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Synthesis of Rhodium Carbonyl Compounds at Atmospheric Pressure. III. Synthesis of $Rh_4(CO)_{12}$ and of $Rh_6(CO)_{16}$

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$Rh_4(CO)_{12}$ was obtained in moderate yield (60 %) by reducing $Rh_2(CO)_4Cl_2$ at atmospheric pressure and room temperature with carbon monoxide in the presence of water. In organic solvents and in the presence of minor quantities of water $Rh_6(CO)_{16}$ was obtained (30%). The same reaction have been carried out under alkaline conditions: $Rh_4(CO)_{12}$ was obtained using hexane containing suspended sodium hydrogen carbonate (82%), and $Rh_6(CO)_{16}$ in water-alcohol in the presence of lithium acetate (77%). These last two syntheses seem to be of particular practical significance, owing to easy availability of $Rh_2(CO)_4Cl_2$, high yield and extreme simplicity. The physical and chemical properties of the two cluster carbonyls are discussed.

Introduction

We have previously[1] reported the synthesis of the anion $[Rh(CO)_4]^-$ by reduction of $Rh_2(CO)_4Cl_2$ at atmospheric pressure with alkali metals and explored several possible reactions with a view to preparing $HRh(CO)_4$ and $Rh_2(CO)_8$. In the present paper it will be shown how the previously reported[2] synthesis of the $[Rh_{12}(CO)_{30}]^{2-}$ anion is related to the problem of obtaining both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ at atmospheric pressure.

These two rhodium cluster carbonyls were previously obtained by Hieber and Lagally[3] by reduction of rhodium trichloride, using a metal as halogen acceptor (Cu, Ag, Zn and Cd) under 200 atm pressure of carbon monoxide. Dodecacarbonyltetrarhodium results at moderate temperature (25°-80°), hexadecacarbonylhexarhodium at higher temperature. During the present work[4] two other syntheses of $Rh_6(CO)_{16}$ were reported: from rhodium trichloride trihydrate in methanol at 60° and 50 atm (80-90% yield),[5] and from $Rh_2(CO)_4Cl_2$ and iron pentacarbonyl at 65°-75° (64% yield).[6]

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(2) P. Chini and S. Martinengo, Part. II, *Inorg. Chim. Acta*, 3, 299, (1969).
(3) W. Hieebr and H. Lagally, *Zeit Anorg. Allg. Chem.*, 251, 96 (1943).
(4) P. Chini and S. Martinengo, *Chem. Comm.*, 251 (1967).
(5) S. H. Chaston and F. G. A. Stone, *J. Chem. Soc.*, (A) 500 (1969).
(6) B. L. Booth, M. J. Else, R. Fields, H. Goldwhite, and R. N. Haszeldine, *J. Organometal. Chem.*, 14, 417 (1968).

Results and Discussion

Reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide and water. Tetracarbonyl-μ-dichlorodirhodium is reduced by carbon monoxide and water at room temperature and atmospheric pressure. Using limited amounts of water in organic solvents such as methanol, acetone and tetrahydrofuran the reaction product was the insoluble $Rh_6(CO)_{16}$, but using larger amounts of water, or pure water, it was $Rh_4(CO)_{12}$ insoluble in these media, but soluble in organic solvents. Table I gives data regarding synthesis of these two different carbonyl compounds: yield increases with increasing water concentration.

Table I. Reduction of $Rh_2(CO)_4Cl_2$ (1 mmole) in aqueous methanol (20 ml) at atmospheric pressure and room temperature. Reaction time 24 hrs.[a]

Water %	$Rh_6(CO)_{16}$ yield %	$Rh_4(CO)_{12}$ yield %	$Rh_4(CO)_{12}+Rh_6(CO)_{16}$ yield %
2	19.5	0	19.5
5	30	0	30
10	13	29	42
20	4	49	53
100	traces	61	61

[a] with vigorous stirring

The two equations are:

$$2Rh_2(CO)_4Cl_2+6CO+2H_2O \rightarrow Rh_4(CO)_{12}+2CO_2+4HCl \quad (1)$$

$$3Rh_2(CO)_4Cl_2+7CO+3H_2O \rightarrow Rh_6(CO)_{16}+3CO_2+6HCl \quad (2)$$

Equation (2) has been confirmed experimentally by the finding that three moles of carbon dioxide and six moles of hydrochloric acid are formed per mole of $Rh_6(CO)_{16}$.

