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# Supported Dichlorotriosmium Clusters: Catalysts for Olefin Isomerization

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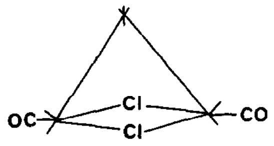
Supported osmium catalysts were prepared from $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ brought in contact with silica, phosphine-functionalized silica, and phosphine-functionalized poly(styrene-divinylbenzene). The preparations yielded physically adsorbed $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ on silica, monosubstituted, surface-bound $[Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL]$, and disubstituted, polymer-bound $[Os_3(CO)_8(\mu\text{-}Cl)_2(PPh_2\text{-}Ⓟ)_2]$. The catalysts were characterized in flow microreactors in the presence of 1-butene or ethylene + hydrogen; samples (some in the working state) were characterized with infrared and uv-visible spectroscopy. Triosmium clusters with coordinative unsaturation resulting from dissociation of CO were catalytically active for isomerization of 1-butene; mononuclear Os complexes formed in cluster fragmentation were active for ethylene hydrogenation.

## INTRODUCTION

Supported metals prepared by surface organometallic chemistry offer the prospect of being simple in structure and selective in catalysis (*1*). Much of the research in this newly developing subject has been done with organo-osmium clusters, since these are among the most stable metal clusters and consequently have a well-developed organometallic chemistry (*2*). Triosmium carbonyl clusters have been supported on polymers (*3*, *4*), on silica (*5*) functionalized with phosphine groups, on silica (*6*) functionalized with –SH groups, and on unfunctionalized oxides [including $SiO_2$ (*7–9*), $Al_2O_3$ (*8–14*), $TiO_2$ (*8*), and MgO (*15*)].

Our goals were to take advantage of the relatively high stability of triosmium clusters and the variety of their known chemistry to prepare supported metal catalysts with (initially) well-defined structures. The catalyst precursor was chosen to be $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$, which has two bridging chloride ligands which act as 3-electron donors. As a consequence, the Os–Os bond between the bridged Os atoms is opened (*16*):



The two pseudo-equatorial CO ligands in this cluster are labile and readily undergo stereospecific $^{13}CO$ exchange (*17*); ligand exchange with triphenylphosphine in solution leads to the disubstituted clusters $[Os_3(CO)_8(PPh_3)_2(\mu\text{-}Cl)_2]$ (*18*). These exchange reactions do not occur with $[Os_3(CO)_{12}]$ under comparably mild conditions.

Supported catalysts prepared from this cluster were tested as catalysts for isomerization and hydrogenation of olefins, since the coordinatively unsaturated $[H_2Os_3(CO)_{10}]$ (*19*, *20*) and its supported analogs (*3*, *4*, *14*, *21*) are catalytically active for these reactions at 70 to 100°C.

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## EXPERIMENTAL METHODS

### *Preparation of Supports*

*Preparation of passivated silica.* A sample of silica (Aerosil 380, Degussa, 340 $m^2/g$) was modified as follows, with the manipulations performed under $N_2$ and with dry solvents. The powder was evacuated to $<10^{-1}$ $N/m^2$ and added to dry methanol and refluxed for 4 h to remove strained siloxane bridges and reduce the density of residual surface -OH groups. The methanol was distilled off and the solid dried under vacuum for 8 h at 70°C. The resulting passivated silica was ready for functionalization with phosphine groups or for use in the preparation of supported osmium clusters by adsorption from solution.

*Functionalization of the silica support.* The passivated silica was held for 18 h in a refluxing solution of benzene and dioxane (1 : 1 by volume), which also contained $[(C_2H_5O)_3Si(CH_2)_2PPh_2]$ at a concentration of 1.05 mmol of silane/g of silica. The silane reacted with surface -OH groups, splitting off ethanol and giving the functionalized silica, $PPh_2(CH_2)_2$-SIL; the solid was washed with a benzene–dioxane solution and dried under vacuum at 70°C for 8 h.

### *Preparation and Functionalization of Polymer Membranes (23)*

The polymers were synthesized from the monomers styrene, divinylbenzene (DVB), and *p*-bromostyrene, which were vacuum distilled immediately prior to the synthesis. The -Br groups were partially converted into $-PPh_2$ groups, which were present in a random distribution in the polymer (*23*). Alternatively, the monomer *p*-styryldiphenylphosphine was used instead of *p*-bromostyrene, giving a block copolymer rather than the random copolymer (*23*). The polymers were prepared in the form of 11-μm-thick membranes, which are well suited to investigation by transmission infrared spectroscopy (*23*).

### *Preparation of the Molecular Metal Cluster* $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$

The cluster $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ was prepared according to literature procedures (*18, 24*). The infrared spectrum of the cluster in cyclohexane solution was in agreement with the literature (*18*).

