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Reversible Interconversions between $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ in the Presence of CO or H_2 on Fully Hydroxylated Magnesia Surface That Mimic Their Reactions in Solution

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Reversible interconversions between the cluster anions $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ on fully hydroxylated magnesia in the presence of H_2 or CO at a pressure of 1 atm have been observed that mimic interconversions of these ions in basic solution. In the presence of H_2, the $[HRu_3(CO)_{11}]^-$ anion on fully hydroxylated magnesia is converted to $[H_3Ru_4(CO)_{12}]^-$, which in turn transforms back to $[HRu_3(CO)_{11}]^-$ when H_2 is removed and CO is added. The organometallic species on the fully hydroxylated magnesia surface are mobile at room temperature, and the interconversion steps are reversible and can be repeated. Possible reaction pathways are proposed.

Introduction

Separation of molecular homogeneous catalysts from reaction media is of considerable practical and fundamental interest. One solution to this problem employs biphasic systems in which the molecular catalyst is solubilized in water *via* water-soluble ligands.[1] This approach is successful at the industrial level. Several hydroformylation biphasic processes are in use.[2] A step forward in this strategy of catalyst separation is the concept of supported aqueous-phase catalysis in which the catalyst is dissolved in the aqueous phase on the hydroxylated inorganic oxide surface.[3] The catalyst solubilized in the physisorbed water layer can, in principle, be removed from the surface by treatment with an excess of water. However, if the catalyst is ionic, leaching from the surface is minimized if the surface serves as the counterion. The anion $[HRu_3(CO)_{11}]^-$ has been identified as a catalyst for the water gas shift reaction in basic media[4] and on a hydroxylated magnesia surface.[5] Solution studies in basic media show that facile interconversion occurs between this anion and $[H_3Ru_4(CO)_{12}]^-$ and is dependent upon the relative amounts of CO and H_2 gases present.[4c] These anions are easily extracted from the hydroxylated magnesia surface when the extracting solvent contains a salt, such as PPNCl (bis(triphenylphosphino)iminium chloride), with the PPN^+ serving as the counterion. These cluster anions are not leached from the surface when no countercation is present.

While numerous studies have been devoted to the thermal treatment of metal carbonyl clusters on oxide surfaces and syntheses and stabilization of cluster species on oxide surfaces,[6] there has been no apparent attempt to examine possible reversible interconversions of potentially catalytic clusters in the aqueous phase on an oxide support under conditions that approximate those in solution. In the present study, we investigate the possible interconversion that might exist between $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ on a hydroxylated MgO surface in the presence of CO and H_2 at room temperature.

Results

Impregnation of $Ru_3(CO)_{12}$ on Fully Hydroxylated Magnesia and Subsequent Reactions with H_2 or CO. Conversion of Supported $[HRu_3(CO)_{11}]^-$ to $[H_3Ru_4(CO)_{12}]^-$. In accord with an earlier investigation,[7] $Ru_3(CO)_{12}$ impregnated on hydroxylated magnesia from a CH_2Cl_2 solution was converted to $[HRu_3(CO)_{11}]^-$. It was identified on the support by its Nujol mull IR spectrum and also identified in the extract (IR and ^1H NMR) when the supported material was treated with PPNCl in CH_2Cl_2 solution.

Hydrogen gas was passed over the supported $[HRu_3(CO)_{11}]^-$ at room temperature. The reaction was monitored as a function of time by IR spectroscopy of Nujol mull samples. As the reaction progressed, the IR spectra (Figure 1) exhibited a decrease in the intensities of bands that are assigned to $[HRu_3(CO)_{11}]^-$ (2077, 2017, and 1940 cm^{-1}) and the appearance of bands that are assigned to $[H_3Ru_4(CO)_{12}]^-$ (2033, 1993, and 1972 cm^{-1}). After 39 h of flowing H_2 through the reaction tube, cluster material on the surface was extracted with

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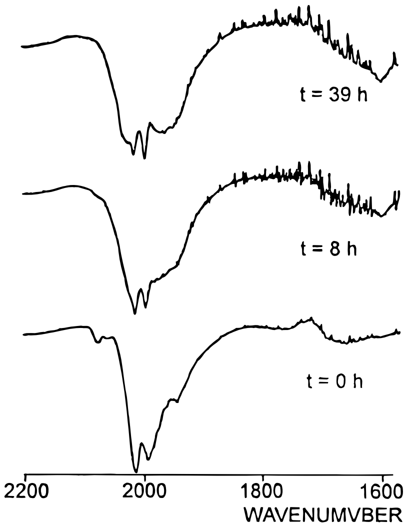

Figure 1. Nujol mull IR spectra of impregnated $Ru_3(CO)_{12}$ on hydroxylated MgO: (a) before H_2 flow, (b) 8 h of H_2 flow, (c) 39 h of H_2 flow.

