Surface-Mediated Organometallic Synthesis: Preparation of $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ on the Basic Magnesium Oxide Surface

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Abstract: High-nuclearity osmium carbonyl clusters have been synthesized by simple means and in high yields on the surface of porous, high surface area magnesium oxide in the presence of CO and CO + H_2. Control of the product distributions was exerted by choice of the temperature, pressure, gas-phase composition, and metal compound precursor. $[Os_{10}C(CO)_{24}]^{2-}$ was prepared from $[H_2OsCl_6]$ adsorbed on MgO treated in equimolar CO + H_2 at 275 °C and 1 atm, and $[Os_5C(CO)_{14}]^{2-}$ was prepared from $[Os_3(CO)_{12}]$ adsorbed on MgO treated in CO at 275 °C and 1 atm. These cluster anions were isolated from the MgO in 65% yield by cation metathesis with [PPN][Cl] in acetone. These syntheses are more efficient than the best known solution syntheses; the results suggest a more general applicability of surface-mediated synthesis.

The established syntheses of high-nuclearity Os and Ru clusters are often characterized by low yields, tedious separations, and less than good reproducibility; many of the reported syntheses are serendipitous, and only recently have rational approaches to cluster synthesis been sought.[1-3] We have communicated[4,5] new methods for synthesis of Os and Ru clusters that exploit the reactivity of metal carbonyls on metal oxide surfaces.[6] These procedures are simple and straightforward and sometimes give higher yields than conventional syntheses. Metal oxide surfaces are attractive replacements for solvent environments in organometallic synthesis because (1) the acid–base and redox properties of the surfaces can be manipulated systematically, (2) high temperature can be used without concern for high autogeneous pressures associated with organic solvents or for solvent degradation, and (3) the isolation of soluble products is generally easy.

The reactivity of organometallic complexes on metal oxide surfaces has begun to be understood in just the preceding few years.[6,7] The patterns of reactivity parallel those in solution, and the variations from one surface to another are often accounted for by differences in acid–base properties. The classes of organometallic reactions that occur on metal oxide surfaces include, for example, deprotonation of hydridometal carbonyls, nucleophilic attack at carbonyl ligands by basic surface groups [e.g., $\{OH^-\}$ and $\{O^{2-}\}$, where the braces denote groups terminating the bulk], oxidative fragmentation of metal carbonyl clusters, and redox condensation and reductive carbonylation leading to the formation of high-nuclearity metal carbonyl clusters.

This latter reaction class is appealing in offering opportunities for efficient surface-mediated synthesis. This paper provides a general description of the methods of surface-mediated synthesis of metal carbonyl cluster anions on the basic surface of magnesia; details are given for efficient syntheses of $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$.

Results

Syntheses of a series of anionic carbonyl clusters on MgO surfaces have been observed, with the product yields and selectivities being controlled by the choices of organometallic or metal salt precursor, gas composition, and pressure. These syntheses involve reactions on a basic surface (that of partially dehydroxylated MgO), with the patterns of surface reactivity paralleling those observed in basic solution. In some cases, the surface-mediated syntheses are so straightforward and efficient that they are recommended instead of the established solution procedures. Details of the individual syntheses follow.

Synthesis of $[Os_5C(CO)_{14}]^{2-}$ from $[Os_3(CO)_{12}]$. A surface-bound precursor was prepared by adsorbing $[Os_3(CO)_{12}]$ from a hexanes solution onto MgO powder that had been partially dehydroxylated and decarbonated by treatment at 400 °C in vacuo. The infrared spectrum of the resultant yellow solid (Figure 1A) is in good agreement with the spectrum of the surface species formulated by Psaro et al.[8] as $[Os_3(CO)_{11}]^{2-}$ tightly ion-paired to the MgO surface. Attempts to extract the organometallic species from the surface by ion exchange with [PPN][Cl] in acetone were unsuccessful, consistent with the results of Psaro et al.[8] The lack of extractability of the surface species argues against a purely ionic interaction between the cluster and the MgO surface.

The supported triosmium cluster was treated with flowing CO in a tubular reactor. At 275 °C and 1 atm, a new pale yellow surface-bound species formed, as evidenced by the infrared spectrum of the resultant solid (Figure 1B). Alternatively, a surface species having the same infrared spectrum was formed by reacting the supported triosmium cluster with CO in an autoclave under 13.6 atm of CO at 300 °C for 4 h.

Extraction of this new surface species with [PPN][Cl] in acetone resulted in a golden yellow solution having the infrared spectrum shown in Figure 1C. This spectrum is virtually identical with that of $[PPN]_2[Os_5C(CO)_{14}]$ (Table I), first reported by Johnson et al.[9] The cluster was isolated in yields of up to 65% based on the Os content of the starting material. X-ray

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(1) Geoffroy, G. L. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; and references cited therein.

(2) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *3*, 123.

(3) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. A., Eds.; Pergamon: Oxford, 1982; Vol. 6, Chapter 40.

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

(5) Lamb, H. H.; Krause, T. R.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1986**, 821.

(6) Lamb, H. H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

(7) Evans, J. In *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*; Basset, J.-M., Gates, B. C., Candy, J. P., Choplin, A., Leconte, M., Quignard, F., Santini, C., Eds.; Kluwer: Dordrecht, 1988.

(8) Psaro, R.; Dossi, C.; Ugo, R. *J. Mol. Catal.* **1983**, *21*, 33.

(9) Johnson, B. G. F.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Puga, J.; Raithby, P. R.; Rosales, M. J.; Schroder, M.; Vargas, M. D. *J. Chem. Soc., Dalton Trans.* **1983**, 2447.

0002-7863/89/1511-8367$01.50/0

Table I. Infrared Stretching Frequencies of Osmium Carbonyl Complexes

sample[a]	ν_{CO}, cm^{-1}	ref
sample prepared by adsorption of $[Os_3(CO)_{12}]$ on MgO_{300}	2073 (s), 2008 (vs), 1949 (s, br)	8
$[PPN]_2[Os_5C(CO)_{14}]$	2040 (w), 2015 (w), 1991 (s), 1975 (vs), 1968 (vs), 1945 (m), 1926 (w), 1720 (w)	9
$[Os_5C(CO)_{14}]^{2-}$ adsorbed on MgO_{400}	2071 (m), 2037 (m, sh), 2031 (m), 2009 (s), 2000 (s), 1974 (sh), 1958 (m), 1935 (m), 1918 (w), 1887 (w), 1869 (w)	4
$[Os_5C(CO)_{14}]^{2-}$ adsorbed on MgO_{400}[b]	2064 (m), 2041 (m), 2024 (m), 2000 (s), 1988 (s), 1965 (m, sh), 1947 (m), 1916 (m), 1868 (w)	this work
$[PPN]_2[Os_{10}C(CO)_{24}]$	2033 (s), 1986 (s)	13
$[Os_{10}C(CO)_{24}]^{2-}$ adsorbed on MgO	2035 (s, br), 1990 (s, br)	5
$[Os_{10}C(CO)_{24}]^{2-}$ adsorbed on MgO	2084 (w), 2045 (vs), 1985 (s)	this work
$[H_4Os_4(CO)_{12}]$	2085 (m), 2066 (s), 2020 (s), 1977 (w)	10
$[Me_4N][H_3Os_4(CO)_{12}]$	2048 (s), 2022 (s), 2000 (s), 1976 (w)	10
sample prepared by adsorption of $[H_4Os_4(CO)_{12}]$ on MgO_{400}	2085 (m), 2053 (s), 2017 (s, sh), 2009 (vs), 1966 (m, sh), 1943 (m, sh)	this work
$[H_3Os_4(CO)_{12}]^-$ adsorbed on MgO_{200}	2087 (m), 2051 (s), 2023 (s), 2004 (vs), 1986 (sh), 1953 (m), 1938 (m), 1914 (w, sh)	11
$[H_{4-n}Os_4(CO)_{12}]^{n-}$ absorbed on MgO_{400} ($n = 1, 2$)	2087 (w), 2056 (m), 2013 (vs), 1998 (s, sh), 1940 (m), 1910 (w)	12

