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RHODIUM CARBONYL CLUSTER CHEMISTRY UNDER HIGH PRESSURE OF CARBON MONOXIDE AND HYDROGEN

VII *. CONVERSION OF $[Rh_{15}(CO)_{27}]^{3-}$ INTO OTHER HIGH NUCLEARITY CLUSTERS: NEW HIGH-YIELD SYNTHESES FOR $[Rh_{13}(CO)_{24}H_2]^{3-}$ AND $[Rh_{14}(CO)_{26}]^{2-}$

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Summary

The interconversions of $[Rh_{13}(CO)_{24}H_2]^{3-}$, $[Rh_{15}(CO)_{27}]^{3-}$, and $[Rh_{14}(CO)_{25}]^{4-}$ have been studied under high pressure of an equimolar mixture of carbon monoxide and hydrogen (12—15 atm; 140—160°C). The three clusters can be selectively prepared from identical reaction mixtures ($Rh(CO)_2acac$, $CsPhCO_2$, in glyme solvent) using different contact times. A new synthesis for $[Rh_{13}(CO)_{24}H_2]^{3-}$ by exposing this solution for less than 0.5 hours to reaction conditions was discovered in this way. This procedure allows the preparation of 5—20 g of the cluster, isolated as the bis(triphenylphosphine) iminium salt with a 95% yield in a 8-hour working period. The fragmentation of $[Rh_{13}(CO)_{24}H_2]^{3-}$ to $Rh_2(CO)_8$ and the aggregation of this dimer with the initial cluster is suggested to form $[Rh_{15}(CO)_{27}]^{3-}$. Conversion of $[Rh_{15}(CO)_{27}]^{3-}$ into $[Rh_{14}(CO)_{25}]^{4-}$ or $[Rh_{14}(CO)_{26}]^{2-}$ occurs subsequently by reaction with carbon monoxide and hydrogen, or by treatment with trifluoromethane sulfonic acid; $[Rh_{15}(CO)_{27}]^{3-}$ has also been converted into $[Rh_{13}(CO)_{24}H_2]^{3-}$ by reaction with formaldehyde in the presence of hydrogen (67 atm, 125°C). The oxidative aggregation of two large clusters to yield an even larger species is promoted by protonic acids: $[Rh_7(CO)_{16}]^{3-}$ and CF_3SO_3H react to give $[Rh_{14}(CO)_{26}]^{2-}$. The effects of the cations on the redox aggregation-fragmentation reactions of the clusters have been noted for the first time during these studies.

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* For part VI see ref. 5g.

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Introduction

The proposed role of clusters as suitable models for surfaces [1] and the predominance of these species in homogeneous systems used for the catalytic hydrogenation of carbon monoxide [2] are responsible in part for the recent studies of these species [3]. These efforts have been hindered by the difficulties in the large scale preparation of the high nuclearity species, in spite of the excellent and devoted efforts of Chini et al. [4a—4d]. The complex mixtures of products usually formed require involved synthetic procedures and obscure the probable reaction paths. The reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with hydrogen is a suitable example [4b] (eq. 1).

$$[Rh_{12}(CO)_{30}]^{2-} + H_2 \xrightarrow[80^\circ C]{1\ atm} [Rh_{13}(CO)_{24}H_3]^{2-} + [Rh_{13}(CO)_{24}H_2]^{3-} + [Rh_{14}(CO)_{25}]^{4-} + [Rh_{15}(CO)_{27}]^{3-} \quad (1)$$

Recent improvements in the syntheses of high nuclearity rhodium carbonyl clusters have resulted from the application of high pressure techniques. Very selective, high-yield preparations of these species are routinely executed in this way. This procedure has been applied to the preparation of new clusters with encapsulated main-group atoms, $[Rh_9E(CO)_{21}]^{2-}$, $[Rh_{10}E(CO)_{22}]^{3-}$, $[Rh_{12}Sb(CO)_{27}]^{3-}$, and $[Rh_{17}S_2(CO)_{32}]^{3-}$ ($E = P, As$) [5a—5d], and to the syntheses of the previously reported homometallic species $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{27}]^{3-}$ [5e,5f]. Operation under high pressure of carbon monoxide and hydrogen allowed us to implicate $[Rh(CO)_4]^-$, $HRh(CO)_4$ and $Rh_2(CO)_8$ in the fragmentation of the clusters (eqs. 2—4) [5g].

