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Molecular Chemistry of Bimetallic Clusters on the Basic γ-Al_2O_3 Surface: Synthesis, Reactivity, and Catalytic Activity of $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ and Related Structures

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Abstract: $[H_2RuOs_3(CO)_{13}]$, $[H_4RuOs_3(CO)_{12}]$, $[Et_4N][HRuOs_3(CO)_{13}]$, and $[Et_4N][H_3RuOs_3(CO)_{12}]$ were synthesized and characterized spectroscopically, and their reactivities with the basic –OH groups on the surface of γ-Al_2O_3 were investigated, the surface species being characterized by infrared and UV–vis spectroscopy and extraction of anions. Surface-bound anions were formed by adsorption of the salts. Alternatively, the surface-bound ion pair $[HRuOs_3(CO)_{13}]^-\{Al\}$ was formed from $[H_2RuOs_3(CO)_{13}]$ by deprotonation on the surface; the anion is bonded to the surface through a bridging carbonyl group interacting with a surface Lewis acid site (Al^{3+} ion). This surface anion is readily converted at 50–70 °C into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$, evidently by reacting with surface water. The latter anion is also formed by deprotonation of $[H_4RuOs_3(CO)_{12}]$ on the surface. $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ is the precursor of a catalyst for isomerization of but-1-ene to give *cis*- and *trans*-but-2-ene at 53–77 °C. The catalytic activity and the Langmuir–Hinshelwood kinetics parameters were the same, whether the catalyst was prepared by adsorption of $[Et_4][H_3RuOs_3(CO)_{13}]$ or from $[H_2RuOs_3(CO)_{13}]$, converted into $[HRuOs_3(CO)_{13}]^-\{Al\}$ and then into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. The catalyst was stable for >2000 turnovers. Infrared spectra showed that $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ was the predominant surface organometallic species on the working catalyst. When the catalyst was used instead for ethylene hydrogenation, the activity changed as the cluster was degraded; metal particles were formed, and these and/or mononuclear metal complexes are the likely catalytic species.

The new field of surface organometallic chemistry[1-5] is concerned with the synthesis, structure, reactivity, and catalytic activity of surface-bound analogues of molecular organometallic structures. The work is motivated[3] by opportunities to use organometallic compounds as probes of the structure and reactivity of surfaces,[5] by opportunities offered by molecular organometallic precursors for formation of new surface structures,[1,3,4,6] and by prospects that these surface structures will have new catalytic properties.[3,4,7-10] The "molecular" surface-bound organometallics are looked upon as models of the supported metal catalysts used in technology, such as the alumina-supported Pt-Re used in reforming of petroleum naphtha[8] and the oxide-supported Pt-Rh used in abatement of automobile exhaust.[9] These technological catalysts have highly complicated structures, incorporating aggregates (crystallites) of metal of various sizes and shapes dispersed on high-area porous metal oxide supports.

Many of these supported metal catalysts used in technology are bimetallics;[10] combinations of metals are often more effective catalysts than single metals. Consequently, there is interest in molecular bimetallic clusters as catalysts and catalyst precursors, in solution[11] and on supports.[12] A number of molecular monometallic clusters have been anchored to the surfaces of metal oxide supports,[13] and a few of these have been investigated as catalysts,[4] including a number for isomerization and hydrogenation of alkenes.[14] Only a few bimetallic clusters have been used as precursors of supported metal catalysts,[12] and, typically, the clusters have not been stable on the supports, often disintegrating easily with segregation of the metals and formation of metal aggregates on the surface. A recent report[15] presents evidence of aggregation of $FeOs_3$ clusters without segregation of the metals.

We have communicated[16] results characterizing $RuOs_3$ clusters on γ-Al_2O_3 supports. These preliminary results showed (1) that molecular cluster anions could easily be formed on basic supports by simple deprotonation of hydrido metal clusters (this method has been found to be quite generally applicable[15,17-20]) and (2) that the cluster anion $[H_3RuOs_3(CO)_{12}]^-$ was relatively stable on the support, apparently being the precursor of a surface-bound molecular catalyst for alkene isomerization.

Here we present a full report of the synthesis, reactivity, and catalytic activity of the supported bimetallic clusters. This paper is concerned with (1) synthesis and characterization of the molecular precursors $[H_2RuOs_3(CO)_{13}]$, $[Et_4N][HRuOs_3(CO)_{13}]$, $[H_4RuOs_3(CO)_{12}]$, and $[Et_4N][H_3RuOs_3(CO)_{12}]$; (2) the reactions of these clusters with the basic γ-Al_2O_3 surface, leading to the formation of adsorbed cluster anions, $[HRuOs_3(CO)_{13}]^-$ and $[H_3RuOs_3(CO)_{12}]^-$; and (3) the catalytic activity of the supported bimetallic clusters for alkene isomerization.

Experimental Methods[21]

A. Synthesis of Molecular Clusters. The organometallic syntheses were carried out under dry N_2 on a Schlenk line. Hydrocarbon solvents were distilled over sodium/benzophenone under N_2, and dichloromethane was distilled over P_2O_5 under N_2. High-pressure experiments were done with a 125-mL stainless-steel Paar bomb.

1. Synthesis of $[H_2RuOs_3(CO)_{13}]$. This compound was first reported

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by Burkhardt and Geoffroy.[22] An alternate synthesis is presented here. $[Ru(CO)_5]$ was prepared by a procedure similar to that reported,[23] as 300 mg (0.765 mmol) of $Ru(C_5H_7O_2)_3$ was placed in the Paar bomb with 20 mL of hexanes. After the bomb had been repeatedly pressurized with a mixture of 67% CO and 33% H_2 and vented to purge the air, it was pressurized to 100 atm with this mixture and heated to 180 °C for 10–12 h. After the bomb had been cooled to room temperature and the gas vented, it was connected to a Schlenk line wrapped with foil to exclude light, and the $[Ru(CO)_5]$ was vacuum transferred to a 100-mL sidearm flask immersed in liquid N_2. A 100-mL sidearm flask containing 330 mg (0.387 mmol) of $[H_2Os_3(CO)_{10}]$[24] in 80 mL of hexane was attached to the Schlenk line and freeze pumped for degassing. When the $[Ru(CO)_5]$ transfer was complete, the liquid N_2 was removed, and the $[H_2Os_3(CO)_{10}]$ solution was transferred into the flask containing the $[Ru(CO)_5]$. This mixture was stirred under N_2 at room temperature for 10–12 h. The resulting solution was purified by chromatography in a 5-cm-diameter by 60-cm-long silica gel column with hexanes as the eluent. A yellow and an orange band developed, identified by infrared spectroscopy as $[Ru_3(CO)_{12}]$ and $[H_2RuOs_3(CO)_{13}]$, respectively. Some uncharacterized orange-brown solid remained at the top of the column. The product band was collected, dried in a rotary evaporator, and recrystallized from petroleum ether. Typical yields were 30–45% based on $[H_2Os_3(CO)_{10}]$.

2. Synthesis of $[H_4RuOs_3(CO)_{12}]$. This compound was prepared from $[H_2RuOs_3(CO)_{13}]$ by heating in octane solution with bubbling of H_2 to cause thermal displacement of a carbonyl ligand by two hydride ligands. Typically, 23 mg (0.24 mmol) of $[H_2RuOs_3(CO)_{13}]$ was placed in a 250-mL three-necked flask with 75 mL of *n*-octane. After H_2 had been bubbled in for 15–20 min at room temperature, the solution was brought to reflux over a period of 30 min. During heating, the $[H_2RuOs_3(CO)_{13}]$ dissolved in the *n*-octane to give a deep orange solution. When reflux temperature had been reached, the solution had turned pale yellow, and a large quantity of yellow solid was observed. The slurry was cooled with continued H_2 sparging and vacuum filtered. The solids were washed with hexane, which remained clear. The product was recrystallized from CH_2Cl_2 to give bright yellow crystals with a typical yield of 85% based on $[H_2RuOs_3(CO)_{13}]$.

3. Synthesis of $[Et_4N][H_3RuOs_3(CO)_{12}]$. This compound was prepared by a procedure similar to that used to prepare $[Ph_4As][H_3Ru_4(CO)_{12}]$.[25] Typically, 253 mg (0.25 mmol) of $[H_4RuOs_3(CO)_{12}]$ was placed in a 100-mL three-necked flask equipped with a nitrogen purge, a rubber septum, and a magnetic stirrer. A solution of 416 mg of KOH in 200 mL of absolute ethanol was prepared. After purging of the air from the flask with N_2, 7 mL of the KOH/ethanol solution containing 0.26 mmol of KOH was injected into the flask by syringe. The flask was heated to 55 °C for 30 min, during which virtually all of the yellow $[H_4RuOs_3(CO)_{12}]$ dissolved to give a deep orange solution. Then 114 mg (0.58 mmol) of Et_4NBr dissolved in 2 mL of absolute ethanol was injected into the flask, and the solution was cooled to −8 °C and held at this temperature overnight; a large quantity of orange crystals precipitated. The ethanol was removed by vacuum filtration, and the solids were washed with a small amount of distilled water to remove KBr and any remaining Et_4NBr and KOH. The solids were then washed with hexanes to remove any remaining $[H_2RuOs_3(CO)_{12}]$. The orange product was insoluble in the hexanes; it was recrystallized from CH_2Cl_2 to give bright orange crystals with a typical yield of 90% based on $[H_4RuOs_3(CO)_{12}]$.

