donor atoms of the ligand are coordinated to the metal ion. In spite of the fact that the Gd(III) ion is surrounded by ligand donor groups, and the complex does not have a coordinated inner-sphere water molecule, it has been shown to exert moderate relaxivity (1.48 m M^{-1} s^{-1} compared to 2.45 m M^{-1} s^{-1} for $Gd^{III}DTPA$) of the NMR water signal in the in vitro tests of its potential as an MRI paramagnetic contrast agent.[12]

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Supplementary Material Available: A textual description of the crystallographic study and tables of the crystallographic data, positional parameters, *B*(eq) values, distances, and angles (9 pages); a listing of structure factors (27 pages). Ordering information is given on any current masthead page.

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(10) Templeton, L. K.; Templeton, D. H.; Zalkin, A.; Ruben, H. W. *Acta Crystallogr., Sect. B* **1982**, *38*, 2155.

(11) Forsellini, E.; Benetollo, F.; Bombieri, G.; Cassol, A.; DePaoli, G. *Inorg. Chim. Acta* **1985**, *109* (3), 167.

(12) Wiegers, C. B.; Welch, M. J.; Martell, A. E.; Permen, W. H.; Madsen, S. L.; Sun, Y.; Chen, D. Paper presented at the Ninth Annual Meeting, Society of Magnetic Resonance in Medicine, New York, 1990.

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Articles

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Surface-Mediated Synthesis of $H_4M_4(CO)_{12}$ (M = Ru, Os) on Hydroxylated Silica

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The surface reactivity with hydrogen of silica-supported $M_3(CO)_{12}$ (M = Ru, Os) has been investigated at atmospheric pressure and temperatures between 25 and 100 °C. Pure $H_4M_4(CO)_{12}$ complexes are selectively obtained and almost quantitatively recovered from the solid sample by solvent extraction. In the case of $H_4Os_4(CO)_{12}$, significative advantages over the conventional synthesis in solution are obtained.

Introduction

Surface organometallic chemistry, particularly concerning the reactivity of transition-metal carbonyl clusters with the surfaces of metal oxides, has been studied in a systematic way.[1] One of the main goals of such studies is to elucidate the elementary steps in surface reactions, hopefully leading to a deeper insight into the mechanism of heterogeneous catalysis.[2] Surface transformations of supported metal clusters can also be regarded as models of sintering processes in heterogeneous systems.

It has been reported, by some of us, that $Rh_4(CO)_{12}$, when physisorbed on silica[3] or alumina,[4] quickly transforms in vacuo into physisorbed $Rh_6(CO)_{16}$. This was the first reported observation of a surface aggregation of a molecular metal cluster to form a new, higher nuclearity species. This surface reactivity could be explained in terms of high surface mobility of the molecular metallic fragments covered with CO, as easily occurring in solution on model compounds.[5] Accordingly, the surface aggregation of $Os^{II}(CO)_n$ or $Ru^{II}(CO)_n$ (n = 2, 3) fragments, covalently linked to the surface of silica, to generate physisorbed $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ has been observed by reductive carbonylation at 250 and 60–80 °C, respectively.[6,7] In the latter reaction, nonnegligible amounts of $Ru_6C(CO)_{17}$ were also formed. Cluster aggregation is often accompanied by incorporation of carbidic carbon atoms, probably deriving from Boudouard reactions.

The activation of H_2 via incorporation into supported molecular clusters has been also observed. The chemisorbed cluster anion $[HRuOs_3(CO)_{13}]^-$ easily transforms to $[H_3RuOs_3(CO)_{12}]^-$ in the presence of CO and H_2.[8]

In other words, metal carbonyl clusters often show a controlled and unexpectedly easy reactivity when supported onto the surface of inorganic oxides. A new approach to the highly selective synthesis of organometallic cluster compounds via "surface-mediated" gas-solid reactions is thus offered.[9,10]

In this context, we now wish to report the selective synthesis of $H_4M_4(CO)_{12}$ species from physisorbed $M_3(CO)_{12}$ (M = Ru, Os) clusters on the surface of silica.

Experimental Section

$Os_3(CO)_{12}$,[11] $H_4Os_4(CO)_{12}$,[12] $Ru_3(CO)_{12}$,[13] and $H_4Ru_4(CO)_{12}$[12] were

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(1) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95. Psaro, R.; Ugo, R. In *Metal Clusters in Catalysis*; Gates, B. C., Knözinger, H., Guczi, L., Eds.; Elsevier: Amsterdam, 1986; p 427. Lamb, H. H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

(2) *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*; Basset, J. M., Gates, B. C., Candy, J. P., Choplin, A., Quignard, F., Leconte, M., Eds.; Kluwer: Dordrecht, The Netherlands 1988. Gates, B. C.; Lamb, H. H. *J. Mol. Catal.* **1989**, *52*, 1. Basset, J. M.; Candy, J. P.; Choplin, A.; Santini, C.; Theolier, A. *Catal. Today* **1989**, *6*, 1.

(3) Theolier, A.; Smith, A. K.; Leconte, M.; Basset, J. M.; Zanderighi, G. M.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1980**, *191*, 415.

(4) Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F.; Basset, J. M.; Smith, A. K.; Zanderighi, G. M.; Ugo, R. *J. Organomet. Chem.* **1978**, *153*, 73. Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F. *Inorg. Chem.* **1979**, *18*, 1395.

(5) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 315.

