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Adsorption of Ruthenium–Cobalt Bimetallic Clusters on Hydroxylated Alumina

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The bimetallic clusters $RuCo_2(CO)_{11}$ and $HRuCo_3(CO)_{12}$ adsorb spontaneously from pentane solution onto hydroxylated aluminum oxide. It is proposed that the former cluster is initially adsorbed as $RuCo_2(CO)_{10}$(ads) which is converted to $RuCo_3(CO)_{12}^-$(ads, solv) after the addition of ether solvents. The hydridic cluster is adsorbed through a deprotonation reaction to also yield the anion $RuCo_3(CO)_{12}^-$(ads). Infrared evidence suggests the absence of bridging carbonyls for this species.

The adsorption of metal carbonyls on refractory supports has been shown, in many cases, to yield highly dispersed supported metal particles which are catalytically active for a wide range of reactions.[1] Also, it has been shown that many heterogeneous[2] and homogeneous[3] bimetallic catalysts have properties that are not derived simply from the additive effects of the two metals. Since many bimetallic and multimetallic carbonyl clusters are well-known, there has also been considerable interest in preparing supported bimetallic catalysts from these materials.[4] The premise is that adsorption of a bimetallic cluster will lead to a surface metallic particle of the same composition. In some cases, however, it has been shown that the two metals phase separate upon heating under catalytic conditions.[5] It is possible, of course, that the composition of a bimetallic cluster may be altered during its deposition on a metal oxide surface. Thus there is no guarantee that the surface composition will exactly reflect the initial composition of the carbonyl cluster.

There are many examples of homogenous ruthenium–cobalt bimetallic catalysts for a wide range of reactions,[6] for example, in the homologation of methanol,[7,8] the water-gas shift reaction,[9] and the hydrogenation of olefins.[10] In some cases the ruthenium–cobalt bimetallic system exhibited superior activity than could be expected from cobalt and ruthenium acting separately.[7] The trinuclear cluster $RuCo_2(CO)_{11}$ (**1**)[11] is a very reactive synthetic precursor to ruthenium–cobalt bimetallic compounds; it is readily capped by a wide variety of substrates and is itself a precursor to a water-gas shift catalyst.[9]

The high reactivity of $RuCo_2(CO)_{11}$ suggested to us that this cluster would be a desirable precursor to supported ruthenium–cobalt bimetallic catalysts. Thus we have investigated the adsorption of **1** onto hydroxylated alumina by in situ infrared spectroscopy. The species that is formed upon adsorption of $RuCo(CO)_{11}$ onto hydroxylated alumina is extremely fragile as evidenced by its reactivity toward PPNCl and solvents. We report here that the bimetallic cluster **1**, adsorbed on alumina, undergoes a rapid disproportionation reaction in the presence of ether solvents to yield predominatly the anion $RuCo_3(CO)_{12}^-$(ads, solv) (**2**(ads, solv)).

Experimental Section

Materials. The aluminum oxide used in this study was CATAPAL SB. This was calcined at 350 °C in oxygen. Hydroxylated alumina (HA) surfaces were prepared by passing helium saturated with water over freshly calcined alumina at 100 °C for $^1/_2$ h. The sample was then purged with dry helium for 1 h at 100 °C. Dicobalt octacarbonyl was purchased from Pressure Chemical Co. Diruthenium hexacarbonyl tetrachloride was either purchased from Aesar Chemical Co. or synthesized by literature procedures from $RuCl_3 \cdot 3H_2O$;[12] the anion $[Co(CO)_4]^-$ was prepared by literature methods;[13] PPNCl was purchased from Strem Chemical Co. The clusters $RuCo_2(CO)_{11}$[11] and $HRuCo_3(CO)_{12}$[14-16] were prepared from $Ru_2(CO)_6Cl_4$ and $[Co(CO)_4]^-$ by literature methods. Both clusters gave satisfactory elemental analysis, infrared spectra, and mass spectra.

The solvents THF and pentane were distilled from sodium–potassium alloy and benzophenone prior to use. Methylene chloride was dried over molecular sieves and degassed by three cycles of freeze, pump, and thaw.

