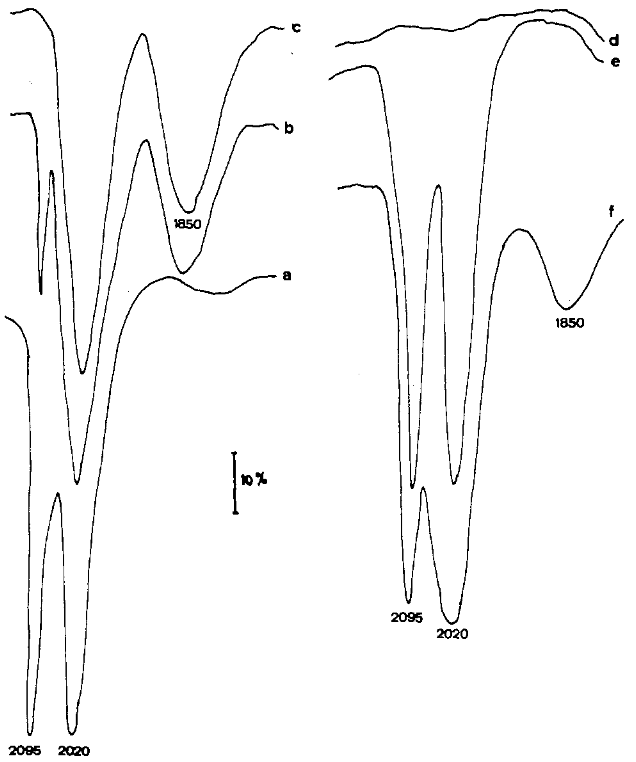


Figure 2. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina after impregnation in air and exposure to CO (30 torr) for 5 min at 25 °C; (b) sample after treatment with H_2 (320 torr) at 70 °C for 24 h; (c) sample after treatment with H_2 (320 torr) at 140 °C for 12 h; (d) sample subsequently exposed to CO_2 (100 torr) at 25 °C for 15 min; (e) same sample exposed to CO (100 torr) at 25 °C for 30 min; (f) same sample heated to 200 °C under CO (100 torr) for 5 h.

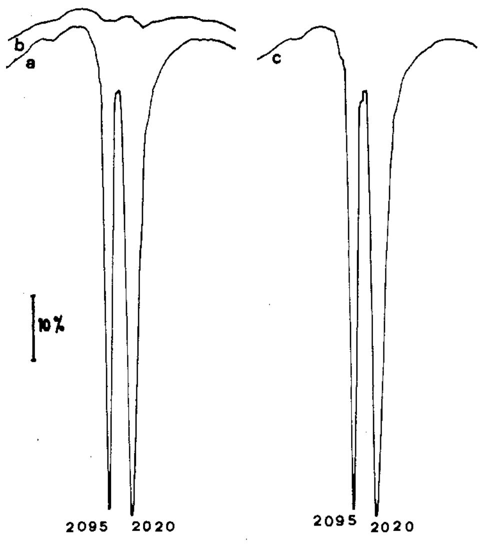


Figure 3. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina after impregnation in air and exposure to CO (30 torr) for 5 min at 25 °C; (b) sample after treatment under vacuum at 200 °C for 15 h; (c) sample subsequently exposed to CO (30 torr) at 25 °C.

Upon treatment under vacuum at increasing temperature of the species characterized by the doublet at 2020 and 2095 cm^{-1}, both carbonyl bands are progressively removed; they disappear at about 150 °C. They are quantitatively reobtained under CO pressure at room temperature, thus proving the reversibility of the decarbonylation process (Figure 3).

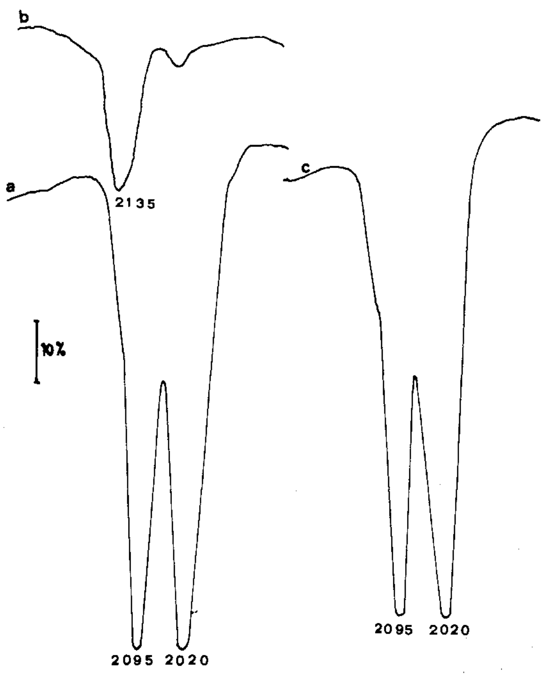


Figure 4. Infrared spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina after impregnation in air and exposure to CO (30 torr) for 5 min at 25 °C; (b) sample after oxygen treatment (500 torr) at 200 °C for 15 h; (c) sample after treatment under CO (400 torr) at 100 °C for 2 h.

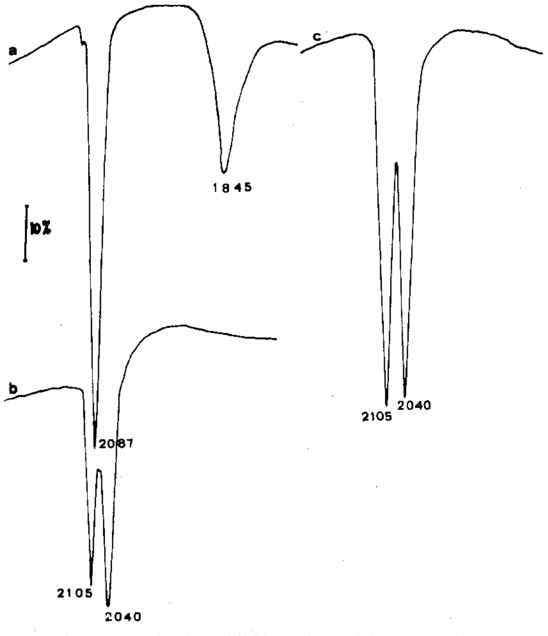


Figure 5. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina previously heated at 500 °C under vacuum, impregnation in absence of air; (b) sample after vacuum treatment at 60 °C for 6 h; (c) same sample after exposure to 200 torr of CO at 25 °C for 12 h.

