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RHODIUM CARBONYL CLUSTER CHEMISTRY. SYNTHESIS AND CHEMICAL CHARACTERIZATION OF THE ANION $[Rh_6(CO)_{14}]^{4-}$

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Summary

The anion $[Rh_6(CO)_{14}]^{4-}$ has been isolated from the reaction of $[Rh_6(CO)_{16}]$ with alkali hydroxides in aqueous solution. It shows high reactivity towards electrophiles and in redox condensations with other rhodium clusters; and is rapidly decomposed by carbon monoxide.

Introduction

In an earlier communication on the synthesis of rhodium carbonyl cluster compounds [1] we briefly mentioned the existence of the anion $[Rh_6(CO)_{14}]^{4-}$ (I) (obtained by reaction of $[Rh_6(CO)_{16}]$ with aqueous alkali hydroxides), whose potassium salt was found to be isomorphous with the corresponding salt of $[Co_6(CO)_{14}]^{4-}$ [2]. However no details of the synthesis were given. We now provide these details, and describe the chemical characterization of the anion.

Results and discussion

Anion I can be prepared by reaction of $[Rh_6(CO)_{16}]$ with a concentrated solution of KOH (25–35% w/w) in water; rapid dissolution of the carbonyl is observed, followed by precipitation of the potassium salt of I as dark red fine crystals, according to the overall reaction 1.

$$Rh_6(CO)_{16} + 8\,OH^- \rightarrow [Rh_6(CO)_{14}]^{4-} + 2\,CO_3^{2-} + 4\,H_2O \qquad (1)$$

Reaction 1 occurs through the intermediate formation of the $[Rh_6(CO)_{15}]^{2-}$ anion, which is immediately reduced to the tetra-anion by the excess of OH^- ions present. A large amount of KOH is required both to create the strongly basic solution required to complete reaction 1 and to furnish the excess of K^+ ions necessary to precipitate the anion from the aqueous solution. Though anion I is sensitive to CO

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(see later), reaction 1 can be carried out either under nitrogen or under CO, probably due to the immediate precipitation of the potassium salt, which prevents further reaction. The mother liquor contains some brown by-products not yet characterized.

The hydrated potassium salt is separated from the mother liquor by filtration and washed with some methyl or ethyl alcohol. Good crystals can be obtained by redissolution in water and precipitation by saturation with KI or KBr. The crystalline potassium salt contains water of solvation which can be eliminated by prolonged pumping in vacuum; water of solvation is also partially removed from the crystals, which become opaque on the surface, by washing with anhydrous methanol, ethanol or 2-propanol. The potassium salt is soluble in water, moderately soluble in acetone and MeCN, sparingly soluble in methanol, and insoluble in THF, propan-2-ol, and aqueous saturated solutions of KBr or KI. The Cs and the tetramethylammonium salts can be obtained as fine powders by metathesis with CsCl or NMe_4Cl in water; the latter requires an excess of NMe_4Cl for the complete precipitation. The Cs salt is sparingly soluble in water, while the tetramethylammonium salt is moderately soluble; both these salts are insoluble in THF. All the salts of anion I are extremely sensitive to oxidation and decompose immediately in air, both in the solid state and in solution. The $[NMe_4]^+$ salt is sometimes pyrophoric.

The IR spectrum of the K salt in MeCN solution (Fig. 1) shows bands at 1899vs, 1735s, 1700(sh) and 1650(sh) cm^{-1} in agreement with the presence of terminal and triple bridging CO molecules; the small shoulder at 1950 cm^{-1} is probably due to

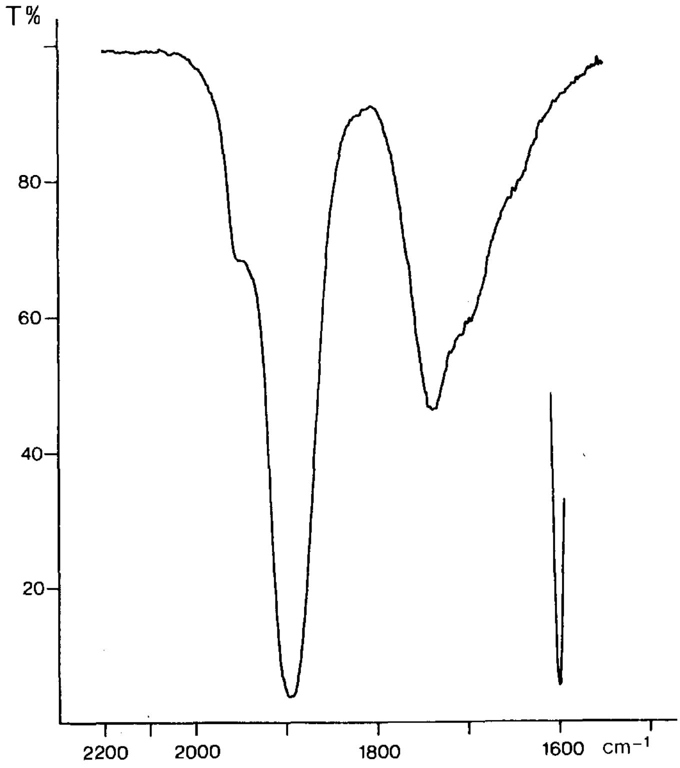

Fig. 1. The IR spectrum of $K_4[Rh_6(CO)_{14}]$ in acetonitrile solution.

traces of $[Rh_7(CO)_{16}]^{3-}$. This spectrum and the isomorphism of the hydrated potassium salt with the corresponding cobalt compound [2], indicate that I must have the same structure, i.e. an octahedron of Rh atoms bearing one terminal CO on every vertex and one triple bridging CO on every triangular face.