$$[Rh_{12}(CO)_{30}]^{2-} + 8\ CO \rightleftharpoons 2\ [Rh_5(CO)_{15}]^- + Rh_2(CO)_8 \quad (2)$$

$$[Rh_5(CO)_{15}]^- + 5\ CO \rightleftharpoons [Rh(CO)_4]^- + 2\ Rh_2(CO)_8 \quad (3)$$

$$[Rh_{13}(CO)_{24}H_3]^{2-} + 18\ CO \rightleftharpoons 2\ [Rh_5(CO)_{15}]^- + 3\ HRh(CO)_4 \quad (4)$$

We studied the chemistry of the clusters formed in the hydrogenation of $[Rh_{12}(CO)_{30}]^{2-}$ (eq. 1) because of their relevance to our systems. The detachment of a mononuclear rhodium fragment from $[Rh_{15}(CO)_{27}]^{3-}$ occurs with several ligands (halides or nitriles [4d], amines, hydrogen, or carbon monoxide mixtures with hydrogen [5f,5g]) and results in the formation of $[Rh_{14}(CO)_{25}]^{4-}$. Thus, we initially turned our attention to the chemistry of $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ in an attempt to understand the relationship of this cluster to the other species formed from $[Rh_{12}(CO)_{30}]^{2-}$.

Experimental

The chemicals used in this work were obtained from the same sources as in our previous work and treated similarly [2,5]. The high pressure equipment and the procedures used in the manipulations of our systems have been also described [2,5]. The infrared spectra were obtained with a Perkin-Elmer 283 spectrometer using 0.125 mm solution cells with calcium fluoride windows and the NMR spectra were obtained in a Varian-XL-100 spectrometer as in our previous reports. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Synthesis of $[Rh_{13}(CO)_{24}H_2]^{3-}$

A solution of cesium benzoate dihydrate (3.41 g, 13.1 mmol) in 40 ml of ethylene glycol was added to a solution of $Rh(CO)_2acac$ (14.0 g, 54.3 mmol) in 840 ml of tetraethylene glycol dimethyl ether. The solution was stirred for 0.5 h under argon and charged to a high-pressure autoclave purged with nitrogen. The reactor was pressurized with an equimolar mixture of carbon monoxide and hydrogen (12 atm) and brought to conditions as quickly as possible (140°C; 15 atm). The system was allowed to react for 5—10 minutes, then it was vented, using Schlenk techniques. The infrared spectra of the solution and of the isolated product (Fig. 1) are similar to that assigned to $[Rh_{13}(CO)_{24}H_2]^{3-}$ [2a]. The final solution was precipitated with ten volumes of toluene, and the resulting oil was washed with isopropanol, redissolved in acetone and either reprecipitated with two volumes of an isopropanol solution of bis(triphenylphosphine) iminium chloride. The final product (13.8 g) corresponded to a yield of 91.0% of $\{[(C_6H_5)_3P]_2N\}_3\ [Rh_{13}(CO)_{24}H_2]$ based on rhodium. The identification of this material was carried out by comparison of its infrared (Fig. 1), ^1H and ^{13}C NMR spectra with those of an authentic sample prepared by the previous procedure [4b], as well as by the full structural characterization of the compound by a tridimensional X-ray single crystal analysis and elemental analysis. Single crystals were obtained by the solvent diffusion method with acetone and isopropanol as solvents. Anal. Found: C, 42.26; H, 2.12; N, 1.04;

