J. Am. Chem. Soc. **1988**, *110*, 2783-2787

Surface Organometallic Chemistry: Hydrogenation of Ethylene with $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi{<})$ and $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$. Evidence for Cluster Catalysis

Agnès Choplin, Bernard Besson, Lindora D'Ornelas, Roberto Sanchez-Delgado,† and Jean-Marie Basset*

Contribution from the Institut de Recherches sur la Catalyse, Laboratoire Propre du CNRS, Conventionné à l'Université Claude Bernard Lyon I, 2 Avenue Albert Einstein, 69626 Villeurbanne Cédex, France. *Received June 3, 1987*

Abstract: The silica-supported cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi{<})$ (**1**) efficiently catalyzes the hydrogenation of ethylene under mild reaction conditions; the reaction is zero order in ethylene and first order in hydrogen. The reaction kinetics as well as volumetric and IR studies of the interaction of **1** with C_2H_4, H_2, and CO indicate a mechanism involving the intact triosmium framework in all the elementary steps conforming the catalytic cycle. The facile $3e^- \rightleftharpoons 1e^-$ interconversion of surface-oxygen ligands provides the appropriate energy balance for cluster catalysis without fragmentation. The reactivity of the molecular analogue $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ (**2**) toward C_2H_4 and H_2 has also been studied by IR and NMR spectroscopy, and the data are in agreement with the proposed hydrogenation cycle for **1**. However, in contrast with **1**, **2** is quickly transformed in solution under catalytic conditions with loss of phenol and formation of $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$. This difference of behavior indicates the stabilizing influence of the silica support.

One of the major challenges in homogeneous catalysis by metal clusters[1] is the stabilization of coordinatively unsaturated species without fragmentation into lower nuclearity complexes or into colloidal metal particles.[2] A possible approach toward the solution of this problem is the stabilization of the molecular cluster by direct attachment to the surface of an oxide, which plays the role of a rigid ligand.

We have proposed that the surface oxygen atoms of silica can behave as 3- (LX) or 1-electron (X) ligand toward a cluster frame;[3] this LX $\rightleftharpoons$ X interconversion provides a low-energy pathway toward stable electron-deficient clusters, capable of effecting a catalytic cycle.

Reaction of $Os_3(CO)_{12}$ with the silanol group of silica yields the grafted cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi{<})$ (**1**),[4a-f] which has been characterized by a variety of techniques and for which the surface structure is now well accepted, although some controversy still exists for the case of alumina.[4g] Also, the molecular analogue $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiEt_3)$ has been structurally characterized, and its spectroscopic data are in agreement with those of the surface species.[5] It is thus reasonable to assume that the surface oxygen atoms in **1** behave as 3-electron ligands, leading to an electron-precise surface cluster.

In this paper we describe the catalytic properties of **1** in the hydrogenation of ethylene, as well as mechanistic studies on this supported cluster, and on its molecular analogue $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ (**2**); the evidence presented herein is in agreement with a catalytic cycle involving only cluster intermediates derived from **1**. A preliminary communication on part of this work has already appeared.[6]

Results and Discussion

When a C_2H_4/H_2 (1:10) mixture is put in contact with the supported cluster (**1**) at 80 °C in a closed vessel, hydrogenation of the double bond takes place. Several hydrogenation runs may be performed up to ca. 100% ethylene conversion without any appreciable loss in catalytic activity. No changes in the IR spectrum of the solid (ν_{CO} region) could be detected after this treatment.

These results suggest the possibility of a cluster-catalyzed reaction; however, catalysis by metal particles or mononuclear species in very small amounts (undetectable by IR spectroscopy) cannot be ruled out solely on this basis.

Consequently, in order to establish the nature of the active species and the elementary steps involved in the hydrogenation reaction, further kinetic and mechanistic studies have been carried out on the supported cluster **1**, as well as on the model compound $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ (**2**).

Kinetics of the Catalytic Hydrogenation of Ethylene with 1. The hydrogenation reaction was carried out at 90 °C and atmospheric pressure (7.3×10^3 Pa C_2H_4, 4.9×10^4 Pa H_2, 4.4×10^4 Pa He) in a flow system (differential reactor). The conversion was found to be proportional to contact time up to 5×10^{-3} g min mL^{-1}; above this value the linear relationship was no longer observed. Consequently, the kinetics of the hydrogenation reaction were studied at a contact time of 2.5×10^{-3} g min mL^{-1}, for which a steady-state activity was attained without an induction period, corresponding to a turnover frequency of 4×10^{-2} mol (mol cluster)$^{-1}$ s^{-1}. No appreciable change of activity could be detected after 1 week of operation, corresponding to an overall turnover of ca. 24 000.