### *Attachment of* $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ *to Supports*

The attachment of $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ to passivated silica and to phosphine-functionalized silica was carried out by refluxing a saturated solution of the cluster in benzene with the support for 2 h. The cluster (10 mg) dissolved in benzene (150 $cm^3$) was brought in contact with 300 mg of pas-

TABLE 1

Analyses of the Solids Incorporating Chlorotriosmium Clusters

| Sample number | Support | Elemental analysis (wt%) Os | Cl | Os/Cl mol/ratio |
|---|---|---|---|---|
| 1 | Silica | 0.55 | 0.092 | 1.1 |
| 2 | Phosphine-functionalized silica | 0.95 | 0.15 | 1.18 |
| 3 | Phosphine-functionalized silica | 0.52 | 0.066 | 1.47 |
| 4 | Phosphine-functionalized membrane (block-copolymer) | 9.42 | — | — |

sivated silica or phosphine-functionalized silica. With the polymer membrane (25 mg), the cluster (20 mg) was first dissolved in tetrahydrofuran (THF, 300 $cm^3$), a good swelling agent for the polymer. The resulting solids were washed thoroughly in benzene or THF, respectively, and then hexane; they were dried under vacuum at room temperature.

The samples were analyzed for Os and Cl by Schwarzkopf Microanalytical Laboratory, Woodside, NY. The results are summarized in Table 1.

### *Catalytic Reaction Experiments and Infrared Spectroscopy*

The catalytic reactions were carried out with a flow reactor system allowing simultaneous measurement of reaction rates and infrared spectra of the functioning catalyst, which was either a membrane of polymer or a wafer of silica incorporating the osmium. The reactant stream contained ethylene (Matheson) and $H_2$, or 1-butene (Phillips), fed from cylinders. The streams of $H_2$, He, and CO were purified with a trap for oxygen (supported Cu catalyst, activated in flowing $H_2$ at 200°C for 2 h before each run) and a trap for water (zeolite 5A, Linde, activated in flowing He at 400°C for 2 h).

The reactants passed through a thermostated flow reactor, which was a stainless-steel gas cell held in the sample compartment of a Nicolet 7199 Fourier transform infrared spectrophotometer. The cell held a catalyst membrane or wafer perpendicular to the beam of infrared radiation. Product gases flowed from this cell through a compensating gas cell (equivalent to the first cell, but lacking any catalyst), and conversions were so low that spectra of the gases in the two cells nearly cancelled. Therefore, the observed spectra were indicative of the catalyst membrane or wafer. Product gases flowing from the reference cell were sampled periodically and injected into an on-line gas chromatograph (Antek model 400) equipped with a flame ionization detector. The ethylene hydrogenation products were separated in a stainless-steel column (2 m × 3.2 mm) packed with Porasil C. The 1-butene hydrogenation/isomerization products were analyzed with a column of the same dimensions packed with Carbopack containing 0.19 wt% picric acid.

### *Diffuse Reflectance Spectroscopy*

Optical spectra in the uv-visible region (250–800 nm) were recorded with the diffuse reflectance technique. The instrument was a Beckman Reflectospectrometer, type DK 2A; the reflectance white standard was Aerosil 380. The quartz cell provided an effective sample thickness of 0.1 cm, which permitted the determination of $R_\infty$ (the reflectance at infinite sample thickness) in the wavelength region investigated. The spectra were evaluated by means of the Kubelka–Munk–Schuster function $F(R_\infty)$ (*25*).

## RESULTS AND DISCUSSION

### *Infrared Characterization of the Supported Clusters*

The sample obtained by refluxing the cluster in the presence of passivated silica for 2 h (sample 1) was a light-yellow powder. The infrared spectrum of this sample in the carbonyl region is compared in Table 2 (also see spectrum A, Fig. 2) with the spectrum of the molecular cluster in cyclohexane solution and with that of crystals of this cluster in a physical mixture with silica. Since the spectra of the molecular and supported osmium species in the carbonyl region are almost identical, we conclude that the cluster was physically adsorbed—intact—on the surface of the passivated silica.

Samples 2 and 3, prepared from $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ and phosphine-functionalized silica, gave an infrared spectrum significantly different from that of the molecular cluster (Fig. 1, Table 2). The spectrum of the supported species is different from that of a diphosphine-substituted cluster (Table 2). There is no reported infrared