4. Synthesis of $[Et_4N][HRuOs_3(CO)_{13}]$. This compound was prepared by a procedure similar to that stated above for $[Et_4N][H_3RuOs_3(CO)_{12}]$. $[H_2RuOs_3(CO)_{13}]$ was treated with a stoichiometric amount of KOH in ethanol. After 10 min at 55 °C, all the $[H_2RuOs_3(CO)_{13}]$ had reacted to give a dark purple solution. After addition of Et_4NBr, the solution was cooled to −8 °C and held at this temperature overnight; no solids were visible. The ethanol was evaporated, and the resulting solids were washed with distilled water and then hexanes; both washes remained clear. The remaining material was dissolved in CH_2Cl_2, leaving a small amount of insoluble brown solid. The solution was evaporated, giving a purple solid, which was recrystallized from $CHCl_3$ to give dark purple crystals in 85% yield based on $[H_2RuOs_3(CO)_{13}]$.

B. Characterization of Compounds. 1. Infrared and UV–Visible Spectroscopy. The infrared spectra of the organometallic compounds in solution were obtained with a Nicolet 7199 Fourier transform spectrophotometer and the UV–vis spectra of solutions with a Cary 219 spectrophotometer.

2. Proton NMR Spectra. The spectra were obtained with a Bruker HFX-90 NMR spectrometer with a variable temperature probe. The chemical shifts were referenced to a TMS internal standard. Because of the low solubilities of the clusters in suitable solvents, the ^1H NMR results were only qualitative.

3. X-ray Crystal Structures. Solid-state structures of $[H_2RuOs_3(CO)_{13}]$ and $[Ph_4As][H_3RuOs_3(CO)_{12}]$ were obtained by single-crystal X-ray diffraction, as reported elsewhere.[26]

C. Characterization of Supported Clusters. The materials prepared by supporting the metal clusters on alumina were characterized by transmission infrared spectroscopy, including in situ experiments to investigate surface reactivities. Other methods were X-ray fluorescence spectroscopy for chemical analysis and reflectance ultraviolet spectroscopy. Cluster anions were also extracted from the surfaces by cation metathesis, with analysis of the resulting solutions by infrared and NMR spectroscopies providing further evidence of the surface species. Details follow.

1. Infrared Spectroscopy. The infrared cell[27] was connected to a gas purification/vacuum system that allowed evacuation and flow of purified gases. Experiments were carried out with thin circular wafers containing about 100 mg of alumina, prepared in a stainless-steel press at 680 atm for 2–8 min. The alumina was Degussa aluminum oxide C. This is a nonporous (primarily γ-phase) alumina prepared by flame hydrolysis of $AlCl_3$. It consists of nearly spherical particles of diameter 5–30 nm and has a BET surface area of about 100 $m^2\ g^{-1}$. A translucent wafer was loaded into the infrared cell, where it was pretreated at the chosen temperature under vacuum for 2–4 h. After cooling of the alumina sample to room temperature, a spectrum was recorded for subtraction from spectra obtained with a metal cluster supported on the wafer. The evacuated cell was then transferred into a nitrogen-filled glovebox. Under this inert atmosphere, the alumina wafer was brought in contact with a solution of the metal cluster. The wafer was washed with additional solvent to remove any physisorbed cluster and then replaced in the infrared cell, which was sealed and transferred to the vacuum/gas handling system. In this way, careful control of the sample environment was maintained for all steps after the alumina pretreatment. The infrared spectrum of the pure support taken before adsorption of the cluster was subtracted from the data. Spectra were collected at 4-cm^{-1} resolution. To determine quantitatively the amount of cluster that had adsorbed on the alumina, the ultraviolet absorbance of the cluster in solution was measured before and after adsorption.

2. X-ray Fluorescence Spectroscopy. A Philips automatic X-ray spectrometer was used to obtain quantitative analyses of Ru and Os in the wafers. The Kα line was used for Ru, the LY5 line for Os. The instrument was calibrated by preparing wafers containing known amounts of Ru and Os.[21] The samples contained about 0.5 wt.% Ru + Os.

3. Ultraviolet Reflectance Spectroscopy.[21] A Cary 219 spectrophotometer equipped with an integrating sphere was used to collect reflectance spectra of wafer samples. A wafer of pure alumina was used as a standard.

D. Catalytic Reaction Experiments. Catalysts were investigated either in the form of pressed wafers in an infrared cell that also served as a flow reactor or in the form of powder in a once-through flow microreactor, as described below. The microreactor design is conventional.[21]

The feed gases hydrogen and helium (UHP grade) passed through traps containing supported Cu_2O held at 75 °C to remove traces of oxygen and then through traps containing 5A zeolite to remove water. Reactant but-1-ene (Phillips) or ethylene (Matheson) were used without further purification. The mixed reactant gases flowed through the tubular reactor mounted in an aluminum block for temperature control. The product gases flowed to an on-line gas chromatograph for periodic analysis with a flame ionization detector. In but-1-ene isomerization experiments, a 0.32-cm × 2-m stainless-steel column packed with 0.19% picric acid on 80/100 mesh Carbopack C was used at room temperature. In ethylene hydrogenation experiments, a 0.32-cm × 6.1-m stainless-steel column packed with phenylisocyanate on 80/100 mesh Porasil C was used at 50 °C.

Each catalyst was prepared under nitrogen in the glovebox by bringing alumina in contact with a solution containing a $RuOs_3$ cluster. The support used in the catalysis experiments was Catapal SB (Conoco), a porous (primarily γ-phase) alumina with a BET surface area of about 270 m^2/g; 40/60 mesh particles were used to ensure the lack of significant mass transfer resistances in catalyst preparation and catalytic re-

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Table I. Infrared Characterization of Tetranuclear Clusters in Solution Measured at Room Temperature

compound	ν_{CO} (terminal, cm^{-1})	ν_{CO} (bridging, cm^{-1})	ref
$[H_2Os_4(CO)_{13}]^a$	2090 s, 2062 s, 2053 s, 2041 w, 2020 vs, 1998 w, 1987 w		28
$[H_2RuOs_3(CO)_{13}]^b$	2081 vs, 2066 vs, 2055 vs, 2028 m, 2023 m, 2017 s, 2007 w	1868 w (br)	this work
$[Et_4N][HRuOs_3(CO)_{13}]^c$	1933 m, 1969 s, 2003 vs, 2014 vs, 2029 vs	1836 w (br)	this work
$[H_4Ru_4(CO)_{12}]^a$	2081 s, 2067 vs, 2030 m, 2024 s, 2009 w		24
$[H_4Os_4(CO)_{12}]^a$	2086 m, 2069 s, 2022 s, 2000 m		24
$[H_4RuOs_3(CO)_{12}]^b$	2085 vs, 2070 vs, 2067 vs, 2026 s, 2022 s, 2012 w, 2004 w, 1998 m		this work
$[Ph_4As][H_3Ru_4(CO)_{12}]^d$	2071 vw, 2040 s, 2034 s, 2019 s, 1978 m, 1950 w, 1932 w		25
$[Et_4N][H_3RuOs_3(CO)_{12}]^c$	2045 vs, 2039 s, 2020 vs, 1998 vs, 1976 s, 1946 m, 1916 w(br)		this work
$[(PPh_3)_2N][HRu_4(CO)_{13}]^c$	1950 s, 1898 m (sh)	1750 s	29

^{a}Cyclohexane solvent. ^{b}Hexane solvent. ^{c}CH_2Cl_2 solvent. ^{d}Acetone solvent.

action. The alumina was pretreated under vacuum for 2–4 h at the desired temperature in a quartz calcining tube. The evacuated tube was transferred into the glovebox, where the alumina was brought in contact with a solution containing a metal cluster; the solid was then washed with solvent to remove any physically adsorbed cluster. The reactor was loaded in the glovebox with 1–2 g of catalyst (held in place by glass wool plugs) and sealed to prevent air exposure during transfer to the flow system.

The catalytic reactor was flushed with helium, the feed gas flow rates set, the reactor brought to temperature, and data collection begun. Partial pressures of reactants were varied systematically, and the reaction rate was measured under each set of conditions. For both isomerization of but-1-ene and hydrogenation of ethylene, the alumina support alone showed no observable catalytic activity. All conversion data were corrected for traces of product present as impurities in the feed. Used catalyst samples were transferred to the drybox in the closed reactor, and air exposure in subsequent experiments was avoided.