The rate dependence on ethylene and hydrogen partial pressures is shown in Figure 1; the reaction is zero order with respect to ethylene and first order in hydrogen, i.e. $r = kp_{H_2}$ ($k = 2.4 \times 10^{-12}$ mol s^{-1} Pa^{-1}). The apparent activation energy in the temperature range 77–99 °C is 32 kJ mol^{-1}. Addition of CO strongly inhibits the catalysis, but the catalytic activity is recovered without an

---

† On leave from IVIC, Caracas.

(1) Whyman, R. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter VIII, and references therein. Jackson, S. D.; Wells, P. B.; Whyman, R.; Worthington, P. *Catalysis (London)* **1981**, *4*, 74.

(2) (a) Sanchez-Delgado, R. A.; Andriollo, A.; Puga, J.; Martin, G. *Inorg. Chem.* **1987**, *26*, 1867. (b) Mutin, R.; Abboud, W.; Basset, J. M.; Sinou, D. *J. Mol. Catal.* **1985**, *33*, 47. (c) Mani, D.; Vahrenkamp, H. *J. Mol. Catal.* **1985**, *29*, 305. (d) King, R. B.; Ohene, F. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 135. (e) Slegeir, W. A. R.; Sapienza, R. S.; Easterling, B. *ACS Symp. Ser.* **1981**, *No. 152*, 325. (f) Warren, B. K.; Dombeck, B. D. *J. Catal.* **1983**, *79*, 334. (g) Suss-Fink, G.; Herrmann, G. *J. Chem. Soc., Chem. Commun.* **1985**, 735. (h) Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4669. (i) Doi, Y.; Koshizuka, K.; Keii, T. *Inorg. Chem.* **1982**, *21*, 2732.

(3) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95.

(4) (a) Besson, B.; Moraweck, B.; Smith, A. K.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 569. (b) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215. (c) Deeba, M.; Gates, B. C. *J. Catal.* **1981**, *67*, 303. (d) Deeba, M.; Streusand, B. J.; Schrader, G. L.; Gates, B. C. *J. Catal.* **1981**, *69*, 218. (e) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1123. (f) Cook, S. L.; Evans, J.; McNulty, G. S.; Greaves, G. N. *J. Chem. Soc., Dalton Trans.* **1986**, 7. (g) Alexiev, V. D.; Binsted, N.; Evans, J.; Greaves, G. N.; Price, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 395.

(5) D'Ornelas, L.; Choplin, A.; Basset, J. M.; Hsu, L.-Y.; Shore, S. G. *Nouv. J. Chim.* **1985**, *9*, 155.

(6) Besson, B.; Choplin, A.; D'Ornelas, L.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 843.

0002-7863/88/1510-2783$01.50/0

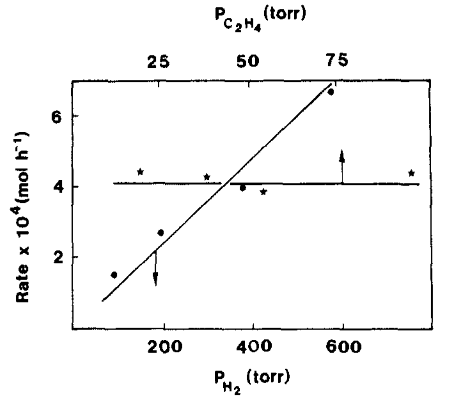


Figure 1. Hydrogenation of ethylene catalyzed by 1: rate dependence on (★) ethylene and (O) hydrogen partial pressures. See text for reaction conditions.

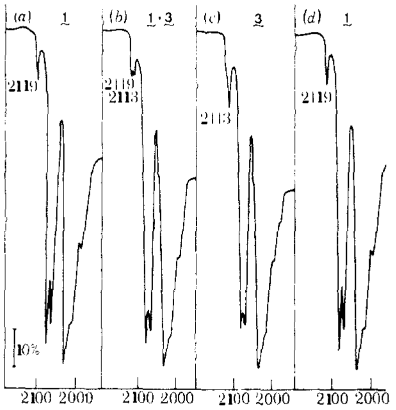


Figure 2. Key: (a) IR spectrum (ν_{CO} region) of 1; (b) after treatment with C_2H_4 [60 °C (3.3 × 10^4 Pa), 1 h]; (c) after treatment with C_2H_4 (80 °C, 1 h); (d) after evacuation of (c) [80 °C (10^{-2} Pa), 3 h].

induction period on removing CO from the gas stream.

Further information was obtained by studying the reaction of 1 with the individual components of the hydrogenation mixture as follows.

Interaction of 1 with C_2H_4, H_2, and CO. The IR spectrum of 1 in the ν_{CO} region remains unchanged upon prolonged contact with ethylene (3.4 × 10^4 Pa) at room temperature. However, several interesting changes take place between 60 and 80 °C, as shown in Figure 2. After 5 h at 80 °C the band at 2119 cm^{-1} has been replaced by a new one at 2113 cm^{-1}; also, a modification of the intensity ratio of the bands at 2079 and 2066 cm^{-1} is observed (Figure 2c). The resulting species (3) is stable under vacuum at room temperature, but the spectral changes are completely reversed at 80 °C under vacuum for 3 h (Figure 2d), indicating the quantitative regeneration of 1. This cycle may be repeated several times without any evidence for cluster degradation on the surface.

