Alumina-Supported Tetraosmium Cluster Anions: Precursors of Catalysts for Isomerization of But-1-ene

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Supported osmium clusters were prepared by the reaction of $[H_4Os_4(CO)_{12}]$ with the surface of γ-Al_2O_3 in refluxing *n*-octane. The surface-bound organometallic was identified as $[H_3Os_4(CO)_{12}]^-$ by its infrared spectrum; this anion could be extracted from the surface as the tetraphenylarsonium salt. The solid was catalytically active for isomerization of but-1-ene at 90°C and 1 atm; the only organometallic on the catalyst surface observed by infrared spectroscopy was $[H_3Os_4(CO)_{12}]^-$, which is identified as the catalyst precursor. At higher temperatures, the clusters broke up and were oxidized by –OH groups on the surface to give $Os(II)(CO)_x$ (x = 2 or 3); these surface-bound complexes had a lower catalytic activity than the clusters. © 1985 Academic Press, Inc.

INTRODUCTION

Metal clusters offer intriguing prospects as catalysts, but since the clusters are typically unstable, there exist only few well-documented catalytic cycles (*1*). Anchoring of metal cluster catalysts to solid supports offers prospects of stabilization of the clusters as a result of their being held apart from each other (*2*); supported clusters also offer the advantages of ease of separation from reaction products and opportunities for investigation of reactions in the absence of solvents. There are numerous examples of metal clusters anchored to functionalized supports [e.g., phosphine-functionalized silica or poly(styrene-divinylbenzene)] but only few anchored to simple metal-oxide supports (*3–5*). Many metal clusters on oxide surfaces easily undergo reactions leading to cluster decomposition and aggregation of the metals (*6*).

Here we report experiments with catalysts prepared from tetraosmium clusters on high-surface-area γ-Al_2O_3; $[H_4Os_4(CO)_{12}]$ was chosen as the parent cluster because it has an interesting reactivity and a relatively robust metal framework

(*7, 8*), offering the prospects of simple, characterizable organometallic surface structures. The results demonstrate that the cluster anion $[H_3Os_4(CO)_{12}]^-$ was formed on the surface and was a precursor of a catalyst for isomerization of but-1-ene.

EXPERIMENTAL METHODS

Cluster synthesis. The neutral cluster $[H_4Os_4(CO)_{12}]$ was prepared from $[Os_3(CO)_{12}]$ and H_2 by a method similar to that of Bhaduri *et al.* (*9*); the mixture in hexane reacted for 30 h at 150°C and 46 atm. The infrared spectrum of the sample in cyclohexane (1969w, 1999s, 2021vs, 2066vs, 2085s cm^{-1}) is in close agreement with that reported in the literature (Ref. (*9*): 1998m, 2021s, 2068s, 2085m cm^{-1}).

The cluster anion $[H_3Os_4(CO)_{12}]^-$ was prepared by the method of Johnson *et al.* (*10*).

Preparation of supported clusters. The support (γ-Al_2O_3, Catapal, 250 m^2/g, or Degussa) was calcined in flowing O_2 at 400°C and 1 atm for 1.5 h, cooled to room temperature, and left in flowing O_2 overnight. Organometallics were brought from solution onto the support surface, as described below; all handling was done with samples under N_2.

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Ninety-five grams of [H₄Os₄(CO)₁₂] was placed in a three-neck 250-cm³ round-bottomed flask with a magnetic stirrer. The γ-Al₂O₃ (5 g) was added, and the flask was evacuated and purged with N₂, and then *n*-octane (80 cm³) was added and the flask reevacuated. The solution, stirred and under N₂ flow, was refluxed for 1 h. It was cooled under flowing N₂ for 1.5 h; then the octane was decanted, hexane (40 cm³) was added, and the solution stirred for a few minutes. After the solid settled, the hexane was decanted and the washing was repeated. The slurry was then left to dry under N₂ flow. The resulting bright-yellow powder was evacuated for 1 h and transferred to a glovebox for storage. The infrared spectrum was obtained with a pressed wafer in air at room temperature. All spectra of supported species were measured at 4 cm⁻¹ resolution.

