

Behavior of $[\text{Ir}_6(\text{CO})_{16}]$ in Solution: Isomerization and Cluster Breakdown to $[\text{Ir}_4(\text{CO})_{12}]$

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Introduction

The hexanuclear carbonyl cluster $[\text{Ir}_6(\text{CO})_{16}]$ exists in two isomeric forms: (i) a red isomer with four face-bridging carbonyl ligands which is easily synthesized;¹ (ii) a black isomer with four edge-bridging carbonyl ligands which is more difficult to prepare.² To our knowledge, the interconversion of these isomers has never been observed.²

We now report that the red form isomerizes easily in solution at room temperature, affording a mixture of the red and the black isomers. Mild thermal treatment of this solution under nitrogen or air causes cluster breakdown to $[\text{Ir}_4(\text{CO})_{12}]$ and metallic particles. This behavior was unexpected, the $[\text{Rh}_6(\text{CO})_{16}]$ analogue with four face-bridging carbonyl ligands being stereochemically rigid even at 70 °C,³ and is unusual because metal carbonyl clusters usually increase their nuclearity by thermal treatment,^{4,5} either in solution or in the solid state. Conversion of $[\text{Ir}_6(\text{CO})_{16}]$ into $[\text{Ir}_4(\text{CO})_{12}]$ and metallic particles occurs at relatively high temperature on a silica surface.⁶

Results and Discussion

Evidence for the Presence in Solution of Both the Isomers of $[\text{Ir}_6(\text{CO})_{16}]$. When the red isomer of $[\text{Ir}_6(\text{CO})_{16}]$ with four face-bridging carbonyl ligands, characterized by a bridging carbonyl band at 1764 cm^{-1} (as KCl pellet, Figure 1a), is dissolved in dichloroethane or tetrahydrofuran, the Fourier-transform infrared spectrum of the resulting brown solution shows two bridging carbonyl bands at 1780 (w) and 1842 (w) cm^{-1} and terminal carbonyl bands at 2106 (vw), 2066 (s), 2042 (sh,w), and 2012 (w) cm^{-1} (Figure 1b). In the solid state, it is known that the red and the black isomers are characterized by one bridging carbonyl band at 1764 and 1840 cm^{-1} , respectively.² Thus, although their infrared spectra have never been reported in solution, by analogy, the carbonyl absorptions observed in solution at 1780 and 1842 cm^{-1} may be assigned to the red and the black isomers.

It is worth pointing out that as soon as the red isomer of $[\text{Ir}_6(\text{CO})_{16}]$ is dissolved, the relative intensities of the two rather weak bridging carbonyl bands are similar and do not change with time. This observation suggests that the equilibrium is reached rapidly.

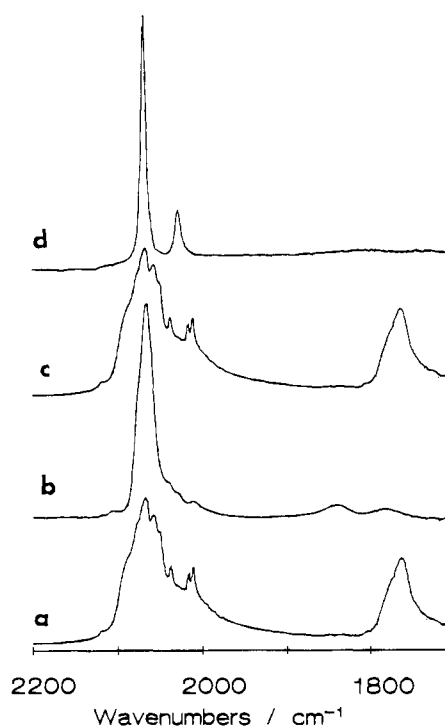


Figure 1. Infrared spectra in the $\nu(\text{CO})$ region: (a) red isomer of $[\text{Ir}_6(\text{CO})_{16}]$, as a KCl pellet; (b) red isomer of $[\text{Ir}_6(\text{CO})_{16}]$ dissolved in dichloroethane to give a mixture of red and black isomers; (c) same as (b) except dried, as KCl pellet; (d) same as (b) except heated at 80 °C under N_2 for 5 h.