[a] The subscript refers to the pretreatment temperature of the MgO. [b] The approximately 10-cm^{-1} downshift of the infrared bands characterizing $[Os_5C(CO)_{14}]^{2-}$ adsorbed on MgO_{400} observed in this work compared with that of ref 4 is associated with the different batches of MgO used in the experiments. Both batches of MgO were calcined at 400 °C, and the difference is tentatively explained by different degrees of surface interaction of the pentanuclear osmium cluster with the different MgO surfaces. Compare the results presented above for $[Os_{10}C(CO)_{24}]^{2-}$ adsorbed on different batches of MgO.

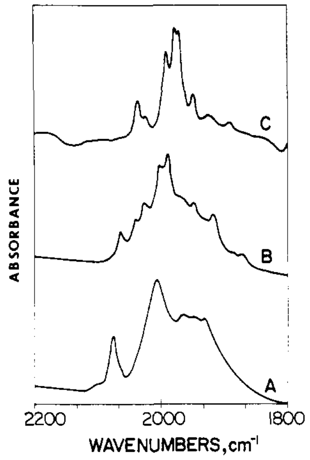

Figure 1. Infrared spectra: A, sample prepared by adsorption of $[Os_3(CO)_{12}]$ from hexanes onto MgO under N_2; B, sample in (A) after 4 h of exposure to CO at 1 atm and 275 °C; C, $[PPN]_2[Os_5C(CO)_{14}]$ in acetone extracted from the surface.

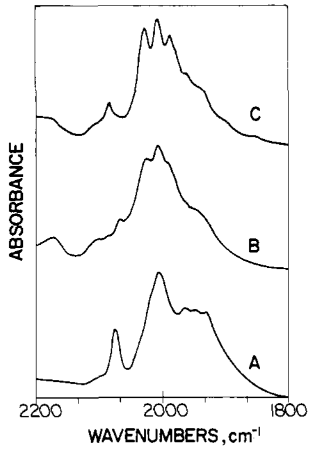

Figure 2. Infrared spectra: A, sample prepared by adsorption of $[Os_3(CO)_{12}]$ from hexanes onto MgO under N_2; B, sample in (A) after 0.5 h of exposure to CO at 1 atm at 75 °C; C, 150 °C.

fluorescence (XRF) analysis of the solid after extraction of $[Os_5C(CO)_{14}]^{2-}$ indicated that loss of Os as volatile carbonyl species was negligible.

The identification of $[PPN]_2[Os_5C(CO)_{14}]$ as the product was confirmed by fast atom bombardment mass spectrometry; there were interactions of the cluster with a number of different matrices, and the molecular ion itself, *m/e* 1366 (^{192}Os), was observed when the "magic bullet" ($CH_3CH_2OSSOCH_2CH_3$) was used as the matrix. Derivatization of the cluster by reaction with $[AuPPh_3Cl]$ gave further confirmation of its identity. The resultant orange red product was $[AuPPh_3]_2[Os_5C(CO)_{14}]$, as expected, with an infrared spectrum identical with that published by Johnson et al.[9]

The formation of $[Os_5C(CO)_{14}]^{2-}$ on the MgO surface under 1 atm of CO was monitored by in situ infrared spectroscopy. The peaks assigned to the initial triosmium surface species broadened upon heating to 75 °C in flowing CO, with formation of new species characterized by bands at 2084 (w), 2024 (s, sh), 2007 (s), 1995 (s, sh), and 1952 (m, sh) cm^{-1} (Figure 2B). After being heated to 150 °C, the parent triosmium complex was nearly completely converted, as evidenced by the disappearance of the 2075-cm^{-1} band and the appearance of bands at 2085 (w), 2029 (s), 1988 (s), 1967 (m, sh), and 1948 (m, sh) cm^{-1} (Figure 2C). The infrared spectrum closely resembles that of $[H_3Os_4(CO)_{12}]^-$ in solution[10] and on the surface of MgO (Table I).[11,12] This surface species persisted on MgO at temperatures up to 200 °C in flowing CO. The infrared spectrum obtained after treatment of the sample for 4 h at 275 °C in CO was identical with that obtained when the reaction was carried out in the flow reactor, as described above. Extraction of the infrared wafer with [PPN][Cl] in acetone gave a solution of pure $[Os_5C(CO)_{14}]^{2-}$, as indicated by infrared spectroscopy.

The tetraosmium surface species formed at 150 °C was characterized in a separate experiment, again with the aid of in situ infrared spectroscopy. A sample prepared by adsorption of $[Os_3(CO)_{12}]$ on MgO was treated in flowing CO at 150 °C for 2 h. Extraction of the resultant yellow wafer with [PPN][Cl] in acetone resulted in a solution having infrared bands at 2049 (s), 2042 (m, sh), 2023 (s), 2002 (vs), 1996 (sh), 1981 (m), 1968 (sh), 1950 (w, sh), and 1922 (w) cm^{-1}. The bands at 2042, 1996, 1981, 1968, 1950, and 1922 cm^{-1} may be assigned to $[Os_5C(CO)_{14}]^{2-}$.[9] The remaining three bands in the spectrum characterizing the extract solution are consistent with the presence of $[H_3Os_4(CO)_{12}]^-$ (Table I).[10]

Recognizing that $[H_3Os_4(CO)_{12}]^-$ might be an intermediate in the formation of $[Os_5C(CO)_{14}]^{2-}$ on MgO, we prepared surface-bound $[H_3Os_4(CO)_{12}]^-$ on MgO by chemisorption of $[H_4Os_4(CO)_{12}]$ from hexanes, resulting in simple deprotonation.[11,12]

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

(11) D'Ornelas, L.; Choplin, A.; Basset, J. M.; Puga, J.; Sanchez-Delgado, R. A. *Inorg. Chem.* **1986**, *25*, 4315.

(12) Lamb, H. H. Ph.D. Dissertation, University of Delaware, 1988.

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

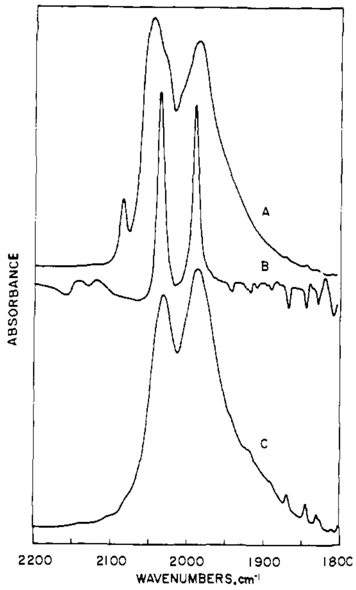

Figure 3. Infrared spectra: A, solid resulting from treatment of sample prepared from H_2OsCl_6 + MgO with flowing CO + H_2 (equimolar) at 275 °C and 1 atm for 5 h; B, $[Os_{10}C(CO)_{24}]^{2-}$ extracted from this sample by ion exchange with [PPN][Cl] in acetone; C, solid sample after extraction with [PPN][Cl]/acetone (the vertical scale is expanded 4-fold).