Because of the high negative charge, anion I is highly reactive towards electrophiles such as acids and the $[Rh(CO)_2(MeCN)_2]^+$ cation, and for the same reason it can readily undergo redox condensations with neutral or less charged rhodium carbonyl clusters. Acids at room temperature act simply as oxidants, with hydrogen evolution, and the nature of the products obtained depends on the H^+/I ratio. Thus, for instance, upon treatment of a MeCN solution of I with a strong acid in 1/2 molar ratio, $[Rh_6(CO)_{15}]^{2-}$ is mainly formed, while with an excess of acid $[Rh_6(CO)_{16}]$ is the main product. With an excess of a weak acid, such as CH_3COOH, $[Rh_{12}(CO)_{30}]^{2-}$ is formed. In all these reactions some unidentified by-products are formed due to partial decomposition.

With the $[Rh(CO)_2(MeCN)_2]^+$ cation there is ready condensation to give $[Rh_7(CO)_{16}]^{3-}$, according to eq. 2.

$$[Rh_6(CO)_{14}]^{4-} + [Rh(CO)_2(MeCN)_2]^+ \rightarrow [Rh_7(CO)_{16}]^{3-} + 2\ MeCN \qquad (2)$$

Examples of redox condensations with other Rh clusters are the reactions of I with $[Rh_6(CO)_{16}]$ or $[Rh_6(CO)_{15}]^{2-}$. Again the products depend on the molar ratio of the reactants. For instance, with $[Rh_6(CO)_{16}]$ in 1/1 molar ratio the anion $[Rh_6(CO)_{15}]^{2-}$ is formed according to eq. 3, while in 1/3 molar ratio the product is $[Rh_{12}(CO)_{30}]^{2-}$ as in eq. 4.

$$[Rh_6(CO)_{14}]^{4-} + [Rh_6(CO)_{16}] \rightarrow 2\ [Rh_6(CO)_{15}]^{2-} \qquad (3)$$

$$[Rh_6(CO)_{14}]^{4-} + 3\ [Rh_6(CO)_{16}] \rightarrow 2\ [Rh_{12}(CO)_{30}]^{2-} + 2\ CO \qquad (4)$$

Similarly anion I can react with $[Rh_6(CO)_{15}]^{2-}$ to give $[Rh_7(CO)_{16}]^{3-}$ according to eq. 5.

$$5\ [Rh_6(CO)_{15}]^{2-} + 2\ [Rh_6(CO)_{14}]^{4-} \rightarrow 6\ [Rh_7(CO)_{16}]^{3-} + 7\ CO \qquad (5)$$

It can be concluded that it is possible, through redox condensations of I with the appropriate Rh carbonyls or carbonyl anions, to generate all of the species observed as intermediates between the neutral rhodium carbonyls and I in the reduction sequences performed at room temperature [1,3].

Anion I is also more reactive towards CO than $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$; unlike these anions, which at atmospheric pressure react only at low temperature [3], anion I is completely decomposed in few minutes at room temperature to a mixture of $[Rh_4(CO)_{11}]^{2-}$ [4] and $[Rh(CO)_4]^-$, according to eq. 6.

$$[Rh_6(CO)_{14}]^{4-} + 5\ CO \rightarrow [Rh_4(CO)_{11}]^{2-} + 2\ [Rh(CO)_4]^- \qquad (6)$$

This behaviour is in agreement with the general trend observed in cluster chemistry that the reactivity towards CO increases at the increase of negative charge; this has been explained in terms of M–M and M–CO mean bond energies [5]; comparison of these energies in the Co and Rh clusters can also account for the different reactivity of the cobalt analogue $[Co_6(CO)_{14}]^{4-}$ which undergoes greater fragmentation, as previously observed for the $[Co_6(CO)_{15}]^{2-}$ and $[Rh_6(CO)_{15}]^{2-}$ anions [3]; furthermore, in the cobalt case the reaction is irreversible, whereas in the rhodium case reaction 6 can be easily reversed by simple elimination of the CO by evaporation to dryness in vacuum. Interestingly, close monitoring by IR of this reverse process reveals that it occurs stepwise, with the intermediate formation of a new compound at present under investigation.

Experimental

All the operations were carried out under oxygen-free nitrogen or carbon monoxide by the Schlenk tube technique. All the solvents were purified by standard methods and stored under nitrogen. $[Rh_6(CO)_{16}]$ was prepared by controlled pyrolysis of $[Rh_4(CO)_{12}]$ in heptane [6], and $[Rh_{12}(CO)_{30}]^{2-}$ as previously reported [7].