Liberation of hydrochloric acid in these reactions has three important consequences. Firstly it is responsible for the conversion of $Rh_4(CO)_{12}$ into $Rh_6(CO)_{16}$ when the reaction is run in a medium in which dodecacarbonyltetrarhodium is soluble. Table II shows the separate effect of adding to a methanol solution of $Rh_4(CO)_{12}$ the substances present during the synthesis. Dodecacarbonyltetrarhodium in the presence of carbon monoxide is stable both in pure and in aqueous methanol, as well as in methanol containing some $Rh_2(CO)_4Cl_2$. It is unstable in the presence of hydrochloric acid, being quantitatively converted to $Rh_6(CO)_{16}$.

Table II. Conversion of $Rh_4(CO)_{12}$ (0.1 g) in $Rh_6(CO)_{16}$ in methanol (10 ml) in a carbon monoxide atmosphere at room temperature. Reaction time 24 hrs

Added substance, %	Reaction product
—	$Rh_4(CO)_{12}$ [a]
water 10	$Rh_4(CO)_{12}$ [a]
$Rh_2(CO)_4Cl_2$ 10	$Rh_4(CO)_{12}$ [a]
1 N aqueous HCl 2	$Rh_6(CO)_{16}$

[a] traces of $Rh_6(CO)_{16}$ are also present

It therefore seems clear that when $Rh_4(CO)_{12}$ is insoluble in the reaction medium, the hydrochloric acid liberated in reaction (1) is unable to convert this compound to $Rh_6(CO)_{16}$.

The second consequence of hydrochloric acid formation is the lowering of hydroxyl ion concentration progressively retarding hydrolysis of $Rh_2(CO)_4Cl_2$. An effect shown by the immediate quantitative reaction of $Rh_2(CO)_4Cl_2$ with alkali as compared with the slow reaction by water. Hence it was expected that the addition of a buffer would result in a better yield of $Rh_4(CO)_{12}$, but such was found not to be the case and buffering at several pH from 5 to 7 with mixtures of Na_2HPO_4 and KH_2PO_4 gave low yield of $Rh_4(CO)_{12}$, because of formation of large amounts of $Rh_6(CO)_{16}$.* Under more alkaline conditions reaction was too rapid, and often separation both of rhodium metal and of $Rh_6(CO)_{16}$ were observed. The same byproducts were obtained in pure water, when it was not first carefully saturated with carbon monoxide. Low rate of solution of carbon monoxide and slow further reduction seem to be responsible for the formation of byproducts.

Finally the third effect of the hydrochloric acid is production of the anion $[Rh(CO)_2Cl_2]^-$ by reaction between chloride anion and $Rh_2(CO)_4Cl_2$:[7]

$$Rh_2(CO)_4Cl_2 + 2Cl^- \rightleftarrows 2[Rh(CO)_2Cl_2]^- \qquad (3)$$

The dicarbonyldichlororhodate(1—) anion is not reduced so easily as $Rh_2(CO)_4Cl_2$ and this is shown by the experiments in Table II, where increasing amounts of lithium chloride were added to the reaction mixture.

The slowing down of the reduction can be used for obtaining $Rh_4(CO)_{12}$ of better purity. Addition of sodium chloride (2 mmoles) in conditions similar to that of Table III gave in water pure $Rh_4(CO)_{12}$ in 47% yield.

$Rh_4(CO)_{12}$ was separated by filtration, and it could be crystallised from pentane at −70°. $Rh_6(CO)_{16}$ was obtained in particularly beatiful crystals when reaction was slow (1% water, 30 days), and it could be purified by extraction in a nitrogen atmosphere using methylenchloride or chloroform.

(*) *Note added in proof*. Good yields have been obtained by buffering at pH 2.