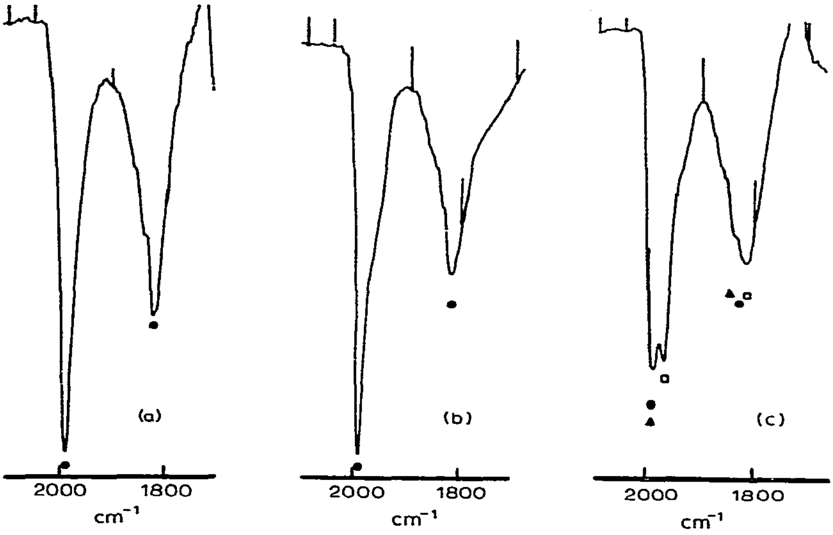

Fig. 1. Infrared spectra of (a) the solution after 5—10 minutes contact time under 15 atm CO : H_2 at 140°C; (b) the isolated Cs^+ or $[(Ph_3P)_2N]^+$ salts of $[Rh_{13}(CO)_{24}H_2]^{3-}$ in acetone; (c) the solution in (a) after a contact time of ca., 1.0 h, under the same conditions. $[Rh_{13}(CO)_{24}H_2]^{3-}$ (●); $[Rh_{15}(CO)_{27}]^{3-}$ (▲); $[Rh_{14}(CO)_{25}]^{4-}$ (■).

P, 4.92; Rh, 37.14. $C_{78}H_{17}NO_{24}P_2Rh_{13}$ Calcd.: C, 43.68; H, 2.56; N, 1.16; P, 5.12; Rh, 36.89%.

Reactions of $[Rh_7(CO)_{16}]^{3-}$, $[Rh_{15}(CO)_{27}]^{3-}$ *and their equimolar mixture with trifluoromethylsulfonic acid*

These reactions were studied following the same procedure and the same results were noted in all instances, with the exception of those specific cases mentioned below. Thus, the study of the system based on $[Rh_7(CO)_{16}]^{3-}$ should be considered typical.

A solution of $\{[(C_6H_5)_3P]_2N\}_3[Rh_7(CO)_{16}]$ (2.0 mmol) in 100 ml of acetone was treated at 0°C by the dropwise addition of ca. 6.0 mmol of a non-oxidizing protonic acid such as trifluoromethylsulfonic acid. An immediate reaction ensued as shown by the change in color from green to brown and by the change of the infrared pattern of the initial solution (2060(sh), 1995s, 1960s, 1821w,

Fig. 2. Infrared spectrum of $[(Ph_3P)_2N]_2[Rh_{14}(CO)_{26}]$ in acetone.

1793m, 1775w, 1745w, cm^{-1}) into a new one with bands at 2020, 1875 and 1855 cm^{-1} (Fig. 2). The product was isolated by precipitation with four volumes of isopropanol, extraction of the resulting tacky solids with acetone and reprecipitation with hexane. The final product (2.69 g) corresponded to a yield of 85.7% of $\{[(C_6H_5)_3P]_2N\}_2[Rh_{14}(CO)_{26}]$ characterized by comparison of the infrared spectrum of the compound with that recently assigned to a fully characterized sample [4], by the absence of detectable resonances corresponding to metal hydrides (acetone-d_6 solution, —90 to 40°C, 20 to 60 ppm) and by its elemental analysis. Found: C, 34.11; H, 1.99; N, 0.94; P, 3.90; Rh, 45.86. Anal. $C_{62}H_{30}N_2O_{26}P_4Rh_{14}$ Calcd.: C, 34.05; H, 1.93; N, 0.89; P, 3.95; Rh, 45.92%. In addition, we have attempted the full structural characterization of the compound by a complete tridimensional X-ray single crystal analysis. Single crystals were obtained by the solvent diffusion method using acetone/isopropanol. The disorder of the carbonyl ligands precluded us from completely solving this structure although it was possible to locate the heavy atoms and those of the three cations, together with eighteen carbonyl ligands. A comparison of the unit cell parameters found by us (orthorhombic, *Pbcn*; $a = 18.565(10)$; $b = 22.525(9)$; $c = 24.809(7)$ Å; $V = 10\,374.0$ Å^3; $Z = 4$) with those reported in the literature (triclinic; $P\bar{1}$; $a = 21.074(6)$; $b = 17.973(6)$; $c = 16.547(6)$ Å; $\alpha = 119.54(4)$; $\beta = 69.34(4)$; $\gamma = 98.92(4)°$; $Z = 2$) suggests that the disorder of the carbonyl ligands may be a result of the different crystalline forms and it can be removed by growing the crystals from methyl ethyl ketone/methanol mixtures.

