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Surface organometallic chemistry: formation of the grafted dianionic cluster $[Rh_6(CO)_{15}]^{2-}$ upon adsorption of $Rh_6(CO)_{16}$ on a partially-hydroxylated magnesia

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Abstract

The adsorption of the cluster $Rh_6(CO)_{16}$ on the surface of partially hydroxylated magnesia leads mainly to the dianionic cluster $[Mg]^{2+}$ $[Rh_6(CO)_{15}]^{2-}$, which has been characterized by in situ infrared spectroscopy, extraction by surface anion exchange, and analysis of gases evolved. It is suggested that $Rh_6(CO)_{16}$ undergoes on the surface a nucleophilic attack at coordinated CO, leading to a $[HRh_6(CO)_{15}]^-$ intermediate, which would undergo a deprotonation by the surface OH^- groups of magnesia.

Introduction

Many studies have demonstrated that on oxide surfaces which bear nucleophilic OH groups (Al_2O_3, MgO), the carbonyl clusters $M_3(CO)_{12}$ (M = Fe [1,2], Ru [3], Os [4]) can be transformed into the hydrido-monoanionic carbonyl species $[HM_3(CO)_{11}]^-$ (M = Fe, Ru, Os), probably by nucleophilic attack of the surface OH^- groups on coordinated CO. Similarly hydridocarbonyl complexes and clusters such as $H_2Os(CO)_4$ [5], $H_2RuOs_3(CO)_{13}$ [6], $H_2FeM_3(CO)_{13}$ [7] (M = Ru, Os), $HFeCo_3(CO)_{12}$ [7,8], $H_4Os_4(CO)_{12}$ [9,10], $H_4Ru_4(CO)_{12}$ [11–13] can be deprotonated to give the corresponding monoanionic species. We report here the results of a study of the behavior of $Rh_6(CO)_{16}$ on hydroxylated magnesia, on which it is transformed into the di-anionic cluster $[Rh_6(CO)_{15}]^{2-}$.

Results and discussion

Previous studies on the chemisorption of $Rh_6(CO)_{16}$ on alumina have demonstrated the marked influence of surface dehydroxylation on the stability or the

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chemical reactivity of this cluster on the surface [14]. This is also true for magnesia which in interaction with $Fe(CO)_5$ presents nucleophilic oxygen anions when the oxide is fully dehydroxylated [15] and nucleophilic OH groups when it is only partially dehydroxylated [1]. In the present paper we consider only partially dehydroxylated magnesias which have been treated either at 25, 200, or 400 °C (MgO_{25}, MgO_{200}, MgO_{400}) (see Experimental section).

When a CH_2Cl_2 (THF or $CHCl_3$) solution of $Rh_6(CO)_{16}$ (0.045 mmole) was brought into contact with MgO_{25} or MgO_{200} (5 g), the reddish solution was decolourized within ca. 10–30 s and the white solid turned deep green suggesting the formation, on the surface, of the well known green dianionic rhodium cluster $[Rh_6(CO)_{15}]^{2-}$ [17].

During this chemisorption process there was no significant amount (less than 0.1 mole/mole of cluster) of gas evolved (CO, H_2, or CO_2). As long as the rhodium content was < 2% wt, all the cluster was chemisorbed on the surface, and it was impossible to wash out any rhodium compound from the surface. Only at higher rhodium content was it possible to extract unchanged $Rh_6(CO)_{16}$ with either CH_2Cl_2 or THF.

The infrared spectrum (Fig. 1) of the solid after chemisorption of $Rh_6(CO)_{16}$ varied slightly depending on the solvent used and the experimental conditions. With most solvents the infrared spectrum mainly exhibited the ν(CO) bands of the dianionic cluster $[Rh_6(CO)_{15}]^{2-}$ (bands at 2046w, 2036sh, 1998sh, 1989s, 1968s, 1827sh(br), 1767m(br) cm^{-1}. In addition in some cases with CH_2Cl_2, or when higher concentrations of $Rh_6(CO)_{16}$ were used, other bands of varying intensity at 2093, 2070, 2059, 2049, 2029 and 1830 cm^{-1} were also observed and these could not be unambiguously ascribed. There is a possibility that unchanged $Rh_6(CO)_{16}$, $[HRh_6(CO)_{15}]^-$, $[ClRh_6(CO)_{15}]^-$, or (Mg-O-)$Rh^I(CO)_2$ could also be present. When MgO_{200} was diluted with an equal amount of $SiO_{2(200)}$ [23*], the resulting infrared spectrum was almost identical to that of $[Rh_6(CO)_{15}]^{2-}$ (Fig. 1), (Table 1).

