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# ON THE THERMAL GROWTH AND DECOMPOSITION OF RHODIUM CARBONYL CLUSTERS

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## Summary

The growth of anionic rhodium carbonyl clusters under pyrolytic conditions depends upon the counterion. The appearance of complexes of higher nuclearity was least favorable with the cesium salts while it occurred more readily with the ammonium salts following the trend: $[R_4N]^+$ (R = alkyl) $< [R_3R'N]^+$ (R' = benzyl) $< [R_3NH]^+ < [R_2NH_2]^+$. A redox reaction between the rhodium carbonyl anion and the ammonium cation is implicated in the thermal growth of clusters. The electron-transfer process between these two moieties may involve the initial fragmentation of the clusters to form $[Rh(CO)_4]^-$, and the reduction of the ammonium counterions by $[Rh(CO)_4]^-$ at high temperatures, although the direct electron transfer from the polynuclear species to the cation cannot be ruled out yet. It appears that electron transfer precedes or, that it is parallel to, the fragmentation of the clusters while the aggregation reactions of the resulting fragments give the observed products. The formation of metallic rhodium from either mono- or poly-nuclear complexes, and the sequential transformations found for these species are in agreement with the expected thermodynamic preference for high nuclearity species. The existence of the independent effect of the amines and the alkali cations when both of them are present resulted in the inhibition of the formation of metallic rhodium and retarded the growth of the clusters. These results correlate with the enhanced rhodium solubility noted for some catalytic systems that are based on rhodium carbonyl clusters with amines and cesium salts added, and which are used to convert $H_2/CO$ mixtures into polyalcohols.

## Introduction

Our interest in the pathways leading to the formation of rhodium carbonyl clusters has been prompted by the suggested involvement of $Rh_2(CO)_8$, $HRh(CO)_4$, $[Rh(CO)_4]^-$ and $[L_xRh(CO)_2]^+$ in their fragmentation and aggregation reactions under high temperatures and pressures of carbon monoxide and hydrogen [1–5], or

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even under milder conditions (eq. 1). Aggregation and fragmentation of the clusters may also occur under ambient pressure as suggested by the formation of $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$, $[Rh_{15}(CO)_{27}]^{3-}$ or $[Rh_{14}(CO)_{25}]^{4-}$ during the pyrolysis of $[Rh_{12}(CO)_{30}]^{2-}$ [6a], or by the formation of $[Rh_{22}(CO)_{35}H_x]^{(5-x)-}$ during the pyrolysis of solutions prepared from $Rh(CO)_2acac$ [7]. Similar reactions have been also observed under ambient conditions upon addition of a non-oxidative protonic acid of a weakly bonding anion such as trifluoromethylsulfonic acid in the absence of other ligands, although they appeared to depend upon the nature of the cation [8] (eq. 2–4). These results suggested that the fragmentation and aggregation reactions of the clusters either at pyrolytic temperatures or under the conditions employed for the synthesis of polyols [1–5] may be related to the redox properties of these species. The changes in cluster size with the temperature and pressure of carbon monoxide indicated to us the inverse effect of these two variables in the growth of clusters [1–5]. This led us to expect a similar behavior for the clusters at high temperature under ambient pressure and under the more drastic conditions used in some catalytic systems [1–5].

$$[Rh_{15}(CO)_{27}]^{3-} \xrightarrow{CO/H_2} [Rh_{13}(CO)_{24}H_2]^{3-} \tag{1}$$

$$[Rh_{22}(CO)_{35}H_x]^{(5-x)-} \xleftarrow[H^+]{CS^+} [Rh_{15}(CO)_{27}]^{3-} + [Rh_7(CO)_{16}]^{3-} \xrightarrow[H^+]{PPN^+} [Rh_{14}(CO)_{26}]^{2-} \tag{2}$$

$$2[Rh_7(CO)_{16}]^{3-} \xrightarrow[H^+]{PPN^+} [Rh_{14}(CO)_{26}]^{2-} \tag{3}$$

$$[Rh_{15}(CO)_{27}]^{3-} \xrightarrow[H^+]{PPN^+} [Rh_{14}(CO)_{26}]^{3-} \tag{4}$$

We decided then to look at the thermal activity of these clusters under ambient pressure because of the implication these studies may have on the behavior of these species under high pressures of carbon monoxide and hydrogen. This work was expected to expand the studies initiated some time ago with the pyrolysis [6a] of $[Rh_{12}(CO)_{30}]^{2-}$. It was also expected that this work would show the sequence involved in the growth of these clusters while indicating the specific pathways leading from the smaller to the bigger species and the influence of the cation on those reactions as suggested by our previous results (eq. 1 and 2). These results are reported below.