TABLE 2

Infrared Spectra of Molecular and Supported Triosmium Clusters

| Sample number | Compound | $\nu_{CO}$ (cm$^{-1}$) | | | | Ref. |
|---|---|---|---|---|---|---|
| | $Os_3(CO)_{10}Cl_2$[a] | 2114w | 2084vs | 2071s | 2029vs | (*18*) |
| | | 2016s | 1993w | 1988w | | |
| | $Os_3(CO)_{10}Cl_2$[a] | 2116w | 2081vs | 2069s | 2027vs | This work |
| | | 2015s | 1993sh | 1989m | | |
| | $Os_3(CO)_{10}Cl_2/SiO_2$ | 2117w | 2088vs | 2072s | 2030vs | This work |
| | (Physical mixture, wafer) | 2020s | 1989m | | | |
| 1 | $Os_3(CO)_{10}Cl_2/SiO_2$ | 2116w | 2085s | 2069s | 2029vs | This work |
| | (Reflux in benzene, wafer) | 2018s,sh | 1992w | | | |
| 2,3 | $Os_3(CO)_9Cl_2PPh_2(CH_2)_2SIL$ | 2102s | 2081m | 2068s | 2018vs | This work |
| | | 1986w | 1977sh | | | |
| | $Os_3(CO)_8Cl_2(PPh_3)_2$[a] | 2079s | 2014s | 2004s | 1967w | (*18*) |
| | | 1943m | | | | |
| 4 | $Os_3(CO)_8Cl_2(PPh_2\text{-Ⓟ})_2$ | 2096sh | 2073s | 2036sh | 2007s | This work |
| | (Block copolymer) | 1997s | 1959w | 1939m | | |
| 5 | $Os_3(CO)_{10}Cl_2/PPh_2\text{-Ⓟ}$ | 2096w | 2073m | 2060sh | 2029sh | This work |
| | (Random copolymer) | 2007s | 1994s | 1955sh | 1940w | |

[a] solvent cyclohexane.

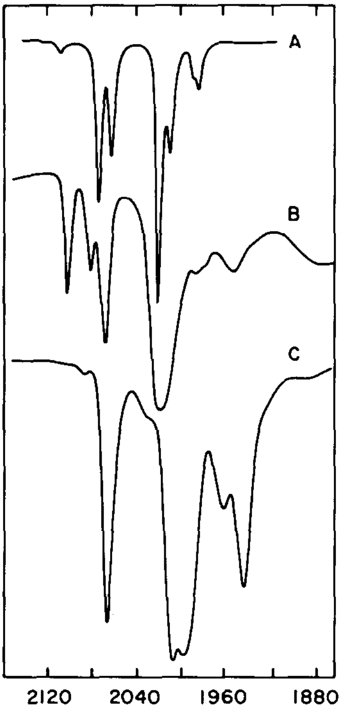


FIG. 1. Infrared spectra of supported triosmium clusters in the carbonyl region: (A) $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ in cyclohexane; (B) $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ (sample 2 or 3); (C) $Os_3(CO)_8(\mu\text{-}Cl)_2(PPh_2\text{-Ⓟ})_2$ (sample 4).

spectrum of the monophosphine-substituted cluster, apparently because in solution in the presence of excess triphenylphosphine, the cluster has a high reactivity determined by the lability of two CO ligands resulting from the presence of the bridging Cl ligands, and the disubstituted cluster forms rapidly.

We infer that the infrared spectra of the osmium species attached to the phosphine-functionalized silica indicate the monosubstituted cluster $Os_3(CO)_9Cl_2PPh_2(CH_2)_2$-SIL, since substitution of CO by phosphine ligands usually shifts the carbonyl bands to lower frequencies {see, for example, the spectra of $[Os_3(CO)_{12}]$, $[Os_3(CO)_{11}PPh_3]$, $[Os_3(CO)_{10}(PPh_3)_2]$, etc. (*18*)}. The greater the number of phosphine ligands, the lower the frequency of the CO band. Consistent with this pattern, the carbonyl bands of the supported cluster inferred to be $Os_3(CO)_9$ $Cl_2PPh_2(CH_2)_2$-SIL fall between those of the unsubstituted and disubstituted clusters (Table 2). This structural inference is consistent with the fact that the phosphine-functionalized silica had a low phosphorus content (0.12 wt%), corresponding to 0.06

ligands/nm$^2$ and an average spacing of 4.1 nm between phosphine groups; we infer that site isolation prevented disubstitution of most of the clusters.

The samples prepared from $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ and the phosphine-functionalized polymers gave different infrared spectra for block (Sample 4) and random copolymers (Sample 5) (Table 2). Attachment of the cluster to the block copolymer gave a species with a spectrum (Fig. 1) having carbonyl bands indicative of disubstitution, i.e., $[Os_3(CO)_8Cl_2(PPh_2\text{-Ⓟ})_2]$ (Table 2). The spectrum of the sample prepared with the random copolymer is not so straightforwardly interpreted. The spectra are consistent with the proposal that both mono- and disubstituted clusters were formed; for example, the band at 2096 cm$^{-1}$ may be compared with the band at 2102 cm$^{-1}$ for the cluster attached to phosphine-functionalized silica (an indication of a monosubstituted cluster). The bands at 2060 and 2029 cm$^{-1}$ also suggest the formation of a monosubstituted cluster. We note that the random copolymer still contained about 40% of the Br groups originally present; these may be involved in nucleophilic attack on the cluster with subsequent cluster fragmentation (*4*).

Shoulders at 2096 and 2036 cm$^{-1}$ in the spectrum of the cluster attached to the block copolymer indicate small amounts of monosubstituted cluster present with the disubstituted cluster. When the sample was heated, these shoulders decreased perceptibly at about 90°C, and they had vanished when the temperature reached about 120°C, indicating the formation of the disubstituted cluster at higher temperatures. Similar results have been reported for monosubstituted iridium clusters attached to phosphine-functionalized silica, which gives the di- and even the trisubstituted clusters at higher temperatures (*26*).