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Table III. Reduction of $Rh_2(CO)_4Cl_2$ (1 mmole) in aqueous methanol (20 ml, 10% water) in the presence of lithium chloride at atmospheric pressure and room temperature. Reaction time 24 hrs

$LiCl/Rh_2(CO)_4Cl_2$ moles	$Rh_4(CO)_{12}+Rh_6(CO)_{16}$ % yield
0	39
2	15
10	traces
100	0

Synthesis of $Rh_4(CO)_{12}$ by reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide and alkali. In a previous paper[2] we showed that using potassium hydroxide in methanol, the first reaction product from $Rh_2(CO)_4Cl_2$ is $Rh_4(CO)_{12}$:

$$4Rh_2(CO)_4Cl_2 + 4KOH + 6CO \xrightarrow{CH_3OH} Rh_4(CO)_{12} + 4K[Rh(CO)_2Cl_2] + 2CO_2 + 2H_2O \qquad (4)$$

Formation of $Rh_4(CO)_{12}$ is followed by its rapid reduction to carbonylrhodates, a reaction which is more rapid than the reduction of the $[Rh(CO)_2Cl_2]^-$ anion. Therefore it is not possible to use, under these conditions, the simple stoichiometric amount of potassium hydroxide in order to convert all the $Rh_2(CO)_4Cl_2$ to $Rh_4(CO)_{12}$.

Reduction of $Rh_4(CO)_{12}$ is suppressed when it is dissolved in a non-polar solvent such as hexane, and when there is no aqueous phase, *e.g.* when solid sodium hydrogen carbonate is used. Under such conditions the yield of $Rh_4(CO)_{12}$ is high (82%) and it is easily separated in a very pure state by cooling to −70° the filtered solution. Some $Rh_6(CO)_{16}$ (7%) is left on the filter and can be separated by washing with water.

$$2Rh_2(CO)_4Cl_2 + 6CO + 4NaHCO_3 \xrightarrow{n-hexane} Rh_4(CO)_{12} + 6CO_2 + 4NaCl + 2H_2O \qquad (5)$$

Poorer results are obtained using sodium carbonate as alkaline reagent, and pentane or toluene as solvent. Powdered sodium hydroxide reacts too rapidly and there is formation of some rhodium metal. In all cases it is important that stirring should not be stopped during the synthesis otherwise lower yields are obtained due to insufficient saturation with carbon monoxide.

Use of a suspension of potassium hydrogen carbonate in tetrahydrofuran gives a mixture of $K_2[Rh_{12}(CO)_{30}]$ with some $Rh_6(CO)_{16}$; a result showing how facile is the further reduction of $Rh_4(CO)_{12}$ when followed by solvation of the ionic product of such a reaction.[2]

Synthesis of $Rh_6(CO)_{16}$ by reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide and alkali. The hexadecacarbonylhexarhodium has been obtained in yield of about 80% by slow addition of the stoichiometric amount of potassium hydroxide to $Rh_2(CO)_4Cl_2$ in methanol or isopropanol:

$$3Rh_2(CO)_4Cl_2 + 6KOH + 7CO \longrightarrow Rh_6(CO)_{16} + 6KCl + 3CO_2 + 3H_2O \qquad (6)$$

The formation of $Rh_6(CO)_{16}$ is definitely assisted by the insolubility of the compound and seems arise from oxidation-reduction between the anions $[Rh_{12}(CO)_{30}]^{2-}$ (rhodium oxidation number −0.166) and $[Rh(CO)_2Cl_2]^-$ (rhodium oxidation number +1). These two anions have been shown to react slowly to give $Rh_6(CO)_{16}$. A similar oxidation-reduction reaction due to other intermediate carbonylrhodates[2] is also possible.