In order to check the presence of $[Rh_6(CO)_{15}]^{2-}$ on the surface, extraction of the adsorbed cluster was attempted by surface anion exchange. The extraction of an anionic species from the surface was possible when an equimolar amount of bis(triphenylphosphine)iminium chloride (PPNCl) was used (see Experimental section). This experiment was repeated several times with the cluster supported on MgO_{25}, MgO_{200} or MgO_{200} diluted with $SiO_{2(200)}$. The infrared spectrum of the extracted complex (Fig. 1c, Table 1), always the same, is characteristic of the anion $[Rh_6(CO)_{15}]^{2-}$ [17]. Analysis of the rhodium remaining on the surface showed that approximately 40% of the supported anion could be extracted from the surface by the exchange reaction with PPNCl. This low yield may be attributable to the presence of other species on the surface. Extraction experiments were also achieved using NEt_4Cl or NPr_4Br and gave similar results. Control reactions between $Rh_6(CO)_{16}$ and PPNCl [16] showed no conversion into $[Rh_6(CO)_{15}]^{2-}$, but instead $[Rh_6(CO)_{15}Cl][PPN]$ was quickly formed (Table 1) [19]. It should also be pointed out that the infrared spectrum of the supported cluster was very similar to that of $[Rh_6(CO)_{15}]^{2-}$ in solution, confirming the fact that the extraction experiment was not perturbing the chemical state of the cluster on the surface. Different results were

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[*] Reference number with asterisk indicates a note in the list of references.

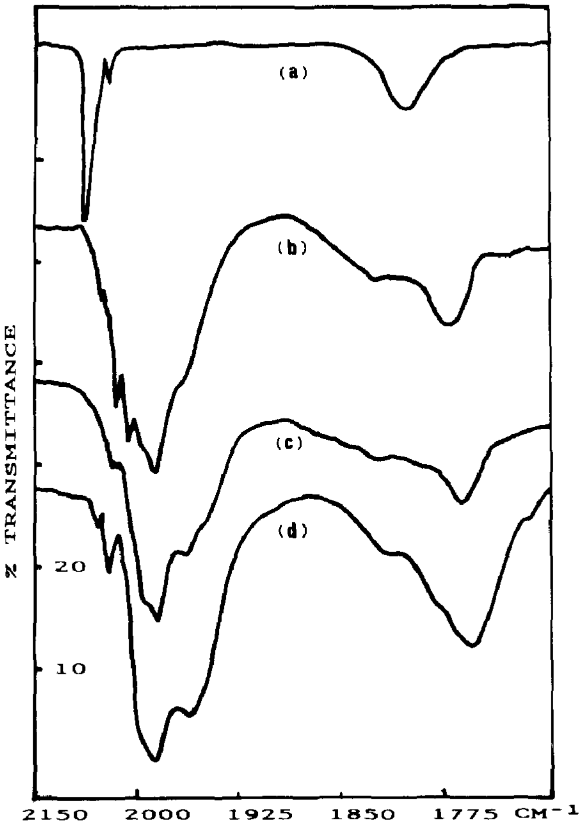


Fig. 1. (a) Infrared spectrum in the ν(CO) region of $Rh_6(CO)_{16}$ in $CHCl_3$; (b) infrared spectrum in the ν(CO) region obtained after adsorption of $Rh_6(CO)_{16}$ on $MgO_{(2100)}$ in CH_2Cl_2; (c) infrared spectrum in the ν(CO) region of $Rh_6(CO)_{16}$ adsorbed on a mechanical mixture of $MgO_{(200)}$ and $SiO_{2(200)}$; (d) infrared spectrum in the ν(CO) region obtained after extraction of $Rh_6(CO)_{15}{}^{2-}$ obtained by adsorption of $Rh_6(CO)_{16}$ on $MgO_{(200)}$ with an equimolar CH_2Cl_2 solution of PPNCl.

