Inorg. Chem. **1992**, *31*, 2939–2947 **2939**

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

Organometallic Chemistry on the Basic Magnesium Oxide Surface: Formation of $[HIr_4(CO)_{11}]^-$, $[Ir_6(CO)_{15}]^{2-}$, and $[Ir_8(CO)_{22}]^{2-}$

Sibudjing Kawi and Bruce C. Gates*

Received January 7, 1992

Samples prepared by adsorption of $[Ir(CO)_2(acac)]$ on partially dehydroxylated MgO and on hydrated MgO were treated in CO at room temperature to form supported $[HIr_4(CO)_{11}]^-$ and $[Ir_8(CO)_{22}]^{2-}$, respectively. A sample prepared by adsorption of $[Ir_4(CO)_{12}]$ on partially dehydroxylated MgO was treated with water-saturated helium at room temperature to form $[Ir_6(CO)_{15}]^{2-}$ on the MgO surface. Each of these anions was extracted in high yield into solution by cation metathesis with [PPN][Cl]. Consecutive formation of $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, and $[Ir_6(CO)_{15}]^{2-}$ on the MgO surface was observed as the temperature of the carbonylation reaction was increased from 25 to 200 °C. The organometallic chemistry occurring on the basic MgO surface is similar to that occurring in basic solution.

Introduction

Numerous reactions of organometallic compounds take place on metal oxide surfaces much as they take place in solutions.[1-3] Condensation reactions on the surface of basic MgO give metal carbonyl cluster anions.[1-8] Most organometallic reactions on surfaces give complicated mixtures, but the reductive carbonylation of mononuclear Os,[6] Ru,[7] and Pt[8] complexes on basic MgO surfaces gives carbonyl cluster anions in high yields. Surface-mediated reactions occasionally provide high yields of metal carbonyl clusters that are not accessible by conventional solution techniques, e.g., $[Os_5C(CO)_{14}]^{2-}$ formed from $[Os_3(CO)_{12}]$ on MgO[6] and $[HOs_3(CO)_{10}(OH)]$ formed from $[Os_3(CO)_{12}]$ on silica,[9] among others.[10,11]

Here we report the carbonylation of iridium complexes formed from $[Ir(CO)_2(acac)]$ on MgO to give efficient syntheses of $[HIr_4(CO)_{11}]^-$, $[Ir_6(CO)_{15}]^{2-}$, or $[Ir_8(CO)_{22}]^{2-}$. The organoiridium chemistry on MgO mimics the reductive carbonylation chemistry in basic solutions reported by Angoletta et al.[12] and that on MgO reported by Maloney et al.[13]

Experimental Section

Methods and Materials. All syntheses and sample transfers were conducted with exclusion of air and moisture on a double-manifold Schlenk line and in a Vacuum Atmospheres drybox. Nitrogen and He with purities of 99.999% were purchased from Matheson and passed through beds of Cu_2O and molecular sieve zeolite to remove traces of oxygen and moisture. CO (Matheson, UHP grade) was passed through a bed of activated alumina heated to a temperature exceeding 200 °C to remove traces of iron carbonyl contaminants and through a bed of molecular sieve zeolite to remove moisture. Dried THF and hexanes were distilled over sodium benzophenone ketyl. All solvents were deoxygenated prior to use. Tetra-*n*-butylammonium bromide, $[NBu_4][Br]$ (Aldrich), and bis(triphenylphosphine)iminium chloride, [PPN][Cl] (Aldrich), were used without purification. Extraction of surface organometallic species was performed with a suspension of [PPN][Cl] in methanol or THF.

Porous, hydrated MgO support, labeled MgO_{25} (where the subscript refers to the treatment temperature in °C), was MgO (MX-65-1 powder, MCB reagents, surface area approximately 70 m^2/g) that had been treated by evacuation at 25 °C for 4 h. Partially dehydroxylated MgO, labeled MgO_{400}, was prepared by treatment of the sample in flowing O_2 (Matheson Extra Dry Grade) at 400 °C for 2 h, followed by evacuation for 14 h. $[Ir_4(CO)_{12}]$ and $[Ir(CO)_2(acac)]$ (Strem) were used without purification.

Infrared spectra were recorded with a Nicolet 7199 spectrometer with a spectral resolution of 4 cm^{-1}. Solution spectra were recorded with samples in a 0.2-mm CaF_2 cell. Spectra of solids were recorded with samples in a heatable, controlled-atmosphere flow cell.[14]

Preparation of $[NBu_4][HIr_4(CO)_{11}]$. The method was similar to that reported.[15]

Preparation of $[NBu_4]_2[Ir_8(CO)_{22}]$. The method was similar to literature procedures.[12,16a]

Preparation of $[Ir(CO)_2Cl_2]^-$. The method was similar to that reported.[17]

Preparation of $[Na]_2[Ir_6(CO)_{15}]$. The synthesis is the same as that reported by Maloney et al.,[18] which is derived from that reported by Stevens et al.[19a]

Preparation of MgO-Supported Samples. The MgO_{25}-supported $[Ir(CO)_2(acac)]$ sample was prepared by dissolving $[Ir(CO)_2(acac)]$ (0.036 g) in nondistilled hexanes (50 mL) in a Schlenk flask under a N_2 blanket. MgO_{25} powder (2.0 g) was added, the mixture was stirred under N_2 for 12 h at room temperature, and the solid was dried by evacuation for 14 h at room temperature. The same procedure was used to prepare MgO_{400}-supported $[Ir(CO)_2(acac)]$, except that freshly distilled hexanes were used. Another sample was prepared by slurrying $[Ir_4(CO)_{12}]$ (0.029 g) in freshly distilled hexanes (50 mL) in a Schlenk flask under a N_2 blanket. Calcined MgO_{400} (2.0 g) was added to the slurry, the mixture was stirred under N_2 for 12 h at room temperature, and the solid was dried by evacuation for 14 h at room temperature. Since the solubility of $[Ir_4(CO)_{12}]$ in hexanes is low, the process of dissolution, transport through the liquid, and adsorption on the MgO was slow; consequently, the slurry was stirred overnight. The solution was clear after this time, indicating a complete uptake of the cluster by the solid.

Characterization of Surface Species by Infrared Spectroscopy. Samples of the solid prepared from $[Ir(CO)_2(acac)]$ on either MgO_{25} or MgO_{400} and from $[Ir_4(CO)_{12}]$ on MgO_{400} were pressed into thin self-supporting wafers in the drybox and loaded into a controlled-atmosphere

---

* To whom correspondence should be addressed.

(1) Gates, B. C., Guczi, L., Knözinger, H., Eds. *Metal Clusters in Catalysis*; Studies in Surface Science and Catalysis, Vol. 29; Elsevier: Amsterdam, 1986.

(2) Ichikawa, M. In *Tailored Metal Catalysis*; Iwasawa, Y., Ed.; Reidel: Dordrecht, The Netherlands, 1986; p 183.

(3) Lamb, H. H.; Wolfer, M.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1296.

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

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

(6) 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.

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

(8) Puga, J.; Patrini, R.; Sanchez, K. M.; Gates, B. C. *Inorg. Chem.* **1991**, *30*, 2479.

(9) Dossi, C.; Fusi, A.; Pizzotti, M.; Psaro, R. *Organometallics* **1990**, *9*, 1994.

(10) Kawi, S.; Gates, B. C. *Catal. Lett.* **1991**, *10*, 263.

(11) Kawi, S.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1991**, 994.

(12) Angoletta, M.; Malatesta, L.; Caglio, G. L. *J. Organomet. Chem.* **1975**, *94*, 99.

(13) Maloney, S. D.; van Zon, F. B. M.; Koningsberger, D. C.; Gates, B. C. *Catal. Lett.* **1990**, *5*, 161.

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

(15) Bau, R.; Chiang, M. Y.; Wei, C.-Y.; Garlaschelli, L.; Martinengo, S.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 4758.

(16) (a) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Raimondi, C.; Martinengo, S.; Canziani, F. *J. Chem. Soc., Chem. Commun.* **1981**, 528. (b) Maloney, S. D.; Kelley, M. J.; Gates, B. C. *J. Organomet. Chem.*, in press.

(17) (a) Forster, D. *J. Inorg. Nucl. Chem. Lett.* **1969**, *5*, 433. (a) Della Pergola, R.; Garlaschelli, L.; Martinengo, S.; Demartin, F.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 2463.

(18) Maloney, S. D.; Kelley, M. J.; Koningsberger, D. C.; Gates, B. C. *J. Phys. Chem.* **1991**, *95*, 9406.

(19) (a) Stevens, R. E.; Lin, P. C. C.; Gladfelter, W. L. *J. Organomet. Chem.* **1985**, *287*, 133. (b) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Martinengo, S. *J. Chem. Soc., Chem. Commun.* **1980**, 903.

