Triosmium Clusters Bonded to Phosphine-Functionalized Supports: Catalysts for Olefin Isomerization

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Analogs of the coordinatively unsaturated cluster [$H_2Os_3(CO)_9PPh_3$] were anchored to crosslinked polystyrene and silica supports through pendent phosphine ligands and identified by their infrared spectra in the carbonyl region. The supported clusters exhibited reactivities with acetylene and olefins nearly the same as those of the analogous soluble cluster. Although the soluble cluster was unstable in solutions of 1-hexene, the supported analogs were stable and catalyzed the formation of internal hexenes. The supported clusters were compared with the coordinatively unsaturated cluster [$H_2Os_2(CO)_{10}$], which is known to catalyze olefin isomerization with the metal framework remaining intact. The initial catalytic activity of the silica-supported cluster for 1-pentene isomerization was about three times greater than that of [$H_2Os_3(CO)_{10}$] at 1 atm and 75°C. Both the supported cluster and [$H_2Os_3(CO)_{10}$] underwent ~10^3 reaction events prior to cessation of catalysis as a result of formation of a coordinatively saturated cluster incorporating a bridging vinyl ligand derived from the olefin. It is concluded that the catalytic nature of the supported cluster is almost identical to that of [$H_2Os_3(CO)_{10}$].

INTRODUCTION

Metal clusters are a class of catalysts expected to have new activities—associated with their offering new combinations of metal centers and surrounding ligands—and high selectivities—associated with their discrete structures. Metal clusters anchored to solid supports may offer these advantages with increased stability, since the supports—by holding the clusters apart from each other—may stabilize the coordinatively unsaturated species required for bonding of reactive ligands to a cluster.

The subject of catalysis by metal clusters (*1–3*) [and especially supported metal clusters (*4*)] is new and largely undeveloped. There are scarcely any well-established catalytic cycles involving metal clusters, the notable exceptions being olefin isomerization and hydrogenation involving triosmium clusters (*5, 6*). Characterization of

supported clusters is at an early stage (*4*), and there are no quantitative comparisons of catalysis by analogous soluble and supported clusters.

The objective of the research reported here was to provide such a comparison by building on the well-known chemistry of triosmium clusters (*5–9*) and the known procedures for preparing supported triosmium clusters (*10, 11*).

EXPERIMENTAL

Materials

Polymeric supports were prepared from macroporous poly(styrene-divinylbenzene) beads [20–50 mesh; average pore diameter about 900 Å; crosslinking approximately 3% divinylbenzene] supplied by Aldrich. The beads were functionalized with phosphine groups by reaction with $LiPPh_2$ (*12*) (typical analysis: 3.7% P). A silica support (Ketjen Akzo F-22; surface area, 382 m²/g) was similarly functionalized by reaction with [$PPh_2(CH_2CH_2)Si(OC_2H_5)_3$] (Strem) refluxing overnight in toluene to give a typi-

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cal P content of 1.25% *(13)*. $[H_2Os_3(CO)_{10}]$ *(14)* and $[H_2Os_3(CO)_9PPh_3]$ *(5)* were prepared by literature methods. Acetylene (Matheson), 1-hexene (Aldrich), 1-pentene (Chemical Samples), and 1-butene (Phillips) were used as received. Solvents, unless otherwise noted, were reagent grade and were used without further purification; for kinetics experiments, the solvents and reactant 1-pentene were distilled and degassed by repeated freeze–pump–thaw cycles. All reactions were carried out under nitrogen.

