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Synthesis of Rhodium Carbonyl Compounds at Atmospheric Pressure. II. Synthesis and Properties of the Derivatives of the $[Rh_{12}(CO)_{30}]^{2-}$ Anion

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Received December 24, 1968

Carbon monoxide in the presence of alkali reduces $Rh_2(CO)_4Cl_2$ to $Rh_4(CO)_{12}$ which is further reduced to the $[Rh_{12}(CO)_{30}]^{2-}$ anion. The use of sodium or potassium acetate in the presence of a tetraalkylammonium salt results in high yields (80-85%) of the $[Rh_{12}(CO)_{30}]^{2-}$ anion. The preparation and characterization of tetralkylammonium and alkali metal derivatives of this anion are reported. The $[Rh_{12}(CO)_{30}]^{2-}$ anion adds reversibly approximately 4 moles of carbon monoxide at atmospheric pressure to yield presumably $[Rh_{12}(CO)_{\sim 34}]^{2-}$ derivatives which on treatment with acids give $Rh_6(CO)_{16}$ and hydrogen. An approximate description of the bonding is suggested for the $[Rh_{12}(CO)_{30}]^{2-}$ anion which represents the first known example of a double octahedral cluster metal-carbonyl system.

Introduction

Our interest in the chemistry of cobalt carbonyl compounds suggested an investigation of similar compounds of rhodium. In a previous paper we reported the preparation of some derivatives of the $[Rh(CO)_4]^-$ anion by reduction of $Rh_2(CO)_4Cl_2$ with alkali metals in the presence of carbon monoxide. The synthesis of these derivatives has led us to make several attempts to obtain $HRh(CO)_4$ and $Rh_2(CO)_8$, but it has not been possible to confirm the existence of these two compounds.[1]

In the present work we report some results from experiments involving the reduction of $Rh_2(CO)_4Cl_2$ by carbon monoxide in the presence of alkaline reagents. Their significance for the synthesis of $Rh_4(CO)_{12}$ and of $Rh_6(CO)_{16}$ at atmospheric pressure[2] will be discussed in part III.[3]

Results

The anion $[Rh_{12}(CO)_{30}]^{2-}$ can be obtained by the reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide in the presence of alkali:

$$6Rh_2(CO)_4Cl_2 + 14OH^- + 13CO \longrightarrow [Rh_{12}(CO)_{30}]^{2-} + 12Cl^- + 7CO_2 + 7H_2O \qquad (1)$$

Further reduction of this violet anion is easily accomplished, the first product being a green anion,[4] which although not to date isolated pure, has an infrared spectrum analogous to that of the $[Co_6(CO)_{15}]^{2-}$ anion.[5] To obtain the $[Rh_{12}(CO)_{30}]^{2-}$ derivatives it is therefore necessary to terminate the reduction process at this stage.

We have found that by the use of either sodium or potassium acetate in aqueous methanol one can obtain high yields (80-85%) of derivatives of the $[Rh_{12}(CO)_{30}]^{2-}$ anion. This is particularly the case when a tetraalkylammonium salt is added, the insoluble tetraalkylammonium salts of the triacontacarbonyldodecarhodium(—2) anion being precipitated and their further conversion hindered. The reaction can be represented by the equation:

$$6Rh_2(CO)_4Cl_2 + 14CH_3COOK + 13CO + 7H_2O \longrightarrow K_2[Rh_{12}(CO)_{30}] + 12KCl + 14CH_3COOH + 7CO_2 \qquad (2)$$

The alkali acetate is probably hydrolyzed to insure sufficient alkalinity, while at the same time the acetic acid liberated in eq. (2) seems to be able to buffer the system and slow down further reduction of the $[Rh_{12}(CO)_{30}]^{2-}$ anion.