(6) Dossi, C.; Fusi, A.; Grilli, E.; Psaro, R.; Ugo, R.; Zanoni, R. *Catal. Today* **1988**, *2*, 585.

(7) Zanderighi, G. M.; Dossi, C.; Ugo, R.; Psaro, R.; Theolier, A.; Choplin, A.; D'Ornelas, L.; Basset, J. M. *J. Organomet. Chem.* **1985**, *296*, 127.

(8) Scott, J. P.; Budge, J. R.; Rheingold, A. L.; Gates, B. C. *J. Am. Chem. Soc.* **1987**, *109*, 7736.

(9) Lamb, H. H.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1986**, 821.

(10) Fung, A. S.; Tooley, P. A.; Kelley, M. J.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1988**, 371.

(11) Johnson, B. F. G.; Lewis, J. *Inorg. Synth.* **1976**, *13*, 92.

(12) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

0020-1669/90/1329-4368$02.50/0

Table I. Infrared Stretching Frequencies for Osmium Carbonyls

compound	Os/SiO_2, wt %	$\nu(CO)$, cm^{-1}				
$Os_3(CO)_{12}$[a]		2068 s	2061 s	2040 ms	2027 s	2015 vs
		1995 s	1984 s			
$Os_3(CO)_{12}$[b]		2068 vs	2034 vs	2013 s	2000 s	
$Os_3(CO)_{12}/SiO_2$[c]	1.0	2069 vs	2035 s	2017 ms	2000 sh	
$Os_3(CO)_{12}/SiO_2$[c]	2.0	2068 s	2037 sh	2028 sh	2014 vs	
		1994 s	1979 s			
$H_4Os_4(CO)_{12}$[a]		2115 vw	2080 sh	2062 vs	2037 sh	2021 vs
		2000 s	1991 s	1977 s		
$H_4Os_4(CO)_{12}$[b]		2085 s	2065 vs	2020 vs	1996 m	
$H_4Os_4(CO)_{12}$[d]		2084 s	2065 vs	2020 vs	1997 m	
$H_4Os_4(CO)_{12}/SiO_2$[c]	1.0	2111 vw	2086 s	2067 vs	2021 s	2000 m, sh
$H_4Os_4(CO)_{12}/SiO_2$[c]	2.0	2115 w	2088 s	2080 s	2068 vs	2027 s, br
		1993 m, sh				

[a] KBr. [b] CH_2Cl_2. [c] As pressed disk. [d] Cyclohexane.

prepared by literature methods, their purity being checked by Fourier transform infrared spectroscopy (FTIR) and thin layer chromatography (TLC).

Silica (Aerosil 200 Degussa),with a nominal surface area of 200 m^{-2}/g, and η-alumina (supplied by Istituto Donegani, Novara, Italy), with a surface area of 250 m^2/g, were used as the support after treatment in vacuo at 25 °C for 16 h (to remove physisorbed water only). A solution of the cluster was contacted under argon with the right amount of silica (as powder or pressed into a self-supporting wafer), to give a metal loading between 1 and 2% by weight. After impregnation, the solvent was removed in vacuo; the impregnated material was evacuated overnight at room temperature and stored under argon or nitrogen. The sample is only slightly air-sensitive, and it can be handled in air. Extraction of physisorbed $H_4Os_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ was conducted with dichloromethane under argon; the organic solution was filtered on a glass frit "in air" and evaporated in vacuo. Temperature-programmed decomposition (TPDE) experiments were performed on 30–100 mg samples in a glass microreactor under a flowing H_2 (5%)/He mixture (10 mL/min) at a heating rate of 2 °C/min from 25 to 400 °C. The gas stream leaving the reactor was periodically analyzed by gas chromatography, as reported elsewhere.[14]

Infrared spectra have been obtained at a resolution of 2 cm^{-1} with Nicolet 10-DX and Digilab FTS-40 Fourier-transform IR spectrophotometers. The samples were pressed in air into self-supporting wafers (18 mm in diameter) and placed in a glass cell with CaF_2 or KBr windows, the cell being attached to a gas and high-vacuum line. Full details have been reported elsewhere.[15]

Results

Surface Reactivity of $Os_3(CO)_{12}$ Physisorbed on Silica in the Presence of Hydrogen. The TPDE of physisorbed $Os_3(CO)_{12}$, carried out in a H_2/He mixture, is reported in Figure 1. The evolution of CO, CO_2, and CH_4 is observed. The first CO peak, centered at about 150 °C, is narrow and symmetric, corresponding to the loss of about 3 mol of CO/mol of cluster ($CO/Os_3 = 3$). The second CO evolution is centered at 200 °C, with the parallel evolution of some CO_2. The evolution of methane becomes significant only above 200 °C. The thermal reactivity of physisorbed $Os_3(CO)_{12}$ in the presence of hydrogen has been also investigated by in situ FT-IR spectroscopy.

When a pressed disk of silica is impregnated with a dichloromethane solution of $Os_3(CO)_{12}$, the infrared spectrum in the $\nu(CO)$ region after evacuation at room temperature closely resembles that of solid $Os_3(CO)_{12}$ (compare parts A and B of Figure 2). Samples containing lower Os loadings showed IR spectra (Figure 2C) more similar to that of $Os_3(CO)_{12}$ in CH_2Cl_2 (Figure 2D). The resolution of the IR spectrum thus depends on the metal loading; this prompted us to work with metal loadings around 1%.