All adsorption experiments and in situ infrared spectroscopy experiments were performed under ultrapure helium (Airco, 99.995) in a reactor system as previously described.[17] Blank experiments showed that immersion of hydroxylated alumina into pentane, THF, or CH_2Cl_2 at room temperature did not result in the evolution of any gases. The neutral clusters **1** and $HRuCo_3(CO)_{12}$ were adsorbed onto alumina from pentane, and the anionic cluster $RuCo_3(CO)_{12}^-$ was adsorbed as its PPN^+ salt from THF. Attempted extractions of surface species were performed in CH_2Cl_2 or CH_2Cl_2/THF mixtures with PPNCl.

A typical adsorption experiment was performed in the following way. A solution of 9.8 mg of **1** in 10 mL of freshly distilled pentane was added to 200 mg of HA under helium. The cluster was extracted from the pentane to give a colorless solution. The pentane solvent was then removed in a flow of helium. The HA

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Table I. Attempted Extraction of Surface Species Following Adsorption of $RuCo_2(CO)_{11}$

total[a] remaining				
1st wash	2nd wash	extracted species	surface metal complex (determined by IR)	% metal
CH_2Cl_2		no carbonyls	"$RuCo_2(CO)_{10}$"	*b*
THF		no carbonyls	$RuCo_3(CO)_{12}^-$	*b*
THF	$PPNCl/CH_2Cl_2$	$RuCo_3(CO)_{12}^{-c}$ + trace $Co(CO)_4^{-d}$	no IR bands in carbonyl region	2% Co 40% Ru
$PPNCl/CH_2Cl_2$		$Co(CO)_4^{-d}$ + trace $RuCo(CO)_{12}^{-d}$	no IR bands in carbonyl region	55% Co 96% Ru

[a] Metal analysis determined by DCP. [b] Not determined. [c] Characterized by IR and UV–vis spectroscopy and protonation to yield the hydride followed by mass spectroscopy. [d] Characterized by IR.

completely extracted the cluster from the pentane; in this manner up to a 2% by weight metal loading could be achieved. Metal analyses were performed by digestion of the alumina with lithium tetraborate and analysis of the solution by direct current plasma spectrometry.

The in situ infrared experiments were performed on self-supporting pellets of aluminum oxide pressed at 10.34×10^3 kPa; the pellets transmitted approximately 50% of the infrared beam intensity. Infrared spectra were recorded on a Nicolet 5DXB spectrometer. The pellets were loaded with the metal carbonyl by immersion into a pentane solution of the metal carbonyl. Metal loadings were less than 1% by weight.

Results

When 1 is adsorbed onto the surface of hydroxylated alumina significant quantities of CO are evolved—up to 1 equiv per cluster in the first 3 h after adsorption with most of that evolved in the first 15 min. After 1 h the adsorbed cluster loses CO very slowly; thus at 10 h a total of 1.4–1.5 equiv of CO/cluster is detected.

Following the initial adsorption of $RuCo_2(CO)_{11}$ onto alumina attempts were made to extract the surface species with PPNCl. The extraction experiments are summarized in Table I. The products extracted from the surface are dependent upon the conditions used for the extraction. When PPNCl in CH_2Cl_2 is used directly to extract surface species, the major product is $[Co(CO)_4]^-$. If the surface is first treated with an ether solvent, for example, THF, then extraction with PPNCl is attempted the major extracted species is $RuCo_3(CO)_{12}^-$. This was identified by infrared and UV–vis spectroscopy by comparison with authentic samples. Protonation yields the known hydride, $HRuCo_3(CO)_{12}$, which was identified by mass spectroscopy. Analysis of the support and extracted species shows that the cluster anion can be synthesized and extracted in 60% yield based on total metal of the starting cluster $RuCo_2(CO)_{11}$.