The cesium and the potassium salts of the $[Rh_{12}(CO)_{30}]^{2-}$ anion, which resemble the tetraalkylammonium derivatives in their low solubility in water, are easily prepared by exchange reactions using the soluble sodium salt. The sodium salt is obtained by the lowering of its solubility through the addition of an excess of sodium chloride. All of these salts, which are dark violet in the solid state, give violet solutions. In acetone containing 2% water the tetrabutylammonium derivative is not completely dissociated as shown by the values of $\frac{\Lambda_o - \Lambda_c}{\sqrt{c}}$ (ref. 6) in Table I.

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[1] P. Chini and S. Martinengo, Part I, *Inorg. Chim. Acta*, 3, 21 (1969).
[2] P. Chini and S. Martinengo, *Chem. Comm.*, 251 (1968).
[3] P. Chini and S. Martinengo, Part III, *Inorg. Chim Acta*, 3, 315 (1969).
[4] P. Chini, S. Martinengo, and V. Albano, work in progress.
[5] P. Chini and V. Albano, *J. Organometal. Chem.*, *15*, 433 (1968).
[6] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Table I. Comparison between the values of $\frac{\Lambda_o-\Lambda_c}{\sqrt{c}}$ for $[NBu_4]_2[Rh_{12}(CO)_{30}]$ and those for 1:1 and 2:1 electrolytes. (In acetone solution containing 2% water, at 25°, $c = 3\times10^{-4}-20\times10^{-4}$ moles/l).

Compound	$\frac{\Lambda_o-\Lambda_c}{\sqrt{c}}$
$[NBu_4]_2[Rh_{12}(CO)_{30}]$	875
$[NBu_4]I$	900
$[NBu_4]_2[PtCl_6]$	1750

In the solid state the $[Rh_{12}(CO)_{30}]^{2-}$ derivatives are moderately resistant to air oxidation, but in solution they rapidly decompose. When heated above 135° they start decomposing with decomposition being very rapid at 150°-160°.

The analytical data agree with the composition $\{Cat[Rh_6(CO)_{15}]\}_n$; the diamagnetism of the trimethylbenzylammonium derivative and the absence of signals in the Rh–H region of the NMR spectrum together indicate that n should be at least equal to 2.

The exact molecular composition was obtained from a single crystal X-ray diffraction determination of the structure of the tetramethylammonium derivative.[7] Figure 1 shows the molecular geometry of the anion.

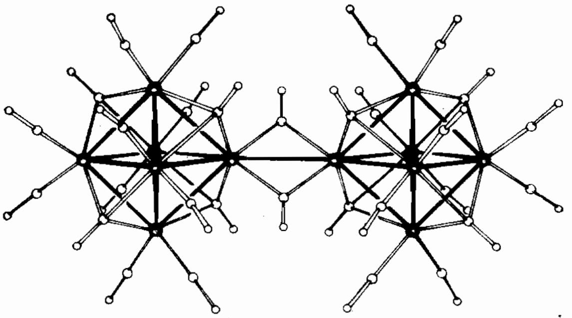

Figure 1. Molecular structure of the $[Rh_{12}(CO)_{30}]^{2-}$ anion[7].

In this double cluster system two octahedral Rh_6-fragments with the basic structure of $Rh_6(CO)_{16}$ [8] are linked together by both a Rh–Rh bond and two bridging carbonyl groups. Of the other 28 carbonyl groups, 20 are terminal and 8 are face bridging. The idealized geometry of the anion possesses D_{2h} symmetry from which selection rules predict that it may contain eight infrared active stretching frequencies $(2B_{1u}+3B_{2u}+3B_{3u})$ for the terminal carbon monoxide groups and five frequencies $(2B_{1u}+B_{2u}+2B_{3u})$ for both the doubly- and triply-bridging carbonyl groups. The IR spectrum in the stretching region is shown in Figure 2; in the tetrahydrofuran solvent only poor resolution is expected.