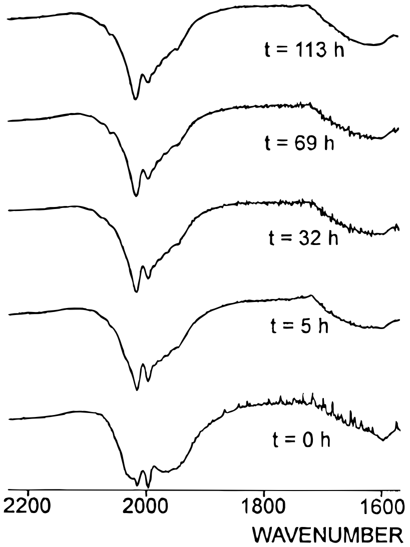

Figure 2. Nujol mull IR spectra of impregnated $Ru_3(CO)_{12}$ on hydroxylated MgO treated with H_2 (39 h): (a) before CO flow, (b) 5 h of CO flow (c) 32 h of CO flow, (d) 69 h of CO flow, (e) 113 h of CO flow.

PPNCl in CH_2Cl_2 and identified as the $[H_3Ru_4(CO)_{12}]^-$ anion by IR and ^{1}H NMR spectroscopies. A very weak singlet at $\delta = -19.32$ ppm indicated the presence of $[H_2Ru_4(CO)_{12}]^{2-}$ which formed from the deprotonation[8] of $[H_3Ru_4(CO)_{12}]^-$ on the basic hydroxylated magnesia surface.

Conversion of Supported $[H_3Ru_4(CO)_{12}]^-$ to $[HRu_3(CO)_{11}]^-$. The $[H_3Ru_4(CO)_{12}]^-$ formed from the reaction above was converted back to $[HRu_3(CO)_{11}]^-$ by passing carbon monoxide over it at room temperature. A Nujol mull IR of the supported cluster as a function of time (Figure 2) exhibited a decrease in the bands assigned to $[H_3Ru_4(CO)_{12}]^-$ and an increase of those assigned to $[HRu_3(CO)_{11}]^-$. Clusters on the surface were extracted with PPNCl in CH_2Cl_2. IR and ^{1}H NMR spectra of the extract reveal the presence of $[HRu_3(CO)_{11}]^-$ as the major product. Additionally, the ^{1}H NMR spectrum contains weak signals ($\delta = -17.07$ and -19.32 ppm) that are indicative of the presence of $[H_3Ru_4(CO)_{12}]^-$ and $[H_2Ru_4(CO)_{12}]^{2-}$. The ^{1}H NMR signals of these tetranuclear clusters became progressively weaker with increased time of flow of CO over the supported cluster material (Figure 3). After 113 h, the proton signals for $[HRu_3(CO)_{11}]^-$, $[H_3Ru_4(CO)_{12}]^-$, and $[H_2Ru_4(CO)_{12}]^{2-}$ were in the ratio of 9:1:1.

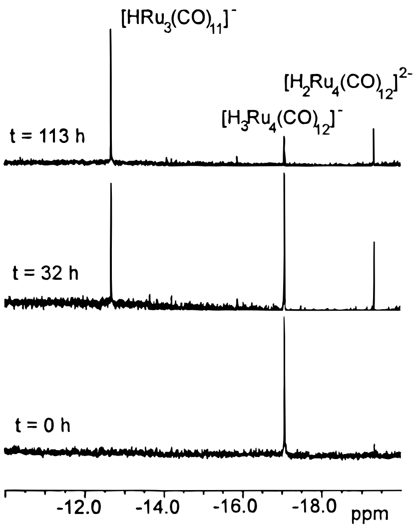

Figure 3. ^{1}H NMR spectra (in CD_2Cl_2) of extracted cluster materials from the impregnated $Ru_3CO)_{12}$ on hydroxylated MgO treated with H_2 (39 h): (a) before CO flow, (b) 32 h of CO flow, (c) 113 h of CO flow.

