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Synthesis of Rhodium Carbonyl Compounds at Atmospheric Pressure. I. Synthesis and Properties of Derivatives of the Tetracarbonylrhodate (-1) Anion

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The alkali salts of the $[Rh(CO)_4]^-$ anion have been obtained by reacting an alkali metal (Li, Na) with a tetrahydrofuran solution of $Rh_2(CO)_4Cl_2$ in the presence of carbon monoxide. In the solid state they are unstable at room temperature. The tetramethylammonium and the tris(o-phenantroline)nickel(II) salts are more stable; they have been obtained by double decomposition and characterized analitically. It has not been possible to obtain any evidence for the existence of either $HRh(CO)_4$ or $Rh_2(CO)_8$. Reaction of $[Rh(CO)_4]^-$ derivatives with acids did not yield the expected $HRh(CO)_4$ and $Rh_2(CO)_8$. $Rh_4(CO)_{12}$ was transformed into $Rh_6(CO)_{16}$ under the experimental conditions reported in the literature for synthesis of $Rh_2(CO)_8$ from rhodium metal and carbon monoxide (220°/500 atm.).

Introduction

The chemistry of the rhodium carbonyls has not so far been thoroughly studied. In 1943 Hieber and Lagally[1] reported the preparation of $HRh(CO)_4$, $Rh_2(CO)_8$, $[Rh(CO)_3]_n$ and $Rh_4(CO)_{11}$ and claimed the characterization of them all by analysis. Later X-ray diffraction studies showed the last two compounds to be $Rh_4(CO)_{12}$ [2] and $Rh_6(CO)_{16}$. [3] They have been more recently obtained using improved methods of synthesis,[4,5,6,7] while complete chemical characterization is proceeding.[7]

Regarding $HRh(CO)_4$ and $Rh_2(CO)_8$ the situation is more unsatisfactory, despite the fact that hese compounds are of great interest due to the extreme high activity of rhodium carbonyls for the oxo process.[8] After the original preparation[1] only a very recent pubblication has mentioned these compounds, where the formulas were assigned to substances obtained in such small amounts that only general characterization by infrared spectroscopy was reported.[4]

The high stability of many salts of the tetracarbonylcobaltate(−1) anion, which, generally, are more stable than $HCo(CO)_4$ and $Co_2(CO)_8$, has prompted us to attempt to synthesize the analogous rhodium salts. The isolation of tetracarbonylrhodates might make possible further transformation into $HRh(CO)_4$ and $Rh_2(CO)_8$ and might therefore contribute to solution of the problem of better characterisation of these latter.

Results and Discussion

Synthesis and properties of salts of the tetracarbonylrhodate(−1) anion. Reduction of a tetrahydrofuran solution of $Rh_2(CO)_4Cl_2$ in the presence of carbon monoxide is a complicated reaction in which many progressively reduced carbonylrhodates are formed, some of which are being studied by X-ray diffraction.[9] With alkali metals the final product is a colourless anion which can also be obtained by reducing $Rh_4(CO)_{12}$ or $[Rh_{12}(CO)_{30}]^{2-}$ derivatives[10]. With sodium or lithium the reduction is slow and requires several days at room temperature; with potassium not only is reduction slow, but the yields are also very low, probably because of inadequate solubility of some intermediate carbonylrhodate.

Evaporation at room temperature gives white solids which in a vacuum darken and decompose rapidly. They are probably solvates such as $[Na(THF)_n][Rh(CO)_4]$, decomposing when the tetrahydrofuran (THF) bonded to the alkali metal is removed. Evaporation at −10° has given the solvate of the sodium salt as white crystals melting with decomposition at about 0°.

An analogous thermal decomposition is known for lithium tetracarbonylcobaltate(−1), the other alkali salts, in this case, being stable. The decomposition is effected by evaporating the solvent diethylether.[11] It seems probable that it is due to acidity of the alkali cation: when such acidity is not preferentially satisfied by the solvent it should operate on the oxygen atoms of the carbonyl groups bonded to the anion, and this interaction may lead to decomposition.