An extraction of the supported osmium species was carried out in the glovebox by adding a wafer to a solution of [Ph₄AsCl] in dry ethanol. It was left standing for 1 h, by which time all the ethanol had evaporated, and the wafer was rinsed three times with dry CH₂Cl₂; the rinses were combined and the spectrum of the solution recorded at 1 cm⁻¹ resolution. A similar extraction procedure was carried out with other samples, including one that had been used for catalytic isomerization of but-1-ene at 90°C; the solution of extracted organometallic was characterized by infrared spectroscopy.

Preparation of the supported cluster from the salt of the anion was done as follows: The salt [(Ph₃P)₂N][H₃Os₄(CO)₁₂] was added to a slurry of γ-Al₂O₃ (Catapal) in hexane at room temperature in the glovebox. The slurry was stirred for 4 h and filtered under vacuum. Then it was dried for 12 h under vacuum. The solid turned pale yellow, indicating that the cluster had been adsorbed on the surface. The supported cluster was mixed with Degussa alumina for recording of the infrared spectrum.

Infrared spectra of catalysts in reactive atmospheres. Samples of the supported os-

mium clusters were characterized in various atmospheres; wafers were mounted in an infrared cell interfaced to a vacuum/gas handling system (*11*). The wafers were loaded and removed from the cell in the glovebox. Helium (Airco grade 5, UHP 99.999%) was further purified by passing through a trap containing activated copper catalyst for O₂ removal and a trap containing zeolite A for water removal. Hydrogen (Matheson, UHP 99.999%) was passed over a zeolite trap. But-1-ene (Phillips, pure grade) was used without further purification.

Catalytic activity measurements. The but-1-ene isomerization reaction was carried out with a flow reactor at atmospheric pressure. The reactor was a vertical stainless-steel tube, 7 mm in diameter and 20 cm in length, surrounded by a close-fitting cylindrical metal heating block. The reactor contained 200–300 mg of the catalyst powder packed between plugs of glass wool. The reactant stream consisted of but-1-ene and He, which flowed through an O₂ trap (incorporating an activated copper catalyst) and a water trap (incorporating particles of zeolite A).

Samples of the product vapor stream were periodically injected into the He carrier gas stream of an on-line gas chromatograph equipped with a 3.2-mm × 1.8-m stainless-steel column packed with 80/100 mesh Carbopak C loaded with 0.19% picric acid. Reactant and product peak areas were measured by electronic integration of the output of a flame ionization detector.

Rates of the catalytic isomerization of but-1-ene to give *cis*-but-2-ene and *trans*-but-2-ene were determined at 90°C, with the partial pressure of but-1-ene varied from 0.1 to 0.9 atm; conversions were so low (0.1–0.5%) that they were assumed to be differential.

RESULTS AND DISCUSSION

Supported osmium catalysts were prepared by reaction of [H₄Os₄(CO)₁₂] with γ-Al₂O₃ in refluxing *n*-octane. The resulting

bright-yellow powders contained 1.2–1.5 wt% Os, as determined by elemental analysis (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) or by X-ray fluorescence.

The infrared spectrum of the supported osmium in the carbonyl region is shown in Fig. 1A, confirming that observed previously (12). This spsectrum (2003s, 2024s, 2053s, 2082w, 2118w cm^{-1}) is almost identical to the reported spectrum (Ref. (10): 1976w, 2000s, 2022s, 2048s, 2083w, 2119w cm^{-1}) and to our observed spectrum of $[H_3Os_4(CO)_{12}]^-$ in solution (Fig. 1B: 1974w, 1999s, 2021s, 2047s cm^{-1}). It is also nearly the same as our observation of the Al_2O_3-supported sample prepared by bringing the salt $[(Ph_3P)_2N]^+$ $[H_3Os_4(CO)_{12}]^-$ in contact with the Al_2O_3 (1978w, 2000s, 2023s, 2049s cm^{-1}). The small peaks observed at 1919, 1944, and 1969 cm^{-1} in Fig. 1B are indicative of the anion $[H_2Os_4(CO)_{12}]^{2-}$ (see Ref. (13)). These small peaks are not observed in the spectrum of the supported cluster (Fig. 1A), but other small peaks are present in this spectrum at 2082 and 2118 cm^{-1}. These peaks are attributed to $[H_4Os_4(CO)_{12}]$ that was not deprotonated. Both these