Physisorbed $Os_3(CO)_{12}$ is stable under hydrogen (600 Torr) for a few hours at 100 °C (Figure 3A). After it was heated for 16 hours, a shoulder at 2086 cm^{-1} appeared in the IR spectrum, together with a new band centered at 2020 cm^{-1}. A further treatment at 100 °C for 48 h caused the complete disappearance of the bands due to physisorbed $Os_3(CO)_{12}$, suggesting its complete transformation into a new surface species.

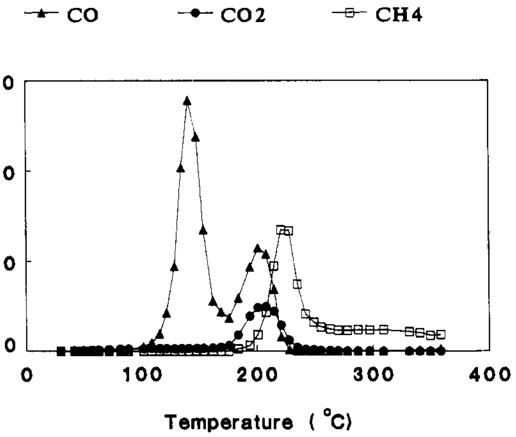

Figure 1. TPDE in H_2 (5%)/He mixture of $Os_3(CO)_{12}$ physisorbed on SiO_2.

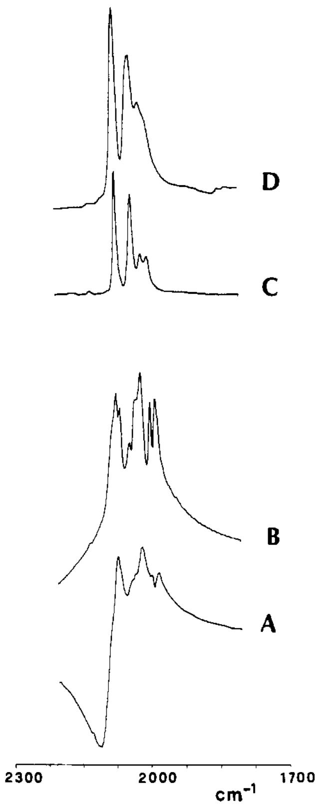

Figure 2. Infrared spectra in the $\nu(CO)$ region: (A) $Os_3(CO)_{12}$ physisorbed on SiO_2 (Os loading = 2 wt %); (B) $Os_3(CO)_{12}$ in solid-state (KBr); (C) $Os_3(CO)_{12}$ in CH_2Cl_2 solution; (D) $Os_3(CO)_{12}$ physisorbed on SiO_2 (Os loading = 1 wt %).

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(13) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

(14) Dossi, C.; Fusi, A. *Anal. Chim. Acta* **1989**, *217*, 197.

(15) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215.

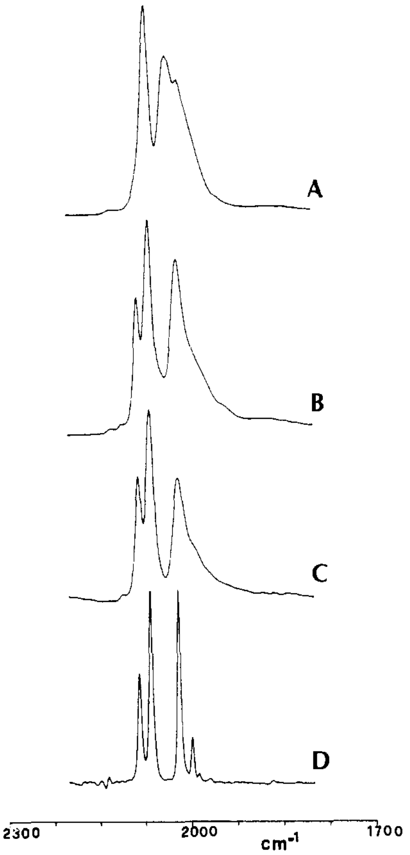

Figure 3. Infrared spectra in the ν(CO) region: (A) $Os_3(CO)_{12}$ physisorbed on SiO_2; (B) $Os_3(CO)_{12}$ physisorbed on SiO_2 after heating in H_2 for 48 h at 150 °C; (C) $H_4Os_4(CO)_{12}$ physisorbed on SiO_2; (D) $H_4Os_4(CO)_{12}$ in cyclohexane solution.

This new surface species is more easily obtained if the thermal treatment is carried out at 150 °C (Figure 3B). It is characterized by strong IR absorptions at 2086, 2067, and 2021 cm^{-1}, which exactly correspond to those of silica-supported $H_4Os_4(CO)_{12}$ (Figure 3C and Table I).

Physisorbed $H_4Os_4(CO)_{12}$ is in fact easily prepared by impregnation of the SiO_2 support with a cyclohexane solution of the tetranuclear cluster. For comparison, the infrared spectrum of the cyclohexane solution of $H_4Os_4(CO)_{12}$ is reported in Figure 3D.

