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# SYNTHESIS AND CHARACTERIZATION OF THE TETRANUCLEAR ANIONS $[Rh_4(CO)_{11}(COOCH_3)]^-$ AND $[Rh_4(CO)_{11}]^{2-}$

S. MARTINENGO, A. FUMAGALLI, P. CHINI *, V.G. ALBANO and G. CIANI

*Centro del C.N.R. per lo studio della sintesi e della stuttura dei composti dei metalli di transizione in basso stato di ossidazione, Via G. Venezian 21, 20133 Milano (Italy)*

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## Summary

The orange $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion has been produced by reaction of sodium methoxide, or anhydrous sodium carbonate, with $Rh_4(CO)_{12}$ in methanol. This anion reacts with potassium hydroxide to give the red $[Rh_4(CO)_{11}]^{2-}$ dianion, which can also be obtained directly from $Rh_4(CO)_{12}$ and potassium hydroxide. Both these anions have been isolated as pure bis(triphenylphosphine)-iminium salts. The carboalkoxy anion is very water sensitive, while the $[Rh_4(CO)_{11}]^{2-}$ dianion is air sensitive and reactive toward carbon monoxide. Both these anions react with $Rh_4(CO)_{12}$, to give $[Rh_6(CO)_{15}(COOCH_3)]^-$ and $[Rh_{12}(CO)_{30}]^{2-}$, respectively.

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## Introduction

We have studied rhodium carbonyls for many years, and have shown that under progressively more reducing conditions and in the presence of carbon monoxide a complex sequence of species containing various numbers of rhodium atoms is formed [1,2]:

$$\begin{tikzcd}
Rh_4(CO)_{12} \arrow[r] & {[Rh_{12}(CO)_{34}]^{2-}} \arrow[r] \arrow[d, shift left] & {[Rh_6(CO)_{15}]^{2-}} \arrow[r] & {[Rh_7(CO)_{16}]^{3-}} \\
 & {[Rh_{12}(CO)_{30}]^{2-} + CO} \arrow[u, shift left] & &
\end{tikzcd} \qquad (1)$$

We have also suggested a mechanism for the formation of the dodecanuclear anions by condensation of tetranuclear species [1]. We now describe the synthesis and characterization of the new $[Rh_4(CO)_{11}(COOCH_3)]^-$ and $[Rh_4(CO)_{11}]^{2-}$ anions, and the possible role of the latter in the formation of the dodecanuclear $[Rh_{12}(CO)_{30}]^{2-}$ dianion.

## Results

### *(a) Synthesis and characterization of the $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion*

$Rh_4(CO)_{12}$ reacts rapidly in methanol with stoichiometric amounts of sodium or magnesium methoxides to give orange red solutions of the carbomethoxy anion:

$$Rh_4(CO)_{12} + CH_3O^- \xrightarrow[CO,\ 25^\circ C]{CH_3OH} [Rh_4(CO)_{11}(COOCH_3)]^- \qquad (2)$$

The reaction is carried out under carbon monoxide in order to stabilize the product; under nitrogen more decomposition products are usually observed. The addition of a slight excess of sodium methoxide is not detrimental because it does not cause any further reaction; furthermore, the $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion is relatively stable in the presence of ten times the stoichiometric amount of methoxide, although in these conditions there is a slow decomposition to the green $[Rh_6(CO)_{15}]^{2-}$ anion, without infrared evidence of other intermediate species.

A similar reaction is also observed with EtONa in ethanol, and, more slowly, with i-PrONa in isopropanol: in both cases the IR spectra in the carbonyl stretching region are identical to those in methanol. No reaction was observed with $(i\text{-}PrO)_3Al$, probably because of the high degree of covalent character of this alkoxide.

