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Chemistry of iridium carbonyl clusters. Preparation of $Ir_4(CO)_{12}$

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Abstract

$Ir_4(CO)_{12}$ has been prepared by a two-step reductive carbonylation of $IrCl_3 \cdot 3H_2O$ in ethanol or of K_2IrCl_6 in 2-methoxyethanol at atmospheric pressure. The iridium trichloride is first transformed into $[Ir(CO)_2Cl_2]^-$, which is subsequently reduced to $Ir_4(CO)_{12}$. A simple method for purification of the metal carbonyl is also described.

Introduction

Simple binary carbonyls are the starting material for the synthesis of many other compounds, and so any improvements in their synthesis are of interest. Since in our studies on iridium carbonyl cluster chemistry we start mainly from $Ir_4(CO)_{12}$ and $Ir_6(CO)_{16}$, we have always sought easier syntheses of these compounds.

Several methods of preparation of $Ir_4(CO)_{12}$ have been described, and mostly require high pressure equipment. For example, $Ir_4(CO)_{12}$ was prepared in good yields from $IrCl_3$ or from Ir^{III} or Ir^{IV} halocomplexes and CO at high pressure and temperature (250 atm, 100–150 °C) [1], or from the "soluble iridium(III) chloride" and carbon monoxide at 50–60 atm [2]. $Ir_4(CO)_{12}$ has also been obtained by reduction of $Na_2IrCl_6 \cdot 6H_2O$ in 2-methoxyethanol in presence of copper bronze at high pressure (100–200 atm) and temperature (100 °C) [3], and, more recently, by reduction of $[Ir(CO)_2(p\text{-toluidine})Cl]$ with zinc under mild pressures (5 atm) [4].

To our knowledge only two methods for synthesis of $Ir_4(CO)_{12}$ at atmospheric pressure have been reported. One involves carbonylation of the hydrated iridium trichloride at 150 °C in a stream of carbon monoxide [5], but gives rather low yields (about 20%). The other starts from Na_2IrCl_6, which is first transformed into Na_3IrCl_6 by reduction with sodium iodide and hence into $Ir_4(CO)_{12}$ in 75% yield by carbonylation in ethanol in the presence of potassium carbonate [6].

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We describe here another atmospheric pressure procedure for the synthesis of $Ir_4(CO)_{12}$ starting from $IrCl_3 \cdot 3H_2O$ or K_2IrCl_6. This involves a one-pot preparation consisting of two steps:
(1) reduction of the iridium(III) salts to $[Ir(CO)_2Cl_2]^-$, by the method described by Forster [7], and
(2) reduction of $[Ir(CO)_2Cl_2]^-$ to $Ir_4(CO)_{12}$ in a buffered solution of the complex. This second step requires very mild conditions (room temperature and 1 atm of CO), and is a clear improvement over the known methods of synthesis.

We report also a simple method for the purification of the $Ir_4(CO)_{12}$.

Results and discussion

$IrCl_3 \cdot 3H_2O$ is quantitatively converted into $[Ir(CO)_2Cl_2]^-$, by refluxing under CO its solutions in ethanol containing 10% of water, according to the equation:

$$IrCl_3 + 3CO + H_2O \rightarrow [Ir(CO)_2Cl_2]^- + Cl^- + 2H^+ + CO_2$$

During about 4 h the dark-brown initial solution changes first to yellow-green then to the characteristic pale-yellow of the $[Ir(CO)_2Cl_2]^-$ anion. At this point the IR spectrum contains carbonyl stretching bands at 2060vs and 1975vs cm^{-1}. The transformation of $IrCl_3 \cdot 3H_2O$ into $[Ir(CO)_2Cl_2]^-$ in ethanol was previously reported by Forster [7], who observed complete conversion to the Ir^I complex in about 48 h. IR monitoring of the solution during the reduction in the Ir^{III} chloride to the Ir^I complex showed the intermediate formation of various halocarbonyl complexes of iridium in keeping with the results obtained by Whyman [3] and Forster [7].

During the reaction there is some formation of $Ir_4(CO)_{12}$, but the acidity of the solution prevents complete reduction of $[Ir(CO)_2Cl_2]^-$ to $Ir_4(CO)_{12}$, which thus can be obtained by buffering the solution with disodium citrate; under these conditions after about 24 h there is complete transformation of the Ir^I derivative into $Ir_4(CO)_{12}$:

$$4[Ir(CO)_2Cl_2]^- + 6CO + 2H_2O \rightarrow Ir_4(CO)_{12} + 2CO_2 + 4H^+ + 8Cl^-$$

$IrCl_3 \cdot 3H_2O$ is the best available starting material for synthesis of dodecacarbonyltetrairidium, but chloro complexes of iridium-(III) or -(IV) can also be used. In these cases however, the first step, i.e. the reduction to $[Ir(CO)_2Cl_2]^-$, is more difficult, and requires more severe conditions, while the ease of the subsequent step to $Ir_4(CO)_{12}$ is almost the same in all cases. For example, starting from K_2IrCl_6, which can be obtained readily from waste iridium [8], a quick reduction to K_3IrCl_6 is first observed, then the reaction slows down and 12 h refluxing of the solution in 2-methoxyethanol containing 10% of water was necessary to complete the first step. A possible factor for this slowness could be the inertness of Ir^{III} halo complexes, which are probably further stabilized by the progressively increasing amount of halide ion set free during the reduction (the inhibiting effect of the halide ions was previously observed in the preparation of $Rh_4(CO)_{12}$ starting from K_3RhCl_6 [9]). Whatever the starting material, great care must be taken to ensure efficient CO saturation of the reaction solution, otherwise iridium metal is formed. The formation of the metal is particularly likely in the first step of the reaction, which is carried out at high temperature, at which the solubility of carbon monoxide in the reaction mixture is low, and is rarely observed in the second step, which is carried out at room temperature.