Consistent with the IR observations, volumetric measurements indicate that ethylene is not adsorbed onto 1 at room temperature, but at 80 °C an ethylene adduct 3 is formed, according to the equilibrium shown in eq 1.

$$\underset{1}{Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\lessdot)} + C_2H_4 \rightleftharpoons \underset{3}{Os_3(CO)_{10}(C_2H_4)(\mu\text{-}H)(OSi\lessdot)} \quad (1)$$

The equilibrium constant K has a value of 1.5 × 10^{-5} Pa^{-1}, corresponding to a transformation of ca. 20% of 1 into 3 at 80 °C (1.4 × 10^4 Pa C_2H_4).

In a separate experiment we have observed that the ν_{CO} pattern of 1 is unmodified by a CO atmosphere. In agreement with this, volumetric measurements show that only about 2% of the CO is adsorbed onto 1 at 80 °C (8.6 × 10^3 Pa). It may seem strange that 1 should form an adduct with ethylene at 80 °C and not with

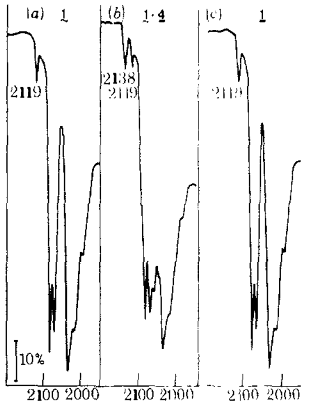


Figure 3. Key: (a) IR spectrum (ν_{CO} region) of 1; (b) after treatment with H_2 [100 °C (3.2 × 10^4 Pa), 3 h]; (c) after evacuation of (b) [100 °C (10^{-2} Pa)].

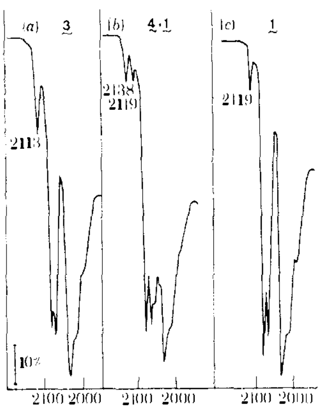
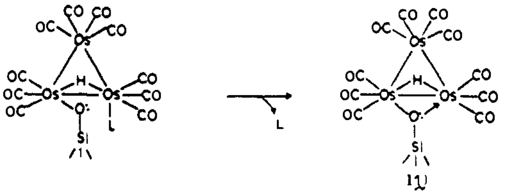


Figure 4. Key: (a) IR spectrum (ν_{CO} region) of 3; (b) after treatment with H_2 [25 °C (3.2 × 10^4 Pa)]; (c) after evacuation of (b) [25 °C (10^{-2} Pa)].

CO, which is generally assumed to be a better ligand. In fact, the reverse reaction has to be considered (eq 2).



(2)

When L = CO, which is highly π-acidic and not particularly bulky, nucleophilic substitution by surface oxygen to regenerate 1 is probably favored; examples of such reactivity have been previously described.[13d] On the other hand, when L = C_2H_4, nucleophilic displacement by ⋗SiO should be less favored due to the greater steric bulk of the ethylene and the higher electron density on the osmium.

Interestingly, addition of CO (1.3 × 10^4 Pa) to the mixture 1 + 3 quantitatively regenerates the IR spectrum of 1. Such a facile ethylene substitution by CO has been observed on related osmium clusters.[11] It is likely that attack by external CO occurs from the less hindered side of the supported cluster, i.e. from the side opposite to the surface. Rapid subsequent displacement of CO by the surface oxygen (eq 2) would then lead to 1 as the only observable product.

On the other hand, when 1 is put in contact with H_2 (3.4 × 10^4 Pa), no adsorption is detected volumetrically below 100 °C, and no changes are observed in the IR spectrum of the solid (ν_{CO} region). After 3 h at 100 °C, however, a new band at 2138 cm^{-1} and two shoulders at 2057 and 2044 cm^{-1} appear, indicating the formation of a new species 4 (Figure 3b). This transformation is reversed under vacuum at the same temperature, regenerating 1 (Figure 3c).