The synthesis of the carbomethoxy derivative can also be readily carried out by reaction of $Rh_4(CO)_{12}$ in dry methanol with an excess of anhydrous sodium carbonate, or with the stoichiometric amount of tetraethylammonium

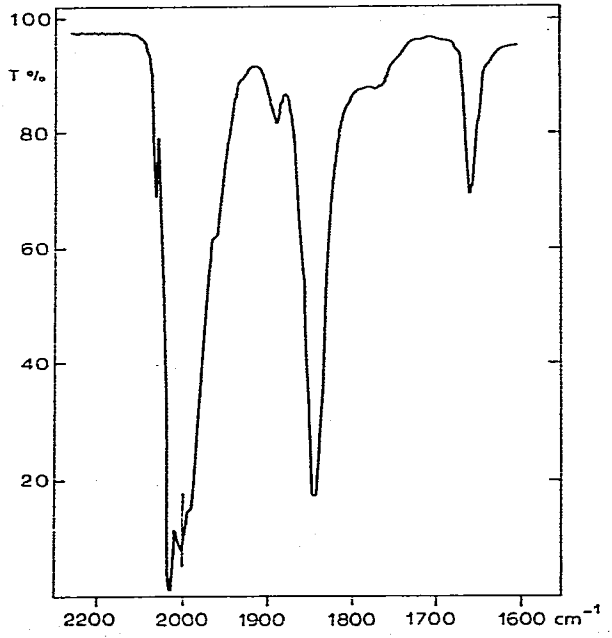


Fig. 1. Infrared spectrum of $[PPN][Rh_4(CO)_{11}(COOCH_3)]$ in THF.

carbonate under carbon monoxide:

$$2\,Rh_4(CO)_{12} + (NEt_4)_2CO_3 + 2CH_3OH \xrightarrow[CO,\ 25^\circ C]{CH_3OH} 2\,NEt_4[Rh_4(CO)_{11}(COOCH_3)] + H_2O + CO_2 \quad (3)$$

More generally, it has been observed by monitoring the IR spectra, that the tetranuclear carboalkoxy derivative is the first product formed when alkaline agents are treated with $Rh_4(CO)_{12}$ in alcoholic solution. This reaction has also been observed with KOH and sodium acetate. Owing to its high reactivity (see later), the isolation of the carboalkoxy anion by conventional techniques, such as precipitation by addition of aqueous solutions of tetraalkylammonium salts, rarely gives pure products. Nearly pure crystalline products were obtained from the methanolic solution of the sodium salt by addition of cobalticinium or bis(triphenylphosphine)iminium (PPN) chlorides at low temperature. These products however, still sometimes contain traces of the hexanuclear $[Rh_6(CO)_{15}(COOCH_3)]^-$ anion, which are very difficult to eliminate.

The IR spectrum of the PPN salt in THF solution (Fig. 1), shows carbonyl absorption bands due to terminal groups, (2075w, 2030vs, 2010s, 1995(sh) and 1965(sh) $cm^{-1}$), to bridging groups, (1892w and 1845s $cm^{-1}$) and to the carbomethoxy group (1655 $cm^{-1}$), while a weak band at 1785 $cm^{-1}$ indicates the presence of traces of the hexanuclear $[Rh_6(CO)_{15}(COOCH_3)]^-$ anion. This spectrum agrees with a structure derived from that of the $Rh_4(CO)_{12}$ by transformation of a terminal carbonyl group into a carbomethoxy group. The exact position at which this transformation occurs has not been determined, but it may involve the apical $Rh(CO)_3$ group. The presence of the carbomethoxy group is confirmed by an IR absorption band at 1040 $cm^{-1}$ (Nujol mull) due to the C—O—C group and, in the NMR spectrum of the PPN salt, (—20°C, $CD_3COCD_3$) by a singlet due to the methyl group ($\tau$ 6.77 ppm) with the correct intensity ratio (1 : 10) relative to the cation phenyl groups ($\tau$ 2.33 ppm).

All the salts isolated ($NMe_3$benzyl, $PPh_4$, PPN and $Co(\pi\text{-}Cp)_2$) are fairly soluble in THF; in methanol the solubility depends on the cation dimensions, and precipitation was observed only with $[Co(\pi\text{-}Cp)_2]Cl$ and [PPN]Cl. The PPN salt is also soluble in benzene or toluene, while other salts are not.