In most cases the $Ir_4(CO)_{12}$ obtained is pure enough for most synthetic purposes, but when the product is dark (owing to the presence of Ir metal), purification can be achieved by refluxing a tetrahydrofuran (thf) suspension of the impure metal carbonyl with sodium iodide, which transforms the insoluble $Ir_4(CO)_{12}$ into the soluble orange-yellow $[Ir_4(CO)_{11}I]^-$ monoanion [10] (ν(CO) 2080w, 2040vs, 2005vs, 1960vw, 1835s, 1830sh cm^{-1}, thf). After filtration to remove insoluble impurities, the $Ir_4(CO)_{12}$ can be recovered quantitatively by simple exposure of the solution to CO:

$$[Ir_4(CO)_{11}I]^- + CO \rightarrow Ir_4(CO)_{12} + I^-$$

In this way a pure crystalline canary-yellow carbonyl is obtained. This purification procedure is of general applicability, and is particularly useful for recovering the pure carbonyl from old samples of $Ir_4(CO)_{12}$, which sometimes become grey.

Experimental

All the reactions were performed under nitrogen or carbon monoxide as specified. 2-Methoxyethanol was distilled under reduced pressure and stored under nitrogen. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. Ethanol Merck analytical grade reagent was used as received.

Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer.

Preparation of $Ir_4(CO)_{12}$ from $IrCl_3 \cdot 3H_2O$

A two-necked, 1-l flask fitted with a reflux condenser is charged with 3 g (8.5 mmol) of commercial $IrCl_3 \cdot 3H_2O$ (Ir 53.6%) and with ethanol containing 10% of water (200 ml). The flask is stoppered, evacuated to degas the solvent, filled with carbon monoxide, and equipped with a gas inlet. The flask is placed in a oil bath and the solution refluxed as a stream of carbon monoxide is bubbled through leaving the flask through the condenser and a mineral oil bubbler. During this treatment the solution usually turns from dark brown to pale yellow, but occasionally turns black owing to traces of iridium metal, which is formed when the flow of CO is inadequate.) The solution is monitored every hour by IR spectroscopy, and the reaction continued until the intensities of the bands of the formed $[Ir(CO)_2Cl_2]^-$ (2060vs, 1975vs cm^{-1}) do not increase further (about 4 h), and the band at 1975vs cm^{-1} is more intense than the other. The intensity ratio between these two bands is important for confirming the complete conversion into $[Ir(CO)_2Cl_2]^-$; this is because one of the intermediate species has an IR band at 2060vs cm^{-1}, and if this band is stronger than that at 1975 cm^{-1} some of this intermediate species is still present. The solution is then heated for a further 2 h, cooled without interruption of the carbon monoxide stream, and left overnight at room temperature under a CO atmosphere. On standing, there is partial formation of $Ir_4(CO)_{12}$, which separates as a pale yellow powder. 50 ml (50 mmol) of an aqueous 1 *M* solution of disodium citrate are then added, and the solution is vigorously stirred at room temperature for about 24 h while the current of CO is maintained. The precipitate is filtered off in the air, washed first with water (4 × 25 ml), to remove the water-soluble salts, then with acetone (2 × 20 ml), then with chloroform (2 × 10 ml), and finally vacuum dried to give 1.52 g (65%) of $Ir_4(CO)_{12}$.

Elemental analysis: Found: C, 13.14; Ir, 69.2; $C_{12}O_{12}Ir_4$ calc: C, 13.04; Ir, 69.58%.

Preparation of $Ir_4(CO)_{12}$ from K_2IrCl_6

In this case it is necessary to use 2-methoxyethanol containing 10% of water as solvent instead of ethanol, and about 12 h at reflux is needed to convert K_2IrCl_6 into $[Ir(CO)_2Cl_2]^-$. At the end the pale-yellow solution is filtered, under CO, through a sintered glass-disk to remove the insoluble materials (mainly KCl) and subsequently treated as above with the solution of disodium citrate and worked up in the same manner.

Purification of $Ir_4(CO)_{12}$

A suspension of 4.32 g (3.91 mmol) of $Ir_4(CO)_{12}$ and 1.80 g of NaI (12 mmol) in 75 ml of thf is refluxed with stirring for 6 h under a slow nitrogen stream. The solution turns dark-red with disappearance of the precipitate and formation of $[Ir_4(CO)_{11}I]^-$. (When lithium iodide is used instead of sodium iodide formation of $[Ir_4(CO)_{11}I]^-$ is observed after 2 h.) The solution is cooled at room temperature and then filtered, under nitrogen, through a fine fritted glass disc into a two-necked flask. The nitrogen is removed from the flask and the solution saturated with carbon monoxide then stirred at room temperature as a carbon monoxide pressure of 1 atm is maintained. After 6 h $[Ir_4(CO)_{11}I]^-$ is quantitatively converted into the insoluble $Ir_4(CO)_{12}$. The suspension is filtered in air through a fine glass frit and the canary-yellow $Ir_4(CO)_{12}$ is washed with water (2 × 10 ml), methanol (2 × 10 ml), and acetone (2 × 10 ml), and vacuum dried. Yield 4.0 g (92%).

Elemental analysis: Found, C, 13.1; Ir, 69.4; $C_{12}O_{12}Ir_4$ calc: C, 13.04; Ir, 69.58%.

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