J. Am. Chem. Soc. **1986**, *108*, 81-89

Table IV. Comparison of Different Fitting Methods in the Derivation of $\Delta\sigma_{corr}^{(-)}(M)$

M^-	$\Delta\sigma_{corr}^{(-)}(M)$; fit type linear	quadratic	cubic
Li^-	0.349	0.384	0.396
Na^-	0.247	0.289	0.302
K^-	0.257	0.259	
Rb^-	0.255	0.272	
Cs^-	0.265	0.282	

and $\Delta\sigma(^-)(Cs)$ in solution suggest that these species are significantly modified upon passing from the gaseous to the condensed phase.

Acknowledgment. We thank the SERC (UK) for their continued support.

Appendix: Calculation of the Correlation Contribution to Ionization Processes Core $s^2 \rightarrow$ Core s

The experimental ionization potentials for the processes core $s^2 \rightarrow$ core s reported in Table III for group IIA, IIIA, and IVA elements are taken from Moore[34-37] except that for La^+.[38] Since the ground configurations of Sc^+ and La^+ are core sd and core d^2, respectively, while those of Sc^{2+}, Y^{2+}, and La^{2+} are core d, the ionization potentials reported for those systems in Table III were calculated from the literature ground-state values[33-37] by incorporation of the appropriate atomic excitation energies.[34-38] The experimental alkali metal values of Table III are electron affinities measured by photodetachment.[39]

The relativistic contribution to the ionization potential ($I_{rel}(Z)$) is given by

$$I_{rel}(Z) = I_{DF}(Z) - I_{HF}(Z) + I_{Br}(Z) + I_{LS}(Z) \quad (A1)$$

Here $I_{DF}(Z)$ is the relativistic Dirac–Fock prediction of the ionization potential calculated as the difference between the total energy of the single configuration wave function for the core s configuration and the energy of the core s^2 configuration. The quantity $I_{HF}(Z)$ is the corresponding prediction of nonrelativistic Hartree–Fock theory, the orbitals of both the relativistic and nonrelativistic calculations being taking to satisfy the usual symmetry and equivalence restrictions.[40,41] The difference $I_{DF}(Z) - I_{HF}(Z)$ constitutes the major portion of the relativistic correction to the ionization potential, only the contribution ($I_{Br}(Z)$) from the Breit interaction,[41,42] that ($I_{LS}(Z)$) from the Lamb shift, and the small relativistic correlation correction not being included. The Breit contributions ($I_{Br}(Z)$) of Table III were computed exactly as the difference between the total Breit energies of the Dirac–Fock wave functions core s and core s^2. The Lamb shift contributions ($I_{LS}(Z)$) were calculated as the estimated Lamb shift energy of the valence electron in the configuration core s minus twice that estimated for one valence electron in the configuration core s^2. The methods used to estimate the Lamb shift of one valence electron are described fully elsewhere.[16]

Linear, quadratic, and cubic approximations to $(\mathrm{d}I_{corr}(Z)/\mathrm{d}Z)_{Z=Z_I}/3c^2$ for the alkali anions of nuclear charge Z_I are presented in Table IV. The linear approximation is calculated as the difference $(I_{corr}(Z_I + 1) - I_{corr}(Z_I))$ between the correlation contribution $(I_{corr}(Z_I + 1))$ to the first ionization potential of the alkaline earth of nuclear charge $(Z_I + 1)$ and that $(I_{corr}(Z_I))$ to the alkali metal electron affinity. The quadratic results (Table IV) are calculated by fitting a quadratic to the three quantities $I_{corr}(Z_I)$, $I_{corr}(Z_I + 1)$, and $I_{corr}(Z_I + 2)$ and therefore require the correlation contributions $(I_{corr}(Z_I + 2))$ to the ionization process core $s^2 \rightarrow$ core s in the group IIIA elements. The cubic approximation used for Li^- and Na^- also requires the correlation contributions $(I_{corr}(Z_I + 3))$ to the ionization process core $s^2 \rightarrow$ core s to enable a cubic to be fitted to $I_{corr}(Z_I)$, $I_{corr}(Z_I + 1)$, $I_{corr}(Z_I + 2)$, and $I_{corr}(Z_I + 3)$. The experimental data for the group IVA elements needed to derive cubic approximations for the heavier alkali anions do not appear to be available. The correlation contributions (Table IV) to the alkali anion–neutral alkali shielding differences predicted from quadratic and cubic approximations to $(\mathrm{d}I_{corr}/\mathrm{d}Z)_{Z=Z_I}$ agree well. Even the values predicted from the linear approximation agree with those from the quadratic one to within 16%. The data required to calculate the contribution to the shielding difference between a neutral alkali atom and its monovalent cation have been reported elsewhere.[16]

---

(33) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327.

(34) Moore, C. E. "Atomic Energy Levels"; U.S. Government Printing Office: Washington D.C., 1949; NBS circular 467, Vol. 1.

(35) Moore, C. E. "Atomic Energy Levels"; U.S. Government Printing Office: Washington, D.C., 1952; NBS Circular 467, Vol. 2.

(36) Moore, C. E. "Atomic Nergy Levels"; U.S. Government Printing Office: Washington, D.C., 1958, NBS Circular 467, Vol. 3.

(37) Moore, C. E. "Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra"; U.S. Government Printing Office: Washington, D.C., 1971; NSRDS-NBS 34.

(38) Martin, W. C.; Zalabus, R.; Hagan, L. "Atomic Energy Levels. The Rare Earth Elements"; U.S. Goverment Printing Office: Washington, D.C.; 1978; NSRDS-NBS 60.

(39) Patterson. T. A.; Hotop, H.; Kashdan, A.; Norcross, D. W.; Linberger, W. C. *Phys. Rev. Lett.* **1974**, *32*, 189.

(40) Nesbet, R. K. *Proc. R. Soc. London, Ser. A* **1955**, *A230*, 312.

(41) Grant, I. P. *Adv. Phys.* **1970**, *19*, 747.

(42) Breit, G. *Phys. Rev.* **1929**, *34*, 553.

Molecular Organoosmium Chemistry and Catalysis on the Basic Magnesium Oxide Surface

H. Henry Lamb and Bruce C. Gates*

Contribution from the Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716.

Received June 21, 1985

Abstract: The complex $[H_2Os(CO)_4]$ is deprotonated upon adsorption on the basic surface of magnesia. The resulting $[HOs(CO)_4]^-$ is held strongly to the surface by a localized carbonyl-Mg^{2+} interaction analogous to the contact anion ion pairing observed for $[Na][HOs(CO)_4]$ in THF. The surface-bound complex is the precursor of surface species that are catalytically active for CO hydrogenation to give methane and higher hydrocarbons at 275 °C and 10 atm. During catalysis, the mononuclear anion is transformed into the stable $[H_3Os_4(CO)_{12}]^-$ and $[Os_{10}C(CO)_{24}]^{2-}$, which become the only surface species detected by infrared spectroscopy and by extraction of surface-bound anions. The chemistry of the molecular condensation reactions of osmium carbonyls on the basic magnesia surface closely parallels that of osmium carbonyls in basic solution. The tetranuclear osmium cluster is suggested to be involved in the CO hydrogenation catalysis.

Supported metal catalysts used in large-scale processes consist of metal crystallites of various sizes and shapes on high-surface-area metal-oxide supports.[1] Understanding of the chemistry of these catalysts is severely hindered by their nonuniformity;

0002-7863/86/1508-0081$01.50/0

consequently, researchers have investigated supported metal complexes and clusters with molecular structures as model catalysts and precursors.[2,3] Under most catalytic reaction conditions, however, the molecular organometallics are unstable on the surfaces, often yielding nonuniform crystallites of supported metal.

In this report, we describe the preparation, spectroscopic characterization, and reactivity of a family of remarkably stable surface-bound organometallics formed from mononuclear carbonylosmate complexes which evolve under conditions of high-temperature CO hydrogenation catalysis into osmium carbonyl clusters with simple molecular structures.

Experimental Methods

Catalyst Synthesis. The MgO support (MX-65-1 powder, MCB Reagents) was calcined at 400, 600, and 800 °C by heating in flowing O_2 (Matheson Extra Dry Grade) for 2 h, followed by evacuation for 12–14 h. A sample of the material treated at 400 °C was exposed at 200 °C for 1 h to flowing He saturated with degassed, deionized water. The rehydrated magnesia was then outgassed at 200 °C for 1 h. The specific surface areas of the magnesia samples pretreated at 200, 400, 600, and 800 °C were 69, 75, 35, and 34 m^2/g, respectively, as determined by N_2 adsorption.