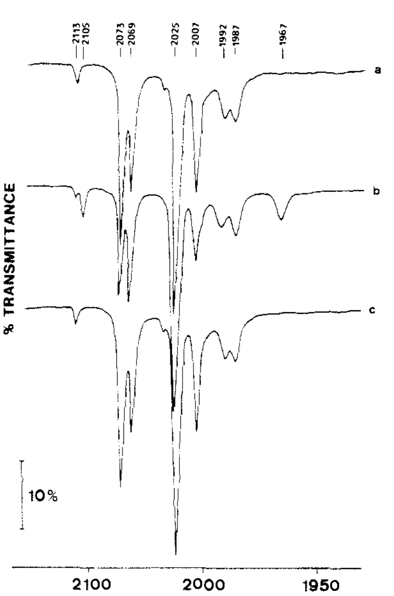


Figure 5. Key: (a) IR spectrum (ν_{CO} region) of **2** in *n*-octane; (b) after treatment with C_2H_4 (90 °C, 10 h); (c) after evacuation of (b) (25 °C).

Species **4** can also be obtained by H_2 treatment of the ethylene adduct **3** at room temperature (Figure 4) and by interaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with silica at 80 °C. A plausible structure for **4** could be $Os_3(CO)_{10}(H)(\mu\text{-}H)(OH\text{-}Si{<})$, although the evidence available does not allow an unambiguous structural assignment.

Interaction of 2 with C_2H_4 and H_2. In order to obtain further mechanistic insight into the hydrogenation reaction catalyzed by **1**, a series of experiments have been performed in solution on a molecular analogue of **1**, namely $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ (**2**).

When ethylene is bubbled through an *n*-octane solution of **2** at 90 °C, significant modifications of the IR spectrum are observed in the ν_{CO} region (Figure 5).

Similar to the case of $\mathbf{1} \rightleftharpoons \mathbf{3}$ (Figure 2), the band at 2113 cm^{-1} is replaced by a new one at 2105 cm^{-1}; simultaneously, a variation of the intensity ratio of the bands at 2073 and 2069 cm^{-1} is observed (Figure 5b), analogous to that occurring for $\mathbf{1} \rightleftharpoons \mathbf{3}$ (Figure 2b). A minor difference detected for **2** is the appearance of a low-intensity band at 1967 cm^{-1}, which in the case of **1** is probably obscured by the strong silica background. This is ascribed to the formation of a new complex **5**. On evacuation at room temperature the spectral changes are totally reversed, and **2** is recovered as the only IR-detectable product.

This indicates that at 90 °C an equilibrium between the starting cluster and a weak ethylene adduct ($\mathbf{2} \rightleftharpoons \mathbf{5}$) is attained, similar to the observed surface equilibrium ($\mathbf{1} \rightleftharpoons \mathbf{3}$). Isolation of **5** has not been possible due to the facile decoordination of ethylene from the cluster (eq 3).

$$\underset{\mathbf{2}}{Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)} + C_2H_4 \rightleftharpoons \underset{\mathbf{5}}{Os_3(CO)_{10}(\mu\text{-}H)(C_2H_4)(OPh)} \quad (3)$$

Further evidence for the nature of **5** comes from the 350-MHz ^1H NMR spectrum of the equilibrium mixture (Figure 6). In addition to the signals characteristic of **2**,[7a] a new spectrum[7b] is observed, consisting of (i) three aromatic signals (phenoxy protons) very similar to those of **2**, but displaced toward higher fields; (ii) a metal–hydride resonance displaced 0.25 ppm to lower field with respect to the hydride signal of **2**; and (iii) an AA′BB′ pattern assigned to an ethylene molecule π-bonded to Os.[7b,8]

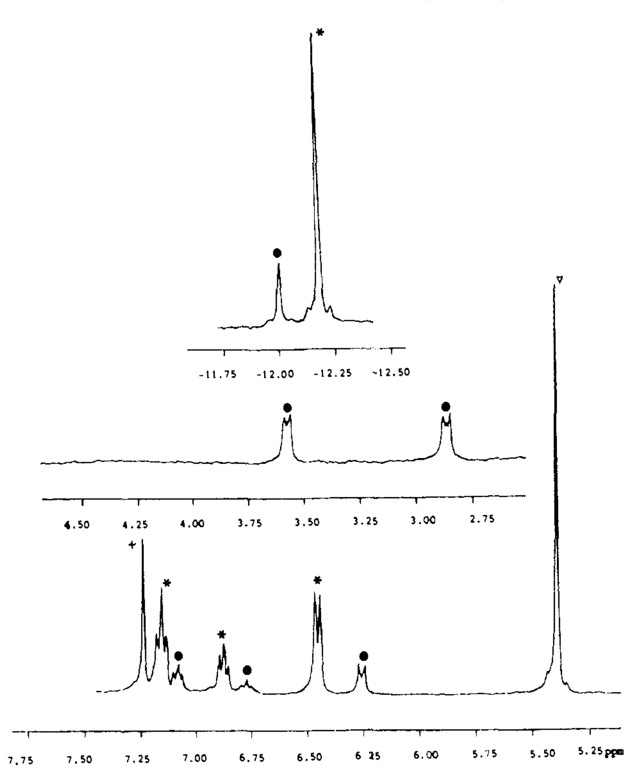
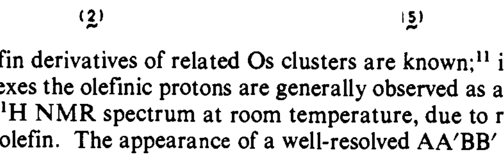


Figure 6. ^1H NMR spectrum of the mixture resulting from **2** + C_2H_4: (*) **2**, (●) **5**, (▽) free C_2H_4, (+) $CHCl_3$ in $CDCl_3$.