(1) Synthesis of $K_4[Rh_6(CO)_{14}]$

$[Rh_6(CO)_{16}]$ (341 mg) was stirred under nitrogen with a deaerated solution of KOH (5 g) in water (10 ml). A rapid dissolution of the carbonyl was observed, followed by formation of a brown-red crystalline precipitate of the potassium salt of the tetraanion; the reaction was complete in about half an hour. The precipitate was filtered off, washed twice with 5 ml of 2-propanol then six times with 5 ml of anhydrous ethanol (which caused the crystals to become opaque as result of partial loss of the water of solvation) and finally vacuum dried. Yields 70–80%. Larger crystals were obtained by dissolving the product from the filter disc with the minimum amount of water allowing the solution to pass directly into a saturated solution of KI in water, and leaving the resulting solution for several hours; the crystals which separated were filtered off, washed 3–4 times with a little methanol, and vacuum dried.

(2) Reaction of $[Rh_6(CO)_{14}]^{4-}$ with acids

$K_4[Rh_6(CO)_{14}]$ (107 mg, 0.091 mmol) was placed in a 15 ml flask equipped with a rubber septum, and dissolved in MeCN (6 ml); the solution was treated with *p*-toluenesulfonic acid 0.1 *M* in MeCN (1.8 ml, molar ratio 1/2). The solution quickly turned green, and the IR spectrum showed appearance of the characteristic absorptions of $[Rh_6(CO)_{15}]^{2-}$, together with minor amounts of $[Rh_7(CO)_{16}]^{3-}$ and other unidentified products. GLC analysis of the gaseous phase revealed the presence of the evolved hydrogen and of traces of CO. A similar reaction performed with an excess of the sulfonic acid caused precipitation of $[Rh_6(CO)_{16}]$, while use of excess of acetic acid gave $[Rh_{12}(CO)_{30}]^{2-}$ as the main product.

(3) Reaction of $[Rh_6(CO)_{14}]^{4-}$ with $[Rh(CO)_2(MeCN)_2]^+$

A solution of $K_4[Rh_6(CO)_{14}]$ (223 mg, 0.191 mmol) in MeCN (10 ml) under nitrogen, was treated dropwise with stirring with a solution of $[Rh(CO)_2(MeCN)_2]BF_4$ (0.0967 *M* in MeCN). The green solution obtained after addition of 2 ml (molar ratio Rh_6/Rh^+ 1/1), showed after a few minutes, the IR absorptions due to the presence of $[Rh_7(CO)_{16}]^{3-}$.

(4) Reaction of $[Rh_6(CO)_{14}]^{4-}$ with $[Rh_6(CO)_{16}]$ (molar ratio 1/1)

$K_4[Rh_6(CO)_{14}]$ (131 mg, 0.112 mmol) and $[Rh_6(CO)_{16}]$ (120 mg, 0.113 mmol) were stirred in MeCN (10 ml) under nitrogen to give within a few minutes a green solution showing the characteristic IR absorptions of the $[Rh_6(CO)_{15}]^{2-}$ anion.

(5) Reaction of $[Rh_6(CO)_{14}]^{4-}$ with $[Rh_6(CO)_{16}]$ (molar ratio 1/3)

$K_4[Rh_6(CO)_{14}]$ (84 mg, 0.072 mmol) and $[Rh_6(CO)_{16}]$ (230 mg, 0.216 mmol) in MeCN (7.5 ml) were stirred under nitrogen to give initially a green solution. After one day the colour had changed to violet, and the IR absorptions of the $[Rh_{12}(CO)_{30}]^{2-}$ anion were observed.

(6) Reaction of $[Rh_6(CO)_{14}]^{4-}$ with $[Rh_6(CO)_{15}]^{2-}$

$K_4[Rh_6(CO)_{14}]$ (84 mg, 0.072 mmol) and $[(PPh_3)_2N]_2[Rh_6(CO)_{15}]$ (366 mg, 0.173 mmol), in a molar ratio of 2.4/1, were stirred in MeCN (7.5 ml) under nitrogen, for one day to give a green solution showing the IR absorptions of $[Rh_7(CO)_{16}]^{3-}$.

(7) Reaction of $[Rh_6(CO)_{14}]^{4-}$ with CO

A solution of $K_4[Rh_6(CO)_{14}]$ in MeCN was stirred under CO at atmospheric pressure. After 10–15 minutes the brown-red solution turned orange-red and the IR spectrum showed complete disappearance of the starting product absorptions, which were replaced by new bands at 1942 and 1813 cm^{-1} due to $[Rh_4(CO)_{11}]^{2-}$ in MeCN, and at 1900 cm^{-1} due to $[Rh(CO)_4]^-$. Evaporation of this solution to dryness in vacuum and redissolution of the residue in MeCN, under N_2, regenerated the original tetra-anion along with only minor by-products. This reverse reaction occurs through the intermediate formation of a new product, which can be more satisfactorily obtained by briefly pumping in vacuum the solution obtained under CO and taking an IR spectrum under nitrogen of the red solution formed; the new product shows bands at 1910 and 1780 cm^{-1}.

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