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Surface organometallic chemistry: formation of $[Ir_8(CO)_{22}]^{2-}$ on magnesium oxide

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Abstract

A sample prepared by adsorption of $[Ir_4(CO)_{12}]$ on MgO powder was treated in CO at 100°C and 1 atm, whereupon the surface species was converted to $[Ir_8(CO)_{22}]^{2-}$ in high yield. The surface-bound cluster anion was characterized by infrared spectroscopy, and it could be extracted into solution by cation metathesis. The chemistry of the iridium carbonyls on the basic MgO surface in the absence of solvents is similar to the chemistry of the iridium carbonyls in basic solutions. The surface chemistry is an alternative method for preparation of $[Ir_8(CO)_{22}]^{2-}$.

Introduction

Surfaces are beginning to be used as media for synthesis of organometallic compounds [1–3]. The method appears to be most successful for reactions of metal carbonyl anions on basic surfaces; the synthesis of some osmium carbonyl cluster anions on surfaces is more efficient than the best known solution syntheses [1,2].

Iridium carbonyl anions are readily interconverted on the basic surface of MgO in the absence of solvents: $[Ir_4(CO)_{12}]$ is adsorbed to give $[HIr_4(CO)_{11}]^-$ with some $[Ir_4(CO)_{11}]^{2-}$ [4], and upon treatment in CO at 200°C and 1 atm, these clusters are converted in high yield to $[Ir_6(CO)_{15}]^{2-}$ [5]. These surface-bound anions have been identified by infrared and extended X-ray absorption fine structure (EXAFS) spectroscopy and by extraction into solution by cation metathesis [4,5].

Here we report the reaction of the MgO-supported tetrairidium carbonyl anions in CO to give $[Ir_8(CO)_{22}]^{2-}$.

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Experimental section

Samples were prepared in the virtual absence of air in a Vacuum Atmospheres glovebox and on a double manifold Schlenk line. $[Ir_4(CO)_{12}]$ (Strem) was used without further purification. Reagent grade hexanes were refluxed over sodium benzophenone ketyl. N_2 (99.999%, Matheson) flowed through Cu_2O and molecular sieve traps to remove traces of O_2 and moisture, respectively. CO (UHP grade, Matheson) flowed through an activated carbon trap heated to $> 200°C$ to remove traces of metal carbonyl contaminants and through a molecular sieve trap to remove moisture.

Partially dehydroxylated MgO (MCB powder) was heated in flowing O_2 to 400°C and held for 2 h. It was then evacuated (approx. 10^{-3} Torr), maintained at 400°C for 14 h, and cooled to room temperature under vacuum and unloaded in the glovebox. The surface area was about 75 m^2/g.

The supported iridium carbonyl was prepared by slurrying $[Ir_4(CO)_{12}]$ (0.029 g) in freshly distilled hexanes (50 mL) under N_2. The pretreated MgO (2.0 g, handled in the absence of air) was added to the slurry. The sample was stirred under N_2 for 4 h at room temperature and dried by evacuation for 14 h at room temperature.

The samples were transferred in the glovebox to a vacuum-tight cell [6] for treatment in flowing gases and measurement of diffuse reflectance Fourier transform infrared spectra (DRIFTS). Following treatment, samples were removed from the cell in the glovebox, and surface-bound organometallic species were extracted into solutions of [PPN][Cl] in THF; the extract solutions were characterized by transmission infrared spectroscopy.

Results

A sample that has been inferred [3–5] to consist predominantly of $[HIr_4(CO)_{11}]^-$ and $[Ir_4(CO)_{11}]^{2-}$ on MgO was prepared by adsorption of $[Ir_4(CO)_{12}]$. This sample was treated in CO at 1 atm and temperatures of 25–100°C. The sample was initially yellow/tan, and it took on a pinkish tinge when brought in contact with CO at 25°C; after treatment at 100°C, the sample was red.

The infrared spectrum of the sample that initially incorporated the adsorbed tetrairidium clusters, following treatment in CO at 100°C and 1 atm, is shown in Fig. 1(A). This sample was brought in contact with [PPN][Cl] in THF, and the organometallic species were extracted, as indicated by the orange color of the solution and the white color of the formerly red solid after the extraction. The infrared spectrum of the extract solution (ν(CO) = 2065w, 2029s, 2016vs, 1983m,br), 1892m, 1803w, Fig. 1(B)) is similar to that of $[Ir_8(CO)_{22}]^{2-}$ prepared by the method of Angoletta *et al.* [7] (Fig. 1(C)).