The silica support (Cabosil, S-17 grade, Cabot) was washed with deionized water, dried, and calcined at 400 °C by the procedure described for magnesia. The surface area of the silica before pretreatment was 380 m^2/g.

Solutions of the complex $[H_2Os(CO)_4]$ (**1**) in mixed hexanes (freshly distilled from sodium/benzophenone) were obtained by two procedures involving the reduction of $[Os_3(CO)_{12}]$ (Strem) by sodium in liquid ammonia followed by protonation of the resulting $[Na]_2[Os(CO)_4]$ with phosphoric acid.[4] In the first synthesis, volatile **1** was absorbed into a hexane layer in contact with the acid solution. In the second synthesis, **1** was vacuum transferred from the aqueous solution onto P_2O_5 and then transferred to a solution of dry mixed hexanes. The product of each synthesis was pure, as indicated by the infrared spectrum [ν_{CO} = 2143 (w), 2067 (m), 2055 (s), 2050 (vs) cm^{-1}].[5]

The complex **1** was adsorbed onto metal-oxide supports from hexane solution. The solid (2 g) was slurried with 100 mL of solution under N_2 for 2 h at 25 °C, recovered by filtration, washed with fresh hexanes (100 mL), then dried in flowing N_2, and stored in a Vacuum Atmospheres drybox.

$[PPN][HOs(CO)_4]$[6] ($[PPN][\mathbf{2}]$) [PPN = $N(PPh_3)_2$] and $[Et_4N]_2[Os_{10}C(CO)_{24}]$[7] ($[Et_4N]_2[\mathbf{3}]$) were prepared by the literature procedures, the purities being confirmed by infrared spectroscopy. The compounds were deposited on magnesia from solutions with THF (freshly distilled from sodium/benzophenone); the contact time was 3 h. The solids were filtered, washed with fresh THF, and then dried and stored.

Osmium loadings of the resulting solids were determined by X-ray fluorescence spectroscopy (XRF) with a Philips PW1410/80 automated X-ray spectrometer calibrated with similar standards.

Infrared Spectroscopy. Infrared spectra of the supported organometallics were obtained with a Nicolet 7199 Fourier transform spectrometer. The spectral resolution was 4 cm^{-1}. The powders were pressed neat, forming self-supporting discs which were placed in a thermostated quartz cell with NaCl windows. The cell could be connected to a gas-handling manifold for evacuation and/or gas dosing.[8]

UV–Visible Spectroscopy. The spectra were obtained with a Cary 219 spectrophotometer equipped with a Model 50413000 diffuse reflectance attachment. Spectra of powders under N_2 were obtained with a Suprasil quartz cell having a 1-mm path length and fitted with a vacuum stopcock. The reported spectra were corrected for the absorption of the magnesia support.

Extraction of Organometallics from the Surfaces. Samples (0.2–0.4 g) of magnesia-supported **1** were treated under N_2 with excess $[Me_4N][Cl]$ in dry THF or 2-propanol. The products of the surface cation metathesis were identified by infrared spectroscopy of the supernatant solutions.

The surface-bound complex was protonated with 85% phosphoric acid and with ethanol. In one experiment, 0.2 g of the solid (the support had been calcined at 800 °C) was added to about 15 mL of absolute ethanol. After 1 h of contact, the solid was recovered by filtration and the supernatant solution and solid examined by infrared spectroscopy.

In a second experiment, 0.93 g of the solid (calcined at 600 °C) was protonated at −78 °C with 10 mL of degassed concentrated phosphoric acid. Dry hexane was transferred onto the frozen aqueous layer and the reaction vessel allowed to warm slowly to room temperature. In the process most of the solid dissolved, leaving a light-yellow aqueous layer. The flask was agitated, the hexane layer removed, and fresh hexane added. The aqueous layer was extracted three times with dry hexane, leaving a slightly discolored aqueous solution containing approximately 0.1 g of suspended white solid. Infrared spectra were obtained of the extract solutions.

Catalytic Hydrogenation of CO. A catalyst sample (0.498 g) prepared from **1** adsorbed on magnesia that had been pretreated at 400 °C was loaded into a copper-lined tubular flow reactor without exposure to air. The catalyst was brought on stream under flowing H_2 + CO (equimolar), and the pressure was raised to 10 atm. The catalyst was then heated in a period of 2 h to 275 °C. The feed composition was changed to 3:1 H_2:CO (molar ratio), the time of the change being defined as zero time on stream under reaction conditions. The total reactant flow rate was 0.31 mL/s (STP). The effluent stream was analyzed for hydrocarbons and oxygenated compounds with an on-line Antek 300 gas chromatograph equipped with flame ionization detectors. Two $^1/_8$-in. stainless steel columns were used, one packed with Porapak PS (Supelco) and the other with activated alumina. The gases were Matheson UHP grade and were purified by passage over activated 5A molecular sieve; the hydrogen also flowed over supported Cu_2O. Any impurity iron carbonyl or nickel carbonyl in the CO feed was decomposed in a trap held at 275 °C. Product compositions were measured as a function of time on stream in the flow reactor. At the conclusion of the experiment, the catalyst was cooled to 25 °C in flowing reactants and then transferred to the drybox without exposure to air.

Results and Discussion

Deprotonation of Transition-Metal Hydrides. Transition-metal hydrides are well-known proton donors.[9] The deprotonation of the osmium carbonyl hydrides $[H_2Os(CO)_4]$[10,11] (**1**) and $[H_4Os_4(CO)_{12}]$[10,12] by soluble bases gives the respective monoanions, $[HOs(CO)_4]^-$ (**2**) and $[H_3Os_4(CO)_{12}]^-$ (**4**). The deprotonation of $[H_4Os_4(CO)_{12}]$[13] and $[H_4RuOs_3(CO)_{12}]$[14] by the surface of hydrated γ-Al_2O_3 has also been reported. Since the surface chemistry of magnesia is dominated by a strong Brønsted basicity[15] exceeding that of γ-Al_2O_3, we expected the formation of surface-bound anions from even weakly acidic metal hydrides on magnesia.

Physisorption of 1 on Silica. To demonstrate the simple physical adsorption of **1** on a metal oxide, this complex was adsorbed on the relatively unreactive and nearly neutral surface of silica that had been dehydrated at 400 °C. The surface infrared spectrum is shown in Figure 1B, with the absorptions in the CO stretching region associated with the silica support removed computationally. A comparison of this spectrum with that of **1** in hexanes (Figure 1A) shows that the effect of adsorption on silica is to induce only little change in the infrared spectrum, with slight broadening and shifting to higher wavenumbers observed for all bands. The complex **1** could be removed from the silica surface by evacuation at room temperature. We conclude that the interaction of this organometallic compound with the silica surface was weak: **1** is simply physisorbed.

---

(1) Anderson, J. R. "Structure of Metallic Catalysts"; Academic Press: New York, 1975.

(2) Psaro, R.; Ugo, R. In "Metal Clusters in Catalysis"; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, in press. (b) Ugo, R.; Psaro, R. *J. Mol. Catal.* **1983**, *20*, 53. (c) Psaro, R.; Dossi, C.; Ugo, R. *J. Mol. Catal.* **1983**, *21*, 331. (d) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95. (e) Deeba, M.; Scott, J. P.; Barth, R.; Gates, B. C. *J. Catal.* **1981**, *71*, 373.

(3) Muetterties, E. L. *Science* **1977**, *196*, 839.

(4) Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, *13*, 1.

(5) Literature ν_{CO} = 2141 (w), 2067 (m), 2055 (s), 2048 (vs) cm^{-1} (heptane): L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1967**, *6*, 2092.

(6) Walker, H. W.; Ford, P. C. *J. Organomet. Chem.* **1981**, *214*, C43.

(7) Hayward, T. C.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.

(8) Barth, R.; Gates, B. C.; Zhao, Y.; Knözinger, H.; Hulse, J. *J. Catal.* **1983**, *82*, 147.

(9) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(10) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179.

(11) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(12) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 673.

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

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

(15) Garrone, E.; Stone, F. S. *Proc. Int. Congr. Catal., 8th* **1984**, *3*, 441.

