

## SYNTHESIS AND CHARACTERISATION OF $[\text{Rh}_7(\text{CO})_{16}\text{X}]^{2-}$ ANIONS (X = Br, I)

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### Summary

The reaction of  $\text{Rh}_6(\text{CO})_{16}$  with an excess of tetraalkylammonium halides in tetrahydrofuran gives the heptanuclear  $[\text{Rh}_7(\text{CO})_{16}\text{X}]^{2-}$  anions (X = Br, I), which have been isolated and characterised. The same anions were obtained by condensation of the  $\text{Rh}_2(\text{CO})_4\text{X}_2$  carbonyl halides with the hexanuclear  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion, or by reaction of the  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  anion with iodine.

### Introduction

In earlier papers, the syntheses of the  $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$  anions (X = Cl, Br, I, CN, SCN, COOR, CONHR) was reported [1], and the analogous hydrido and acyl anions (X = H [1], COR [2]) were briefly mentioned. All these anions can be formally derived from  $\text{Rh}_6(\text{CO})_{16}$ , by replacement of a carbonyl group by an  $\text{X}^-$  ligand, but different reaction products were obtained using more severe conditions; this paper reports the preparation of the  $[\text{Rh}_7(\text{CO})_{16}\text{X}]^{2-}$  anions (X = Br, I) by use of long reaction times.

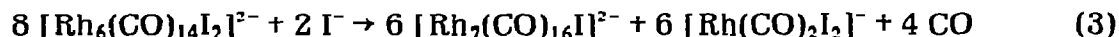
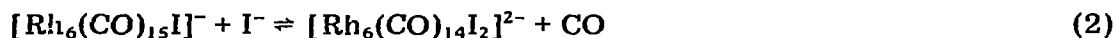
### Results and discussion

During some studies on the substitution reactions of  $\text{Rh}_6(\text{CO})_{16}$  with halide ions, it was observed [1] that initially this carbonyl reacts with tetraethylammonium iodide at  $50^\circ$  in THF to give  $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$  anion, as in eqn. 1.



However, after longer reaction times, following the appearance in the IR spectrum of some new absorption bands ( $\nu(\text{CO})$  2030s,  $1765\text{m cm}^{-1}$ ), probably due to an intermediate unstable anion such as  $[\text{Rh}_6(\text{CO})_{14}\text{I}_2]^{2-}$ , a solution of the

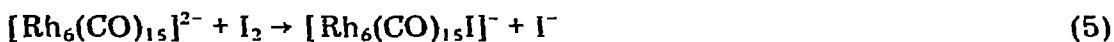
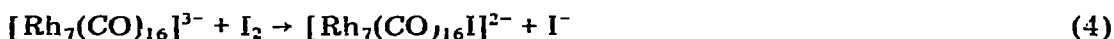
known  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  anion ( $\nu(\text{CO})$  2055s, 1985s  $\text{cm}^{-1}$ ) and a dark brown crystalline precipitate of  $[\text{NEt}_3]_2[\text{Rh}_7(\text{CO})_{16}\text{I}]$  were formed:



The same reactions were observed when  $\text{NEt}_3\text{Br}$  was used, and the crystalline product  $[\text{NEt}_3]_2[\text{Rh}_7(\text{CO})_{16}\text{Br}]$  was obtained.

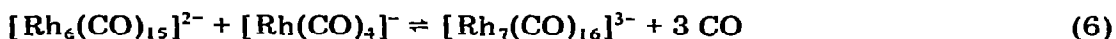
It is noteworthy that the reaction of  $\text{Rh}_6(\text{CO})_{16}$  with an excess of halide ion stops at the heptanuclear anions only when they separate out from the reaction mixture as they are formed. In solvents such as acetone, in which no precipitation occurs, the reaction proceeds further to give other brown anions, as yet unidentified, and thus the choice of the appropriate tetraalkylammonium halide and the solvent is very important. The best results were obtained using tetramethyl- or tetraethyl-ammonium halides in THF.