Table 1

Infrared data of some rhodium clusters

Clusters	ν(CO) cm^{-1}
$Rh_6(CO)_{16}$	2077s, 2046w, 1804m(br) [a]
$[Rh_6(CO)_{15}]^{2+}$ Mg^{2+} (surface)	2046w, 2036sh, 1998sh, 1989s, 1968s, 1827sh(br) 1767m(br)
$[Rh_6(CO)_{15}]^{2-}$ $[PPN]_2{}^+$ (extracted from MgO)	2046w, 1999sh, 1990s, 1965s, 1817w(br), 1784sh 1757s(br), 1714sh [b]
$[Rh_6(CO)_{15}]^{2-}$ $[NBu_4]_2{}^+$	2048w, 1990s, 1960s, 1815w(sh), 1760s [c]
$[Rh_6(CO)_{15}Cl]^-$ $[PPN\}^+$	2095vw, 2059s, 2050sh, 2024m, 1981w(br), 1783m(vbr) [b]
$[Rh_6(CO)_{15}Cl][NBu_4]$	2095w, 2060s, 2028w, 1823w, 1790s, 1785sh [d]

[a] In $CHCl_3$. [b] In CH_2Cl_2. [c] In CH_3CN, from ref. 17. [d] In THF, from ref. 19.

obtained on a magnesia$_{400}$. In this case the $Rh_6(CO)_{16}$ was found to remain intact on the surface, in agreement with published results [14a], with the formation of only trace amounts of $[Rh_6(CO)_{15}]^{2-}$. Finally, it seems that the anionic cluster $[Rh_6(CO)_{15}]^{2-}$ may be stable at the surface of magnesia only in the presence of solvents such as THF: in fact the deep green solid was found to turn brown after the removal of THF from the solid under vacuum, but it was not possible to identify the obtained product.

The results indicate that $Rh_6(CO)_{16}$ can be readily chemisorbed as $[Rh_6(CO)_{15}]^{2-}$ on the surface of fairly hydroxylated magnesia; this behaviour seems to occur on magnesia$_{(25)}$ and on magnesia$_{(200)}$, but not on magnesia$_{(400)}$; in the last case, $Rh_6(CO)_{16}$ seems to remain intact on the surface. The fact that it was not possible to wash out the anion from the surface with any solvent strongly suggests that the counter ion is Mg^{2+} from the surface. It should, however, be pointed out that there is no shift in the $\nu(CO)$ vibrations on going from $[Rh_6(CO)_{15}][Mg^{2+}]$ to $[Rh_6(CO)_{15}][NBu_4]_2$ (Table 1), and consequently there seems to be no detectable interaction between the bridging carbonyls and Mg^{2+} from the surface.

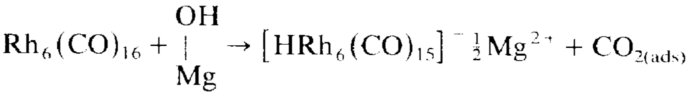
Formation of $[Rh_6(CO)_{15}]^{2-}$ has previously been observed by Chini and coworkers [17] upon reaction of $Rh_6(CO)_{16}$ with methanolic NaOH or KOH under nitrogen (eq. 1):

$$Rh_6(CO)_{16} + 4NaOH \xrightarrow{MeOH} [Rh_6(CO)_{15}]Na_2 + Na_2CO_3 + 2H_2O \qquad (1)$$

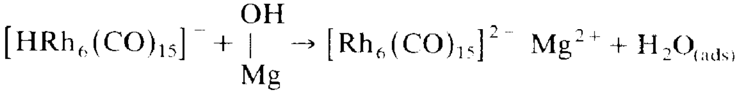
If the OH concentration is higher, the tetraanion $[Rh_6(CO)_{14}]^{2-}$ can be obtained [18]:

$$Rh_6(CO)_{16} + 8\ KOH \xrightarrow{H_2O} [Rh_6(CO)_{14}]K_4 + 2K_2CO_3 + 4H_2O$$