0020-1669/92/1331-2939$03.00/0

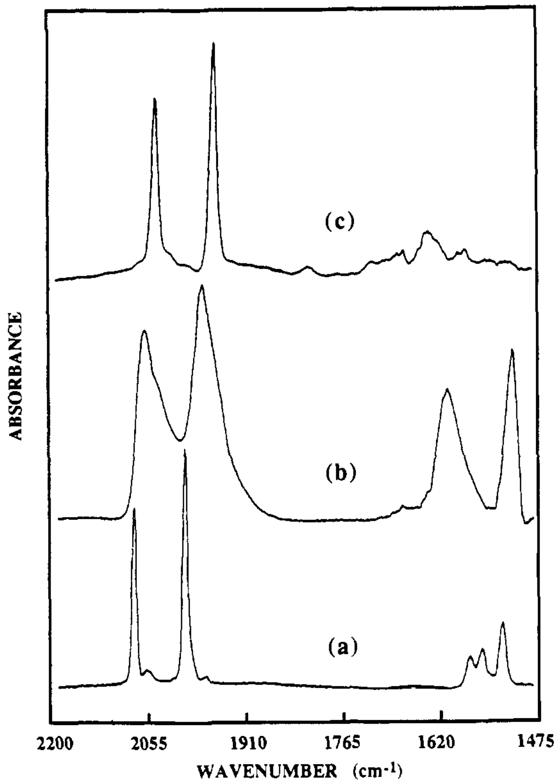


Figure 1. Infrared spectra of (a) [Ir(CO)$_2$(acac)] dissolved in hexanes, (b) species formed by adsorption of [Ir(CO)$_2$(acac)] on MgO$_{400}$ or MgO$_{25}$, and (c) extract solution formed from bringing the sample of spectrum b in contact with [PPN][Cl] in THF.

infrared cell.[14] Flowing gas, CO or H$_2$O-saturated He, was brought in contact with the wafer after thorough purging of the lines with He. For high-temperature treatment, the temperature was typically raised in steps of 20–30 °C and maintained for 30 min after each change to allow equilibration. The sample was scanned 32 or more times, and the signal was averaged.

Extraction of Iridium Carbonyls from the MgO Surface. Surface-bound iridium carbonyls were extracted from MgO as the solid sample in the drybox was brought in contact with a solution of [PPN][Cl] in freshly distilled THF or methanol. The liquid was transferred by pipet into the solution infrared cell. The liquid sample was sealed in the cell, removed from the drybox, and scanned quickly. In some cases, extraction of iridium carbonyls from MgO was carried out on the Schlenk line; the liquid was carefully transferred by cannula from the Schlenk flask to the solution infrared cell without air contamination and the sample was scanned quickly. The infrared data for the sample were ratioed to the background atmosphere in the spectrometer, and the infrared bands for THF or methanol were subtracted from the spectrum.

Results

Chemisorption of [Ir(CO)$_2$(acac)] on MgO. When a solution of [Ir(CO)$_2$(acac)] in hexanes under N$_2$ was brought in contact with MgO$_{25}$ or MgO$_{400}$, the initially white MgO powder became beige and the initially light black solution became clear. The infrared spectrum of the solid prepared from either MgO sample was characterized by two strong carbonyl bands at about 2057 and 1973 cm^{-1} (Figure 1b). A comparison with the spectrum of [Ir(CO)$_2$(acac)] in hexanes (Figure 1a) shows that adsorption of [Ir(CO)$_2$(acac)] on either of the MgO surfaces led to a broadening and shifting of the carbonyl bands to lower wavenumbers. The band broadening is characteristic of adsorbed metal carbonyls, being consistent with the interaction of the metal complex with several chemically distinct surface sites. The shifting of carbonyl bands to lower wavenumbers indicates electron transfer from the MgO to the iridium.

Table I. Infrared Spectral Data in the Carbonyl Stretching Region of MgO-Supported Species Formed from Adsorption of [Ir(CO)$_2$(acac)] or [Ir$_4$(CO)$_{12}$]

sample	ν_{CO}, cm^{-1}	ref
[Ir(CO)$_2$(acac)] in hexanes	2073 vs, 2054 vw, 1998 vs, 1968 vw, 1579 mw, 1562 mw, 1532 m	this work
sample prepared by adsorption of Ir(CO)$_2$(acac) on MgO$_{25}$ or MgO$_{400}$	2057 s, 1973 s, 1613 m, 1518 m	this work
extract of above sample with dilute HCl and [PPN][Cl] in THF	2042 s, 1957 s	this work
K[Ir(CO)$_2$Cl$_2$] in THF	2040 s, 1955 s	17
[Ir$_4$(CO)$_{12}$] in THF	2110 vw, 2067 vs, 2026 mw	this work
sample prepared by adsorption of [Ir$_4$(CO)$_{12}$] on MgO$_{400}$	2073 w, 2044 s, 2008 m, 1985 w, 1768 vw	this work
extract of above sample with [PPN][Cl] in CH$_3$OH	2030 sh, 2017 vs, 1990 m, 1980 sh, 1812 w	this work
[P(CH$_2$C$_6$H$_5$)(C$_6$H$_5$)$_3$][HIr$_4$(CO)$_{11}$] in THF	2015 vs, 2005 vs, 1985 s, 1970 s, 1800 m	15
[NEt$_4$][HIr$_4$(CO)$_{11}$] in THF	2067 w, 2030 s, 2017 vs, 1986 m, 1978 m, 1832 m, 1806 m	20
Na[HIr$_4$(CO)$_{11}$] in diethyl ether	2072 w, 2039 s, 2020 vs, 1990 m, 1984 m, 1730 m, 1830 w	20

The surface species could not be extracted from either of the MgO surfaces with THF alone, as shown by the result that the infrared spectrum of the THF solution did not have any carbonyl bands corresponding to [Ir(CO)$_2$(acac)]. However, when dilute HCl and [PPN][Cl] in THF was added to the slurry, the solution became light yellow with an infrared spectrum (ν_{CO}: 2042 s, 1957 s cm^{-1}) (Figure 1c) similar to that of [Ir(CO)$_2$Cl$_2$]$^-$ [17] (Table I). Since [Ir(CO)$_2$(acac)] is soluble in THF, any physisorbed [Ir(CO)$_2$(acac)] on MgO would have been extracted by THF. These results indicate that [Ir(CO)$_2$(acac)] had been chemisorbed on the MgO surfaces.

To test for the possibility of removal of acac ligands from [Ir(CO)$_2$(acac)] as a result of chemisorption on MgO, an experiment was carried out to show whether the acac ligand of [Ir(CO)$_2$(acac)] could be displaced by anionic ligands in solution. When [Ir(CO)$_2$(acac)] was dissolved in dry THF, the solution became dark brown with an infrared spectrum having strong ν_{CO} bands at 2069 and 1991 cm^{-1} and bands at 1562 and 1534 cm^{-1} that could be Ir–O stretching bands (Figure 2a). When [PPN][Cl] was added to the THF solution of [Ir(CO)$_2$(acac)] and stirred under N$_2$ for 3 h, the solution became orange-yellow with an infrared spectrum including bands at 2069 w, 2042 s, 1991 w, and 1957 s cm^{-1} (Figure 2b). The bands at 2069 and 1991 cm^{-1} are indicative of unreacted [Ir(CO)$_2$(acac)]. The two strong bands at 2042 and 1957 cm^{-1} are assigned to [Ir(CO)$_2$Cl$_2$]$^-$.[17] Stirring of the solution for a longer time (>6 h) under N$_2$ converted all the [Ir(CO)$_2$(acac)] to [Ir(CO)$_2$Cl$_2$]$^-$, as indicated by the infrared spectra (not shown). The bands at 1562 and 1534 cm^{-1} diminished in intensity. The acac ligand, initially bonded to iridium, as indicated by bands at 1562 and 1534 cm^{-1}, is suggested to have reacted with the counterion to form [PPN][acac].

Chemisorption of [Ir$_4$(CO)$_{12}$] on MgO$_{400}$. When [Ir$_4$(CO)$_{12}$] was slurried with MgO$_{400}$ in hexanes under N$_2$ for 12 h, the white MgO powder became light yellow. The infrared spectrum of the resultant solid has absorption bands at 2073 sh, 2044 s, 2008 m, 1985 sh, and 1768 vw cm^{-1} (Figure 3b). A comparison with the spectrum of [Ir$_4$(CO)$_{12}$] in THF (Figure 3a) shows that adsorption of [Ir$_4$(CO)$_{12}$] on MgO$_{400}$ led to broadening and a shift of the terminal carbonyl bands to lower wavenumbers and to the appearance of a bridging carbonyl band. Extraction of the surface species with [PPN][Cl]-saturated methanol gave a yellow solution with an infrared spectrum similar to that of [HIr$_4$(CO)$_{11}$]$^-$ [15] (ν_{CO}: 2030 sh, 2017 vs, 1990 m, 1980 sh, 1812 w cm^{-1}) (Figure 3c). This result indicates that [Ir$_4$(CO)$_{12}$] was chemisorbed on the

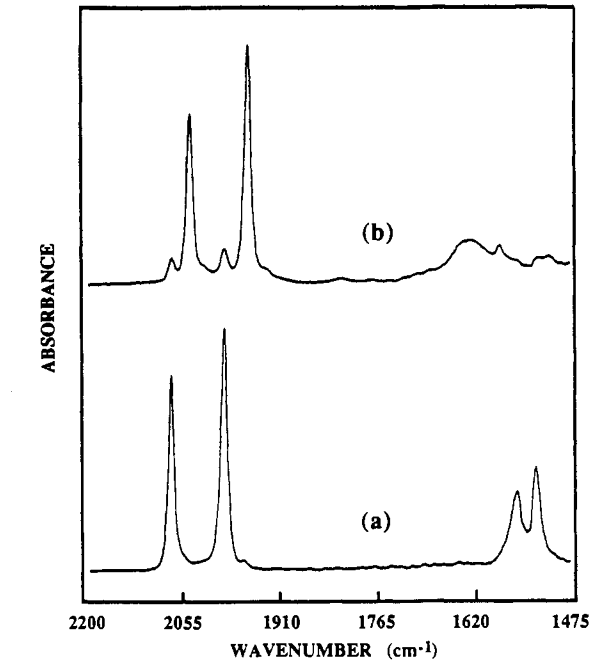


Figure 2. Infrared spectra of (a) [$Ir(CO)_2(acac)$] dissolved in THF and (b) solution formed by bringing the sample of spectrum a in contact with [PPN][Cl] in THF under N_2 and stirring for 3 h.