The displacement of the phenoxy signals to higher fields on passing from **2** to **5** is consistent with an increase in the electron density on the aromatic ring, probably resulting from the opening of the Os–O–Os bridge. The chemical shift of the high-field signal is typical of a *bridging* hydride in Os_3 clusters[9,10] and very close to that of **2**. These data are in agreement with a reaction pathway similar to that proposed for the silica-supported cluster, involving the opening of the Os–O–Os bridge (eq 4).



(4)

Olefin derivatives of related Os clusters are known;[11] in these complexes the olefinic protons are generally observed as a singlet in the ^1H NMR spectrum at room temperature, due to rotation of the olefin. The appearance of a well-resolved AA′BB′ pattern in our case may be due to restricted movement of the coordinated ethylene imposed by the presence of the phenoxy ligand on a vicinal Os atom. No coupling was observed between the olefinic protons and the metal hydride.

---

[7] Relevant ^1H NMR data (assignment, δ (Me_4Si), multiplicity, coupling constants in hertz). (a) **2** ($CDCl_3$): 2 H (Ph), 6.46, d, *J* = 8.75; 1 H (Ph), 6.87, t, *J* = 7.0; 2 H (Ph), 7.16 m; M – H, 12.25, s. (b) **5** ($CDCl_3$): 2 H (Ph), 6.25, d, *J* = 8.75; 1 H (Ph), 6.77, t, *J* = 7.0; 2 H (Ph), 7.08 m; 2 H (C_2H_4), 3.57 pseudo t; 2 H (C_2H_4), 2.86 pseudo t; M – H, 12.0, s. (c) Free PhOH ($CDCl_3$): 5 H (Ph), 6.65, m; OH 4.11, s. (d) $Os_3(\mu\text{-}H)_2(COe_{10}$: M – H, 11.36, s (Knox, S. A. P.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942). (e) $H_4Os_4(CO)_{12}$: M – H, 20.35, s; $H_2Os_4(CO)_{13}$, M – H, 21.23, s (Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 838).

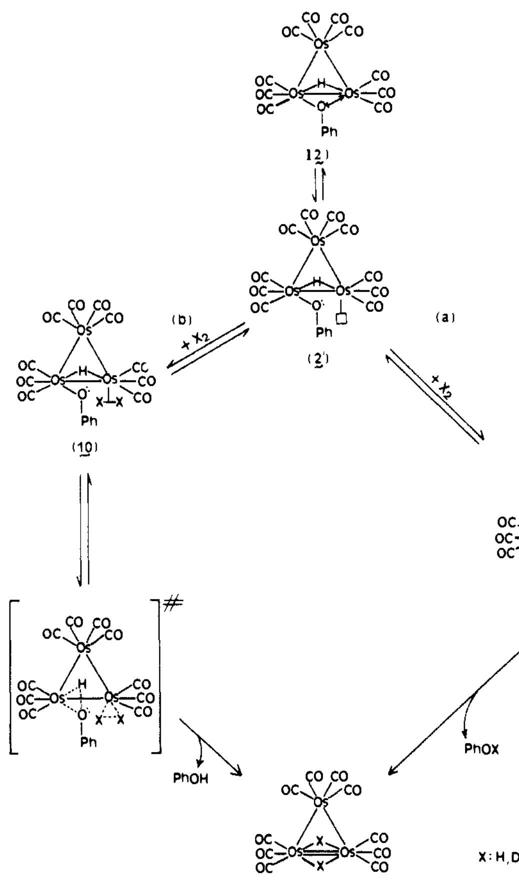
[8] For a discussion of the NMR spectra of η^2-ethylene–metal complexes, see: Benn, R. *Org. Magn. Reson.* **1983**, *21*, 723.

[9] Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975**, *88*, C21; **1976**, *114*, 313. Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

[10] Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304. Shapley, J. R.; Keister, J. B.; Churchill, M. W.; De Boer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145.

[11] (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (b) Dawoodi, Z.; Henrick, K.; Mays, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 696. (c) Dawoodi, Z.; Mays, M. J.; Raithby, P. R.; Henrick, K.; Clegg, W.; Weber, G. *J. Organomet. Chem.* **1983**, *249*, 149. (d) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Organomet. Chem.* **1981**, *213*, 249.