Surface Synthesis of $H_4Os_4(CO)_{12}$. As reported above, $H_4Os_4(CO)_{12}$ can be selectively prepared on a SiO_2 disk from physisorbed $Os_3(CO)_{12}$. As the next step, this synthesis has been tried on a preparative scale. In a typical large-scale experiment, $Os_3(CO)_{12}$ (157 mg, 2.0 wt % Os) was dissolved in 200 mL of degassed dichloromethane and added under argon to silica (5 g). The slurry was stirred under argon at room temperature for 24 h in order to obtain an uniform distribution of $Os_3(CO)_{12}$ onto the silica surface. After removal of the solvent, the impregnated material was dried under vacuum (10^{-5} Torr) at room temperature. The infrared spectrum of the yellow powder showed the typical carbonyl bands of physisorbed $Os_3(CO)_{12}$. A partial pressure of H_2 (700 Torr) was then introduced. A thermal treatment at 100 °C for 24 h did not produce any significant effect or color change. However, when the temperature was raised up to 150 °C, a relevant sublimation immediately occurred.

The infrared spectrum of the sublimate, in a dichloromethane solution, is very complicated (Figure 4). A more detailed analysis of the IR spectrum reveals that two sets of bands, one at 2085, 2066, 2020, and 1999 cm^{-1} and the other one at 2066, 2034, 2020, and 1999 cm^{-1}, are simultaneously present. By comparison with the reported infrared spectra of Os clusters (see Table I), the presence of $H_4Os_4(CO)_{12}$ and unreacted $Os_3(CO)_{12}$ is suggested, and this was confirmed by thin-layer chromatography.

The surface synthesis was then repeated at lower temperature (100 °C), in order to avoid any sublimation. After 5 days under

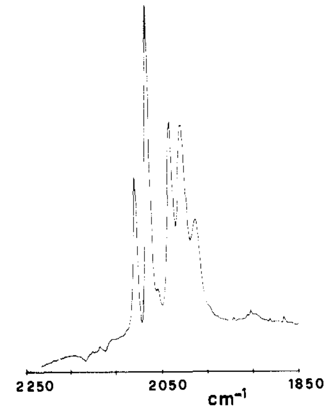

Figure 4. Infrared spectrum in the ν(CO) region of the CH_2Cl_2 solution of the sublimate obtained from the synthesis of $H_4Os_4(CO)_{12}$ (see text).

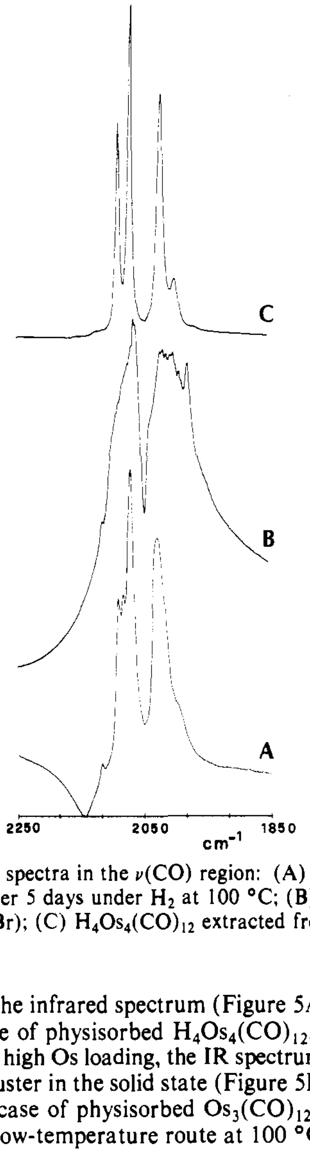

Figure 5. Infrared spectra in the ν(CO) region: (A) $Os_3(CO)_{12}$ physisorbed on SiO_2 after 5 days under H_2 at 100 °C; (B) $H_4Os_4(CO)_{12}$ in the solid state (KBr); (C) $H_4Os_4(CO)_{12}$ extracted from the surface as CH_2Cl_2 solution.

H_2 atmosphere, the infrared spectrum (Figure 5A) clearly shows only the presence of physisorbed $H_4Os_4(CO)_{12}$.

Because of the high Os loading, the IR spectrum resembles that of the hydrido cluster in the solid state (Figure 5B), as previously observed in the case of physisorbed $Os_3(CO)_{12}$. We therefore recommend the low-temperature route at 100 °C to obtain pure $H_4Os_4(CO)_{12}$.

The tetranuclear hydride was extracted from the surface with dichloromethane (200 mL). The yellow-orange solution showed the typical infrared spectrum of pure $H_4Os_4(CO)_{12}$ (Figure 5C).[12] Accordingly, the ^1H NMR spectrum showed only one intense signal, at −20.5 ppm from TMS, in agreement with the known value for $H_4Os_4(CO)_{12}$.[16] Its purity has been also checked by

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(16) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1976**, 838.

Table II. Infrared Stretching Frequencies for Ruthenium Carbonyls

compound	Ru/SiO_2, wt %	$\nu(CO)$, cm^{-1}				
$Ru_3(CO)_{12}$[a]		2060 vs	2030 s	2011 m		
$Ru_3(CO)_{12}/SiO_2$[b]	1.0	2063 vs	2032 s	2018 m, sh		
$H_4Ru_4(CO)_{12}$[a]		2080 s	2066 vs	2030 m, sh	2024 s	2009 vw
$H_4Ru_4(CO)_{12}/SiO_2$[b]	1.0	2082 s	2068 vs	2027 ms		

[a] Hexane. [b] As pressed disk.