Lower yields on the final compound (75 and 82%) were obtained upon using $[Rh_{15}(CO)_{27}]^{3-}$ or an equimolar mixture of this cluster with $[Rh_7(CO)_{16}]^{3-}$, respectively. The same procedure was followed to study the reactions of the cesium salts of these clusters.

The ^{13}C NMR spectra were obtained by either enriching a sample of the final reaction product with 45% ^{13}CO (1 atm; ambient temperature; acetone-d_6 solution) or by using previously enriched starting materials.

The complete results from the tridimensional single crystal X-ray diffraction studies for the $[(C_6H_5)_3P]_2N^+$ salts of $[Rh_{13}(CO)_{24}H_2]^{3-}$ and $[Rh_{14}(CO)_{26}]^{2-}$ are included as supplementary material *.

Results and discussion

The preparation of $[Rh_{13}(CO)_{24}H_2]^{3-}$ by this method offers a simple procedure for the preparation of bulk amounts of this cluster starting with commercially available materials. In contrast, the previously reported procedure for the preparation of this anion requires the synthesis of $Rh_4(CO)_{12}$ or $[Rh_{12}(CO)_{30}]^{2-}$ and the separation of the mixture of products by fractional crystallization (Scheme 1) [4b]. The cluster prepared by the high pressure procedure described here has been identified by comparison of the infrared, ^{1}H and ^{13}C NMR spectra of the $\{[(C_6H_5)_3P]_2N\}^+$ salt with those of a sample prepared by the previous

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SCHEME 1

PREVIOUS SYNTHESIS [4a–g]

$$RhCl_3 \cdot 3\,H_2O \rightarrow Rh_4(CO)_{12} \rightarrow [Rh_{12}(CO)_{30}]^{2-} \xrightarrow{H_2\ (1\ atm,\ 140^\circ C)} \begin{matrix}[Rh_{13}(CO)_{24}H_x]^{(5-x)-}\ (x = 2, 3)\\ [Rh_{15}(CO)_{27}]^{3-}\\ [Rh_{14}(CO)_{25}]^{4-}\end{matrix} \xrightarrow[\text{procedures}]{\text{Tedious separation}} [Rh_{13}(CO)_{24}H_2]^{3-}$$

85% yield [a] 30 hours	85% yield [a] 7 hours	10–20% yield [b] 70 hours

NEW SYNTHESIS (This work)

$$Rh(CO)_2ACAC \xrightarrow{CO/H_2\ (15\ atm,\ 140^\circ C;\ 5\ min)} [Rh_{13}(CO)_{24}H_2]^{3-}$$

90% yield
8 hours

[a] Yields and times are taken for each step from ref. 8. [b] P. Chini, personal communication.

procedure [4b,c]. In addition, a tridimensional single-crystal X-ray diffraction study showed the crystal and molecular structure of the compound to be in perfect agreement with that recently described by Martinengo, et al. [4c].