Although Chini and coworkers [17] did not speculate about the mechanism of formation of $[Rh_6(CO)_{15}]^{2-}$ from $Rh_6(CO)_{16}$, they observed that $[Rh_6(CO)_{15}COOR]^-$ can be obtained by nucleophilic attack of an alcohol on coordinated CO in the presence of Na_2CO_3 [19]. In our case, although we have no real evidence for it, we can assume, as already observed for most simple carbonyls and hydroxylated magnesia [1], the intermediate formation of $[Rh_6(CO)_{15}(COOH)]^-$ and $[HRh_6(CO)_{15}]^-$ [20] by nucleophilic attack of a surface OH group with formation of surface carbonate. The anionic hydride would then undergo a proton abstraction such as occurs on basic supports with many hydrido clusters [6–13] (eq. 2 and 3).



$$Rh_6(CO)_{16} + \underset{Mg}{\overset{OH}{|}} \rightarrow [HRh_6(CO)_{15}]^- \tfrac{1}{2}Mg^{2+} + CO_{2(ads)} \qquad (2)$$



$$[HRh_6(CO)_{15}]^- + \underset{Mg}{\overset{OH}{|}} \rightarrow [Rh_6(CO)_{15}]^{2-}\ Mg^{2+} + H_2O_{(ads)} \qquad (3)$$

The occurrence of these two reactions is consistent with previous observations on the surface organometallic chemistry of carbonyl and hydrido clusters. The fact that $[Rh_6(CO)_{14}]^{4-}$ was not observed on $MgO_{(200)}$ even for low concentration of $Rh_6(CO)_{16}$ (which could permit a high $OH^-/Rh_6(CO)_{16}$ ratio) may reflect the low mobility on the surface of the dianion, which may be interacting sufficiently with a Mg^{2+} cation to prevent surface migration.

Experimental

Materials and general procedures

CH_2Cl_2 was distilled over P_2O_5 and stored under Ar over freshly activated zeolites. THF was distilled prior to use over sodium benzophenone under Ar. Magnesia was prepared by dehydroxylation of $Mg(OH)_2$. It was kept under O_2 (1 atm) at 400 ° C for 10 h and then under vacuum (10^{-5} torr) at the same temperature for 0.5 h in order to eliminate most of the surface carbonates. The support was then rehydrated by equilibration with well degassed water at 25 ° C for 14 h. Finally it was thermally dehydroxylated at 25, 200 or 400 ° C under vacuum for 16 h (MgO_{25}, MgO_{200}, MgO_{400}). The surface area was about 100 m^2/g.

All experiments were carried out with strict exclusion of air by standard break-seal systems or Schlenk tube techniques. In situ IR experiments were performed following procedures already described [22], and spectra recorded with a Nicolet M 100 FT Spectrometer.

Extraction experiment

The surface reactions were usually carried out with 1 g of MgO under vacuum. This was treated in a close vessel with a THF (10 ml) solution of $Rh_6(CO)_{16}$, the Rh contents being 0.5, 1, and 2% by weight, respectively, in three experiments.

The solid was washed twice with THF and the THF removed, and a solution of PPNCl (equimolar to $Rh_6(CO)_{16}$) in 15 ml of CH_2Cl_2 or EtOH was brought into contact with the resulting surface supported species with strict exclusion of air. The green resulting extract was characterized in an IR cell directly connected to the reaction vessell.

Reaction of $Rh_6(CO)_{16}$ with PPNCl

A red-brown suspension of $Rh_6(CO)_{16}$ (20 mg) in CH_2Cl_2 (10 ml) was stirred under Ar with a excess of PPNCl. After 10 min the red solution showed the typical ν(CO) stretching spectrum of $[Rh_6(CO)_{15}Cl]^-[PPN]^+$: bands at 2095vw, 2059s, 2050sh, 2024m, 1981w(br), 1783m(vbr) cm^{-1}.

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