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Contribution from the Institut de Recherches
sur la Catalyse, CNRS, 69626 Villeurbanne, France,
and The Chemistry Center, Instituto Venezolano
de Investigaciones Cientificas, Caracas 1020A, Venezuela

Surface Organometallic Chemistry: Relative Reactivity of Carbonyl, Hydride, and Halide Ligands in $H_4Os_4(CO)_{12}$ and $H_3Os_4(CO)_{12}I$ toward Magnesia

Lindora D'Ornelas,[1a] Agnès Choplin,[1a] Jean-Marie Basset,*[1a]
José Puga,[1b] and Roberto A. Sanchez-Delgado*[1b]

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Surface organometallic chemistry, particularly concerning metal clusters, has been a subject of much recent interest, since it may lead to the identification of well-defined surface species. It is thus possible to propose some elementary steps in surface reactions and hopefully in heterogeneous catalysis.[2–10]

It is now well-established that the OH groups of oxide supports oxidatively add across a metal–metal bond in a cluster;[2–4] with basic supports the OH groups can act as nucleophiles toward coordinated CO to yield either surface anionic species[5,6] or surface formate.[7] It has also been shown that these OH groups can deprotonate hydrido mixed-metal clusters to give the corresponding anions.[6,8–10]

In this paper we report the reactivity of $H_4Os_4(CO)_{12}$ (**1**) and $H_3Os_4(CO)_{12}I$ (**2**) with the surface of partially hydroxylated magnesia (as well as lanthanum and zinc oxides), which shows the following: (i) An iodo ligand can be abstracted as I^+. Such a reaction has never been observed on a surface.

(ii) Proton abstraction seems now to be a general process[8–10] on a basic support: it is a facile reaction.

(iii) These two reactions occur on the surface with apparently no nucleophilic attack on coordinated CO taking place under the reaction conditions.

Results and Discussion

$H_4Os_4(CO)_{12}$ (1). When a suspension of **1** in CH_2Cl_2 is contacted with MgO(200) (see Experimental Section), the support becomes yellow in a few minutes. After removal of the solvent, no metal complex can be extracted from the solid with CH_2Cl_2. The FTIR spectrum of the supported complex (Figure 1) differs considerably from that of the starting cluster **1**[11] and closely resembles that of the anionic species $[H_3Os_4(CO)_{12}]^-$ (**3**).[12a]

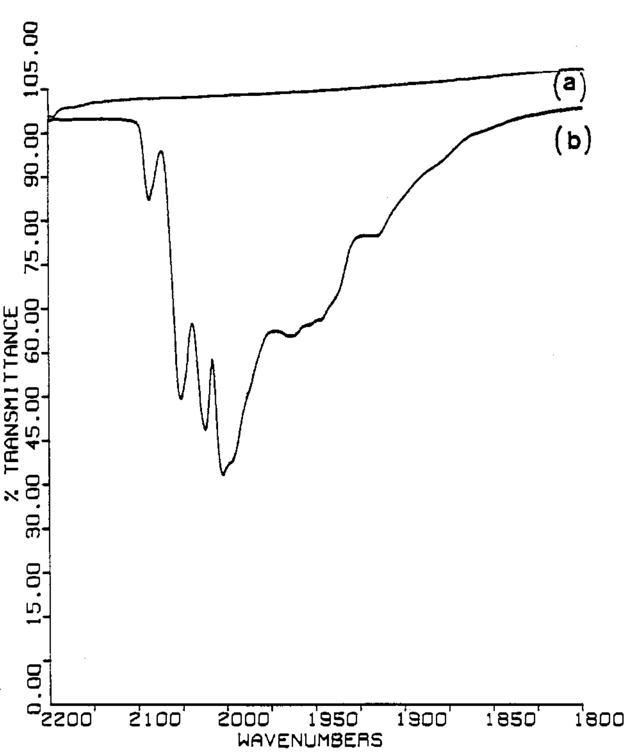

Figure 1. FTIR spectra in the region 2200–1800 cm^{-1}: (a) MgO(200); (b) $H_4Os_4(CO)_{12}$ adsorbed on MgO(200) (band maxima at 2087 m, 2051 s, 2023 s, 2004 vs, 1986 sh, 1953 m, 1938 m, and 1914 w, sh cm^{-1}).

