

A new convenient method for the high-yield synthesis of $\text{Ir}_4(\text{CO})_{12}$

F.P. Pruchnik, K. Wajda-Hermanowicz, M. Koralewicz

Institute of Chemistry University of Wrocław, 14 Joliot-Curie street, 50 383 Wrocław (Poland)

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Abstract

The complex $\text{Ir}_4(\text{CO})_{12}$ has been prepared by a new, simple method, involving heating of solutions of Ir^{III} or Ir^{IV} chlorides in 98% formic acid. Reaction at 100°C gave pure $\text{Ir}_4(\text{CO})_{12}$ in 100% yield.

Introduction

The rapid development of the studies of the cluster compounds observed in the past decade is due to their growing importance in synthesis and catalysis. $\text{Ir}_4(\text{CO})_{12}$ is important because of its application in catalysis and use as a starting material for the preparation of various derivatives. It can act as a catalyst, or catalyst precursor for hydrogenation, carbonylation, reduction of CO, CO_2 and related reactions [1–4]. Several methods for its preparation have been described, but all were very time-consuming, involved several stages, and mostly required high pressure equipment. $\text{Ir}_4(\text{CO})_{12}$ was first prepared by Hieber and Lagally [5] from the anhydrous iridium(III) or iridium(IV) halides and carbon monoxide in the presence of halide acceptors (Cu or Ag) under rather severe conditions (350 atm, $150\text{--}200^\circ\text{C}$), no yields were given. Others [6] have obtained good yields by using a water-insoluble form of iridium trichloride and temperatures of 240°C and pressure of 230–250 atm. Chaston and Stone [7] found that the reaction proceeds under milder conditions (50 atm, 60°C) in methanol in the absence of any halide acceptor (yield 60–70%). Whyman [8] employed copper bronze and 2-methoxyethanol at 100–200 atm at 100°C make $\text{Ir}_4(\text{CO})_{12}$ from $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (yield 70–90%).

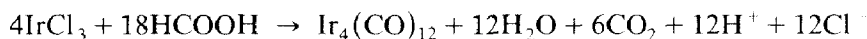
$\text{Ir}_4(\text{CO})_{12}$ has also been obtained by reduction of a monovalent iridium species $\text{IrCl}(\text{CO})_2$ (*p*-toluidine) with zinc in a mixture of 2-methoxyethanol and water in the presence of carbon monoxide under mild pressure (5 atm) [9] (yield 65%). Some $\text{Ir}_4(\text{CO})_{12}$ is formed, but only in low yield (10%) when a stream of carbon monoxide at atmospheric pressure is passed over $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ at 150°C [10]. Two good-yield syntheses of $\text{Ir}_4(\text{CO})_{12}$ at atmospheric pressure have been reported. Thus Malatesta,

Caglio and Angoletta [11] prepared it in 74–78% yield by treatment of Na_2IrCl_6 or Na_3IrCl_6 with NaI in methanol under one atmosphere of CO followed by treatment with base. Recently Pergola and Garlaschelli [12] have used a two-step reductive carbonylation of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol or K_2IrCl_6 in 2-methoxyethanol at atmospheric pressure. The iridium trichloride is first transformed into $[\text{IrCl}_2(\text{CO})_2]$, which is subsequently reduced to give $\text{Ir}_4(\text{CO})_{12}$ in 65% yield.

It has been shown that formic acid in the presence of the appropriate halogen acid reacts with halogeno-complexes of iridium(IV) or iridium(III) to give a number of products containing iridium(III), (II) or (I) species [12–15], e.g., $[\text{IrX}_5(\text{CO})]^{2-}$, $[\text{IrX}_4\text{CO}(\text{MeOH})]^-$, $[\text{IrX}_4(\text{CO})_2]^-$, $[\{\text{IrX}_3(\text{CO})_2\}_2]^{2-}$, $[\text{Ir}_4\text{X}_8(\text{CO})_8]^{2-}$, $[\text{Ir}_2(\text{CO})_2]^-$. W.P. Griffith et al. [15] observed that formic acid alone reacts with $[\text{IrCl}_6]^{3-}$, to give a mixture of $[\text{IrCl}_5(\text{CO})]^{2-}$ and complex formate derivatives. We describe below the quantitative preparation of $\text{Ir}_4(\text{CO})_{12}$ by a very simple route.

Results and Discussion

Our method involves heating the hydrated iridium(III) chloride (or the iridium(III) and iridium(IV) chloride complexes) with 98% formic acid at 100°C for 12 h in a sealed vessel. The formic acid decomposes with evolution of carbon monoxide, and the carbon monoxide pressure generated is sufficient for quantitative transformation of the chlorides into $\text{Ir}_4(\text{CO})_{12}$.



No iridium compounds were found dissolved in the formic acid, but Cl^- ions were detected in solution. The canary-yellow product was insoluble in the reaction medium. Analysis and IR spectroscopy showed it to be $\text{Ir}_4(\text{CO})_{12}$. The IR spectra (KBr discs) in the range $4000\text{--}300\text{ cm}^{-1}$ show bands at 2108m, 2085sh, 2058vs, 2040m, 2022s, 2002m, 532s, 497vs, 472m, 442vs, consistent with literature data for $\text{Ir}_4(\text{CO})_{12}$ [16].

Our method of synthesis of $\text{Ir}_4(\text{CO})_{12}$ is simple and more efficient than those previously available. It is not necessary to use a high pressure of CO , and the readily available and cheap formic acid is used both as a reactant and solvent. The one-step synthesis is quantitative, and for most purposes the product requires no purification.

Experimental

In a glass tube of 15 cm^3 volume were placed 0.2 g $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and 5 cm^3 98% HCOOH or 0.2 g $(\text{NH}_4)_2\text{IrCl}_6$ and 8 ml 98% HCOOH . The tube was sealed within a stainless steel jacket and kept for 12 h at 100°C . (Sealed glass ampoules cannot be used because the pressure of CO is too high.) The canary-yellow reaction product was filtered off, washed 3 times with water and methanol, and dried in vacuo. Elemental analysis. Found C 13.02; $\text{Ir}_4\text{C}_{12}\text{O}_{12}$ calcd.: 13.05%.

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