Far more convenient is the reduction of $Rh_2(CO)_4Cl_2$ in the presence of lithium acetate. In a previous paper[2] it was shown that sodium and potassium acetate give rise to $[Rh_{12}(CO)_{30}]^{2-}$ derivatives, which are decomposed by subsequent addition of acids with formation of $Rh_6(CO)_{16}$. More simply the two reactions can be carried out simultaneously using lithium acetate; probably the lesser alkalinity of the lithium is not great enough to buffer the acetic acid liberated during the formation of $Li_2[Rh_{12}(CO)_{30}]$. The reaction time is about 24 hrs at room temperature, the $Rh_6(CO)_{16}$ yields being about 80%.

Chemical and physical properties of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. Red $Rh_4(CO)_{12}$ decomposes under nitrogen at about 130°-140° (lit. 150°)[3,6] giving $Rh_6(CO)_{16}$. In solution decomposition proceeds more readily, *e.g.* n-heptane at 50°-60°. Dark brown $Rh_6(CO)_{16}$ * decomposes under nitrogen at 197°-208° (lit. 220°[4] and 235°[6]), and the IR spectrum shows that no other carbonyl compounds are formed.

In the solid state both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are stable to air oxidation, and $Rh_4(CO)_{12}$ is also moderately stable in hexane solution. In n-pentane the solubility of $Rh_4(CO)_{12}$ is particularly high (~12 g/l at 25°), the compound is also well soluble in n-heptane, toluene and tetrahydrofuran (~10 g/l at 25°), in methanol the solubility is much lower. On the other hand $Rh_6(CO)_{16}$ is very slightly soluble in organic solvents, the highest solubilities being in methylenchloride and chloroform. It also has low solubility at 150°-170° in tetralin.

In methanol solution under nitrogen $Rh_4(CO)_{12}$ is slowly transformed in $Rh_6(CO)_{16}$, the latter solid not reacting further. Decomposition of $Rh_4(CO)_{12}$ in methanol is suppressed in a carbon monoxide atmospere, suggesting that some kind of dissociation occurs. This behaviour is very different from that of the corresponding cobalt compounds for which a disproportionation reaction is observed.[8,9]

Neither $Rh_6(CO)_{16}$ at 70°, nor $Rh_4(CO)_{12}$ at 25° react with carbon monoxide at 300 atm. At 70°-120°/360-420 atm $Rh_4(CO)_{12}$ in n-heptane is transformed in $Rh_6(CO)_{16}$ suggesting that even in these conditions there is a slow irreversible decomposition in $Rh_6(CO)_{16}$.[1]

Both $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ react easily with excess triphenylphosphine giving, after recrystallisation under carbon monoxide, pale yellow $Rh_2(CO)_4(PPh_3)_4$, a compound recently obtained from $HRh(CO)(PPh_3)_3$ and carbon monoxide.[10] This reaction involves several intermediates stages such as $Rh_4(CO_{10}(PPh_3)_2$, which are at present being investigated.[11]

Under carbon monoxide both these carbonyls react with alkaline reagents to give carbonylrhodates, the composition of the reaction products being highly dependent on the experimental conditions.[2] We are at present making X-ray diffraction studies of the structures of several of these carbonylrhodates such as $[Rh_7(CO)_{16}]^{3-}$ and $[Rh_6(CO)_{14}]^{4-}$.[11]

Halides such LiCl and $[N(CH_3)_4]I$ react readily with solutions of $Rh_4(CO)_{12}$ giving compounds such as $[N(CH_3)_4][Rh_6(CO)_{15}I]$ which are also at present under X-ray investigation.[11]

The infrared spectra of $Rh_4(CO)_{12}$ in n-hexane and in nujol are shown in Figure 1.