Scheme I



If, on the other hand, H_2 comes in contact with a cyclohexane-d_{12} solution of **2** in a sealed NMR tube, no reaction is apparent below 100 °C. After 16 h at 120 °C the 350-MHz ^1H NMR spectrum of the mixture shows the presence of **2**[7a] and free phenol;[7c] besides, the metal–hydride signals of $H_2Os_3(CO)_{10}$[7d] and small amounts of $H_4Os_4(CO)_{10}$[7e] are observed. When D_2 was used instead of H_2, the spectrum of free phenol was again clearly observed after 16 h at 120 °C, but the hydride signals of $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$ were extremely weak. In the absence of H_2 or D_2, no changes were observed in the NMR spectrum of **2** after 16 h at 120 °C (under Ar).

Consistent with the NMR observations, the solution IR spectrum of **2** is unchanged under H_2 below 100 °C; at 120 °C a series of changes are observed, leading to a complex pattern in the ν_{CO} region, which may be interpreted as a superposition of the spectra of **2**, $H_2Os_3(CO)_{10}$, and $H_4Os_4(CO)_{12}$.

These results can be explained in terms of the reaction represented by eq 5.

$$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh) + X_2 \rightleftharpoons PhOH + Os_3(CO)_{10}(\mu\text{-}X)_2 + ... \qquad X = H, D \tag{5}$$

This reaction may occur by sequential oxidative addition of H_2 or D_2 and reductive elimination of phenol via an intermediate trihydride **9** (Scheme I, pathway a). However, this type of intermediate containing terminal and bridging hydrides is expected to lead to rapid H–D exchange as previously demonstrated for complexes of the type $H_2Os_3(CO)_{10}L$;[9,10] consequently, a mixture of PhOH, PhOD, $HDOs_3(CO)_{10}$, and $D_2Os_3(CO)_{10}$ should be produced, which is not the case.

Alternatively, the experimental data are best explained by a concerted mechanism, which involves oxidative addition of H_2 (or D_2) on one Os atom taking place simultaneously with reductive elimination of phenol from a second Os atom. In view of the number of recent publications on metal complexes of molecular hydrogen,[12] one could also envisage the formation of such a transient $Os(H_2)$ intermediate (**10**), after opening of the phenoxy bridge (Scheme I, pathway b).

Further evidence in support of eq 3 comes from the reaction of $H_2Os_3(CO)_{10}$ with phenol in refluxing *n*-octane (eq 6).

$$H_2Os_3(CO)_{10} + PhOH \rightleftharpoons Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh) + H_2 + ... \tag{6}$$

After 2 h of reaction, the IR spectrum of the mixture (in the ν_{CO} region) is essentially identical with that obtained from the reaction of **2** with H_2. Furthermore, the ^1H NMR spectrum of this mixture shows the hydride signal corresponding to $H_2Os_3(CO)_{10}$,[7d] the phenyl and hydride peaks of **2**,[7a] and hydride resonances typical of $H_4Os_4(CO)_{12}$[7e] and $H_2Os_4(CO)_{13}$.[7e] This represents the reverse of eq 3, in accord with the set of reactions summarized in Scheme I.

Ethylene as well as styrene hydrogenation has been carried out in *n*-octane solution with complex **2** [80–100 °C (1 atm)]. However, after a few turnovers, the catalyst is transformed mainly into $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$ with loss of the phenoxy ligand (in the form of phenol). The same reaction occurs between **1** and H_2 in the absence of the olefin (eq 5 and Scheme I).

Mechanism of Catalytic Hydrogenation with 1. Scheme II depicts a catalytic hydrogenation cycle and a set of peripheral reactions consistent with the experimental data presented above.

Formation of **3** as the first step in the catalytic cycle is in agreement with the zero-order dependence on ethylene pressure. This reversible transformation of **1** into **3** is also clearly shown by the IR and volumetric measurements described above and adequately modeled by the soluble analogues **2** and **5** (eq 2), as demonstrated by IR and NMR studies.

Precedents for this type of transformation of a 3-electron LX into a 1-electron X ligand are available in the literature.[13] An alternative reaction pathway involving CO displacement by ethylene may be ruled out in view of the facile regeneration of **1** by evacuation of **3** (eq 1) and of **2** by evacuation of **5** (eq 2).

Hydride migration to the coordinated olefin in **3** with concomitant transfer of the 1-electron OSi< ligand from Os_1 to Os_2 (see Scheme II) leads to the coordinatively unsaturated alkyl intermediate **3′**. A closely related triosmium–ethyl complex has been recently synthesized by Shapley and co-workers.[14] Oxidative addition of H_2 ($3' \rightarrow 3''$) and subsequent reductive elimination of the product alkane ($3'' \rightarrow 1'$) complete the catalytic cycle.