### *(b) Synthesis and characterization of the $[Rh_4(CO)_{11}]^{2-}$ anion*

The reaction of the $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion with alkali hydroxides gives the $[Rh_4(CO)_{11}]^{2-}$ dianion (eq. 4). The reaction is best carried out by

$$[Rh_4(CO)_{11}(COOCH_3)]^- + 3\,OH^- \rightarrow [Rh_4(CO)_{11}]^{2-} + CH_3OH + CO_3^{2-} + H_2O \quad (4)$$

adding a methanolic solution of $Na[Rh_4(CO)_{11}(COOCH_3)]$ dropwise into a concentrated solution of KOH and [PPN]OH in isopropanol. The product separated out immediately as red orange flakes, and this hinders further reaction.

Similarly the addition of a concentrated solution of $Rh_4(CO)_{12}$ in $CH_2Cl_2$ to the same solution of KOH and [PPN]OH in isopropanol gives a product containing significant amounts of the $[PPN]_2[Rh_4(CO)_{11}]$ salt. Because of the reactivity of the dianion towards $Rh_4(CO)_{12}$ (see later), this reaction is not as good as the first one, but it is important for understanding the mechanism of reduction of $Rh_4(CO)_{12}$:

$$Rh_4(CO)_{12} + 4\ OH^- \rightarrow [Rh_4(CO)_{11}]^{2-} + CO_3^{2-} + 2\ H_2O \qquad (5)$$

Substitution of [PPN]OH with [$NEt_4$]OH gives poorer yield: the precipitation is slower and the product is pyrophoric.

The PPN salt was crystallised from THF and isopropanol by the slow diffusion technique. It is soluble in THF and acetonitrile, but sparingly soluble in methanol and insoluble in isopropanol. The crystals are stable in air for hours, while the solution is immediately oxidized.

A subsequent X-ray investigation [3] has confirmed the analytical data and elucidated the structure of the anion, which is schematically depicted in Fig. 2. It consists of a distorted tetrahedron of rhodium atoms each bearing a terminal CO group; there are five bridging groups on five edges of the tetrahedron, and the remaining two on the sixth edge. The IR spectrum of the PPN salt in THF solution (Fig. 3) is consistent with such a structure, showing absorption bands due both to terminal (1930vs $cm^{-1}$) and bridging (1810s $cm^{-1}$) carbonyl groups, while the very weak band at 1984 $cm^{-1}$ is probably due to the presence of some $[Rh_6(CO)_{15}]^{2-}$.

### *(c) Chemical characterization of the $[Rh_4(CO)_{11}(COOCH_3)]^-$ and $[Rh_4(CO)_{11}]^{2-}$ anions: the formation of the $[Rh_6(CO)_{15}(COOCH_3)]^-$ and $[Rh_{12}(CO)_{30}]^{2-}$ species*

The $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion reacts with an excess of acids, such as $CH_3COOH$ or $H_2SO_4$ in methanol, to give $Rh_4(CO)_{12}$ (eq. 6). The solutions of

$$[Rh_4(CO)_{11}(COOCH_3)]^- + H^+ \xrightarrow{CH_3OH} Rh_4(CO)_{12} + CH_3OH \qquad (6)$$

the PPN salt in THF under carbon monoxide are stable for a few hours under anhydrous conditions at room temperature, and for some days at —10 to —15°C, but the addition of traces of water causes rapid decomposition to give mainly the $[Rh_{12}(CO)_{30}]^{2-}$ anion with other unidentified products.

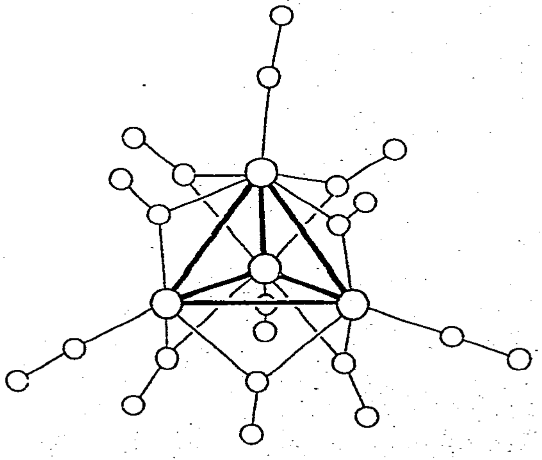


Fig. 2. Molecular structure of the $[Rh_4(CO)_{11}]^{2-}$ dianion.