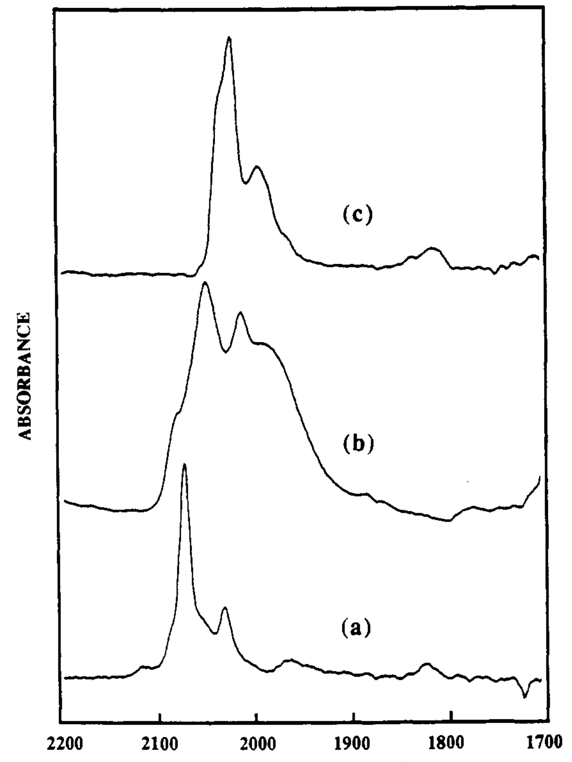


Figure 3. Infrared spectra of [$Ir_4(CO)_{12}$] and the sample prepared by adsorption of [$Ir_4(CO)_{12}$] on MgO_{400}: (a) spectrum of [$Ir_4(CO)_{12}$] in THF; (b) spectrum of fresh sample prepared by adsorption of [$Ir_4(CO)_{12}$] on MgO_{400}; (c) solution spectrum of the species extracted with [PPN][Cl] in methanol.

MgO surface to yield surface-bound [$HIr_4(CO)_{11}$]$^-$. This conclusion verifies earlier results; the same surface species has been identified by infrared and extended X-ray absorption fine structure spectroscopies and by extraction of the anion into solution and identification by infrared spectroscopy.[13]

The solution infrared spectrum of [PPN][$HIr_4(CO)_{11}$] in methanol (Figure 3c) is different from the spectrum of [$HIr_4(CO)_{11}$]$^-$ on the MgO surface (Figure 3b). The differences are

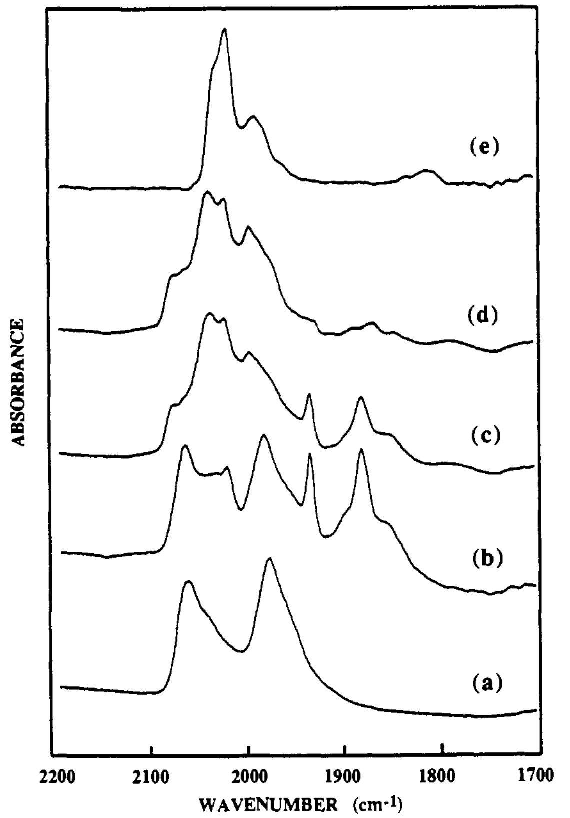


Figure 4. Infrared spectra of the sample prepared by adsorption of [$Ir(CO)_2(acac)$] on MgO_{400} followed by treatment in CO at 1 atm and room temperature: (a) freshly supported sample; (b) sample a after 5 min; (c) sample a after 2 h; (d) sample a after 8 h; (e) extract solution formed by treating the sample of spectrum d with [PPN][Cl] in methanol.

the shift of about 27 cm^{-1} of the terminal carbonyl bands to higher energies and the shift of about 44 cm^{-1} of the bridging carbonyl band to lower energy. These shifts[20a,b] are consistent with effects of ion pairing to the Mg cations of the surface (Table I), as discussed below.

Room-Temperature Synthesis of Iridium Carbonyl Clusters on MgO Treated at Different Temperatures. The nature of the iridium carbonyl clusters formed from iridium complexes on MgO depends on the composition of the MgO surface, which is easily varied by the temperature of treatment.[5] Details are reported in the following six sections.

Formation of [$HIr_4(CO)_{11}$]$^-$ on MgO_{400} by Reductive Carbonylation of [$Ir(CO)_2(acac)$]. The carbonylation of surface species formed from [$Ir(CO)_2(acac)$] on MgO_{400} (Figure 4a) was monitored by infrared spectroscopy with the solid in the presence of flowing CO at 1 atm. A few minutes after exposure of the sample to CO at room temperature, new infrared bands appeared at 2019 w, 1931 m, and 1878 m (ν_{CO}, cm^{-1}) and increased proportionately in intensity, whereas the bands at 2057 and 1973 cm^{-1} decreased in intensity (Figure 4b). The simultaneous appearance of the three carbonyl bands suggests that only one new species, designated **1**, was produced on the MgO surface. As CO continued to flow through the sample at room temperature, new bands appeared at 2072, 2038, 2017, and 1995 cm^{-1}, and the bands at 2057, 1973, 1931, and 1878 cm^{-1} decreased in intensity (Figure 4c). This result indicates that supported [$Ir(CO)_2(acac)$] (ν_{CO}: 2057 and 1973 cm^{-1}) reacted with **1** (ν_{CO}: 2019, 1931, 1878 cm^{-1}) under CO to produce a new surface species with bands at 2038, 2017, and 1995

---

(20) (a) Vandenberg, D. M. Ph.D. Dissertation, University of California, Santa Barbara, 1986. (b) Vandenberg, D. M.; Choy, T. C.; Ford, P. C. *J. Organomet. Chem.* **1989**, *366*, 257. (c) Vandenberg, D. M.; Friedman, A. E.; Ford, P. C. *Inorg. Chem.* **1988**, *27*, 594. (d) Vandenberg, D. M.; Suzuki, T. M.; Ford, P. C. *J. Organomet. Chem.* **1984**, *272*, 309.

Table II. Infrared Spectral Data in the Carbonyl Stretching Region of MgO-Supported Species Formed from Carbonylation of $[Ir(CO)_2(acac)]$ or $[Ir_4(CO)_{12}]$ at 1 atm and 25 °C and Related Molecular Clusters

sample	ν_{CO}, cm^{-1}	ref
$[Ir(CO)_2(acac)]$ adsorbed on MgO_{400}, followed by treatment in CO at 25 °C for >8 h	2072 sh, 2038 s, 2017 sh, 1995 m, 1975 sh, 1786 vw	this work
extract of above sample with [PPN][Cl] in CH_3OH	2030 sh, 2017 vs, 1990 m, 1980 sh, 1812 w	this work
$[Ir(CO)_2(acac)]$ adsorbed on MgO_{25}, followed by treatment in CO at 25 °C for >8 h	2072 sh, 2038 sh, 2021 s, 1995 m, 1975 sh, 1830 w	this work
extract of above sample with [PPN][Cl] in THF	2074 vw, 2042 m, 2030 sh, 2017 vs, 1985 m, 1975 m, 1820 mw	this work
$[PPh_4]_2[Ir_8(CO)_{22}]$ in THF	2070 vw, 2040 m, 2020 vs, 1970 m, 1820 m	16a
$[Na]_2[Ir_8(CO)_{22}]$ in THF	2067 w, 2023 s, 2017 vs, 1985 m, 1820 w	16b
$[Ir_4(CO)_{12}]$ adsorbed on MgO_{400}, followed by treatment in water-saturated He at 25 °C for 15 min	2062 sh, 2035 sh, 2017 sh, 1986 s	this work
extract of above sample with [PPN][Cl] in THF	2015 m, 1980 s, 1961 m, 1922 sh, 1896 mw, 1820 w, 1770 m, 1760 sh	this work
$Na_2[Ir_6(CO)_{15}]$ in THF	1993 s, 1984 s, 1928 w, 1788 m, 1735 m	18
$[NMe_4]_2[Ir_6(CO)_{15}]$ in THF	2030 sh, 1970 s, 1910 sh, 1775 s, 1735 s	12
$K_2[Ir_4(CO)_{11}]$ in THF	1960 s, 1927 m, 1760 m	15
$Na[Ir(CO)_4]$ in THF	2000 w, 1898 s, 1868 sh	12

cm^{-1}. Continuation of the CO flow for 8 h led to an infrared spectrum with bands at 2072 sh, 2038 s, 2017 sh, 1995 m, 1975 sh, and 1786 vw cm^{-1} (Figure 4d). The carbonylated sample was then removed from the cell in the drybox; it was yellow. Extraction of the surface species with a dry methanol solution of [PPN][Cl] gave a yellow solution, and the infrared spectrum was immediately recorded (ν_{CO}: 2030 sh, 2017 vs, 1990 m, 1980 sh, 1812 w cm^{-1}) (Figure 4e). This spectrum is essentially the same as that of the sample formed by adsorption of $[Ir_4(CO)_{12}]$ on MgO_{400}; the adsorbed species is identified as $[HIr_4(CO)_{11}]^-$.