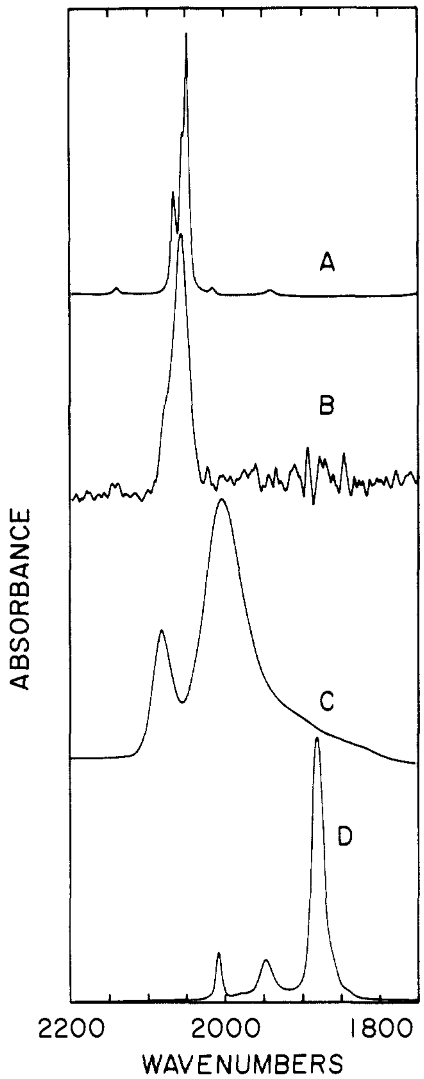

Figure 1. Infrared spectra of (A) [$H_2Os(CO)_4$] in hexane, (B) [$H_2Os(CO)_4$] physisorbed on silica, (C) [$H_2Os(CO)_4$] adsorbed on magnesia, and (D) [PPN][$HOs(CO)_4$] in THF.

Chemisorption of 1 by Deprotonation on Dehydrated Magnesia. When a colorless solution of **1** in hexanes was brought in contact with magnesia pretreated at 800 °C, the initially white magnesia powder became light yellow. The infrared spectrum of the resulting solid (Figure 1C) has strong absorptions at 2084 and 2006 cm^{-1} and weak absorptions at 1905, 1860, and 1825 cm^{-1}. This spectrum is clearly different from that of **1** in hexane solution (Figure 1A) and different from the spectrum of [PPN][**2**] in THF (Figure 1D). The surface species is stable under vacuum at 25 °C, as indicated by infrared spectroscopy. The solid displays strong UV-visible absorption only in the region $\lambda < 400$ nm, consistent with its light-yellow color. This color is suggestive of the formation of the monoanion, since **2** is yellow in the solid state and in solution.[16,17]

To test the hypothesis of deprotonation of **1** upon reaction with the magnesia surface, the salt, [PPN][**2**], was adsorbed onto magnesia from THF solution. The infrared spectrum of the resulting solid (in the absence of washing with THF) is shown in Figure 2C. The intense band near 1900 cm^{-1} is assigned to the adsorbed anion, still associated with the bulky PPN cation.[18] However, the bands at 1997 and 2070 cm^{-1} are similar to those observed following adsorption of **1** on magnesia. The former assignment was confirmed by the removal of most of the weakly bound salt by washing of the solid with THF. The spectrum of the remaining (surface-bound) complex (Figure 2B) may be compared directly with that obtained from adsorption of **1** (Figure 2A). (The subtle differences between the spectra of Figures 1C and 2A result from the exposure of the surface to THF vapor; this effect is discussed below.) These results are consistent with the inference that the product of the interaction of **1** with the magnesia surface is the anion **2**, but the three-band infrared spectrum of **2** is strongly perturbed by the interaction of the complex with the magnesia surface.

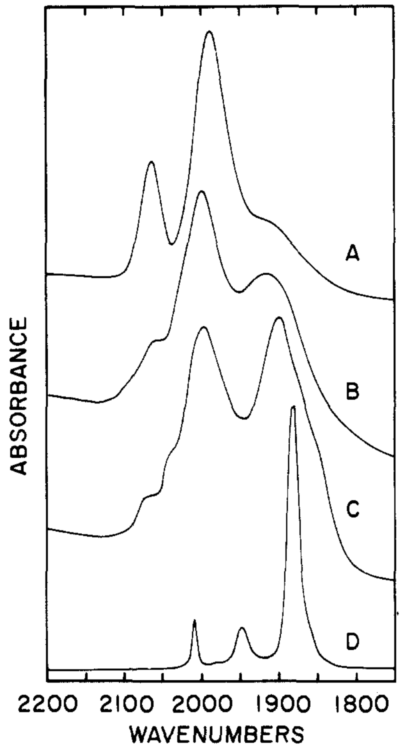

Figure 2. Infrared spectra of (A) [$H_2Os(CO)_4$] adsorbed on magnesia (sample exposed to THF vapor), (B) [PPN][$HOs(CO)_4$] adsorbed on magnesia (sample washed with THF), (C) sample of spectrum B before washing with THF, and (D) [PPN][$HOs(CO)_4$] in THF.

Extraction of the Surface-Bound Complex. To test for the presence of **2** on samples prepared by adsorption of **1**, a series of experiments was performed with the goal of isolating the anion or its conjugate acid in solution for positive identification. Treatment of the solid with [Me_4N][Cl] in THF resulted in the isolation of [Me_4N][**2**] [ν_{CO} = 2015 (m), 1951 (m), 1890 (s sh) 1880 (s), 1820 (m) cm^{-1}].[19] The results of this experiment demonstrate that **2** is available at the surface to be extracted into solution by simple cation metathesis. The neutral complex **1** was recovered from the magnesia surface following protonation with phosphoric acid. After contacting the solid with concentrated H_3PO_4 at −78 °C, significant quantities of **1** were isolated by extraction of the resulting aqueous solution with hexanes. The neutral complex was also released from the surface as a result of treating of the solid with absolute ethanol. Pure **1** was obtained with either technique.

When [Me_4N][Cl] was added to dry 2-propanol and used in an attempt to remove the carbonylosmate anion from the surface by ion exchange, a complication was encountered which can be traced to the protic solvent. Instead of pure [Me_4N][**2**], a mixture of species was obtained. Infrared bands of the solution were observed at 2082 (w), 2070 (w), 2049 (m), 2024 (s), 1995 (s), 1958 (s br), and 1897 (vs br) cm^{-1}. The bands at 2024, 1958, and 1897 cm^{-1} are unambiguously assigned to [Me_4N][**2**][18] and

---

[16] Walker et al.[10] followed the deprotonation of [$H_2Os(CO)_4$] by observing the appearance of an absorption at 350 nm.

[17] L'Eplattenier, F. *Inorg. Chem.* **1969**, *8*, 965.

[18] [PPN][**2**] in 2-propanol has infrared absorptions at 2022 (m), 1959 (m), and 1897 (vs) cm^{-1}; comparison with the bands observed in THF solution (ν_{CO} = 2010 (m), 1949 (m), 1882 (vs) cm^{-1}) indicates that the band positions are solvent sensitive.

[19] A single extraction with excess [Me_4N][Cl] in THF was insufficient to remove quantitatively the surface-bound anion; the extracted solid retained its yellow color and an infrared spectrum similar to that of the fresh material.

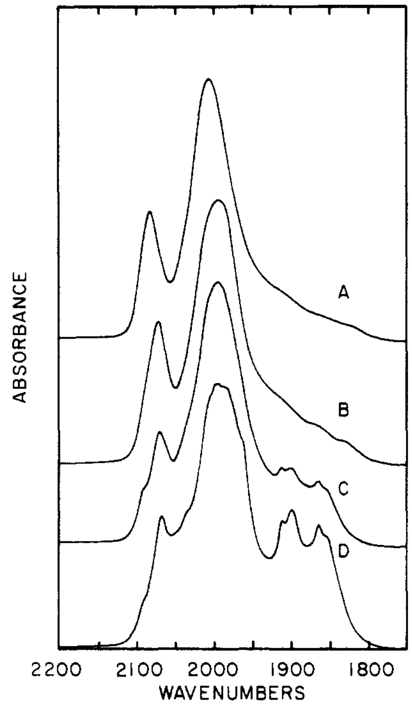

Figure 3. Infrared spectra of $[HOs(CO)_4]^-$ on magnesia pretreated at 800 °C (A), 600 °C (B), 400 °C (C), and 200 °C (D).

those at 2070 and 2049 cm^{-1} to **1**. The bands at 2082 and 1995 cm^{-1}, in conjunction with those at 2024 and 1958 cm^{-1}, are assigned to $[Me_4N][HOs_3(CO)_{11}]$.[20]

The presence of $[HOs_3(CO)_{11}]^-$ in the alcoholic extract solution is understandable since **2** has been shown to undergo condensation in protic media to form the trinuclear cluster anion.[21] The stoichiometry is suggested to be comparable to that observed for $[K][HRu(CO)_4]$:[21]

$$HOs(CO)_4^- + BH \rightarrow H_2Os(CO)_4 + B^- \tag{1a}$$

$$2H_2Os(CO)_4 + HOs(CO)_4^- \rightarrow HOs_3(CO)_{11}^- + CO + 2H_2 \tag{1b}$$

where BH represents a Brønsted acid. The presence of both **1** and **2** in the extract solution supports this suggestion. This condensation process may also be important on the magnesia surface, as discussed below.