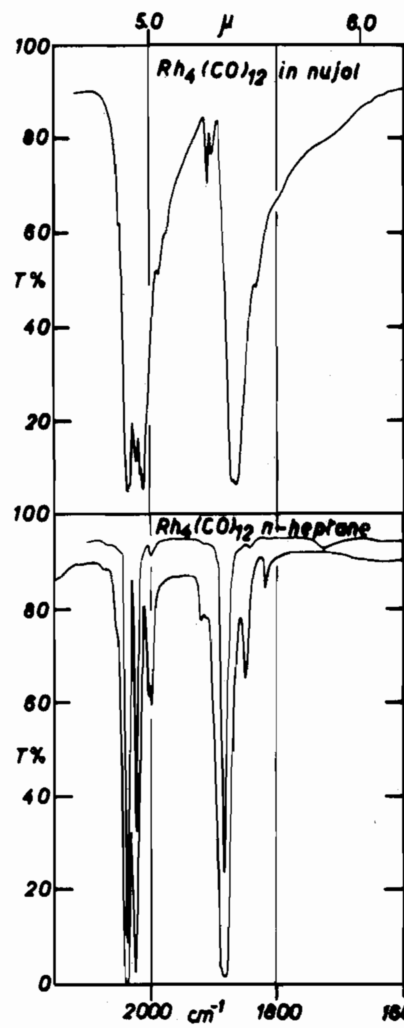

Figure 1. Infrared spectra of $Rh_4(CO)_{12}$ in the carbonyl stretching region. (Registered on a Perkin Elmer 457 spectrophotometer).

In nujol the stretching band of the bridging carbonyl groups is double and there is also an highly complicated pattern in the terminal region, probably because of the simultaneous presence of solid and dissolved $Rh_4(CO)_{12}$. It has not been possible to obtain the spectrum in KBr, owing to decomposition

(*) Crystals of $Rh_6(CO)_{16}$ are black with a violet nuance, but in mull the colour is dark brown.

(8) P. Chini and V. Albano, *J. Organometal. Chem.*, *15*, 433 (1968) and references therein.
(9) P. Chini, *Inorg. Chem. 8*, 1206 (1969).
(10) D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.*, (A) 2660 (1968).
(11) P. Chini, S. Martinengo, and V. Albano, work in progress.

to $Rh_6(CO)_{16}$.[12,13] The IR spectrum of $Rh_6(CO)_{16}$ has been already reported in detail.[9]

Preliminary reports have been made of the structures of both of these compounds.[14,15]

Interpretation of the results. The initial product of the reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide in the presence of water or alkaline agents is $Rh_4(CO)_{12}$. The latter is easily converted into $Rh_6(CO)_{16}$ which therefore is a thermodynamically more stable phase. The initial formation of $Rh_4(CO)_{12}$ must be due to kinetic factors. The slowness of this synthesis both at low pH and at high concentration of Cl^- ions agree with a slow initial substitution:

$$Rh_2(CO)_4Cl_2 + H_2O \overset{slow}{\rightleftarrows} Rh_2(CO)_4(OH)Cl + HCl \qquad (7)$$

The initial formation of $Rh_4(CO)_{12}$ is consistent with futher reaction according to:

$$Rh_2(CO)_4(OH)Cl + xCO \xrightarrow{rapid} \{Rh_2(CO)_{3+x}\} + CO_2 + HCl \qquad (8)$$

$$\{Rh_2(CO)_{3+x}\} + Rh_2(CO)_4Cl_2 \xrightarrow[H_2O]{CO} Rh_4(CO)_{12} + CO_2 + 2HCl \qquad (9)$$

We have observed the intermediate formation of an yellow product, possibly an intermediate of reaction (9), but unfortunately this compound was of so low stability that isolation was not possible.

Conversion of $Rh_4(CO)_{12}$ in $Rh_6(CO)_{16}$ takes place under several different conditions, and at present it is impossible to speculate generally about the mechanism of the reaction. Intermediate formation of a Rh_{12} cluster has been previously proved for synthesis in the presence of alkali acetates.[2]

Experimental Section

Synthesis of $Rh_6(CO)_{16}$ by reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide and water, with determination of liberated CO_2 and HCl. (a) A solution of $Rh_2(CO)_4Cl_2$[16] (2.84 g) in THF (25 ml) was saturated with carbon monoxide, water (1 ml) added and the mixture left standing for 30 days. The reaction flask was cooled to –70°, connected to another flask and then the whole evacuated in high vacuum. By gentle heating the volatile products were distilled into the second flask at –70°. After adding water, the hydrochloric acid which came over was titrated with 0.1 N NaOH (42.6 ml). The solid residue in the first flask was suspended in THF and the $Rh_6(CO)_{16}$ filtered off, washed and vacuum dried (0.747 g; 28% yield). *Anal.* Found.: C, 18.0. $Rh_6(CO)_{16}$ calcd.: C, 18.0. The ratio HCl: $Rh_6(CO)_{16}$ was 6.09.