Table II shows the changes in the carbonyl stretching frequencies of the $[Rh_{12}(CO)_{30}]^{2-}$ anion that occur on reaction with carbon monoxide at atmospheric pressure in THF. During the addition of carbon monoxide the colour changes from violet to reddish-violet, about four moles of carbon monoxide being absorbed at 20° for every mole of $[Rh_{12}(CO)_{30}]^{2-}$ derivative. The reaction is reversible and under vacuum the original anion is immediately formed again. Unfortunately, it has not been possible to isolate any derivative of this carbonylated $[Rh_{12}(CO)_{30}]^{2-}$ anion: precipitation with an excess of water gives the original anion. Such facile decomposition to the original compound suggests that the Rh_{12} unit is not destroyed during reaction and makes the formula $[Rh_{12}(CO)_{\sim34}]^{2-}$ highly probable.

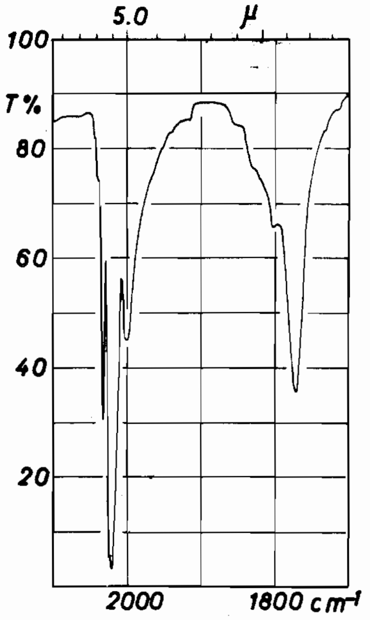

Figure 2. Infrared spectrum of $[NMe_3Bz]_2[Rh_{12}(CO)_{30}]$ in the carbonyl stretching region (in THF) registered on a Perkin Elmer 457 spectrophotometer.

Table II. Changes in the IR spectrum of $[NMe_3Bz]_2[Rh_{12}(CO)_{30}]$ on addition of carbon monoxide. (In tetrahydrofuran at 25°/1 atm).

$[Rh_{12}(CO)_{30}]^{2-}$	2070 w, 2053 s, 2040 s, 2007 w, 1823 w, 1807 w, 1771 s cm^{-1}
$[Rh_{12}(CO)_{\sim34}]^{2-}$	2087 w, 2055 s, 2010 vs, 1868 m, 1838 ms, 1785 m cm^{-1}

The derivatives of the $[Rh_{12}(CO)_{30}]^{2-}$ anion were easily hydrolyzed by gentle heating in aqueous alcohol with formation of $Rh_6(CO)_{16}$. With acids they gave an intermediate product, as yet uncharacterised, which subsequently decomposes to $Rh_6(CO)_{16}$. Analysis shows that 0.5 moles of hydrogen are liberated for each mole of $Rh_6(CO)_{16}$, produced but the exact course of the reaction depends on the presence of carbon monoxide.[4]

Discussion

Reduction of $Rh_2(CO)_4Cl_2$ with carbon monoxide in the presence of alkaline reagents involves a complex

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(7) P. Chini, V. Albano, and S. Martinengo, in Progress in Coordination Chemistry, Ed. M. Cais, Elsevier, 1968, p. 211.

(8) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, *85*, 1202 (1963).

sequence of reactions. The first product in this sequence which could be isolated was not the anion $[Rh_{12}(CO)_{30}]^{2-}$, but the neutral carbonyl $Rh_4(CO)_{12}$. The latter was obtained with a 1:1 $Rh_2(CO)_4Cl_2$: KOH ratio; the yield was about 50% that expected from equation(3):

$$4Rh_2(CO)_4Cl_2 + 4KOH + 6CO \longrightarrow Rh_4(CO)_{12} + 4K[Rh(CO)_2Cl_2] + 2CO_2 + 2H_2O \qquad (3)$$

After separation of the $Rh_4(CO)_{12}$, the resulting solution showed the IR spectrum of the $[Rh(CO)_2Cl_2]^-$ anion.[9] Moreover during the addition of potassium hydroxide the IR spectrum of the solution did not reveal any considerably quantity of other products.