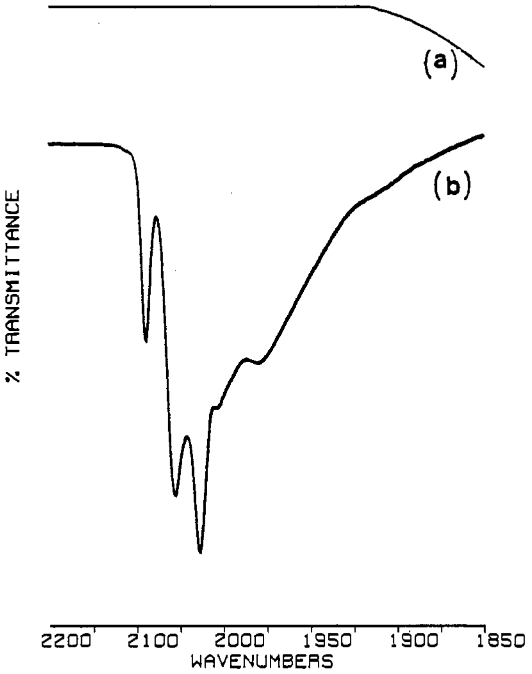

Figure 2. FTIR spectra in the region 2200–1800 cm^{-1}; (a) MgO(200); (b) $H_3Os_4(CO)_{12}I$ adsorbed on MgO(200) (band maxima at 2089 m, 2055 s, 2026 s, 2006 w, sh, and 1978 w cm^{-1}).

Extraction of the surface species with $[N(PPh_3)_2]Cl$ in CH_2Cl_2 at room temperature produces excellent yields of **3** in solution, as identified by its IR[12a] and ^1H NMR[12b] spectra. A blank reaction between **1** and $[N(PPh_3)_2]Cl$ in CH_2Cl_2 under similar reaction conditions did not lead to the formation of **3** after 5 h.

These results indicate that an ionic chemisorption of **1** onto the surface of MgO(200) has taken place by a deprotonation reaction

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(1) (a) Institut des Recherches sur la Catalyse. (b) Instituto Venezolano de Investigaciones Cientificas.

(2) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95 and references therein. Ugo, R.; Psaro, R.; Zanderighi, G. M.; Basset, J. M.; Theolier, A.; Smith, A. K. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 579. Besson, B.; Moraweck, B.; Smith, A. K.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 569. Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Organomet. Chem.* **1980**, *192*, C31. Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. *Ibid.* **1981**, *213*, 215. D'Ornelas, L.; Choplin, A.; Basset, J. M.; Hsu, L. Y.; Shore, S. G. *Nouv. J. Chim.* **1985**, *9*, 155. Drezdzon, M. A.; Tessier-Youngs, C.; Woodcock, C.; Blonsky, P. M.; Leal, O.; Teo, B. K.; Burwell, R. L., Jr.; Shriver, D. F. *Inorg. Chem.* **1985**, *24*, 2349. Yermakov, V. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981. Ichikawa, M. *CHEMTECH* **1982**, 674. Collier, G.; Hunt, D. J.; Jackson, S. D.; Moyes, R. B.; Pickering, I. A.; Wells, P. B.; Simpson, A. F.; Whyman, R. *J. Catal.* **1983**, *80*, 154–171.

(3) Deeba, M.; Gates, B. C. *J. Catal.* **1981**, *67*, 303.

(4) Watson, P. L.; Schrader, G. L. *J. Mol. Catal.* **1980**, *9*, 125.

(5) Hughes, F.; Basset, J. M.; Ben Taarit, Y.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020.

(6) Pierantozzi, R.; Valagene, E. G.; Nordquist, A. F.; Dyer, P. N. *J. Mol. Catal.* **1983**, *21*, 189.

(7) Basset, J. M.; Choplin, A.; Theolier, A. *Nouv. J. Chim.* **1985**, *9*, 655.

(8) Choplin, A.; Huang, L.; Basset, J. M.; Mathieu, R.; Siriwardane, U.; Shore, S. G. *Organometallics* **1986**, *5*, 1547.

(9) Budge, J. R.; Scott, J. P.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1983**, 342.

(10) Guglielminotti, E.; Osella, D.; Stanghellini, P. L. *J. Organomet. Chem.* **1985**, *281*, 291.

(11) **1** in CH_2Cl_2 has absorption bands at 2085 (m), 2066 (s), 2018 (m), and 1995 (w) cm^{-1}.