Formation of $[Ir(CO)_4]^-$ as an Intermediate Species on MgO_{400}. In an attempt to identify the surface species **1** formed during the short exposure of $[Ir(CO)_2(acac)]$ supported on MgO_{400} to CO at room temperature, a similar infrared experiment was carried out with a sample prepared from $[Ir(CO)_2(acac)]$ brought in contact with MgO_{400} (Figure 5a). After flow of CO over the sample at room temperature for 5 min, the spectrum (Figure 5b) was virtually identical to that of **1** (Figure 4b). The infrared cell was then purged with He for 15 min; there was no noticeable change in the spectrum. The wafer, unloaded immediately in the drybox, was beige. Extraction with [PPN][Cl] in THF gave a light yellow solution with an infrared spectrum, obtained immediately after the extraction, having bands at 2042 s, 1957 s, and 1892 s cm^{-1} (Figure 5c). The bands at 2042 and 1957 cm^{-1} are attributed to $[Ir(CO)_2Cl_2]^-$, and that at 1892 cm^{-1} to $[Ir(CO)_4]^-$, which, in THF solution, is characterized by a ν_{CO} band at 1898 cm^{-1} [12,13] (Table II).

A sample of $[Ir(CO)_2(acac)]$ adsorbed on MgO_{400} was placed in a Schlenk flask, and a stream of CO at 1 atm flowed over it at room temperature. After 2 h, the light yellow sample was transferred to an infrared cell in the drybox. The ν_{CO} spectrum

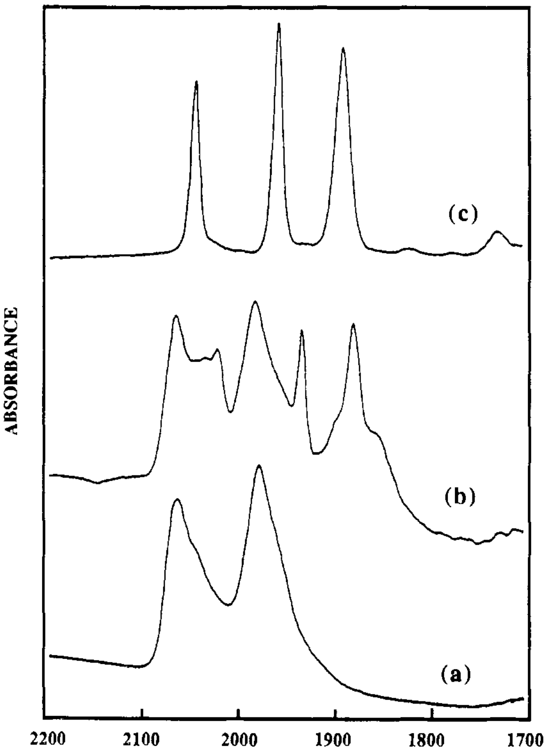


Figure 5. Infrared spectra of the sample prepared by adsorption of $[Ir(CO)_2(acac)]$ on MgO_{400} followed by short exposure to 1 atm of CO at room temperature: (a) freshly prepared supported sample; (b) sample after exposure to CO for 5 min; (c) extract solution formed by bringing the sample of spectrum b in contact with [PPN][Cl] in THF.

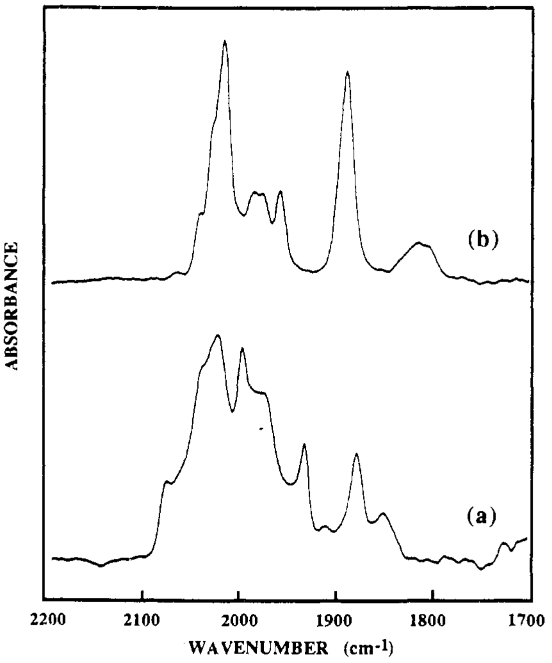


Figure 6. Infrared spectra of the sample prepared by adsorption of $[Ir(CO)_2(acac)]$ on MgO_{400} followed by exposure to CO at 1 atm and room temperature: (a) sample after exposure to CO for 2 h; (b) extract solution formed by bringing the sample of spectrum a in contact with [PPN][Cl] in THF.

(2072 sh, 2060 w, 2038 sh, 2020 s, 1995 m, 1973 sh, 1931 mw, 1878 mw cm^{-1}) is shown in Figure 6a. The bands at 2060 and 1973 cm^{-1} are attributed to $[Ir(CO)_2(acac)]$; those at 2072, 2038, 2020, and 1995 cm^{-1} to $[HIr_4(CO)_{11}]^-$; and those at 1931 and 1878 cm^{-1} to $[Ir(CO)_4]^-$ on the MgO surface. Extraction of the surface species with a THF solution of [PPN][Cl] gave a yellow solution, and the infrared spectrum was immediately recorded (ν_{CO}:

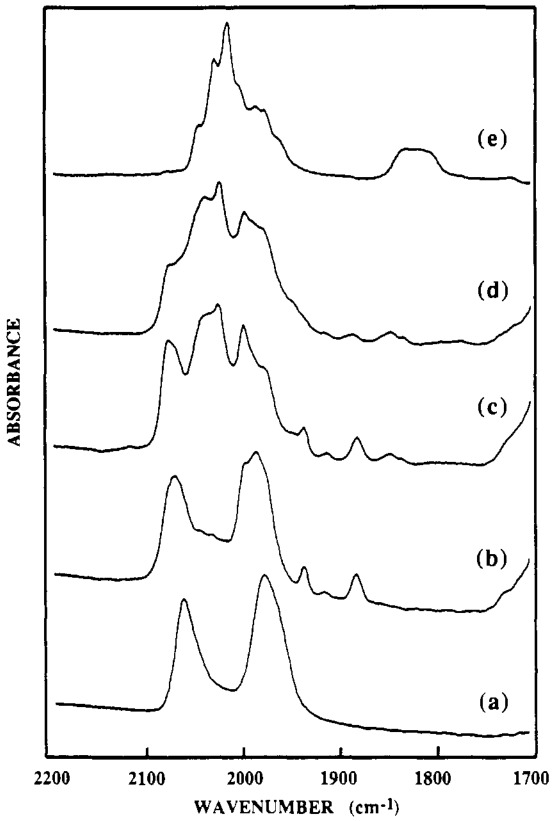


Figure 7. Infrared spectra of the sample prepared by adsorption of [Ir(CO)$_2$(acac)] on MgO$_{25}$ followed by CO at 1 atm and room temperature: (a) freshly supported sample; (b) sample a after 10 min; (c) sample a after 2 h; (d) sample a after 8 h; (e) extract solution formed by bringing the sample of spectrum d in contact with [PPN][Cl] in THF (without light exposure).

2042 w, 2027 sh, 2017 vs, 1984 mw, 1975 mw, 1957 mw, 1892 s, 1815 w cm^{-1}) (Figure 6b). The bands at 2042 and 1957 cm^{-1} are attributed to [Ir(CO)$_2$Cl$_2$]$^-$, those at 2027, 2017, 1984, 1975, and 1815 cm^{-1} are attributed to [HIr$_4$(CO)$_{11}$]$^-$, and that at 1892 cm^{-1} is attributed to [Ir(CO)$_4$]$^-$. The identification of these species suggests that [Ir(CO)$_4$]$^-$ is an intermediate in the carbonylation of the MgO$_{400}$-supported [Ir(CO)$_2$(acac)] to give surface-bound [HIr$_4$(CO)$_{11}$]$^-$.

One-Step Synthesis of [HIr$_4$(CO)$_{11}$]$^-$ on MgO$_{400}$. The abovementioned synthesis of [HIr$_4$(CO)$_{11}$]$^-$ on MgO$_{400}$ involves the adsorption of [Ir(CO)$_2$(acac)] on MgO$_{400}$ and then the reductive carbonylation of the surface species. A simpler synthesis has also been effected, as follows: [Ir(CO)$_2$(acac)] and MgO$_{400}$ powder were loaded into a Schlenk flask in the drybox, and a solution of CO-saturated, freshly distilled hexanes was canulated into the flask. The slurry was stirred in the presence of flowing CO at 25 °C. After 8 h, the slurry became yellow. The mixture was then filtered under CO and dried in vacuo for 2 h. The infrared spectrum of the resultant yellow solid (ν_{CO}: 2072 w, 2040 s, 2020 m, 1995 m, 1780 w cm^{-1}) is similar to that of Figure 4d, suggesting the formation of [HIr$_4$(CO)$_{11}$]$^-$ on MgO$_{400}$. The extraction of the surface species with [PPN][Cl] in methanol gave a yellow solution, and the infrared spectrum (ν_{CO}: 2030 sh, 2018 vs, 1990 m, 1980 m, 1815 w cm^{-1}) confirms the formation of [HIr$_4$(CO)$_{11}$]$^-$.