Influence of Surface Hydration. The results discussed above pertain to samples prepared from magnesia pretreated at 800 °C. Following calcination at this temperature, the magnesia surface is highly dehydroxylated[22] and free of carbonate contamination. The simplicity of the surface treated in this way suggests that **1** may be deprotonated at surface $\{Mg^{2+}O^{2-}\}$ pairs (where the braces imply surface species); analogous behavior has been observed for organic Brønsted acids:[15]

$$H_2Os(CO)_4 + \{Mg^{2+}O^{2-}\} \rightarrow \{Mg^{2+}[HOs(CO)_4]^-\} + \{OH^-\} \tag{2}$$

where $\{OH^-\}$ is a surface hydroxyl group. Hugues et al.[23] and Guglielminotti and Zecchina[24] observed the adsorption of $[Fe(CO)_5]$ on hydroxylated and dehydroxylated magnesia surfaces, respectively. Hugues et al. inferred the formation of $\{HFe_3(CO)_{11}^-\}$ from $[Fe(CO)_5]$ adsorbed on hydroxylated magnesia. The cluster formation may be postulated to result from the initial formation of $\{HFe(CO)_4^-\}$ via nucleophilic attack of a surface hydroxyl group at a carbonyl ligand followed by condensation of the anion in the presence of surface water to form $\{HFe_3(CO)_{11}^-\}$.[21] Guglieliminotti and Zecchina inferred the formation of $\{Fe(CO)_4(CO_2)Mg\}$ from the adsorption of $[Fe(CO)_5]$ on the highly dehydroxylated surface. These sharply contrasting results motivated us to investigate the surface chemistry of **1** adsorbed on magnesia with varying degrees of hydration, controlled by the pretreatment temperature.

Table I. Effect of Pretreatment on the Extent of $[H_2Os(CO)_4]$ Adsorption on Magnesia

MgO pretreatment temp, °C	specific surface area, m^2 g^{-1}	loading,[a] wt % of Os	surface density, Os atoms nm^{-2}
200	69	1.1	0.49
400	75	1.2	0.50
600	35	0.82	0.75
800	34	0.76	0.71

[a] Loadings were determined for samples prepared with aliquots of a single hexane solution containing **1**.

The infrared spectra of the solids obtained following adsorption of **1** on magnesia dehydrated at 800, 600, 400, and 200 °C are shown in Figure 3. The spectra are similar, but the two strong bands observed at 2084 and 2006 cm^{-1} characterizing the highly dehydrated surface treated at 800 °C shift monotonically to lower wavenumbers with increasing surface hydration. Four low-frequency features in the 1850–1900 cm^{-1} region appear in the spectra of the hydrated surfaces (pretreated at 400 and 200 °C). These bands are suggested to be associated with weakly interacting **2** in a solvent-like environment on the surface. The broad and asymmetric nature of the bands observed for these hydrated materials suggests the presence of a mixture of species, with **2** being predominant.

These results indicate that on all the surfaces, regardless of the degree of hydration, **1** was deprotonated to form the anion **2**. This hypothesis is supported by the spectroscopic data and also by data (Table I) showing that the osmium loading varies only weakly with surface pretreatment temperature.[25] The extent of adsorption, expressed as the surface density of complexes, is approximately 50% higher on the highly dehydroxylated surfaces pretreated at 600 and 800 °C. The osmium carbonyl hydride was deprotonated not only by the basic hydroxyl groups present on the hydrated surfaces but also at $\{Mg^{2+}O^{2-}\}$ pairs characteristic of the dehydrated surface (eq 2).[26] We suggest that the major role of adsorbed water is simply to control the degree of local interaction achieved between the organoosmium anion and the surface.

To confirm the possible role of adsorbed water in shifting the infrared bands, a sample prepared by adsorption of **1** on magnesia pretreated at 800 °C was exposed to increasing amounts of water vapor; the shifts of the two strong bands of the surface-bound anion to lower frequency were observed as expected.[27] In another experiment, stringent precautions were taken to prevent water contamination of the solution of **1** prior to its being brought in contact with the magnesia; preparation of **1** by the second method mentioned above ensured a thoroughly dry solution. Adsorption of **1** from such a solution onto dehydrated magnesia led to an infrared spectrum with strong bands at 2104 and 2019 cm^{-1}. A new low-frequency band also appeared at 1760 cm^{-1} (Figure 4A). The high-frequency absorptions are shifted in the direction opposite to that observed on addition of water. The sensitivity of the surface complex to coadsorbed water further supports the hypothesis that the degree of surface hydration influences the strength of the anion–surface interaction.

---

[20] Literature ν_{CO} = 2083 (w), 2020 (s), 1996 (s), 1958 (m), 1667 (w br) cm^{-1} (CH_2Cl_2): Eady, C. R.; Guy, J. J.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 602.

[21] Bricker, J. C.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1984**, *3*, 201.

[22] Anderson, P. J.; Horlock, R. F.; Oliver, J. F. *Trans. Faraday Soc.* **1965**, *61*, 2754.

[23] Hugues, F.; Basset, J. M.; Ben Taarit, Y.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020.

[24] Guglielminotti, E.; Zecchina, A. *J. Mol. Catal.* **1984**, *24*, 331.

[25] Negligible adsorption of **1** occurred on magnesia surfaces contaminated by carbonates.

[26] From the data of Anderson et al.[22] we estimate surface hydroxyl group densities of <2 $\{OH^-\}$/nm^2 for pretreatment temperatures >600 °C and >10 $\{OH^-\}$/nm^2 for pretreatment temperatures <400 °C.

[27] In the limit of multilayer adsorption of water followed by brief evacuation, the peak maxima shifted to 2060 and 1988 cm^{-1}.

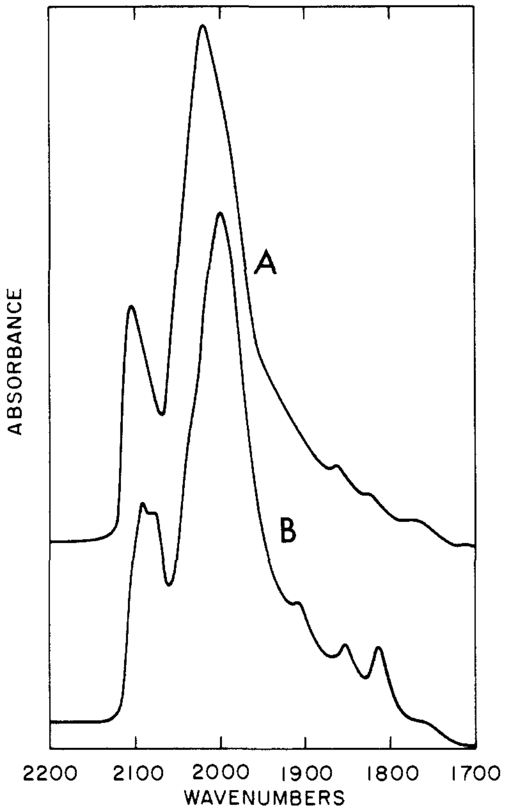

Figure 4. Infrared spectrum of $[HOs(CO)_4]^-$ on magnesia pretreated at 800 °C (A) and 600 °C (B). The preparations were carried out with strict exclusion of water.

Evidence of Surface Ion Pairs. The nature of the interactions between soluble hydrido carbonylate anions, such as $[HFe(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$, and alkali metal ions has been the subject of recent investigations.[28,29] Adduct formation between neutral metal carbonyls and Lewis acids, both in solution[30] and on surfaces,[31] has also been investigated. It has been demonstrated that $[HFe(CO)_4]^-$, which exhibits C_{3v} symmetry as the PPN^+ salt in THF, engages in contact ion pairing via a single equatorial carbonyl group as the Na^+ salt in THF.[28] To test for a similar phenomenon involving the isostructural osmium anion, a 4:1 excess of sodium tetraphenylboron was added to a THF solution of [PPN][**2**]. The infrared spectra of the solution before and after metathesis are shown in Figure 5. The most notable change was the appearance of a low-frequency band at 1850 cm^{-1};[32] the bands originally located at 2010, 1949, and 1882 cm^{-1} were broadened and shifted at most 2 cm^{-1} to higher wavenumbers.[33] The presence of the low-frequency absorption following metathesis is evidence of a localized interaction between the Na^+ ion and a particular carbonyl group of the carbonylosmate anion.[28] The spectrum (Figure 5B) suggests that a mixture of contact ion pairs and solvent-separated ion pairs exists for [Na][**2**] in THF, consistent with previous observations for $[Na][HFe(CO)_4]$.