E. Infrared Characterization of Catalysts in Reactive Atmospheres. To characterize changes in the surface organometallic species in contact with reactants, including those used in the catalysis experiments, the catalyst samples were prepared in the form of pressed wafers and mounted in the infrared cell which was also a flow reactor.

F. X-ray Photoelectron Spectroscopy. Samples were prepared as wafers, just as for infrared spectroscopy. Brief air exposure occurred during introduction of the samples into the instrument (a Physical Electronics AES/XPS system, Model 550). Since the metal loadings of the samples were low, long data collection times were necessary, resulting in changes in the appearance of the samples; all samples were dark brown after data collection.

G. Transmission Electron Microscopy.[21] High-resolution transmission electron microscopy of catalyst samples was carried out by A. Datye and J. Schwank of the University of Michigan. The JEOL JEM-100 cx microscope was equipped with an ultrahigh resolution pole piece, a top entry stage, and a LaB_6 emitter operated at 100 keV. The samples were placed on 2.3-mm copper grids, and the magnification was calibrated by using the lattice fringes of partially graphitized carbon.

Results and Discussion

A. Synthesis and Characterization of $[H_2RuOs_3(CO)_{13}]$. The high yield of this compound (30–45% based on $[H_2Os_3(CO)_{10}]$, compared with 23% reported by Burkhardt and Geoffroy[22]) is attributed to the high initial concentration of $[Ru(CO)_5]$ monomer available to react with the unsaturated triosmium cluster. As shown by infrared spectra, $[Ru(CO)_5]$ was the only detectable ruthenium carbonyl species initially present; as it slowly decomposed, $[Ru_3(CO)_{12}]$ formed, as indicated by its infrared spectrum. Presumably, the unsaturated complexes $[Ru(CO)_4]$ and/or $[Ru(CO)_3]$ are intermediates in this decomposition, reacting with $[H_2Os_3(CO)_{10}]$ to give $[H_2RuOs_3(CO)_{13}]$.[22] The lower yield obtained by Burkhardt and Geoffroy[22] (who relied on prolonged photolysis of a solution of $[Ru_3(CO)_{12}]$ and $[H_2Os_3(CO)_{10}]$ in hexane to produce the Ru carbonyl monomers) may have resulted in part from the loss of $[H_2Os_3(CO)_{10}]$ as a consequence of its slight photoactivity.

The solution infrared spectrum of $[H_2RuOs_3(CO)_{13}]$ (agreeing with the literature[22]) is given in Table I. There is a single broad bridging carbonyl band in the infrared spectrum, consistent with a structure like that of $[H_2Ru_4(CO)_{13}]$. This single broad band may be an indication of easy deformation of the bridging carbonyl ligands in the molecule in solution. The two independent structures determined for $[H_2RuOs_3(CO)_{13}]$ in the solid state,[26] which exhibit differences in the orientations of the bridging carbonyl ligands, may reflect this deformation during crystal growth.

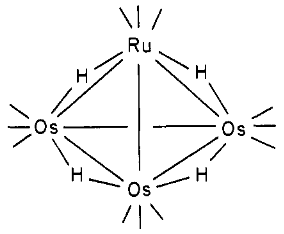
Table II. UV–vis and NMR Spectra of Tetranuclear Clusters in Solution Measured at Room temperature

compound	UV–vis absrbncs, nm	^1H NMR peaks ppm (temp, °C)
$[H_2RuOs_3(CO)_{13}]$	287, 312, 465 (sh)	τ 31.11 (27, 35)
$[H_4RuOs_3(CO)_{12}]$	325	τ29.5 (50) τ 29.03 (br), 30.04 (br) (−35)
$[Et_4N][H_3RuOs_3(CO)_{12}]$	327	τ 29.54, 29.10 (w, br) (50) τ 27.66 (br), 28.64, 29.62 (br) (−35)
$[Et_4N][HRuOs_3(CO)_{13}]$	323, 380 (sh), 528 (sh)	τ 29.28 (50) τ 27.68, 28.64, 29.63 (−35)

B. Synthesis and Characterization of $[H_4RuOs_3(CO)_{12}]$. The near quantitative synthesis of $[H_4RuOs_3(CO)_{12}]$ by the reaction of H_2 with $[H_2RuOs_3(CO)_{13}]$ parallels the reaction of H_2 with the isoelectronic $[H_2FeRu_3(CO)_{13}]$[24] as well as with other tetranuclear mixed-metal clusters.[24,30]

A comparison of the infrared spectrum of $[H_4RuOs_3(CO)_{12}]$ with the spectra of $[H_4Ru_4(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$ (Table I) suggests a lower symmetry for $[H_4RuOs_3(CO)_{12}]$. The spectrum of $[H_4RuOs_3(CO)_{12}]$ bears more resemblance to that of $[H_4FeRu_3(CO)_{12}]$ [2085 s, 2070 s, 2054 s, 2031 m (br), 2012 w, 1998 w, 1990 w, cm^{-1}]. The spectrum of $[H_4RuOs_3(CO)_{12}]$ gives no indication of bridging carbonyls, as is true also for the spectra of $[H_4Ru_4(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, and $[H_4FeRu_3(CO)_{12}]$.

No crystal structure was obtained; the infrared and ^1H NMR and ultraviolet characterizations (Table II) suggest that $[H_4RuOs_3(CO)_{12}]$ has the following structure in solution.



C. Synthesis and Characterization of $[Et_4N][H_3RuOs_3(CO)_{12}]$. The near quantitative deprotonation of $[H_4RuOs_3(CO)_{12}]$ by KOH to give $[H_3RuOs_3(CO)_{12}]^-$ is analogous to the reactions demonstrated for the preparation of $[H_3Ru_4(CO)_{12}]^-$ from $[H_4Ru_4(CO)_{12}]$[25] and of $[H_3Os_4(CO)_{12}]^-$ from $[H_4Os_4(CO)_{12}]$.[31] The infrared spectrum of $[Et_4N][H_3RuOs_3(CO)_{12}]$ closely resembles that of $[Ph_4As][H_3Ru_4(CO)_{12}]$ (Table I).

The characterization of $[H_3RuOs_3(CO)_{12}]^-$ by infrared and ^1H NMR spectroscopy (Table II) suggests that in solution two

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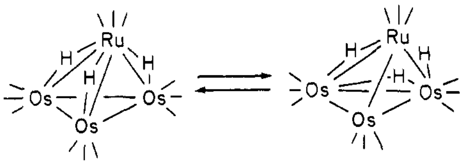
structural isomers are in equilibrium; the structure on the left corresponds to the solid-state structure determined for $[H_3RuOs_3(CO)_{12}]^-$.[26]



D. Synthesis and Characterization of $[Et_4N][HRuOs_3(CO)_{13}]$. The deprotonation of $[H_2RuOs_3(CO)_{13}]$ by KOH to yield $[HRuOs_3(CO)_{13}]^-$ was successful (85% yield), whereas a reported attempt to deprotonate $[H_2Ru_4(CO)_{13}]$ by reaction with KH led instead to the formation of $[H_3Ru_4(CO)_{12}]^-$ instead of $[HRu_4(CO)_{13}]^-$.[32] $[HRu_4(CO)_{13}]^-$ has been prepared by protonation of $[Ru_4(CO)_{13}]^-$ obtained by reduction of $[Ru_3(CO)_{12}]$ with potassium–benzophenone.[33] $[HFeRu_3(CO)_{13}]^-$, which is isoelectronic to $[HRuOs_3(CO)_{13}]^-$, has been prepared by reaction of $[(Ph_3P)N][HFe(CO)_4]$ with $[Ru_3(CO)_{12}]$ in refluxing THF.[34]

The anion $[HRuOs_3(CO)_{13}]^-$ represents the second of the compounds reported for the series $[HRu_nOs_{4-n}(CO)_{13}]^-$. The infrared spectrum (Table I) suggests that it has a tetrahedral structure and contains bridging carbonyl ligands which may adopt a range of orientations in solution, a behavior similar to that encountered for $[H_2RuOs_3(CO)_{13}]$. The ^1H NMR spectra (Table II) suggest that the hydride ligand can occupy three different edge-bridging positions and that rapid scrambling between positions occurs at elevated temperatures.

E. Preparation and Characterization of γ-Al_2O_3-Supported Clusters. 1. Adsorption of $[H_2RuOs_3(CO)_{13}]$ and $[Et_4N][HRuOs_3(CO)_{13}]$. A primary objective of this research was to prepare alumina-supported $RuOs_3$ catalysts with well-defined structures. The following section is an evaluation of the preparation and characterization of the supported clusters resulting from adsorption of each of the $RuOs_3$ clusters described above.