Furthermore, evaporation of a dichloroethane or tetrahydrofuran solution of the $[\text{Ir}_6(\text{CO})_{16}]$ isomers leads to the complete conversion into the isomer with four face-bridging carbonyl ligands as shown by the infrared spectrum of the resulting powder, taken as a KCl pellet (Figure 1c). This behavior is in agreement with the observation that the red isomer is more easily isolated and synthesized than the black isomer.

$[\text{Ir}_6(\text{CO})_{16}]$ isomers interconvert in solution at room temperature. This contrasts with the behavior of $[\text{Rh}_6(\text{CO})_{16}]$ which exists only in the isomer with four face-bridging carbonyls and is stereochemically rigid even at 70 °C.³

The isomerization of $[\text{Ir}_6(\text{CO})_{16}]$ in solution explains why the black isomer of $[\text{Ir}_6(\text{CO})_{16}]$ has the same reactivity as the red isomer in solution.² It may also explain why the bridging carbonyl arrangement of the Ir_6 clusters $[\text{Ir}_6(\text{CO})_{15}(\text{COEt})]^-$, $[\text{Ir}_6(\text{CO})_{15}(\text{CO}_2\text{R})]^-$, and $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ have four *edge-bridging* carbonyls while the corresponding rhodium complexes have four *face-bridging* carbonyls.⁷

Thermal Conversion in Solution of $[\text{Ir}_6(\text{CO})_{16}]$ to $[\text{Ir}_4(\text{CO})_{12}]$. When a dichloroethane solution of the $[\text{Ir}_6(\text{CO})_{16}]$ isomers (Figure 1b) is heated at 80 °C under N_2 , $[\text{Ir}_4(\text{CO})_{12}]$,⁸ characterized by $\nu(\text{CO})$ at 2068 (s) and 2028 (m) cm^{-1} , is slowly formed as suggested by infrared spectroscopy. After 5 h, the carbonyl bands typical of $[\text{Ir}_6(\text{CO})_{16}]$ completely disappear and a clean infrared spectrum of $[\text{Ir}_4(\text{CO})_{12}]$ is obtained (Figure 1d).

Interestingly, the conversion of $[\text{Ir}_6(\text{CO})_{16}]$ to $[\text{Ir}_4(\text{CO})_{12}]$ is faster in the presence of oxygen than under nitrogen. In fact, this cluster breakdown reaction is complete after 2 h when a

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dichloroethane solution of the $[\text{Ir}_6(\text{CO})_{16}]$ isomers is heated at 80 °C in air, as shown by infrared spectroscopy. Evaporation of the solution affords a dark brown powder, suggesting that some metallic iridium has been formed along with yellow $[\text{Ir}_4(\text{CO})_{12}]$, as also occurs on a silica surface.⁶ The dodecacarbonyl tetrairidium cluster is easily purified (see Experimental Section), showing that the $[\text{Ir}_6(\text{CO})_{16}]$ breakdown reaction affords $[\text{Ir}_4(\text{CO})_{12}]$ in 83% isolated yield, assuming that 1 mol of $[\text{Ir}_6(\text{CO})_{16}]$ should give 1 mol of $[\text{Ir}_4(\text{CO})_{12}]$.

Because the formation of 1.5 mol of $[\text{Ir}_4(\text{CO})_{12}]$ from 1 mol of $[\text{Ir}_6(\text{CO})_{16}]$ would require CO, a solution of $[\text{Ir}_6(\text{CO})_{16}]$ was heated at 80 °C under CO for 6 h. No reaction occurred as shown by infrared spectroscopy. Obviously, the presence of excess CO inhibits the breakup of the $[\text{Ir}_6(\text{CO})_{16}]$ metal cage, which probably occurs via CO dissociation as first step. The reported syntheses of $[\text{Ir}_6(\text{CO})_{11}(\text{P}(\text{OMe})_3)_5]$ ⁹ and $[\text{Ir}_6(\text{CO})_{12}(\text{P}(\text{OPh})_3)_4]$ ¹⁰ by thermal treatment in toluene of $[\text{Ir}_6(\text{CO})_{16}]$ with excess $\text{P}(\text{OMe})_3$ or $\text{P}(\text{OPh})_3$ is another case where the presence of excess soft ligands such as phosphites stabilizes the Ir_6 cluster cage.