(b) A solution of $Rh_2(CO)_4Cl_2$ (1.03 g) in methanol (25 ml) was saturated with carbon monoxide, water (2 ml) added, and the mixture left to stand for 48 hrs. The carbon monoxide was swept out with a stream of nitrogen and, after washing in water, reacted with an excess of 0.403 N baryta water (25 ml). The excess of alkali was titrated with 0.2 N HCl (42.65 ml). The $Rh_6(CO)_{16}$ was filtered off, washed and vacuum dried (0.28 g; 29.7% yield). The ratio CO_2: $Rh_6(CO)_{16}$ was 2.94.

Synthesis of $Rh_4(CO)_{12}$ by reduction of $Na[Rh(CO)_2Cl_2]$ with carbon monoxide in water. A solution of NaCl (0.102 g) in water (20 ml) was carefully saturated with carbon monoxide, and $Rh_2(CO)_4Cl_2$ (0.2032 g) added with vigorous stirring. After 24 hrs the red solid was filtered off, washed and dried in vacuum (0.093 g; 47.5% yield). *Anal.* Found: C, 19.64. $Rh_4(CO)_{12}$ calcd.: C, 19.2.

Synthesis of $Rh_4(CO)_{12}$ in n-hexane in the presence of $NaHCO_3$. A solution of $Rh_2(CO)_4Cl_2$ (2.07 g) in n-hexane (200 ml) in a 500 ml two necked flask was saturated with carbon monoxide and solid $NaHCO_3$ (1.1 g) added. The mixture was vigorously stirred for 24 hrs (incidental interruption of stirring lowered the yield). After filtering the solid residue was extracted with pentane (100 ml and the combined solution cooled to –70°. The $Rh_4(CO)_{12}$ was filtered off at –70° using a sintered glass filter, washed with a little iced pentane and vacuum dried (1.65 g; 82.5% yield). The residual solid was washed with water, when some $Rh_6(CO)_{16}$ (0.13 g; 7% yield) remained.

Synthesis of $Rh_6(CO)_{16}$ in alcohol in the presence of KOH. A 0.2 N KOH solution in methanol (13.1 ml, 2.62 mmoles) was slowly dropped over a period of two hrs into a solution of $Rh_2(CO)_4Cl_2$ (0.51 g, 1.31 mmoles) in methanol (25 ml) in a carbon monoxide atmosphere. After 48 hrs stirring the $Rh_6(CO)_{16}$ was filtered off, washed and vacuum dried (0.39 g; 83% yield). Isopropanol similarly gave a 84% yield in $Rh_6(CO)_{16}$.

Synthesis of $Rh_6(CO)_{16}$ from $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh(CO)_2Cl_2]^-$. A solution of $Rh_2(CO)_4Cl_2$ (0.022 g) in methanol (4 ml) was saturated with carbon monoxide and LiCl (0.01 g) added. By further addition of a solution of $Na_2[Rh_{12}(CO)_{30}]$[2] (0.106 g) in methanol (6 ml) there was formation of $Rh_6(CO)_{16}$ which, after 48 hrs, was filtered off, washed and vacuum dried (0,078 g; 62.8% yield).

Synthesis of $Rh_6(CO)_{16}$ in acqueous methanol in the presence of CH_3COOLi. A solution of $Rh_2(CO)_4Cl_2$ (0.5 g) in methanol (30 ml) was saturated with carbon monoxide, lithium acetate (0.4 g) and water (1 ml) added with vigorous stirring. The colour changed to violet and $Rh_6(CO)_{16}$ began to separate. After 24 hrs the $Rh_6(CO)_6$ was filtered off, washed and vacuum dried (0.35 g; 77.5% yield).

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(16) J. A. McCleverty and G. Wilkinson, *Inorg. Synth. 8*, 211 (1966).