Chemistry in Cages: Synthesis and Reversible Decarbonylation of $[Ir_6(CO)_{16}]$ Isomers in NaY Zeolite

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$[Ir(CO)_2(acac)]$ in the cages of NaY zeolite is converted in CO at 1 bar (1 bar = 10^5 Pa) to the isomer of $[Ir_6(CO)_{16}]$ with edge-bridging CO ligands and in CO + H_2 at 20 bar to the isomer of $[Ir_6(CO)_{16}]$ with face-bridging ligands, either of which can be reversibly decarbonylated (Hacac = pentane-2-4-dione).

The synthesis of metal clusters in zeolite cages gives stable supported catalysts with novel selectivities.[1–5] Metal sulphide and semiconductor clusters in these cages are potential quantum dots.[6–8] Here we report the simple synthesis of two isomers of $[Ir_6(CO)_{16}]$ **1** from $[Ir(CO)_2(acac)]$ **2** in the supercages of NaY zeolite and IR evidence that they can be *reversibly* decarbonylated to give species that are suggested to be naked Ir_6.

The samples, typically containing 1.8 wt% Ir, were prepared by slurrying **2** with crystalline NaY zeolite in hexanes at 298 K for 1 day. A sample in an IR cell after treatment in CO (1 bar) at 313 K for 4 h gave an IR spectrum almost identical to that of $[Ir_4(CO)_{12}]$ **3** in tetrahydrofuran (thf) solution [Fig. 1(*a*)].[9] When the temperature was increased to 398 K, a bridging carbonyl band appeared at 1816 cm^{-1} and increased in intensity, and the terminal carbonyl bands shifted to higher frequencies. The steady-state spectrum [Fig. 1(*b*)] was observed after 4 h at 398 K; the sample was light yellow in colour. The spectrum is very similar to that of the isomer of $[Ir_6(CO)_{16}]$ with four edge-bridging CO ligands **1a**,[10] except that the frequencies of the terminal CO bands of the zeolite-supported cluster are shifted to higher wavenumbers and that of the bridging ligand is shifted to a lower frequency. (Such a pattern of band shifts has been observed for $[Rh_6(CO)_{16}]$ in NaY zeolite.[3]) A similar IR spectrum has been observed before for an iridium carbonyl in a zeolite and assigned incorrectly as **3**,[11] but this report appeared prior to the identification of the isomers of **1**.

With the sample still in CO at 1 bar, the temperature was raised to 498 K. The band at 1816 cm^{-1} decreased slightly in intensity, the terminal carbonyl peaks shifted *ca.* 10 cm^{-1} to higher frequencies, and a small peak appeared at 1730 cm^{-1}; the sample was light yellow in colour. The 1730 cm^{-1} band is characteristic of the isomer of $[Ir_6(CO)_{16}]$ with four face-bridging carbonyl ligands **1b**.[12,13] Evidently the zeolite-encaged **1a** was partially converted (only about 20%) to **1b**. However, when the sample originally prepared from **2** was treated in flowing CO + H_2 (equimolar) at 20 bar and 548 K for 3 days, it became yellow in colour and had an IR spectrum [Fig. 1(*c*)] very similar to that of **1b**; there was no evidence of **1a**. Again, the pattern of shifts in the terminal and bridging carbonyl bands is as stated above.

Attempts to extract iridium carbonyls from samples containing either **1a** or **1b** with thf or [PPN][Cl] in thf were unsuccessful. The supernatant solutions remained colourless and had no ν_{CO} absorptions, consistent with the stable entrapment of the clusters in the supercages of the zeolite.

The zeolite incorporating **1a** was treated in flowing H_2 at 1 bar and 373 K for 30 min, with no change in the IR spectrum. However, as the temperature was increased beyond 398 K, the bands broadened, decreased in intensity, and shifted to lower frequencies. After 2 h at 573 K in H_2, the ν_{CO} bands disappeared. The sample was then evacuated at 573 K for 30 min and cooled under vacuum to 298 K; it was beige in colour. This decarbonylated sample was then heated in CO at 1 bar; at 348 K, IR bands appeared at 2082, 2040 and 1816 cm^{-1}. After