(12) (a) **3** (as its $N(PPh_3)_2^+$ salt) in CH_2Cl_2 has absorption bands at 2075 (vw), 2046 (vs), 2040 (sh), 2021 (vs), 1999 (vs), 1979 (s, br), 1964 (sh), 1945 (m), and 1916 (w) cm^{-1}. (b) ^1H NMR (−30 °C, $CDCl_3$): −19.26, −19.89, −21.96 ppm.

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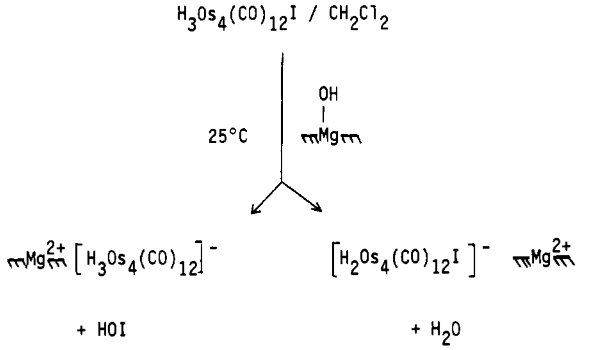
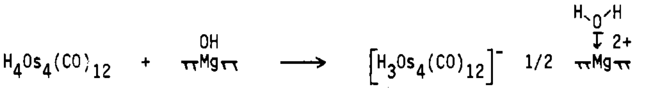
Scheme I



leading to the formation of surface-bound **3**, according to eq 1. Analogous results are obtained when **1** is reacted with ZnO(200) or La_2O_3(200) surfaces.



$$H_4Os_4(CO)_{12} + \overset{OH}{\text{Mg}} \longrightarrow [H_3Os_4(CO)_{12}]^- \; 1/2 \; \overset{\overset{H \diagdown O \diagup H}{\updownarrow\, 2+}}{\text{Mg}} \qquad (1)$$

This shows that the tendency of the surface OH groups to act as deprotonating agents is greater than their nucleophilic character toward coordinated CO. This is also the case for γ-Al_2O_3.[13] In a recent paper the formation of **3** from the mononuclear precursor $H_2Os(CO)_4$ on a MgO surface was described.[14]

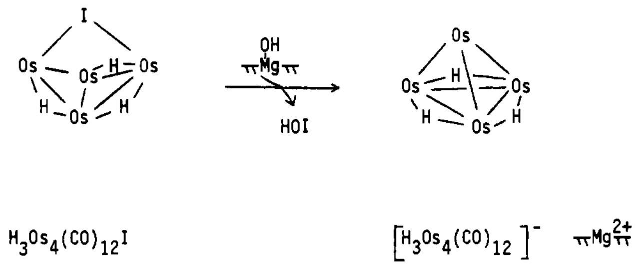
$H_3Os_4(CO)_{12}I$ (2). In view of the results obtained for **1** it was interesting to study the reactivity of MgO(200) surfaces toward a cluster containing carbonyl, hydride, and halide ligands. A CH_2Cl_2 solution of **2** is immediately decolorized upon contact with the oxide, which in turn becomes yellow. The FTIR spectrum of the supported species (Figure 2) differs from that of **2**[15] and can be interpreted as a superposition of the spectra corresponding to **3**[12] and $[H_2Os_4(CO)_{12}I]^-$ (**4**).[16]

Extraction of the surface species with $[N(PPh_3)_2]Cl$ leads to a mixture of **3** and **4** in CH_2Cl_2 solution, characterized by comparison of their IR and ^1H NMR spectra with those of authentic samples. Although **3** is the predominant species in the extraction solution, the relative intensities in the IR spectrum of the solid before extraction indicate that comparable amounts of **3** and **4** are present on the surface. Therefore, we conclude that the interaction of the iodide-containing anion **4** with the surface is probably stronger than that of **3**.

Thus, chemisorption of **2** onto MgO(200) is also of an ionic nature and takes place by abstraction of a proton or an iodonium cation by the surface OH groups, according to Scheme I.

Proton abstraction by basic supports[8-10] as well as by bases in solution[17,19,21] is well-documented. Abstraction of I^+ is certainly a novel reaction on surfaces and has only been observed once in solution.[20] The deprotonation of **2** to **4** in solution has been shown to occur with concomitant metal framework (butterfly–tetrahedral) rearrangement.[17] A similar butterfly–tetrahedron skeletal rearrangement on the surface is conceivable also in this case (Scheme II).