Upon treatment under oxygen of the species characterized by the doublet at 2020 and 2095 cm^{-1}, the carbonyl groups are progressively removed (as CO_2) and are almost completely eliminated at 200 °C. The only band remaining at this temperature is a broad peak at 2135 cm^{-1} (presumably due to a carbonyl group chemisorbed on a more oxidized rhodium species). The doublet at 2020 and 2095 cm^{-1} is then reobtained under CO (400 torr) at 100 °C (Figure 4).

Ib. Impregnation in the Absence of Air. The advantage of this method is that it is possible to pretreat the support at any temperature before deposition of the cluster; also, since the adsorption of the cluster is carried out in a close vessel, it is possible in some cases to analyze by chromatography the gases evolved during adsorption and further treatment.

Impregnation of η-Al_2O_3 previously treated at 500 °C for 16 h under high vacuum (10^{-5} torr) with a chloroform solution of $Rh_6(CO)_{16}$ results in a spectrum having an intense peak at 2087 cm^{-1} and a less intense peak at 1848 cm^{-1} (Figure 5a). This spectrum resembles that of the original cluster but is not identical since the linear and triply bridged ν(CO) vibrations are shifted respectively by 11 and 39 wavenumbers to higher frequencies. In order to verify if the modification of the infrared spectrum of $Rh_6(CO)_{16}$ adsorbed on alumina$_{500}$ was due to a simple interaction between the original cluster $Rh_6(CO)_{16}$ and the surface or to substituted species such as $Rh_6(CO)_{16-n}Y_n$, we carried out the extraction of the cluster from the surface by washing with an excess of $CHCl_3$ under Ar. A quantitative recovery of $Rh_6(CO)_{16}$ was made possible, indicating that probably the cluster had retained its integrity on the surface.

This cluster can be kept as such for several days under vacuum at room temperature. If O_2 (100 torr) is introduced at room temperature, no modification of the infrared spectrum is observed. If traces of water (10^{-1} torr) are introduced to the supported cluster, the latter is transformed instantaneously into a carbonyl species characterized by two ν(CO) vibrations at 2105 and 2040 cm^{-1} (Figure 5b), probably an oxidized species; simultaneously, at the same temperature CO_2 and H_2 appear in the gas phase with a molar ratio of 2:0.7 and 2:0.9 depending on the amount of water introduced (10^{-1} and 1 torr, respectively). Due to the small amount of $Rh_6(CO)_{16}$ adsorbed on the alumina a quantitative determination of the ratio of CO_2 evolved/mol of cluster was not very accurate; nevertheless the values obtained for CO_2 indicated a ratio of about 2–4 mol of CO_2/mol of $Rh_6(CO)_{16}$ depending on the vapor pressure of water (10^{-1} and 1 torr, respectively). It must be pointed out that the amount of CO_2 measured may be lowered by adsorption on the support (carbonates are always observed on aluminas and are characterized by strong bands at 1440 and 1360 cm^{-1} (monodentate carbonates)). Concerning H_2 the value obtained at 60 °C may also be lowered since hydrocarbons, corresponding to combined hydrogen, are already observed at 100 °C in similar experimental conditions.[13]

If the cluster supported on Al_2O_3(500) is heated at 60 °C under vacuum for 60 h, the same type of behavior is observed: formation of two symmetric peaks at 2105 and 2040 cm^{-1} having the same intensity. Upon admission of CO these two peaks reach an intensity comparable to that of the starting cluster (Figure 5c). It must be pointed out here that the alumina surface pretreated at 500 °C still retains 3 OH/100 Å^2.

If the η-alumina is previously treated at 200 °C, impregnation with $Rh_6(CO)_{16}$ again gives a spectrum close to that of $Rh_6(CO)_{16}$, with an intense peak at 2058 cm^{-1} and a broad peak at 1830 cm^{-1}. Nevertheless the linear carbonyl band is shifted by almost 19 cm^{-1} to lower wavenumbers and the band due to the triply bridged carbonyl is much broader than in the starting cluster. The cluster is much less stable than in the previous case since it decomposes at room temperature under vacuum after 4 h to give the "oxidized" rhodium species (peaks at 2091 and 2021 cm^{-1}) (Figure 6).

If the η-alumina is previously treated at 25 °C, for 16 h, the cluster remains as such for just a few minutes. In this case it is characterized by an intense peak at 2050 cm^{-1} and a broad peak at 1820 cm^{-1}. It decomposes very fast into a rhodium species characterized by peaks at 2087 and 2014 cm^{-1} of equal intensity (Figure 7).

Whatever the pretreatment temperature of the alumina, the "oxidized" species are reduced at moderate temperature under hydrogen to metallic rhodium characterized by broader bands at 2020 and 1850 cm^{-1}. This modification of the infrared spectrum results in a moderate decrease of the intensity of the 2020-cm^{-1} band, suggesting that an aggregation to a metallic particle of higher nuclearity may be occurring but not to a great extent. This metallic rhodium gives back easily the "oxidized" rhodium surface carbonyl species by an O_2–CO sequence at room temperature. The H_2–O_2–CO sequence can be repeated several times without significant modification of the carbonyl bands coordinated to metallic rhodium or to "oxidized" rhodium.