When a hexane solution of $[H_2RuOs_3(CO)_{13}]$ was brought in contact with a wafer of alumina (pretreated at 150 °C), adsorption of the cluster occurred. The wafer, after washing in hexane, was dark brown. The infrared spectrum of the sample (Figure 1) showed that there was a shift in carbonyl frequencies to lower wavenumbers upon adsorption, suggesting that a negative charge formed on the cluster, the adsorption leading to increased electron donation from the metals to the π^* antibonding orbitals of the CO ligands. This effect can be observed in the comparison of the solution spectrum of the neutral $[H_2RuOs_3(CO)_{13}]$ with that of $[HRuOs_3(CO)_{13}]^-$ (Table I). The UV–vis spectrum of the adsorbed cluster has a maximum at 324 nm, nearly matching that of $[HRuOs_3(CO)_{13}]^-$ in solution. There was no CO (or other gas) evolved upon adsorption of $[H_2RuOs_3(CO)_{13}]$ onto alumina,[35] a result that allows us to rule out a reaction similar to that observed for adsorption of $[Os_3(CO)_{12}]$ onto alumina, whereby a surface hydroxyl group on the alumina oxidatively adds to the $[Os_3(CO)_{12}]$, forming the surface species $(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-O-Al}\}$ (where the curly brackets {} denote surface groups) and evolving CO.[36]

To test the possibility that the adsorption of $[H_2RuOs_3(CO)_{13}]$ was dissociative, involving deprotonation of the cluster to form the anion $[HRuOs_3(CO)_{13}]^-$, the salt $[Et_4N][HRuOs_3(CO)_{13}]$ was adsorbed from CH_2Cl_2 solution onto alumina pretreated at 150 °C. The infrared spectrum of the resulting wafer retained the essential features of the spectrum of $[HRuOs_3(CO)_{13}]^-$ in solution (Figure 1), but there were some changes resulting from adsorption, namely, a band broadening and a shift in the bridging carbonyl frequency, discussed below, and the appearance of a small peak at 2082 cm^{-1}, suggestive of the neutral cluster as an impurity (Table I). The adsorbed $[HRuOs_3(CO)_{13}]^-$ was not removed from the surface by repeated washing in CH_2Cl_2 (a solvent in which $[Et_4N][HRuOs_3(CO)_{13}]$ is highly soluble), and it is concluded that the $[HRuOs_3(CO)_{13}]^-$ ion on the surface was no longer associated with the $[Et_4N]^+$ ion. Instead, the $[HRuOs_3(CO)_{13}]^-$ is inferred to have been paired with an aluminum ion at the surface.

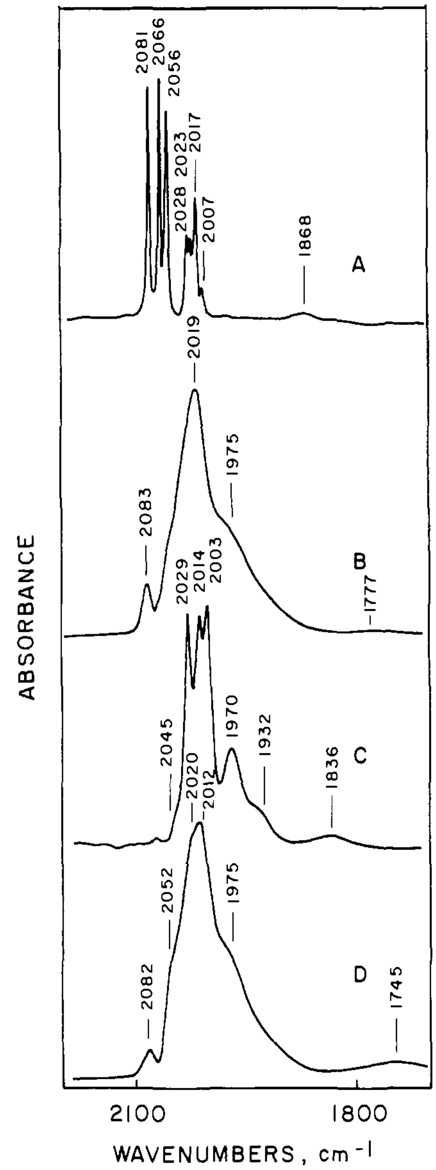


Figure 1. Infrared spectra of $RuOs_3$ clusters in solution and on γ-Al_2O_3: (A) $[H_2RuOs_3(CO)_{13}]$ in hexane, (B) sample formed by adsorption of $[H_2RuOs_3(CO)_{13}]$ on γ-Al_2O_3, (C) $[Et_4N][HRuOs_3(CO)_{13}]$ in CH_2Cl_2, (D) $[Et_4N][HRuOs_3(CO)_{13}]$ adsorbed on γ-Al_2O_3.

The principal point illustrated by Figure 1 is that the spectrum of the product of adsorption of $[H_2RuOs_3(CO)_{13}]$ on alumina is almost the same as the spectrum of $[Et_4N][HRuOs_3(CO)_{13}]$ adsorbed on alumina. We infer that the same metal carbonyl anion is present on the surface in both instances. These spectra are concluded to be indicative of the surface-bound cluster anion $[HRuOs_3(CO)_{13}]^-\{Al\}$. This anion can be formed by abstraction of a proton from $[H_2RuOs_3(CO)_{13}]$ by a basic site on the alumina or by adsorption of the anion $[HRuOs_3(CO)_{13}]^-$ onto an anion vacancy or by ion exchange of $[HRuOs_3(CO)_{13}]^-$ with a surface hydroxyl group.

The proposed reaction of $[H_2RuOs_3(CO)_{13}]$ with a basic site on the alumina surface to give $[HRuOs_3(CO)_{13}]^-\{Al\}$ is consistent

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(32) Inkrott, K. E.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 2817.

(33) Nagel, C. C.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1980**, 530.

(34) Takusagawa, F.; Fumagalli, A.; Kaetzle, T. F.; Steinmetz, G. R.; Rosen, R. P.; Gladfelter, W. L.; Geoffroy, G. L.; Bruck, M. A.; Bau, R. *Inorg. Chem.* **1981**, *20*, 3823.

(35) Careful experiments with degassed solvents were carried out to detect even very small quantitites of evolved gas. The methods are described in a thesis,[21] where the detection limits are also given.

(36) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215.

with the observed reaction between $[H_2RuOs_3(CO)_{13}]$ and OH^- in solution, which was observed to occur quickly under mild conditions (85% converted in 10 min at 55 °C) to give $[HRuOs_3(CO)_{13}]^-$.

Consistent with this conclusion, the Brønsted acidities of several clusters that are chemically similar to $[H_2RuOs_3(CO)_{13}]$, namely, $[H_2Ru_4(CO)_{13}]$ ($pK_a = 11.0$), $[H_4Ru_4(CO)_{12}]$ ($pK_a = 11.7$), and $[H_4Os_4(CO)_{12}]$ ($pK_a = 12.0$), have been confirmed by measurement of their ability to protonate CH_3O^- in CH_3OH.[37]

This model of the adsorption requires basic sites on the γ-Al_2O_3 surface. It has been concluded[38] that alumina partially dehydroxylated at temperatures <400 °C has basic hydroxyl groups and Lewis base sites consisting of coordinatively unsaturated surface oxygens (formed by condensation of two hydroxyl groups to form water during dehydroxylation).[38a] The formation of an adsorbed pyridine species on alumina accompanied by H_2 evolution has been taken as evidence for the existence of strongly basic OH^- groups on the surface, their density being $\sim 10^{13}$ cm^{-2}.[39] This estimate is consistent with an estimate of the maximum number of basic sites on alumina covered with three or more monolayers of water, $\sim 10^{14}$ cm^{-2}.[38b]

There are several reports of reactions of hydrido metal clusters with alumina that are consistent with cluster deprotonation on the surface.[16,17,19,40,41] $[H_3Ru_4(CO)_{12}]^-$ evidently forms upon adsorption of $[H_4Ru_4(CO)_{12}]$,[40,41] and $[H_3Os_4(CO)_{12}]^-$ forms upon adsorption of $[H_4Os_4(CO)_{12}]$.[17] Similar chemistry occurs on the strongly basic surface of magnesia.[19,42]

Some further inferences can be drawn from the spectra in Figure 1. The bridging carbonyl bands in the spectra of the supported $[HRuOs_3(CO)_{13}]^-$ prepared by adsorption of $[H_2RuOs_3(CO)_{13}]$ or by adsorption of $[Et_4N][HRuOs_3(CO)_{13}]$ are shifted by 65 to 91 cm^{-1} to lower frequencies relative to the bridging carbonyl band for $[Et_4N][HRuOs_3(CO)_{13}]$ in solution. Similar results have been interpreted by Tessier-Youngs et al.[5] as an indication of a strong interaction of the oxygen of the bridging carbonyl group with a Lewis acid center (Al^{3+} ion) of the surface. Consequently, we infer that the supported $[HRuOs_3(CO)_{13}]^-$ was present in ion pairs on the alumina surface, interacting with the Al^{3+} ion through bridging carbonyl groups.[43] All of the carbonyl bands in the spectra of the alumina-supported anion are broadened relative to the bands of the clusters in solution. This result is typical of supported metal carbonyl clusters and is consistent with local variations in the surface structure and the presence of a distribution of similar species, each described approximately as $[HRuOs_3(CO)_{13}]^-\{Al\}$.