Analyses

Infrared spectra of catalysts were obtained with a Nicolet Model 7199 Fourier transform infrared spectrometer in the range 400–4000 cm^{-1} with a 4-cm^{-1} resolution. Proton NMR spectra of catalytic reaction products were recorded on a Perkin-Elmer Model R-12, 60-MHz spectrometer, with shifts reported relative to internal TMS. Gas chromatographic analyses of catalytic reaction products were performed
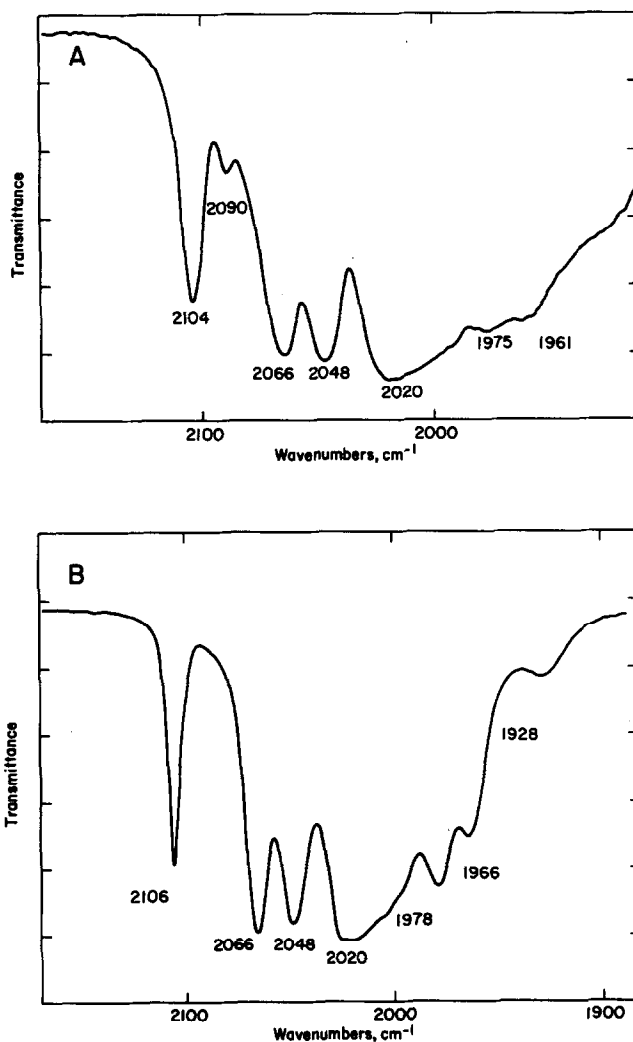

FIG. 1. Infrared spectra of (A) polymer-supported triosmium cluster $[H_2Os_3(CO)_{10}PPh_2-$Ⓟ$]$ and (B) the molecular analog $[H_2Os_3(CO)_{10}PPh_3]$.

with an Antek Model 300 equipped with an electronic integrator. A 7-ft column of *n*-octane on Porasil C (80–100 mesh) was used with helium carrier gas flowing at 50 cm^3/min. Separations of butene isomers were performed at 37°C, pentene isomers at 30–35°C, and hexane and hexene isomers over the range 70–100°C, with a programmed temperature increase of 4°C/min. Elemental analyses of catalysts were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Catalyst Preparations

Preparation of [$H_2Os_3(CO)_9PPh_2$–Ⓟ]. Functionalized polymer beads (typically 200 mg) and excess [$H_2Os_3(CO)_{10}$] (240 mg, 2.81×10^{-4} mol) were stirred in hexane at ambient temperature for 2 hr. After solvent had been decanted, the beads were washed with hexane; they were lightly yellow tinted. Infrared spectra in the carbonyl stretching region indicated the formation of [$H_2Os_3(CO)_{10}PPh_2$–Ⓟ], as inferred from the comparison of the spectrum with that of the molecular analog (Fig. 1, Table 1). The supported osmium carbonyl cluster was decarbonylated by heating in refluxing hexane for 24 hr to yield the green [$H_2Os_3(CO)_9PPh_2$–Ⓟ], again identified by its infrared spectrum (Table 1).

Preparation of [$H_2Os_3(CO)_9PPh_2C_2H_4$–SIL]. As described by Brown and Evans (*10*), [$H_2Os_3(CO)_{10}$] reacts with phosphine-functionalized silica ([PPh$_2$C$_2$H$_4$–SIL]) in hexane at ambient temperature (2 hr) to yield the yellow [$H_2Os_3(CO)_{10}PPh_2C_2H_4$–SIL], identified by its infrared spectrum (Fig. 2, Table 1). Decarbonylation was achieved by heating for 2 hr in refluxing hexane, the resulting product being identified from its infrared spectrum (Fig. 2, Table 1) as [$H_2Os_3(CO)_9PPh_2C_2H_4$–SIL], which was dark green. A typical elemental analysis was P, about 1%; Os, about 14%.

Reaction Experiments

Reaction of [$H_2Os_3(CO)_9PPh_2$–SUPPORT] *with* C_2H_2. Acetylene was passed through a trap at $-63°C$ and bubbled through a hexane suspension containing [$H_2Os_3(CO)_9PPh_2$–Ⓟ] or [$H_2Os_3(CO)_9PPh_2C_2H_4$–SIL] at ambient temperature and pressure for 4 hr. Each solid changed in color from green to yellow. The solvent was decanted, and the product was washed with hexane, dried, and characterized by infrared spectroscopy. Reaction of the soluble molecular metal cluster [$H_2Os_3(CO)_9PPh_3$] with acetylene was performed similarly.