This preparation of $[Rh_{13}(CO)_{24}H_2]^{3-}$, and those of $[Rh_{15}(CO)_{27}]^{3-}$ and $[Rh_{14}(CO)_{25}]^{4-}$ recently described by us [5f], results from exposing a solution of the same composition to high pressure of carbon monoxide and hydrogen for different lengths of time. These results confirm the sequential transformations of these clusters previously suggested by monitoring the solution with infrared spectroscopy (eq. 5). They also indicate some of the inter-relations existing between the clusters formed in the reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with hydrogen (eq. 1). For instance, the exclusive presence of $[Rh_{13}(CO)_{24}H_2]^{3-}$ in our systems is detected at reaction times shorter than 0.5 hours under our conditions (12—15 atm; H_2 : CO, 1 : 1; 140—160°C) but $[Rh_{15}(CO)_{27}]^{3-}$ slowly appears afterwards. The formation of $Rh_2(CO)_8$ by fragmentation of $[Rh_{13}(CO)_{24}H_2]^{3-}$ followed by the aggregation of these two species could explain this result. The conversion of $[Rh_{15}(CO)_{27}]^{3-}$ into $[Rh_{13}(CO)_{24}H_2]^{3-}$ occurs only by reaction with formaldehyde and hydrogen (67 atm H_2; 125°C; sulfolane solution; added paraformaldehyde) (eq. 6), but $[Rh_{14}(CO)_{25}H_x]^{(4-x)-}$ ($x = 0, 1$) is obtained instead by reaction with carbon monoxide, hydrogen and a mixture of these gases [5f,5g]. These changes show the influence of the substrates in the detachment of either one or two apical rhodium atoms from $[Rh_{15}(CO)_{27}]^{3-}$.

$$\begin{array}{lll} \mathrm{Rh(CO)_2acac,} \xrightarrow{0.5\ h} & [Rh_{13}(CO)_{24}H_2]^{3-} \xrightarrow{1\ h} & [Rh_{15}(CO)_{27}]^{3-} \xrightarrow{3\ h} \\ \mathrm{CsPhCO_2, R_3N} & 1990, 1820\ \mathrm{cm^{-1}} & 1990, 1845\ \mathrm{cm^{-1}} \\ & & [Rh_{14}(CO)_{25}H]^{3-}, [Rh_{14}(CO)_{25}]^{4-} \qquad (5) \end{array}$$

$$[Rh_{15}(CO)_{27}]^{3-} + CH_2O \xrightarrow{H_2} [Rh_{13}(CO)_{24}H_2]^{3-} + \text{other products} \qquad (6)$$

The fragmentation of $[Rh_{15}(CO)_{27}]^{3-}$ to Rh_{14} clusters attracted our attention. For instance, contrary to our expectations we found that $[Rh_{15}(CO)_{27}]^{3-}$ is inert to hydrogen in the absence of carboxylates (67 atm; 125°C) [5g,5f]. On the other hand, this cluster reacted very readily with CF_3SO_3H, forming the recently reported cluster $[Rh_{14}(CO)_{26}]^{2-}$ (Scheme 2) [4e], as concluded from the elemental analysis and the infrared and ^{13}C NMR spectra of the product (Figs. 2 and 3). The full structural characterization of the compound by a

SCHEME 2

$$\begin{tikzcd}
 & {[Rh_{15}(CO)_{27}]^{3-}} \arrow[dr, "{[PPN]^+\ \mathrm{salt}}", "{CF_3SO_3H}"'] & \\
{Rh_{22}(CO)_{35}H_x]^{(5-x)-}} \arrow[r, shift right, "{CF_3SO_3H}"'] & {[Rh_{15}(CO)_{27}]^{3-} + [Rh_7(CO)_{16}]^{3-}} \arrow[l, shift right, "{Cs^+\ \mathrm{salt}}"'] \arrow[r, "{[PPN]^+\ \mathrm{salts}}", "{CF_3SO_3H}"'] & {[Rh_{14}(CO)_{26}]^{2-}} \\
 & {[Rh_7(CO)_{16}]^{3-}} \arrow[ur, "{[PPN]^+\ \mathrm{salt}}", "{CF_3SO_3H}"'] &
\end{tikzcd}$$