Impregnation of $H_4Ru_4(CO)_{12}$ on Fully Hydroxylated MgO and Subsequent Reactions with CO or H_2. Conversion of Supported $[H_3Ru_4(CO)_{12}]^-$ to $[HRu_3(CO)_{11}]^-$. In accord with earlier investigations,[5,9] $H_4Ru_4(CO)_{12}$ impregnated on hydroxylated magnesia from a CH_2Cl_2 solution was deprotonated to form $[H_3Ru_4(CO)_{12}]^-$. It was identified on the support by its Nujol mull IR spectrum and also identified in the extract (IR and ^{1}H NMR) when the supported material was treated with PPNCl in CH_2Cl_2 solution.

Carbon monoxide gas was passed over the supported $[H_3Ru_4(CO)_{12}]^-$ at room temperature, and the product was analyzed by IR and ^{1}H NMR spectroscopies in the same manner as the samples discussed in the preceding section. The Nujol mull IR spectrum of the supported cluster showed the appearance of $[HRu_3(CO)_{11}]^-$. After 27 h of passing CO over the sample, cluster material was extracted from the hydroxylated magnesia surface with PPNCl in CH_2Cl_2. The IR spectrum of the extract showed bands due to both $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_3(CO)_{11}]^-$. The ^{1}H NMR spectrum of the extracted clusters showed three singlets at -12.67, -17.07, and -19.32 ppm due to $[HRu_3(CO)_{11}]^-$, $[H_3Ru_4(CO)_{12}]^-$, and $[H_2Ru_4(CO)_{12}]^{2-}$ in the respective ratio of 5:4:1.

Conversion of Supported $[HRu_3(CO)_{11}]^-$ to $[H_3Ru_4(CO)_{12}]^-$. The $[HRu_3(CO)_{11}]^-$ formed from the reaction above was converted back to $[H_3Ru_4(CO)_{12}]^-$ by passing H_2 over it. The Nujol mull IR spectrum of the supported cluster material showed the reappearance of the bands attributed to $[H_3Ru_4(CO)_{12}]^-$ and a decrease in the intensities of the bands assigned to $[HRu_3(CO)_{11}]^-$. The product after 53 h of exposure to flowing H_2 was

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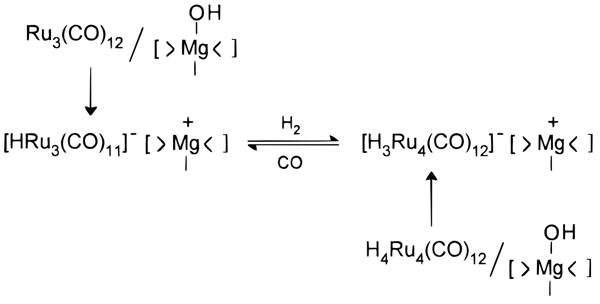
Scheme 1. Reversible Interconversions of the Cluster Anions $[HRu_3CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ on Hydroxylated Magnesia Surface



extracted from the support by treatment with PPNCl in CH_2Cl_2. IR and ^1H NMR spectra of the extract revealed the presence of $[H_3Ru_4(CO)_{12}]^-$ as the only cluster product.

Condensation of $[HRu(CO)_4]^-$ to $[HRu_3(CO)_{11}]^-$ in the Presence of Fully Hydroxylated MgO. The $[HRu(CO)_4]^-$ anion was converted to $[HRu_3(CO)_{11}]^-$ in a slurry of [PPN][HRu(CO)$_4$] and hydroxylated magnesia in CH_2Cl_2. It was identified from IR and ^1H NMR spectra.

Impregnation of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ on Partially Hydroxylated Magnesia. $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ impregnated on partially hydroxylated magnesia (MgO_{200}) produced $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$, respectively, on the support. But additional species were formed that could not be identified or extracted from the oxide surface. Furthermore, clean interconversions between the trinuclear and tetranuclear clusters in the presence of H_2 or CO could not be achieved on the partially hydroxylated magnesia (MgO_{200}) surface.

