Table III. Infrared[a] and Optical[b] Data (cm^{-1}) for (1) $[(C_2H_5)_4N]MoO(C_5H_4CS_2)_2$ and (2) $[(C_2H_5)_4N]_2Mo(C_5H_4CS_2)_3$

Ir

(1) 1188 m, 1178 s, 1080 s, 1015 sh, 1004 m, *942 s, br,* 897 m, 808 s, 787 w, 756 m, 728 m, 640 m, 382 m, br

(2) 1380 m, 1345 m, 1170 br, 1063 m, 1022 m, 1000 sh, 947 m, 816 s, 790 sh, 744 m, 643 w, 342 m, 336 sh

Optical

(1) 23,256, 26,316, 27,248, 31,446 (ϵ 7)

(2) 22,727, 26,455, 29,851, 35,714, 37,453, 40,816

[a] Obtained in Nujol mulls. [b] Obtained in CH_3CN solution.

the one-electron spin–orbit coupling constants for chlorine and bromine [587 and 2460 cm^{-1}, respectively (λ_F is only 272 cm^{-1} [25])].

For the dithiolate system studied here, $g_\perp$ is greater than $g_\parallel$ as for most other MoO^{3+} systems. However, $g_\perp$ is larger than $g_\parallel$ by a much smaller margin for the dithiolate than for the fluoride complex. Employing Manoharan and Rogers' argument, then a reasonable spin–orbit coupling constant for the sulfur in this dithiolate system would be that for the sulfhydryl sulfur (382 cm^{-1}).

Infrared and uv–visible spectral data for $MoO(C_5H_4CS_2)_2^-$ and $Mo(C_5H_4CS_2)_3^{2-}$ are given in Table III. All the electronic transitions for the molybdenyl complex are of sufficient intensity to be charge transfer in origin. The low-energy $^2B_2 \rightarrow {}^2E$ transition, normally found near 14,000 cm^{-1} in MoO systems, is not observed here apparently because of its low intensity. The intense bands found above 26,000 cm^{-1} for $MoOCl_5^{2-}$ have all been accounted for by Gray and Hare[26] in terms of excitation of an electron from filled π orbitals on oxygen to empty d orbitals on the metal. This scheme however, fails fully to account for the spectrum of the somewhat more covalent $MoOBr_5^{2-}$ system where it is probable that π interactions of the bromine atoms contribute to the charge-transfer bands.[27]

On the basis of the electron spin resonance spectrum of bis(cyclopentadienedithiocarboxylato)oxomolybdate(V), it is obvious that the in-plane π-donor ability of the dithiolate ligand plays an important part in the electronic character of the system. Certainly, some of the charge-transfer peaks must arise from dithiolate ligand to metal transitions.

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Surface-Supported Metal Cluster Carbonyls. I. Decarbonylation and Aggregation Reactions of Rhodium Clusters on Alumina

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The adsorption of carbon monoxide on supported metal particles has been an area of interest in the chemistry and physics of surfaces for some time. Such factors as metal particle size, methods of reduction and sintering, and the type of support used often appear to affect the details of CO adsorption on the surface of these particles. The interest in CO adsorption on metals and obvious parallels with metal carbonyl compounds suggest that surface-supported metal carbonyls, especially polynuclear carbonyls, might have interesting and important properties as catalysts and as models of metal particles.

The interactions of nickel carbonyl with alumina and silica have been reported by Parkyns;[1] on the silica surface the carbonyl appears simply to physisorb while the alumina surface catalyzes a reaction yielding materials which have an ir spectrum typical of CO adsorbed on nickel metal. Studies of catalyst systems formed from molybdenum hexacarbonyl supported on a variety of oxide supports have also been reported.[2–6] In addition, there have been recent studies in which metal carbonyls, including polynuclear carbonyls, were bonded to modified polymer supports such as chemically modified polystyrene.[7–9] However, we are not aware of any studies reporting the interaction of polynuclear cluster carbonyls with simple oxide surfaces.

Because of our interest in metal cluster carbonyls and the belief that, under appropriate conditions, such metal cluster species should exhibit unique catalytic properties and perhaps model the behavior of very small metal particles, we have begun an investigation of oxide-supported metal cluster carbonyls. We report here the reactions which occur when the rhodium carbonyls $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Rh_2(CO)_4Cl_2$ are adsorbed on alumina.