Surface-bound $[H_3Os_4(CO)_{12}]^-$ was heated gradually under CO and the surface species monitored by infrared spectroscopy. After reaction at 275 °C for 4 h, the infrared bands of $[H_3Os_4(CO)_{12}]^-$ on MgO had disappeared and a new set of bands had appeared, consistent with the formation of $[Os_5C(CO)_{14}]^{2-}$. The surface species were extracted with [PPN][Cl] in acetone, and the infrared spectrum of the acetone solution confirmed the presence of the pentaosmium cluster anion.

Synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ from $[H_2OsCl_6]$. An aqueous solution of $[H_2OsCl_6]$ was used to impregnate partially dehydroxylated MgO, a typical initial step in the preparation of a classical supported osmium catalyst. A sample was placed in a tubular reactor and treated at 275 °C in flowing equimolar CO + H_2 at 1 atm for 5 h; the resultant material had infrared bands at 2035 (s, br) and 1990 (s, br) cm^{-1}, consistent with the presence of $[Os_{10}C(CO)_{24}]^{2-}$ (Table I), and a UV–visible spectrum indistinguishable from that of $[Et_4N]_2[Os_{10}C(CO)_{24}]$ adsorbed on MgO from a THF solution.[5] Extraction of the surface species with [PPN][Cl] in acetone gave a reddish brown solution having infrared bands in good agreement with the spectrum of $[PPN]_2[Os_{10}C(CO)_{24}]$ (Table I). The unit cell dimensions of a crystal of $[PPN]_2[Os_{10}C(CO)_{24}]$ prepared by this procedure were found by X-ray crystallography to be the same, within experimental error, as those reported by Jackson et al.[14]

The synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ on MgO was monitored by in situ infrared spectroscopy. The wafer was initially transparent in the carbonyl region, but upon heating in flowing equimolar CO + H_2 at 200 °C, it soon exhibited an infrared spectrum [ν_{CO} = 2105 (m), 2030 (s), and 1936 (s) cm^{-1}] indicative of osmium(II) di- and tricarbonyl species. These well-characterized species are also formed by the oxidative fragmentation of triosmium clusters on MgO.[8,15] When the reaction temperature was increased to 275 °C, ν_{CO} bands suggestive of the presence of $[Os_{10}C(CO)_{24}]^{2-}$ appeared. The intensities of bands at 2080 (w), 2040 (s), and 1980 (s) cm^{-1} increased rapidly during the first hour at 275 °C and continued to increase, but more slowly, for 4–5 h. The ν_{CO} infrared spectrum of the product, recorded at 25 °C in vacuo after reaction for 5 h, has three principal absorptions that we assign to $[Os_{10}C(CO)_{24}]^{2-}$ adsorbed on MgO (Figure 3A, Table I). When the wafer was removed from the infrared cell and treated with [PPN][Cl] in acetone, a deep reddish brown solution was produced that contained pure $[PPN]_2[Os_{10}C(CO)_{24}]$ [ν_{CO} = 2036 (s) and 1990 (s) cm^{-1} (Figure 3B)]. The only osmium carbonyl species remaining on the MgO after extraction of $[Os_{10}C(CO)_{24}]^{2-}$ and rinsing with acetone was residual decaosmium carbido carbonyl, as evidenced by the infrared spectrum [ν_{CO} = 2030 (s) and 1986 (vs) cm^{-1} (Figure 3C)].

XRF analysis of solids after treatment with CO + H_2 and after extraction with [PPN][Cl] in acetone established that the yield of $[PPN]_2[Os_{10}C(CO)_{24}]^{2-}$ was 65% and that Os loss as volatile carbonyls was negligible. The Os contents of the starting mixture ($[H_2OsCl_6]$ + MgO) (1.49 wt %) and the resultant $[Os_{10}C(CO)_{24}]^{2-}$/MgO (1.44 wt %) are equivalent within the limits of experimental precision. The Os content of the extracted solid was 0.50 wt %, from which the yield of $[Os_{10}C(CO)_{24}]^{2-}$ was estimated.

The preparation of $[Os_{10}C(CO)_{24}]^{2-}$ also was effected in an autoclave. Under 1 atm of equimolar CO + H_2, 1 g of material prepared from $[H_2OsCl_6]$ and MgO was allowed to react for 5 h at 275 °C. $[Os_{10}C(CO)_{24}]^{2-}$ was extracted by cation metathesis with [PPN][Cl] in acetone.

Effects of Precursor and Gas Environment on Osmium Cluster Growth. Additional experiments were performed to examine the roles of the precursor and gas environment in determining the nuclearity of the osmium clusters formed on the MgO surface. Treatment of a sample derived from the adsorption of $[Os_3(CO)_{12}]$ on MgO for 4 h in flowing CO + H_2 (equimolar) at 275 °C and 1 atm resulted in a mixture of surface-bound cluster anions. The clusters were extracted with [PPN][Cl] in acetone, and the infrared spectrum of the resultant solution [ν_{CO} = 2049 (m), 2039 (w), 2023 (s), 2001 (s), 1990 (s), 1978 (s), 1970 (s), 1948 (w), and 1922 (w) cm^{-1}] is suggestive of a mixture of $[H_3Os_4(CO)_{12}]^-$ and $[Os_5C(CO)_{14}]^{2-}$ (Table I). Treatment of $[H_3Os_4(CO)_{12}]^-$ on MgO, prepared by chemisorption of $[H_4Os_4(CO)_{12}]$, with flowing CO + H_2 (equimolar) at 275 °C and 1 atm for 1.5 h did not result in loss of molecular species from the surface or in a significant conversion to higher nuclearity carbonyl clusters; $[H_3Os_4(CO)_{12}]^-$ was stabilized on MgO under these conditions.

When the supported triosmium cluster was first decomposed by treatment in He for 2 h at 275 °C, osmium(II) subcarbonyl species [ν_{CO} = 2019 (s) and 1915 (br) cm^{-1}] were formed.[8,15] Treatment of the supported Os^{II} complexes with equimolar CO + H_2 at 275 °C and 1 atm for 2 h, followed by extraction of the resultant solid with [PPN][Cl] in acetone, gave a solution of $[Os_{10}C(CO)_{24}]^{2-}$ [ν_{CO} = 2035 (s) and 1990 (s) cm^{-1}].

$[H_3Os_4(CO)_{12}]^-$ was produced by reductive carbonylation of a sample prepared from $[H_2OsCl_6]$ + MgO with flowing CO + H_2 (equimolar) at 275 °C and 11 atm for 12 h. The resultant yellow orange solid was extracted with [PPN][Cl] in CH_2Cl_2 to yield a yellow solution characterized by ν_{CO} infrared bands at 2046 (s), 2021 (s), 1998 (s), and 1979 (m) cm^{-1}, consistent with the presence of $[H_3Os_4(CO)_{12}]^-$ (Table I). Unassigned infrared bands at 1967 (m, sh), 1944 (w), and 1920 (w) cm^{-1} were also observed. XRF analysis of portions of the $[H_2OsCl_6]$-derived materials before and after reaction indicated that 42% of the initial Os content was lost, presumably as volatile neutral carbonyls.