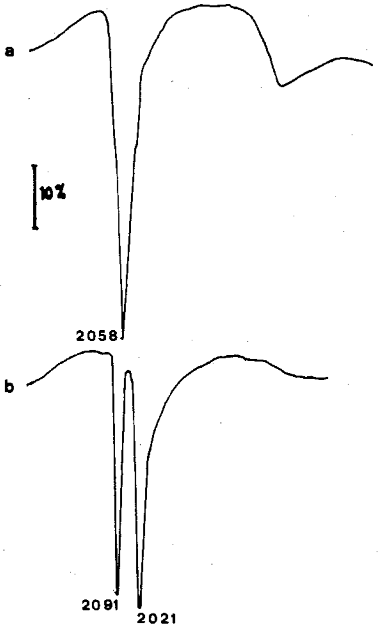


Figure 6. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina previously heated at 200 °C for 16 h under vacuum of 10^{-4} torr, impregnation in absence of air; (b) same sample after leaving under vacuum of 10^{-4} torr at 25 °C for 4 h.

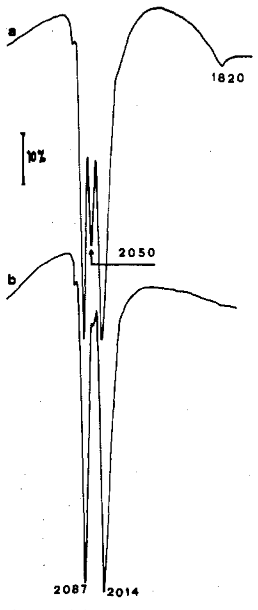


Figure 7. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina previously treated at 25 °C for 16 h under vacuum of 10^{-4} torr, impregnation in absence of air; (b) same sample after leaving under vacuum at 25 °C for 15 min.

It must be pointed out here that "chemisorption" of $Rh_6(CO)_{16}$ on alumina with varying water contents results in a modification of the infrared spectrum of $Rh_6(CO)_{16}$ (Table I). A remarkable electronic interaction occurs between the cluster and the surface depending on the water content of the

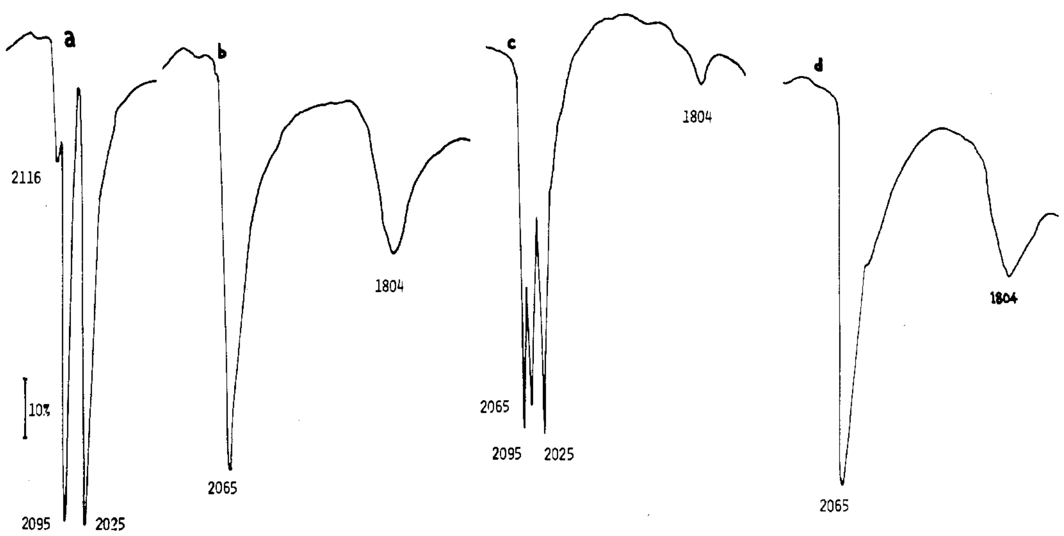


Figure 8. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on alumina previously treated at 300 °C for 16 h under vacuum of 10^{-4} torr and subsequently evacuated at 50 °C for 4 h; (b) same sample after introduction of H_2O (2 torr) and CO (350 torr) for 12 h (25 c); (c) same sample after treatment under a vacuum of 10^{-4} torr for 2 h (25 °C; (d) same sample after treatment under CO (350 torr) for 2 h.

Table I. ν(CO) Vibrations of the Various Species Resulting from the Chemisorption of $Rh_6(CO)_{16}$ on Silica, Alumina, Silica-Alumina, and Magnesia

		ν(CO), cm^{-1}		
support	pretreatment temp, °C	starting cluster on the surface	$(Rh^I(CO)_2)_n$ on the surface	"metallic surface carbonyl species"
alumina	25	2050–1820	2087–2014	
	200	2058–1830	2091–2021	2025–1850
	500	2087–1845	2105–2040	
silica	300	2083–1804	2093–2038	2054–1898
silica-alumina	500	2090–1828		
magnesia	25		2085–2007	1990–1820
	500	2058–1830	2093–2025	
no		2080–1800^a	2105 sh, 2090–2030^b	

^{a} $Rh_6(CO)_{16}/CHCl_3$. ^{b} $(Rh(CO)_2Cl)_2/CHCl_3$.

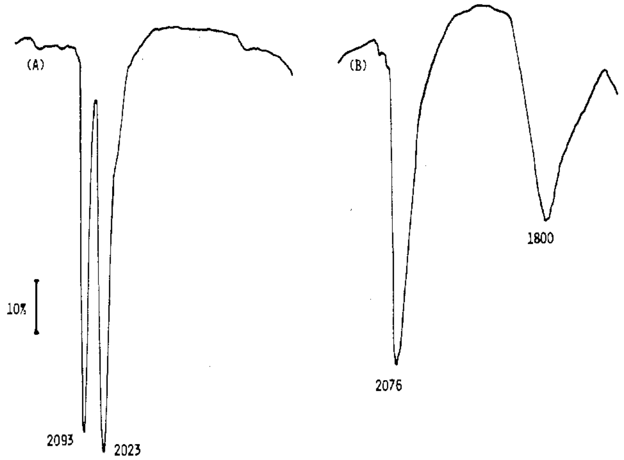


Figure 9. IR spectra in the ν(CO) region: (A) $(Rh(CO)_2Cl)_2$ on alumina previously treated at 300 °C under vacuum of 10^{-4} torr for 16 h; (B) same sample after introduction of CO (350 torr) and H_2O (4 torr) at 25 °C for 60 h

surface: the lower the water content of the support, the higher the frequency of the linear and bridged carbonyls. This also occurs for the oxidized rhodium surface carbonyl species. It should be noted that the intensity ratio of linear and bridged bands of CO coordinated to metallic rhodium derived from $Rh_6(CO)_{16}$ also depends on the water content of the support.