### *Behavior of Supported Clusters under Reaction Conditions*

*$Os_3(CO)_{10}(\mu\text{-}Cl)_2/SiO_2$ (Sample 1).* Sample 1 was tested as a 1-butene isomerization catalyst at 45 to 160°C with a partial pressure of $4.2 \times 10^4$ N m$^{-2}$ of 1-butene in helium. Exposure of the catalyst to flowing 1-butene even at 45°C resulted in changes in the infrared spectrum, as shown by comparison of the initial spectrum A with spectrum B in Fig. 2. The intensities of the bands at 2116, 2085, and 2069 cm$^{-1}$, which are typical of the adsorbed $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ cluster (Fig. 1, spectrum A), are reduced in intensity, and new bands are present at 2106 and 2096 cm$^{-1}$. Subsequent exposure of the sample to CO at 45°C led to a rapid restoration of the original spectrum (spectrum C, Fig. 2). We attribute this behavior to a replacement of one or two labile

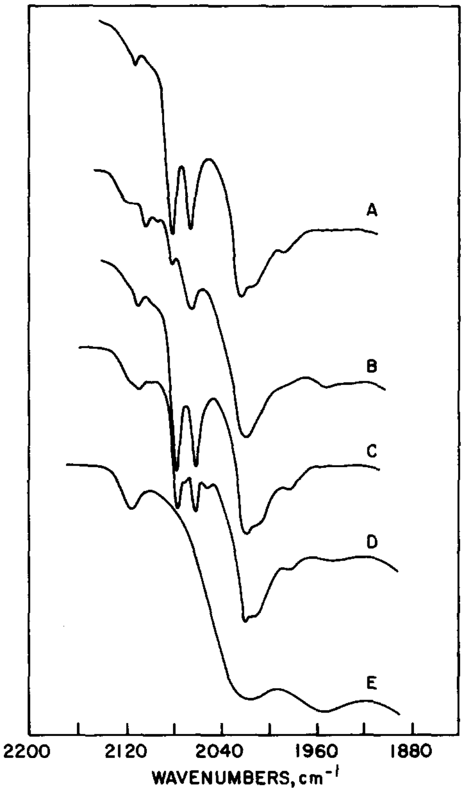


FIG. 2. Changes in the infrared spectra of $Os_3(CO)_{10}(\mu\text{-}Cl)_2/SiO_2$ (sample 1) in the carbonyl region: (A) initial spectrum; (B) after flowing 1-butene at 45°C for 2h; (C) after carbonylation at 45°C for ½ h; (D) after flowing 1-butene at 65°C for 4 h and subsequent carbonylation at 65°C for ½ h; (E) after flowing 1-butene at 165°C for 6 h.

CO ligands by 1-butene, this process being easily reversed on reexposure of the sample to CO. Rates of catalytic isomerization were immeasurably low at these low temperatures.

Reexposure of this sample to the CO after treatment with 1-butene for 4 h at 65°C led to spectrum D of Fig. 2. Under these conditions, irreversible changes occurred in the spectrum as indicated by the appearance of new bands at 2076 and 2058 cm$^{-1}$. These bands can be attributed to surface-bound clusters of the type $Os_3(CO)_{10}(\mu\text{-Cl})(\mu\text{-O-SIL})$ or $Os_3(CO)_{10}(\mu\text{-O-SIL})_2$, which may be formed via a nucleophilic attack involving one or two silanol groups. The molecular cluster $[Os_3(CO)_{10}(\mu\text{-OPh})_2]$ has an infrared spectrum (*8*) with bands at 2108(w), 2076(vs), 2058(s), 2018(vs), 1999(s), and 1986(m) cm$^{-1}$, which is very similar to the one observed for the sample suggested to incorporate the surface-bound oxygen-bridged cluster. Bands at 2076 and 2058 cm$^{-1}$ were clearly observed at intermediate temperatures; the two other strong bands of the phenoxy-bridged cluster at 2018 and 1999 cm$^{-1}$ may be superimposed on the bands of the original chloro-osmium cluster at 2016 and 1993 cm$^{-1}$.

Once the oxygen-bridged species had formed on the silica surface, it rapidly decomposed at increasing temperatures (>125°C), as indicated by infrared bands at 2121, 2024, and 1958 cm$^{-1}$. A typical spectrum, obtained after heating the sample to 165°C, is shown in Fig. 2, spectrum E. The three observed bands can be assigned to mononuclear di- and tricarbonyl species (*11, 13*).

Although dissociation of the labile CO ligands from the cluster and coordination of 1-butene were observed at 45°C, measurable catalytic isomerization activity was not detected at temperatures <90°C. The 1-butene conversion increased slightly with time on stream at temperatures <130°C, and steady-state conversions were observed after approximately 3 h. *Cis/trans* ratios of the product 2-butene were <1 and decreased with temperature and with time on stream during the initial 3-h period.