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The solvate $[Na(THF)_n][Rh(CO)_4]$ is not only thermally unstable, but also very sensitive to hydrolysis and to oxidation by air. It has been dissolved in ice water and rapidly precipitated by adding a tetraalkylammonium salt or tris(*o*-phenantroline)nickel(II) chloride. Tetramethylammonium tetracarbonylrhodate is a white crystalline solid, stable up to about 100° and moderately soluble in water. Tris(*o*-phenantroline)nickel(II) tetracarbonylrhodate is a yellow solid, stable in the solid state, but slowly decomposing in solution; like the tetracarbonylcobaltate[12] the solid is moderately resistant to air oxidation.

The tetracarbonylrhodate(−1) anion is a strong reducing agent; *e.g.* mercury(II) chloride is immediately reduced to mercury metal and $Rh_4(CO)_{12}$ to cluster carbonylrhodates.[13] In solution the low stability of the tris(*o*-phenantroline)nickel(II) salt is probably due to slow reduction of the cation; a related reduction of nickel(II) salts has been reported using $[Co(CO)_4]^-$ derivatives.[14]

Figure 1 shows the great similarity between the infrared spectra of THF solutions of sodium tetracarbonylrhodate and tetracarbonylcobaltate. The presence of several bands in the carbonyl stretching region in a THF solution of $Na[Co(CO)_4]$ was previously observed by Edgell and ascribed to loss of the tetrahedral symmetry through formation of ion pairs.[15] Great similarity between infrared spectra is also found with $Co_4(CO)_{12}$ [24] and $Rh_4(CO)_{12}$,[7] and for $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$.[16] In all these cases the rhodium compounds absorb at slightly higher frequencies (10-20 cm^{-1}) indicating less back-donation from rhodium to carbon monoxide.

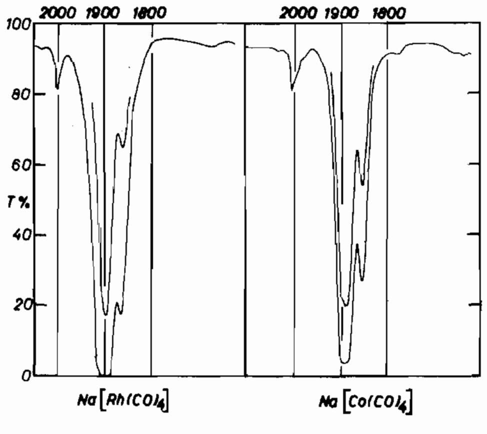

Figure 1. Infrared spectra of $Na[Co(CO)_4]$ and $Na[Rh(CO)_4]$ in THF solution in the carbonyl stretching region. (Registered on a Perkin Elmer 457 spectrophotometer.)

Comparison between these analogous cobalt and rhodium carbonyl derivatives shows that the chemical stability, which is related both to thermal and chemical resistance, varies in opposite ways for the two metals, the arrows below denoting increasing stability:

←

$Na[Co(CO)_4]$	$Co_4(CO)_{12}$	$Co_6(CO)_{16}$
$Na[Rh(CO)_4]$	$Rh_4(CO)_{12}$	$Rh_6(CO)_{16}$

→

In the cobalt series the more stable compound is $Na[Co(CO)_4]$, but in the rhodium one it is $Rh_6(CO)_{16}$. Moreover $Rh_6(CO)_{16}$ is much more stable than $Co_6(CO)_{16}$, while $Na[Co(CO)_4]$ is much more stable than $Na[Rh(CO)_4]$. This behaviour reflects on the one hand strenghtening of the metal-metal bonds, and from the other parallel loss of back-donation capacity.

Attempted syntheses of $HRh(CO)_4$ and of $Rh_2(CO)_8$. It has been reported that the yellow $HRh(CO)_4$ decomposes slightly over its melting point (−10°/−12°), giving the orange $Rh_2(CO)_8$ decomposing at 76°.[1] Therefore reaction between acids and tetracarbonylrhodates would be expected to give different products depending on temperature. Moreover it has been reported that water, acids and bases decompose $Rh_2(CO)_8$ immediately with gas evolution,[1] and these substances would be expected to give rise to different derivatives.

Several experiments run at room temperature in the presence of excess acid (exps 1 to 4 in Table I) confirm these results. More surprisingly we failed to obtain $HRh(CO)_4$ even at low temperature (exps 5 to 7 in Table I). Concentrated phosphoric acid (85%) at −25° gave $Rh_4(CO)_{12}$, and the stoichiometric amount of hydrochloric acid gave cluster carbonylrhodates at −50°. In no case was it possible to detect the expected products, nor did we observe the characteristic smell of hydrocarbonyl reported by Hieber and Lagally,[1] and well known for $HCo(CO)_4$.