In another set of experiments $Rh_6(CO)_{16}$ was adsorbed on an alumina previously treated at 300 °C under a vacuum of 10^{-5} torr for 16 h. After impregnation of the cluster the solid was evacuated under vacuum (10^{-5} torr) for 6 h so that the spectrum exhibited the two symmetric peaks at 2025 and 2095 cm^{-1} plus a small shoulder at 2116 cm^{-1} (Figure 8a). After introduction of CO (350 torr) and water (2 torr) for 1 day at room temperature the spectrum was quite characteristic of $Rh_6(CO)_{16}$(adsorbed) with an intense peak at 2065 cm^{-1} and a broader one at about 1804 cm^{-1} (Figure 8b). Obviously the synthesis of $Rh_6(CO)_{16}$ from an "oxidized" rhodium carbonyl species had occurred in a similar way to that described by Chini and Martinengo, who observed the drastic effect of H_2O on the synthesis of $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ from $(Rh(CO)_2Cl)_2$ and CO.[18] It was observed that the removal of the excess water under vacuum resulted in the destruction of the cluster frame again with the appearance of the two ν(CO) bands at about 2095 and 2025 cm^{-1} (Figure 8c). A new synthesis of $Rh_6(CO)_{16}$ could be carried out easily under CO and excess water (Figure 8d). It must be pointed out that no band that one could attribute to $Rh_4(CO)_{12}$ (bridged carbonyl) around 1890 cm^{-1} was observed.

II. Behavior of $(Rh(CO)_2Cl)_2$ on an Alumina Surface. The adsorption of $(Rh(CO)_2Cl)_2$ in $CHCl_3$ solution on the surface of an η-alumina previously treated at 300 °C under vacuum (10^{-4} torr) for 16 h results in two symmetric ν(CO) bands at 2093 and 2024 cm^{-1} (Figure 9A). The ν(OH) bands of the starting alumina are not significantly modified after chemisorption of the complex and removal of the solvent. After introduction of CO (350 torr) at room temperature no modification of the intensity of the ν(CO) bands was observed, indicating that the $(Rh(CO)_2Cl)_2$ had probably kept all its carbonyl ligands upon adsorption. If the complex is allowed to stay under CO for several days, no modification of the IR spectrum can be detected.

However by treatment of the chemisorbed complex under CO (350 torr) plus H_2O (4 torr) at room temperature, there is a slow appearance of $Rh_6(CO)_{16}$ characterized by intense peaks at 2076 and 1800 cm^{-1} (Figure 9B). After 60 h the only bands remaining are those of the cluster $Rh_6(CO)_{16}$ with no strong modification compared to that of $Rh_6(CO)_{16}$ in $CHCl_3$ solution. It must be pointed out here that the frequencies of $Rh_6(CO)_{16}$(adsorbed) obtained in this way are quite different from those obtained by supporting $Rh_6(CO)_{16}$ on alumina$_{25}$, alumina$_{203}$, or alumina$_{500}$. In the latter case the alumina has been dehydrated to such an extent that only a monolayer of

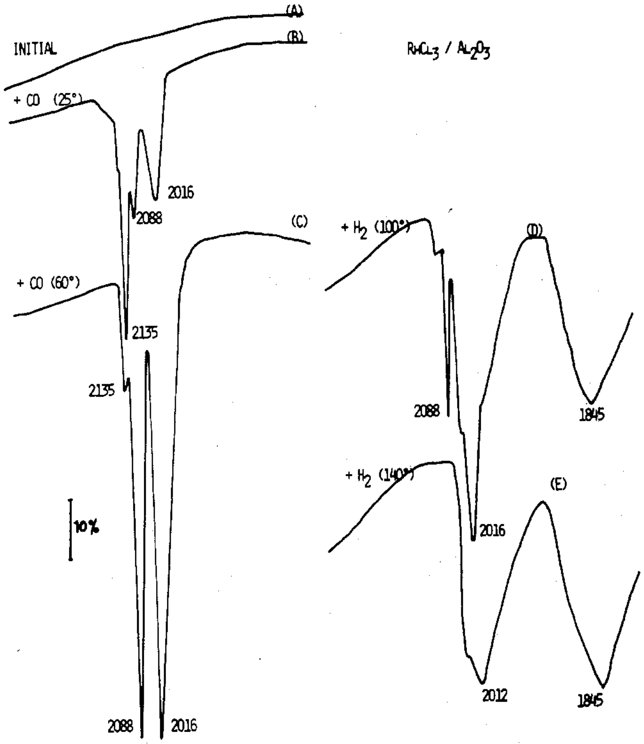


Figure 10. IR spectra of $RhCl_3{\cdot}nH_2O$ on alumina: (A) sample after impregnation of $RhCl_3{\cdot}nH_2O$ on alumina in air; (B) same sample after exposure to CO (20 torr) at 25 °C for 10 min; (C) same sample after treatment with CO (200 torr) at 60 °C for 6 h; (D) same sample treated with H_2 (200 torr) at 100 °C for 15 h; (E) same sample treated with H_2 (200 torr) at 140 °C for 6 h.

hydroxyl groups or molecular water is left on the surface so that the chemisorbed cluster is already strongly interacting with surface hydroxyl groups. In the present case the physisorption of molecular water on the surface results in a capillary condensation of water in the pores of the alumina so that the $Rh_6(CO)_{16}$ thus produced is almost in a water solution and probably away from the surface so that strong electronic surface interaction is avoided. This phenomenon also accounts for $Rh_6(CO)_{16}$ in this case being more stable than when the support has been dehydrated to such an extent that OH groups are present (vide infra).