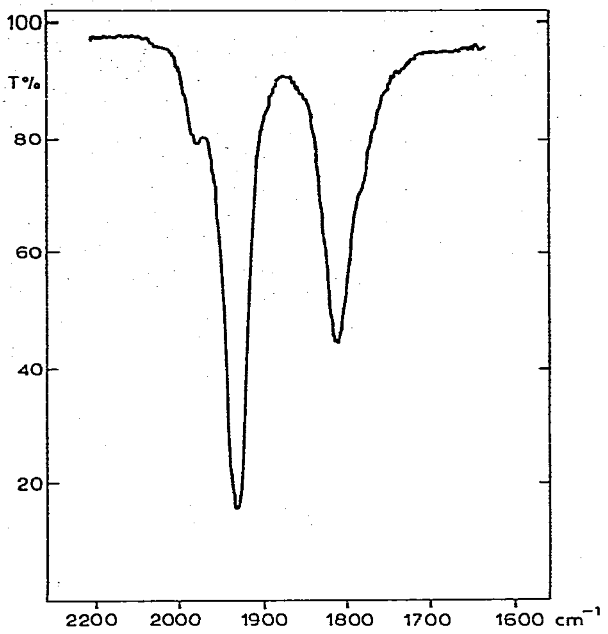


Fig. 3. Infrared spectrum of $[PPN]_2[Rh_4(CO)_{11}]$ in THF.

In methanol the stability of the $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion is higher; this is probably due to the following equilibrium [7]:

$$OH^- + CH_3OH \rightleftharpoons CH_3O^- + H_2O$$

and to the consequent continuous regeneration of the carbomethoxy species.

The condensation between the $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion and $Rh_4(CO)_{12}$ has been investigated in dry methanol under carbon monoxide by treating 3 mol of $Rh_4(CO)_{12}$ with only 2 mol of $CH_3ONa$, in order to leave 1 mol of $Rh_4(CO)_{12}$ for the subsequent condensation. A rapid formation of $Na[Rh_4(CO)_{11}(COOCH_3)]$ was observed, followed by the slow dissolution of the third mol of $Rh_4(CO)_{12}$, while the IR spectrum showed the progressive transformation into the hexanuclear $[Rh_6(CO)_{15}(COOCH_3)]^-$ anion, which was complete after 18 h:

$$\begin{tikzcd}[column sep=small] 3\,Rh_4(CO)_{12} + 2\,CH_3ONa \arrow[r, "\text{fast}"] & 2\,Na[Rh_4(CO)_{11}(COOCH_3)] + Rh_4(CO)_{12} \arrow[d, "\text{slow}"'] \\ & 2\,Na[Rh_6(CO)_{15}(COOCH_3)] + 4\,CO \end{tikzcd} \qquad (7)$$

The analogous reaction between the $[Rh_4(CO)_{11}]^{2-}$ anion and $Rh_4(CO)_{12}$ cannot be carried out under carbon monoxide, owing to the reactivity of this anion towards this reagent. A rapid degradation, represented by eq. 8, is indicated

$$2[Rh_4(CO)_{11}]^{2-} + CO \xrightarrow[1\text{ atm}]{25^\circ C} [Rh_6(CO)_{15}]^{2-} + 2\,[Rh(CO)_4]^- \qquad (8)$$

by the IR spectra. This reaction has been confirmed by $^{13}$C NMR spectroscopy at room temperature [8] while $^{13}$C NMR spectra indicate that at —70°C the reaction is as shown in eq. 9 [8] in agreement with the known behaviour of

$$5[Rh_4(CO)_{11}]^{2-} + 11\ CO \xrightarrow[-70^\circ C]{THF} [Rh_{12}(CO)_{\sim 34}]^{2-} + 8\ [Rh(CO)_4]^- \qquad (9)$$