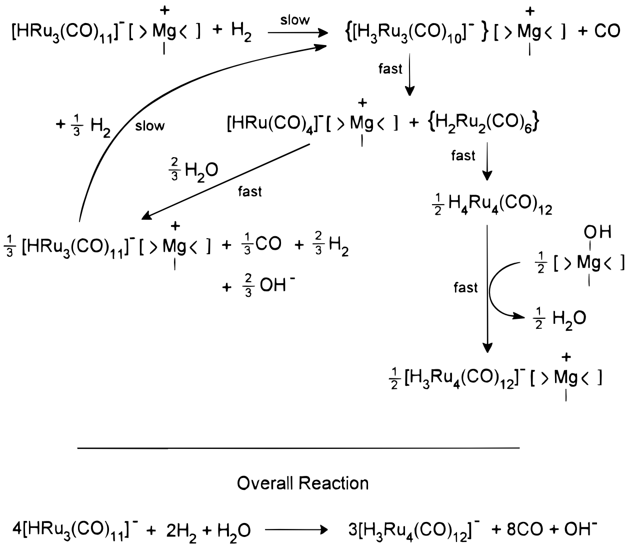
Discussion

While there are previous examples of reactions of clusters on oxide surfaces,[6] the present work represents the first example of reversible interconversions of cluster species on an oxide surface (Scheme 1) at ambient temperature that mimics a documented reversible system in solution. However, partially hydroxylated magnesia (MgO_{200}) does not yield the clean results obtained on fully hydroxylated magnesia (MgO_{25}).

Noteworthy features of these reactions on a fully hydroxylated magnesia surface are that the organometallic species are mobile at room temperature and that the interconversion steps are reversible and can be repeated. Thus, after $[HRu_3(CO)_{11}]^-$ is converted to $[H_3Ru_4(CO)_{12}]^-$ in the presence of H_2, it is reconstituted when the H_2 is removed and CO is added. By the same token, after $[H_3Ru_4(CO)_{12}]^-$ is converted to $[HRu_3(CO)_{11}]^-$ in the presence of CO, it is reconstituted when the CO is removed and H_2 is added. No carbonyl species were observed on the surface after the extraction procedure to remove the products of the reactions with CO and H_2. In the extracts, $[H_2Ru_4(CO)_{12}]^{2-}$ was the only organometallic species observed other than $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$.

Previous studies in solution[4c,10,11] provide clues to possible reaction pathways (Scheme 2) by which

Scheme 2. Proposed Pathway for Conversion of $[HRu_3(CO)_{11}]^-$ to $[H_3Ru_4(CO)_{11}]^-$ in the Presence of H_2[a]



$$4[HRu_3(CO)_{11}]^- + 2H_2 + H_2O \longrightarrow 3[H_3Ru_4(CO)_{12}]^- + 8CO + OH^-$$

[a] { } indicates a proposed unstable intermediate.

$[HRu_3(CO)_{11}]^-$ is converted to $[H_3Ru_4(CO)_{12}]^-$ in the presence of H_2. Earlier we showed that $[HRu_3(CO)_{11}]^-$ loses CO in vacuum, and a kinetic study of $^{13}CO-^{12}CO$ exchange between carbon monoxide and $[HRu_3(CO)_{11}]^-$ revealed parallel dissociative and associative pathways for the exchange process.[11] Therefore, a reasonable first step in Scheme 2 is the replacement of CO by H_2 to form $[H_3Ru_3(CO)_{10}]^-$. The osmium analog $[H_3Os_3(CO)_{10}]^-$ is known; it is unstable at room temperature.[12] In the present case, the resulting $[H_3Ru_3(CO)_{10}]^-$ could disproportionate into an unsaturated species $H_2Ru_2(CO)_6$ which rapidly associates to form $H_4Ru_4(CO)_{12}$ and is in turn deprotonated by the basic surface to produce the $[H_3Ru_4(CO)_{12}]^-$ anion. The second proposed product of the disproportionation of $[H_3Ru_3(CO)_{10}]^-$ is $[HRu(CO)_4]^-$. In the present study, it was shown that this ion is rapidly converted to $[HRu_3(CO)_{11}]^-$ on the hydroxylated magnesia surface. Additionally, earlier we showed that this condensation reaction occurs in basic solution.[10]

Scheme 3 provides a proposed pathway by which $[H_3Ru_4(CO)_{12}]^-$ is converted to $[HRu_3(CO)_{11}]^-$ in the presence of CO. In an earlier study[4c] in the absence of a basic medium, it was shown that CO displaces H_2 from $[H_3Ru_4(CO)_{12}]^-$ to yield $[HRu_4(CO)_{13}]^-$, which in turn reacts with additional CO to yield $[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$. In Scheme 3, the reaction of CO with $[HRu_4(CO)_{13}]^-$ is proposed to form an intermediate species $[HRu_4(CO)_{14}]^-$ that reacts with additional CO to cleave the cluster to produce $[HRu_3(CO)_{11}]^-$ and Ru(CO)$_4$, which trimerizes to $Ru_3(CO)_{12}$. The $Ru_3(CO)_{12}$ is in turn converted to $[HRu_3(CO)_{11}]^-$ upon reaction with the basic magnesia surface.