It should be noted also that the rate of $Rh_6(CO)_{16}$ synthesis is much slower when starting from chemisorbed $(Rh(CO)_2Cl)_2$ than when starting from $Rh_6(CO)_{16}$ oxidized on the alumina surface. It is quite likely that in the former case the "oxidized" rhodium carbonyl species are in a close vicinity whereas in the second case a slow surface diffusion is necessary to carry out the synthesis of $Rh_6(CO)_{16}$.

III. Behavior of $RhCl_3{\cdot}nH_2O$ on Alumina Surface. In order to elucidate the nature of the various species obtained by supporting $Rh_6(CO)_{16}$, we have investigated the adsorption of carbon monoxide on $RhCl_3$ supported on η-alumina. Impregnation of η-alumina was carried out by using an ethanol solution of $RhCl_3$ so that the rhodium content was equal to 4 wt %. Under carbon monoxide (20 torr) the spectrum exhibits first a high-intensity band at 2135 cm^{-1} attributed to CO coordinated to a surface Rh^{III} species[19] (Figure 10B). Upon treatment under CO at 60 °C two sharp bands of equal intensity appear at 2088 and 2016 cm^{-1} probably due to a $(Rh(CO)_2Cl)_2$ species formed and adsorbed on the surface, whereas the band at 2135 cm^{-1} decreases in intensity (Figure 10C). The reduction under hydrogen of the rhodium(I) species is not observed under 60 °C. At 100 °C under hydrogen, it is possible to observe simultaneously the presence of CO on metallic rhodium (bands at 2015 and 1845 cm^{-1}) as well as CO coordinated to rhodium(I). The reduction to metallic rhodium seems to be complete at 165 °C (Figure 10D,E). Oxidation with O_2, followed by CO, regenerates two strong absorption bands at about 2090 and 2020 cm^{-1} typical of the oxidized surface species.

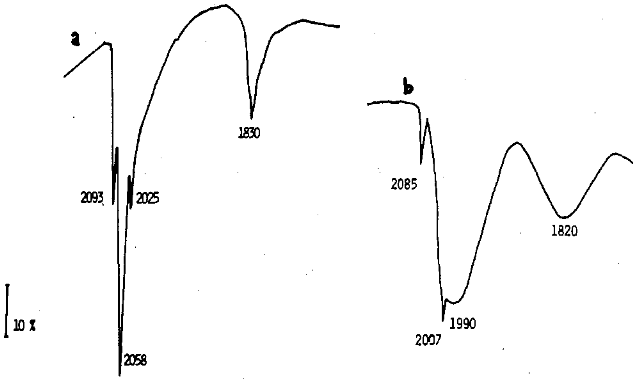


Figure 11. IR spectra in the ν(CO) region: (a) $Rh_6(CO)_{16}$ on magnesia previously treated at 500 °C under high vacuum (10^{-5} torr) for 16 h; (b) same sample after 1 day under 26 torr of H_2O.

If the sample of $RhCl_3$ supported on alumina is treated first with hydrogen at 50 °C and then with CO, the only bands observed are the two peaks at 2089 and 2018 cm^{-1}.

IV. Behavior of $Rh_6(CO)_{16}$ on Magnesia. The impregnation of a chloroform solution of $Rh_6(CO)_{16}$ onto a magnesia support previously treated at 500 °C under high vacuum (10^{-5} torr) for 16 h results in a spectrum showing ν(CO) bands due to the supported cluster at 2058 (vs) and 1830 (m) cm^{-1} as well as bands of medium intensity attributed to an oxidized rhodium carbonyl species at 2093 and 2025 cm^{-1} (Figure 11a). The addition of water (25 torr) at room temperature leads to a shift in the ν(CO) frequencies of the oxidized rhodium species to 2085 and 2007 cm^{-1} (Figure 11b). The formation of a "metallic" rhodium species is also indicated by somewhat broad bands at 1990 (s) and 1820 (m) cm^{-1}. After 3 days under 25 torr of H_2O, only the bands at 1990 and 1820 cm^{-1} remain.

V. Behavior of $Rh_6(CO)_{16}$ on a Silica–Alumina Surface. $Rh_6(CO)_{16}$ in chloroform solution was impregnated onto a silica–alumina previously treated overnight at 500 °C under 10^{-5} torr. The infrared spectrum obtained was similar to that of the starting cluster complex but shifted to higher frequencies (2090 (s) and 1828 (m, br) cm^{-1}). The cluster was kept as such on the surface for several days without noticeable change of the IR spectrum.

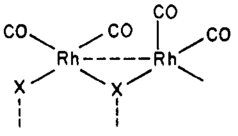
Discussion

The behavior of $Rh_6(CO)_{16}$ chemisorbed on alumina, silica–alumina, and magnesia surfaces differs from that of $Rh_6(CO)_{16}$ supported on silica.[12] On silica, the infrared spectra of adsorbed $Rh_6(CO)_{16}$ are identical with those obtained in solution: the results suggest that $Rh_6(CO)_{16}$ can easily keep its integrity on the surface; on alumina and on magnesia it is quite difficult to keep the cluster in its molecular form due to a very fast oxidation of the rhodium cage. Nevertheless it seems that a strong dehydration of the alumina support above 300 °C before chemisorption of the cluster favors the stability of the molecular cluster as such on the surface (Figure 5a and Table I). On magnesia it is almost impossible to keep only the cluster on the surface as such and we always observe an "oxidized rhodium carbonyl" simultaneously on the surface (Figure 11a). On silica–alumina the cluster can be kept as such on the surface (Figure 12). In all cases, except silica, we have observed an electronic interaction between the cluster–carbonyl and the surface, which is evidenced by modifications in the shapes and frequencies of the carbonyl bands with respect to the solution or Nujol spectra.