When $RuCo_3(CO)_{12}^-$ is extracted with $THF/CH_2Cl_2/PPNCl$, some $Co(Co)_4^-$ is present in the extract. Since $Co(CO)_4^-$ is not present on the surface prior to extraction (vide infra), it seems likely that the anion $RuCo_3(CO)_{12}^-$ undergoes some decomposition upon extraction. If $RuCo_2(CO)_{11}$ is stirred in a solution of PPNCl and CH_2Cl_2, the anion $RuCo_3(CO)_{12}^-$ is formed very rapidly. When $RuCo_2(CO)_{11}$ is stirred in CH_2Cl_2, no IR evidence for the formation of $RuCo_3(CO)_{12}^-$ is found after 1 h. The addition of ether solvents to the surface appears to initiate a transformation of the surface species to yield $RuCo_3(CO)_{12}^-$(ads). In all of the attempted extractions additional CO evolution is observed during the extraction, no other gases, e.g. CO_2, are detected.

Additional information concerning the surface transformation is obtained by in situ infrared spectroscopy. Figure 1 compares the solution infrared spectrum of 1 in pentane (Figure 1A) with the spectra for the same cluster during adsorption onto HA (Figure 1B). The top spectrum in Figure 1B was recorded immediately following the addition of the ruthenium–cobalt cluster. There are no bands in this spectrum that can be assigned to any of the starting cluster which may simply be physisorbed on the surface. The bottom spectrum of Figure 1B was recorded 1 h after the adsorption of the cluster. All of the bands in the top trace have disappeared, and two new bands have appeared. These are in the terminal region and occur at 2027 and 1973 cm^{-1}. No further changes are observed in the spectrum after this time.

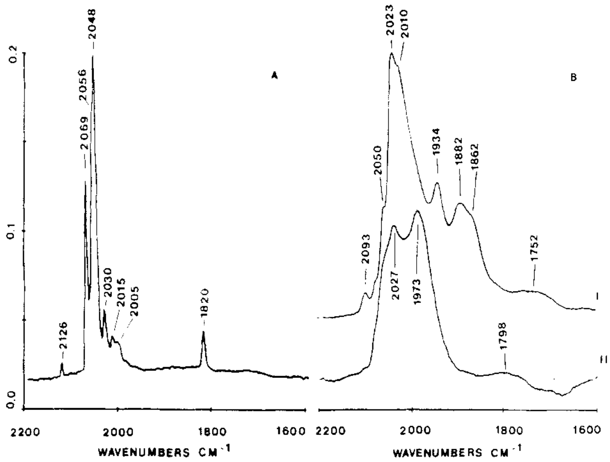

Figure 1. A. Solution spectrum of $RuCo_2(CO)_{11}$ in pentane for comparison with surface species. B. Top trace, I: infrared spectrum immediately following addition of $RuCo_2(CO)_{11}$ to hydroxylated surface. Bottom trace, II: the spectrum of the pellet after 1 h.

Given the simplicity of the final infrared spectrum (two terminal bands and no bridging carbonyls) generated in the in situ adsorption experiment, the quantitative removal of the cluster from pentane solution, and close to 1 equiv of CO evolved during the initial adsorption, it is possible to describe the surface species as "$RuCo_2(CO)_{10}$(ads)" bonded to a surface hydroxyl group. The infrared spectra obtained immediately following adsorption of the cluster are quite complex. The band at 1882 cm^{-1} suggests the possible presence of $Co(CO)_4^-$, during the adsorption; this band disappears as the steady-state spectrum is obtained. Although $Co(CO)_4^-$ is extracted as the major surface species with PPNCl in CH_2Cl_2, there is no evidence for this species by infrared spectroscopy once the steady-state infrared spectrum is obtained.

The identity of the surface compound or compounds responsible for the bottom trace in Figure 1B is difficult to assign from the infrared spectrum; it does not correspond to the solution spectrum of any of the well-known ruthenium–cobalt clusters that have been reported in the literature, such as $RuCo_2(CO)_{11}$,[11] $Ru_2Co_2(CO)_{12}$,[11] $Ru_3Co(CO)_{13}^-$,[18] $RuCo_3(CO)_{12}^-$,[15,18] or simple substituted[16] or