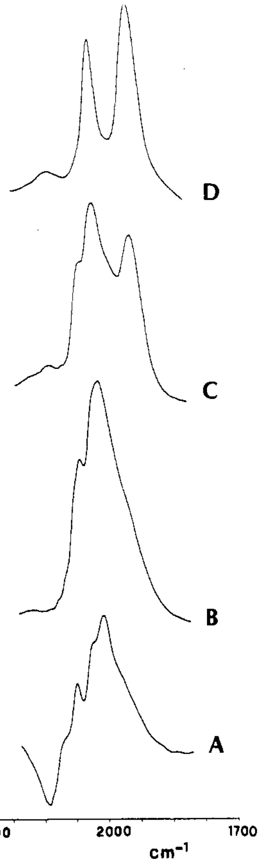

Figure 6. Infrared spectra in the $\nu(CO)$ region: (A) $Os_3(CO)_{12}$ physisorbed on Al_2O_3; (B) $Os_3(CO)_{12}$ physisorbed on Al_2O_3 after heating in H_2 for 1 h at 100 °C; (C) $Os_3(CO)_{12}$ physisorbed on Al_2O_3 after heating in H_2 for 24 h at 150 °C; (D) $Os_3(CO)_{12}$ physisorbed on Al_2O_3 after further 20 h in H_2 at 250 °C.

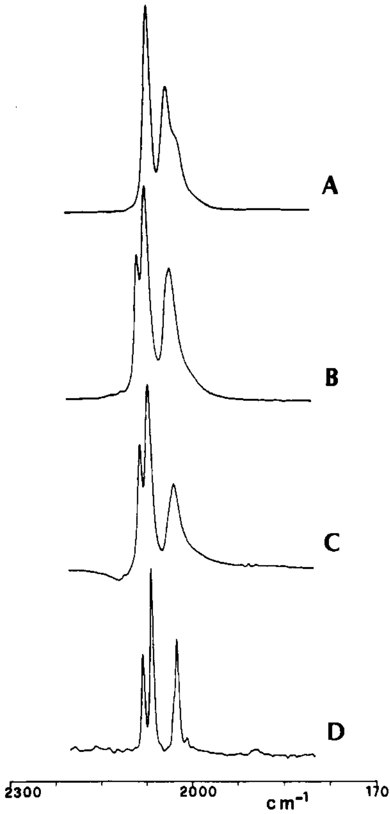

Figure 7. Infrared spectra in the $\nu(CO)$ region: (A) $Ru_3(CO)_{12}$ physisorbed on SiO_2; (B) $Ru_3(CO)_{12}$ physisorbed on SiO_2 after heating in H_2 for 12 h at 25 °C; (C) $H_4Ru_4(CO)_{12}$ physisorbed on SiO_2; (D) $H_4Ru_4(CO)_{12}$ in hexane solution.

TLC. The dichloromethane solution was dried in vacuum, and the yellow powder of $H_4Os_4(CO)_{12}$ was stored in air (yield 97.4 mg, 68% with respect to $Os_3(CO)_{12}$).

Surface Reactivity of $Os_3(CO)_{12}$ Physisorbed on Alumina in the Presence of Hydrogen. The IR spectrum of physisorbed $Os_3(CO)_{12}$ on Al_2O_3 (Figure 6A) showed a negative absorption centered at about 2120 cm^{-1} and attributed to the Christiansen effect. This was removed after heating the sample in H_2 for 1 h at 100 °C; at the same time, the 2065-cm^{-1} band disappeared quite completely, while new ones grew at 2051 and 2007 cm^{-1} (Figure 6B). Subsequent thermal treatments in H_2 only produced a slow transformation of the surface species, without relevant decarbonylation. After the sample was heated at 150 °C for 6 h, new bands at 2016 and 1928 cm^{-1} appeared. Prolonged treatments at 150 °C caused the appearance of sharp bands at 2013 and 1926 cm^{-1} with a shoulder at 2044 cm^{-1} (Figure 6C). These bands are stable at 250 °C in H_2 for long time (Figure 6D).

Surface Reactivity of $Ru_3(CO)_{12}$ Physisorbed on Silica in the Presence of Hydrogen. A pressed disk of silica was impregnated with a pentane solution of $Ru_3(CO)_{12}$. After evacuation of the solvent at room temperature, the infrared spectrum in the $\nu(CO)$ region unequivocally indicates the presence of physisorbed $Ru_3(CO)_{12}$ on silica[7] (Figure 7A and Table II). The surface cluster is not stable in H_2 even at room temperature; after 12 h, the complete disappearance of the IR spectrum of physisorbed $Ru_3(CO)_{12}$ was observed (Figure 7B). The new spectrum shows the typical features of physisorbed $H_4Ru_4(CO)_{12}$, as further confirmed by deposition of pure $H_4Ru_4(CO)_{12}$ on silica via solvent impregnation (Figure 7C). For comparison, the IR spectrum of pure $H_4Ru_4(CO)_{12}$ in hexane solution is shown in Figure 7d.

Surface Synthesis of $H_4Ru_4(CO)_{12}$. The surface synthesis of $H_4Ru_4(CO)_{12}$ was then tested on a preparative basis. In a typical experiment, silica (4.3 g) was impregnated with 200 mL of a degassed pentane solution of $Ru_3(CO)_{12}$ (91 mg, 1.0 wt % Ru). The slurry was stirred under argon at 25 °C for 16 h. After removal of the solvent, the orange powder was dried in vacuo (10^{-3} Torr) at room temperature. Its IR spectrum showed the typical carbonyl bands of physisorbed $Ru_3(CO)_{12}$. A partial pressure of H_2 (760 Torr) was then introduced. In a result different from those of the experiments carried out on silica wafers, at room temperature the transformation into $H_4Ru_4(CO)_{12}$ was not complete even after 87 h. The surface synthesis was thus repeated at 50 °C, in order to have a faster reaction rate. After 4 days, the infrared spectrum clearly showed only the presence of $H_4Ru_4(CO)_{12}$.