Since no bands which could be attributed to surface Rh–CO:→Al species are observed,[20] it is not possible to invoke the Lewis acidity of alumina or silica–alumina as being responsible for this interaction which is also observed on magnesia (Table I). It could be suggested here that hydroxyl surface groups can interact with the cluster unit especially with nondehydrated alumina (alumina$_{25}$) or partially dehydrated magnesia (magnesia$_{500}$); this would occur through hydrogen bonding between hydroxyl groups and carbonyl groups in agreement with the lowering of the stretching frequencies of both the linear and bridged carbonyl groups with increasing hydroxyl group coverage of the alumina.[21] This kind of interaction can also explain various phenomena observed by heating $Rh_6(CO)_{16}$ on alumina and magnesia, that is, water gas shift reaction and hydrocarbon formation[13] and destruction of the cluster cage and oxidation of the rhodium atoms.[22] Such kind of oxidation by surface OH groups of alumina has been shown to occur in the case of $Mo(CO)_6$ supported on alumina.[22]

The oxidized surface species, which is characterized by two symmetric ν(CO) bands of equal intensity, can be obtained in many ways: on alumina$_{25}$ it is obtained under vacuum at room temperature in a few minutes whereas on alumina$_{500}$ it is necessary to introduce traces of water to obtain this oxidation. On silica this oxidation does not occur under these conditions, an oxygen treatment at 100 °C of supported $Rh_6(CO)_{16}$ being necessary. On magnesia it is readily obtained at room temperature whatever the pretreatment temperature of the support. For all the supports it is also obtained by oxygen treatment of small particles of metallic rhodium at room temperature followed by a simple chemisorption of CO at room temperature.

The relative intensity and position of the carbonyl absorption bands of the "oxidized" rhodium species would suggest the presence of surface $Rh^I(CO)_2$ groups on both silica[12] and alumina and magnesia supports. In fact both the position and intensity of the two carbonyl bands are in good agreement with those of Rh^I complexes of the type $(Rh(CO)_2X)_2$ where X is a bridging ligand oxygen donor atom such as SO_4^{2-}.[23] ν(CO) frequencies obtained by chemisorption of $(Rh(CO)_2Cl)_2$ on alumina also support this hypothesis. In addition it is quite likely that the $Rh^I(CO)_2$ species is chemically bonded to the support by Al–O– or Mg–O– bonds. This is indicated by the ν(CO) dependency on the nature of the support (Table I). The sharpness of these bands suggests the absence of any strong internuclear vibrational coupling (which should be facilitated in a polynuclear aggregate by strong intermetallic metal–metal bonds[24]) so that a surface structure of the oxidized species having weak metal–metal interactions may be described as shown.

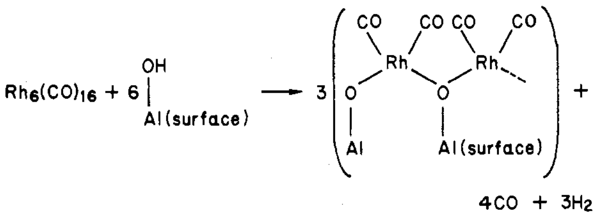


X = O, O–Al, or O–Mg

It must be pointed out here that in some cases (Figure 5b,c) the slightly varying ratio of the intensities of bands at 2105 and 2040 cm^{-1} could suggest that these two bands could arise from two different species than one $Rh^I(CO)_2$ species. In fact this phenomenon is due to a small contribution of a carbonyl band corresponding to a very small amount of metallic rhodium. The simultaneous presence of metallic rhodium and $Rh^I(CO)_2$ species is quite remarkable on Figure 1c. In any case, within experimental error, the intensity ratio of the two bands is constant during any vacuum treatment of a solid exhibiting these two bands, suggesting the existence of a single species $Rh^I(CO)_2$. As a matter of fact an identical behavior is also observed when $Rh(CO)_2Cl)_2$ is chemisorbed on alumina: reversible thermal dissociation of the carbonyl groups with a constant intensity ratio of the two ν(CO) bands.

In any case these oxidized species are probably weakly bound to each other, since owing to the relatively low temperature at which all the reversible transformations take place we may suppose that no drastic changes of nuclearity occur when $Rh_6(CO)_{16}$ is oxidized to the rhodium(I) surface carbonyl species. The very facile reduction under hydrogen to a "metallic" rhodium carbonyl species also suggests that in the oxidized species we still have an aggregate of metal atoms or that the $(Rh^I(CO)_2)$ moieties are in a close vicinity on the surface. This fact is confirmed by the relatively fast synthesis of $Rh_6(CO)_{16}$ from the oxidized species under CO + H_2O, a synthesis which is much faster than when starting from $(Rh(CO)_2Cl)_2$ chemisorbed on alumina. A limiting case concerning the rhodium(I) carbonyl species obtained on silica would be the formation by O_2 oxidation of $Rh_6(CO)_{16}$ of a simple oxo cluster of rhodium such as $Rh_6O_3(CO)_{12}$, a suggestion which is not impossible because oxo or hydroxo carbonyl clusters have been reported and characterized for osmium[25] or molybdenum and tungsten.[26] As a matter of fact the mean shift of ν(CO) stretching frequencies in going from a zerovalent cluster such as $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$[27] to an oxidized oxo cluster such as $(OsO(CO)_3)_4$[25] is quite similar to that observed on going from $Rh_6(CO)_{16}$ to our oxidized Rh^I surface carbonyl species.