The reductive carbonylation of a sample prepared from $[H_2OsCl_6]$ + MgO was investigated by slowly heating this material in flowing CO alone at 1 atm and simultaneously monitoring the surface reaction by in situ infrared spectroscopy. At temperatures <275 °C the only surface carbonyl species detected were the osmium(II) di- and tricarbonyls, also observed at these temperatures under CO + H_2. Broad ν_{CO} bands at 2034 and 1990 cm^{-1}, suggestive of the formation of $[Os_{10}C(CO)_{24}]^{2-}$, appeared abruptly upon heating to 275 °C. After 1.5 h at 275 °C, the sample was cooled to 25 °C in flowing CO, and the infrared cell was evacuated; the infrared spectrum of the resultant material (Figure 4A) is suggestive of $[Os_{10}C(CO)_{24}]^{2-}$/MgO in addition to unconverted osmium(II) subcarbonyls. The presence of this cluster was confirmed by extraction of the $[Os_{10}C(CO)_{24}]^{2-}$ from the surface by cation metathesis (Figure 4B). The species that remained on the surface were examined by infrared spectroscopy; the spectrum (Figure 4C) indicates the presence of the covalently bound os-

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[14] Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1982**, 2099.

[15] Deeba, M.; Scott, J. P.; Barth, R.; Gates, B. C. *J. Catal.* **1981**, *71*, 373.

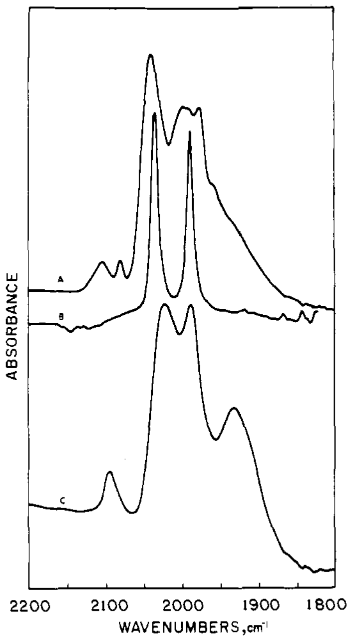

Figure 4. Infrared spectra: A, solid resulting from treatment of sample prepared from H_2OsCl_6 + MgO with flowing CO at 275 °C and 1 atm for 1.5 h; B, $[Os_{10}C(CO)_{24}]^{2-}$ extracted from the sample by ion exchange with [PPN][Cl] in acetone; C, sample after extraction with [PPN][Cl]/acetone.

mium(II) subcarbonyls. Additional experiments suggested that the yield of $[Os_{10}C(CO)_{24}]^{2-}$ by reductive carbonylation of samples prepared from $[H_2OsCl_6]$ + MgO and treated with CO alone was limited by the stability of the osmium(II) subcarbonyl species. Heating a sample in CO at 275 °C for 5.5 h did not result in complete reduction of the mononuclear complexes, whereas essentially complete conversion of these species was observed after 5 h in CO + H_2 (above).

Discussion

The simple, efficient surface-mediated syntheses of $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_5C(CO)_{14}]^{2-}$ reported here may presage a broad class of organometallic syntheses involving solid surfaces. The reactions observed to occur on MgO typically have parallels in basic solutions, and we infer that the strongly basic character of the MgO surface is essential.[16] In this section, we attempt to place the surface organometallic chemistry in the perspective of known solution organometallic chemistry and known surface chemistry, with a goal being to draw attention to the broader possibilities for the application of surface-mediated synthesis.

The synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ by treatment of samples prepared from $[H_2OsCl_6]$ adsorbed on MgO with CO or CO + H_2[5] represents the first example of reductive carbonylation[17] of a metal halo salt to produce a high-nuclearity Os cluster. The yield of $[Os_{10}C(CO)_{24}]^{2-}$ is equivalent to that obtained in conventional synthesis by reaction of $[Os_3(CO)_{12}]$ with Na or by pyrolysis of $[Os_3(CO)_{11}(C_5H_5N)]$,[14] but the chloroosmic acid precursor is less expensive than $[Os_3(CO)_{12}]$, and the surface-mediated synthesis is more rapid and convenient. The byproducts of the pyrolysis of $[Os_3(CO)_{11}(C_5H_5N)]$ at 250 °C for 64 h are $[PPN][HOs_5(CO)_{15}]$ (24% yield), $[H_4Os_4(CO)_{12}]$ (6%), and $[PPN][HOs_5C(CO)_{14}(NC_5H_4)]$ (4%). In the surface-mediated synthesis there are no apparent osmium carbonyl byproducts; the decaosmium clusters which are retained by the MgO after extraction (and reduce the yield) perhaps are entrapped by the matrix.[18] It seems likely that straightforward extensions of this chemistry will lead, for example, to the surface-mediated synthesis of high-nuclearity Rh and Pt clusters, which are known products of reductive carbonylation in solution.[17]

The key requirements for efficient synthesis of $[Os_{10}C(CO)_{24}]^{2-}$, whether in solution, in the solid state, or on a metal oxide surface, are (1) a reaction temperature between 230 and 270 °C and (2) a suitable reducing agent. Temperatures in this range are consistent with formation of the encapsulated carbon ligand by CO disproportionation.[19] The short reaction time (5 h) for surface-mediated synthesis on MgO, as compared to reaction times (64–70 h) for the syntheses from triosmium carbonyl precursors, may be attributed to the higher reaction temperature. In the conversion of $[Os_3(CO)_{12}]$ to $[Os_{10}C(CO)_{24}]^{2-}$ in solution, metallic Na is added as a reducing agent[13] and the reaction temperature is limited by the boiling point of the solvent tetraglyme. In the vacuum pyrolytic conversion of $[Os_3(CO)_{11}(C_5H_5N)]$ to $[Os_{10}C(CO)_{24}]^{2-}$, the pyridine ligand may react as a base, allowing synthesis in the absence of solvent.[14] The surface-mediated synthesis on a refractory metal oxide such as basic MgO in the absence of solvent provides a unique flexibility; high reaction temperatures can be used without the need for high pressures or concern for solvent stability.

The only precedents for reductive carbonylation of supported metal ions are reactions that produce polynuclear rhodium carbonyls at room temperature. Rhodium(I) *gem*-dicarbonyl species on Al_2O_3, produced from the decomposition of $[Rh_6(CO)_{16}]$, react with CO + H_2O at 25 °C and 1 atm to regenerate the hexarhodium carbonyl cluster.[20] The reductive carbonylation of Rh ions in the supercages of faujasitic zeolites has also been reported;[21] polynuclear carbonyls form by CO + H_2 treatment of Rh^{III} ions in hydrated zeolite Y at 25 °C and 1 atm. The low reaction temperatures in these syntheses suggest a growth mechanism involving redox condensation reactions, known to be facile for rhodium carbonyls in solution.[17] Basset et al.[20] suggested that, in the synthesis of $[Rh_6(CO)_{16}]$ on Al_2O_3, reductive carbonylation was initiated by attack of adsorbed H_2O on $Rh(CO)_2\{OAl\}\{HO\text{-}Al\}$ to generate the mobile nucleophile $Rh(CO)_4]^-$:

$$Rh(CO)_2\{OAl\}\{HO\text{-}Al\} + H_2O \xrightarrow{CO} [Rh(CO)_4]^- + \{H^+\} + 2\{HO\text{-}Al\} + CO_2 \quad (1)$$

Cluster growth was envisaged to result from redox condensation of $[Rh(CO)_4]^-$ and $Rh(CO)_2\{OAl\}\{HO\text{-}Al\}$ species.