The course of further reduction depends on the way in which the alkali hydroxide is added. Rapid addition of two moles of potassium hydroxide for every mole of $Rh_2(CO)_4Cl_2$ gave a violet solution containing the $[Rh_{12}(CO)_{30}]^{2-}$ anion, but slow addition gave $Rh_6(CO)_{16}$.[3] This further reduction is probably complicated by slow oxidation-reduction reactions between carbonylrhodates (where the rhodium has oxidation number from-1 to -0.166) and dicarbonyldichlororhodates (where the rhodium oxidation number is $+1$). To obtain additional information on the synthesis of the $[Rh_{12}(CO)_{30}]^{2-}$ anion it is therefore more convenient to study reduction starting from $Rh_4(CO)_{12}$.

The reduction of $Rh_4(CO)_{12}$ proceeds very readily, and a violet solution of $[Rh_{12}(CO)_{30}]^{2-}$ is obtained with two moles of KOH per three moles of $Rh_4(CO)_{12}$ in a nitrogen atmosphere. The IR spectrum shows that all the $Rh_4(CO)_{12}$ reacts. This equation is:

$$3Rh_4(CO)_{12} + 2OH^- \rightarrow [Rh_{12}(CO)_{30}]^{2-} + CO_2 + 5CO + H_2O \qquad (4)$$

This reaction shows that the $[Rh_{12}(CO)_{30}]^{2-}$ cluster can be obtained by condensation of three Rh_4 units, a process which should involve intermediate formation of a Rh_8 cluster. This probably occurs, because the IR spectrum during the addition of the potassium hydroxide shows intermediate formation of new bands. This intermediate has been isolated by an effecting of the reduction in carbon monoxide followed by the addition of an aqueous solution of a tetraalkylammonium salt. Analysis indicates the presence of one cation and of one carbomethoxy group (–COOMe) for every four rhodium atoms in agreement with the composition expected for either a Rh_4 or a Rh_8 cluster.[4]

Further evidence is necessary for a clear understanding of the mechanism of formation of the Rh_{12} cluster by the sequence:

$$Rh_2 \longrightarrow Rh_4 \longrightarrow Rh_8(?) \longrightarrow Rh_{12}$$

Isolation of the $[Rh_{12}(CO)_{30}]^{2-}$ derivatives raises some particular problems regarding representation of the bonds of the double octahedral rhodium cluster, which departs from the noble gas rule. We have previously suggested a simple approximate picture of the bonding in the octahedral cluster $[Co_6(CO)_{15}]^{2-}$;[10] this bonding scheme can now be extended to the double octahedral cluster $[Rh_{12}(CO)_{30}]^{2-}$. In this latter anion with the consideration of only the carbonyl groups, the coordination about each rhodium atom is fairly well represented by a tetrahedron,[7] and sp^3 hybridisation at the rhodium atoms can be reasonably assumed. Of the molecular orbitals (obtained from the 4d and $5sp^3$ orbitals of the rhodium atoms and the ligand orbitals) some are assumed to be more conveniently represented as essentially localised between metal atoms and terminal ligands, others as essentially delocalised on the faces of the octahedron and engaged in the bonding of the face bridging carbonyl groups, yet others as essentially delocalised over the octahedral part of the cluster and involved in the metal-metal bonds, and finally the rest as delocalised over the whole cluster and also involved in metal-metal bonds. The 170 electrons are accounted for in the following way 40 are required for the 20 sp^3 bonds to the 20 terminal carbonyl groups, 8 are used up in the 4 sp^3 bonds of the two carbonyl groups bridging the octahedra, 48 are needed for the 24 sp^3 orbitals delocalised over 8 faces ($8a_1 + 8e$ in C_{3v} symmetry) and engaged in bonding with the 8 face bridging carbonyl groups. Of the remaining 4 d orbitals the 12 d_{xy} and the 12 $d_{x^2-y^2}$ ones are assumed to be essentially involved in the backbonding to the terminal groups and are occupied by 48 electrons. The 12 d_{xz} and the 12 d_{yz} ones pointing along the edges of the octahedra are combined in O_h symmetry to give eight triply degenerate orbitals ($2t_{1g} + 2t_{2g} + 2t_{1u} + 2t_{2u}$), and 24 electrons are assigned to the two t_{2g} and two t_{1u} combinations. The remaining 12 $d_z{}^2$ orbitals pointing to the centers of the two octahedra are combined under localized O_h symmetry to give 12 molecular orbitals ($2a_{1g} + 2e_g + 2t_{1u}$); the two a_{1g} orbitals correspond in D_{2h} symmetry to two non-equivalent orbitals ($a_{1g} + a_{2u}$), and two electrons are assigned to the a_{1g} bonding combination.[14]