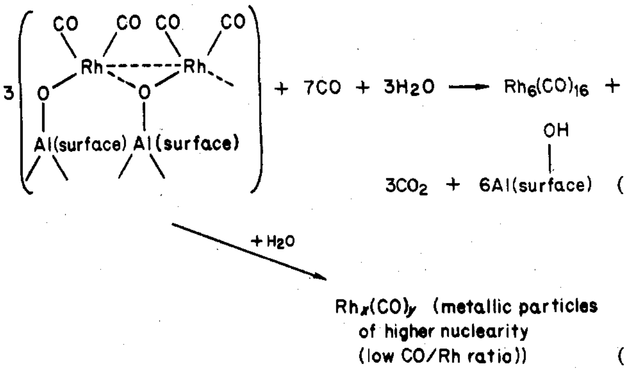
A possible equation for the formation of the rhodium(I) carbonyl species from surface OH groups $Rh_6(CO)_{16}$ is given in eq 1. This would explain why this oxidation is followed



(1)

by the formation of H_2 detected at low temperature as well as hydrocarbon formation observed at higher temperature (above ca. 100 °C)[13] from $Rh_6(CO)_{16}$ supported on alumina. It may be possible that the proton attack takes place either on $Rh_6(CO)_{16}$ as such or on a hydrido carbonyl species formed by nucleophilic attack of surface water which we have observed in the case of $Fe_3(CO)_{12}$ supported on alumina and magnesia (formation of $HFe_3(CO)_{11}^-$).[28] Equation 1 does not explain the formation of CO_2 also observed but we will see in the following that in the presence of CO and water the rhodium(I) carbonyl species can be easily reduced to a metallic particle or to a molecular cluster with formation of CO_2. The reduction to metal particle or to molecular cluster will depend on the reaction conditions.

Under CO plus excess water, $Rh_6(CO)_{16}$ is easily regenerated as in a classical synthesis of $Rh_6(CO)_{16}$ from $(Rh(CO)_2Cl)_2$ in aqueous methanol solution.[18] The cycle $Rh_6(CO)_{16}$ synthesis from $Rh^I(CO)_2$ under CO + H_2O and $Rh^I(CO)_2$ formation under vacuum can be repeated several times. Any vacuum treatment leading to isolated hydroxyl groups results in an oxidation of the cluster frame to the rhodium(I) carbonyl species: excess of water on both alumina or magnesia surfaces destroys these isolated hydroxyl groups and molecular water leads, in the presence of a coordinated carbonyl ligand, to the reduction of the rhodium(I) carbonyl species. If the treatment under water occurs in the absence of gaseous CO, then the reduction of the rhodium(I) carbonyl species gives rise to metallic particles. The following reduction by CO + H_2O seems to occur:



(2)

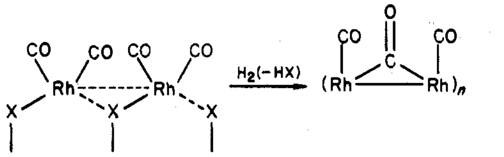
(3)

Similar reaction must occur during the reduction by CO + H_2O of $Rh_2(CO)_4Cl_2$ supported on alumina or during the reduction by CO + H_2O of the rhodium(I) carbonyl species supported on magnesia.

It is interesting to note here the very strong analogy observed for the surface synthesis of $Rh_6(CO)_{16}$ from a surface $Rh^I(CO)_2$ species and the synthesis of $Rh_6(CO)_{16}$ from $(Rh(CO)_2Cl)_2$ under CO atmosphere which requires traces of water. Chini and co-workers have proposed eq 4 for $Rh_6(CO)_{16}$ synthesis.[32] It is likely that in our case H^+ is present as a hydroxyl group.

$$3(Rh(CO)_2Cl)_2 + 7CO + 3H_2O \rightarrow Rh_6(CO)_{16} + 3CO_2 + 6H^+ \quad (4)$$

The rhodium(I) carbonyl species can also be reduced by hydrogen at moderate temperature ($T = 100$ °C) to a metallic rhodium carbonyl and it is suggested from intensity considerations of the ν(CO) bands that in this process a linear carbonyl is transformed into a bridged carbonyl probably by increasing the metal–metal bond interaction. A smooth intramolecular rearrangement of carbonyl ligands seems to occur (eq 5).

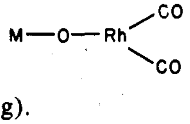


(5)

X = O, O–Al, or O–Mg

Concerning the metallic state characterized by linear and bridged carbonyls, the stretching frequencies of these carbonyls depend on whether the support is magnesia, silica, or alumina (Table I). Two explanations can be advancced to account for this behavior. On silica the particle may be smaller than on alumina and therefore more electron deficient.[3,15] Although we have previously found that on platinum the frequency of CO adsorbed is much less size dependent than the frequency of NO adsorbed,[15] the second explanation would be to consider, as in the previous case, an electronic interaction with the surface of the small metal particles.[29]

We have summarized in Figure 12 the overall cycles which occur on alumina and magnesia (cycles I and II) and to a lesser extent on silica[12] (cycle II), with CO, O_2, H_2, and H_2O. The first cycle describes the oxidation of the adsorbed cluster by isolated OH groups of the alumina or magnesia. On silica or probably silica–alumina such an oxidation by surface OH groups does not proceed in this way and consequently the resulting rhodium(I) carbonyl species obtained under O_2 at 100 °C probably do not have such a structure with an



$$M{-}O{-}Rh(CO)_2$$

linkage (M = Al, Mg).

