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IMPROVED SYNTHESIS OF DODECACARBONYLTETRARHODIUM AT ATMOSPHERIC PRESSURE

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SUMMARY

A convenient two step synthesis of $Rh_4(CO)_{12}$ at room temperature and atmospheric pressure is reported. This involves reduction of the hexachlororhodate(III) anion to dicarbonyldichlororhodate(I) anion with copper metal, followed by further reduction with carbon monoxide and water in presence of sodium citrate buffer. Yields of 86–99% are obtained.

INTRODUCTION

We have previously described a synthesis of $Rh_4(CO)_{12}$ from $Rh_2(CO)_4Cl_2$, carbon monoxide and sodium hydrogen carbonate at atmospheric pressure[1], but it involved a rather tedious transformation of Na_3RhCl_6 or K_3RhCl_6, into $Rh_2(CO)_4Cl_2$[2]. We now report a preparation of $Rh_4(CO)_{12}$ which starts direct from the alkali hexachlororhodate(III), and is therefore considerably more convenient.

RESULTS AND DISCUSSION

The new synthesis involves reduction of the hexachlororhodate(III) anion by powdered copper metal followed by further reduction of the dichlorodicarbonylrhodate(I) anion by carbon monoxide and water; it is represented by eqns. (1) and (2):

$$(RhCl_6)^{3-} + 2\,Cu + 2\,CO \xrightarrow[H_2O]{25°,\ 1\ atm} [Rh(CO)_2Cl_2]^- + 2\,CuCl + 2\,Cl^- \qquad (1)$$

$$4[Rh(CO)_2Cl_2]^- + 6\,CO + 2\,H_2O \xrightarrow[H_2O]{25°,\ 1\ atm} Rh_4(CO)_{12} + 2\,CO_2 + 4\,Cl^- + 4\,HCl \qquad (2)$$

The reactions are carried out in aqueous solution, because use of a medium in which carbon monoxide has a higher solubility is prevented by the low stability of $Rh_4(CO)_{12}$ in polar organic solvents[1]. In water it is very important that reactions (1) and (2) are slowed down in such a way that the solution remains continuously saturated with carbon monoxide, otherwise formation of $Rh_6(CO)_{16}$ or rhodium metal is observed. For the same reason efficient stirring is needed throughout the synthesis.

The first reduction, reaction (1), is conveniently carried out using a slight excess of powdered copper metal [ratio Cu to Rh^{III} of about 3] and ca. 0.02 *M* aqueous hexachlororhodate(III). It usually takes about 12–14 h, as shown by precipitation of the $[Rh(CO)_2Cl_2]^-$ anion as the tetrabutylammonium salt. Since reaction (2) takes place to some extent alongside with reaction (1), some $Rh_4(CO)_{12}$ is also formed and the pH is about ca. 2.

Reaction (2), is carried out at a pH of ca. 4, the pH being controlled by use of a buffer such as a solution of disodium citrate, or of magnesium acetate, or by addition of magnesium oxide. At a lower pH this reduction is too slow, while at a higher pH $Rh_6(CO)_{16}$ or rhodium metal is formed[1]. The reaction takes 24–36 h at room temperature and atmospheric pressure.

Reaction (2) involves nucleophilic attack at a carbon atom of a carbonyl group: probably the small amounts of $Rh_2(CO)_4Cl_2$ which are in equilibrium with the $[Rh(CO)_2Cl_2]^-$ anion are attacked both by water and by hydroxyl ion, which would account for the sensitivity of the rate to pH and chloride ion concentration[1]. Use of an excess of sodium or potassium chloride, as *e.g.*, when the raw hexachlororhodate(III) obtained by chlorination of rhodium metal in the presence of alkali chlorides is employed, lowers the reaction rate, as shown by experiments 4 and 5 in Table 1. Noble metal impurities must be avoided, for in their presence the formation of byproducts is easier*, and recrystallisation of the K_3RhCl_6 from water saturated with potassium chloride[3] is recommended.