Comparison to Rhodium. A solution of both the $[\text{Ir}_6(\text{CO})_{16}]$ isomers leads, by mild thermal treatment, to cluster breakdown and formation of $[\text{Ir}_4(\text{CO})_{12}]$. This decrease of nuclearity is an unusual reaction in the chemistry of metal carbonyl clusters; for instance the opposite process occurs with the related rhodium carbonyl clusters.⁴ Obviously, $[\text{Ir}_4(\text{CO})_{12}]$ is characterized by a very high stability. In agreement with this statement, the molecular ion peak of $[\text{Ir}_6(\text{CO})_{16}]$ could not be detected in the mass spectrum of $[\text{Ir}_6(\text{CO})_{16}]$ by electron impact and thermal vaporization while that of $[\text{Rh}_6(\text{CO})_{16}]$ could be easily observed in the mass spectrum of $[\text{Rh}_6(\text{CO})_{16}]$. The mass spectrum of $[\text{Ir}_6(\text{CO})_{16}]$ simply showed the presence of $[\text{Ir}_4(\text{CO})_{12}]$ and successive losses of CO. Interestingly, the molecular ion peak of $[\text{Rh}_4(\text{CO})_{12}]$ could not be detected by mass spectroscopy, this cluster being too rapidly thermally converted to $[\text{Rh}_6(\text{CO})_{16}]$. The high stability of $[\text{Ir}_4(\text{CO})_{12}]$ occurs only in neutral conditions. In basic solution, $[\text{Ir}_4(\text{CO})_{12}]$ increases its nuclearity to give anionic clusters such as $[\text{Ir}_8(\text{CO})_{22}]^{2-}$ and $[\text{Ir}_6(\text{CO})_{15}]^{2-}$.¹

Experimental Section

The red isomer of $[\text{Ir}_6(\text{CO})_{16}]$ was prepared according to the literature.¹ 1,2-Dichloroethane (puriss. pa purchased from Fluka) was used as received while tetrahydrofuran was dried over sodium/benzophenone and distilled under nitrogen prior to use. Infrared spectra were recorded on a Nicolet MX-1 FT spectrometer, while a VG analytical 7070EQ spectrometer was used for mass spectral determinations.

Conversion of $[\text{Ir}_6(\text{CO})_{16}]$ to $[\text{Ir}_4(\text{CO})_{12}]$. In a typical experiment, $[\text{Ir}_6(\text{CO})_{16}]$ (0.144 g; 0.090 mmol) was added to dichloroethane (75 mL) and heated under reflux (80 °C) in air. The reaction was monitored by infrared spectroscopy. After 2 h, a clean spectrum of $[\text{Ir}_4(\text{CO})_{12}]$ was obtained showing that the cluster breakdown of $[\text{Ir}_6(\text{CO})_{16}]$ was complete. The solvent was evaporated affording a dark brown powder of $[\text{Ir}_4(\text{CO})_{12}]$ contaminated most probably by metallic iridium. $[\text{Ir}_4(\text{CO})_{12}]$ was purified as follows. LiBr (0.0234 g; 0.270 mmol) and anhydrous tetrahydrofuran (20 mL) were added to the dark brown residue under N_2 . The mixture was refluxed for 7 h, affording a reddish-brown solution of $[\text{Ir}_4(\text{CO})_{11}\text{Br}]\text{Li}$.¹¹ The solution was filtered and placed under CO atmosphere at room temperature. $[\text{Ir}_4(\text{CO})_{12}]$ began to precipitate as a yellow powder already after 1 h. After 14 h, the suspension was filtered in air and the canary-yellow powder was washed with water (2 mL) and vacuum dried, affording pure $[\text{Ir}_4(\text{CO})_{12}]$ (0.065 g; 0.059 mmol; 66% yield, assuming that 1 mol of $[\text{Ir}_6(\text{CO})_{16}]$ should give 1 mol of $[\text{Ir}_4(\text{CO})_{12}]$). In a blank experiment, it was found that the conversion of $[\text{Ir}_4(\text{CO})_{12}]$ to $[\text{Ir}_4(\text{CO})_{11}\text{Br}]$ followed by reconversion to $[\text{Ir}_4(\text{CO})_{12}]$ has a global yield of 80%. Assuming the same global yield for the $[\text{Ir}_4(\text{CO})_{12}]$ purification process, the cluster breakdown reaction of $[\text{Ir}_6(\text{CO})_{16}]$ afforded $[\text{Ir}_4(\text{CO})_{12}]$ in 83% yield. Similarly, the thermal behavior of $[\text{Ir}_6(\text{CO})_{16}]$ dissolved in dichloroethane was investigated under N_2 and CO.

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