$[Rh_6(CO)_{15}]^{2-}$ at this temperature [2]. Because of this degradation the reaction of $[Rh_4(CO)_{11}]^{2-}$ with $Rh_4(CO)_{12}$ has been studied under nitrogen in THF solution. The reaction is rapid, and its path depends on whether the $Rh_4(CO)_{12}$ is added to the $[Rh_4(CO)_{11}]^{2-}$ anion, or the latter is to the $Rh_4(CO)_{12}$. In the first case, the initial reaction which is observed upon addition of 0.5 mol of $Rh_4(CO)_{12}$, is the complete transformation of the $[Rh_4(CO)_{11}]^{2-}$ anion mainly into the $[Rh_6(CO)_{15}]^{2-}$ anion; this hexanuclear anion reacts further upon addition of 1.5 mol of $Rh_4(CO)_{12}$, to give the $[Rh_{12}(CO)_{30}]^{2-}$ anion, according to eq. 10.

$$[Rh_4(CO)_{11}]^{2-} \xrightarrow[(a)-2\ CO]{0.5\ Rh_4(CO)_{12}} [Rh_6(CO)_{15}]^{2-} \xrightarrow[(b)-3\ CO]{1.5\ Rh_4(CO)_{12}} [Rh_{12}(CO)_{30}]^{2-} \qquad (10)$$

In the second case, clean and apparently direct formation of $[Rh_{12}(CO)_{30}]^{2-}$ is observed (eq. 11).

$$2\ Rh_4(CO)_{12} + [Rh_4(CO)_{11}]^{2-} \rightarrow [Rh_{12}(CO)_{30}]^{2-} + 5\ CO \qquad (11)$$

In both cases, the evolved carbon monoxide also gives rise to the known equilibrium [1]:

$$[Rh_{12}(CO)_{30}]^{2-} + 4\ CO \rightleftharpoons [Rh_{12}(CO)_{\sim 34}]^{2-}$$

Finally the $[Rh_4(CO)_{11}]^{2-}$ dianion also reacts with $Rh_6(CO)_{16}$, to give the $[Rh_{12}(CO)_{30}]^{2-}$ species (eq. 12).

$$4\ Rh_6(CO)_{16} + 3[Rh_4(CO)_{11}]^{2-} \rightarrow 3[Rh_{12}(CO)_{30}]^{2-} + 7\ CO \qquad (12)$$

## Discussion

The $[Rh_4(CO)_{11}(COOCH_3)]^-$ and $[Rh_4(CO)_{11}]^{2-}$ anions differ in their reactivity towards carbon monoxide. The reactivity of the dianion is probably associated with a more favourable enthalpy variation, arising from an enhancement of the Rh—CO bond energy due to the presence of a second negative charge and increased back-donation [6]. It is interesting to note that the related clusters $[Rh_6(CO)_{15}(COOCH_3)]^-$ and $[Rh_6(CO)_{15}]^{2-}$ do not behave similarly, and at room temperature a similar degradation in the hexanuclear series occurs only for the $[Rh_6(CO)_{14}]^{4-}$ tetraanion [5], in which the ratio between the number of metal atoms and of negative charges (MA/NC) becomes even lower than in $[Rh_4(CO)_{11}]^{2-}$ dianion. A comparison between the chemical behaviour of the tetranuclear series (MA/NC values in brackets):

$Rh_4(CO)_{12}$ (—); $[Rh_4(CO)_{11}(COOCH_3)]^-$ (4); $[Rh_4(CO)_{11}]^{2-}$ (2)