Since the temperature range of onset of measurable catalytic activity coincides with the temperature range in which chemical transformations of the initially physisorbed cluster were first detected, the characterization of the catalytically active species is difficult. The 1-butene isomerization activity at low temperatures might be speculatively attributed to the intact cluster activated by loss of the labile CO ligands. The cluster fragmentation at higher temperatures, leading to formation of mononuclear osmium carbonyl complexes, corresponds to reduced isomerization activity and increased hydrogenation activity; we speculate that the mononuclear complexes are active for ethylene hydrogenation.

*$Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ (Samples 2 and 3).* The infrared spectra of sample 2 during exposure to 1-butene at 4.2 × 10$^4$ N m$^{-2}$ at 45°C are shown in Fig. 3. The initial spectrum changed in an atmosphere of 1-butene even at room temperature; the change was more rapid at 45°C. A new band at 2090 cm$^{-1}$ developed with increasing time on stream as the characteristic bands of the original cluster at 2102 and 2068 cm$^{-1}$ decreased in intensity (spectrum B, Fig. 3). Simultaneously, the band at 2018 cm$^{-1}$ was shifted to 2015 cm$^{-1}$. Exposure of the sample to an atmosphere of He or $H_2$ at 45°C following the exposure to 1-butene caused a decrease in the intensity of the band at 2090 cm$^{-1}$ (spectrum C, Fig. 3). Subsequent exposure to CO at 45°C restored the original spectrum of the carbonylated cluster (spectrum D, Fig. 3). These changes continued to be reversible for >2 days.

When this sample was held in 1-butene for 24 h at 45°C, the bands characteristic of the original cluster vanished. The spectrum in the carbonyl region then showed an intense band at 2068 cm$^{-1}$, an intense broad band at 2015 cm$^{-1}$, and a shoulder at 1957 cm$^{-1}$. We infer that this infrared spectrum indicates the $\pi$-coordination of 1-butene to the osmium after loss of the labile CO li-

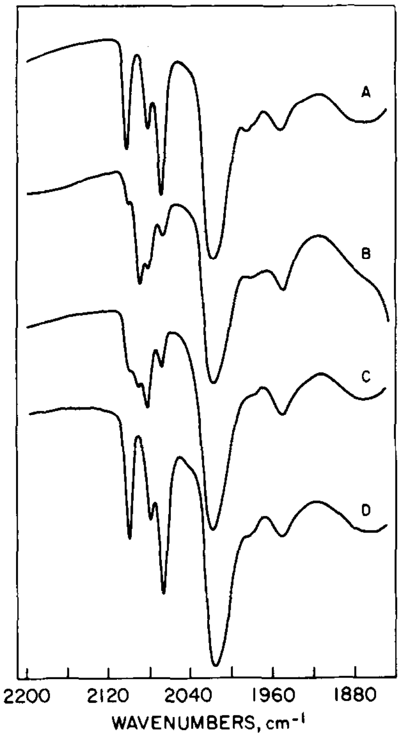


FIG. 3. Changes in the infrared spectra of $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ (sample 2) in the carbonyl region: (A) initial spectrum; (B) after flowing 1-butene at 45°C for 2 h; (C) after flowing He or $H_2$ at 45°C for ½ h; (D) after carbonylation at 45°C for ½ h.

gand to form a surface-bound cluster of the type $Os_3(CO)_8(\mu\text{-}Cl)_2(C_4H_8)PPh_2(CH_2)_2$ SIL.

The infrared spectrum of this species is expected to include features similar to those of a disubstituted dichloroosmium cluster, since both species incorporate the same $Os_3(CO)_8$ unit. The data bear out the expectation, as can be seen by comparison of the spectrum with that of sample 4, $Os_3(CO)_8(\mu\text{-}Cl)_2(PPh_2\text{-}Ⓟ)_2$ (Table 2), except that the bands are located at higher frequencies for the former species. The intense bands at 2073 cm$^{-1}$ and at 2007 and 1997 cm$^{-1}$ observed for sample 4 should correspond to the intense band at 2086 cm$^{-1}$ and the broad unresolved band at 2015 cm$^{-1}$ of the above species, respectively. [The shoulder at 2096 cm$^{-1}$ occurring in the spectrum of sample 4 is attributed to the presence of some mono-substituted clusters in sample 4 (Table 2).]

The coordination of 1-butene after dissociation of the labile CO ligand may be considered to be the first step in a catalytic cycle for 1-butene isomerization, although the 1-butene conversion at 45°C is still negligibly slow. The bonding of 1-butene to the cluster is weak, as shown by its easy removal in He or $H_2$.

Heating of sample 3 to 85°C under 1-butene did not lead to any further significant change in the spectrum. At temperatures >85°C, however, the intensity of the band at 2090 cm$^{-1}$ decreased again. The spectrum then was closely similar to the one obtained for the same sample under He or $H_2$ at lower temperatures (cf. spectrum C, Fig. 3), indicating dissociation of the 1-butene ligand at these temperatures, even in the presence of 1-butene in the gas phase.