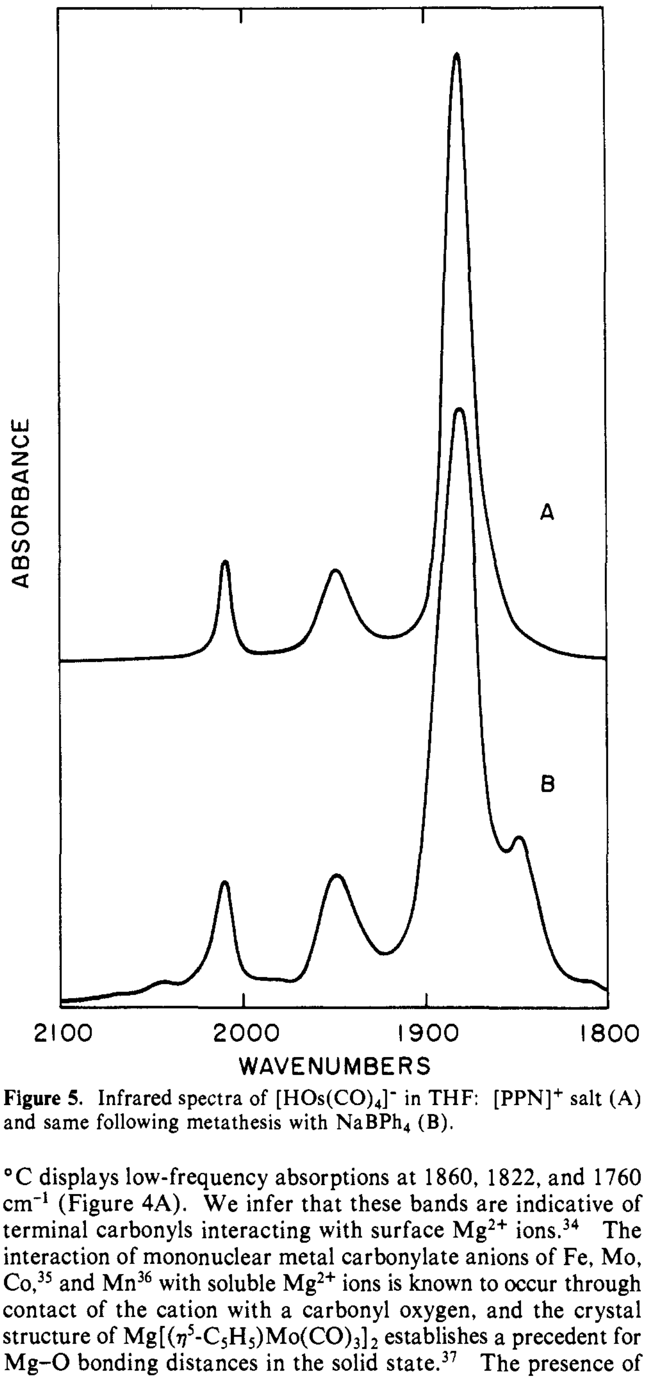

Figure 5. Infrared spectra of $[HOs(CO)_4]^-$ in THF: $[PPN]^+$ salt (A) and same following metathesis with $NaBPh_4$ (B).

By analogy to the contact ion pairs formed in solution, we interpret the infrared spectrum of **2** on the magnesia surface as suggestive of a strong interaction of the complex with surface Mg^{2+} ions. The spectrum of the surface-bound anion prepared by adsorbing **1** from dry hexanes onto magnesia pretreated at 800 °C displays low-frequency absorptions at 1860, 1822, and 1760 cm^{-1} (Figure 4A). We infer that these bands are indicative of terminal carbonyls interacting with surface Mg^{2+} ions.[34] The interaction of mononuclear metal carbonylate anions of Fe, Mo, Co,[35] and Mn[36] with soluble Mg^{2+} ions is known to occur through contact of the cation with a carbonyl oxygen, and the crystal structure of $Mg[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ establishes a precedent for Mg–O bonding distances in the solid state.[37] The presence of multiple low-frequency bands in the infrared spectrum may be explained (1) by several chemically distinct sites for carbonyl interaction or (2) by more than one carbonyl of the anion interacting with Mg^{2+}.[38] The former explanation seems more plausible since the strong high-frequency bands are broad and asymmetric, suggesting that they are the superposition of absorptions indicative of several chemically distinct species.[39] The observation of multiple binding sites for **2** on magnesia confirms the intrinsic heterogeneity of the highly dehydroxylated surface. Three types of magnesia surface site have been identified by UV

---

(28) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297.

(29) Schick, K. P.; Jones, N. L.; Sekula, P.; Boag, N. M.; Labinger, J. A.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 2204.

(30) Hodali, H. A.; Shriver, D. F. *Inorg. Chem.* **1979**, *18*, 1236.

(31) Tessili-Youngs, C.; Correa, F.; Ploch, D.; Burwell, R. L., Jr.; Shriver, D. F. *Organometallics* **1983**, *2*, 898.

(32) This low-frequency band of [Na][**2**] in THF had been tentatively assigned to an Os–H vibration;[17] Jordan and Norton[11] suggested that a similar band for [K][**2**] was due to tight ion pairs.

(33) Weak absorptions were observed at 2046, 1983, and 1811 cm^{-1} following metathesis.

(34) One of these bands could arise from the Os–H vibration.

(35) McVicker, G. B. *Inorg. Chem.* **1975**, *14*, 2087.

(36) Pribula, C. D.; Brown, T. L. *J. Organomet. Chem.* **1974**, *71*, 415.

(37) Ulmer, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4469.

(38) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

(39) The attribution of the relative broadness of surface infrared bands to the heterogeneity of surface sites is common in the literature,[31] but rarely have unambiguously resolved splittings, like those observed here for the low-frequency bands, been reported.

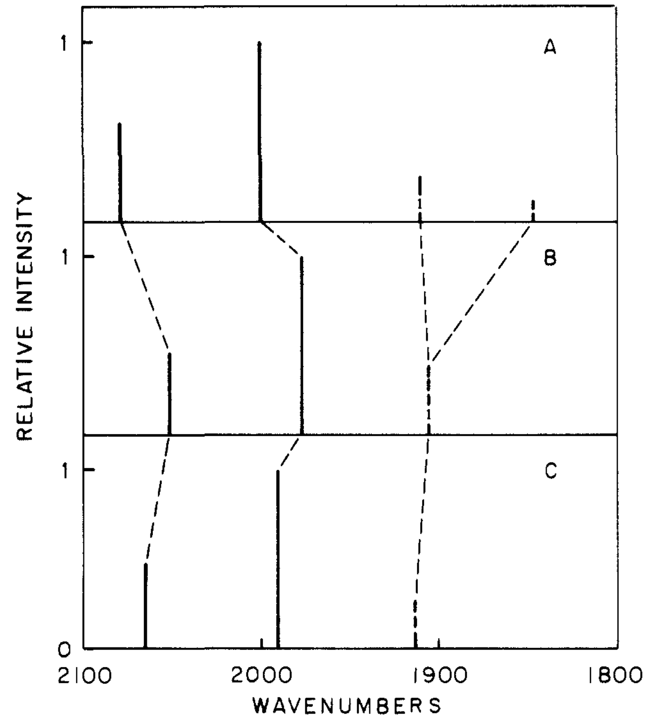

Figure 6. Schematic representation of the infrared spectral changes accompanying THF adsorption on magnesia incorporating surface-bound $[HOs(CO)_4]^-$: fresh sample (A); following exposure to 50 torr of THF vapor (B); after brief evacuation (C). (Dashed bars indicate shoulders; spectrum B has been corrected for absorptions of THF vapor.)

diffuse reflectance and fluorescence spectroscopies. These are characterized by three-, four-, and fivefold Mg coordination at the surface.[15,40] The spectrum of **2** on magnesia pretreated at 600 °C (Figure 4B) illustrates particularly well the presence of related but chemically distinct surface species. After momentary exposure of this sample to air, the low-energy bands at 1824 and 1772 cm^{-1} disappeared, and the high-energy absorptions coalesced to form two single symmetric bands at 2072 and 2000 cm^{-1}.