FIG. 1. Infrared spectra of sample (A) prepared from $[H_4Os_4(CO)_{12}]$ and γ-Al_2O_3, in air, at room temperature, and (B) $[(Ph_2P)_2N]^+$ $[H_3Os_4(CO)_{12}]^-$ in CH_2Cl_2 at room temperature.

bands decreased in intensity after exposure of the sample to He at 90°C.

The samples prepared from $[H_4Os_4(CO)_{12}]$ and from $[(Ph_3P)_2N]^+$ $[H_3Os_4(CO)_{12}]^-$ were subjected to extraction with $[Ph_4AsCl]$ or $(Ph_3P)_2NCl$ in CH_2Cl_2. The solutions of the extracted organometallics were characterized by infrared spectroscopy. The results agree with the spectrum of $[H_3Os_4(CO)_{12}]^-$, demonstrating that this anion was extracted from the surface of each sample and confirming that it was the predominant surface organometallic species.

The foregoing results show that $[H_4Os_4(CO)_{12}]$ reacted with basic sites on Al_2O_3 (14), being deprotonated. Similarly, deprotonation of $[H_4Os_4(CO)_{12}]$ occurs in methanolic KOH (10).

Infrared Spectra of Supported Catalysts in Reactive Atmospheres

Experiments with reactant gases in the presence of the supported catalyst were carried out with 100-mg wafers of the sample prepared from Degussa alumina (which gives excellent spectra) and, in one case, a mixture of Catapal and Degussa aluminas, which gave equivalent (but lower quality) spectra. The wafers were introduced into the infrared cell under N_2 in a dry box; they were then brought in contact with He, CO, or but-1-ene, with the following results.

A sample of the supported catalyst was initially evacuated at room temperature, the spectrum (Fig. 2A): 2002vs, 2023vs, 2054s, 2065sh, 2085w, 2113vw cm^{-1}) indicating the presence of $[H_3Os_4(CO)_{12}]^-$ and $[H_4Os_4(CO)_{12}]$. When He at 1 atm flowed over the sample for 1 h at 90°C, there was a decrease in intensity of the band at 2023 cm^{-1} accompanied by the disappearance of the shoulder at 2065 cm^{-1} (Fig. 2B), consistent with disappearance of the neutral cluster. The cell was then evacuated and CO at 1 atm was allowed to flow over the sample at 90°C for 30 min, without a significant change in the spectrum. The wafer was then subjected to extraction with a solution
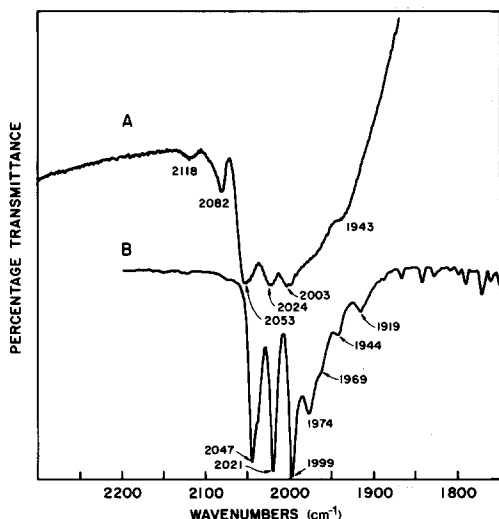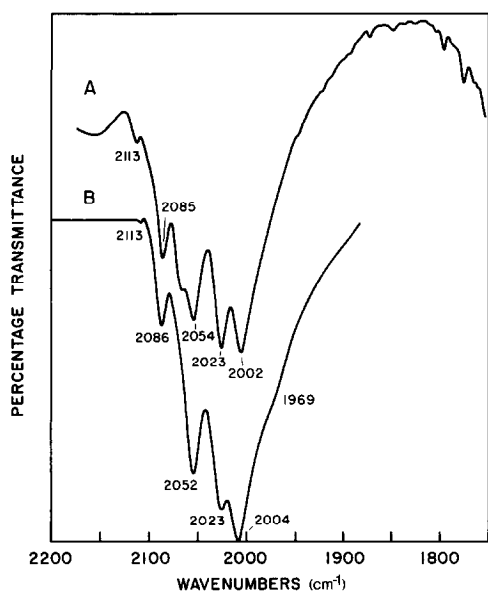
FIG. 2. Infrared spectra of sample prepared from [H₄Os₄(CO)₁₂] and γ-Al₂O₃. (A) Under vacuum at room temperature. (B) After 1 h at 90°C in flowing He.