Formation of [Ir$_8$(CO)$_{22}$]$^{2-}$ on MgO$_{25}$ by Reductive Carbonylation of [Ir(CO)$_2$(acac)]. An infrared experiment was performed to investigate the carbonylation of species formed from [Ir(CO)$_2$(acac)] on MgO$_{25}$ (Figure 7a) in the presence of flowing CO at 1 atm. Within 10 min of exposure of the sample to CO, the spectrum showed the simultaneous appearance of carbonyl bands at 2019 w, 1931 m, and 1878 m cm^{-1} and a decrease in the intensities of the bands at 2056 and 1972 cm^{-1} (Figure 7b). This result is similar to that observed in the carbonylation of [Ir(CO)$_2$(acac)] on MgO$_{400}$ and suggests the formation of [Ir(CO)$_4$]$^-$ on the surface. With continuing CO flow over the sample at room temperature, new bands appeared at 2072, 2038, 2021, and 1995 cm^{-1}, and the bands at 2056, 1972, 1931, and 1878 cm^{-1} decreased in intensity (Figure 7c). This result suggests that supported [Ir(CO)$_2$(acac)] (ν_{CO}: 2056, 1972 cm^{-1}) reacts with [Ir(CO)$_4$]$^-$ on the surface (ν_{CO}: 2019, 1931, 1878 cm^{-1}) in the presence of CO to give a new surface species with infrared bands at 2072, 2038, 2021, and 1995 cm^{-1}. This reaction is similar to the carbonylation of [Ir(CO)$_2$(acac)] on MgO$_{400}$. Continuation of the CO flow for 8 h led to an infrared spectrum with bands at 2072 sh, 2038 sh, 2021 s, 1995 m, 1975 sh, and 1830 w cm^{-1} (Figure 7d). The carbonylated sample was removed from the cell in the drybox; it was reddish pink. Extraction with [PPN][Cl] in THF gave a red solution, and the spectrum was recorded immediately (ν_{CO}: 2074 vs, 2042 m, 2027 sh, 2015 vs, 1985 m, 1975 m, 1820 mw cm^{-1}) (Figure 7e). The spectrum is virtually identical to that of [Ir$_8$(CO)$_{22}$]$^{2-}$.[16]

The solution was allowed to stand in the drybox, and the color changed from red to yellow in 15 min. However, the infrared spectrum of the yellow solution was virtually identical to that of the original red solution. This color change of the THF solution of [Ir$_8$(CO)$_{22}$]$^{2-}$ has been observed by Vandenberg et al.[20a,c] and explained as the result of photolysis of [Ir$_8$(CO)$_{22}$]$^{2-}$ to give [HIr$_4$(CO)$_{11}$]$^-$ in the THF solution. The inference was confirmed by experiments done with samples in the dark.

One-Step Synthesis of [Ir$_8$(CO)$_{22}$]$^{2-}$ from [Ir(CO)$_2$(acac)] on MgO$_{25}$. The foregoing synthesis of [Ir$_8$(CO)$_{22}$]$^{2-}$ on MgO$_{25}$ involves the adsorption of [Ir(CO)$_2$(acac)] on MgO$_{25}$ and then the reductive carbonylation of the supported organometallic species. A simpler synthesis was done as follows: [Ir(CO)$_2$(acac)] and MgO$_{25}$ powder were loaded into a Schlenk flask in the drybox, and a solution of CO-saturated nondistilled hexanes was canulated into the flask. The slurry was stirred under flowing CO at 25 °C, and after 8 h it became reddish pink. The mixture was filtered under CO and dried in vacuo for 2 h. The infrared spectrum of the reddish-pink solid (ν_{CO}: 2072 sh, 2038 sh, 2020 s, 1995 m, 1975 sh, 1830 w cm^{-1}) is similar to that of Figure 7e, suggesting the formation of [Ir$_8$(CO)$_{22}$]$^{2-}$ on MgO$_{25}$. Extraction of the surface species with [PPN][Cl] in THF gave a red solution, and the infrared spectrum (ν_{CO}: 2074 vw, 2042 sh, 2030 sh, 2017 vs, 1985 m, 1975 m, 1820 mw cm^{-1}) confirms the formation of [Ir$_8$(CO)$_{22}$]$^{2-}$.

Formation of [Ir$_6$(CO)$_{15}$]$^{2-}$ on MgO$_{400}$ Dosed with Water. The reactivity of MgO$_{400}$-supported [Ir$_4$(CO)$_{12}$], which, as stated above, is inferred to give adsorbed [HIr$_4$(CO)$_{11}$]$^-$, was monitored by infrared spectroscopy with the solid in the presence of flowing water-saturated He at 1 atm. After exposure for 5 min, the infrared spectrum of the sample changed from 2072 w, 2042 s, 2010 m, and 1985 sh cm^{-1} to 2062 sh, 2035 sh, 2017 sh, and 1986 s cm^{-1} (Figure 8a,b). The spectrum did not change significantly after treatment for an additional 1 h. This observation suggests the relatively rapid transformation of surface-bound [HIr$_4$(CO)$_{11}$]$^-$ in the presence of water. In an attempt to extract and identify the resultant surface species, 1 g of the MgO$_{400}$-supported sample prepared from [Ir$_4$(CO)$_{12}$] was placed in a flask with about 100 mg of [PPN][Cl]. A stream of water-saturated He flowed over the sample at room temperature. Within 10 min, the color changed from the beige characteristic of the freshly supported species to light brown. The flow was continued for an additional 50 min to ensure complete reaction. Undried THF was then added to the flask. Extraction of the surface species yielded a reddish-brown solution with a spectrum (Figure 8c) (ν_{CO}: 2015 m, 1980 s, 1961 m, 1922 sh, 1896 mw, 1820 w, 1770 m, 1760 sh cm^{-1}) attributed to a mixture of [Ir$_6$(CO)$_{15}$]$^{2-}$ [12,18,19] (ν_{CO}: 1980, 1770 cm^{-1}), [HIr$_4$(CO)$_{11}$]$^-$ (ν_{CO}: 2015, 1980, 1820 cm^{-1}), [Ir$_4$(CO)$_{11}$]$^{2-}$ [15] (ν_{CO}: 1961, 1922, 1760 cm^{-1}), and [Ir(CO)$_4$]$^-$ (ν_{CO}: 1896 cm^{-1}) (Table II). The hexairidium carbonyl cluster was estimated from the spectra to be roughly 70% of the metal carbonyl species. The predominance of [Ir$_6$(CO)$_{15}$]$^{2-}$ in the extract solution is also confirmed by the extract color of reddish brown, which is exactly the color of hexairidium carbonyl anion in THF.[12,18,19] The presence of [Ir(CO)$_4$]$^-$ suggests that the decomposition of the higher-nuclearity species took place in solu-

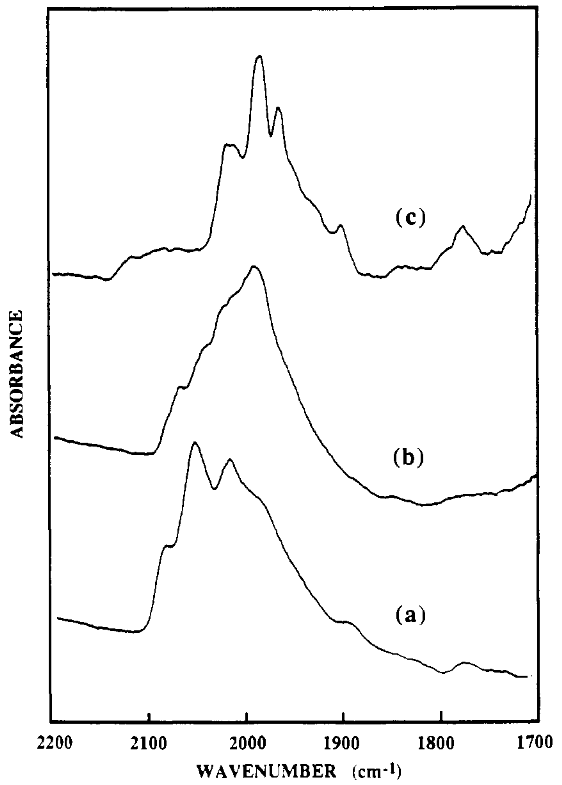


Figure 8. Infrared spectra of the sample prepared by adsorption of $[Ir_4(CO)_{12}]$ on MgO_{400} followed by exposure to water-saturated He flowing at room temperature: (a) freshly adsorbed $[Ir_4(CO)_{12}]$ on MgO_{400}; (b) sample a after 5 min of exposure to water-saturated He; (c) extract solution formed by bringing the sample of spectrum b in contact with [PPN][Cl] in THF.

tion.[13] Indeed, the formation of $[Ir(CO)_4]^-$ has been shown to occur in the presence of Na in THF.[12]

High-Temperature Formation of $[Ir_6(CO)_{15}]^{2-}$ on MgO. Reductive carbonylation of supported iridium species on MgO was monitored by infrared spectroscopy with the samples in flowing CO at 1 atm. After the formation of new surface species, samples were unloaded in the drybox for notation of color and extraction of surface species. The infrared results are summarized in Table III. Details are given in the following three sections.