Further evidence of a localized interaction between the organoosmium anion and surface cations was obtained by examining the effect of coadsorption of Lewis bases on the infrared spectrum of the former. The results of Figure 6 illustrate the effect of THF adsorption at 25 °C on a sample prepared by the first method described above. The low-frequency shoulder appearing at 1845 cm^{-1} for the fresh material was removed, apparently coalescing in the presence of THF with the band at about 1900 cm^{-1}. Concomitantly, the strong, high-frequency bands shifted 28 and 24 cm^{-1} to 2051 and 1977 cm^{-1}, respectively. These changes were partially reversed by evacuation of the sample at room temperature. When other lone-pair donors such as water, pyridine, and ethanol were adsorbed, similar shifts in the CO stretching region were observed. The strong high-frequency bands assigned to the surface anion were shifted 5–30 cm^{-1} to lower wavenumbers, depending on the coadsorbing molecule, and the low-frequency bands observed for the freshly prepared materials were removed from the spectrum. The low-frequency CO stretching bands observed for these samples and the water-free materials discussed above, together with removal of the splitting upon exposure of the surface to base, suggest that (1) the surface-bound anion interacts directly via a carbonyl ligand with a surface Mg^{2+} ion and (2) this interaction may be moderated by the coadsorption of competing lone-pair donors. The shift of the bands assigned to the noninteracting carbonyl ligands to lower frequency following exposure to base is a secondary effect consistent with the increase in metal electron density expected following the attenuation of the interaction.

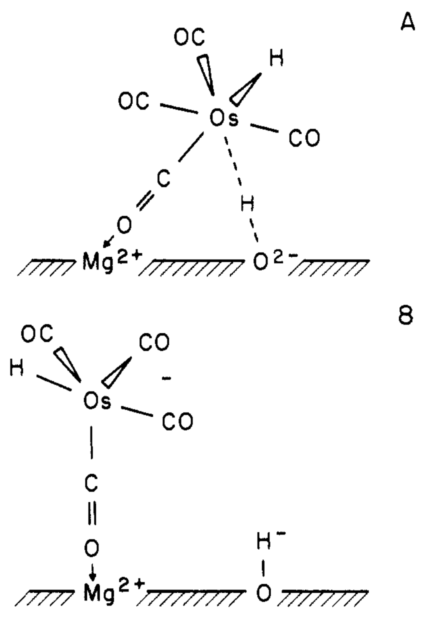

Figure 7. Structures of surface species formed by adsorption of $[H_2Os(CO)_4]$ on dehydrated magnesia.

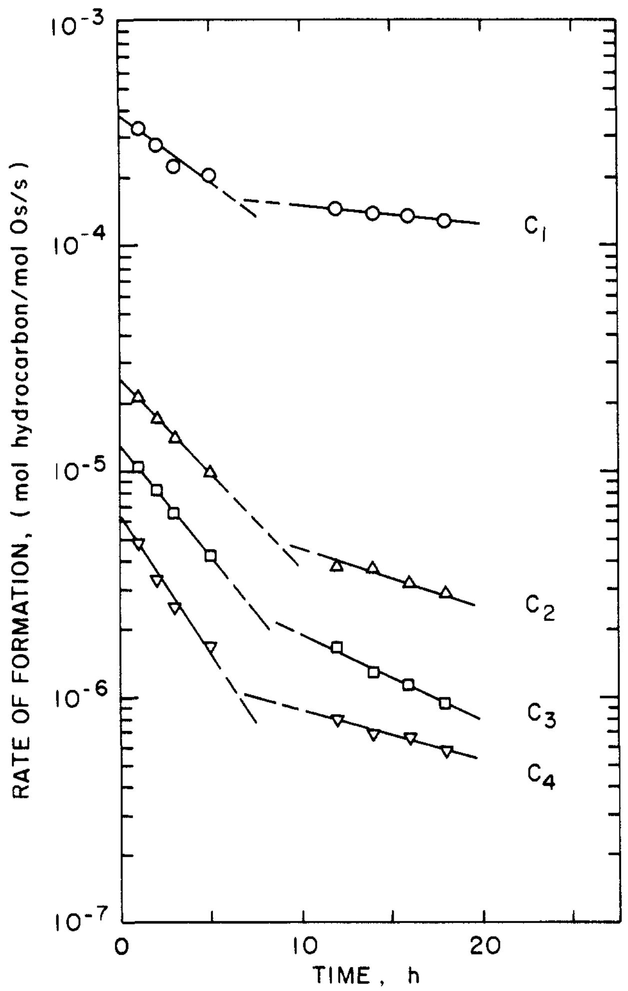

Figure 8. Catalytic hydrogenation of CO in a flow reactor at 275 °C and 10 atm. The catalyst was prepared by adsorption of $[H_2Os(CO)_4]$ on magnesia.

A scheme for the adsorption of **1** on the highly dehydroxylated magnesia surface is suggested in Figure 7. The initial interaction of the complex with the surface is envisioned to occur at a $\{Mg^{2+}O^{2-}\}$ site (Figure 7A), followed by deprotonation of the complex to form the supported anion and a surface hydroxyl group

---

[40] Zecchina, A.; Lofthouse, M. G.; Stone, F. S. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1476.

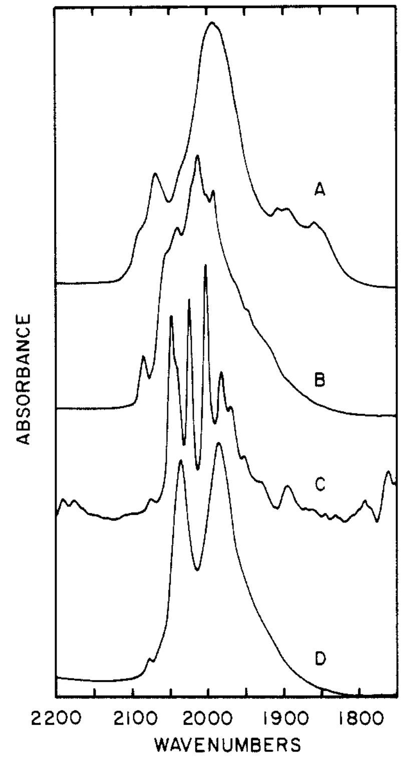

Figure 9. Infrared spectra of (A) fresh catalyst prepared from [$H_2Os(CO)_4$] and magnesia, (B) sample after use as a CO hydrogenation catalyst, (C) [Me_4N][Cl] extract of used catalyst, and (D) solid after extraction.

(Figure 7B).[41] Consistent with the arguments presented above, the strength of the carbonylate anion–Mg^{2+} ion interaction should be greatest at sites with highest coordinative unsaturation of the Mg^{2+} ions. Coadsorption of lone-pair donors would be expected to attenuate or eliminate this direct anion–Mg^{2+} binding, since the adsorbed base would coordinate with surface Mg^{2+} ions. The results for the hydrated and base-dosed samples confirm this hypothesis.

Catalytic Chemistry of CO Hydrogenation. A sample of supported **2** prepared from the adsorption of **1** on magnesia pretreated at 400 °C was tested as a catalyst for CO hydrogenation. The sample was heated at 275 °C in a mixture of flowing 1:1 (molar) H_2:CO at 10 atm., without any other pretreatment. The feed to the flow reactor was then switched to a 3:1 (molar) H_2:CO mixture, the time of the switch being defined as zero time under reaction conditions.

Analysis of the catalytic reaction products by on-line gas chromatography showed that C_1–C_4 hydrocarbons were formed, with a distribution that appears to conform to the Schulz–Flory polymerization model (Figure 8). The activity of the catalyst, defined as the rate of CO hydrogenation (calculated on the basis of the assumption that the low observed conversions (<0.7%) were differential), was initially relatively high and characterized by a rapid loss of activity ($t_{1/2}$ = 5 h) followed by a period of slow deactivation (Figure 8). The activity after 12 h was 1.5×10^{-4} molecules of hydrocarbon/Os atom·s. For comparison, a rate of 28.5×10^{-4} molecules of hydrocarbon/Os atom·s was reported for an Os/γ-Al_2O_3 catalyst prepared from [$Os(CO)_5$] and decarbonylated before catalytic testing; this catalyst consisted of small aggregates of Os metal on the surface.[42]

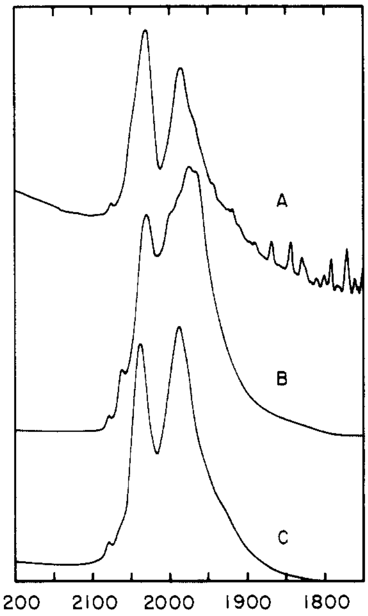

Figure 10. Infrared spectra of (A) [Et_4N]$_2$[$Os_{10}C(CO)_{24}$] in KBr, (B) [Et_4N]$_2$[$Os_{10}C(CO)_{24}$] adsorbed on magnesia, and (C) used CO hydrogenation catalyst following extraction with [Me_4N][Cl].