$$HOs_3(CO)_{10}-O-Al,$$

which had been prepared from Al_2O_3 and $[Os_3(CO)_{12}]$ (*3, 15, 16*). The spectrum is similar to that of $[Os(II)(CO)_2I_2]$ (Ref. (*17*): 1988, 2045, 2119 cm^{-1}), which presumably is oligomeric. The surface species prepared from the triosmium cluster have been identified as $Os(II)(CO)_x$, where $x = 2$ or 3 (*3, 15, 16*). We infer that the same surface species were formed from the tetraosmium clusters on the support; evidently, the clusters broke up at temperatures of 120–150°C, reacting with surface –OH groups to become oxidized (*18, 19*).

Another sample of the supported cluster anion was held for 2.5 h at 90°C under He flow and then subjected to a flow of but-1-ene at 1 atm for 4 h at 90°C. This treatment had the same effect as the treatment with He alone at 90°C. When the temperature of
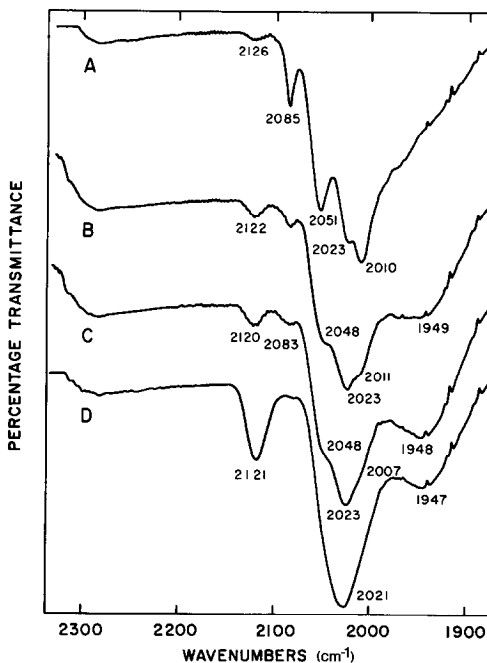
of [Ph₄AsCl]; the infrared spectrum of the extract solution showed $[H_3Os_4(CO)_{12}]^-$ as the only detectable metal carbonyl. Evidently, this cluster was stable on the surface in He and CO at 90°C.

Another sample of the alumina-supported cluster anion was maintained under He flow at 120°C for 1 h, which led to a broadening and a decrease in intensity of the bands; the band at 2022 cm^{-1} became almost a shoulder (Fig. 3A). The temperature was then raised to 150°C, resulting in more broadening and a shift of the bands to higher frequencies. After 2 h, a band at 1949 cm^{-1} started to appear, those at 2011 and 2048 cm^{-1} became shoulders, and the one at 2114 cm^{-1} moved to 2122 cm^{-1} and became more intense (Fig. 3B). After 3 h, a three-band pattern (1948, 2023, and 2120 cm^{-1}) became apparent (Fig. 3C). A flow of CO over the sample for 2 h at 150°C did not lead to any significant change in the spectrum (Fig. 3D).