Reaction of olefins in the presence of

TABLE 1

Infrared Spectra: Carbonyl Stretching Frequencies of Anchored and Soluble Triosmium Clusters[a]

Metal Cluster	ν_{CO} (cm^{-1})						
[$H_2Os_3(CO)_{10}PPh_3$][b]	2106m	2066s	2048s	2020vs	1978m	1966m	1928w
[$H_2Os_3(CO)_{10}PPh_2$–Ⓟ]	2104m	2090w	2066s	2048s	2020vs	1975w	
[$H_2Os_3(CO)_{10}PPh_2C_2H_4$–SIL]	2106m	2092w	2066s	2050s	2021vs	1981m	
[$H_2Os_3(CO)_9PPh_3$][b]	2090m	2053s	2021vs	1992sh			
[$H_2Os_3(CO)_9PPh_2$–Ⓟ]	2090m	2051s	2005vs	1977sh			
[$H_2Os_3(CO)_9PPh_2C_2H_4$–SIL]	2099m	2054s	2011vs	1988m			
[$HOs_3(CH=CH_2)(CO)_9PPh_3$]	2087m	2038s	2015sh	1998vs	1983sh		
[$HOs_3(CH=CH_2)(CO)_9PPh_2$–SUPPORT]	2090m	2041s	2008vs				
[$HOs_3(vinyl)(CO)_9PPh_2$–SUPPORT][c]	2089m	2045s	2010vs				

[a] Spectra of samples in KBr pellets.
[b] Ref. (*5*).
[c] Typical spectrum from reaction of [$H_2Os_3(CO)_9PPh_2$–SUPPORT] with α-olefins.

[$H_2Os_3(CO)_9PPh_2$–SUPPORT]. Reactions of 1-pentene and of 1-hexene were performed similarly by adding the liquid olefin (0.5–2.0 ml) to [$H_2Os_3(CO)_9PPh_2$–Ⓟ] or [$H_2Os_3(CO)_9PPh_2C_2H_4$–SIL] (50–150 mg) suspended in 4 ml of toluene (or of C_6D_6, for NMR studies). The mixture was stirred overnight at ambient temperature and pressure, and then the solvent and excess (and isomerized) olefin were removed. The supported cluster was then washed, dried, and characterized by infrared spectroscopy. Analysis of olefin isomerization products was achieved either by examination of the olefinic region of the NMR spectrum (in the case of hexene) or by gas chromatography. Samples taken periodically during the reaction determined the activity of the catalyst. In the event of complete conversion to internal olefins, more reactant olefin (in 1-ml increments) was added to the reaction mixture until catalytic activity had ceased.
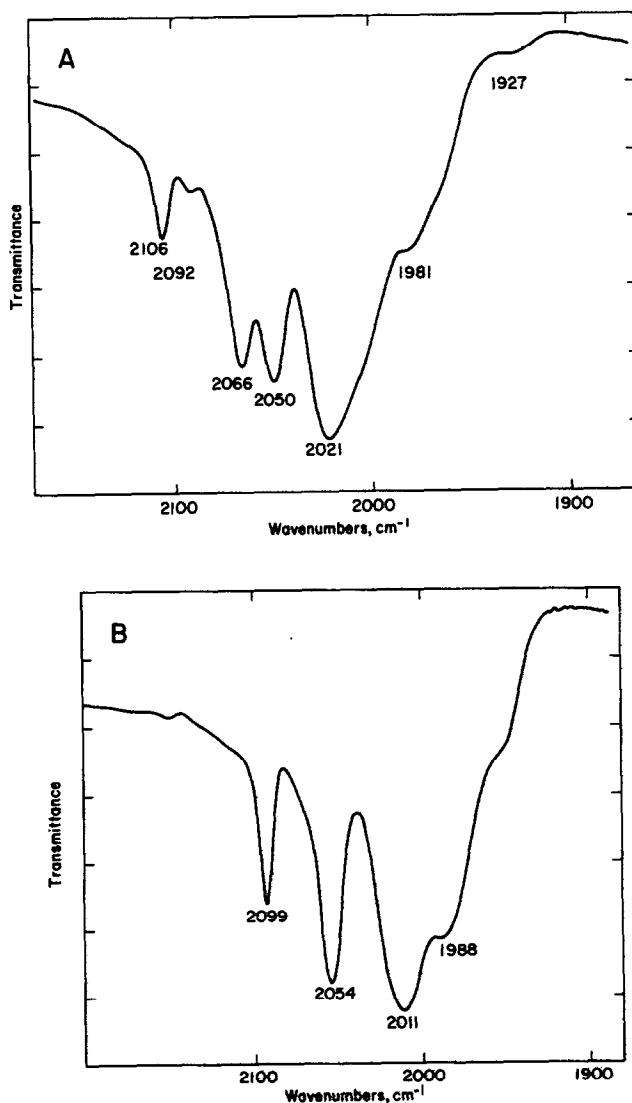