In contrast to the chemistry of rhodium carbonyls on Al_2O_3 and in zeolites, the osmium(II) di- and tricarbonyl intermediates on MgO are quite stable under CO and CO + H_2 and are reduced to give anionic Os clusters only at temperatures approaching 275 °C. The reduction of the osmium(II) subcarbonyl species and the initiation of cluster growth in the presence CO or CO + H_2 were found to coincide with the loss of chemically bound water from the MgO, which becomes significant only at temperatures exceeding 250 °C. Thermogravimetric analysis demonstrated that water loss in flowing He at 275 °C from a sample made from $[H_2OsCl_6]$ and MgO was complete after ~2 h and amounted to 40 H_2O molecules/Os atom.[12] In situ infrared spectroscopy indicated that reduction of osmium(II) subcarbonyls ceased after ~2 h at 275 °C in CO alone. We suggest that the reductive

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[16] MgO is one of the most strongly basic solids known (Tanabe, K. *Solid Acids and Bases*; Academic Press: New York, 1970), able to deprotonate even such weak Brønsted acids as ammonia (pK_a = 36) (Garrone, E.; Stone, F. S. *Proc. Int. Congr. Catal. 8th* **1984**, *3*, 441), and it is easily prepared as a porous high surface area powder.

[17] Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

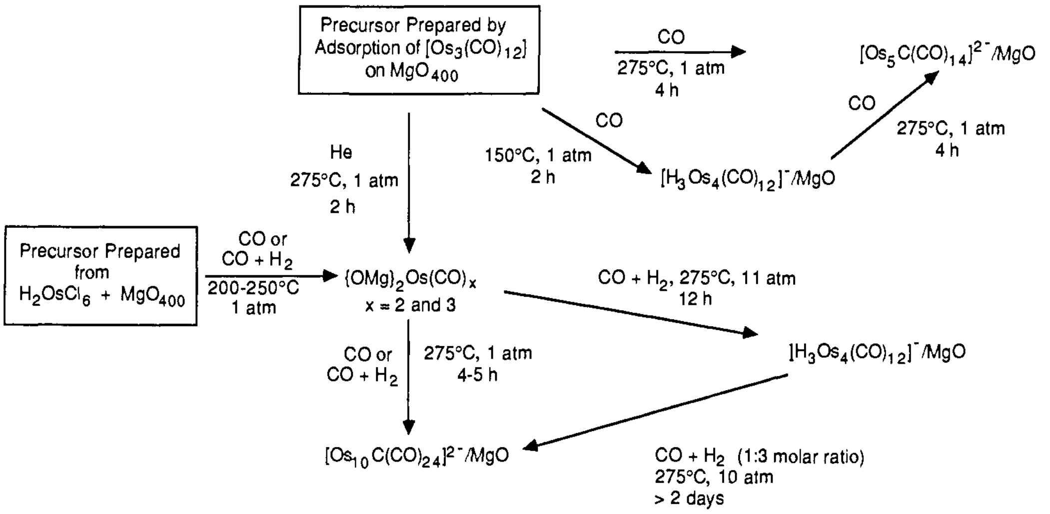
[18] It has been proposed on the basis of electron microscopy that metal aggregates can be encapsulated by the MgO support: Stastic, A. G.; Schwank, J. *J. Catal.* **1986**, *98*, 191.

[19] Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606.

[20] (a) 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*, 3104. (b) Basset, J. M.; Theolier, A.; Commereuc, D.; Chauvin, Y. *J. Organomet. Chem.* **1985**, *279*, 147.

[21] (a) Shannon, R. D.; Vedrine, J. C.; Naccache, C.; Lefebre, F. *J. Catal.* **1984**, *88*, 431. (b) Mantovani, E.; Palladino, M.; Zanoki, A. *J. Mol. Catal.* **1977**, *3*, 285. (c) Ichikawa, M.; et al. To be published. Kosugi, N.; Kuroda, H.; Rao, L. F.; Fukuoka, A.; Ichikawa, M. Preprints of 60th Meeting of Catalysis Society of Japan, 1987, 2D04, p 438. (d) Gallezot, P. In *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*; Basset, J.-M., Gates, B. C., Candy, J.-P., Choplin, A., Leconte, M., Quignard, F., Santini, C., Eds.; Kluwer: Dordrecht, 1988; p 143.

Scheme I. Reactivity of Surface-Bound Osmium Carbonyls in Open-Flow Systems



carbonylation of Os^{II} species on MgO in the presence of CO alone could be initiated by nucleophilic attack of adsorbed water (or basic surface hydroxyl groups):

$$\{OMg\}_2Os(CO)_3 + 3\{MgO\} + 3H_2O \xrightarrow{CO} [HOs(CO)_4]^- + 2\{Mg{-}OH\} + 3\{Mg(HCO_3)\} \quad (2)$$

We have reported the condensation of $[HOs(CO)_4]^-$ to give $[Os_{10}C(CO)_{24}]^{2-}$ on MgO at 275 °C and 10 atm,[22] and Bhattacharya et al.[23] have reported the redox condensation of $[HOs(CO)_4]^-$ and its conjugate acid in solution at 100 °C to give $[HOs_3(CO)_{11}]^-$. Nearly complete conversion of osmium(II) subcarbonyls on MgO was accomplished in flowing CO + H_2 at 275 °C, perhaps because an additional reduction pathway was operative, e.g.

$$\{OMg\}_2Os(CO)_3 + \tfrac{3}{2}H_2 \xrightarrow{CO} [HOs(CO)_4]^- + 2\{HO{-}Mg\} \quad (3)$$

However, at these high temperatures, reactions of coordinatively unsaturated osmium subcarbonyls could contribute to cluster growth. When the pressure of equimolar CO + H_2 was increased to 11 atm, the predominant product from the $[H_2OsCl_6]$ + MgO precursor at 275 °C was $[H_3Os_4(CO)_{12}]^-$, as opposed to $[Os_{10}C(CO)_{24}]^{2-}$. The higher partial pressures of CO and of H_2 inhibited the growth of high-nuclearity clusters and stabilized the trihydridotetraosmium anion on MgO. Infrared spectroscopy of binary osmium carbonyl clusters at high pressures in solution has demonstrated that $[H_2Os(CO)_4]$ and $[H_4Os_4(CO)_{12}]$ are the stable neutral species under pure H_2 or CO + H_2 mixtures.[24] Similarly, the anionic derivative $[H_3Os_4(CO)_{12}]^-$ was stabilized on the basic MgO surface, but 42% of the Os was lost from the surface as volatile products, probably, we suggest, in the form of $[H_2Os(CO)_4]$.