Further changes in the spectrum of this sample in the presence of 1-butene occurred with increasing temperature. When the temperature reached 125°C, weak bands appeared at 2051 and 1997 cm$^{-1}$; at higher temperatures these disappeared. These carbonyl bands might be attributed to dinuclear osmium species analogous to the compound $[Os(CO)_2PPh_3Cl_2]_2$ (*18*), which gives rise to carbonyl bands at 2051 and 1981 cm$^{-1}$. When the temperature reached 145°C, new shoulders were observed at 2038, 2027, and 1968 cm$^{-1}$. The bands at 2038 and 1968 cm$^{-1}$ may be an indication of the formation of a mononuclear phosphine-substituted surface analog of the complex $[Os(CO)_2(PPh_3)_2Cl_2]$, the latter giving rise to carbonyl bands at 2043 and 1971 cm$^{-1}$ (*27*).

After sample 3 had been exposed to 1-butene at 165°C for 2 h, a spectrum was observed with bands at 2080(s), 2024(s,sh), 2013(s,sh), and 1958 cm$^{-1}$. Subsequent exposure of the sample to CO at the same temperature led to the appearance of strong bands at 2073 and 2005 cm$^{-1}$, as the bands at 2080 and 2013 cm$^{-1}$ almost disappeared. These observations are tentatively interpreted as indications of a severe decarbonylation leading to the formation of open coordination sites, where butene or perhaps additional phosphine ligands may bond. Hence, the bands at 2073 and 2005 $cm^{-1}$ can be attributed to a disubstituted surface cluster $Os_3(CO)_8(\mu\text{-}Cl)_2(PPh_2(CH_2)_2SIL)_2$. This assignment is based on the comparison with the characteristic spectrum of the diphosphine-substituted cluster attached to polymer supports (Table 2).

Since the average Os–Os bond strength in $[Os_3(CO)_{12}]$, for example, is only 130 kJ $mol^{-1}$ as compared to the average Os–CO bond strength of 188 kJ $mol^{-1}$ (*28*), simultaneous cluster fragmentation with Os–Os bond scission cannot be completely excluded.

In separate experiments, the thermal stability of $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ was investigated by diffuse reflectance spectroscopy. The $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ cluster in cyclohexane shows an electronic transition at 348 nm. A band at 330 nm is reported for $[Os_3(CO)_{12}]$ and attributed to a $\sigma \rightarrow \sigma^*$ transition (*29*), i.e., to a d–d transition which is typical of metal–metal bonds in the cluster framework. We infer that the band observed for $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ at 348 nm is to be attributed analogously to a $\sigma \rightarrow \sigma^*$ transition in the cluster framework. As shown in Fig. 4, the initial sample $Os_3(CO)_{10}(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ gives rise to a strong absorption at 350 nm, which corresponds to the $\sigma \rightarrow \sigma^*$ transition mentioned above for $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$.

In addition, there is a weaker band in the uv-visible spectrum at 305 nm, which is attributed to surface clusters which have lost the labile CO ligand. Removal of a CO ligand should lead to an increased energy separation of the frontier molecular orbitals of the Os fragments of which the cluster is built up, and consequently to a blue-shift of the $\sigma \rightarrow \sigma^*$ transition (*29, 30*). This assignment is supported by the temperature dependence of the two bands. Evacuation of the sample at 65 and 84°C (spectrum B, Fig. 4) reduced the intensity of the band at 350 nm and simultaneously increased that of the band at 305 nm. Reexposure of the sample to CO immediately regenerated the initial spectrum (spectrum C, Fig. 4). The same behavior was also observed during heating of the sample in an ethylene atmosphere. Evacuation at 105°C (spectrum D, Fig. 4) and recarbonylation (spectrum E, Fig. 4) resulted in irreversible changes in the spectrum. The intensity of the 350-nm band was significantly reduced, and a new shoulder appeared at 373 nm. This change may be associated with the formation of a diphosphine-substituted cluster and/or fragmentation products. We conclude that the electronic spectra support the conclusions deduced from the infrared spectra.

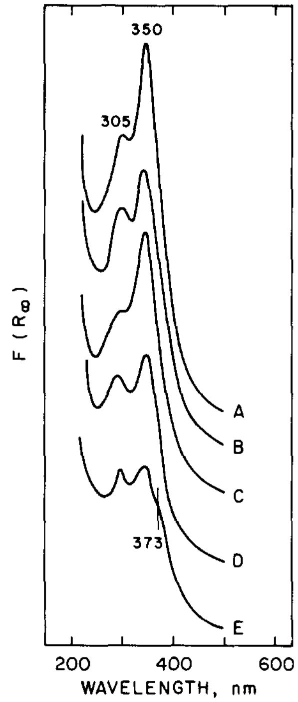


FIG. 4. Diffuse reflectance spectra of $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$: (A) initial sample; (B) after evacuation at 85°C for 8 h; (C) After subsequent exposure to CO ($10^5$ N $m^{-2}$) at 25°C for 10 h. (D) After evacuation at 105°C for 16 h; (E) After subsequent exposure to CO ($10^5$ N $m^{-2}$) at 25°C for 10 h.