Experimental Section

Materials. The three rhodium carbonyls were prepared by literature methods[10–12] starting from $RhCl_3 \cdot nH_2O$ purchased from Engelhard Industries. Aluminas and silicas were from a variety of sources and of purity varying from chromatographic grade to high-purity materials.

Details of the chemical and physical observations and of the ν(CO) spectrum obtained were independent of the type of alumina used as long as the sample was primarily in the γ phase. The Vycor used was powdered Corning high-purity porous glass adsorbent (lot no. 8144). The $^{18}O_2$ was from Yeda Research and Development Ltd. and was 98.1% enriched.

Ir Spectra. All spectra were obtained using a Beckman IR-9 spectrophotometer. Where noted, the spectra were recorded for Nujol mulls or solutions. Otherwise, all spectra were obtained by plating the alumina sample out of a chloroform slurry onto the inner surface of the window of an ir gas cell which was jointed to provide ready access. The high scattering of these solid samples required relatively wide slit settings in order to obtain sufficient signal levels.

Surface Adsorption of Cluster Carbonyls. Solutions of $Rh_6(CO)_{16}$ in chloroform were used to deposit the metal carbonyl on the alumina or silica surfaces. Typically, 25 mg of the carbonyl in ~50 ml of chloroform was stirred at 50° with 0.5 g of the oxide for about 10 min. The alumina was then filtered, washed several times, and air-dried briefly. The rhodium carbonyl in the wash or that remaining in the chloroform solvent exhibited only the ir spectrum typical of $Rh_6(CO)_{16}$. Both $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ were similarly deposited out of Skelly B solution. In each case the carbonyl remaining in solution appeared unaffected by interaction with the alumina.

Results and Discussion

When hexadecacarbonyl hexarhodium, $Rh_6(CO)_{16}$, is stirred in a chloroform solution over alumina at 50° for several minutes, the oxide surface acquires a light tan color; the very dark color of the $Rh_6(CO)_{16}$ solution also lightens perceptibly because of reduction in concentration. After filtration and air-drying, the rhodium carbonyl–alumina material retains the light tan color or changes slightly to a golden hue; the product exhibits a spectrum in the ν(CO) region like that in Figure 1c. This spectrum changes and finally disappears over several hours' exposure to air as shown by the sequence of spectra in Figure 1c–e. However, under an atmosphere of CO the color of the alumina-supported material changes to a deep violet and an intense ν(CO) spectrum returns (Figure 1b). This spectrum closely resembles that of solid $Rh_6(CO)_{16}$ (compare Figure 1b and a). Exposure to air or to dry oxygen again leads to gradual frequency and intensity changes until, after 1 day or more, the ν(CO) spectrum disappears completely. This sequence can be repeated several times without noticeably diminishing the intensities for the fully carbonylated material and without the appearance of new bands besides those present in Figure 1b–e. In addition, when the surface-supported sample is in the fully carbonylated violet form, $Rh_6(CO)_{16}$ can be removed from the alumina surface into refluxing chloroform if the system is maintained under an atmosphere of CO. We interpret these results as evidence that a gradual decarbonylation of the Rh_6 cluster is catalyzed on the alumina surface and that the Rh_6 cluster either retains its integrity or fragments into smaller units which remain in very close proximity in the decarbonylated form.

Under $^{18}O_2$ the formation of oxygen-labeled CO_2 occurs concomitantly with the disappearance of the ν(CO) spectrum. Alumina blanks treated in the same fashion gave no detectable CO_2. The precise nature of the rhodium species remaining after this carbon monoxide oxidation is not yet known, although the easy reversibility of these reactions suggests that molecular oxygen is adsorbed at the coordination sites vacated by the oxidized CO as in the reaction step

$$Rh_6(CO)_{16}\cdot Al_2O_3 + (m + n/2)O_2 \rightarrow Rh_6(CO)_{16-n}(O_2)_m\cdot Al_2O_3 + nCO_2$$

The formation of at least one stable intermediate during the decarbonylation process is indicated by the simultaneous appearance of two bands between 2000 and 2100 cm^{-1} followed by their disappearance as the reaction progresses (see Table I).