Nearly this same three-band spectrum has been observed upon similar treatment of supported triosmium clusters

FIG. 3. Infrared spectra of sample prepared from [H₄Os₄(CO)₁₂] and γ-Al₂O₃. (A) After 1 h at 120°C in flowing He. (B) After 2 h at 150°C in flowing He. (C) After 3 h at 150°C in flowing He. (D) After 2 h at 150°C in flowing CO.
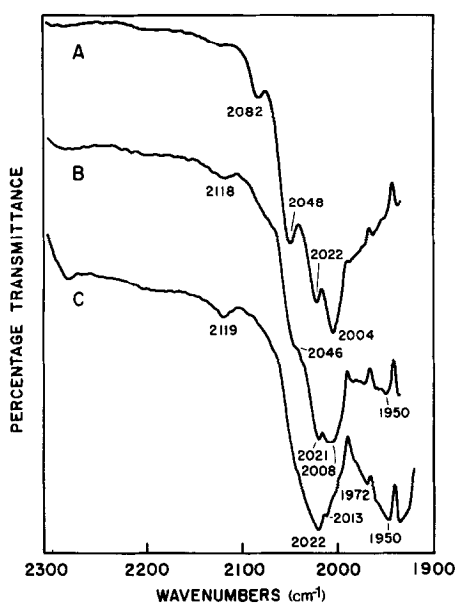
FIG. 4. Infrared spectra of sample prepared from [H$_4$Os$_4$(CO)$_{12}$] and γ-Al$_2$O$_3$. (A) After 2.5 h at 90°C in flowing He followed by 4 h at 90°C in flowing but-1-ene then 2 h at 120°C in flowing but-1-ene; the spectrum was taken under vacuum. (B) After 13 h at 120°C in flowing but-1-ene; the spectrum was taken under vacuum. (C) After 2 h at 150°C in flowing He.

the sample in but-1-ene was increased to 120°C, a pattern of changes took place as in He (Fig. 4A), until after 13 h the sample showed the three-band pattern attributed to divalent Os carbonyls (Fig. 4B). A subsequent flow of He at 1 atm and 120°C for 3 h had a negligible effect, but after 2 h at 150°C, the bands at 1950 and 2118 cm^{-1} became more intense and those at 2008 and 2021 cm^{-1} nearly merged into one at 2022 cm^{-1} (Fig. 4C).

Subsequent flow of but-1-ene at 1 atm and 150°C for 12 h caused no change in the spectrum, apart from a slight accentuation of the three-band pattern. Cooling under vacuum led to no change. These results demonstrate that the cluster decomposition to give the mononuclear carbonyl complexes occurred in the presence of but-1-ene just as it occurred in He and CO.

Catalytic Isomerization of But-1-ene

A flow reactor was loaded with 240 mg of

the sample prepared from [H$_4$Os$_4$(CO)$_{12}$] and Catapal alumina (1.2 wt% Os) and left overnight under a flow of 40 cm^3 of He/min at room temperature. The temperature was then raised to 90°C over a period of 10 min, and a but-1-ene flow of 10 cm^3/min was started, giving a feed stream with partial pressures of but-1-ene and He equal to 0.2 and 0.8 atm, respectively. After ~1 h had been allowed for attainment of steady state, six injections of product into the gas chromatograph were made over a period of 2 h, giving mean conversions of 0.12% to cis-but-2-ene and 0.27% to trans-but-2-ene; the corresponding reaction rates are 0.16 and 0.36 molecules/(Os$_4$ cluster · s), respectively.