Owing to the probable high reactivity of $HRh(CO)_4$ and $Rh_2(CO)_8$ these experiments cannot be considered conclusive and we sought other independent evidence. The behaviour of the analogous cobalt compounds immediately suggests the equilibria:

$$2\ HRh(CO)_4 \rightleftarrows Rh_2(CO_8 + H_2 \qquad (1)$$

$$2\ Rh_2(CO)_8 \rightleftarrows Rh_4(CO)_{12} + 4\ CO \qquad (2)$$

$$3\ Rh_4(CO)_{12} \rightleftarrows 2\ Rh_6(CO)_{16} + 4\ CO \qquad (3)$$

In the case of cobalt reactions (1) and (2) are reversed even at moderate temperature (< 100°),[17,18] and formation of $Co_4(CO)_{12}$ by reaction between carbon monoxide and $Co_6(CO)_{16}$ is known qualitatively.[16] On the other hand in the case of rhodium equilibria (2) and (3) are pratically irreversible under pressure at 25°-100° as the experiments of Table II show. Despite the high carbon monoxide pressure a partial transformation of $Rh_4(CO)_{12}$ into $Rh_6(CO)_{16}$ is observed even at 70°/360 atm in n-heptane (exp. 3), and complete conversion occurs at 120°/420 atm (exp. 4). This behaviour corresponds to slow irreversible decomposition of $Rh_4(CO)_{12}$ at moderate temperature.

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Table I. Study of the reaction between tetracarbonylrhodates and acids.

Exp. n°	Starting salt	Acid	Temp. C°	Solvent	Reaction product
1	$Na(THF)_n$	HCl 2 N	25	water	$Rh_4(CO)_{12}$
2	$Na(THF)_n$	H_3PO_4	0	water[a]	$Rh_4(CO)_{12}$
3	$N(CH_3)_4$	p.toluene sulphonic	25	toluene	$Rh_4(CO)_{12}$
4	$N(CH_3)_4$	CH_3COOH	25	THF	cluster carbonylrhodates
5	$Na(THF)_n$	H_3PO_4(85%)	–25	—	$Rh_4(CO)_{12}$
6	$N(CH_3)_4$	HCl[b]	–50	THF	cluster carbonylrhodates[c]
7	$N(CH_3)_4$	HCl[d]	–70	—	cluster carbonylrhodates

[a] In a carbon monoxide atmosphere. [b] Stoichiometric amount. [c] By infrared analysis at –50°. [d] In the presence of carbon monoxide.

Table II. Behaviour of $Rh_4(CO)_{12}$ and of $Rh_6(CO)_{16}$ to carbon monoxide pressure.

Exp.n°	Starting carbonyl	Solvent	Temp. C°	CO pressure atm[a]	H_2 pressure	Reaction time hrs	Reaction product
1	$Rh_4(CO)_{12}$	n-heptane	25	300	—	48	$Rh_4(CO)_{12}$
2	$Rh_4(CO)_{12}$	—	25	300	50	72	$Rh_4(CO)_{12}$
3	$Rh_4(CO)_{12}$	n-heptane	70	360	—	24	$Rh_4(CO)_{12}$ + + $Rh_6(CO)_{16}$
4	$Rh_4(CO)_{12}$	n-heptane	120	420	—	24	$Rh_6(CO)_{16}$
5	$Rh_4(CO)_{12}$	—	220	535	—	20	$Rh_6(CO)_{16}$
6	$Rh_6(CO)_{16}$	toluene	70	365	—	24	$Rh_6(CO)_{16}$
7	$Rh_6(CO)_{16}$	toluene	100	135	—	6	$Rh_6(CO)_{16}$ [b]
8	$Rh_6(CO)_{16}$	toluene	170	110	30	4	$Rh_6(CO)_{16}$ [b]

[a] At the temperature of reaction. [b] Along with traces of unidentified products.