FIG. 2. Infrared spectra of silica-supported triosmium clusters: (A) [$H_2Os_3(CO)_{10}PPh_2C_2H_4$–SIL]; (B) [$H_2Os_3(CO)_9PPh_2C_2H_4$–SIL].

A few preliminary experiments were done with 1-butene as the reactant olefin. Beads of polymer-supported catalyst or particles of silica-supported catalyst were held in a thermostated tubular flow reactor of conventional design, interfaced to a gas chromatograph. Reactant 1-butene passed over the catalyst at 25–100°C and atmospheric pressure. In some experiments hydrogen flowed with the 1-butene.

Reactions of the soluble clusters $[H_2Os_3(CO)_{10}]$ and $[H_2Os_3(CO)_9PPh_3]$ with 1-pentene and 1-hexene were carried out in the liquid phase at ambient temperature and pressure. The procedures were almost the same as those applied with these olefins and the solid catalysts.

Kinetics of 1-pentene isomerization. Weighed amounts of catalyst {10–30 mg of $[H_2Os_3(CO)_{10}]$ or 100–150 mg of $[H_2Os_3(CO)_9PPh_2C_2H_4–SIL]$} and 1-pentene (0.5–2 ml) were placed in a preheated batch reactor, also containing 4 ml of toluene (distilled from sodium and stored over anhydrous molecular sieve desiccant). The extent of the olefin isomerization reaction was monitored by gas chromatographic analyses of products withdrawn at intervals of 2–10 min. The initial rate was determined from the conversion vs time plot, which was linear. At least six samples were taken for each experimental determination of a rate. The olefin concentration and the amount of catalyst were varied independently; the temperature was held constant at 75 ± 1°C.

Hydrogenation of olefins in the presence of $[H_2Os_3(CO)_9PPh_2C_2H_4–SIL]$. A pressure bottle was charged with 300 mg of $[H_2Os_3(CO)_9PPh_2C_4H_4-SIL]$, 6 ml of octane, and 1 ml of 1-hexene. The mixture was brought up to pressure with hydrogen (4.0 atm) and then held at 75°C with stirring for 45 hr. The products were analyzed by gas chromatography for hexenes and hexane.

RESULTS AND DISCUSSION

Both acetylene and the various olefins

reacted with the supported triosmium clusters in just the manner expected from the known chemistry of the soluble analog of the supported clusters, $[H_2Os_3(CO)_{10}]$. An important characteristic of the triosmium clusters $[H_2Os_3(CO)_{10}]$, $[H_2Os_3(CO)_9PPh_3]$, and $[H_2Os_3(CO)_9PPh_2–SUPPORT]$ is their coordinative unsaturation. Each has 46 bonding electrons, whereas each of the saturated triosmium clusters (e.g., $[Os_3(CO)_{12}]$ and $[H_2Os_3(CO)_{10}PPh_3]$) has 48. The unsaturated clusters are reactive, undergoing ligand association in the presence of electron-pair donors such as acetylenes, olefins, and phosphines, giving saturated clusters (7–9).

It is the coordinative unsaturation that accounts for the catalytic activity of the 46-electron cluster $[H_2Os_3(CO)_{10}]$ for olefin isomerization and hydrogenation; the olefin is π-bonded at the site of unsaturation, and the isomerization results from hydrogen transfers shown in the catalytic cycle of Fig. 3. This cycle is ultimately blocked after the cluster has been completely converted into a saturated species having a bridging vinyl ligand, $[HOs_3(vinyl)(CO)_{10}]$ (Fig. 3).