The synthesis of $[Os_5C(CO)_{14}]^{2-}$ on MgO illustrates the influence of the surface-bound precursor. In contrast to the formation of $[Os_{10}C(CO)_{24}]^{2-}$ from chloroosmic acid on MgO, the surface species derived from the adsorption $[Os_3(CO)_{12}]$ on MgO, upon treatment with CO at 275 °C, is converted in high yield to $[Os_5C(CO)_{14}]^{2-}$. The simplicity and efficiency of this synthesis are contrasted to the literature procedure, whereby a yield of <5% is obtained by vacuum pyrolysis of $[Os_3(CO)_{12}]$ to give $[Os_5C(CO)_{15}]$[19] followed by reduction in alcoholic base to give $[Os_5C(CO)_{14}]^{2-}$.[9] The synthesis of $[Os_5C(CO)_{15}]$ has been refined recently,[9] but byproducts are numerous and yields still low. The surface-mediated synthesis is recommended, and it may be expected to facilitate the development of the chemistry of the family of pentaosmium carbido carbonyl clusters.

The reaction pathway producing $[Os_5C(CO)_{14}]^{2-}$ on MgO was investigated by heating the surface species derived by adsorption of $[Os_3(CO)_{12}]$ on MgO with CO at 150 °C. After 2 h, the major product was $[H_3Os_4(CO)_{12}]^-$, with only a small quantity of $[Os_5C(CO)_{14}]^{2-}$. The synthesis of $[H_3Os_4(CO)_{12}]^-$ from the triosmium carbonyl precursor on MgO appears to be analogous to the reaction of $[Os_3(CO)_{12}]$ in refluxing KOH–isobutyl alcohol to yield the tetranuclear anionic cluster.[25] Pyrolysis of $[HOs_3(CO)_{11}]^-$ in refluxing isobutyl alcohol also gives $[H_3Os_4(CO)_{12}]^-$ as the major product.[25] Surface hydroxyl groups are evidently the source of hydrogen in the formation of $[H_3Os_4(CO)_{12}]^-$ from the triosmium carbonyl on MgO in the presence of CO. Treatment of surface-bound $[H_3Os_4(CO)_{12}]^-$ on MgO[11,12] with CO at 275 °C and 1 atm resulted in its conversion to $[Os_5C(CO)_{14}]^{2-}$. These results suggest that $[H_3Os_4(CO)_{12}]^-$ might be an intermediate in the formation of $[Os_5C(CO)_{14}]^{2-}$ from the triosmium carbonyl on MgO at 275 °C under 1 atm of CO. In contrast, $[H_3Os_4(CO)_{12}]^-$ is stabilized on MgO under equimolar CO + H_2 at 275 °C and 1 atm. Earlier work demonstrated that $[H_3Os_4(CO)_{12}]^-$ remained the predominant surface species even after treatment with H_2 + CO in a 3:1 molar ratio at 275 °C and 10 atm for 14 h.[26]

When the supported triosmium cluster precursors were first oxidatively fragmented by treatment in He at 275 °C, a different chemistry was observed. Deeba et al.[15] demonstrated that the oxidative fragmentation of triosmium species, derived from the chemisorption of $[Os_3(CO)_{12}]$ on MgO, results in cluster breakup to yield osmium(II) subcarbonyl species; this result was confirmed by Psaro et al.[8] We infer on the basis of the close agreement with the ν_{CO} infrared spectra reported by Deeba et al.[15] that $\{L\}\{OMg\}Os(CO)_{2and3}$ (where L = OH^- or O^{2-}) species are also formed by treatment of our triosmium precursor on MgO under He at 275 °C. Exposure of these mononuclear surface species to CO or CO + H_2 at 275 °C and 1 atm resulted in the formation of $[Os_{10}C(CO)_{24}]^{2-}$ on MgO, which was extracted from the surface with [PPN][Cl] in acetone. After fragmentation and oxidation of the triosmium precursor, the surface organoosmium chemistry is closely similar to that observed in the reductive carbonylation of samples prepared from $[H_2OsCl_6]$ + MgO.

Scheme I is a summary of the transformations observed for surface-bound osmium carbonyls on MgO. Osmium(II) subcarbonyl complexes $[H_3Os_4(CO)_{12}]^-$, $[Os_5C(CO)_{14}]^{2-}$, and $[Os_{10}C(CO)_{24}]^{2-}$ were found to be particularly stable on MgO

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[22] Lamb, H. H.; Gates, B. C. *J. Am. Chem. Soc.* **1986**, *108*, 81.

[23] Bhattacharya, A. A.; Nagel, C. C.; Shore, S. G. *Organometallics* **1983**, *2*, 1187.

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

[25] Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; Braga, D.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2151.

[26] Lamb, H. H.; Krause, T. R.; Gates, B. C. *Proc. Int. Congr. Catal. 9th* **1988**, 3, 1378.

in the presence of CO and CO + H_2 mixtures. The surface species formed evidently depend on both thermodynamics and kinetics. The easily controlled variables are temperature, pressure, and gas-phase composition. Additional control of the product distribution is exercised through the choice of the surface-bound precursor. Reductive carbonylation of Os^{II} complexes on MgO at low pressures in the presence of CO or CO + H_2 results in rapid cluster growth and synthesis of robust $[Os_{10}C(CO)_{24}]^{2-}$. Alternatively, growth from preformed triosmium species on MgO in the presence of CO under similar conditions results in high yields of $[Os_5C(CO)_{14}]^{2-}$. Preformed triosmium clusters and Os^{II} complexes can serve as precursors of $[H_3Os_4(CO)_{12}]^-$ on MgO; this supported trihydridoosmium cluster is most stable under high partial pressures of hydrogen.

The pentanuclear and decanuclear carbido cluster anions are highly stable on MgO in the presence of CO and CO + H_2. $[Os_{10}C(CO)_{24}]^{2-}$ has a tetracapped octahedral core, which has been demonstrated to be extremely resistant to fragmentation.[27] On MgO, the decaosmium cluster dianion does not fragment under CO or CO + H_2 at the temperatures of this investigation, and, upon heating in an inert atmosphere, it decomposes only at temperatures exceeding 300 °C.[12] The structures of the carbido carbonyl anions are closely related as both are based on a fundamental octahedron of six Os atoms and have seven skeletal electron pairs for cluster bonding.[28] The interconversion of $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ on MgO was not observed, possibly, we suggest, because this conversion would require (a presumably slow) fragmentation of the Os_5C or $Os_{10}C$ cluster core.[29]

To summarize, although many of the details of the surface chemistry remain to be elucidated, it is clear that surface-mediated syntheses giving metal carboyl clusters are sometimes efficient and simple. This may be only a beginning for surface-mediated synthesis. Earlier research in surface organometallic chemistry has provided a foreshadowing of the possibilities (e.g., the synthesis of $[Rh_6(CO)_{16}]$ on γ-Al_2O_3 from mononuclear fragments[20] and the synthesis of neutral metal carbonyl clusters in the supercages of a sodium form faujasite zeolite[21]). The syntheses of $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$ reported here appear to be the first examples of surface-mediated syntheses that are more efficient than the best known solution syntheses. The opportunities seem to be many; the surface medium can be chosen to provide the desired acidic, basic, or redox groups or anchored ligands, thereby playing a role usually reserved for solvents, and possibly simplifying the product purification.