The tetranuclear hydride was extracted from the surface with dichloromethane (200 mL). The ^1H NMR spectrum of the solution showed only one intense signal at −17.78 ppm from TMS, in agreement with the known value for $H_4Ru_4(CO)_{12}$.[16] Its purity has been also checked by TLC.

The CH_2Cl_2 solution was then dried in vacuo, and the yellow powder of $H_4Ru_4(CO)_{12}$ stored in air (61.7 mg, 78% yield with respect to $Ru_3(CO)_{12}$).

Discussion

In the TPDE in H_2/He mixture of $Os_3(CO)_{12}$ physisorbed on silica, the first CO evolution peak at 150 °C is very sharp and symmetric, suggesting the occurrence of a single surface reaction in this temperature range. In addition, it does not overlap significantly with the other peaks; the accurate integration of the TPDE peak is thus possible. The obtained CO/Os stoichiometry, about 3.0 mol of evolved carbon monoxide/mol of supported $Os_3(CO)_{12}$, is consistent with the surface reaction

$$4\ Os_3(CO)_{12} + 6H_2 \rightarrow 3H_4Os_4(CO)_{12} + 12CO$$

$$CO/Os_3 \text{ molar ratio} = 3$$

involving the nucleation of the starting Os_3 cluster into an Os_4 hydrido species.

The subsequent formation of methane, together with a small evolution of CO_2, is then corresponding to the typical trend previously found in the low-pressure CO hydrogenation with supported osmium catalysts.[17]

The infrared characterization is in agreement with the TPDE data. The transformation of physisorbed $Os_3(CO)_{12}$ into $H_4Os_4(CO)_{12}$ is easily and completely obtained in a single step between 100 and 150 °C.

This surface reaction can be profitably used to prepare the tetranuclear hydrido cluster on a preparative scale. After reaction, pure $H_4Os_4(CO)_{12}$ is recovered in high yield (68%) by solvent extraction of the silica powder at room temperature.

On the contrary, when a solution of $Os_3(CO)_{12}$ in octane is heated at 120 °C under atmospheric pressure of H_2, $H_4Os_4(CO)_{12}$ is obtained in low yield (29%) after chromatographic separation.[12] The use of water as hydrogen source has been reported.[16] After pyrolysis of $Os_3(CO)_{12}$ with water in a Carius tube at 230 °C, a complex mixture of hydrido carbonyls, based on Os_4, Os_5, Os_6, and Os_7 units, is obtained.[16] The tetranuclear hydride was then recovered in low yield (15%) by cooling the filtrate. Higher yields in $H_4Os_4(CO)_{12}$, comparable to that of the surface-mediated synthesis, can be obtained only by working at 100 °C under high H_2 pressure, typically 120 atm.[18]

The highly reactive $Ru_3(CO)_{12}$ was thus used as a probe for testing the effectiveness and specificity of the proposed heterogeneous route.

As expected, silica-supported $Ru_3(CO)_{12}$ is much more reactive than the Os homologue; $H_4Ru_4(CO)_{12}$ is already slowly being formed in hydrogen atmosphere at 25 °C on the silica surface. The synthesis was actually carried out at 50 °C, to have a faster reaction rate. Higher reaction temperatures should, however, be avoided, since $H_4Ru_4(CO)_{12}$ starts to decompose to metallic Ru above 70 °C.

The obtained yield of $H_4Ru_4(CO)_{12}$ was high (78%) and comparable to that reported in the reaction of $Ru_3(CO)_{12}$ with H_2 in octane at atmospheric pressure (88%).[12] The transformation of $M_3(CO)_{12}$ into $H_4M_4(CO)_{12}$ (M = Ru, Os) is mechanistically a complex reaction, since incorporation of H_2 and increase in cluster nuclearity must occur. Knox et al.[12] showed that $Os_3(CO)_{12}$ in octane solution at 120 °C, under hydrogenation at atmospheric pressure, formed $H_2Os_3(CO)_{10}$ as the first step. $H_4Os_4(CO)_{12}$ was subsequently obtained by additional treatment of the trinuclear hydride cluster with H_2. The same two-step mechanism happened in the high-yield synthesis under hydrogen pressure.

In the case of the ruthenium system, the one-step transformation was reported;[19] $H_2Ru_3(CO)_{10}$ was unstable at 90 °C and quickly reacted with H_2 to form $H_4Ru_4(CO)_{12}$.[20]

A remarkable peculiarity of the surface-mediated route is that $H_2Os_3(CO)_{10}$ does not seem to be formed as a stable intermediate on silica, as suggested by our FTIR data and the presence of a single decomposition step in the TPDE profile of SiO_2-supported $Os_3(CO)_{12}$.

In addition, a mechanism of $H_4M_4(CO)_{12}$ (M = Ru, Os) formation involving surface –OH groups of the support cannot be rejected. However this reactivity, leading to the formation of the grafted surface species $HM_3(CO)_{10}(OSi{<})$, according to the oxidative addition of a silanol group into a metal–metal bond of the cluster frame, is possible only in the absence of hydrogen.[7,15] The chemisorbed cluster does not transform into $H_4M_4(CO)_{12}$ if subsequently heated in hydrogen atmosphere. Consequently, in the reported surface synthesis of $H_4M_4(CO)_{12}$, it is very important to avoid any chemical interactions of the cluster precursor with the surface sites of the silica.