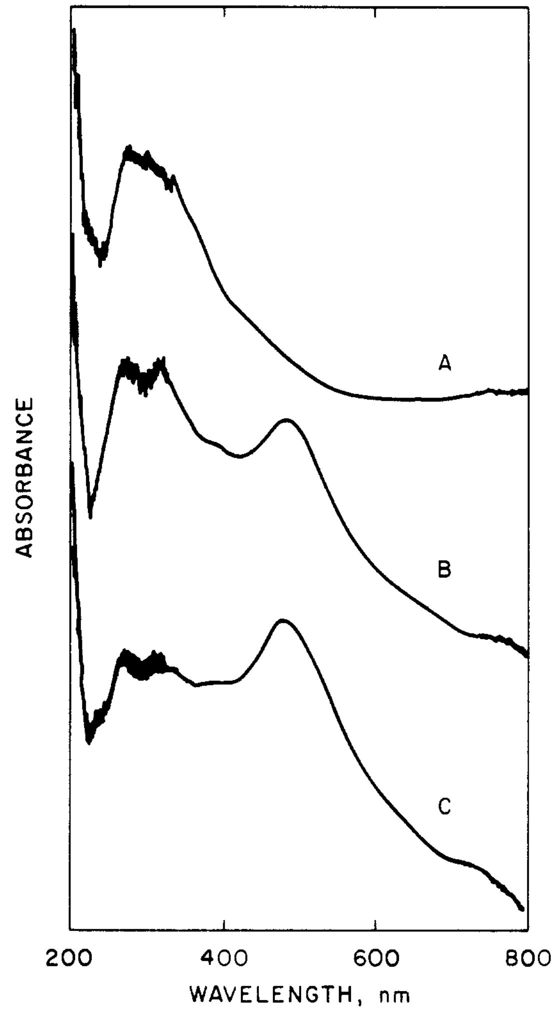

Figure 11. Electronic spectra of (A) sample prepared from [$H_2Os(CO)_4$] and magnesia, (B), used catalyst, and (C) [Et_4N]$_2$[$Os_{10}C(CO)_{24}$] adsorbed on magnesia.

When the used magnesia-supported catalyst was removed from the reactor, it was reddish-brown with no visible indication of metallic osmium. Analysis indicated that 36% of the osmium had

---

[41] The possibility that the proton remains within the coordination sphere of the osmium anion must be considered. F. Calderazzo, G. Fachinetti, and F. Marchetti (*J. Chem. Soc., Chem. Commun.* **1981**, 181) reported the crystal structure of [NEt_3H][$Co(CO)_4$], formally an anionic complex derived from the deprotonation of [$HCo(CO)_4$] by NEt_3. The hydrogen atom was found to retain a distinct coordination site at Co with simple elongation of the Co–H distance. This solid-state structure may be taken as a basis for the structure postulated in Figure 7A.

[42] Odebunmi, E. O.; Zhao, Y.; Knözinger, H.; Tesche, B.; Manogue, W. H.; Gates, B. C.; Hulse, J. *J. Catal.* **1984**, *86*, 95.

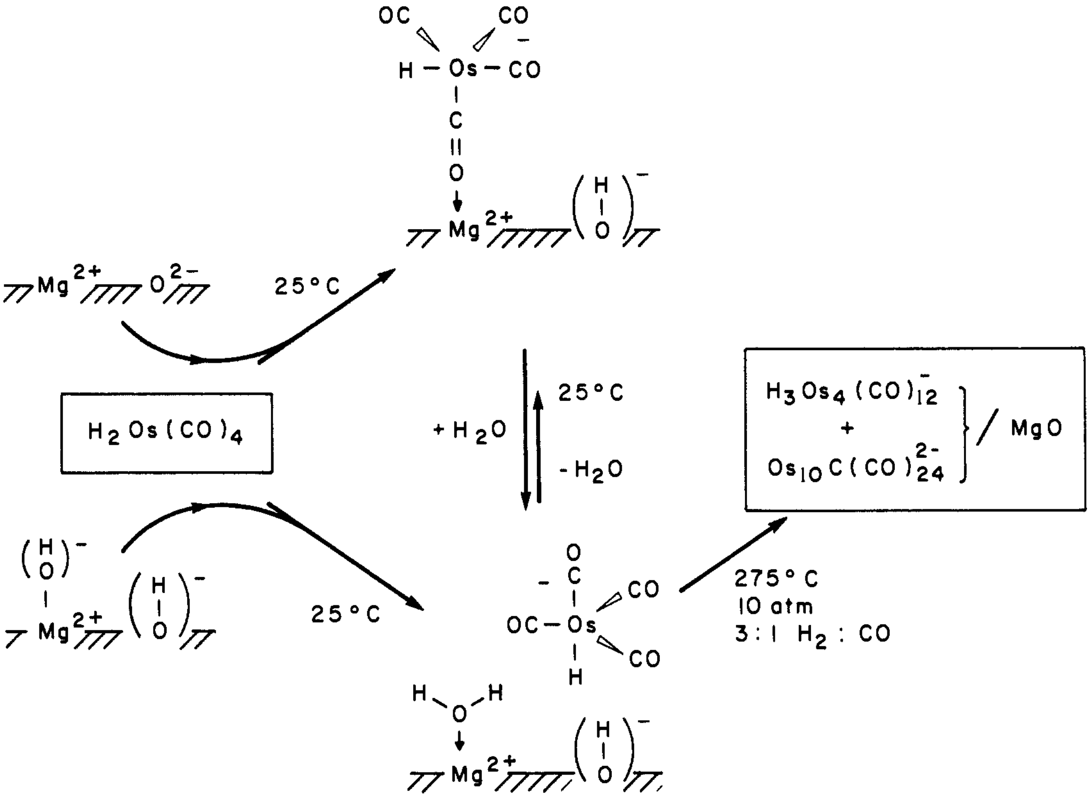

Figure 12. Schematic representation of the transformations of $[H_2Os(CO)_4]$ on magnesia following adsorption and during catalysis of CO hydrogenation.

been lost from the catalyst during the experiment, presumably as the volatile **1**.

The used catalyst (handled in the absence of air) was examined by infrared spectroscopy after removal from the reactor. The spectra in the ν_{CO} region of the fresh and used catalysts are shown in Figure 9. A comparison shows that the organoosmium precursor was transformed during catalysis. When a portion of the reddish-brown sample was treated with $[Me_4N][Cl]$ in 2-propanol, a yellow extract solution was obtained that exhibited the infrared spectrum shown in Figure 9C. This spectrum is nearly the same as that of $[H_3Os_4(CO)_{12}]^-$ (**4**).[43] After extraction, the solid was red, and its simple infrared spectrum (Figure 9D) suggested that a molecular metal carbonyl remained on the surface.

The remaining surface species was identified as the highly stable $[Os_{10}C(CO)_{24}]^{2-}$ (**3**) by its infrared and UV-visible spectra. This compound was not extracted from the surface; this cluster anion has negligible solubility in 2-propanol. The infrared spectrum of the surface species is compared in Figure 10 with that of $[Et_4N]_2$[**3**][44] in KBr and adsorbed on magnesia. The agreement is good, although there are slight differences, ascribed to variations in the local environments between the different samples. Confirmation of the identity of the red surface species was obtained from UV-visible spectroscopy. The comparison of the electronic spectra of the fresh and used catalysts with that of the $[Et_4N]_2$[**3**] on magnesia (Figure 11) shows that the strong absorption at 485 nm is common to the used catalyst and **3**, being associated with their reddish appearance.

To repeat, two well-characterized molecular metal clusters have been identified on the surface of magnesia following CO hydrogenation catalysis, one being the extractable anion **4** and the other being the decanuclear dianion **3**; there was no evidence of any other osmium structures on the used catalyst. In earlier work,[2e] the involvement of molecular osmium carbonyl clusters on magnesia as intermediates in CO hydrogenation catalysis had been suggested; the reported spectra[2e] are consistent with those observed in this work, but they are not sufficient for structural inferences such as those stated above.