2. Adsorption of $[H_4RuOs_3(CO)_{12}]$ and $[Et_4N][H_3RuOs_3(CO)_{12}]$. $[H_4RuOs_3(CO)_{12}]$ reacts with the surface of alumina in a manner similar to that characterizing $[H_2RuOs_3(CO)_{13}]$. When an alumina wafer pretreated at 150 °C was brought in contact with a solution of $[H_4RuOs_3(CO)_{12}]$ in CH_2Cl_2, the cluster was adsorbed onto the alumina to give a pale yellow solid with the infrared spectrum of Figure 2B. This spectrum is very similar to the spectrum of $[Et_4N][H_3RuOs_3(CO)_{12}]$ in solution (Figure 2A, Table I), but the presence of a small peak at 2084 cm^{-1} suggests the presence of some neutral cluster that had not been deprotonated (Table I). When a solution of $[Et_4N][H_3RuOs_3(CO)_{12}]$ in CH_2Cl_2 was brought in contact with alumina, the spectrum of the resulting wafer was virtually identical with that of the structure formed by adsorption of $[H_4RuOs_3(CO)_{12}]$ on alumina.[21] The adsorbed $[Et_4N][H_3RuOs_3(CO)_{12}]$ could not be removed by repeated washing with CH_2Cl_2, a solvent in which this salt is highly soluble. Its UV–vis spectrum had a maximum at 326 nm, nearly matching that of the anion in solution. From these observations, we infer that the anion $[H_3RuOs_3(CO)_{12}]^-$ is paired with a positively charged site on the alumina surface, being present as $[H_3RuOs_3(CO)_{12}]^-\{Al\}$.

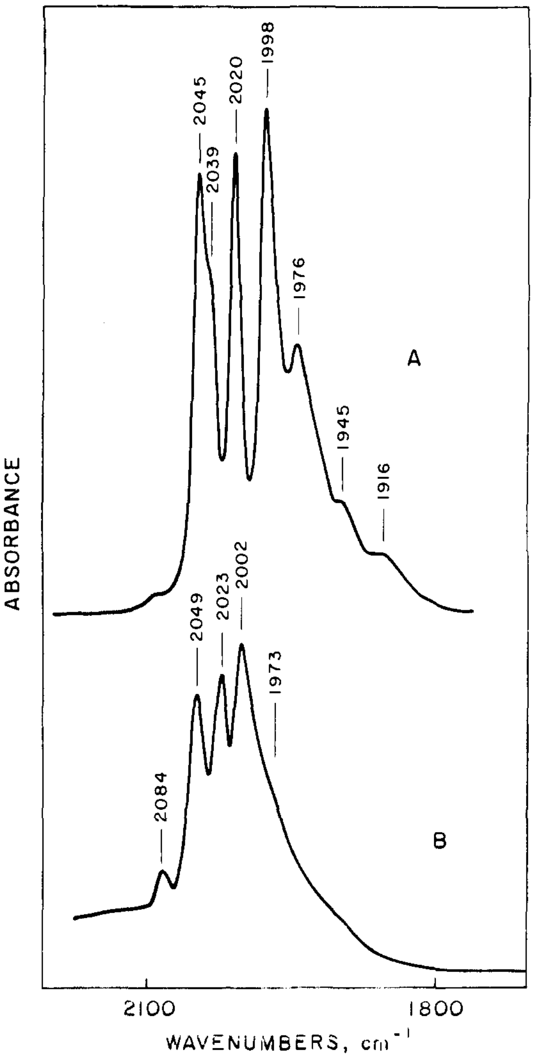

Figure 2. Infrared spectra of (A) $[Et_4N][H_3RuOs_3(CO)_{12}]$ in CH_2Cl_2 and (B) $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ formed by adsorption of $[H_4RuOs_3(CO)_{12}]$; the spectrum was taken at 25 °C with the sample under vacuum.

This conclusion is confirmed by the results of experiments in which the cluster anion was extracted from the surface with Et_4NBr in CH_2Cl_2. The salt $[Et_4N][H_3RuOs_3(CO)_{12}]$ was formed in solutions in contact with each of the samples containing the surface species having the infrared spectrum associated with $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. All the surface carbonyl species could be removed (as evidenced by the lack of carbonyl absorption in the spectrum of the extracted wafers), and the infrared and NMR spectra of the extract solutions indicated that $[Et_4N][H_3RuOs_3(CO)_{12}]$ was virtually the only organometallic species present. Since a solution of CH_2Cl_2 alone did not remove the surface species from these samples, it is concluded that the anions were paired with surface cation sites and that the extraction proceeded by cation metathesis.

In summary, the cluster obtained by adsorption of $[H_4RuOs_3(CO)_{12}]$ or $[Et_4N][H_3RuOs_3(CO)_{12}]$ on alumina was the surface-bound anion $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. This species can be obtained by deprotonation of $[H_4RuOs_3(CO)_{12}]$ by a basic site on the surface or by adsorption of $[H_3RuOs_3(CO)_{12}]^-$ from solution onto an anion vacancy on the surface or by ion exchange of $[H_3RuOs_3(CO)_{12}]^-$ with a hydroxyl group on the surface. The nature of the bonding of the anion to the surface cation is not evident from the spectra.

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[43] The literature of analogous ion pairs in solution has been reviewed by Darensbourg (Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221).

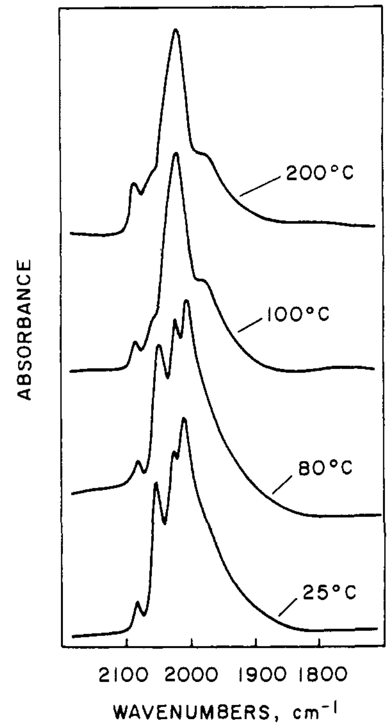

Figure 3. Infrared spectra of cluster anions formed from adsorption of $[H_2RuOs_3(CO)_{13}]$ on γ-Al_2O_3 pretreated at various temperatures.

3. Effect of Alumina Pretreatment Temperature on Adsorption of $[H_2RuOs_3(CO)_{13}]$. The surface composition was varied by changing the pretreatment temperature of the γ-Al_2O_3.[38,44] Solutions of $[H_2RuOs_3(CO)_{13}]$ were brought in contact with supports pretreated for 2 h under vacuum at 25, 80, 100, and 200 °C, according to the procedure described above. The infrared spectra of the resulting wafers are shown in Figure 3.

The spectra of the samples pretreated at 200 and 100 °C indicated that the cluster anion $[HRuOs_3(CO)_{13}]^-$ had formed by deprotonation upon adsorption, as described above. In contrast, the spectra of the samples pretreated at 80 and 25 °C indicated the presence of $[H_3RuOs_3(CO)_{12}]^-$ on the surface. These latter two samples had hydrated surfaces,[45] whereas the former two had been dehydrated and "rehydroxylated"[45] at the higher pretreatment temperature. Both the hydrated and "rehydroxylated" surfaces are basic and, we infer, able to deprotonate $[H_2RuOs_3(CO)_{13}]$. We suggest that the resulting anion reacted with water on the hydrated surfaces to give $[H_3RuOs_3(CO)_{12}]^-$ and CO_2. A similar reaction of $[Rh_6(CO)_{16}]$ with H_2O on silica has been observed.[46] The analogous molecular chemistry of $RuOs_3$ clusters in solution was not observed, but related chemistry, illustrated by eq 1, has been observed for $[H_2FeRu_3(CO)_{12}]$[24] and

$$H_2FeRu_3(CO)_{13} + H_2 \xrightarrow[\text{hexane}]{\Delta,\ 6\ \text{h}} H_4FeRu_3(CO)_{12} + CO \quad (1)$$

other tetranuclear bimetallic clusters.[47,48] The reaction of eq 1 involves H_2, not H_2O, but it has been suggested that H_2O adsorbed on γ-Al_2O_3 is activated by the polar surface.[39] The reaction is favored thermodynamically by the reduction in steric crowding resulting from replacement of a CO ligand by two hydride ligands.