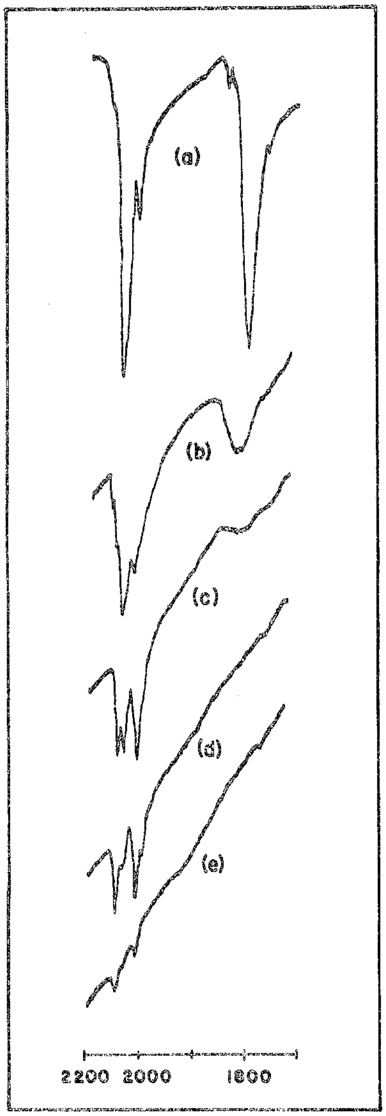

Figure 1. Ir spectra in the ν(CO) region showing various stages of decarbonylation of the Rh_6 cluster on alumina. Spectra shown are for (a) solid $Rh_6(CO)_{16}$ as Nujol mull, (b) fully carbonylated $Rh_6(CO)_{16}$ on alumina after exposure to 1 atm of CO for more than 1 day, (c) the same sample after exposure to 1 atm of dry O_2 for several hours, (d) the same sample after exposure to dry O_2 for more than 1 day, and (e) the same sample after exposure to dry O_2 for several days.

Table I. ν(CO) Bands for Species of Interest

Species	ν(CO) terminal[a]	ν(CO) bridging[a]
$Rh_6(CO)_{16}$[b]	2105 w, 2070 s, 2047 w, 2022 m, 2020 m	1833 w, 1793 s
Fully carbonylated $Rh_6(CO)_{16}$–Al_2O_3	2095 w, 2060 s, 2010 m	1805 s
Bands assigned to intermediate species	2080 s, 2000 s	
$Rh_2(CO)_4Cl_2$[c]	2105 m, 2089 s, 2080 w, 2035 s, 2003 w	
$Rh_2(CO)_4Cl_2$–Vycor[b] (carbonylated)	2105 sh, 2096 s, 2038 s, 2005 w	

[a] Frequencies in wave numbers. [b] As Nujol mull. [c] Solution spectrum.

Attempts to observe ir bands typical of complexed molecular oxygen in the region 800–1300 cm^{-1} were unsuccessful. However, this region is partially obscured by strong alumina absorptions. Indirect evidence for complexation of oxygen on the surface-bound rhodium derives from the observation that a substantial quantity of oxygen remains even after evacuation

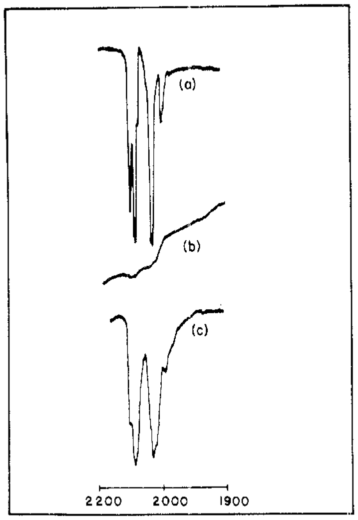

Figure 2. Ir spectra in the ν(CO) region of (a) solid $Rh_2(CO)_4Cl_2$ as Nujol mull, (b) $Rh_2(CO)_4Cl_2$ supported on Vycor after exposure to air for more than 1 day, and (c) the material obtained after exposing fully decarbonylated dimer to CO for 1 hr.

under conditions which remove oxygen from an alumina surface. The presence of this adsorbed oxygen was demonstrated by exposure of a sample to $^{18}O_2$, evacuation to remove physisorbed oxygen, and then exposure to CO. Substantial quantities of $C^{16}O^{18}O$ were formed along with lesser amounts of $C^{18}O_2$.