As expected (5, 6) we observed that $[H_2Os_3(CO)_{10}]$ catalyzed isomerization of 1-hexene to internal hexenes, producing 510 moles of internal hexenes per mole of $[H_2Os_3(CO)_{10}]$, after which no further conversion was observed.[3] The color of the solution changed from purple to yellow, and infrared spectra demonstrated the complete disappearance of $[H_2Os_3(CO)_{10}]$ and formation of a saturated complex, inferred to be $[HOs_3(CH_3(CH_2)_3C=CH_2)(CO)_{10}]$, which has a bridging vinyl ligand.

In similar experiments, attempts were made to measure rates of isomerization of 1-hexene catalyzed by $[H_2Os_3(CO)_9PPh_3]$. No quantitative results were obtained, since decomposition of the cluster occurred

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[3] Deeming and Hasso (5) reported that 5400 moles of olefin were isomerized per mole of $[H_2Os_3(CO)_{10}]$ prior to cessation of catalysis. Recalculation with Deeming and Hasso's data gave a value of 540, which is in good agreement with the result stated above.
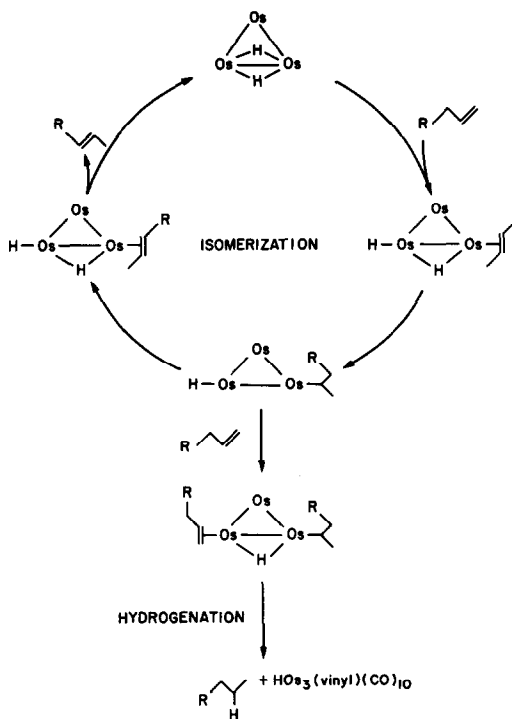
FIG. 3. Catalytic cycle for isomerization of α-olefins catalyzed by triosmium clusters in solution (5, 6). The carbonyl ligands are omitted for simplicity.

(giving unidentified species, possibly disproportionation products and mononuclear osmium complexes).

In the quantitative kinetics experiments with [H$_2$Os$_3$(CO)$_{10}$] and 1-pentene, data were obtained (typified by those of Fig. 4) which are consistent with the following rate equation:

$$r = k_1 C_{\text{Os cluster}} C_{\text{1-pentene}} \text{ mole}/(1 \cdot \text{s}), \quad (1)$$

where k_1 = 0.026 ± 0.005 1/(mole · s) at 75°C. The color change of the solution from purple to yellow was evident at a conversion of about 10% of the 1-pentene.

These results compare well with the results of Ferrari et al. (15), who determined kinetics of 1-pentene isomerization in the presence of [H$_2$Os$_3$(CO)$_{10}$] in toluene solvent at a temperature about 5°C less than that used in our work, namely, 70.4°C. These authors found that the reaction was first order in the catalyst concentration

(consistent with the results given above) and independent of the CO partial pressure (varied over a narrow range) (consistent with the mechanism of Fig. 3). Their observed initial rates are approximately equal to those reported here, being 18 to 38% greater than the values predicted by Eq. (1).

In experiments with the supported clusters, it was found that the coordinatively unsaturated clusters, i.e., [H$_2$Os$_3$(CO)$_9$PPh$_2$-Ⓟ] and [H$_2$Os$_3$(CO)$_9$PPh$_2$C$_2$H$_4$–SIL], were also catalytically active for olefin isomerization, whereas the coordinatively saturated supported clusters and the supports themselves were inactive.