The use of a more active metal oxide, like alumina, was unsuccessful. $Os_3(CO)_{12}$ is rapidly chemisorbed after impregnation, and a different surface chemistry, not leading to $H_4Os_4(CO)_{12}$, is observed upon heating in hydrogen. Vannice et al.[21] recently reported the decomposition of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ supported on an oxygen-free, highly unreactive carbon surface. Decomposition in H_2 flow produced $H_4M_4(CO)_{12}$, as the first step in the decomposition process to give highly dispersed metallic crystallites. In agreement with our results, the transformation rate of $Ru_3(CO)_{12}$ to $H_4Ru_4(CO)_{12}$ was much more rapid than that for $Os_3(CO)_{12}$.[22,23]

The relative inertness, in H_2 atmosphere, of the surface of silica toward $M_3(CO)_{12}$ is the only similarity with the surface of carbon and must be regarded as a key factor to obtain high selectivity in the surface-mediated synthesis. This surface reactivity is another example of the unexpected mobility of molecular metal carbonyl clusters on the surface of inorganic oxides.[1] The effect of chemisorption is likely to suppress, or to reduce to a large extent, the cluster mobility at the surface, as observed on alumina.

A high-pressure infrared study of the stability of some ruthenium and osmium clusters under H_2 pressure demonstrated that the tetranuclear species $H_4M_4(CO)_{12}$ seem to be the favored products.[24] As a result of these observations, we believe that the surface topology of silica is likely to play a significant role in the stabilization and consequently in the selective formation of organometallic compounds.

The examples of surface-mediated organometallic synthesis are not limited to the surface of silica. Fung et al.[10] reported that $Os_3(CO)_{12}$ on the surface of MgO under CO is converted into $[Os_5C(CO)_{14}]^{2-}$; this one-step synthesis is far simpler and gives much higher yields than the conventional synthesis. The surface of magnesium oxide is particularly effective in this respect; the anionic $[Os_{10}C(CO)_{24}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ clusters are conveniently synthesized by reductive carbonylation of MgO-supported H_2OsCl_6 and $RuCl_3$.[25]

At the moment, the documented cases of "surface-mediated" organometallic reactions are still few;[25] it is nevertheless possible to propose some general trends. When silica, or other hydrophobic supports of low chemical reactivity, is used as reaction media, the synthesis is directed toward neutral molecular clusters; on the contrary, basic surfaces, such as MgO, tend to favor the formation of anionic clusters.

Conclusions

In summary, organometallic reactions can be easily conducted on the surface of inorganic oxides, acting as "nonconventional" reaction media. Although the reported examples are still few,

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(17) Deeba, M.; Scott, J. P.; Barth, R.; Gates, B. C. *J. Catal.* **1981**, *71*, 373. Knözinger, H.; Zhao, Y.; Tesche, B.; Barth, R.; Epstein, R.; Gates, B. C.; Scott, J. P. *Faraday Discuss. Chem. Soc.* **1982**, *72*, 53. Hunt, D. J.; Jackson, S. D.; Moyes, R. B.; Wells, P. B.; Whyman, R. *J. Catal.* **1984**, *86*, 333. Jackson, S. D.; Moyes, R. B.; Wells, P. B.; Whyman, R. *J. Catal.* **1984**, *86*, 342.

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

(19) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1978**, *26*, 150.

(20) Poë, A. J. In *Metal Clusters*; Moskovits, M., Ed.; John Wiley & Sons: New York, 1986; p 86.

(21) Venter, J. J.; Vannice, M. A. *J. Mol. Catal.* **1989**, *56*, 117.

(22) Venter, J. J.; Vannice, M. A. *Inorg. Chem.* **1989**, *28*, 1634.

(23) Venter, J. J.; Vannice, A. *J. Am. Chem. Soc.* **1989**, *111*, 2377.

(24) Nicholls, A. P.; Farror, D. H.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1395.

(25) Lamb, H. H.; Fung, A. S.; Tooley, P. A.; Puga, J.; Krause, T. R.; Kelley, M. J., Gates, B. C. *J. Am. Chem. Soc.* **1989**, *111*, 8367.

Inorg. Chem. **1990**, *29*, 4373-4376 **4373**

they nevertheless show promising possibilities, since high selectivity and high yields can be achieved through new reaction pathways.

In particular, the surface-mediated synthesis of $H_4M_4(CO)_{12}$ (M = Ru, Os) from silica-supported $M_3(CO)_{12}$ presents significant advantages over the conventional synthesis in solution: (1) milder reaction conditions; (2) direct formation of the products via one-step reactions, leading to higher yield and selectivity (absence of unreacted $M_3(CO)_{12}$ and other cluster compounds); (3) easy recovering of the products by simple solvent extraction at room temperature.

Therefore, a new field of preparative inorganic chemistry on the gas-solid interphase is now being developed, with unexpected and promising improvements over the conventional methods in solution.