The partial pressures of but-1-ene and the diluent He were then varied systematically, with reaction rates being determined at each condition. The data, plotted as rate as a function of reactant partial pressure (Fig. 5) for formation of each of the but-2-ene isomers, show a pattern typical of Langmuir kinetics. The shapes of the curves suggest that the catalytic sites approached saturation with reactant but-1-ene at a partial pressure of about 0.5 atm.

The rate data for formation of each of the two but-2-ene products are well represented by an equation of the form
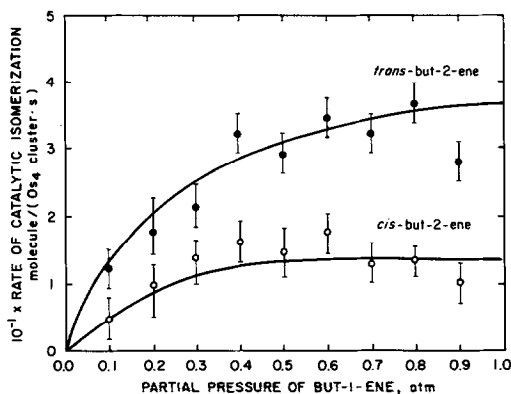

FIG. 5. Kinetics of isomerization of but-1-ene at 90°C and 1 atm catalyzed by alumina-supported [H$_3$Os$_4$(CO)$_{12}$]$^-$. The curves are predictions of Eq. (1) with the parameter values of Table 1.

$$r = \frac{kK_{\text{but-1-ene}}P_{\text{but-1-ene}}}{1 + K_{\text{but-1-ene}}P_{\text{but-1-ene}}}, \qquad (1)$$

where r is catalytic reaction rate and P is partial pressure. The values of the parameters k and $K_{\text{but-1-ene}}$, estimated by a standard nonlinear least-squares routine, are summarized in Table 1. The goodness of fit to the data is shown in Fig. 5.

When the catalyst was maintained in operation for 12 h and the experiment repeated at the initial condition, lower rates were observed than those observed initially. The rates of formation of cis- and trans-but-2-ene were 0.10 and 0.21 molecules/(Os$_4$ cluster · s), respectively. These results indicate that the catalyst had undergone a slow change in activity and, presumably, structure. Subsequent experiments confirmed the pattern of catalyst deactivation.

After a series of kinetics measurements demonstrating the deactivation, the reactor was cooled down in flowing He, and the He flow was continued overnight at room temperature. The following morning the catalyst was reheated in flowing He to 90°C over a period of 10 min, and the measurements of catalytic reaction rate were repeated. The data were in agreement with those measured initially (and shown in Fig. 5), within experimental error; the catalyst had been reactivated.

The cycle of deactivation and reactivation of the catalyst and collection of kinetics data was repeated. The sample was held in flowing He again, as before, and then

TABLE 1

Kinetics Parameters for Isomerization of But-1-ene at 90°C and 1 atm[a]

Product	Organometallic precursor	k (molecule cluster · s)	$K_{\text{but-1-ene}}$ (atm^{-1})
cis-But-2-ene	[H$_4$Os$_4$(CO)$_{12}$]	0.17	3.7
trans-But-2-ene	[H$_4$Os$_4$(CO)$_{12}$]	0.44	4.4
cis-But-2-ene	[(Ph$_3$P)$_2$N][H$_3$Os$_4$(CO)$_{12}$]	0.16	8.9
trans-But-2-ene	[(Ph$_3$P)$_2$N][H$_3$Os$_4$(CO)$_{12}$]	0.37	4.7

[a] Parameters for Eq. (1).

transferred to the glovebox for extraction with a solution of [Ph$_4$AsCl]. The extracted organometallic was characterized by infrared spectroscopy, and again the only detected species was [H$_3$Os$_4$(CO)$_{12}$]$^-$. We conclude from these results and the aforementioned infrared spectra that the predominant surface osmium species was [H$_3$Os$_4$(CO)$_{12}$]$^-$; this cluster anion is identified as the catalyst precursor.