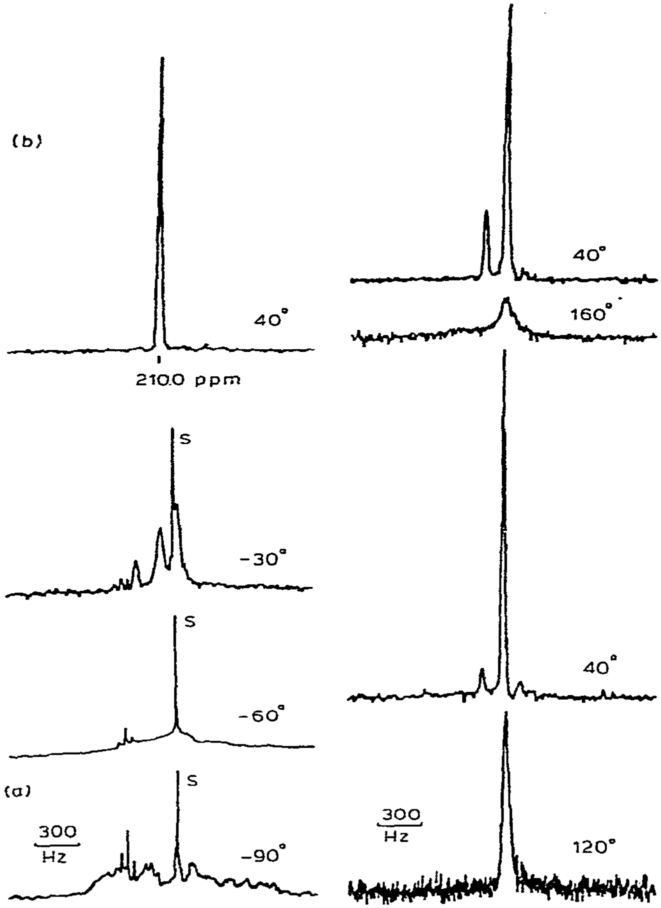

Fig. 3. ^{13}C NMR variable temperature study of $[(Ph_3P)_2N]_2[Rh_{14}(CO)_{26}]$ in acetone-d_6 (—90 to 40°C) and sulfolane (40—160°C).

single crystal X-ray diffraction study was precluded by the disorder of the carbonyls, but it was established that this product consisted of a double charged fourteen-atom rhodium cluster with the same inter-atomic distances and angles found in the polyhedron of $[Rh_{14}(CO)_{26}]^{2-}$ [4e]. The formation of hydrogen in this system was confirmed after the analysis of the gas phase by mass spectroscopy. These results suggest that a redox reaction occurs between the proton and $[Rh_{15}(CO)_{27}]^{3-}$. Cluster fragmentation caused by the coordination of a very weak ligand as the $CF_3SO_3^-$ anion to the detached mononuclear fragment should give a more reduced cluster since formally the "$Rh(CO)_2^+$" fragment should be removed (eq. 7). Rather we suggest that the redox reaction causes the fragmentation responsible for the formation of $[Rh_{14}(CO)_{26}]^{2-}$ instead of $[Rh_{14}(CO)_{25}]^{4-}$. The comparison between the solution and solid state (Fig. 4) structures of $[Rh_{14}(CO)_{26}]^{2-}$ by ^{13}C NMR was precluded by the scrambling of some of the carbonyls at —90°C (Fig. 3), but exchange involving all the ligands occurs between —30 and 40°C, as indicated by a single coalescence band at 210.0 ppm. The thermal instability of $[Rh_{14}(CO)_{26}]^{2-}$