While it is known that oxide surfaces can provide an appropriate environment for the syntheses of cluster materials,[6] this study provides an additional aspect. The fully hydroxylated surface provides a medium upon which facile, reversible reactions involving anionic

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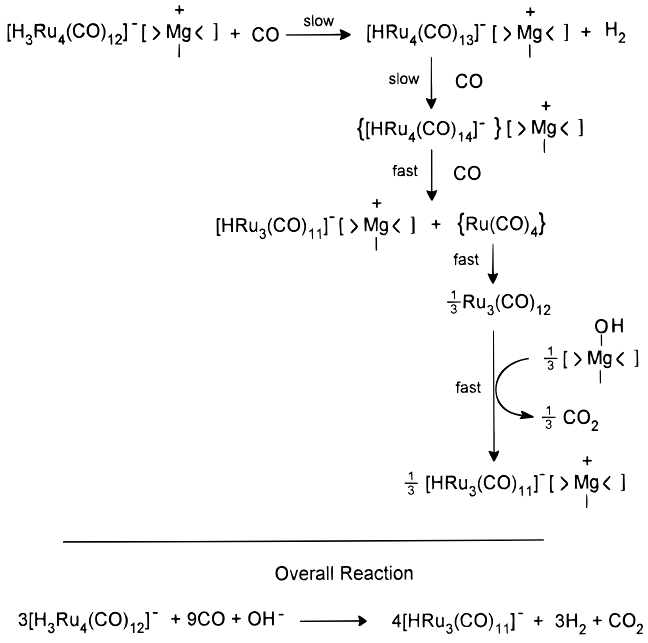
Scheme 3. Proposed Pathway for Conversion of $[H_3Ru_4(CO)_{12}]^-$ to $[HRu_3(CO)_{11}]^-$ in the Presence of CO[a]



[a] { } indicates a proposed unstable intermediate.

cluster species can occur. The countercation, magnesium, is immobilized and is effectively shielded from the anions by surface hydroxyl groups.[13] Thus, there is only a weak ion pairing between the anionic clusters and the countercation, thereby providing a weak barrier for random motion of the ionic species on the surface, permitting reactions to occur that resemble those in basic media.

Experimental Section

Carbon monoxide (99.5%) and hydrogen (99.9%) (Liquid Carbonic) were used without further purification. Methylene chloride (J. T. Baker) was dried over P_4O_{10} for 7 days before being distilled for use. Tetrahydrofuran, THF (J. T. Baker), was dried with Na/benzophenone solution and then distilled from the solution immediately prior to use. Bis(triphenylphosphino)iminium chloride, PPNCl, (Aldrich) was dried under vacuum at 100 °C overnight. $Ru_3(CO)_{12}$,[11b] $[PPN][HRu(CO)_4]$,[14] and hydroxylated magnesia (MgO_{25} or MgO_{200})[7] were prepared as previously reported. Hydrated $RuCl_3$ (Strem Chemicals) was used as received. Preparation of the hydroxylated magnesia support and the loading of ruthenium clusters on the support were performed on the vacuum line or in a glovebox.

^{1}H NMR spectra were recorded on a Bruker AM-250 instrument. Infrared spectra were obtained on a FT-IR Mattson Polaris spectrophotometer.

Impregnation of $Ru_3(CO)_{12}$ on Fully Hydroxylated MgO and Subsequent Reactions with H_2 or CO. The procedure for impregnating $Ru_3(CO)_{12}$ (97 mg) on hydroxylated MgO (2.9 g) to form impregnated $[HRu_3(CO)_{11}]^-$ was taken from the literature, with a minor modification.[7]

(a) Conversion of Supported $[HRu_3(CO)_{11}]^-$ to $[H_3Ru_4(CO)_{12}]^-$. A 1 g quantity of hydroxylated MgO, supporting $[HRu_3(CO)_{11}]^-$ (30 mg, 0.05 mmol), was introduced into a tubular vessel, through which H_2 was allowed to flow slowly for 39 h at room temperature and 1 atm of pressure. Extraction from the solid by 32 mg (0.05 mmol) of PPNCl in 20 mL of CH_2Cl_2 yielded $[H_3Ru_4(CO)_{12}]^-$. IR (CH_2Cl_2, ν_{co}): 2036 (m), 2016 (s), 1997 (vs), 1975 (m, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −17.07 (s), −19.32 (s, barely observed). On the basis of the appearance of the solid (change in color from orange-red to white) and its IR spectrum, removal of the cluster from the hydroxylated magnesia was complete.