Experimental Section

All operations were carried out under nitrogen or carbon monoxide, solvents being saturated with nitrogen before use. $Rh_2(CO)_4Cl_2$ was prepared as described in the literature.[11] The analytical data

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(9) L. M. Vallarino, *Inorg. Chem.*, *4*, 161 (1965).

(10) V. Albano, P. Chini, and V. Scatturin, *J. Organometal. Chem.*, *15*, 423 (1968).

(11) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, *8*, 211 (1966).

(12) W. Geilmann and W. Gebauhr, *Fresenius' Z. Anal. Chem.*, *139*, 161 (1953).

(13) N. Cheronis and T. S. Ma, Organic Functional Analysis by Mioro and Semimicro Methods, Interscience, 1964, p. 544.

(14) *Note added in proof.* The predominant influence of the sp^3 rhodium-carbon bonds agrees with differences found in the rhodium-carbon and rhodium-rhodium distances.[15] Owing to stronger backdonation to four bridging carbonyl groups the two inner rhodium atoms (Rh_1) bridging the cluster are more electron deficient and induce a regular set of deformations on each octahedral part of the cluster. Each triple bridging carbonyl group bonded to the Rh_1 atoms and to two of the four equatorial rhodium atoms (Rh_1) present a short Rh_1—C and two long Rh_2—C distances. This induces further deformation and each triple bridging group bonded to the Rh_2 and to the apical rhodium atoms (Rh_3) present two short distances to the Rh_2 and a long one to the Rh_3. The net effect on the four equatorial Rh_2 atoms is the presence of a rectangle of alternate long and short Rh_2—Rh_2 distances, and the whole process corresponds to transfer of electronic charge from Rh_3 to Rh_1.

(15) V. Albano, P. L. Bellon, *J. Organometal. Chem.*, in press.

Table III. Comparison between the solubilities of several derivatives of the $[Rh_{12}(CO)_{30}]^{2-}$ anion at room temperature.

Cation	water	methanol	tetrahydrofuran	acetone
NMe_4	—	—	—	+
NM_3Bz and NBu_4	—	—	+	+
Cs	—	+	+	+
K	few	+	+	+
Na	+	+	—	+

(— insoluble; + soluble)

were obtained thus: the sample was dissolved or suspended in aqueous methanol containing some hydrochloric acid and decomposed by the addition of dilute H_2O_2. The excess H_2O_2 was destroyed by boiling, and at the same time the methanol evaporated off. In the clear solution tetraalkylammonium, cesium, and potassium ions were determined as tetraphenylborates.[12,13] Rhodium was amalgamated with magnesium and, after the decomposition of the excess magnesium, separated by filtration and determined as rhodium metal by heating at 900°. When only volatile elements were present, rhodium was obtained by direct cautious ashing of a sample at 900°. Carbon monoxide has been obtained by a two stage decomposition in vacuum: the sample was first reacted with excess iodine in quinoline at room temperature, then excess 1,2-bis(diphenylphosphino)ethane added and the mixture heated for a short time (10 min) at 150°-180°. The evolved gas was transferred with a Toepler pump and measured.