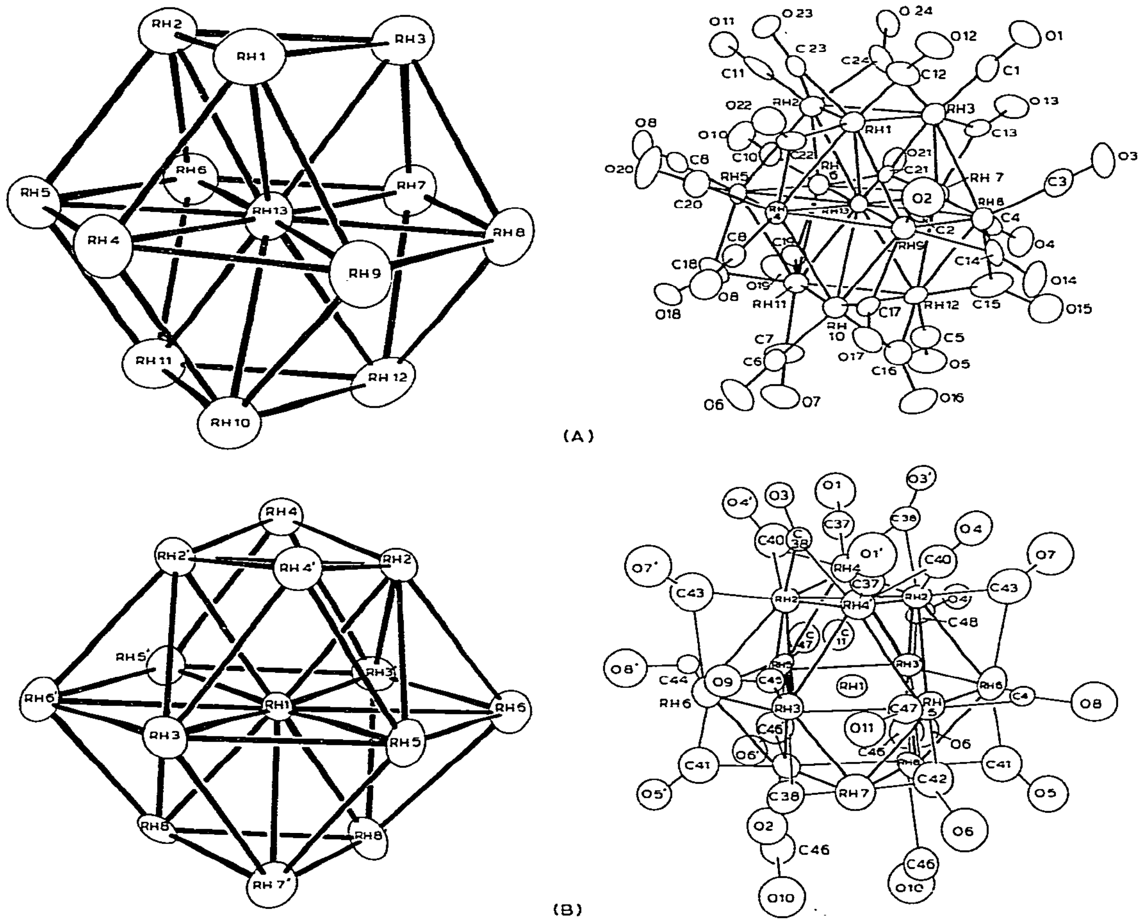

Fig. 4. ORTEPS of: (a) $[Rh_{13}(CO)_{24}H_2]^{3-}$ with and without the carbonyls and (b) $[Rh_{14}(CO)_{26}]^{2-}$ with the carbonyls found in this study and without them. The complete structure for the latter cluster has been reported by Martinengo et al. [4e].

(bis(triphenylphosphine)iminium salt) resulted in the partial degradation of the anion after 2-hours each at 120 and 160°C, while the related species, $[Rh_{14}(CO)_{25}]^{4-}$ (benzyl triethyl ammonium salt) was found to be inert under these conditions. We initially expected, on the basis of the similarity of the two polyhedra [4d,4e,5e] and the known increase in the reactivity of the clusters with the degree of reduction [4a] that the tetra-anion would be the least stable, but our more recent results [7] have shown the determining role of the counter-ion in the thermal reactivity of the clusters.

$$[RhX_2(CO)_2]^- + [Rh_{14}(CO)_{25}]^{4-} \xleftarrow{2\,X^-} [Rh_{15}(CO)_{27}]^{3-} \xrightarrow[-\text{``Rh(CO)''}]{CF_3SO_3H} [Rh_{14}(CO)_{26}]^{2-} + H_2 + 2\,CF_3SO_3^- \quad (7)$$