Carbonylation of $[Ir(CO)_2(acac)]$ Supported on MgO_{25}. As shown above, treatment of $[Ir(CO)_2(acac)]$ on MgO_{25} in flowing CO at 25 °C for 8 h gave surface-bound $[Ir_8(CO)_{22}]^{2-}$. The infrared spectrum was maintained after treatment of the sample at 75 °C for 2 h, and the wafer was still reddish pink; this result indicates the stability of MgO-supported $[Ir_8(CO)_{22}]^{2-}$ in CO. However, when the sample was treated in CO at 200 °C for 2 h, the infrared spectrum showed bands at 2020 sh, 2002 s, 1990 s, and 1730 vw cm^{-1}. The sample unloaded in the drybox was light brown; extraction with [PPN][Cl] in THF gave a reddish-brown solution, and the immediately recorded infrared spectrum (ν_{CO}: 2020 sh, 1980 s, 1910 vw, 1770 mw cm^{-1}) is virtually identical to that of $[Ir_6(CO)_{15}]^{2-}$.[12,19] Comparison of the infrared spectra of $[Ir_6(CO)_{15}]^{2-}$ on MgO and $[Ir_6(CO)_{15}]^{2-}$ in THF solution shows a shift of the terminal carbonyl bands of the supported cluster of about 22 cm^{-1} to higher energy and a shift of the bridging carbonyl band of about 40 cm^{-1} to lower energy. The shifts are explained by the ion pairing of $[Ir_6(CO)_{15}]^{2-}$ with the Mg^{2+} ions of the surface, similar to that observed for $Na_2[Ir_6(CO)_{15}]$ in solution.[18,19a]

Carbonylation of $[Ir(CO)_2(acac)]$ Supported on MgO_{400}. Following treatment of $[Ir(CO)_2(acac)]$ on MgO_{400} in flowing CO at 25 °C for 8 h, the infrared spectrum showed bands characteristic of $[HIr_4(CO)_{11}]^-$ (ν_{CO}: 2072 w, 2038 s, 2020 sh, 1995 m, 1975 sh, 1786 w cm^{-1}); the sample unloaded in the drybox was light yellow. When the temperature was increased to 75 °C and held for 2 h, the infrared bands were slightly shifted from the positions found for the sample formed at 25 °C (ν_{CO}: 2072 sh, 2034 sh, 2018 s, 1990 m, 1830 vw cm^{-1}), and the sample unloaded in the drybox was reddish pink, indicating the formation of $[Ir_8(CO)_{22}]^{2-}$. This result indicates that the tetrairidium cluster anions dimerized to form the more stable $[Ir_8(CO)_{22}]^{2-}$, in which two tetrahedral Ir_4 clusters are connected by an Ir–Ir bond.

Table III. Infrared Spectral Data in the Carbonyl Stretching Region of MgO-Supported Species Formed from Carbonylation of $[Ir(CO)_2(acac)]$ or $[Ir_4(CO)_{12}]$ at 1 atm and Different Temperatures

sample	ν_{CO}, cm^{-1}
$[Ir(CO)_2(acac)]$ adsorbed on MgO_{25}, followed by treatment in CO at 25 °C for 8 h (1A)	2072 sh, 2038 sh, 2021 s, 1995 m, 1975 sh, 1830 w
sample 1A, followed by treatment in CO at 75 °C for 2 h (1B)	2034 sh, 2023 s, 1994 m, 1975 m, 1825 vw
sample 1B, followed by treatment in CO at 200 °C for 2 h (1C)	2020 sh, 2002 s, 1990 s, 1730 vw
extract of sample 1C with [PPN][Cl]	2020 sh, 1980 s, 1910 w, 1770 mw
$[Ir(CO)_2(acac)]$ adsorbed on MgO_{400}, followed by treatment in CO at 25 °C for 8 h (2A)	2072 sh, 2038 s, 2020 sh, 1995 m, 1975 sh, 1786 w
sample 2A, followed by treatment in CO at 75 °C for 2 h (2B)	2072 sh, 2034 sh, 2018 s, 1990 m, 1830 vw
sample 2B, followed by treatment in CO at 200 °C for 2 h (2C)	2020 sh, 1995 s, 1735 vw
extract of sample 2C with [PPN][Cl]	2020 vw, 1980 s, 1910 w, 1766 w
$[Ir_4(CO)_{12}]$ adsorbed on MgO_{400}, followed by treatment in CO at 75 °C for 2 h (3A)	2072 w, 2040 w, 2020 s, 1990 m, 1825 w
sample 3A, followed by treatment in CO at 200 °C for 2 h (3B)	2020 w, 2000 s, 1730 vw
extract of sample 3B with [PPN][Cl]	2025 w, 1982 s, 1915 w, 1771 mw

The sample was then treated at higher temperatures, and bands characteristic of $[Ir_6(CO)_{15}]^{2-}$ slowly appeared at about 200 °C. After treatment of the sample at 200 °C for 2 h, the infrared spectrum showed bands at 2020 sh, 1995 s, and 1735 vw cm^{-1}, indicating the formation of surface-bound $[Ir_6(CO)_{15}]^{2-}$. Extraction of the resultant light-brown solid with [PPN][Cl] in THF gave a reddish-brown solution, and the infrared spectrum (ν_{CO}: 2020 vw, 1980 s, 1910 vw, 1766 w cm^{-1}) is indistinguishable from that of $[Ir_6(CO)_{15}]^{2-}$.

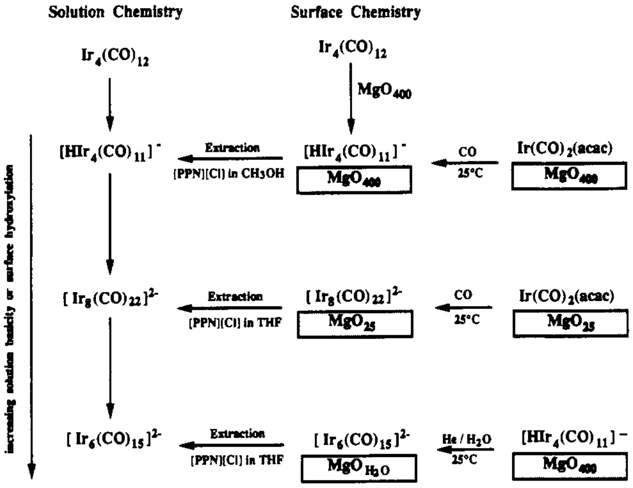
Carbonylation of $[Ir_4(CO)_{12}]$ Supported on MgO_{400}. When the fresh sample was exposed to CO at room temperature, the infrared spectrum began to change. As the temperature was increased at a rate of approximately 5 °C/min to 75 °C, the spectrum became more distinct. After exposure to CO at 75 °C for 2 h, the spectrum included bands at 2072 w, 2040 w, 2020 s, 1990 m, and 1825 w cm^{-1}, which agree well with the spectrum of $[Ir_8(CO)_{22}]^{2-}$. The sample unloaded in the drybox was reddish pink, confirming the formation of $[Ir_8(CO)_{22}]^{2-}$. When the treatment temperature was slowly increased to 200 °C, the infrared spectrum began to change again. After 2 h at this temperature, the spectrum included bands at 2020 w, 2000 s, and 1730 vw cm^{-1}. This spectrum is similar to that of the carbonylated sample formed from MgO-supported $[Ir(CO)_2(acac)]$ in CO at 200 °C, indicating the formation of surface-bound $[Ir_6(CO)_{15}]^{2-}$. Extraction of the surface species with [PPN][Cl] in THF yields a reddish-brown solution having an infrared spectrum (ν_{CO}: 2025 w, 1982 s, 1915 w, 1771 mw cm^{-1}) similar to that of $[Ir_6(CO)_{15}]^{2-}$.

All these results showing the formation of $[Ir_6(CO)_{15}]^{2-}$ on MgO are consistent with results of Maloney et al.,[18] who prepared it from $[Ir_4(CO)_{12}]$ on MgO.

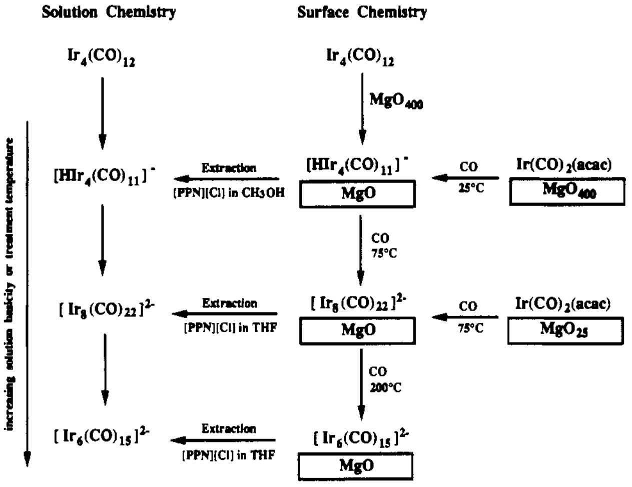
Discussion

The reaction of $[Ir_4(CO)_{12}]$ with K_2CO_3 in methanol, KOH in methanol, or Na in THF (all under CO) was reported by Angoletta et al.[12] to yield a series of iridium carbonyl anions with metal frameworks having 4, 6, or 8 Ir atoms. The reaction of $[Ir_4(CO)_{12}]$ with K_2CO_3 in methanol gives $[HIr_4(CO)_{11}]^-$; the

Scheme I. Reactions of Iridium Carbonyls in Basic Solutions and on MgO with Various Degrees of Hydration



Scheme II. Reactions of Iridium Carbonyls in Basic Solutions and Molecular Condensation of Iridium Carbonyls on MgO



reaction of $[Ir_4(CO)_{12}]$ with KOH in methanol gives $[Ir_8(CO)_{22}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$; and the reaction of $[Ir_4(CO)_{12}]$ with Na in THF gives mainly $[Ir_6(CO)_{15}]^{2-}$ and $[Ir(CO)_4]^-$.

Under all these conditions, the initial product is $[HIr_4(CO)_{11}]^-$. With the weak base K_2CO_3, the reaction stops at this stage. With the stronger base KOH, the reaction continues, to produce $[Ir_8(CO)_{22}]^{2-}$ and then $[Ir_6(CO)_{15}]^{2-}$. With the very strong base Na, the reaction proceeds further to give $[Ir(CO)_4]^-$.