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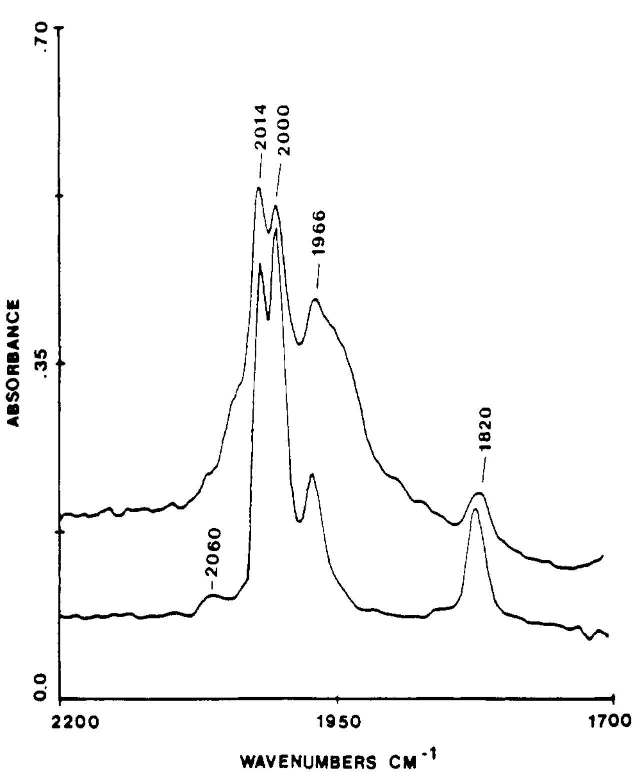

Figure 2. Top trace, I: infrared spectrum obtained after the addition of THF to $RuCo_2(CO)_{11}$ adsorbed on HA. Bottom trace, II: solution spectrum of $RuCo_3(CO)_{12}^-$ in THF.

capped derivatives.[11,19] Nor is this spectrum similar to either $Co_4(CO)_{12}$[20] or $Ru_3(CO)_{12}$[21] adsorbed on hydroxylated alumina.

The trinuclear cluster $RuCo_2(CO)_{11}$ is well-known to be unstable in solution, and its decomposition, in fact, forms the basis for the preparation of $Ru_2Co_2(CO)_{12}$.[11] When we use nucleophilic solvents such as diglyme or tetrahydrofuran, THF, to model the reactivity of the HA surface, we find that $RuCo_3(CO)_{12}^-$ is formed in good yield.[22] Protonation yields the known hydrido cluster $HRuCo_3(CO)_{12}$.[15]

The formation of the anion **2** on hydroxylated alumina is confirmed by the infrared spectroscopy experiment shown in Figure 2. The trinuclear cluster **1** is adsorbed on HA from pentane to give an infrared spectrum as shown in the bottom trace of Figure 1B. When THF is added to this sample, the top trace of Figure 2 is obtained. A bridging band is now observed at 1820 cm^{-1}, and well-defined terminal bands are observed at 2014, 2000, and 1966 cm^{-1}. For comparison the spectrum of $RuCo_3(CO)_{12}^-$ in THF is shown in the bottom trace of Figure 2. The major bands present on the surface are accounted for by postulating the presence of the tetranuclear anion. However, there are broad shoulders in the infrared spectrum shown in the top trace of Figure 2 that remained unassigned. This is not surprising since a disproportionation reaction to yield $RuCo_3(CO)_{12}^-$ must be very complex; for example, the formation of either ruthenium- or cobalt-containing cations is expected.