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Low-Temperature Reactions of Atomic Nickel with Diazomethane

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The reactions of atomic nickel with diazomethane have been investigated by FTIR matrix-isolation spectroscopy. In argon matrices, $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ are formed spontaneously. Photolysis of the matrix with $\lambda \approx$ 400–500 nm radiation enhances the yield of $N_2Ni{=}CH_2$, suggesting that photoinduced diffusion of reagents may become important under these conditions. Dihydrogen reacts with $Ni{=}CH_2$ to give methane, whereas $N_2Ni{=}CH_2$ is less reactive to hydrogenolysis. Ultraviolet photolysis of a $Ni/CH_2N_2/H_2/Ar$ matrix yields CH_3NiH from insertion of photoexcited nickel atoms into the C–H bonds of methane. In nitrogen matrices, $(N_2)_xNi{=}CH_2$ complexes are formed spontaneously. The yield of these species can be increased by photolysis with $\lambda \approx$ 400–500 nm radiation or by ultraviolet photolysis.

Introduction

Since the landmark paper by Fischer and Massböl[1] in 1964 describing the synthesis of (methoxymethylcarbene)pentacarbonyltungsten, the synthesis and characterization of transition-metal carbene complexes has occupied a critical position in the development of organometallic chemistry. Indeed, the chemistry of metal–carbon double bonds is now well entrenched in organometallic chemistry and is even used in efforts to understand surface chemistry and homogeneous catalysis.[2] In this paper, we describe the synthesis and characterization of naked $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ by FTIR matrix-isolation spectroscopy.[3]

Experimental Section

A description of the multisurface matrix-isolation apparatus[4] as well as the preparation of CH_2N_2, CD_2N_2, $CHDN_2$, and $^{13}CH_2N_2$ has been reported previously.[5] Nickel atoms were generated by vaporizing nickel (MC&B, 99.5%) from an alumina crucible enclosed in a resistively heated tantalum furnace over the range 1250–1420 °C. Argon (99.9995%) and dinitrogen (99.9995%) were obtained from Matheson Chemical Co. Hydrogenation studies were carried out by introducing dihydrogen (Air Products, 99.9995%) or dideuterium (Air Products, 99.99%) into the matrix during deposition (H_2/Ar or $D_2/Ar \approx$ 15–50 mmHg/1000 mmHg). Matrices were usually irradiated subsequent to deposition by exposure to a focused 100-W medium-pressure short-arc Hg lamp. The typical exposure time was 10 min. A water filter with various Corning long-pass cutoff filters and a band filter, 280–360 nm (UV), were used for wavelength-dependent photolysis studies. In a typical experiment, nickel atoms and diazomethane were cocondensed with argon onto a rhodium-plated copper surface over a period of 30 min at 12 K.

Results

Although the infrared spectra exhibited by the products of atomic nickel and diazomethane are complicated by additional absorptions arising from residual dihydrogen[6] reacting with nickel atoms and clusters, the primary products can be characterized readily as $Ni{=}CH_2$ and $N_2Ni{=}CH_2$. The infrared spectra from a study in which the concentration of nickel is increased gradually are shown in Figure 1. The product absorptions associated with $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ are labeled a and b, respectively.

A small amount of CO was added to provide NiCO[7] (c band) as an internal standard. Log–log plots[8] of the intensities of bands corresponding to each species versus the absorption of NiCO at 1994.5 cm^{-1} (Figure 2) suggest that the absorption labeled e, as well as those assigned to the carbenes, correspond to atomic nickel reactions. The d band may arise from a Ni_2 reaction product.

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(1) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(2) For comprehensive coverage, see also: *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983. For several relevant reviews, see: Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545–574. Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487–613. Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, pp 189–233. Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122. Fischer, H. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley: Chichester, England, 1982; pp 181–231. Dötz, K. H. Carbene Complexes of Groups VIa; VIIa and VIIIa. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: London. Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407–423. Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353–372. Kreiter, C. G.; Fischer, E. O. In *XXIII International Congress of Pure and Applied Chemistry*; Butterworths: London, 1971; pp 151–168. Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857–870. Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651. Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139. Casey, C. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley: New York, 1981; Vol. 2, pp 135–174. Fischer, E. O.; Fischer, H. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; Verlag Chemie: Weinheim, FRG, 1986. Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

(3) For representative nickel carbene complexes that have been isolated, see: Fischer, E. O.; Kreissl, F. R.; Winkler, E.; Kreiter, C. G. *Chem. Ber.* **1972**, *105*, 588. Cetinkaya, B.; Dixneuf, P.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1827. Fraser, P. J.; Roper, W. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 102. Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172. Dean, W. K.; Charles, R. S.; Van Derveer, D. G. *Inorg. Chem.* **1977**, *16*, 3328. Ogura, K.; Wada, M.; Okawara, R. *J. Organomet. Chem.*, **1978**, *159*, 417. Hoberg, H.; Burkhart, G.; Krüger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1981**, *222*, 343. Miki, K.; Tomiguchi, H.; Koi, Y.; Kasai, N.; Nichiwaki, K.; Wadi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1178.

(4) Hauge, R. H.; Fredin, L.; Kafafi, Z. H.; Margrave, J. L. *Appl. Spectrosc.* **1986**, *40*, 588.

(5) Chang, S.-C.; Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 4508.

(6) The dihydrogen probably arises from cracking of the diffusion pump oil.

(7) DeKock, R. L. *Inorg. Chem.* **1971**, *10*, 1205.

(8) Moskovits, M.; Ozin, G. A. *Cryochemistry*; Wiley-Interscience: New York, 1976.

0020-1669/90/1329-4373$02.50/0