After filtration of the reaction mixture, dodecacarbonyltetrarhodium is obtained in high yield (86–99%) by dissolution in methylene chloride and subsequent rapid evaporation in a carbon monoxide stream. Hexadecacarbonylhexarhodium is

TABLE 1

SYNTHESIS OF $Rh_4(CO)_{12}$ AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE FROM K_3RhCl_6 (0.02 *M* AQUEOUS SOLUTION)

Exp. no.	Reducing agent (mol/g-at Rh)	Buffering agent (mol/g-at Rh)	Reaction time (h)	Conversion (%)	$Rh_4(CO)_{12}$ yield (%)
1	Formic acid (2)	Disodium citrate[a] (3)	72	54	~43[b]
2	CO	Magnesium acetate[c] (3)	72	65	~52[b]
3	$CO+H_2$[d]	Magnesium acetate[c] (6)	65	69	46[b]
4	Cu (3)	Disodium citrate[a] (1)	24	96.0–99.5[e]	86–99[b,e]
5[f]	Cu	Disodium citrate[a]	24	38	
	(3)	(1)	168	96	81[b]

[a] Added as 1 *M* aqueous solution after 18 h. [b] $Rh_6(CO)_{16}$ is also present in 10–15% yields. [c] Added at the beginning. [d] Ratio CO/H_2 of 3. [e] Values obtained from 7 different experiments. [f] In the presence of additional 34 mol KCl/mol K_3RhCl_6.

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* In our experience commercial salts of rhodium can be impure for sizable amounts of platinum salts.

somewhat soluble in CH_2Cl_2, and furthermore during this separation small amounts of $Rh_6(CO)_{16}$ are also formed, when pure $Rh_4(CO)_{12}$ is required it recrystallised from pentane at $-70°$[1].

The synthesis can be also carried out under acidic conditions using a number of different reducing agents, such as formic acid[4,5], hydrogen/carbon monoxide, or water/carbon monoxide[6-8]. These reducing agents are attractive because they do not produce solid by-products, but unfortunately the slowness of the reaction or the easy formation of by-product is found in all the cases examined, as shown by experiments 1 to 3 in Table 1.

EXPERIMENTAL

A 0.02 *M* aqueous solution (1 l) of recrystallised $K_3RhCl_6 \cdot H_2O$ (9.02 g; 2.06 g of rhodium)* contained in a 2 l Buchner flask equipped with a Teflon-covered magnetic bar is well degassed under vacuum and then saturated with carbon monoxide. Powdered copper metal (4.0 g) is then added, and carbon monoxide is added as required during about 12 h of stirring to maintain at atmospheric pressure. The red solution becomes pale-yellow and some $Rh_4(CO)_{12}$ is precipitated.

A 1 *M* solution of disodium citrate (20 ml) is added and the mixture is stirred for a further 12 h. The solid is filtered off, washed with water and dried in vacuum. Some rhodium is still present in the original solution (10–80 mg, 99.5–96 % of conversion)*. The dry solid is extracted with methylene chloride (75 ml) pre-saturated with carbon monoxide, and the filtered solution is quickly evaporated in a carbon monoxide stream to give $Rh_4(CO)_{12}$ (3.2–3.7 g, 86–99 % yield). The IR spectrum of the product shows only a small shoulder at 1800 cm^{-1} due to the presence of $Rh_6(CO)_{16}$[1]. Some $Rh_6(CO)_{16}$ can usually be extracted from the residual solid by prolonged washing with chloroform (0.03–0.3 g, 1–9 %).

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REFERENCES

1 P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 3 (1969) 315.
2 J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8 (1966) 211.
3 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press, London, Vol. II, 1965, p. 1588.
4 R. Colton, R. H. Farthing and J. Knapp, *Proceedings of the XIII ICCC*, Sydney, Australia, 1969, pp. 162–164.
5 M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, (1969) 372.
6 J. A. Stanko, G. Petrov and C. K. Thomas, *Chem. Commun.*, (1969) 1100.
7 B. R. James and G. L. Rempel, *J. Chem. Soc. A*, (1969) 78.
8 D. Forster, *Inorg. Chem.*, 8 (1969) 2556.

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* Determined by atomic absorption.