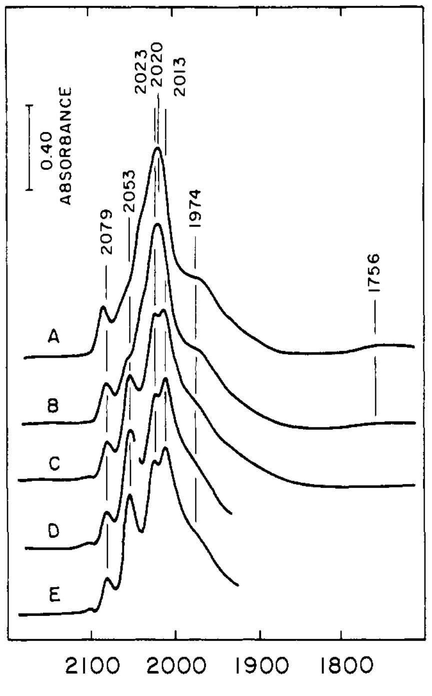

Figure 4. Infrared evidence of the conversion of $[HRuOs_3(CO)_{13}]^-\{Al\}$ into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. The sample was prepared from $[H_2RuOs_3(CO)_{13}]$ and γ-Al_2O_3 pretreated at 110 °C: (A) fresh sample at 25 °C under vacuum, indicative of $[HRuOs_3(CO)_{13}]^-\{Al\}$, (B) after heating to 50 °C in He, (C) after 3 h at 50 °C in He, (D) after temperature had been raised to 70 °C with sample in He, and (E) sample under vacuum at 25 °C after 1 h at 70 °C in He. The final spectrum is that of $[H_3RuOs_3(CO)_{12}]^-\{Al\}$.

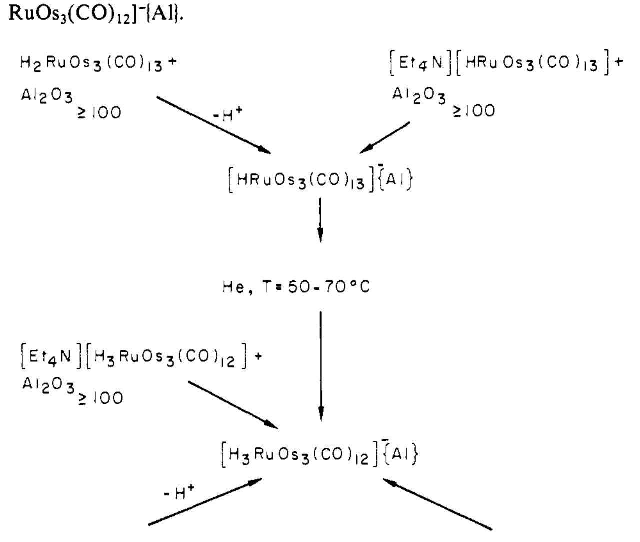

Figure 5. Summary of the reactions of $RuOs_3$ carbonyl clusters with and on the basic γ-Al_2O_3 surface. The subscripts on Al_2O_3 refer to the pretreatment temperature in °C.

F. Conversion of $[HRuOs_3(CO)_{13}]^-\{Al\}$ into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. To test the hypothesis that $[HRuOs_3(CO)_{13}]^-\{Al\}$ reacted with water on the surface to give $[H_3RuOs_3(CO)_{12}]^-\{Al\}$,

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[44] Variation of the pretreatment temperature of a metal oxide support is the most straightforward method for systematic variation of the support surface composition. Increasing pretreatment temperature reduces the degree of hydration of the γ-Al_2O_3 surface and, at temperatures higher than those used in this work, results in further dehydration that reduces the surface hydroxyl group concentration and creates exposed Al^{3+} sites.[39] Psaro et al.[37] investigated the effect of the pretreatment temperature of Al_2O_3 on the adsorption of $[Os_3(CO)_{12}]$, and others investigated the effect on adsorption of $[Rh_6(CO)_{16}]$: Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F. *Inorg. Chem.* **1979**, *18*, 3104. Watters, K. L.; Howe, R. F.; Chojnaki, T. P.; Fu, C. M.; Schneider, R. L.; Wong, N. B. *J. Catal.* **1980**, *66*, 424.

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Table III. Kinetics of But-1-ene Isomerization in the Presence of Catalysts Incorporating Alumina-Supported $[H_3RuOs_3(CO)_{12}]^-$

cluster used to prepare catalyst	temp, °C	$10^3 \times k$,[a] mol (mol of $RuOs_3)^{-1}$ s^{-1} atm^{-1}		K,[a] atm^{-1}	
		for *cis*-but-2-ene	for *trans*-but-2-ene	for *cis*-but-2-ene	for *trans*-but-2-ene
$[HRuOs_3(CO)_{13}]$[b]	67	34 ± 12	69 ± 21	7.0 ± 1.5	7.7 ± 1.5
$[Et_4N][H_3RuOs_3(CO)_{12}]$[c]	66	26 ± 6	50 ± 11	4.8 ± 0.8	4.6 ± 0.8

[a] In eq 1. [b] Ru + Os (0.59 wt%) in catalyst. [c] Ru + Os (0.39 wt%) in catalyst.

an experiment was done with the former sample (prepared as described above by adsorption of $[H_2RuOs_3(CO)_{13}]$ on a wafer of γ-Al_2O_3 pretreated at 110 °C). The sample was heated in helium, and the infrared spectrum was measured periodically. The spectra (Figure 4) confirm that $[HRuOs_3(CO)_{13}]^-\{Al\}$ was converted into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ at 50–70 °C.

G. Summary of Surface Structures and Reactivities. The results provide a basis for understanding the synthesis chemistry and reactivity of the surface-bound cluster anions $[HRuOs_3(CO)_{13}]^-\{Al\}$ and $[H_3RuOs_3(CO)_{12}]^-\{Al\}$, summarized in Figure 5. The synthetic chemistry on the basic alumina surface involves simple deprotonation of the neutral clusters $[H_2RuOs_3(CO)_{13}]$ and $[H_4RuOs_3(CO)_{12}]$; the resulting anions are evidently ion-paired with Al^{3+} sites on the surface.

H. Catalytic Activity of $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ for Isomerization of But-1-ene. 1. Catalyst Prepared by Adsorption of $[H_2RuOs_3(CO)_{13}]$ on γ-Al_2O_3. Adsorption of $[H_2RuOs_3(CO)_{13}]$ on γ-Al_2O_3 takes place with deprotonation of the cluster and formation of the surface ion pair $[HRuOs_3(CO)_{13}]^-\{Al\}$. This solid was tested as a catalyst for isomerization of but-1-ene; thorough kinetics measurements were made with the microflow reactor, and infrared spectra of separate samples were measured under reaction conditions.

The material catalyzed isomerization of but-1-ene, giving *cis*- and *trans*-but-2-ene and no other products in detectable amounts. Measurements of kinetics were made with a sample (2.22 g) containing approximately 8.5 μmol of $RuOs_3$ cluster per gram.[49] The catalyst was brought on stream at room temperature and 1.01 atm with a flow of but-1-ene in helium, and rates of isomerization were measured as the temperature was brought to 67 °C and held there. There was an induction period of roughly 50 h after this temperature had been reached, then the catalyst was stable, and kinetics were measured as the partial pressures of but-1-ene and helium in the feed stream were varied. Reaction rates were calculated from conversions less than 15%; the conversions were differential, the slope of the conversion vs inverse space velocity plot[21] being the reaction rate.

The dependence of the rate of formation of each of the two isomers of but-2-ene on the partial pressure of reactant but-1-ene at 67 °C is shown in Figure 6. These data are well represented (Figure 6) by a rate equation of the simple Langmuir–Hinshelwood (Michaelis–Menten) form (eq 2). The best values of the parameters[50] in eq 2 are summarized in Table III.

$$r = \frac{kKP_{\text{but-1-ene}}}{1 + KP_{\text{but-1-ene}}} \tag{2}$$

Experiments were also done to determine the dependence of rate on temperature in the range 53–77 °C at a but-1-ene partial pressure of 0.26 atm. The reaction rate data[51] determine apparent activation energies of 16.3 ± 0.7 kcal/mol for *cis*-but-2-ene and 14.9 ± 3.8 kcal/mol for *trans*-but-2-ene formation.

The catalyst had maintained its activity for >2000 turnovers (molecules of but-1-ene converted per cluster) when the experiment was stopped. After the kinetics data had been collected, the reactor was cooled with flowing CO and taken into the glovebox, where the catalyst was recovered without exposure to air. Its color had changed from brown to light yellow. A sample was analyzed by X-ray fluorescence for Os and Ru and found to contain 8.5 ± 0.3 μmol of $RuOs_3$/g based on the Os analysis and 8.4 ± 0.9 μmol of $RuOs_3$/g based on the Ru analysis; the metal loading had not changed during the catalysis.