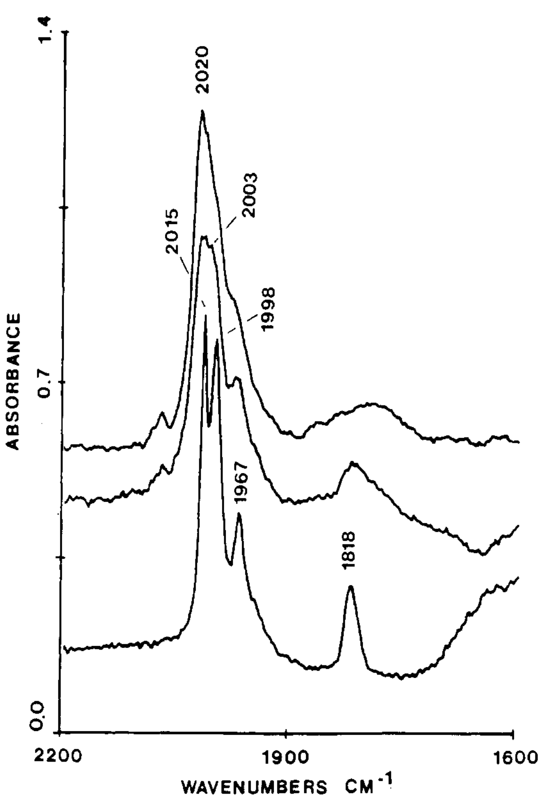

Figure 3. Trace I: infrared spectrum immediately following the adsorption of $HRuCo_3(CO)_{12}$ onto hydroxylated alumina. Trace II: the spectrum after 3 h. Trace III: the spectrum immediately following the addition of THF to the surface.

The direct adsorption of $HRuCo_3(CO)_{12}$ onto HA yields an infrared spectrum that is identical with the spectrum of **2** in THF. Very little CO is evolved during this adsorption: (0.15 ± 0.03) CO per cluster (average of seven experiments), consistent with a simple deprotonation reaction.[27,28] This provides confirmation for the presence of $RuCo_3(CO)_{12}^-$(ads) from the reaction of **1** with HA following the addition of THF. Figure 3 shows the in situ infrared spectra obtained upon adsorption of $HRuCo_3(CO)_{12}$ onto alumina from pentane solution. The bridging carbonyl band is lost during the adsorption; after 3 h the band at 1820 cm^{-1} has nearly disappeared. This band is regenerated upon the addition of THF; after the addition of THF the spectrum is virtually identical with the spectrum of $RuCo_3(CO)_{12}^-$ in THF and with the spectrum obtained after the addition of THF to **1**(ads) (Figure 2).

Discussion

The adsorption of $RuCo_2(CO)_{11}$ and $HRuCo_3(CO)_{12}$ onto hydroxylated alumina can be represented by eq 1 and 2.

$$RuCo_2(CO)_{11} \xrightarrow[\text{pentane}]{Al_2O_3} A + CO \xrightarrow{\text{THF}} RuCo_3(CO)_{12}^-(\text{ads, solv}) + CO + B \quad (1)$$

$$HRuCo_3(CO)_{12} \xrightarrow[\text{pentane}]{Al_2O_3} RuCo_3(CO)_{12}^-(\text{ads}) \xrightarrow{\text{THF}} RuCo_3(CO)_{12}^-(\text{ads, solv}) \quad (2)$$

The second reaction is an example of cluster deprotonation which is well documented for the adsorption of cluster hydrides.[23] The adsorbed species $RuCo_3(CO)_{12}^-$(ads) shows no bridging carbonyl in the infrared spectrum. The

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(22) When the decomposition of $RuCo_2(CO)_{11}$ in THF is monitored by infrared spectroscopy, it is observed that the disproportionation is complete in 24 h. In solution traces of $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$ are observed by IR. During the solution decomposition, the intensity of the bridging carbonyl band of $Co_4(CO)_{12}$ is less than 5% of the bridging carbonyl band of $RuCo_3(CO_{12})^-$.

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bridging carbonyl band appears only upon the addition of solvent; thus a distinction is made between two types of adsorbed $RuCo_3(CO)_{12}^-$. After the addition of solvent the infrared spectrum is indistinguishable from that observed in solution for this reason it is referred to as solvated. Addition of solvent alone, however, does not extract any metal carbonyls; thus the surface species is described as adsorbed.