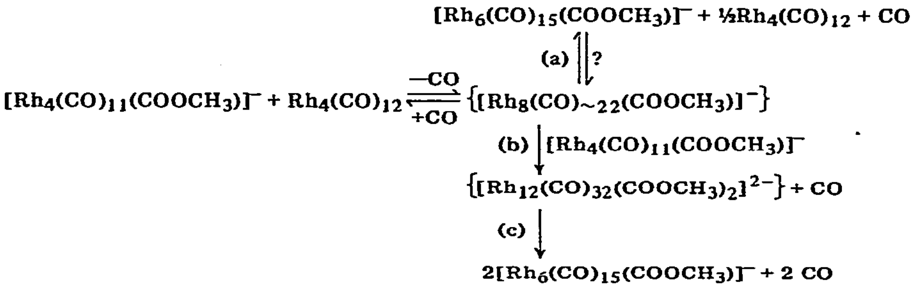
and the corresponding hexanuclear series [2,4,5]:

$Rh_6(CO)_{16}$ (—); $[Rh_6(CO)_{15}(COOCH_3)]^-$ (6); $[Rh_6(CO)_{14}(COOCH_3)_2]^{2-}$ (3);

$[Rh_6(CO)_{15}]^{2-}$ (3); $[Rh_6(CO)_{14}]^{4-}$ (1.5)

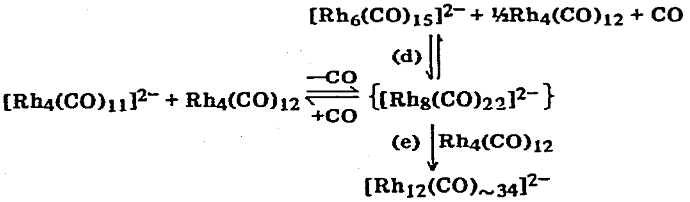
is in good qualitative agreement with the variation of MA/NC. Thus for example, the sensitivity to hydrolysis decreases in the series: $[Rh_6(CO)_{14}(COOCH_3)_2]^{2-} > [Rh_4(CO)_{11}(COOCH_3)]^- > [Rh_6(CO)_{15}(COOCH_3)]^-$ in keeping with the sequence of MA/NC. Also lack of evidence for a dicarboalkoxy species in the reaction of $[Rh_4(CO)_{11}(COOCH_3)]^-$ with an excess of methoxide ions contrasts with the reactivity of the $[Rh_6(CO)_{15}(COOCH_3)]^-$ anion [4], and can be related to that same factor. Finally, the sensitivity to oxidation by atmospheric oxygen also increases with a decrease in MA/NC. The redox condensation reactions [6] between the new tetranuclear anions and $Rh_4(CO)_{12}$ are particularly significant. The redox condensation 7 which proceeds with formation of a hexanuclear $[Rh_6(CO)_{15}X]^-$ species, is probably widespread, and can also explain the synthesis of $[Rh_6(CO)_{15}I]^-$ from $Rh_4(CO)_{12}$ and $I^-$ [4]. This condensation possibly involves an initial addition of $Rh_4(CO)_{12}$ to give an unstable octanuclear species which can be regarded as a reactive activated complex. Of the many possible reaction paths open to this intermediate, the simplest involve rearrangement to hexanuclear species with expulsion of a $Rh_2(CO)_6$ group (path a), or further reaction with another tetranuclear species present in solution to give a dodecanuclear species (paths b and c) (see Scheme 1).

SCHEME 1



Similar mechanisms can be proposed for the analogous redox condensation between the $[Rh_4(CO)_{11}]^{2-}$ dianion and $Rh_4(CO)_{12}$ (Scheme 2). Path d can explain the intermediate formation of $[Rh_6(CO)_{15}]^{2-}$ in reaction 10, while the path e can account for reaction 11. More complicated mechanisms are probably

SCHEME 2



involved in the redox condensation reactions 10b and 12, for which, at present, we have no simple explanation.

Finally the transformation of the $[Rh_4(CO)_{11}(COOCH_3)]^-$ anion into the $[Rh_{12}(CO)_{30}]^{2-}$ dianion in the presence of traces of water can be interpreted as resulting from disproportionation into $Rh_4(CO)_{12}$ and $[Rh_4(CO)_{11}]^{2-}$ according to the concurrent reactions 4 and 6 followed by condensation (eq. 11).