The supported catalysts were much more stable than the soluble analog, [H$_2$Os$_3$(CO)$_9$PPh$_3$]. With the silica-supported cluster, the isomerization of roughly 10^3 moles of 1-hexene per mole of triosmium was observed before cessation of catalytic activity [as measured by NMR spectroscopy and by gas chromatography]. The used catalyst had changed color to bright yellow, and an infrared spectrum confirmed the formation of a saturated species, inferred to have a bridging vinyl ligand (Table 1). Qualitative isomerization catalysis experiments with the silica-supported cluster and other olefins yielded similar results. An experiment was also done with 1-hexene and the polymer-supported triosmium cluster, and, again, ≥10^3 molecules of isomers were formed before the cessation of catalysis.

The roughly twofold greater yield of catalytic reaction products formed in the presence of the supported clusters compared with the soluble cluster [H$_2$Os$_3$(CO)$_{10}$] suggests the importance of steric effects associated with the support. The formation of the catalytically inactive saturated cluster with a bridging vinyl ligand requires coordination of two molecules of olefin per cluster, as shown in Fig. 3. We suggest that the polymer or silica support, functioning essentially as a large ligand, may sterically hinder coordination of the second molecule
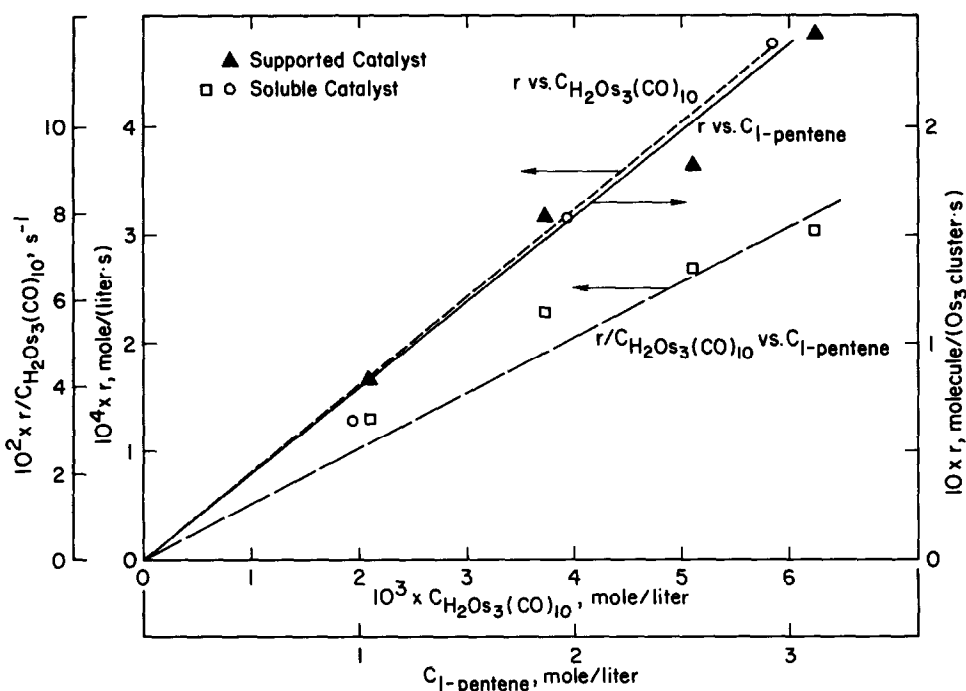
FIG. 4. Kinetics data: isomerization of 1-pentene catalyzed by [H$_2$Os$_3$(CO)$_{10}$] and by [H$_2$Os$_3$(CO)$_9$PPh$_2$C$_2$H$_4$–SIL] in toluene at 1 atm and 75°C. Representative data (averages of several points) are shown with lines predicted by Eqs. (1) and (2) for the soluble and supported catalysts, respectively. The data for the plot of rate vs the concentration of [H$_2$Os$_3$(CO)$_{10}$] were obtained for a fixed value of the concentration of 1-pentene, namely, 3.12 moles/liter. The solid catalyst contained 0.97% P and 15.1% Os.

of olefin, thus favoring the competing (catalytic) reactions.

Kinetics of the 1-pentene isomerization catalyzed by [H$_2$Os$_3$(CO)$_9$PPh$_2$C$_2$H$_4$–SIL] was also investigated to allow a comparison with the soluble cluster [H$_2$Os$_3$(CO)$_{10}$]. No catalyst decomposition was detected during the determinations of initial rates, as indicated by the spectra of representative samples. Consistent with the previously mentioned results for the soluble catalyst, rates of 1-pentene isomerization catalyzed by [H$_2$Os$_3$(CO)$_9$PPh$_2$C$_2$H$_4$–SIL] were found to be approximately proportional to the olefin concentration (Fig. 4). The rate data are well represented by the equation

$$r = k_2 C_{\text{1-pentene}} \text{ molecules/}$$
$$(\text{Os}_3 \text{ cluster} \cdot \text{s}), \quad (2)$$

where $k_2 = 0.08 \pm 0.02$ 1/(mole of Os$_3$ · s) at 75°C.