In order to determine whether other compounds would exhibit similar behavior and to see whether the reaction of small clusters to form larger ones was facile on the alumina surface, we studied $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ under conditions similar to those described above. Both compounds adsorb out of alkane solvents onto the surface where they are fully decarbonylated in a short period of time. Exposure to an atmosphere of CO then produces a deep violet material with a ν(CO) spectrum identical with that in Figure 1b. The ν(CO) spectrum progresses gradually through the Figure 1b–e decarbonylation sequence upon exposure to air. In addition, $Rh_6(CO)_{16}$ can be extracted into refluxing chloroform from the violet fully carbonylated form. The alumina surface apparently acts as a very effective catalyst for the conversion of these two compounds to $Rh_6(CO)_{16}$ under an atmosphere of CO. This parallels the solution behavior in which both $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ can be converted to $Rh_6(CO)_{16}$[11-13] under strongly basic conditions. This suggests that the strongly basic nature of the alumina surface hydroxyl groups is at least partially responsible for the course of these surface reactions.

These results on alumina surface contrast sharply with our observations using silica and Vycor support materials. All three rhodium carbonyls appear to undergo physical adsorption or crystallization onto silica surfaces where the ir spectra remain virtually identical with those of the free solids for days if the samples are maintained at room temperature. A notable exception is the system $Rh_2(CO)_4Cl_2$ on Vycor. Dramatic color changes ensue upon exposure to oxygen and the ν(CO) spectrum disappears although no new bands are observed during this decarbonylation. Under exposure to CO the color and ir spectrum typical of the dimer return with no apparent conversion to the hexanuclear carbonyl; this again contrasts with the behavior on the alumina surface. These spectral changes are shown in Figure 2.

Our studies also suggest that initiation of the observed alumina-catalyzed reaction is sensitive to the manner by which adsorption onto the alumina surface is achieved. Several samples for which deposition occurred by evaporation of a saturated chloroform solution over alumina showed none of the behavior described above. The ν(CO) spectrum was simply that of crystalline $Rh_6(CO)_{16}$ and the spectrum remained unchanged for days or weeks. Only carefully controlled adsorption out of a subsaturated solution, presumably as a monolayer or less, led to the behavior described above. It also occurred that these reactions only took place when at least a substantial fraction of the alumina adsorbent was in the γ phase. Pure β-trihydrate and α-phase samples failed to initiate the decarbonylation reactions.

These studies show that interesting reactions of metal carbonyls are catalyzed by oxide surfaces and that the exact course of the reaction is very sensitive to the type of surface involved. This is consistent with the observations of Parkyns[1] for nickel carbonyl on silica and alumina. Studies of supported catalysts derived from molybdenum hexacarbonyl[2-6] have already suggested that metal carbonyls can be used reproducibly to form supported metal catalysts by mild heating in vacuo. Our results suggest that the proper choice of metal carbonyl and oxide support may form decarbonylated metal clusters by simple room-temperature oxidation. Mild reduction conditions might then succeed in forming very active catalyst systems consisting essentially of uniform size metal clusters of just a few atoms. Synthetic and catalytic applications of these oxide-supported metal cluster carbonyls are deserving of further study.

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Registry No. $Rh_6(CO)_{16}$, 28407-51-4; $Rh_4(CO)_{12}$, 19584-30-6; $Rh_2(CO)_4Cl_2$, 14523-22-9; Al_2O_3, 1344-28-1.

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Resonance Raman Spectra of Superoxide-Bridged Binuclear Complexes. $[(CN)_5CoO_2Co(CN)_5]^{5-}$ and $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ [1]

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Resonance Raman spectroscopy affords the potential of elucidating both vibrational and electronic transitions, since their coupling produces resonance enhancement of Raman bands.[2,3] The technique offers particular promise in biological systems,[4] where vibrations of chromophoric groupings can be