Scheme II



In conclusion, our study of the relative reactivities of H, I, and CO ligands toward magnesia shows that the OH groups of basic supports can easily abstract a proton from **1** and both a proton and I^+ from **2**, to yield the chemisorbed anions **3** and **3** + **4**, respectively. Under these conditions there is no evidence for any other surface reaction taking place.

Complexes **1**–**4** are known to be efficient catalyst precursors for hydrogenation reactions in solution.[18] Work is now in progress to determine the catalytic properties of the supported systems herein reported.

Experimental Section

All manipulations were carried out under vacuum or inert atmosphere. Solvents and reagents were purified by conventional methods as required. $H_4Os_4(CO)_{12}$ and $H_3Os_4(CO)_{12}I$ were prepared by published procedures.[19a]

The supports (MgO, 70 $m^2\ g^{-1}$; ZnO, 43 $m^2\ g^{-1}$; La_2O_3) were slowly heated under vacuum (10^{-5} torr) up to 400 °C. Subsequently, several cycles of introduction of oxygen (2 h) followed by evacuation (10^{-5} torr, 0.5 h) at 400 °C were carried out in order to eliminate carbonates, adsorbed water, and volatiles from the solids. The supports were then rehydrated with water vapor at 25 °C for 2 h and finally dehydrated at 200 °C under vacuum (10^{-5} torr) for 16 h to yield samples named MgO(200), ZnO(200), and La_2O_3(200).

The impregnation of the clusters on the supports was carried out as previously described,[5] with use of the necessary amounts of clusters to obtain a 1% concentration of Os on the solid. FTIR spectra were obtained on a Nicolet 10-MX instrument.

For the extraction experiments, 2 g of the solid containing the supported clusters (0.056 mmol for **1**, 0.068 mmol for **2**) was put in contact with a CH_2Cl_2 solution of $N(PPh_3)_2Cl$ (0.054 mmol for **1**, 0.074 mmol for **2**) at room temperature for 1 h. The resulting solutions were filtered and the IR spectra obtained immediately. For NMR measurements, the solvent was removed and the resulting solid was redissolved in $CDCl_3$.

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Registry No. **1**, 12375-04-1; **2**, 67966-16-9; **3**, 104550-42-7; **3**·PPN, 104550-43-8; **4**, 98331-77-2; **4**·PPN, 98331-78-3; ZnO, 39377-65-6; La_2O_3, 12195-45-8; partially hydroxylated magnesia, 12710-11-1.

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(13) Krause, T. A.; Davies, M. E.; Lieto, J.; Gates, B. C. *J. Catal.* **1985**, *94*, 195.

(14) Lamb, H. H.; Gates, B. C. *J. Am. Chem. Soc.* **1986**, *108*, 81.

(15) **2** in CH_2Cl_2 has IR absorption bands at 2110 (w), 2085 (vs), 2066 (vs), 2019 (s), 2009 (m), 1998 (sh), and 1982 (vw) cm^{-1}.

(16) **4** (as its $N(PPh_3)_2^+$ salt) in CH_2Cl_2 has IR absorption bands at 2081 (m), 2049 (vs), 2016 (vs), 1987 (m, br), 1978 (sh), and 1947 (vw) cm^{-1}.

(17) Puga, J.; Sanchez-Delgado, R.; Braga, D. *Inorg. Chem.* **1985**, *24*, 3971. Puga, J.; Sanchez-Delgado, R.; Andriollo, A.; Ascanio, J.; Braga, D. *Organometallics* **1985**, *4*, 2064.

(18) Sanchez-Delgado, R. A.; Puga, J.; Rosales, M. *J. Mol. Catal.* **1984**, *24*, 221. Sanchez-Delgado, R. A.; Puga, J.; Andriollo, A.; Martin, G., to be submitted for publication.

(19) (a) Johnson, B. F. G.; Lewis, J.; Raithby, P.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 673. (b) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179.

(20) Winter, A.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1982**, *282*, 47.

(21) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647. The observation that nucleophilic attack of OH^- results in deprotonation of **1** parallels the observation that a nucleophile such as Cl^- can deprotonate the hydrido cluster $H_4Ru_4(CO)_{12}$ (in tetrahydrofuran) under ambient conditions.