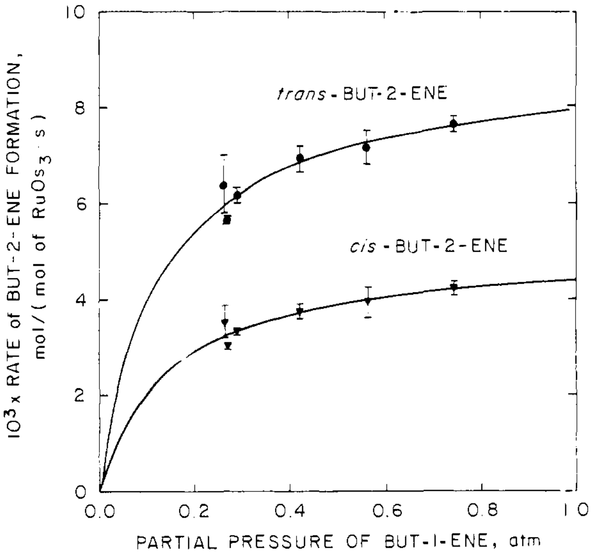

Figure 6. Kinetics of but-1-ene isomerization at 67 °C in the presence of a catalyst prepared from $[H_2RuOs_3(CO)_{13}]$. The curves are the fits to eq 2 with the parameter values of Table III.

The infrared results presented above (section E3) show that heating of the surface-bound cluster $[HRuOs_3(CO)_{13}]^-\{Al\}$ in helium led to its complete conversion into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ at 50–70 °C. This same transformation is expected to have occurred in the catalytic reactor; the induction period observed during the catalysis is inferred to be an indication of this transformation. The UV–vis spectra of the fresh and used catalysts are consistent with this inference.[21] As a further test, an infrared experiment was done with a wafer of the supported cluster $[HRuOs_3(CO)_{13}]^-\{Al\}$ (prepared from $[H_2RuOs_3(CO)_{13}]$) in the presence of but-1-ene at 0.32 atm in helium at 90 °C. The infrared spectra show the conversion of this cluster into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ under these conditions. As expected, this anion was the only metal carbonyl removed from the surface by cation metathesis after the experiment, as shown by infrared spectroscopy.

In summary, the data support the conclusion that the observed butene isomerization catalysis is associated with the surface-bound cluster anion $[H_3RuOs_3(CO)_{12}]^-$.

2. Catalyst Prepared by Adsorption of $[Et_4N][H_3RuOs_3(CO)_{12}]$ on γ-Al_2O_3. To test the inference that the catalytically active species were associated with the anion $[H_3RuOs_3(CO)_{12}]^-$ (and not the other clusters or cluster degradation products), a series of experiments was done with the salt of this anion deposited directly onto the Al_2O_3 surface, as described above. Alumina pretreated at 150 °C was brought in contact with a CH_2Cl_2 solution of $[Et_4N][H_3RuOs_3(CO)_{12}]$ to give a pale yellow catalyst. A sample of this was analyzed by X-ray fluorescence and found to contain 5.9 ± 0.2 μmol of $RuOs_3$/g based on the Os analysis and 5.5 ± 0.9 μmol of $RuOs_3$/g based on the Ru analysis; the average analysis was used in the rate calculations.

The reactor was loaded with 1.70 g of this catalyst and placed on stream at a pressure of 1.02 atm; the temperature was brought slowly to 66 °C as conversion data were being collected. Differential (<7.5%) conversions of but-1-ene were observed. There was no evidence of an induction period like that observed with the catalyst made from $[H_2RuOs_3(CO)_3]$. At 66 °C, rate data were collected; they are virtually indistinguishable from the data

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(49) The analysis of the catalyst by X-ray fluorescence showed 9.4 μmol of $RuOs_3$/g based on the Os analysis and 7.5 μmol of $RuOs_3$/g based on the Ru analysis. The average was used in calculating reaction rates.

(50) The parameters in the equation were estimated with a standard nonlinear least-squares program.[21]

characterizing the catalyst prepared from $[H_2RuOs_3(CO)_{13}]$, following its induction period. The lack of an induction period for the catalyst prepared from $[Et_4N][H_3RuOs_3(CO)_{12}]$ and the nearly identical activities of the two catalysts lead us to the conclusion that they incorporated the same catalytically active species, evidently associated with $[H_3RuOs_3(CO)_{12}]^-$. Rates determined at various temperatures confirm this conclusion. The apparent activation energies[51] found for the catalyst prepared from $[Et_4N][H_3RuOs_3(CO)_{12}]$ are 14.8 ± 2.8 kcal/mol for *cis*-but-2-ene and 13.2 ± 2.2 kcal/mol for *trans*-but-2-ene, agreeing within experimental error with the values observed for the catalyst prepared from $[H_2RuOs_3(CO)_{13}]$.

In further experiments with the catalyst prepared from $[Et_4N][H_3RuOs_3(CO)_{13}]$, the partial pressure of but-1-ene was systematically varied with the temperature held at 66 °C and the pressure held at 1.05 atm. As was observed with the catalyst prepared from $[H_2RuOs(CO)_{13}]$, the catalytic reaction rate data are excellently represented by eq 2; the parameter values[50] (summarized in Table III) are the same, within experimental error, as those determined for the catalyst prepared from $[H_2RuOs_3(CO)_{13}]$.

After collection of these data, the reactor was cooled with flowing CO and transferred into the glovebox, where the still pale yellow catalyst was recovered. The infrared and UV-vis spectra of the sample are consistent with the presence of $[H_3RuOs_3(CO)_{12}]^-$ on the catalyst surface; there was no evidence of other organometallic species. The sample was analyzed by X-ray fluorescence, the results indicating 4.7 ± 0.2 μmol of $RuOs_3$/g based on the Os analysis and 5.0 ± 0.8 μmol of $RuOs_3$/g based on the Ru analysis; the average is 15% lower than was indicated by the analysis of the fresh catalyst; considering the accuracy of the data, we infer that no Ru or Os had been lost during the catalysis.

In summary, all the analytical and spectroscopic characterizations of both catalysts are consistent with the inference that the anion $[H_3RuOs_3(CO)_{12}]^-$ was the catalyst precursor; the quantitative comparison of the two catalysts in terms of the kinetics of the but-1-ene isomerization reaction strongly supports the inference.

To provide a further test of this inference, an infrared experiment was done to characterize the surface organometallic species present during catalysis. A wafer of alumina pretreated at 150 °C was brought in contact with a solution of $[Et_4N][H_3RuOs_3(CO)_{12}]$. Adsorption of the cluster caused the wafer to turn pale yellow. The wafer was placed in the infrared cell, and the sample was brought in contact with a mixture of 32% but-1-ene in helium. The cell was then heated to 90 °C and held for 16 h. The spectra during this period were closely similar to those of the supported $[Et_4N][H_3RuOs_3(CO)_{12}]$.

3. Extraction of $[H_3RuOs_3(CO)_{12}]^-$ from Used Catalysts. Each of the used catalysts prepared by each of the methods described above was brought in contact with a solution of Et_4NBr in CH_2Cl_2; the resulting solutions were yellow and were shown by infrared and NMR spectroscopy to contain $[H_3RuOs_3(CO)_{12}]^-$, consistent with the inferences drawn above. Analyses of the extract solutions and the remaining solids and catalytic activities of the extracted solids are reported elsewhere.[21] The data are of only qualitative value; they show that the extractions removed a fraction of the Ru + Os and that some catalytic activity remained after the extraction. It is likely that the extraction procedure led to contamination of the catalysts.

4. Interpretation of the Kinetics. There is no direct evidence of the catalytic intermediates that may be formed from the $[H_3RuOs_3(CO)_{12}]^-$ precursor, but some suggestions can be made on the basis of the literature and examined on the basis of the catalytic kinetics. A cycle for alkene isomerization catalyzed by the hydrido triosmium cluster $[H_2Os_3(CO)_{10}]$ has been elucidated;[52,53] it involves coordination of the alkene at an unsaturated metal center followed by an insertion step forming a σ-alkyl intermediate. A similar mechanism has been proposed[54] for the formation of $[H_4Os_4(CO)_{11}(CHCH_2)]$ from $[H_4Os_4(CO)_{12}]$ and ethylene and for the isomerization of alkenes catalyzed by alumina-supported $[H_3Os_4(CO)_{12}]^-$.[17] We speculate that the rate-determining step in the catalytic cycle[55] is insertion of coordinated but-1-ene into an Os-H bond to give a σ-butyl ligand. If the steps following alkene coordination are approximated as irreversible and the usual assumptions regarding steady-state concentrations of the catalytic intermediates are made, then an analysis of the kinetics[21] leads to a rate equation of the form of eq 2. (The same form of equation also results, however, if it assumed that coordination of but-1-ene to a metal center is the rate-determining step.)