Attempts to isolate the intermediate  $[\text{Rh}_6(\text{CO})_{14}\text{X}_2]^{2-}$  anions from the reaction mixtures failed, which accords with the previously observed instability of these anions [1]. The heptanuclear nature of the  $[\text{Rh}_7(\text{CO})_{16}\text{X}]^{2-}$  anions was chemically confirmed by reaction 4, which is closely similar to the known [1]



reaction 5. This reaction with iodine is complicated by the concurrent formation of minor amounts of other products, probably due to oxidation reactions, but in the IR spectrum the absorption bands of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion are clearly distinguishable. The corresponding reaction with bromine is very complex, and no clear information could be obtained.

It was previously reported [3] that the heptanuclear  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  anion can be prepared by condensation of a seventh rhodium atom with the hexanuclear  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion as in eqn. 6, and it was of interest to extend this



synthetic scheme. In the present case, this could be done in two ways: (a) by the condensation of  $[\text{Rh}(\text{CO})_4]^-$  with the  $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$  anions, and (b) by the condensation of  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  with  $\text{Rh}_2(\text{CO})_4\text{X}_2$ .

In the first case, the reaction proceeds further, and the only result observed is the formation of the  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion as in eqn. 7. This is probably due to



the extremely high reducing power of the  $[\text{Rh}(\text{CO})_4]^-$  anion.

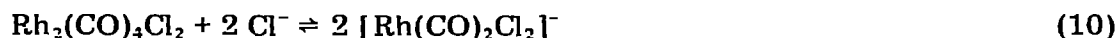
Procedure (b) effectively gives the expected products from both the bromo- and iodo-carbonyls (eqn. 8). This represents another interesting example



(X = Br, I)

of an increase in the cluster nuclearity by condensation of species in different oxidation states. The reaction gives a good yield in the case of the iodo derivative, while in the case of the bromo derivative some other by-products are present, in agreement with the lower stability of the bromo compound.

When rhodium carbonyl chloride is used in place of the bromide or iodide, an oxidation to the  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  anion is mainly observed, according to eqns. 9 and 10. The carbon monoxide required by reaction 9 probably comes



from minor decomposition processes. The existence of equilibrium 9 was confirmed by treatment of the  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  anion with a large excess of chloride ion. Under these conditions, the removal of the rhodium carbonyl chloride to give the stable  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$  anion is responsible for the disproportionation into  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  and  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ , along with minor amounts of other unidentified anions.

When  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  was treated with an excess of iodide ions, a similar reaction sequence was expected, but since equilibrium 8 lies to the right hand side, and since the carbon monoxide formed is eliminated from the system, the final result is that formation of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion still predominates.

The instability of the solutions of the  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  anion in the presence of halide ions agrees well with the observed reactivity of this anion towards other ligands such as carbon monoxide [4], and is an example of the rather common destruction of clusters by these non innocent ions.

#### *Characterisation of the $[\text{Rh}_7(\text{CO})_{16}\text{X}]^{2-}$ anions ( $X = \text{Br}, \text{I}$ )*

Both anions were obtained as the crystalline tetramethyl- and tetraethylammonium salts. These salts are soluble in acetone and acetonitrile, slightly soluble in THF and isopropanol, and insoluble in water. The corresponding tetrabutyl- and trimethylbenzyl-ammonium salts were obtained only as oils or powders, and are also soluble in THF. Solutions of all salts are unstable in air, while the crystals are stable for a few days. Thermogravimetric measurements show that the  $[\text{NEt}_4]_2[\text{Rh}_7(\text{CO})_{16}\text{I}]$  salt begins to decompose at about  $150^\circ$ .

Infrared spectra in acetonitrile in the carbonyl stretching region show absorptions at 2058m, 2018s, 1996m, 1777(sh) and 1763s  $\text{cm}^{-1}$  for the iodo compound, and at 2062m, 2018s, 1997m, 1774(sh) and 1767  $\text{cm}^{-1}$  for the bromo compound.