The sample $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ showed measurable catalytic activity for isomerization of 1-butene at $4.2 \times 10^4$ N

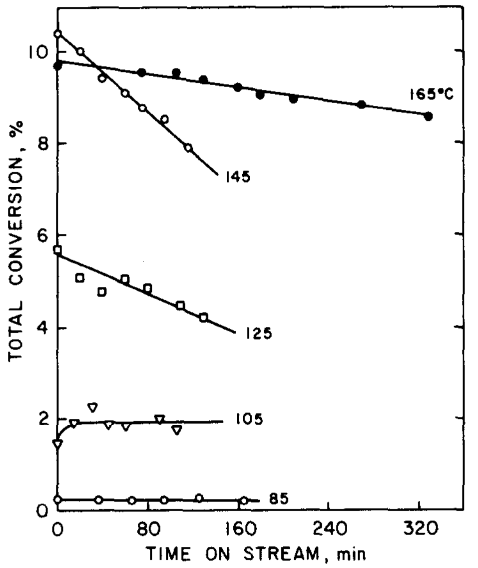


FIG. 5. Time dependence of the 1-butene isomerization activity of $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ (sample 3). The pressure was atmospheric; the mass of catalyst was 200 mg, and the feed flow rate was 0.57 $cm^3$ at STP/s.

$m^{-2}$ in He at >60°C (Fig. 5). Steady-state activity was achieved at ≤120°C, and a continuous decrease in activity was observed with time on stream at higher temperatures (Fig. 5). Initial conversions increased with temperature up to 145°C and then declined at higher temperatures. This behavior implies that there was a transformation of catalytically active species into less active species at the higher temperatures; the decrease in activity observed with time on stream at 165°C was less severe than at lower temperatures. The *cis*/*trans* ratio of the product 2-butene decreased with temperature (and time on stream) from about 1.2 at 80°C to 0.35 at 165°C.

The activity of $Os_3(CO)_9(\mu\text{-}Cl)_2PPh_2(CH_2)_2SIL$ for ethylene hydrogenation (with $8.6 \times 10^4$ N $m^{-2}$ of $H_2$ and $2.1 \times 10^4$ N $m^{-2}$ of $C_2H_4$) was extremely low at temperatures <100°C. Hydrogenation activity at 105°C increased with time on stream while isomerization activity declined under similar conditions. Only at 145°C did hydrogenation activity start to decline with time on stream.

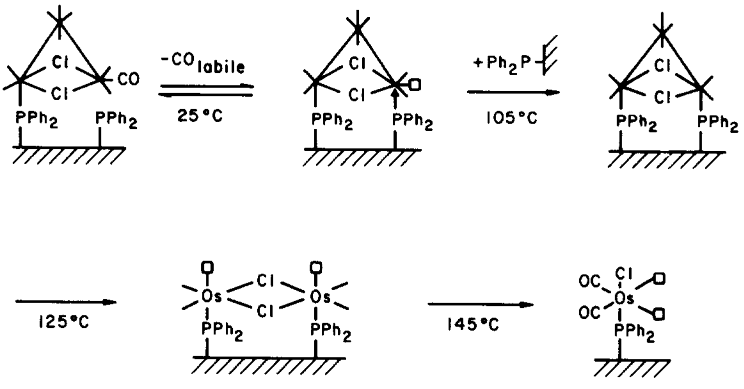
The spectroscopic characterization of this sample suggested that the supported chloro-osmium clusters were stable at temperatures up to approximately 120°C. In this range, reversible dissociation of the labile CO ligand and coordination of butene were observed. Steady-state isomerization activity was observed in the same temperature range, whereas hydrogenation activity was negligible or very low. Therefore, we infer that the intact cluster was the catalytically active species for 1-butene isomerization in this temperature range. Since the cluster can provide only one free coordination site by loss of the one labile CO ligand, it apparently has no hydrogenation activity.

At intermediate temperatures (near 120°C), the beginning of cluster fragmentation was suggested by the infrared spectra. The fragmentation products may be responsible for ethylene hydrogenation (which was first observed at 105°C), and they also appear to have a lower isomerization activity than the initial cluster. The final fragmentation products—inferred to be mononuclear osmium complexes—which are the dominant species at >140°C, appear to have significant hydrogenation activity but much lower isomerization activity than the initial coordinatively unsaturated cluster. Scheme 1 is a summary of the tentatively suggested transformation of the surface-bound organometallics.

$Os_3(CO)_8(\mu\text{-}Cl)_2(PPh_2\text{-}\textcircled{P})_2$ *(Sample 4)*. This sample has no labile CO ligand. Experiments showed it to have negligible activity for 1-butene isomerization at temperatures <125°C and for ethylene hydrogenation at temperatures <160°C. No changes in the infrared spectra were observed with the sample in flowing 1-butene at temperatures <125°C. The results demonstrate that the coordinatively saturated cluster is relatively stable and catalytically inactive.