The reappearance of the bridging bands upon addition of THF may be consistent with poisoning of the Lewis base sites. This last explanation is often invoked for surface metal carbonyls,[1b,24] and often there is good evidence for this interaction.[1b,25] However, in the present case we do not find bands below 1600 cm^{-1} which can be assigned to such an interaction. Also, it is difficult to imagine how all three of the bridging carbonyls in $RuCo_3(CO)_{12}^-$ could interact simultaneously with the surface. An alternative explanation is that an alternative isomeric form of $RuCo_3(CO)_{12}^-$ which has no bridging CO's is stabilized on the surface. Such isomers for $M_4(CO)_{12}$ systems have been discussed recently by Lauher.[26]

In the reactions represented by eq 1 above it is clear that predominantly $RuCo_3(CO)_{12}^-$(ads, solv) is formed as the major product following the addition of THF. The stoichiometry of the transformation, however, is not clear. Other products, B in eq 1, must be formed. Broad peaks are observed in the infrared spectrum (Figure 2) consistent with other products but are not assigned. The reaction of A with THF to yield **2** on the surface is described as a disproportionation since the other possible reduction pathway utilizing CO as the reductant must generate CO_2, and this is not observed either in the gas phase or on the surface as carbonate.

The species represented by A in this scheme is characterized by the following facts: (1) It is formed with the apparent stoichiometry $RuCo_2(CO)_{10}$. (2) It decomposes in the presence of PPNCl to give predominantly $Co(CO)_4^-$. (3) It is converted predominantly to $RuCo_3(CO)_{12}^-$(ads, sol) upon addition of THF. (4) Its infrared spectrum is very simple consisting of only two terminal bands. Without being able to model this species with a known molecular analogue, we propose the assignment to be $RuCo_2(CO)_{10}$(ads) in which a surface hydroxyl group occupies a bridging position between the two cobalt atoms.

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Registry No. 1, 78456-89-0; $HRuCo_3(CO)_{12}$, 24013-40-9.

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Synthetic Applications of Trialkylaluminum Reagents: Alkylation and Reduction of Transition-Metal-Complexed π-Hydrocarbon Ligands

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Trialkylaluminum compounds (AlR_3, R = Me, Et) interact with the organotransition-metal cations $[(arene)Mn(CO)_3]^+$ (**1**) and $[Co(C_5H_5)]^+$ (**2**) to form "liquid clathrate" phases. Thermal decomposition of these phases results in isolation of a series of neutral cyclohexadienyl, **3a–d**, or cyclopentadiene, **4**, products which are simple addition products except in the case of **1d** (arene = mesitylene), for which, depending upon the reaction conditions, isomeric forms of the novel dimer $(C_{18}H_{24})[Mn(CO)_3]_2$ (**5a** or **5b**) have been isolated. It was found that preformed "liquid clathrates" containing the anions $[Al_2R_6Cl]^-$ (R = Me, Et), which possess a much higher degree of air stability than the corresponding free trialkylaluminum compounds, reacted with **1** and **2** to give the same range of products. The structures of **5a** and **5b** have been determined crystallographically. **5a**: triclinic; $P\bar{1}$; a = 8.529 (3) Å, b = 9.189 (2) Å, c = 8.488 (3) Å; α = 104.21 (3)°, β = 118.10 (3)°, γ = 89.43 (3)°, V = 564.4 Å^3; Z = 1; ρ = 1.524 g cm^{-3}; R = 0.041. **5b**: monoclinic; $P2_1/c$; a = 12.2916 (19) Å, b = 15.8372 (21) Å, c = 12.2308 (13) Å; β = 101.757 (11)°; V = 2331.0 Å^3; Z = 4; ρ = 1.477 g cm^{-3}; R = 0.057. The structure of the addition product **3d** (R = Me) was also crystallographically determined, and exo addition of the methyl was thereby confirmed. **3d**: monoclinic; $P2_1/n$; a = 11.956 (1) Å, b = 11.441 (1) Å, c = 10.104 (1) Å; β = 104.28 (1)°; V = 1339.4 Å^3; Z = 4; ρ = 1.360 g cm^{-3}; R = 0.042.

Introduction

Activation of π-hydrocarbon compounds toward nucleophilic addition via transition-metal complexation is one of the most widely studied phenomena in the field of organotransition-metal chemistry.[2] In this context addition of carbanionic moieties to monocationic organotransition-metal substrates has been a particularly widely studied reaction as the neutral addition products are often

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