Figure 1 shows the IR spectrum of the iodo compound. The position of the terminal carbonyl absorption bands in the IR spectrum agrees well with that expected for a ratio of 0.286 between the negative charge and the number of metal atoms [5].

Figure 2 shows the structure of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion, which has been determined for the tetraethylammonium salt [6]. It consists of an irregular monocapped octahedron with 10 terminal, 2 edge-bridging and 4 face-bridging carbonyl groups. The iodine atom is in a bridging position on the edge of the tetrahedral unit, thus causing an excess of two electrons in the electronic

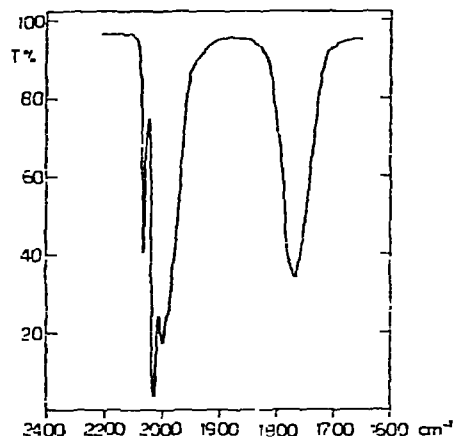


Fig. 1. Infrared spectrum of  $[\text{NEt}_4]_2[\text{Rh}_7(\text{CO})_{16}\text{I}]$  in  $\text{CH}_3\text{CN}$ .

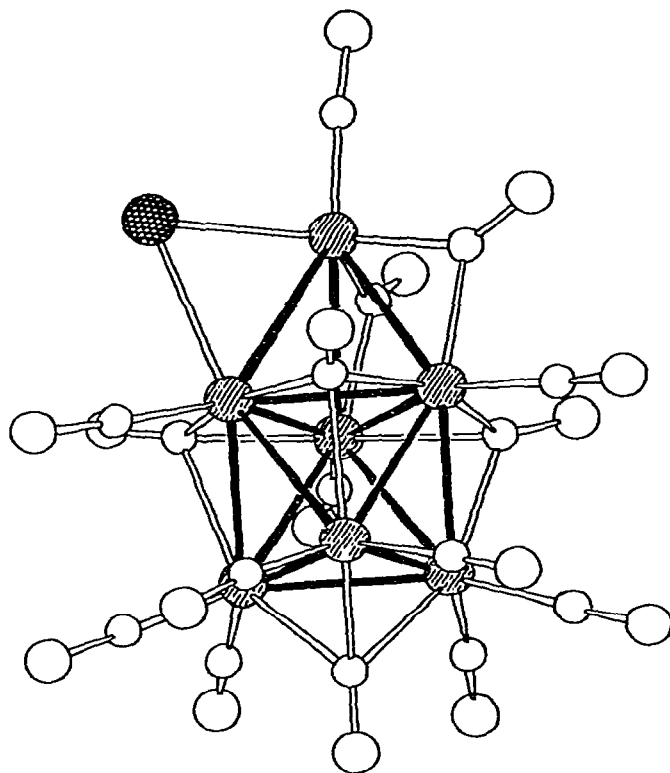


Fig. 2. The molecular structure of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  dianion.

situation with respect to that in the  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  anion. The effect of this two-electron excess on the metal-metal bond lengths in the cluster is discussed in more detail in another paper [6]. In acetonitrile solution the iodo compound reacts with carbon monoxide at atmospheric pressure, taking up about 2.8 moles of gas, while the IR spectrum changes completely, and new absorption bands appear at 2060w, 2025ms, 1992vs, 1820s and 1775s  $\text{cm}^{-1}$ , which do not belong to any known cluster species. The reaction is reversible, and flushing with nitrogen or precipitation with water gives back the starting compound almost quantitatively. The  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion reacts with iodine in acetonitrile solution to give, initially, a mixture of  $[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$  and  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ , and then a complete decomposition occurs to give a mixture of  $\text{Rh}_2(\text{CO})_4\text{I}_2$  and  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ .

The iodo compound is stable towards water in acetonitrile, while the bromo compound is unstable, and decomposes with predominant formation of the  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  anion; it is therefore necessary to operate in anhydrous media in the synthesis and manipulations of this anion. In the  $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$  series of anions only the chloro substituted species shows similar behaviour, and this indicates a marked decrease in stability for the heptanuclear dianions.

## Experimental

All solvents were purified and dried by the usual methods and stored under nitrogen. All operations were carried out under nitrogen. The analytical data were obtained as previously reported [1]. Infrared spectra were recorded on Perkin-Elmer model 457 or 621 spectrophotometers.

The  $[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$ ,  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ ,  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ ,  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  and  $[\text{Rh}(\text{CO})_4]^-$  anions, and  $\text{Rh}_6(\text{CO})_{16}$  were prepared as described previously [1, 3, 4, 7, 8].  $\text{Rh}_2(\text{CO})_4\text{Br}_2$  and  $\text{Rh}_2(\text{CO})_4\text{I}_2$  were prepared in low yields by reaction of  $\text{Rh}_4(\text{CO})_{12}$  [9] with HBr and HI.

(a) *Synthesis of  $[\text{NEt}_3]_2[\text{Rh}_7(\text{CO})_{16}\text{I}]$  from  $\text{Rh}_6(\text{CO})_{16}$ .*  $\text{Rh}_6(\text{CO})_{16}$  (1.07 g) in THF (30 ml) was stirred for 6 h at  $50^\circ$  with  $\text{NEt}_3\text{I}$  (2.57 g). The dark brown precipitate was filtered, washed with THF and water, and vacuum dried. This product was purified by dissolution in acetone, addition of isopropanol, and concentration under vacuum followed by filtration and vacuum drying. Yield 80%. Analysis found: I, 8.49; Rh, 47.07;  $\text{NEt}_3^+$ , 16.85.  $\text{C}_{32}\text{H}_{40}\text{IN}_2\text{O}_{16}\text{Rh}_7$  calcd.: I, 8.30; Rh, 47.15;  $\text{NEt}_3^+$  17.05%.

(b) *Synthesis of  $[\text{NEt}_3]_2[\text{Rh}_7(\text{CO})_{16}\text{Br}]$  from  $\text{Rh}_6(\text{CO})_{16}$ .*  $\text{Rh}_6(\text{CO})_{16}$  (1.43 g) in THF (25 ml) was stirred for 3 h at  $50^\circ$  with  $\text{NEt}_3\text{Br}$  (2.05 g). The precipitate was filtered, washed with THF and vacuum dried. This product was extracted with acetone (50 ml), and solution was treated with anhydrous isopropanol (30 ml) and concentrated in vacuum to about 50 ml volume. The precipitated product was filtered from the brown mother liquor and twice recrystallised from acetone-isopropanol. Yield 50%. Analysis found: C, 25.72; H, 2.77; N, 1.80; Rh, 47.21;  $\text{NEt}_3^+$ , 16.5.  $\text{C}_{32}\text{H}_{40}\text{BrN}_2\text{O}_{16}\text{Rh}_7$  calcd.: C, 25.47; H, 2.67; N, 1.85; Rh, 47.74;  $\text{NEt}_3^+$ , 17.26%.

(c) *Reaction of  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  with iodine.* To a stirred solution of  $[\text{NMe}_4]_3\text{Rh}_7(\text{CO})_{16}$  (0.069 g) in acetonitrile (4.5 ml) a solution of iodine (0.05 N) in acetonitrile was added dropwise. The green solution turned reddish-brown, and when the molar ratio  $[\text{Rh}_7(\text{CO})_{16}]^{3-}/\text{I}_2$  was 1/1, the IR spectrum showed the absorption bands characteristic of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion in addition to weak bands at 1965(sh) and  $1815\text{ cm}^{-1}$  of another unidentified anion.