Discussion

There are numerous results that indicate close parallels between the chemistry of osmium carbonyl anions on the basic MgO surface and the chemistry of these anions in basic solutions [2]. The emerging data for iridium carbonyl anions on MgO [4,5] and in basic solutions [7,8] indicate similar parallels. The chemistry of iridium carbonyls in KOH in methanol and in THF in the presence of Na has been

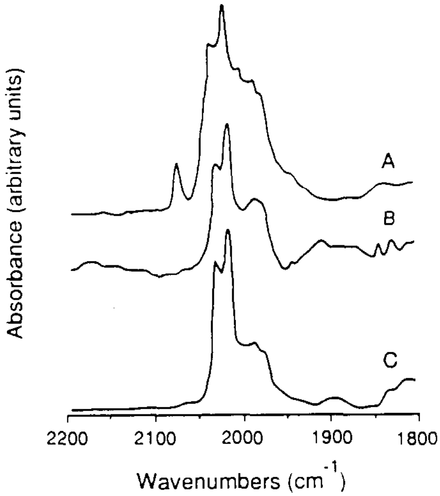

Fig. 1. Infrared spectra of $[Ir_8(CO)_{22}]^{2-}$ in solution and on MgO. (A) DRIFTS of the sample prepared by adsorption of $[Ir_4(CO)_{12}]$ on MgO followed by treatment in CO at 100°C and 1 atm for 1 h; (B) transmission spectrum of the solution resulting from extract of the solid sample with [PPN][Cl] in THF; (C) transmission spectrum of $[Ir_8(CO)_{22}]^{2-}$ prepared by the method of Angoletta *et al.* [7].

reported by Angoletta *et al.* [7] and Stevens *et al.* [8]; this chemistry involves formation of higher-nuclearity clusters from $[Ir_4(CO)_{12}]$, as follows (where the key reagent is listed over the arrow in each case):

$$Ir_4(CO)_{12} \xrightarrow{KOH} [HIr_4(CO)_{11}]^- \xrightarrow{KOH} [Ir_8(CO)_{22}]^{2-} \xrightarrow{KOH} [Ir_8(CO)_{20}]^{2-} \xrightarrow{KOH} [Ir_6(CO)_{15}]^{2-} \qquad (1)$$

$$Ir_4(CO)_{12} \xrightarrow{Na} [HIr_4(CO)_{11}]^- \xrightarrow{Na} [Ir_8(CO)_{22}]^{2-} \xrightarrow{Na} [Ir_8(CO)_{20}]^{2-} \xrightarrow{Na} [Ir_6(CO)_{15}]^{2-} \xrightarrow{Na} [Ir(CO)_4]^- \qquad (2)$$

A comparison of the colors of the samples investigated here with those of the clusters in solution (the tetrairidium carbonyls are yellow, the $[Ir_8(CO)_{22}]^{2-}$ is red) suggests that the chemistry of $[Ir_8(CO)_{22}]^{2-}$ synthesis in basic solutions is an indication of the chemistry occurring on MgO, and that the principal product formed from $[Ir_4(CO)_{12}]$ in the surface reaction at 100°C is $[Ir_8(CO)_{22}]^{2-}$. The infrared spectra confirm this suggestion, as shown by the comparison of Fig. 1(B) and 1(C) for the species extracted from the surface and authentic $[Ir_8(CO)_{22}]^{2-}$, respectively; the principal difference between these spectra is the broad peak at about 1992 cm^{-1} in the spectrum of the extracted species; this peak is identified with $[Ir(CO)_4]^-$, which is also formed in solution from iridium carbonyl clusters in the presence of Na in THF [7,8]; it is likely that it was formed in solution during and after the extraction, as indicated by the lack of this peak in the spectrum of the supported species (Fig. 1(A)).

The infrared spectrum of the surface-bound metal carbonyl (Fig. 1(A)) is similar to that of $[Ir_8(CO)_{22}]^{2-}$, but there is a significant peak at 2076 cm^{-1}. The position of this band suggests an iridium carbonyl with less negative charge than

$[Ir_8(CO)_{22}]^{2-}$, and the absence of this peak in the extract solution is consistent with its identification as a neutral species. We suggest that it is unconverted $[Ir_4(CO)_{12}]$, which has only a low solubility in THF (the extract solvent) and has peaks in THF solution at 2068vs and 2027m cm^{-1}; we suggest that the former corresponds to the 2076 cm^{-1} peak in the spectrum of the surface species and that the other peak overlaps the strong nearby peaks in this spectrum.

In summary, the analogy between the basic solution and basic surface chemistry of the iridium carbonyls, the colors of the solid samples, and the similarity of the infrared spectra of $[Ir_8(CO)_{22}]^{2-}$ in solution and that of the surface species formed in CO at 100°C and that of the anionic species extracted from the surface are all consistent with the conclusion that $[Ir_8(CO)_{22}]^{2-}$ formed on the MgO surface.

As treatment of the supported iridium carbonyl at higher temperatures in CO leads to formation of $[Ir_6(CO)_{15}]^{2-}$ [5], we suggest that $[Ir_8(CO)_{22}]^{2-}$ is an intermediate in the formation of the hexairidium cluster anion. It is logical to infer that the Ir cluster framework was broken prior to the formation of the octahedral hexairidium framework from the dimers of Ir_4 tetrahedra. The surface intermediates, which are unknown but likely mononuclear, must undergo facile reaction and transport on the MgO surface. The surface-mediated synthesis provides an alternative to the solution chemistry for preparation of $[Ir_8(CO)_{22}]^{2-}$ and related iridium carbonyl anions.

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