Experimental Section

General Procedures. All syntheses and sample transfers were conducted with exclusion of air and moisture on a double-manifold Schlenk line, in a Vacuum Atmospheres drybox, a batch autoclave, or a copper-lined stainless steel tubular reactor with a flow system designed to prevent contamination of the sample with adventitious metal carbonyls. Hexanes and tetrahydrofuran (THF) were dried and distilled from sodium/benzophenone ketyl. Acetone was dried over activated 4A molecular sieves and stored under nitrogen. Methylene chloride was dried and distilled from phosphorus pentoxide. 2-Propanol was used as received. $H_2OsCl_6{\cdot}6H_2O$ (H_2OsCl_6) and $[Os_3(CO)_{12}]$ were purchased from Strem and used as received. MgO powder (MX-65-1) was obtained from MCB Reagents. [PPN][Cl] (Strem), $[Et_4N][Cl]$ (Eastman), and $[t\text{-}Bu_4N][Br]$ (Eastman) were used as received. $[H_4Os_4(CO)_{12}]$[10] and $[Et_4N]_2[Os_{10}C(CO)_{24}]$[13] were prepared according to literature methods. The gases, CO, CO + H_2 (equimolar), and H_2, were purchased from Matheson as UHP grade and further purified by passage over 4A molecular sieves to remove water; the hydrogen also flowed over supported Cu_2O to remove oxygen. A trap of alumina maintained at 300 °C was also used for purification of CO, removing by decomposition any traces of nickel and iron carbonyls. Oxygen (extra-dry grade) was purchased from Matheson.

Instrumentation. Infrared spectra were recorded with a Nicolet 7199 Fourier transform spectrometer with a spectral resolution of 4 cm^{-1}. Solution samples were measured in 0.2-mm CaF_2 cells. Solid samples were pressed into self-supporting wafers and examined in transmission mode in a controlled-atmosphere quartz cell with fitted NaCl windows. UV–visible spectra were measured by diffuse reflectance with a Cary 219 spectrophotometer; spectra of powders were obtained with a Suprasil quartz cell having a 1-mm path length and fitted with a vacuum stopcock. X-ray fluorescence measurements to determine metal contents of the solids were effected with a Philips PW1410/80 automated X-ray spectrometer. Fast atom bombardment mass spectrometry was carried out with a Vacuum Generators ZAB-E (BE) instrument. The clusters were placed in a "magic bullet" matrix and bombarded with 8-keV Xe. The instrument achieved unit resolution throughout the mass range explored.

Surface Preparation. The MgO support was calcined by heating to 400 °C under flowing oxygen for 2 h, followed by evacuation (10^{-3}–10^{-4} Torr) for 12 h. The surface area of the powder treated in this manner was determined to be 75 m^2/g by N_2 adsorption.

Preparation of Precursors. $[Os_3(CO)_{12}]$ was brought in contact with MgO from hexanes solutions. A slurry of $[H_4Os_4(CO)_{12}]$ microcrystals and MgO in hexanes was used in the preparation of $[H_3Os_4(CO)_{12}]^-$/MgO, since the neutral cluster is only slightly soluble in hexanes at 25 °C. Typically, 5 g of MgO was used in these preparations with enough of the metal carbonyl precursor to give a metal loading of 1 wt %; approximately 30 mL of solvent was used in each preparation. After the slurries were stirred for 4–6 h at 25 °C, hexanes were removed by either filtration [in the case of $[H_4Os_4(CO)_{12}]$] or evacuation. Samples of $[H_3Os_4(CO)_{12}]^-$ were washed exhaustively with fresh hexanes. The solids were dried under vacuum for 12 h. X-ray fluorescence of the supported materials showed them to contain 0.8–1.0 wt % Os.

Samples of MgO impregnated with chloroosmic acid and having Os loadings of approximately 1 and 3 wt % were prepared as follows: sufficient H_2OsCl_3 to impregnate 5 g of MgO was dissolved in 10 mL of deionized water (2 mL of water/g was required to wet the MgO). The solution was combined rapidly with freshly calcined MgO in an alumina crucible open to the atmosphere to form a heavy, bluish gray paste. The paste was dried under vacuum at 70 °C for 4 h; the resultant light blue gray solid was crushed and then stored in a desiccator.

Preparation of $[Os_5C(CO)_{14}]^{2-}$. In the drybox, 2 g of the sample prepared by adsorption of $[Os_3(CO)_{12}]$ on MgO was placed in a $^1/_2$-in. copper-lined stainless steel reactor tube. The tube was sealed, brought outside the drybox, and introduced into a flow system without exposure of the sample to the atmosphere. A flow of CO at 1 atm, 60 mL/min, was begun and the reactor heated to 275 °C at 3 °C/min and maintained at this temperature for 4 h. With the CO flow continuing, the reactor was allowed to cool to room temperature, and then it was sealed and transferred back to the drybox. The pale yellow solid removed from the reactor was extracted with an excess of [PPN][Cl] in acetone, producing a white solid and a golden yellow supernatant solution. The solution exhibited infrared bands at ν_{CO} = 2039 (w), 2023 (w), 1991 (s), 1977 (vs), 1970 (vs), 1947 (s), 1926 (w), and 1891 (w) cm^{-1}. After solvent evaporation and recrystallization from THF/hexanes, a yellow brown crystalline solid resulted. The product isolated in this manner was 20 mg of $[Os_5C(CO)_{14}]^{2-}$ (65% yield).

Alternatively, the synthesis was carried out in an autoclave. In the drybox, 2 g of the sample prepared by adsorption of $[Os_3(CO)_{12}]$ on MgO was sealed inside a 100-mL stainless-steel autoclave. Outside the drybox, the autoclave was pressurized to 13.6 atm with CO. The reaction temperature was brought to 300 °C and maintained for 5 h. The autoclave was then cooled to room temperature and the pressure released to 1 atm. The autoclave was placed in the drybox, and the solid sample was removed and extracted with [PPN][Cl]/acetone to yield pure $[Os_5C(CO)_{14}]^{2-}$. The identification was verified by infrared spectroscopy.

Preparation of $[AuPPh_3]_2[Os_5C(CO)_{14}]$.[9] Ten milligrams of $[PPN]_2[Os_5C(CO)_{14}]$, 15 mg of $[AuPPh_3Cl]$, and 5 mg of Tl_2SO_4 were combined in a 50-mL Schlenk tube. The flask was evacuated for 1 h, and then 10 mL of CH_2Cl_2 was added. Within 10 min, the starting golden yellow CH_2Cl solution turned red orange: ν_{CO} = 2085 (w), 2051 (vs), 2036 (m, sh), 1965 (w), 1936 (w), and 1902 (w) cm^{-1}.

Preparation of $[Os_{10}C(CO)_{24}]^{2-}$. Samples (ca. 0.5 g) of the material prepared from MgO impregnated with H_2OsCl_6 were suspended by glass wool plugs in Pyrex tubes and treated with flowing equimolar CO + H_2 [50 mL/min (NTP)]. Typically, the samples were heated directly from room temperature to 275 °C at 6 °C/min and then held at this temperature for 5 h. (Alternatively, some samples were dried at 150° C in flowing He for 1 h before cooling to room temperature and the start of the treatment in CO + H_2; the drying did not affect the synthesis of the

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(27) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Nicholls, J. N.; Vargas, M. D. *J. Organomet. Chem.* **1983**, *249*, 255.