## Experimental

All the solvents were purified and dried by conventional methods, and stored under nitrogen. All operations were carried out under nitrogen or carbon monoxide. The analytical data were obtained as previously reported [1]. Infrared spectra were recorded on a Perkin—Elmer 457 spectrophotometer, and NMR spectra on a Varian NV-14 spectrometer. $Rh_4(CO)_{12}$ was prepared as previously described [9].

### *Synthesis of [PPN][Rh$_4$(CO)$_{11}$(COOCH$_3$)]*

All operations were carried out under carbon monoxide. A suspension of $Rh_4(CO)_{12}$ (0.72 g) and anhydrous $Na_2CO_3$ (0.36 g) in dry $CH_3OH$ (15 ml) was stirred until all the carbonyl had reacted (~15 min). The resulting dark red solution of the sodium salt was quickly filtered, to remove the excess of $Na_2CO_3$, the filtrate being collected on solid [PPN]Cl (2.5 g). After a short induction period crystallization started, and was completed by cooling to —70°C. The crystals were filtered off at this temperature, washed with cold methanol until free of [PPN]Cl, and vacuum dried. Yield: 60—70%. The product is best stored under CO. Analysis found: Rh, 32.93; PPN, 40.99. $C_{49}H_{33}NO_{13}P_2Rh_4$ calcd.: Rh, 31.25; PPN, 40.88%.

The cobalticinium salt can be obtained analogously by using a stoichiometric amount of $[Co(\pi\text{-}C_5H_5)_2]Cl$ in place of the excess of [PPN]Cl.

The trimethylbenzylammonium salt was obtained by adding the methanolic solution of the sodium salt, prepared as above from 0.5 g of $Rh_4(CO)_{12}$, dropwise to a stirred solution of $[NMe_3benzyl]Cl$ (1.5 g) in water (60—70 ml), filtering, washing with water and drying in vacuo. Analysis found: Rh, 44.0; $NMe_3$-benzyl, 15.82; CO, 33.10. $C_{23}H_{19}NO_{13}Rh_4$ calcd.: Rh, 44.31; $NMe_3$benzyl, 16.17; CO, 33.16%.

The tetraphenylphosphonium salt was obtained similarly.

### *Synthesis of [PPN]$_2$[Rh$_4$(CO)$_{11}$]*

A solution of $Na[Rh_4(CO)_{11}(COOCH_3)]$ prepared as above from $Rh_4(CO)_{12}$ (0.32 g) and $Na_2CO_3$ (0.3 g) in dry methanol (7 ml), was added dropwise with stirring under nitrogen into a solution of [PPN]OH and KOH obtained by dissolving [PPN]Cl (0.75 g) and KOH (2.5 g) in isopropanol (30 ml) and filtering off the precipitated KCl. The product separated out immediately as orange-red flakes, which were filtered, washed with isopropanol (2 × 10 ml), water (10 ml), then again with isopropanol (4 × 5 ml), and finally dried in vacuo. It was purified by extraction with THF (which leaves some oily material undissolved) followed by addition of isopropanol and concentration in vacuo to complete the precipitation. Yield: ~70%. Although this product still contains small amounts of the $[Rh_6(CO)_{15}]^{2-}$ dianion, which is also soluble in THF, it is sufficiently pure for most purposes. The solutions of the product in THF should be quickly used, as small amounts of the insoluble impurities are reformed on standing.

Because of the presence of these insoluble impurities, the analysis was carried out on a filtered THF solution, and gave a ratio PPN/Rh = 2.19 (calcd. 2.0).

*Reaction of $Na[Rh_4(CO)_{11}(COOCH_3)]$ with $Rh_4(CO)_{12}$*

A suspension of $Rh_4(CO)_{12}$ (0.221 g, ~0.3 × $10^{-3}$ *m*) in anhydrous methanol (10 ml), was treated under carbon monoxide with a 0.2 *M* solution of $CH_3ONa$ in methanol (1 ml). There was an immediate reaction to give a mixture of $Na[Rh_4(CO)_{11}(COOCH_3)]$ and unreacted $Rh_4(CO)_{12}$ followed by a slow complete transformation into the brown $[Rh_6(CO)_{15}(COOCH_3)]^-$ anion, as shown by the progressive increase of the IR bands characteristic of the hexanuclear species at 2085w, 2045vs, 2020w, 1825w, 1785s and 1620w $cm^{-1}$.