Direct oxidative addition of H_2 to **1** (presumably via **1′**), which occurs at 100 °C in the absence of ethylene to produce **4**, does not seem to intervene in the catalytic cycle. Furthermore, the observed reaction of **3** with H_2, which also yields **4**, may be explained by the sequence $3 \rightarrow 3' \rightarrow 3'' \rightarrow 1' \rightarrow 4$ (Scheme II). Alternatively, displacement of ethylene by H_2 could form a transient molecular hydrogen adduct **4′**, which would quickly rearrange into the hydride form **4**.[12] The analogous solution reaction of **2** with H_2 to yield $H_2Os_3(CO)_{10}$ plus free phenol (Scheme I) provides further support for this mechanism.

Similarly, the reaction of **3** with CO may proceed by displacement of ethylene to yield a labile intermediate $Os_3(CO)_{11}(\mu\text{-}H)(OSi<)$ (**4″**), which easily loses CO to regenerate the most

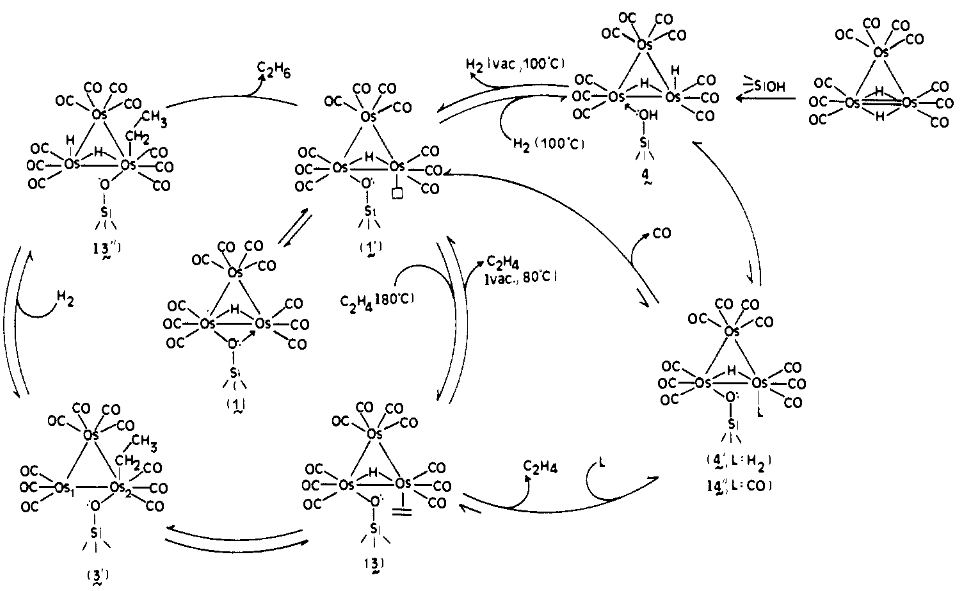
---

(12) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 451. Kubas, G.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. Morris, R. H.; Sayer, J. F.; Shiralian, M.; Zubkowski, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 5581. Crabtree, R. H.; Hamilton, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3124. Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. Conroy-Lewis, F. M.; Simpson, S. *J. Chem. Soc., Chem. Commun.* **1986**, 506. Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. Church, S. P.; Grevels, F. W.; Hermann, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30. Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374. Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *101*, 6587.

(13) (a) Puga, J.; Sanchez-Delgado, R. A.; Andriollo, A.; Ascanio, J.; Braga, D. *Organometallics* **1985**, *4*, 2064. (b) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Whitmire, K. *J. Chem. Soc., Dalton Trans.* **1983**, 787. (c) Cowie, A. G.; Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 2311. (d) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1977**, 330.

(14) Cree-Uchiyama, M.; Shapley, J. R.; St-George, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316.

Scheme II



stable surface species, **1**. This facile ethylene substitution, which has been observed on a related cluster,[11d] could thus be responsible for the inhibition of the hydrogenation catalysis observed on addition of CO to the reaction mixture.

Finally, species **4** can also be obtained by interaction of $H_2Os_3(CO)_{10}$ with silica, in a manner analogous to the known reactions of this dihydride with Lewis bases to yield $Os_3(CO)_{10}(H)(\mu\text{-}H)L$.[9]

It is interesting to note that the catalytic behavior of **1** is quite different from that of its molecular analogue **2**. The structure of **1** seems to be preserved on the surface, whereas that of **2** is quickly transformed in solution with loss of phenol and formation of $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$. This fragmentation in solution is now a quite commonly recognized phenomenon.[2a-e]

This difference of behavior indicates the stabilizing influence of the silica support, probably due to the presence of an extended array of OH groups able to trap coordinatively unsaturated clusters before they undergo fragmentation.

Conclusions. We have demonstrated that the oxide-bound triosmium cluster **1** is an efficient catalyst for the hydrogenation of ethylene. The kinetic, as well as the spectroscopic, data presented allow us to deduce a mechanism that involves the intact trinuclear framework in all the elementary steps conforming the catalytic cycle. The observed reactivity of the molecular analogue **2** provides further support for this proposal.