This result lends itself to comparison with Eq. (1) rearranged into the form

$$\frac{r}{C_{\text{Os}_3 \text{ cluster}}} = k_1 C_{\text{1-pentene}} \text{ molecules/}$$
$$(\text{Os}_3 \text{ cluster} \cdot \text{s}) \quad (3)$$

[where $k_1 = 0.026 \pm 0.005$ 1/(mole · s)].

The important result is the approximate equality of the activities of the soluble and supported triosmium cluster catalysts. We suggest that the threefold greater activity of the supported cluster reflects the influence of the electron-donating phosphine ligand, and that, otherwise, the support effect is negligible.

It has been established that the soluble triosmium cluster with the metal framework intact is the catalytically active species for olefin isomerization (Fig. 3). We therefore conclude from all the similarities

in reactivity and catalytic activity and stability of the soluble and supported clusters that the supported clusters were also catalytically active for olefin isomerization. These results provide the best example documenting catalysis by a supported cluster itself, rather than fragments (mononuclear complexes) or aggregates of metal. We emphasize that neither of the supports without attached clusters nor any of the saturated catalyst precursors, [H_2 $Os_3(CO)_{10}PPh_2$–SUPPORT], was active as an isomerization catalyst; among the supported clusters referred to above, only those designated [$H_2Os_3(CO)_9PPh_2$–SUPPORT] were active.

The supported cluster [$H_2Os_3(CO)_9$ $PPh_2C_2H_4$–SIL] has also been found to be an olefin hydrogenation catalyst, as is the soluble cluster [$H_2Os_3(CO)_{10}$] (5, 6). Reaction of 1-hexene in the presence of the silica-supported cluster (for 45 hr at 75°C and 4.0 atm in an autoclave) resulted in conversion of 19% to hexane and 79% to internal hexenes (2% remained unconverted); no catalyst decomposition was observed by infrared spectroscopy. The formation of internal hexenes is consistent with the observed failure of [$H_2Os_3(CO)_{10}$] to catalyze hydrogenation of internal olefins (6). All the results are in agreement with the previously observed results for hydrogenation of 1-hexene catalyzed by [$H_2Os_3(CO)_{10}$]; for similar reaction conditions, Keister and Shapley reported conversion of 1-hexene to 19% hexane and 81% internal hexenes with no catalyst decomposition (6). This comparison therefore provides further evidence of the strong similarity between [$H_2Os_3(CO)_{10}$] and the coordinatively unsaturated supported triosmium cluster catalysts.

CONCLUSIONS

The comparisons of the soluble and supported triosmium clusters—on the basis of (1) their structures determined by infrared spectra, (2) their reactivities in the presence of acetylene and olefins, and (3) their catalytic activities and stabilities for olefin isomerization and hydrogenation—all demonstrate that the catalytically active species on the support were unsaturated triosmium clusters analogous to [$H_2Os_3(CO)_9PPh_3$]. The results show that the catalysis was associated with the coordinatively unsaturated triosmium cluster itself, and not with other osmium species. The mechanism of the solution catalysis is well established (Fig. 3), and we infer that the mechanism involving the supported cluster is almost the same. The supported catalyst was much more stable than [$H_2Os_3(CO)_9PPh_3$], presumably because the support held the clusters apart from each other and prevented reactions such as disproportionation and decomposition. The supported clusters were also slightly more stable than [$H_2Os_3(CO)_{10}$], presumably because the support exerted a steric influence restricting formation of a cluster with a bridging vinyl ligand, which is saturated and catalytically inactive. The supported cluster was also about three times as active as [$H_2Os_3(CO)_{10}$] in solution, and we attribute the difference to the electron-donor character of the phosphine ligand, and not to any other influence of the support.

APPENDIX: NOMENCLATURE

C	concentration, mole/liter
k	reaction rate constant, variable dimensions
Ⓟ	polymer support, crosslinked polystyrene
r	reaction rate, variable dimensions
SIL	silica
SUPPORT	silica or crosslinked polystyrene

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