(28) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley Interscience: Chichester, U.K., 1980; Chapter 3.

(29) Similarly, we suspect that cluster growth starting with preformed triosmium species on MgO ceases with formation of $[Os_5C(CO)_{14}]^{2-}$ or $[H_3Os_4(CO)_{12}]^-$ under CO or CO + H_2, respectively, at 275 °C and 1 atm, because fragmentation of these robust clusters, a process required to supply monomeric units for further growth, is energetically unfavorable.

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decanuclear cluster.) The flow of CO + H_2 was maintained while the reactor was cooled to room temperature. The resultant bright pinkish brown solids were removed from the sealed reactor tubes in the drybox. Extraction of the solids was carried out with a 10-fold excess of [PPN][Cl] or $[Et_4N][Cl]$ in reagent acetone (100 mL each). Deep reddish brown solutions formed immediately, but agitation of the suspensions under N_2 was continued for at least 1 h. After filtration, the solvent was evaporated to give a solution volume of 5–10 mL, and 2-propanol was added dropwise to precipitate red microcrystals, which were recovered by filtration and washed with several volumes of deionized water. The red $[PPN]_2[Os_{10}C(CO)_{24}]$ prepared in this manner exhibited an infrared spectrum with ν_{CO} = 2036 (s) and 1990 (s) cm^{-1}.

Altenatively, the synthesis was carried out in an autoclave. One gram of the material prepared by impregnation of MgO with H_2OsCl_6 was placed inside a 100-mL autoclave, which was purged with CO + H_2 (equimolar) at 1 atm and sealed. The autoclave was heated to 300 °C, held for 5 h, and then cooled to room temperature. The material was removed from the reactor in the drybox and extracted with [PPN][Cl] in acetone to yield pure $[Os_{10}C(CO)_{24}]^{2-}$. The identification was verified by infrared spectroscopy.

Acknowledgments. We thank A. L. Rheingold of the University of Delaware for the X-ray diffraction and J. Lazar of E. I. du Pont de Nemours and Co. for the mass spectrometry. The research at the University of Delaware was supported by the National Science Foundation (Grant CBT 8605699).

Registry No. MgO, 1309-48-4; $[PNN]_2[Os_5C(CO)_{14}]$, 88567-87-7; $Os_3(CO)_{12}$, 15696-40-9; CO, 630-08-0; $[PPn]_2[Os_{10}C(CO)_{24}]$, 75117-74-7; $[H_4Os_4(CO)_{12}]$, 12375-04-1.

Intermediates in the Time-Resolved and Matrix Photochemistry of (η^5-Cyclopentadienyl)rhodium Complexes: Roles of Alkane Activation and Rhodium–Rhodium Bond Formation

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Received March 24, 1989

Abstract: Pulsed laser photolysis studies of solutions of $Cp_2Rh_2(CO)_3$, $CpRh(CO)_2$, and $CpRh(C_2H_4)CO$ (Cp = η^5-C_5H_5) are reported using UV/vis and IR detection. The identification of the transients is supported by earlier studies of $Cp_2Rh_2(CO)_3$ in hydrocarbon glasses, by prior matrix studies of $CpRh(CO)_2$ and $CpRh(CO)(C_2H_4)$, and by matrix isolation experiments on $Cp_2Rh_2(CO)_3$ reported here. Matrix photolysis (20 K, Ar, N_2, CH_4, and CO matrices) of $Cp_2Rh_2(CO)_3$ generates $[CpRh(\mu\text{-}CO)]_2$ reversibly. Isotopic labeling and polarized photolysis demonstrates that the $Rh_2(CO)_2$ unit is planar with CO bridges perpendicular to the RhRh axis. Metal–metal bond fission of $Cp_2Rh_2(CO)_3$ is observed only in CO-doped matrices. The major photoproduct of $Cp_2Rh_2(CO)_3$ in solution is $[CpRh(\mu\text{-}CO)]_2$, which reacts with CO to re-form starting material with $k_2 = (1.2 \pm 0.1) \times 10^3$ dm^3 mol^{-1} s^{-1} at 292 K ($\Delta H^\ddagger$ = 22.3 ± 2.5 kJ mol^{-1}, $\Delta S^\ddagger$ = −110 ± 10 J mol^{-1} K^{-1}). The first observable product of photolysis of $CpRh(CO)_2$ in cyclohexane at room temperature is $CpRh(CO)(C_6H_{11})H$, formed by insertion of CpRhCO into the solvent C–H bonds within 400 ns. In the absence of other ligands, $CpRh(CO)(C_6H_{11})H$ decays by complex kinetics (probably by reaction with its reductive elimination product CpRhCO) to form $[CpRh(\mu\text{-}CO)]_2$ and then slowly to $Cp_2Rh_2(CO)_3$. The formation of $[CpRh(\mu\text{-}CO)]_2$ is quenched by high concentrations of other ligands (Et_3SiH, $P(OPh)_3$). The reactions with ligands exhibit saturation kinetics, from which the rate of reductive elimination of $CpRh(CO)(C_6H_{11})H$ is measured as $k_{-1} = (2.7 \pm 0.3) \times 10^3$ s^{-1}. The IR experiments show that photolysis of $CpRh(C_2H_4)CO$ gives a higher yield of $CpRh(CO)(C_6H_{11})H$ than that from $CpRh(CO)_2$. These experiments show that matrix isolation and room-temperature photolysis experiments are fully consistent, that the kinetics of formation of CpRh(CO)(alkyl)H are favorable, but that this C–H activation product is exceptionally unstable with respect to formation of other products via reductive elimination of alkane.

The ability of some complexes of general formula (η^5-C_5R_5)ML_2 and (η^5-C_5R_5)$ML(H)_2$ (M = Rh, Ir; R = Me, H; L = CO, PMe_3, C_2H_4) to yield products derived from insertion into the C–H bonds of unactivated alkanes and arenes has generated much excitement among organometallic chemists.[2] There is considerable evidence to indicate that these reactions proceed via intermediates of the type (η^5-C_5R_5)ML. However, not all of the intermediates produced by photolysis of the parent complexes are capable of carrying out C–H activation reactions. The nature of the balance required between the electronic and steric properties of the C_5R_5 and L groups and the metal is not yet fully understood.

The photochemistry of $CpRh(CO)_2$, $CpRh(C_2H_4)CO$ (Cp = η^5-C_5H_5), and related complexes has been investigated previously both in solution and in low-temperature matrices (Charts I and II).[3-9]

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(1) (a) University of York. (b) Max-Planck Institut für Strahlenchemie.

(2) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (c) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (d) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

(3) (a) Haddleton, D. M.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 1810. (b) Haddleton, D. M. *J. Organomet. Chem.* **1986**, *311*, C21. (c) Earlier assignments[3a,5] of $CpRh(CO)(CH_3)H$ depended on the observation of ν(CO) alone. In recent experiments with $CpRh(^{13}CO)(C_2H_4)$ in methane matrices we have identified ν(Rh–H) as a broad, weak pair of bands at 2056 and 2069 cm^{-1}.

(4) (a) Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *10*, 337. (b) Hill, R.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2622. (c) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1.

(5) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1181.

(6) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562.

(7) (a) Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1121. (b) Wasserman, E. P.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1988**, *110*, 6076.

0002-7863/89/1511-8373$01.50/0