The basic surface of MgO is known to be an efficient medium for the synthesis of anionic metal carbonyl clusters.[5] The published results show that the chemistry of iridium carbonyl clusters on the surface of partially hydroxylated MgO parallels the chemistry of the iridium carbonyl clusters in basic solutions,[13,18] but the comparison is incomplete. The experiments reported here with a mononuclear iridium carbonyl precursor on MgO provide the basis for extending the comparison. This chemistry is summarized in Schemes I and II. It is discussed in the following paragraphs.

Chemisorption of $[Ir(CO)_2(acac)]$ on MgO. $[Ir(CO)_2(acac)]$ is a convenient precursor for iridium carbonyl clusters on surfaces because it is readily available and because the acac ligand (in contrast to chloride, for example) was not expected to affect substantially the properties of MgO, which are important in regulating the organometallic chemistry.[21] After contacting of the support under N_2 with a hexane solution of $[Ir(CO)_2(acac)]$, a fast chemisorption took place, as evidenced by the color change of the solution and shifting to lower energy of the carbonyl bands in the infrared spectrum. The primary surface reaction of $[Ir(CO)_2(acac)]$ with MgO is suggested to take place through the protolysis of the acac ligand by the hydroxyl groups of the MgO surface, with the concomitant formation of Mg–O–Ir linkages:

$$Ir(CO)_2(acac) + 2\{Mg{-}OH\} \rightarrow CH_3COCH_2COCH_3 + Ir(CO)_2\{OMg\}\{HOMg\} \quad (1)$$

(Here the braces denote species terminating the bulk solid; it is not known whether those bonded to Ir are {OMg} or {HOMg} or both.)

A similar interpretation has been suggested by Dossi et al.[21] for the formation of $Rh(CO)_2\{OMg\}_2$ as a result of adsorption of $[Rh(CO)_2(CH_3COO)]_2$ on MgO. The basic O^{2-} or OH^- sites of the MgO surface are expected to donate electron density to the Ir atoms, the net effect being a shift to lower energy of the stretching frequencies of the two carbonyl bands.

$[Ir(CO)_2(acac)]$ adsorbed on MgO could not be extracted with THF alone (although $[Ir(CO)_2(acac)]$ is soluble in THF). However, treatment of the sample with dilute HCl and [PPN][Cl] led to the extraction of $[Ir(CO)_2Cl_2]^-$. Similar chemistry has been observed for rhodium subcarbonyls on MgO,[21] and by analogy, the following transformation is suggested (but the statement is incomplete):

$$Ir(CO)_2\{OMg\}\{HOMg\} + 5HCl + [PPN][Cl] \rightarrow [PPN][Ir(CO)_2Cl_2] + 2MgCl_2 + 2H_2O \quad (2)$$

In summary, the inference that $[Ir(CO)_2(acac)]$ reacts with MgO by displacement of the acac ligand with surface ligands to form $Ir(CO)_2\{OMg\}\{HOMg\}$ is consistent with the following results: (1) the shift to lower energy of the carbonyl bands of the supported species formed from $[Ir(CO)_2(acac)]$, (2) the lack of extraction of $[Ir(CO)_2(acac)]$ from the MgO surface with THF alone, (3) the extraction of $[Ir(CO)_2Cl_2]^-$ with HCl and [PPN][Cl] in THF, and (4) the result that the acac ligand could be displaced by Cl^- ligands in solution to form $[Ir(CO)_2Cl_2]^-$. The displaced acac ligand is expected to have been adsorbed on the MgO, as indicated by bands at 1613 and 1518 cm^{-1} (Figure 1b), but it is not known how it is bonded to the MgO surface.

Chemisorption of $[Ir_4(CO)_{12}]$ on MgO. Chemisorption of $[Ir_4(CO)_{12}]$ on MgO has been shown to yield a surface species that could be extracted with [PPN][Cl]-saturated methanol to give $[HIr_4(CO)_{11}]^-$. The formation of this surface anion is suggested to occur by nucleophilic attack of a surface hydroxyl group on a polarized CO ligand bonded to Ir:

$$Ir_4(CO)_{12} + OH^- \rightarrow [Ir_4(CO)_{11}(COOH)]^- \quad (3)$$

Similar chemistry has been observed in solution when $[Ir_4(CO)_{12}]$ was treated with base in an alcoholic medium, as in the synthesis of the $[HIr_4(CO)_{11}]^-$.[22] The formation of the surface hydrido species is then suggested to occur as follows:

$$[Ir_4(CO)_{11}(COOH)]^- + OH^- \rightarrow [HIr_4(CO)_{11}]^- + HCO_3^- \quad (4)$$

This hydrido carbonyl anion could be simply extracted from the MgO surface with [PPN][Cl] in methanol solution. When the extraction of the surface species was instead carried out with a [PPN][Cl]-saturated THF solution, $[HIr_4(CO)_{11}]^-$, $[Ir_4(CO)_{11}]^{2-}$, and $[Ir(CO)_4]^-$ were identified in the extract solution by infrared spectroscopy.[13] $[Ir(CO)_4]^-$ is suggested to have formed from further reaction of the anions in the extract solution, which is consistent with the reaction of $[Ir_4(CO)_{12}]$ with Na in THF.[12] This result shows the importance of the solvent in the extraction of the surface carbonyl species.

A comparison of the spectrum of $[HIr_4(CO)_{11}]^-$ on MgO (Figure 3b) with that of the extracted $[PPN][HIr_4(CO)_{11}]$ in methanol (Figure 3c) shows a shift of the major terminal carbonyl band of the supported species of about 27 cm^{-1} to higher frequency and a shift of the bridging carbonyl band of about 44 cm^{-1} to lower frequency. These shifts are consistent with ion pairing of [H-

---

(21) Dossi, C.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1989**, *359*, 105.

(22) Garlaschelli, L.; Martinengo, S.; Chini, P.; Canziani, F.; Bau, R. *J. Organomet. Chem.* **1981**, *213*, 379.

$Ir_4(CO)_{11}]^-$ with the Mg cations of the surface, similar to the ion pairing of $[HIr_4(CO)_{11}]^-$ with Na^+ in diethyl ether.[20a,b] The relatively large shift of the bridging carbonyl band characteristic of MgO-supported $[HIr_4(CO)_{11}]^-$ suggests a strong interaction of the bridging carbonyl oxygen of the anion with Mg cations of the surface. Such an interaction is expected to result in a net electron withdrawal from the cluster, decreasing the back-bonding to the terminal carbonyl ligands, strengthening the carbon–oxygen bonds, and shifting the terminal carbonyl bands to higher frequencies.

Formation of $[Ir(CO)_4]^-$. Reductive carbonylation of the MgO-supported species formed from $[Ir(CO)_2(acac)]$ leads to rapid formation of an intermediate species, suggested on the basis of the infrared spectra to be $[Ir(CO)_4]^-$. The formation of this mobile mononuclear anion may be initiated by nucleophilic attack of surface hydroxyl groups on iridium subcarbonyl species, as follows:[5]

$$Ir(CO)_2\{OMg\}\{HOMg\} + OH^- + 3CO \rightarrow [Ir(CO)_4]^- + 2\{HOMg\} + CO_2 \quad (5)$$

Basset et al.[23] similarly inferred that $[Rh(CO)_4]^-$ was the key intermediate (although they did not observe it) in the reductive carbonylation of $Rh(CO)_2\{OAl\}\{HOAl\}$ to form $[Rh_6(CO)_{16}]$ on the surface of γ-Al_2O_3. The process was suggested to be initiated by the nucleophilic attack of adsorbed water on $Rh(CO)_2\{OAl\}\{HOAl\}$, generating mobile mononuclear carbonyl rhodate ions.

The solution infrared spectrum of $[PPN][Ir(CO)_4]$ in THF, which has only a single carbonyl band at 1892 cm^{-1},[12,13] is quite different from the spectrum of $[Ir(CO)_4]^-$ on the MgO surface, which has carbonyl bands at 2019, 1931, and 1878 cm^{-1}. Similar results have also been observed for $[Co(CO)_4]^-$[24] and $[HOs(CO)_4]^-$[25] on the surface of MgO. The lower symmetry of the surface species in comparison with the anions in solution indicates the complexity of the interaction of the anions with the MgO surface. We postulate interactions of the carbonyl oxygens with Mg^{2+} ions at the surface, comparable to ion pairing in solutions; these effects are to be discussed separately.[26]

Formation of Anionic Iridium Carbonyl Clusters on MgO by Condensation Reactions. Formation of iridium carbonyl clusters was observed following the formation of $[Ir(CO)_4]^-$. The surface chemistry can be explained as a condensation reaction involving $[Ir(CO)_4]^-$. Two condensation processes could be suggested for the syntheses of these anionic iridium carbonyl clusters:

(a) Self-Condensation. Several studies[25,27] have been reported concerning the abilities of mononuclear anions of the type $[HM(CO)_4]^-$ (M = Fe, Ru, Os) to form cluster anions through self-condensation. Bricker et al.[27a] observed the condensation of $[HM(CO)_4]^-$ to give $[HM_3(CO)_{11}]^-$ in protic media and under conditions favoring the water gas shift reaction. Lamb et al.[26] observed that when $[HOs(CO)_4]^-$ was extracted from MgO, $[HOs(CO)_4]^-$ and $[HOs_3(CO)_{11}]^-$ could be identified in the extract solution. The formation of the triosmium carbonyl was explained by the condensation of the mononuclear anion. Hugues et al.[27c] observed the formation of $[HFe_3(CO)_{11}]^-$ from $[Fe(CO)_5]$ adsorbed on hydroxylated MgO. 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 $[HFe_3(CO)_{11}]^-$.[27] The sequence of steps might be generalized as follows, but the generalization is likely oversimplified:

$$[HM(CO)_4]^- + H_2O \rightarrow H_2M(CO)_4 + OH^- \quad (6A)$$

$$2H_2M(CO)_4 + [HM(CO)_4]^- \rightarrow [HM_3(CO)_{11}]^- + CO + 2H_2 \quad (6B)$$

$$M = Fe, Ru, Os$$

If the analogous chemistry pertains to iridium, $[Ir(CO)_4]^-$ would be expected to be protonated to form $[HIr(CO)_4]$ as an intermediate, which then would be expected to undergo rapid reaction with $[Ir(CO)_4]^-$ to form $[HIr_4(CO)_{11}]^-$ or $[Ir_8(CO)_{22}]^{2-}$, depending on the degree of surface hydration. Although $[HIr(CO)_4]$ has been reported to be formed by protonation of $[Ir(CO)_4]^-$ with anhydrous phosphoric acid under severe conditions (100 °C, 680 atm of CO[28]), the formation of this species on MgO under mild conditions has not been demonstrated.