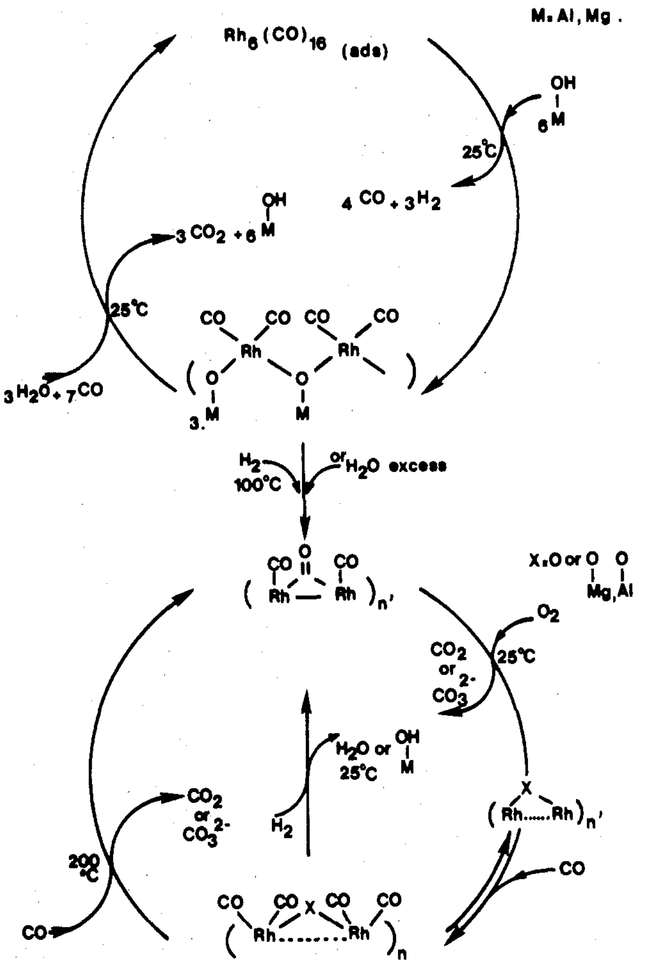


Figure 12. Catalytic cycles which occur with $Rh_6(CO)_{16}$ supported on divided oxides.

The transition from cycle I to cycle II corresponds in fact to a transition from a highly dispersed rhodium(I) carbonyl species (probably in close vicinity to each other) to a metallic particle of rhodium covered with linear and bridged carbonyl groups. Once the metallic particle is formed, cycle II can be repeated several times without any detectable change of nuclearity.

Registry No. $Rh_6(CO)_{16}$, 28407-51-4; $(Rh(CO)_2Cl)_2$, 14523-22-9; $RhCl_3$, 10049-07-7; silica, 12060-65-0; alumina, 1344-28-1; magnesia, 1309-48-4.

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Coordination Chemistry of New Sulfur-Containing Ligands. 16.[1] Crystal and Molecular Structure of Tris(pyrrole-*N*-carbodithioato)iron(III)–Hemikis(dichloromethane), $Fe(S_2CNC_4H_4)_3\cdot 0.5CH_2Cl_2$, a Low-Spin Dithiocarbamate Complex of Iron(III)

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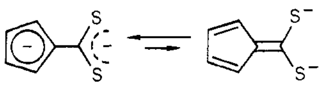
The detailed molecular structure of the low-spin iron(III) complex $Fe(S_2CNC_4H_4)_3$ has been determined from a single-crystal X-ray diffraction study. The complex crystallizes from dichloromethane/methanol in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 11.298$ (3) Å, $b = 18.095$ (3) Å, $c = 11.007$ (2) Å, $\beta = 111.32$ (2)°, and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using Mo Kα radiation. The iron and sulfur atoms were located from a Patterson synthesis, all other nonhydrogen atoms were located via difference-Fourier techniques, and hydrogen atoms were placed in calculated positions. Refinement converged with $R_F = 5.50\%$ and $R_{wF} = 4.21\%$ for all 2755 symmetry-independent reflections with $4° < 2\theta < 45°$ (none rejected). The crystals contain discrete, well-separated monomeric molecules of $Fe(S_2CNC_4H_4)_3$ and dichloromethane of solvation (which occupies positions of C_i symmetry and is disordered); the overall composition of the material is thus $Fe(S_2CNC_4H_4)_3\cdot 0.5CH_2Cl_2$. Individual iron–sulfur distances range from 2.280 (1) to 2.314 (1) Å. The average value of 2.297 ± 0.014 Å for the iron–sulfur distance in this low-spin iron(III) complex is markedly shorter than the average iron–sulfur distance of 2.432 ± 0.009 Å for the structurally similar, *but high-spin*, iron(III) complex tris(pyrrolidine-*N*-carbodithioato)iron(III), $Fe(S_2CNC_4H_8)_3$, previously studied by Sinn. This and other geometric considerations clearly indicate that the low-spin (strong-field) dithiocarbamate complexes of iron(III) are associated with dithiocarbamate ligands in which there is a ligand structure rich in the delocalized dithio acid form $R_2NCS_2^-$ rather than in the dianionic dithio form, $R_2N^+{=}CS_2^{2-}$.

Introduction

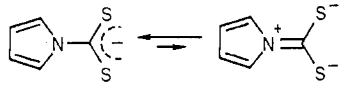
In recent years we have been interested in synthesizing new sulfur-containing ligands which promise to induce "unusual" electronic properties at the metal center.[1,3–16] With this in mind, we have recently investigated the coordination chemistry of several new dithiocarbamate ligands derived from the heterocyclic nitrogenous bases pyrrole, indole, carbazole, imidazole, and indoline. As a result of our extensive studies on the relationship between ligand resonance structure and metal bonding in the cyclopentadienedithiocarboxylate ligand[1,3,4,6–8,10] (see Scheme I), we felt confident that certain specific resonance structures of these new dithiocarbamate ligands might dominate the metal-bonding scheme. Thus, the pyrrole-*N*-carbodithioate ligand should have *little* contribution from the "normal" resonance structure proposed for dithiocarbamates (i.e., that where positive charge builds up on the nitrogen atom, IV), since this would tend to disrupt the aromaticity of the pyrrole ring (see Scheme II).

Scheme I



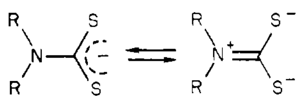
I II

Scheme II



III IV

Scheme III



V VI

Since the early 1930's it has been known that tris bidentate chelate complexes of iron(III) can possess magnetic moments intermediate between the low-spin value ($\mu_{\text{eff}} \simeq 2.0\ \mu_B$) and the high-spin value ($\mu_{\text{eff}} \simeq 5.9\ \mu_B$).[17,18] This is particularly true of dithiocarbamate complexes and it has been assumed that variations in magnetic moment can here be attributed to differing percentage contributions from the two limiting

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