(d) *Reaction of  $[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$  with  $[\text{Rh}(\text{CO})_4]^-$ .* A solution of  $\text{Na}[\text{Rh}(\text{CO})_4]$  (0.236 M) in THF was added dropwise to a stirred solution of  $[\text{NEt}_3][\text{Rh}_6(\text{CO})_{15}\text{I}]$  (0.140 g) in THF (7 ml). When the molar ratio  $[\text{Rh}(\text{CO})_4]^-/[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$  was 1/1 the IR spectrum showed the  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion absorption bands along with those of the unreacted  $[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$ , which disappeared completely when the molar ratio was 3/1, while the green solution showed the IR bands of the  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion at 2045w, 1980s, 1960ms and  $1765\text{ s cm}^{-1}$ , and a weak band of the  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  anion at  $1950\text{ cm}^{-1}$ .

(e) *Reaction of  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  with  $\text{Rh}_2(\text{CO})_4\text{I}_2$ .* To a stirred solution of  $[\text{NBu}_4]_2[\text{Rh}_6(\text{CO})_{15}]$  (0.157 g) in THF (8 ml) a solution of  $\text{Rh}_2(\text{CO})_4\text{I}_2$  (0.041 M) in THF was added dropwise. When the molar ratio between  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  and  $\text{Rh}_2(\text{CO})_4\text{I}_2$  was 1/0.5, the IR spectrum showed the characteristic absorption bands of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion at 2060m, 2018s, 1990m and  $1765\text{ s cm}^{-1}$ .

(f) *Reaction of  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  with  $\text{Rh}_2(\text{CO})_4\text{Br}_2$ .* This reaction was

performed as in (e): the IR spectrum showed the characteristic absorption bands of the  $[\text{Rh}_7(\text{CO})_{16}\text{Br}]^{2-}$  anion at 2060m, 2019s, 1990m and 1765  $\text{cm}^{-1}$  along with weak bands at 2050, 1980 and 1825  $\text{cm}^{-1}$ .

(g) *Reaction of  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  with  $\text{I}^-$ .* To a stirred solution of  $[\text{NBu}_4]_2[\text{Rh}_{12}(\text{CO})_{30}]$  (0.163 g) in THF (15 ml) a solution of  $\text{NBu}_4\text{I}$  (0.016 M) in THF was added dropwise with monitoring of the IR spectrum of the mixture. The addition was stopped when the molar ratio of  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  to  $\text{I}^-$  was 1/2, and after 3 h the IR spectrum showed the presence of the characteristic absorption bands of the  $[\text{Rh}_7(\text{CO})_{16}\text{I}]^{2-}$  anion with other weak bands at 2040, 1970, 1825 and 1800  $\text{cm}^{-1}$ .

(h) *Reaction of  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  with  $\text{Cl}^-$ .*  $\text{Cs}_2[\text{Rh}_{12}(\text{CO})_{30}]$  (0.030 g) was stirred at 25° with bis(triphenylphosphine)iminium chloride (PPNCl) (0.060 g) in THF (3 ml). After 2 h the violet solution turned green, while a small quantity of a brown precipitate mixed with the undissolved PPNCl was formed. The IR spectrum of the green solution showed bands at 2045w, 1980s, 1960ms, and 1765s  $\text{cm}^{-1}$  of the  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion, together with the bands at 2060w, and 1975w  $\text{cm}^{-1}$  of the  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$  anion, and at 1820w and 1970vw  $\text{cm}^{-1}$ .

The brown precipitate in acetonitrile solution showed IR bands at 1980-1950s(br) and at 1820ms  $\text{cm}^{-1}$ . Prolonging the reaction time causes the complete disappearance of the green  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  anion, which, after 12 h, was completely transformed into a mixture of the insoluble brown anions, while the solution contained only the  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$  anion and a trace of the brown anions.

## Acknowledgements

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