(b) Redox Condensation. Alternatively, a redox condensation reaction involving $[Ir(CO)_4]^-$ can be suggested to explain the formation of iridium carbonyl clusters following the formation of $[Ir(CO)_4]^-$ from $Ir(CO)_2\{OMg\}\{HOMg\}$. The surface chemistry is presumably analogous to the redox condensation that leads to the formation of rhodium carbonyl cluster anions in basic solutions.[29] The facile nature of redox condensation reactions is attributed in part to the strong nucleophilicity of mononuclear carbonylate anions. The formation of $[HIr_4(CO)_{11}]^-$ on MgO_{400} and of $[Ir_8(CO)_{22}]^{2-}$ on MgO_{25} is therefore suggested to occur by nucleophilic attack of $[Ir(CO)_4]^-$ on $Ir(CO)_2\{OMg\}\{HOMg\}$ in the presence of CO, as follows:

$$[Ir(CO)_4]^- + 3Ir(CO)_2\{OMg\}\{HOMg\} + CO \rightarrow [HIr_4(CO)_{11}]^- + 4\{MgO\} + 2\{Mg\text{–}OH\} \quad (7)$$

$$2[Ir(CO)_4]^- + 6Ir(CO)_2\{OMg\}\{HOMg\} + 2CO \rightarrow [Ir_8(CO)_{22}]^{2-} + 6\{MgO\} + 6\{MgOH\} \quad (8)$$

Consistent with the suggestions, $[Ir(CO)_4]^-$ and $Ir(CO)_2\{OMg\}\{HOMg\}$ were both consumed in the reactions to produce $[HIr_4(CO)_{11}]^-$ and $[Ir_8(CO)_{22}]^{2-}$, as confirmed by the infrared results.

There is not yet sufficient evidence to distinguish between the suggested possibilities.

Influence of Surface Hydration. The selectivity of the cluster synthesis, whereby $[HIr_4(CO)_{11}]^-$ is formed on MgO_{400} and $[Ir_8(CO)_{22}]^{2-}$ is formed on MgO_{25}, both from the above reductive carbonylation of supported $[Ir(CO)_2(acac)]$, indicates the importance of the composition of the MgO surface. The chemistry of the formation of iridium carbonyl clusters on MgO parallels the chemistry of formation of these clusters in basic solution (Scheme I). $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, and $[Ir_6(CO)_{15}]^{2-}$ are formed, sequentially, from the reductive carbonylation of $[Ir_4(CO)_{12}]$ as the solution basicity is increased.[13] There is evidently a parallel between the solution and surface chemistry, as the base strength of MgO increases with increasing temperature of treatment.[5] In addition to the base strength of the MgO surface, the degree of surface hydroxylation or hydration of MgO is also expected to influence the surface chemistry,[5,25] since the OH groups or water are expected to play a role, and the present results show that water plays a role in the conversion of tetrairidium carbonyl anions to hexairidium cluster anions on MgO. Reduction of the tetrairidium carbonyl clusters might be accompanied by oxidation of CO, presumably by nucleophilic attack of water on coordinated CO groups to form CO_2, H_2, and protons (although

---

(23) (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.

(24) Homs, N.; Choplin, A.; de la Piscina, P. R.; Huang, L.; Garbowski, E.; Sanchez-Delgado, R.; Theolier, A.; Basset, J.-M. *Inorg. Chem.* **1988**, *27*, 4030.

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

(26) Kawi, S.; Gates, B. C. To be published.

(27) (a) Bricker, J. C.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1984**, *3*, 201. (b) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179. (c) Hugues, F.; Basset, J. M.; Ben Taarit, Y.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020.

(28) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249.

(29) (a) Chini, P. *J. Organomet. Chem.* **1990**, *200*, 37. (b) Fumagalli, A.; Koetzle, T.; Takusagawa, F.; Chini, P.; Martinengo, S.; Heaton, B. T. *J. Am. Chem. Soc.* **1980**, *102*, 1740. (c) Washecheck, D. M.; Wucherer, E. J.; Dahl, L. F.; Ceriotti, A.; Longoni, G.; Manassero, M.; Sansoni, M.; Chini, P. *J. Am. Chem. Soc.* **1979**, *101*, 6110. (d) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

experiments to detect these gaseous products have not been done):

$$3[HIr_4(CO)_{11}]^- + 4H_2O \rightarrow 2[Ir_6(CO)_{15}]^{2-} + H_3O^+ + 3CO_2 + 4H_2 \quad (9)$$

Production of CO_2 and H_2 in similar chemistry has been observed for iridium carbonyls in basic solution,[20a,d] but the identification of the iridium carbonyl products is not definitive. The nature of the iridium carbonyl clusters present on the surface may reflect a competition between reduction by water and the reverse oxidation associated with surface acidity. The effect of water in the reduction of metal carbonyl anions has also been shown for platinum carbonyl clusters.[8,30] We also recognize that since the mass balance information that would be required to determine exact stoichiometries is lacking, there are other plausible explanations for the surface chemistry. For example, instead of CO and OH^- providing the reducing equivalents, some of the iridium itself could end up as Ir^{3+} in what would be a surface-mediated disproportionation.

Formation of Iridium Carbonyl Clusters by Thermal Treatment. Formation of iridium carbonyl anions of various nuclearities on partially hydroxylated MgO is inferred to result from reductive carbonylation of the surface carbonyl species, with the products depending on the treatment temperature. $[Ir_8(CO)_{22}]^{2-}$ is formed under relatively mild conditions by dimerization of tetrahedral clusters; thus, the Ir cluster frame is not broken at this stage. Formation of $[Ir_6(CO)_{15}]^{2-}$ occurs at higher temperature, consistent with the possibility that $[Ir_8(CO)_{22}]^{2-}$ is an intermediate. Whether it is or not, the results imply that tetrahedral Ir frameworks were broken prior to the formation of the octahedral hexairidium framework of $[Ir_6(CO)_{15}]^{2-}$. The surface intermediates, which are unknown but likely mononuclear, must undergo facile reaction and transport on the MgO surface. The chemistry of the molecular condensation reactions of iridium carbonyls on the basic MgO surface thus closely parallels that of iridium carbonyls in basic solution (Scheme II).

The formation and stability of hexairidium clusters on the MgO surface at high temperature has been shown recently[18] and is not unexpected since $[Ir_6(CO)_{16}]$ was observed[11] when $[Ir(CO)_2(acac)]$ in the cages of NaY zeolite was treated with CO at temperatures between 125 and 200 °C. It is inferred[10,11] that the monovalent iridium dicarbonyl, $Ir(I)(CO)_2$, was transformed through $[Ir_4(CO)_{12}]$ to give the hexanuclear iridium carbonyl, and the hexanuclear species was more stable than the tetranuclear at the higher temperatures. Stability of this zeolite-supported hexairidium cluster under conditions of CO hydrogenation catalysis in flowing CO + H_2 (equimolar) at 20 atm and 275 °C has been demonstrated. Similarly, it has been found that NaX zeolite-supported $[Ir(CO)_2(acac)]$ could be carbonylated to form first $[HIr_4(CO)_{11}]^-$ and then form $[Ir_6(CO)_{15}]^{2-}$ in the zeolite cages.[31] The stability of $[Ir_6(CO)_{15}]^{2-}$ in the zeolite in flowing CO + H_2 (equimolar) at 20 atm and 225 °C was also demonstrated. The stability of hexairidium carbonyl clusters and the basic character of the MgO surface may also suggest that $[Ir_6(CO)_{15}]^{2-}$ on MgO may be stabilized under catalytic CO hydrogenation conditions and might be a catalyst precursor.[32]

Conclusions

The MgO surface is a medium for the reductive carbonylation of species formed from adsorbed $[Ir(CO)_2(acac)]$ under mild conditions to give $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, and $[Ir_6(CO)_{15}]^{2-}$. The supported anionic clusters are stabilized by the basic support in the presence of CO. The cluster formation is suggested to involve $[Ir(CO)_4]^-$ as a nucleophilic intermediate. $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, and $[Ir_6(CO)_{15}]^{2-}$ are formed sequentially. High yields of each can be obtained by choice of the conditions of synthesis. The anions can be extracted into solution by cation metathesis. The selectivity is controlled by the degree of surface hydroxylation of the MgO and the treatment temperature. There is a parallel between the organometallic surface chemistry and that occurring in basic solutions.

Acknowledgment. This work was supported by the National Science Foundation (Grant CTS 9012910).

---

(30) (a) Bhaduri, S.; Sharma, K. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1412. (b) Basu, A.; Bhaduri, S.; Sharma, K. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2315.

(31) Kawi, S.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1992**, 702.

(32) Kawi, S.; Gates, B. C. To be published.