New Rhodium Carbonyl Cluster Compounds

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Summary Chemical evidence is presented for the existence of the anions $[Rh_7(CO)_{16}]^{3-}$, $[Rh_6(CO)_{14}]^{4-}$, and $[Rh_3(CO)_{10}]^{-}$.

TETRACARBONYL-μ-DICHLORODIRHODIUM is reduced by carbon monoxide and water to $Rh_4(CO)_{12}$[1] and in the presence of alkali there is further reduction to carbonylrhodates; similar reduction products have been also obtained using alkali metals in tetrahydrofuran (THF). Reduction is very complicated, the products so far isolated and characterised being:

$$Rh_2(CO)_4Cl_2 \xrightarrow[H_2O]{CO} \underset{\text{orange}}{Rh_4(CO)_{12}} \xrightarrow[OH^-]{CO} \underset{\text{violet}}{[Rh_{12}(CO)_{30}]^{2-}} \xrightarrow[OH^-]{CO}$$

$$\longrightarrow \underset{\text{dark-green}}{[Rh_7(CO)_{16}]^{3-}} \xrightarrow[OH^-]{CO} \underset{\text{dark-red}}{[Rh_6(CO)_{14}]^{4-}} \xrightarrow[Na]{CO} \underset{\text{colourless}}{[Rh(CO)_4]^-}$$

Infrared spectra recorded during reduction support an extended version of the above scheme, indicating a much more complex reaction sequence giving rise to other intermediates as yet incompletely characterised.

Anions $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh(CO)_4]^-$ have been previously characterised:[2,3] we now present chemical evidence for the existence of the anions $[Rh_7(CO)_{16}]^{3-}$, $[Rh_6(CO)_{14}]^{4-}$, and $[Rh_3(CO)_{10}]^-$. The last anion was not included in the reaction scheme, because its relative position is still unclear.

The salt $K_3[Rh_7(CO)_{16}]$ could be obtained by slow reduction of $Rh_2(CO)_4Cl_2$ with an excess of KOH in aqueous alcohol in the presence of carbon monoxide:

$$7\,Rh_2(CO)_4Cl_2 + 20\,KOH + 14\,CO \rightarrow$$
$$2\,K_3[Rh_7(CO)_{16}] + 10\,CO_2 + 14KCl + 10\,H_2O$$

The same anion was obtained by reaction between wet morpholine and $Rh_4(CO)_{12}$, when some morpholine carbonate was isolated, thus proving the reducing agent to be carbon monoxide. The dark-green anion was precipitated as the tetramethyl-, tetraethyl-, or trimethylbenzylammonium salt and then recrystallised from water–acetone. Analyses agreed with the formula $[Rh_7(CO)_{16-17}]^{3-}$, the precise number of carbonyl groups being obtained by *X*-ray analysis.[4] The n.m.r. spectra lacked any Rh–H signal, and the i.r. spectrum had stretching carbonyl bands at 1990w, 1950s, 1820w, 1770s, 1740sh, and 1720sh cm.$^{-1}$ (MeCN solution) in agreement with the presence both of terminal and bridging carbonyl groups. The existence of the unusual seven metal-atom cluster $[Rh_7(CO)_{16}]^{3-}$ indicates the possibility of other related new types of clusters.

On account of ease of reduction and difficulty in separating the intermediate compounds formed in the reduction sequence we prepared the $[Rh_6(CO)_{14}]^{4-}$ anion using a more specific reaction. The salt $K_4[Rh_6(CO)_{14}]$ was obtained as dark-red crystals by reacting 30% aqueous potassium hydroxide with $Rh_6(CO)_{16}$ in carbon monoxide. The corresponding cesium and tetramethylammonium salts were prepared by metathesis. They were extremely sensitive to air oxidation and completely consistent analytical data could not be obtained. The formula $[Rh_6(CO)_{14}]^{4-}$ was deduced from *X*-ray studies[5] which showed the potassium salt to be isomorphous with the analogous $K_4[Co_6(CO)_{14}]6H_2O$.[6] The solid potassium salt had stretching carbonyl bands at 1970w, 1945sh, 1892s, 1725s, and 1665s cm.$^{-1}$ (Nujol mull).

Crystals of $K[Rh_3(CO)_{10}]$ and $[NMe_3(C_7H_7)][Rh_3(CO)_{10}]$ were obtained as a by-product in the preparation of the $[Rh_7(CO)_{16}]^{3-}$ anion. Analyses were satisfactory and i.r. spectrum had stretching carbonyl bands at 2030w, 1993s, 1883m, 1843s, and 1831s cm.$^{-1}$ (THF solution). At present there is no satisfactory method of synthesizing derivatives of this yellow anion.

Compounds $Rh_4(CO)_{11}(PPh_3)$ (red), $Rh_4(CO)_{10}(PPh_3)_2$ (dark-red), and $Rh_4(CO)_9(PPh_3)_3$ (brownish red) have now been prepared by reacting $Rh_4(CO)_{12}$ with a stoicheiometric amount of triphenylphosphine in THF. These crystalline compounds were stable in air and had i.r. spectra analogous to those of the homologous compounds $Co_4(CO)_{11}(PPh_3)$,[7] $Ir_4(CO)_{10}(PPh_3)_2$,[8] and $Ir_4(CO)_9(PPh_3)_3$.[8]

We thank Prof. L. Malatesta and Dr. V. Albano for their interest in the work and the CNR for financial support.

(*Received, July 25th*, 1969; *Com.* 1125.)

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