*Reaction of $[Rh_4(CO)_{11}]^{2-}$ with $Rh_4(CO)_{12}$*

*Addition of $[Rh_4(CO)_{11}]^{2-}$ to $Rh_4(CO)_{12}$.* A solution of $[PPN]_2[Rh_4(CO)_{11}]$ (0.129 g, 0.72 × $10^{-4}$ *m*) in THF (7.4 ml), was dropped into a stirred solution/suspension of $Rh_4(CO)_{12}$ (0.107 g, 1.43 × $10^{-4}$ *m*) in THF (5 ml). The IR spectra showed the progressive disappearance of the $Rh_4(CO)_{12}$ bands and the parallel appearance of the characteristic bands of the violet $[Rh_{12}(CO)_{30}]^{2-}$ dianion at 2070mw, 2055 and 2045vs, 2035(sh), 2010m and 1770s $cm^{-1}$. During the reaction there was some formation of $Rh_6(CO)_{16}$, due to the decomposition of $Rh_4(CO)_{12}$; this seems to be accelerated by the $[Rh_{12}(CO)_{30}]^{2-}$ anion, which probably acts as an intermediate reversible CO acceptor.

*Addition of $Rh_4(CO)_{12}$ to $[Rh_4(CO)_{11}]^{2-}$.* A solution of $Rh_4(CO)_{12}$ (0.047 g) in THF (20 ml) was slowly added dropwise to a stirred solution of $[PPN]_2$-$[Rh_4(CO)_{11}]$ (0.057 g) in THF (5 ml), the reaction being monitored by means of IR spectra, When the ratio between $Rh_4(CO)_{12}$ and $[Rh_4(CO)_{11}]^{2-}$ was 0.5 : 1, the $[Rh_4(CO)_{11}]^{2-}$ dianion had completely disappeared, while the spectrum of the green-black solution showed the characteristic bands of the green $[Rh_6(CO)_{15}]^{2-}$ dianion at 2050vw, 1990(sh), 1984s, 1960m, 1790w and 1767ms $cm^{-1}$ and a trace of the $[Rh_{12}(CO)_{30}]^{2-}$ dianion. The further addition of $Rh_4(CO)_{12}$ caused the progressive transformation of the green $[Rh_6(CO)_{15}]^{2-}$ dianion into the dodecanuclear $[Rh_{12}(CO)_{30}]^{2-}$ violet dianion, which was complete when the ratio was 2 : 1.

*Reaction of $[Rh_4(CO)_{11}]^{2-}$ with carbon monoxide*

A solution of $[PPN]_2[Rh_4(CO)_{11}]$ (0.077 g) in THF (5 ml) was stirred under carbon monoxide at 28°C. The orange-red solution slowly turned green, while the IR spectra showed a progressive transformation into a mixture of the green $[Rh_6(CO)_{15}]^{2-}$ dianion and the colourless $[Rh(CO)_4]^-$ anion (1898 $cm^{-1}$); this was complete after 24 h at this temperature (or after 4 h at 40°C).

*Reaction of $[Rh_4(CO)_{11}]^{2-}$ with $Rh_6(CO)_{16}$*

To a suspension of finely powdered $Rh_6(CO)_{16}$ (0.072 g) in THF (5 ml) under nitrogen was added dropwise, with stirring, a solution of $[PPN]_2[Rh_4(CO)_{11}]$

(96% purity) (0.095 g) in THF (6.3 ml). The IR spectra taken during the addition showed the progressive formation of the $[Rh_{12}(CO)_{30}]^{2-}$ dianion, which was complete at the end of the addition, when all the $Rh_6(CO)_{16}$ had reacted to give a clear violet solution of the dodecanuclear species.

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