This shows that the frequently encountered problem of cluster fragmentation during catalysis in solution may be overcome by the use of oxide surfaces as ligands. The surface oxygen atoms are capable not only of functioning as either 3- or 1-electron donors but also of easily interconverting between these two forms. As a result, an appropriate energy balance is attained, allowing the formation of reactive electron-deficient intermediates, without competing rupture of metal–metal bonds.

One can never completely rule out the possibility of the presence of trace amounts of small metal particles (undetectable by IR spectroscopy or electron microscopy) on the silica support. However, the evidence presented in this paper strongly favors a cluster-catalyzed reaction on the surface.

Experimental Section

Materials. Solvents and gases were dried and deoxygenated by standard methods. $Os_3(CO)_{12}$ (Johnson Matthey) was used as received. $H_2Os_3(CO)_{10}$,[7d] $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$,[15] and $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi{<})$[4b] were prepared according to the published procedures.

The Os concentration was 1.5% wt; at this metal loading the IR spectrum of the solid showed only the presence of **1**. The silica used was a nonporous Aerosil O from Degussa with a surface area of ca. 200 $m^2\ g^{-1}$; the support was thermally dehydroxylated at 200 °C before reaction with $Os_3(CO)_{12}$.[4b] The supported cluster **1** is air stable.

Instrumentation. IR spectra were recorded on Perkin-Elmer 225 or Nicolet 10-MX (FT) instruments. NMR spectra were recorded at 100 or 350 MHz on a Varian XL-100 or a CAMECA-350 spectrometer, respectively.

Catalytic Reactions. Dynamic hydrogenation runs were carried out in a differential reactor at atmospheric pressure. In a typical experiment the catalyst (**1**) (0.1 g) was introduced into the reactor, which was then connected to a gas manifold. The desired partial pressures of C_2H_4 and H_2 were adjusted to constant flow by diluting with He. The reactor was heated to the desired temperature (60–90 (±1 °C)) by means of an electric oven; the reaction temperature was measured by means of a thermocouple placed directly on the catalyst bed. No detectable changes in temperature could be observed at low conversions; ethylene and ethane were analyzed by gas chromatography on an IGC 12 F instrument fitted with a flame ionization detector and a Porapak Q column, using N_2 as the carrier gas.

Homogeneous hydrogenation of ethylene and styrene with **2** was carried out by the method described in ref 2a.

Other Reactions of 1. The procedure for studying the interaction of **1** with C_2H_4, H_2, and CO by IR spectroscopy and by volumetric measurements was essentially identical with those previously described for related experiments.[4b]

Reaction of 2 with Ethylene. A solution of **2** (0.05 g, 5.3×10^{-2} mmol) in *n*-octane (20 mL) was heated to 90 °C under ethylene. The IR spectrum of the mixture was recorded at appropriate intervals. After 10 h of reaction the resulting solution was treated in two different manners: (i) The solvent was evaporated under vacuum, and the residue was redissolved in *n*-octane or $CDCl_3$ in order to obtain the IR and NMR spectra, which showed only the presence of **2**. (ii) The solvent was evaporated under a current of ethylene, and the residue was redissolved in $CDCl_3$ in order to obtain the NMR spectrum of the mixture **2** + **5**.

Reactions of 2 with H_2 or D_2. The procedure for following the IR spectral changes during reaction of **2** with H_2 was similar to that used for the ethylene reaction, except that the *n*-octane solution was kept under reflux (120 °C). For the NMR experiments, a cyclohexane-d_{12} solution of **2** was sealed under H_2, D_2, or Ar in an NMR tube, and the spectral changes were followed by measuring the spectra at appropriate intervals after the mixture had been heated to 120 °C.

Reaction of $H_2O_3(CO)_{10}$ with Phenol. A solution of $H_2Os_3(CO)_{10}$ (0.1 g, 1.2×10^{-2} mmol) and phenol (1.2×10^{-1} mmol) in *n*-octane was refluxed for 5 h, during which time the reaction was followed by IR spectroscopy. The solvent was then evaporated under vacuum, and the dry residue was dissolved in $CDCl_3$ for NMR measurements.

Acknowledgment. We thank Prof. H. D. Kaesz for helpful discussions and M. Yea-Jer Chen of his laboratory for having repeated the reaction of **2** with ethylene. A Graduate Fellowship from CDCH-UCV (Caracas) to L.D. is also gratefully acknowledged. We thank the CNRS for an Associate Researcher Position to R.S.-D. and the Chemistry Center at IVIC (Caracas) for a sabbatical leave.

---

[15] Azam, K. A.; Deeming, A. J.; Kimber, R. E.; Shukla, P. R. *J. Chem. Soc., Dalton Trans.* **1976**, 1853.