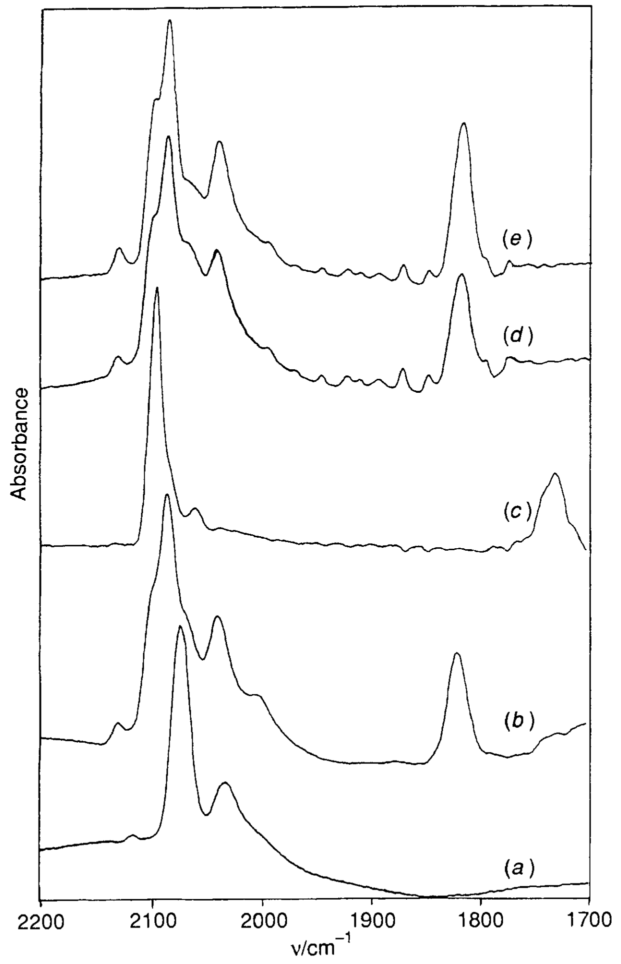
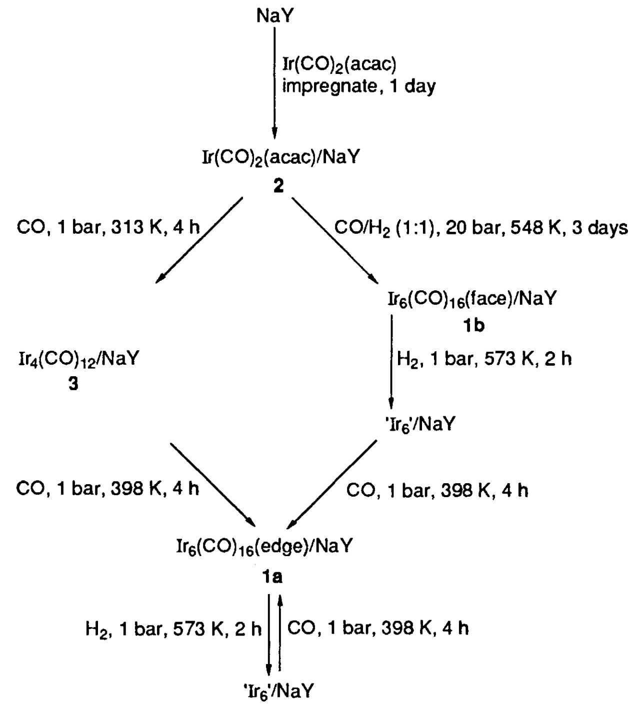


Fig. 1 Infrared spectra taken during treatment of the samples made from [Ir(CO)$_2$(acac)] and NaY zeolite: (*a*) sample after treatment in CO at 313 K and 1 bar for 4 h; (*b*) after treatment in CO at 398 K and 1 bar for 4 h; (*c*) after treatment in CO + H$_2$ (equimolar) at 548 K and 20 bar for 3 days; (*d*) sample from (*b*) after recarbonylation in CO at 398 K and 1 bar for 4 h; and (*e*) sample from (*c*) after recarbonylation in CO at 398 K and 1 bar for 4 h



Scheme 1 Chemistry of iridium clusters in NaY zeolite. The terms edge and face refer to the isomers with edge- and face-bridging carbonyl ligands, respectively.

4 h at 398 K, the spectrum became almost identical to that observed prior to decarbonylation [Fig. 1(*d*)]; the sample was again a light-yellow colour. Compound **1a** had been formed again.

The zeolite incorporating **1b** was treated with H$_2$ in the same way. The sample was stable in H$_2$ at 373 K for 30 min, but at higher temperatues the ν_{CO} IR bands decreased proportionately in intensity with almost no change in frequencies. These bands disappeared after 2 h in H$_2$ at 573 K. The sample was then evacuated at 573 K for 30 min and cooled under vacuum to room temperature; it was beige in colour. When this decarbonylated sample was heated to 348 K in flowing CO at 1 bar, IR bands slowly increased in intensity at 2082, 2040 and 1816 cm^{-1}. At 398 K, a steady-state spectrum was observed after 4 h [Fig. 1(*e*)], being that of **1a**. The ν_{CO} band at 1730 cm^{-1} did not reappear; the sample was again light-yellow in colour.

The spectra showed that the carbonylation–decarbonylation process was reversible for at least three cycles for each sample. Thus when either of the [Ir$_6$(CO)$_{16}$] isomers was decarbonylated in H$_2$, it formed species that could be recarbonylated cleanly to give **1a**. The results suggest that the decarbonylated clusters might have retained their nuclearity of six. The iridium cluster chemistry in the zeolite cages (summarised in Scheme 1) is an example of surface-mediated synthesis of metal carbonyls.[14,15] The chemistry is straightforward and easily controllable; perhaps the encagement of the clusters by the zeolite and the absence of solvents simplify the chemistry by hindering cluster–cluster interactions. The encaged decarbonylated clusters are among the simplest supported metals.

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