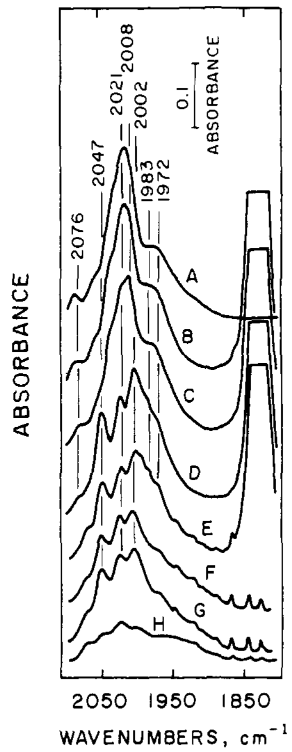

Figure 7. Infrared spectra showing the effect of but-1-ene on a sample prepared by adsorption of $[H_2RuOs_3(CO)_{13}]$ on γ-Al_2O_3: (A) fresh sample at 25 °C under vacuum, (B) sample at 25 °C under but-1-ene + He, (C) after heating to 90 °C under but-1-ene + He, (D) after 1 h, (E) after 16 h under but-1-ene + He, (F) after evacuation at 90 °C, (G) at 25 °C under vacuum after cooling in CO, (H) sample at 25 °C under vacuum after extraction with Et_4NBr in CH_2Cl_2.

If this speculative mechanism were correct, then *K* in eq 2 (the adsorption equilibrium constant according to the Langmuir formalism) would have the same value for the *cis*-but-2-ene formation as for the *trans*-but-2-ene formation. This condition is satisfied within experimental error (Table III).

Although the infrared spectra do not allow an identification of catalytic intermediates, they provide a clue. The spectrum of the fresh $[HRuOs_3(CO)_{13}]^-\{Al\}$ formed by adsorption of $[H_2RuOs_3(CO)_{13}]$ showed virtually no change upon exposure of the sample to but-1-ene at room temperature (Figure 7). Heating to 90 °C under but-1-ene initially left the spectrum still virtually unchanged (Figure 7). However, following the conversion into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$, the spectrum of the sample in the presence of but-1-ene at 90 °C (Figure 7) showed a shoulder at 1983 cm^{-1}

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[51] These values were determined from the temperature dependence of the reaction rate itself (not the rate constant *k*), since the rate equation (and *k*) were determined for only one temperature.

(52) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056.

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(55) A speculative catalytic cycle and an analysis of the kinetics are presented in ref 21.

that was not present in the spectrum of $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. The shoulder can be attributed to a reduction in symmetry of the cluster resulting from the coordination of but-1-ene. The lack of a similar, rapid change in the spectrum of $[HRuOs_3(CO)_{13}]^-\{Al\}$ upon exposure to but-1-ene suggests that this cluster cannot simply coordinate the alkene, consistent with its lack of catalytic activity.

I. Ethylene Hydrogenation Activity of Supported Metallic Catalysts Derived from $RuOs_3$ Clusters. 1. Catalyst Prepared by Adsorption of $[H_2RuOs_3(CO)_{13}]$. A catalyst was prepared from $[H_2RuOs_3(CO)_{13}]$ and γ-Al_2O_3, initially containing 8.60 ± 0.03 μmol of $RuOs_3$ per gram. The reactor was loaded in the glovebox with this catalyst and placed in the microflow reactor, where flows of H_2 and ethylene mixed with helium were set so that the partial pressures of H_2 and ethylene were 0.44 and 0.34 atm, respectively. The reactor was heated to 70 °C at a pressure of 1.01 atm, and rates of ethylene hydrogenation were measured at low (<0.1%) conversions that were shown to be differential. The rate of ethane formation initially was 3×10^{-3} mol (mol of $RuOs_3$·s)$^{-1}$; the rate increased gradually, appearing to approach an asymptotic value of 24×10^{-3} mol (mol of $RuOs_3$·s)$^{-1}$ after 30 h onstream.

These results suggest that the cluster initially present on the catalyst decomposed and that the catalytically active species finally present were not metal clusters. The catalyst, after extraction with Et_4NBr in absolute ethanol, was gray, suggesting the presence of metal particles on the support. Characterization of the used catalyst by transmission electron microscopy confirmed the presence of the particles, which had an average diameter of about 40 Å. These results are consistent with the inference that metal particles catalyzed the ethylene hydrogenation.

2. Catalyst Prepared by Adsorption of $[H_4RuOs_3(CO)_{12}]$. To test these ideas, another catalyst was prepared as $[H_4RuOs_3(CO)_{12}]$ was adsorbed by bringing alumina (pretreated at 150 °C) in contact with a solution of $[H_4RuOs_3(CO)_{12}]$ in CH_2Cl_2; the sample contained about 0.64 μmol of $[H_3RuOs_3(CO)_{12}]^-$ per gram. The reactor was loaded with this catalyst, and rates of ethylene hydrogenation were measured at 75 °C and conditions otherwise the same as those stated above. The activity increased from 2.6×10^{-2} to 11.1×10^{-2} mol (mol of $RuOs_3$·s)$^{-1}$ during 9 h onstream, again suggesting that metal particles had formed.

3. Infrared Evidence of Degradation of Supported Clusters in the Presence of H_2. When a wafer of $[HRuOs_3(CO)_{13}]^-\{Al\}$ was prepared by adsorption of $[H_2RuOs_3(CO)_{12}]$ onto alumina pretreated at 100 °C, the initial infrared spectrum was that expected for this supported cluster. Heating to 100 °C under H_2 resulted in several changes in the infrared spectrum: new bands appeared at 2012 and 2052 cm^{-1}, and the shoulder at 1975 cm^{-1} became less pronounced. Except for a shift of 7 cm^{-1} in frequency of the band at 2012 cm^{-1} from its expected position at 2005 cm^{-1}, these changes are consistent with the beginning of a transformation of $[HRuOs_3(CO)_{13}]^-\{Al\}$ into $[H_3RuOs_3(CO)_{12}]^-\{Al\}$. However, after 1 h at 100 °C under H_2, the band at 2012 cm^{-1} disappeared; the other features of the spectrum remained essentially unchanged. No indication of the band which might have been expected at 2005 cm^{-1} was present in this spectrum. Heating to 150 °C under H_2 left the spectrum virtually unchanged. After 0.5 h at 150 °C under H_2, however, the carbonyl spectrum had changed to a single very broad band at 2021 cm^{-1} with shoulders at 1975, 2052, and 2082 cm^{-1}. A reduction in total absorbance had also occurred. The loss in total carbonyl absorbance and the absence of distinct carbonyl bands in this final spectrum suggest that heating under H_2 led to partial decarbonylation and degradation of the $[HRuOs_3(CO)_{13}]^-\{Al\}$. These results confirm the complexity of the surface organometallic chemistry when supported metal clusters are brought in contact with hydrogen. We suggest that cluster degradation and metal aggregate formation on surfaces are to be expected with some generality with group VIII metals under such conditions.

Conclusions

The results show that the alumina-supported anion cluster $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ is formed either from $[HRuOs_3(CO)_{13}]^-\{Al\}$ or by direct deposition of $[Et_4N][H_3RuOs_3(CO)_{12}]$ on the alumina, according to the chemistry summarized in Figure 5. $[H_3RuOs_3(CO)_{12}]^-\{Al\}$ is inferred to be the precursor of a catalyst for isomerization of but-1-ene to give *cis*- and *trans*-but-2-ene. The catalyst is stable for more than 2000 turnovers at temperatures of 53–77 °C. The observed Langmuir–Hinshelwood kinetics and infrared spectra of the catalyst under reaction conditions suggest that the catalytic cycle involves coordination of the alkene to osmium in the intact molecular cluster. In contrast, when the catalyst is used for ethylene hydrogenation, its activity increases, accompanied by cluster degradation; the catalytic species evidently include metal particles.

These results not only demonstrate the role of supported metal clusters in catalysis but also confirm the general conclusion that the use of intact metal clusters as catalysts is severely limited by their lack of stability. The value of supported metal clusters in catalysis may be less in their application as catalysts themselves and more in the opportunities they offer for preparation of novel surface catalytic sites. For example, isolated rhenium carbonyl complexes on MgO have been formed from oxidation of mononuclear complexes and found to be catalytically active for alkene hydrogenation but not for alkane hydrogenolysis. In contrast, catalysts formed from trirhenium clusters evidently formed ensembles consisting of three rhenium centers and were active for both the hydrogenation and hydrogenolysis reactions.[6] Cluster precursors can in prospect be used to prepare surface structures of controlled nuclearity and composition, and with proper choice of the metals, support, and reactants, these may be more stable and catalytically interesting than the clusters themselves.

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Registry No. $H_2RuOs_3(CO)_{13}$, 75901-26-7; $H_4RuOs_3(CO)_{12}$, 65268-93-1; $[Et_4N][H_3RuOs_3(CO)_{12}]$, 109901-34-0; $[Et_4N][HRuOs_3(CO)_{13}]$, 111004-75-2; $Ru(CO)_5$, 16406-48-7; $Ru(C_5H_7O_2)_3$, 14284-93-6; $H_2Os_3(CO)_{10}$, 41766-80-7; $[H_3RuOs_3(CO)_{12}]^-$, 109901-32-8; $[HRuOs_3(CO)_{13}]^-$, 106531-06-0; Al_2O_3, 1344-28-1; H_2O, 7732-18-5; but-1-ene, 106-98-9; ethylene, 74-85-1.