The formation of these two stable osmium surface clusters from **2** under catalytic conditions may be accounted for on the basis of known organoosmium solution chemistry. $[H_4Os_4(CO)_{12}]$ and **1** were identified by Nicholls et al.[45] as the stable osmium carbonyls existing in the presence of H_2 or H_2/CO mixtures. Further, $[H_4Os_4(CO)_{12}]$ is itself deprotonated on magnesia to form **4**.[46] The synthesis of the carbido osmium cluster is known to be promoted by basic conditions; Hayward and Shapley[7] reported the formation of this cluster from $[Os_3(CO)_{12}]$ in the presence of metallic sodium at 260–265 °C. We infer that in our experiment the magnesia serves as a reducing agent, by deprotonating **1** to form **2**, which can then condense to form the higher-nuclearity osmium complexes.

To summarize the surface organometallic chemistry, a scheme is proposed (Figure 12) illustrating the formation of the stable clusters **3** and **4** from **1** adsorbed on hydrated magnesia. The initial condensation product of **2**, namely $[HOs_3(CO)_{11}]^-$, is suggested as an intermediate in the formation of **3** and **4** on magnesia. The formation of $[H_3Ru_4(CO)_{12}]^-$ from $[HRu_3(CO)_{11}]^-$ and $[Ru_3(CO)_{12}]$ in solution has been observed by Bricker et al.,[47] and $[Os_6(CO)_{18}]^{2-}$ has been observed as an intermediate product in the homogeneous synthesis of **3**.[7] We speculate that this hexanuclear cluster anion may have been an intermediate in the surface synthesis of **3** on magnesia. If this were correct, then a trinuclear cluster anion, such as $[HOs_3(CO)_{11}]^-$ or $[Os_3(CO)_{11}]^{2-}$, could be a common precursor for both **3** and **4** on the magnesia surface. The parallels observed between the homogeneous and surface cluster chemistry of osmium appear to be strong; the basic character of the surface is essential.

The identification of the catalytically active surface species requires more data, but mononuclear complexes are considered unlikely intermediates, since C=O bond-breaking and C—C bond-forming reactions are believed to require neighboring metal centers. The formation of **3**, which contains an interstitial carbon

---

[43] Observed ν_{CO} = 2047 (s), 2023 (s), 2002 (s), 1981 (m) cm^{-1}; literature ν_{CO} = 2048 (s), 2022 (s), 2000 (s), 1976 (w) cm^{-1}.[11]

[44] Literature ν_{CO} = 2034 (s), 1992 (s) cm^{-1} (acetone).[7]

[45] Nicholls, J. N.; Farrar, D. H.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1395.

[46] Lamb, H. H., et al., to be published.

[47] Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444.

atom, implies that the precursor(s) of this compound had the capacity to reduce CO.[48] However, the decanuclear cluster is highly stable, and under catalytic reaction conditions it might be expected to remain coordinatively saturated and hence inactive. Therefore, of the compounds observed on the used catalyst, the tetranuclear cluster seems to be a plausible candidate for involvement in a catalytic cycle,[49] and the formation of the carbido osmium cluster may be associated with the deactivation of the catalyst.[50]

Several investigators have reported the formation of small zerovalent metal particles of Fe, Ru, and Os following thermal treatment of the respective surface-bound carbonyl complexes in vacuum or under inert atmospheres.[24,42,51] Experiments with **2** adsorbed on magnesia pretreated at 800 °C indicate that a similar agglomeration to give metallic osmium occurs upon heating the sample to 150 °C under vacuum; a blackening of the sample was observed. Since there was no evidence of metallic osmium on the used magnesia-supported CO hydrogenation catalyst, we infer that the presence of stabilizing CO was critical in preventing destruction of the molecular organometallics that occurs readily on less basic surfaces, especially in the absence of CO.

Conclusions

Adsorption of **1** on the basic surface of magnesia results in the formation of surface-bound **2**, regardless of the degree of hydration of the surface. The major role of surface water or other adsorbed lone-pair donors is to moderate the degree of interaction achieved between a carbonyl ligand of the mononuclear anion and a surface Mg^{2+} ion. Under conditions of catalytic reduction of CO by H_2, the mononuclear anion initially present undergoes condensation, yielding the stable cluster anions **3** and **4**. The formation of these molecular metal clusters on the basic magnesia surface parallels the homogeneous chemistry of osmium cluster synthesis. The tetranuclear cluster may be the precursor of the catalytically active species; the formation of the carbido osmium cluster may be associated with the catalyst deactivation.

Acknowledgment. This work was supported by grants from the National Science Foundation (CPE8218311), the Exxon Education Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

[48] (a) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2099. (b) Braga, D. P.; Henrick, K.; Johnson, B. F. G. Lewis, J.; McPartlin, M.; Nelson, W. J. H.; Sironi, A.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1983**, 1131.

[49] The reduction of CO ligands on the face of a triosmium cluster has been documented under conditions of low-temperature noncatalytic reaction: Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559. Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783.

[50] The formation of $[Os_{10}C(CO)_{24}]^{2-}$ on the surface of magnesia has been observed during the first 6 h of reaction by in situ high-pressure infrared spectroscopy.

[51] Basset, J. M.; Besson, B.; Choplin, A.; Hugues, F.; Leconte, M.; Rojas, D.; Smith, A. K.; Theolier, A.; Chauvin, Y.; Commereuc, D.; Psaro, R.; Ugo, R.; Zanderighi, Griaziani, M. In "Fundamental Research in Homogeneous Catalysis"; Giongo, M., Griaziani, M., Ed.; Plenum, New York and London, 1984; Vol. 4, p 19.

Photochemical Reduction of $CpW(CO)_3CH_3$ (Cp = η^5-C_5H_5) to $CpW(CO)_3^-$; An Isolobal Analogy to the Disproportionation of $Cp_2Mo_2(CO)_6$

Alan S. Goldman and David R. Tyler*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received November 2, 1984*

Abstract: Irradiation (λ > 380 nm) of $CpW(CO)_3Me$ in inert solvents in the presence of PPh_3 gives $[PPh_3CH_3^+][CpW(CO)_3^-]$ as well as the substitution product $CpW(CO)_2(PPh_3)Me$ ($\phi_{\mathrm{disappearance\ CpW(CO)_3Me}} = 0.45 \pm 0.005$, $\phi_{\mathrm{appearance\ CpW(CO)_3^-}} = 0.04 \pm 0.01$). The mechanism of $CpW(CO)_3^-$ formation was studied. Experiments suggest that $CpW(CO)_2(PPh_3)Me$ may be an intermediate in the reaction but direct reductive elimination of PPh_3Me^+ from this species or from $CpW(CO)(PPh_3)_2Me$ was ruled out. Experiments using $PTol_3$ demonstrated that PAr_3Me^+ (Ar = aryl) is formed from exogenous, not coordinated, phosphine. The mechanism proposed for the reduction of $CpW(CO)_3Me$ involves the intermediate formation of phosphoranyl radicals, $\cdot PPh_3Me$, formed by addition of Me radicals (from W–CH_3 homolysis) to PPh_3. Phosphoranyl reduction of a variety of metal species which are present in solution is shown to lead to $CpW(CO)_3^-$. The proposed mechanism is isolobal with a mechanism we proposed for the photochemical disproportionation of metal–metal bonded dimers (e.g., $Cp_2Mo_2(CO)_6$) involving 19-valence-electron intermediates.

Irradiation of the complex $CpW(CO)_3Me$ (Cp = η^5-C_5H_5) in the presence of various ligands, L, is well-known to give the substitution products $CpW(CO)_2(L)Me$.[1-4] Some time ago,

$$CpW(CO)_3Me + L \xrightarrow{h\nu} CpW(CO)_2(L)Me + CO \quad (1)$$

however, we reported[4] that irradiation of $CpW(CO)_3Me$ in the presence of PPh_3 also leads to the formation of $CpW(CO)_3^-$:

$$CpW(CO)_3Me \xrightarrow[PPh_3]{h\nu} CpW(CO)_3^- \quad (2)$$

(The cation formed in reaction 2 was not identified, but it is not a carbonyl-containing species.)

Our interest in reaction 2 was recently reawakened because the $CpW(CO)_3Me$ complex is isolobal[5] with the $Cp_2M_2(CO)_6$ complexes (M = Mo, W) ($\mathrm{Me} \leftarrow\!\!\bigcirc\!\!\rightarrow \mathrm{CpM(CO)_3}$). We have been studying[6] the photochemical disproportionation reactions of the

---

* Address correspondence to this author at the Department of Chemistry, University of Oregon, Eugene, OR 97403.

[1] Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294-299.

[2] Alt, H. G. *J. Organomet. Chem.* **1977**, *124*, 167-174.

[3] Severson, R. G.; Wojcicki, A. *J. Organomet. Chem.* **1978**, *157*, 173-185.

[4] Tyler, D. R. *Inorg. Chem.* **1980**, *20*, 2257-2261.

[5] Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711-724.

0002-7863/86/1508-0089$01.50/0