(b) Conversion of Supported $[H_3Ru_4(CO)_{12}]^-$ to $[HRu_3(CO)_{11}]^-$. Carbon monoxide at 1 atm of pressure was passed over $[H_3Ru_4(CO)_{12}]^-$ on a hydroxylated MgO support that was formed as described in (a) above. The clusters on the surface were extracted with PPNCl in CH_2Cl_2. One portion of the solid was extracted after 32 h under a CO atmosphere. The remaining portion was extracted after 113 h of exposure to flowing CO. The material extracted after 32 h of CO treatment showed IR (CH_2Cl_2, ν_{co}) frequencies at 2074 (w), 2060 (w), 2037 (m, sh), 2016 (vs), 1996 (s, sh), 1987 (s), and 1951 (m, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −12.67 (s), −17.07 (s), −19.32 (s) (intensity ratio of $[HRu_3(CO)_{11}]^-$, $[H_3Ru_4(CO)_{12}]^-$, and $[H_2Ru_4(CO)_{12}]^{2-}$ was 2.5:3:1). The extracted clusters after 113 h of exposure to flowing CO showed IR (CH_2Cl_2, ν_{co}) frequencies at 2073 (w), 2060 (w), 2016 (vs), 1988 (s), 1955 (m, br), and 1707 (m, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −12.67 (s), −17.07 (s), −19.32 (s) (intensity ratio of $[HRu_3(CO)_{11}]^-$, $[H_3Ru_4(CO)_{12}]^-$, and $[H_2Ru_4(CO)_{12}]^{2-}$ was 9:1:1).

Impregnation of $H_4Ru_4(CO)_{12}$ on Fully Hydroxylated MgO and Subsequent Reactions with CO or H_2. The procedure for impregnating $H_4Ru_4(CO)_{12}$ (43 mg) on hydroxylated MgO (1.8 g) to form impregnated $[H_3Ru_4(CO)_{12}]^-$ was taken from the literature, with a minor modification.[9] The interconversions between $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_3(CO)_{11}]^-$ were performed in the same manner as described above.

Condensation of $[HRu(CO)_4]^-$ to $[HRu_3(CO)_{11}]^-$. A 50 mg quantity of $[PPN][HRu(CO)_4]$ in 20 mL of CH_2Cl_2 solution was mixed with 0.5 g of hydroxylated MgO and was stirred for 1 h. The color of the solution slowly turned from yellow to tan. The reaction product was extracted from the hydroxylated MgO with CH_2Cl_2. IR (CH_2Cl_2, ν_{co}): 2073 (w), 2016 (vs), 1987 (s), 1951 (m, br), 1708 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −12.67 (s), −17.07 (s), −19.32 (s) (intensity ratio of $[HRu_3(CO)_{11}]^-$, $[H_3Ru_4(CO)_{12}]^-$, and $[H_2Ru_4(CO)_{12}]^{2-}$ was 12:1:2).

Impregnation of $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ on Partially Hydroxylated MgO_{200} and Subsequent Reactions with CO or H_2. The impregnation of $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ on partially hydroxylated MgO_{200} and interconversions between $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ were performed in the same method as described above. The impregnation of $Ru_3(CO)_{12}$ on partially hydroxylated magnesia, MgO_{200}, yielded $[HRu_3(CO)_{11}]^-$, and the impregnation of $H_4Ru_4(CO)_{12}$ on partially hydroxylated magnesia, MgO_{200}, yielded $[H_3Ru_4(CO)_{12}]^-$. However, in both cases, unidentified species were formed that were tightly bound to the oxide surface and could not be removed by extraction with CH_2Cl_2 containing PPNCl. The reactions of $[HRu_3(CO)_{11}]^-$ with H_2 and $[H_3Ru_4(CO)_{12}]^-$ with CO on the partially hydroxylated magnesia surface produced $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_3(CO)_{11}]^-$, respectively, but tightly bound unidentifiable species were observed as well.

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