## CONCLUSIONS

1. The supported triosmium clusters prepared from $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$ can be made coordinatively unsaturated—and therefore



SCHEME 1

catalytically active for olefin isomerization—by dissociation of CO labilized by the bridging chloride ligands.

2. If this labilization of the CO ligands is not provided, as, for example, in the $Os_3(CO)_8(\mu\text{-}Cl)_2(PPh_2\text{-}\textcircled{P})_2$ sample, open coordination sites can be created only by Os–Os or Os–L bond scission under relatively severe conditions leading to cluster fragmentation even on such inert supports as the block copolymer.

3. The stability of supported clusters is strongly dependent on the nature of the support surface. The phosphine ligands attached to the silica surface stabilized the cluster against nucleophilic attack by silanol groups, whereas even the passivated silica was found to be reactive with $[Os_3(CO)_{10}(\mu\text{-}Cl)_2]$.

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## REFERENCES

1. Gates, B. C., and Lieto, J., *CHEMTECH* **195,** 248 (1980).
2. Deeming, A. J., *in* "Transition Metal Clusters" (B. F. G. Johnson, Ed.), p. 391. Wiley, Chichester, 1980.
3. Freeman, M. B., Patrick, M. A., and Gates, B. C., *J. Catal.* **73,** 82 (1982).
4. Nguini Effa, J.-B., Lieto, J., and Aune, J.-P., *J. Mol. Catal.* **15,** 367 (1982).
5. Brown, S. C., and Evans, J., *J. Chem. Soc. Chem. Commun.* 1053 (1978).
6. Castrillo, T., Knözinger, H., and Wolf, M., *Inorg. Chim. Acta* **45,** L 235 (1980).
7. Barth, R., Gates, B. C., Zhao, Y., Knözinger, H., and Hulse, J., *J. Catal.* **82,** 147 (1983).
8. Psaro, R., Ugo, R., Zanderighi, G. M., Besson, B., Smith, A. K., and Basset, J. M., *J. Organomet. Chem.* **213,** 215 (1981).
9. Deeba, M., and Gates, B. C., *J. Catal.* **67,** 303 (1981).
10. Watson, P. L., and Schrader, G. L., *J. Mol. Catal.* **9,** 129 (1980).
11. Knözinger, H., and Zhao, Y., *J. Catal.* **71,** 337 (1981).
12. Deeba, M., Streusand, B. J., Schrader, G. L., and Gates, B. C., *J. Catal.* **69,** 218 (1981).
13. Knözinger, H., Zhao, Y., Tesche, B., Barth, R., Epstein, R., Gates, B. C., and Scott, J. P., *Faraday Disc. Chem. Soc.* **72,** 53 (1981).
14. Li, X.-J., Onuferko, J. H., and Gates, B. C., *J. Catal.* **85,** 176 (1984).
15. Deeba, M., Scott, J. P., Barth, R., and Gates, B. C., *J. Catal.* **71,** 373 (1981).
16. Allen, V. F., Mason, R., and Hitchcock, P. B., *J. Organomet. Chem.* **140,** 297 (1977).
17. Bryan, E. G., Johnson, B. F. G., and Lewis, J., *J. Chem. Soc. Chem. Commun.* 329 (1977).
18. Deeming, A. J., Johnson, B. F. G., and Lewis, J., *J. Chem. Soc.* (*A*) 897 (1970).
19. Deeming, A. J., and Hasso, S., *J. Organomet. Chem.* **114,** 313 (1976).
20. Keister, J. B., and Shapley, J. R., *J. Amer. Chem. Soc.* **98,** 1056 (1976).
21. Brown, S. C., and Evans, J., *J. Mol. Catal.* **11,** 143 (1981).
22. Lewis, J., and Johnson, B. F. G., *Gaz. Chim. Ital.* **109,** 271 (1979).
23. Minkiewicz, J. V., Milstein, D., Lieto, J., Gates, B. C., and Albright, R. L., *ACS Symp. Ser.* **192,** 9 (1982).

*24.* Johnson, B. F. G., Lewis, J., and Kilty, P. A., *J. Chem. Soc.* (*A*) 2859 (1968).

*25.* Kortüm, G., "Reflexionsspektroskopie." Springer, Berlin, 1969.

*26.* Castrillo, T., Knözinger, H., Wolf, M., and Tesche, B., *J. Mol. Catal.* **11,** 151 (1981).

*27.* Hales, L. A. W., and Irving, R. J., *J. Chem. Soc.* (*A*) 1932 (1967).

*28.* Muetterties, E. L., Rhodin, T. N., Band, E., Brucker, C. F., and Pretzer, W. R., *Chem. Rev.* **79,** 91 (1979).

*29.* Tyler, D. R., Levenson, R. A., and Gray, H. B., *J. Amer. Chem. Soc.* **100,** 7888 (1978).

*30.* Schilling, B. E. R., and Hoffmann, R., *J. Amer. Chem. Soc.* **101,** 3456 (1979).