Hence it seems improbable that Hieber and Lagally obtained $HRh(CO)_4$ and $Rh_2(CO)_8$ at high temperature and pressure (200°-220°/500 atm), but nevertheless we reacted $Rh_4(CO)_{12}$ with carbon monoxide under the conditions reported for synthesis of $Rh_2(CO)_8$ from rhodium metal and carbon monoxide. Only $Rh_6(CO)_{16}$ was obtained at 220°/535 atm, showing once more that this is the stable phase at high temperature; a fact in accord with the results obtained in other laboratories, where it has not been possible to reproduce the original preparation of $Rh_2(CO)_8$.[8,19,20,25]

It is now perfectly clear that $Rh_2(CO)_8$, if it exists, is not stable under the high temperature conditions reported for its synthesis; and that it is not obtained either starting from $Rh_4(CO)_{12}$ and carbon monoxide at moderate temperatures, or starting from tetracarbonylrhodates and acids. Trifluorophosphine is a ligand similar to carbon monoxide[22] and it is of interest that while $HCo(PF_3)_4$ begin to decompose at 250°, $HRh(PF_3)_4$ decomposes slowly at room temperature.[21,22]

Experimental Section

All operations were carried out under nitrogen and all the solvents saturated with nitrogen before use. Tetrahydrofuran was distilled over $LiAlH_4$. The starting rhodium carbonyls were prepared as described in the literature ($Rh_2(CO)_4Cl_2$,[23] $Rh_4(CO)_{12}$ [7] and $Rh_6(CO)_{16}$ [7]). The analytical data were obtained as reported in Part II.[10]

Synthesis of $[N(CH_3)_4][Rh(CO)_4]$. Sodium in small pieces (1 g) was added to a solution of $Rh_2(CO)_4Cl_2$ (1.02 g) in THF (30 ml) presaturated with carbon monoxide, and the mixture vigorously stirred. The solution first turned violet, then green and next red, ultimately becoming colourless, while some black precipitate was formed. Reaction was complete in 2-3 days. Filtration through a G3 sintered glass filter than gave a colourless solution, but occasionally fil,tration was so slow that decantation was necessary. The filtrate contained 50-60% of the rhodium originally reacted.

The THF was removed under high vacuum at –10°, the white crystalline residue dissolved in ice water (15 ml) and a solution of $[N(CH_3)_4]Cl$ (2 g) in ice water (20 ml) immediately added. The white precipitate was filtered off, washed with ice water and vacuum dried. *Anal.* Found: $N(CH_3)_4$, 24.0; Rh, 34.6. $N(CH_3)_4$/Rh 1.035 . $[N(CH_3)_4][Rh(CO)_4]$ calcd.: $N(CH_3)_4$, 25.65; Rh, 35.59. $N(CH_3)_4$/Rh 1.00. It begin to decompose at about 100°, it is soluble in water, methanol, THF and acetone. The infrared spectrum is very close to that of the sodium salt (Figure 1).

Synthesis of $[Ni(o\text{-}phen)_3][Rh(CO)_4]_2$. This was obtained by double decomposition using $[Ni(o\text{-}phen)_3]Cl_2$ as in the previous preparation. It was purified by solution in acetone and precipitating with

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water. *Anal.* Found: C, 51.17; H, 2.81; N, 7.87; CO, 20.5. $C_{44}H_{24}O_8N_6NiRh_2$. Calcd. C, 51.35; H, 2.35; N, 8.16; CO, 21.77. The infrared spectrum of this compound is also very close to that of the sodium salt (Figure 1).

Reaction between $[Na(THF)_n][Rh(CO)_4]$ *and* H_3PO_4 *at –25°.* A solution of $Na[Rh(CO)_4]$ in THF was evaporated under high vacuum at –10° until a white crystalline solid was obtained (about 0.3 g). The temperature was lowered to –25° and 85% H_3PO_4 (5 ml) was added. The mixture turned brown and some gas was evolved. Extraction with pentane gave a red solution shown by IR spectroscopy to contain only $Rh_4(CO)_{12}$.

Reaction between $Rh_4(CO)_{12}$ *and carbon monoxide at 220°/535 atm.* An autoclave (100 ml) was charged with $Rh_4(CO)_{12}$ (0.5 g), evacuated, and then charged with carbon monoxide (305 atm). The autoclave was heated at 220° during 20 hrs (530-540 atm). After cooling to room temperature the gas was vented through a –80° trap, where no condensate was obtained. The IR spectrum of the product, some of which have sublimed in beautiful crystals, showed only $Rh_6(CO)_{16}$.

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