The used catalyst was extracted with a solution of excess (Ph$_3$P)$_2$NCl in CH$_2$Cl$_2$. The infrared spectrum (1919w, 1943w, 1968w, 1979m, 1998s, 2021s, 2046s cm^{-1}) showed the major product extracted was the anion [H$_3$Os$_4$(CO)$_{12}$]$^-$, a minor component being [H$_2$Os$_4$(CO)$_{12}$]$^{2-}$. Extraction of a fresh catalyst sample gave similar results.

The extracted catalyst was filtered, dried under vacuum, and reloaded into the reactor. The but-1-ene isomerization experiments were repeated, with the support after extraction showing no catalytic activity. These results confirm the conclusion that the tetranuclear cluster anion was the catalyst precursor.

To provide further confirmation that [H$_3$Os$_4$(CO)$_{12}$]$^-$ was the catalyst precursor, a sample prepared from [(Ph$_3$P)$_2$N][H$_3$Os$_4$(CO)$_{12}$] was also tested for isomerization of but-1-ene. The performance of this catalyst was virtually indistinguishable from that of the catalyst prepared from the neutral cluster (Table 1).

Since the infrared spectra indicated that the surface-bound cluster was not stable at temperatures exceeding about 120°C, a different catalytic performance was expected at these temperatures. The results of further experiments with a sample prepared from [H$_4$Os$_4$(CO)$_{12}$] and Al$_2$O$_3$ confirmed this expectation. The catalytic activity at 150°C, for example, decreased relatively rapidly with time on stream (too rapidly to allow determination of a rate equation). The activity approached a value approximately an order of magnitude lower than that characteristic of the supported tetraosmium cluster. We infer that the activity was

associated with mononuclear osmium complexes on the Al_2O_3 surface; such activity has been reported for similar catalysts prepared by the decomposition of triosmium clusters on Al_2O_3 (20, 21).

The catalytic action of the supported cluster anions is consistent with the known solution chemistry of tetraosmium clusters. Bhaduri et al. (9) reported the reactions of alkenes with $[H_4Os_4(CO)_{12}]$, a possible structure of the product being suggested to be the following:
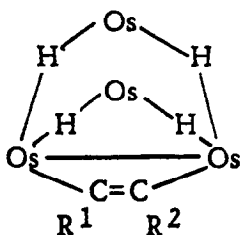
These workers (7, 9) pointed out the similarity in the chemistry of alkenes and tetraosmium clusters, on the one hand, and of alkenes and triosmium clusters, on the other. The latter chemistry is better understood and includes a well-characterized catalytic cycle for alkene isomerization (22, 23), whereby the alkene is coordinated to Os in the unsaturated $[H_2Os_3(CO)_{10}]$, then undergoing insertion with a hydride ligand, rearrangement, and dissociation of the product. Such a cycle might pertain with the tetraosmium cluster as well. The mechanism for generation of sites of coordinative unsaturation for bonding of butene remains to be elucidated; Lewis and Johnson (7) speculated that reaction of ethylene with tetraosmium clusters occurred via an associative Os–Os bond-breaking mechanism. Since the only surface organoosmium species detected by infrared spectroscopy was the coordinatively saturated anion, we infer that any unsaturated species and reaction intermediates were present in only very small concentrations. The slow deactivation of the catalyst in operation at 90°C is similar to what was observed with $[H_2Os_3(CO)_{10}]$ in the homogeneous catalysis (22, 23)—in that case the deactivation was attributed to the formation of a bridging vinyl species which drained catalytically active triosmium clusters from the cycle. A similar species might have formed with the supported cluster, being desorbed under He flow, but with our analytical capability it was not detected.

The results reported here indicate a close similarity in the chemistry of alumina-supported tetraosmium cluster anions and the analogous ruthenium–triosmium cluster anions (5)

$$[H_3RuOs_3(CO)_{12}]^- \overset{+}{Al}$$
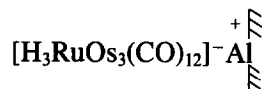
the similarity may extend to tetraruthenium anions (24).

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