We examined the reaction of $[Rh_7(CO)_{16}]^{3-}$ with trifluoromethanesulfonic acid in an attempt to detect $[Rh_7(CO)_{16}H_x]^{(3-x)-}$ ($x = 1, 2$), whose existence was postulated by analogy with its halide and pseudo-halide analogs [6] and because it could be an intermediate in the formation of $[Rh_{14}(CO)_{26}]^{2-}$ or $[Rh_{14}(CO)_{25}H_x]^{(4-x)-}$ ($x = 0, 1$). We found (bis(triphenylphosphine)iminium salt of the cluster; acetone solution; 0°C) that $[Rh_{14}(CO)_{26}]^{2-}$ was the only product detected by monitoring the system with ^{13}C NMR spectroscopy (salt enriched with 45% ^{13}CO; 1 atm; 25°C). The absence of the characteristic resonances of metal-bonded hydrides expected in the ^1H NMR spectra (acetone-d_6 or acetone solution, —90 to 40°C; 0 to 60 ppm) indicates the absence of detectable amounts of $[Rh_{14}(CO)_{25}H_x]^{(4-x)-}$ ($x > 0$) and $[Rh_7(CO)_{16}H_x]^{(3-x)-}$. The formation of this hydride in excess of acid is suggested by the selective formation of $[Rh_{14}(CO)_{26}]^{2-}$ from $[Rh_7(CO)_{16}]^{3-}$ and trifluoromethanesulfonic acid (Scheme 2).

The formation of $[Rh_{14}(CO)_{26}]^{2-}$ in the reaction of $[Rh_7(CO)_{16}]^{3-}$ with CF_3SO_3H indicates the enhancement of the oxidative aggregation of two high nuclearity clusters to form even larger species in the presence of that acid. It is inferred from the non-oxidative character of trifluoromethanesulfonic acid that this enhancement probably is due to the decrease in the energy of activation for such a process caused by the protonation of the clusters. We tested this idea by studying the aggregation of $[Rh_7(CO)_{16}]^{3-}$ with $[Rh_{15}(CO)_{27}]^{3-}$ in the presence of CF_3SO_3H (acetone solution; 0°C). It was expected from previous structural observations that $[Rh_{22}(CO)_{35}H_x]^{(5-x)-}$ would be formed in that reaction [5h]. Instead, it was found that $[Rh_{14}(CO)_{26}]^{2-}$ was the sole product of the reaction in the case of the bis(triphenylphosphine)iminium salts and that the expected twenty-two-atom rhodium cluster was formed upon using the cesium salts of the clusters (Scheme 2). These results show the influence of the cationic counterions in the aggregation-fragmentation reactions of the anionic rhodium carbonyl clusters, and the probable involvement of the cations in determining the pathway for the redox reactions of the clusters. The degradation of the bis(triphenylphosphine)iminium cation in the acidic medium could have facilitated the aggregation reactions responsible for the formation of $[Rh_{14}(CO)_{26}]^{2-}$ from $[Rh_7(CO)_{16}]^{3-}$ and of the twenty-two-atom rhodium species from $[Rh_7(CO)_{16}]^{3-}$ and $[Rh_{15}(CO)_{27}]^{3-}$. We are investigating these possibilities [7].

This work has also shown that the fragmentation of $[Rh_{15}(CO)_{27}]^{3-}$ may result in the formation of $[Rh_{13}(CO)_{24}H_2]^{3-}$, $[Rh_{14}(CO)_{26}]^{2-}$ or $[Rh_{14}(CO)_{26}H_x]^{(4-x)-}$ depending on the reaction conditions. It also indicates that the mixture of clusters formed in the hydrogenation of $[Rh_{12}(CO)_{30}]^{2-}$ (eq. 1) may be due to the pyrolysis of $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ to form $[Rh_{15}(CO)_{27}]^{3-}$ and to the further transformation of this cluster into $[Rh_{14}(CO)_{26}]^{2-}$ and $[Rh_{14}(CO)_{25}H_x]^{(4-x)-}$ ($x = 0, 1$). These results explain the formation of $[Rh_{14}(CO)_{26}]^{2-}$ and $[Rh_{22}(CO)_{37}H_x]^{4-}$ during the pyrolysis of $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ [4e,4f]. These observations have led to the discovery of a convenient, rapid, procedure for the synthesis of $[Rh_{23}(CO)_{24}H_2]^{3-}$ which overcomes the difficulties of the previous synthesis [4b].

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