Synthesis of some tetraalkylammonium derivatives of the $[Rh_{12}(CO)_{30}]^{2-}$ *anion.* A solution of $Rh_2(CO_4Cl_2$ (1.81 g) in methanol (50 ml) was saturated with carbon monoxide, and potassium acetate (2 g) in methanol (10 ml), trimethylbenzylammonium chloride (2 g) in methanol (10 ml), and water (7 ml) added. The mixture was stirred for 48 hrs, then the dark violet precipitate filtered off, washed with water and isopropanol and vacuum dried (1.5 g, 82% yield). It could be recrystallised from acetone by the slow addition of isopropanol. *Anal.* Found: C, 25.28; H, 1.44; N, 1.15; $N(CH_3)_3(C_7H_7)$, 12.65; CO, 34.35; Rh, 52.1. $C_{50}H_{32}O_{30}N_2Rh_{12}$ calcd.: C, 25.25; H, 1.35; N, 1.18; $N(CH_3)_3(C_7H_7)$, 12.62; CO, 35.35; Rh, 52.10. The salt is diamagnetic, it begins to decompose at about 135°.

The tetramethylammonium derivative was similarly obtained (76% yield). *Anal.* Found: C, 20.51; H, 1.08. $C_{38}H_{24}O_{30}N_2Rh_{12}$ calcd.: C, 20.50; H, 1.08. It begins to decompose at about 150°.

The tetrabutylammonium derivative was similarly obtained (84% yield).

Synthesis of some alkali metal salts of the $[Rh_{12}(CO)_{30}]^{2-}$ *anion.* A solution of $Rh_2(CO)_4Cl_2$ (1 g) in THF (25 ml) was saturated with carbon monoxide, $CH_3COONa \, . \, 3H_2O$ (1 g) added and the whole stirred for 5 hrs. The solution was vacuum evaporated to about 15 ml, water (70 ml) containing NaCl (1 g) added, and the rest of the THF evaporated off under vacuum. The crystalline violet sodium salt was filtered off, washed with a diluted solution of NaCl, then with a little water and vacuum dried (0.8 g, 88% yield). The salt is anhydrous, it begins to decompose at about 150°.

The cesium and potassium salts were obtained from the sodium salt by double decomposition in water. A comparison between the solubility of several derivatives is reported in Table III.

Reaction between $[NMe_3Bz]_2[Rh_{12}(CO)_{30}]$ *and carbon monoxide.* A gas measuring apparatus was charged with THF (10 ml) and carbon monoxide. Solid $[NMe_3Bz]_2[Rh_{12}(CO)_{30}]$ (0.448 g) was added and the solution was stirred for 24 hrs at 20° and atmospheric pressure, when carbon monoxide was absorbed (18.1 Nml; 4.3 moles/mole of $[NMe_3Bz]_2[Rh_{12}(CO)_{30}]$.

Isolation of $Rh_4(CO)_{12}$ *in the reduction of* $Rh_2(CO)_4Cl_2$. A solution of $Rh_2(CO)_4Cl_2$ (0.8 g) in methanol (25 ml) was saturated with carbon monoxide and with vigorous stirring a 0.2 N solution of KOH in methanol (9 ml) slowly added. The resulting suspension of $Rh_4(CO)_{12}$ was cooled to −70° and the $Rh_4(CO)_{12}$ was filtered off, extracted with pentane (40 ml) and crystallised out by cooling to −70° (0.202 g; 54% yield). The residual methanol solution showed bands in the carbonyl stretching region at 2080 s and 2002 s cm^{-1} due to the $[Rh(CO)_2Cl_2]^-$ anion.

Acknowledgments. We thank Prof. L. Malatesta for his interest in this work and the CNR for financial assistance.