## Experimental

Commercially available solvents were purified and dried by literature procedures [1]. Sulfolane was obtained from Philips Chem. Co.; methanol from Kodak Chem. Co.; tetraethylene glycol dimethyl ether from Ansul Chem. Co., acetone and acetone-$d_6$ from Aldrich Chemical Co. Other chemicals were obtained from usual sources: $Rh(CO)_2acac$ was supplied by Mathey, Bishop and Co.; cesium benzoate trihydrate from Strem Chem. Corp.; and the remaining inorganic reagents from Alfa Chem. Corp. The gases used in this work were obtained from the Linde Division of Union Carbide Corp. These chemicals were used as supplied. The synthesis of the salts of the rhodium carbonyl complexes were conducted by new procedures in the cases of $[Rh(CO)_4]^-$ [2], $[Rh_{12}(CO)_{30}]^{2-}$ [9a], $[Rh_{15}(CO)_{27}]^{3-}$ [4], $[Rh_{14}(CO)_{25}]^{4-}$ [9b], and $[Rh_{13}(CO)_{24}H_2]^{3-}$ [8], by modification of the literature methods in the cases of $[Rh_7(CO)_{16}]^{3-}$ [9c], and $[Rh_{13}(CO)_{24}H_3]^{2-}$ [6a], and by the literature procedures in the cases of $[Rh_5(CO)_{15}]^-$ [9d], $[Rh_6(CO)_{15}X]^-$ [9e] and $[Rh_7(CO)_{16}X]^{2-}$ (X = Br, I) [9f]. Infrared spectra were obtained with a Perkin–Elmer 283 spectrometer using matched 0.15 mm calcium fluoride cells; $^1H$ and $^{13}C$ NMR spectra were run in acetone-$d_6$ for the lower thermal range, (−90 to 40°C), and in sulfolane at higher temperatures. We usually employed saturated solutions prepared by using 3–4 ml of the solvent in a Schlenk tube and transferred via syringe into a 12 mm NMR tube. The tube was capped under argon and sealed with wax. The spectra were collected on a Varian XL-100 FT-NMR spectrometer. The parameters used varied with each sample. In general, $^1H$ spectra were collected in the range of +30 to −50 ppm, while $^{13}C$ spectra were studied from 0 to 300 ppm downfield from tetramethylsilane used as external standard. Samples were enriched by ex-

TABLE 1

$^{13}C$ NMR CHEMICAL SHIFTS FOR SOME RHODIUM CARBONYL COMPLEXES

| Compound | Temperature (°C) | Chemical shift (ppm) | Reference |
|---|---|---|---|
| $Rh(CO)_2acac$ | 20 | 183.7(d) | 23e |
| $[Rh(CO)_2(CH_3CN)_2]^+$ | 20 | 181.6(d) | 23e |
| $[Rh(CO)_4]^-$ | 20 | 206.3(d) | 23e |
| $[Rh(CO)_2Br_2]^-$ | 20 | 181.4(d) | 23e |
| $[Rh(CO)_2Cl_2]^-$ | 20 | 183.2(d) | 23e |
| $Rh_4(CO)_4Cl_2$ | 20 | 180.4(d) | 23e |
| $Rh_2(CO)_4Br_2$ | 20 | 179.9(d) | 23e |
| $Rh_2(CO)_3(\eta\text{-}C_5H_5)_2$ | 20 | 203.8(t) | 23d |
| | −80 | 191.8(d); 231.8(t) | |
| $Rh_4(CO)_{12}$ | 50 | 189.5(q) | 23b |
| | −65 | 175.5; 181.8; 183.4; 228.8(d) | |
| $Rh_6(CO)_{16}$ | 70 | 180.1(ds); 231.5(qs) | 23f |
| $[Rh_6(CO)_{15}]^{2-}$ | −70 | 209.2(sep) | 23f |
| $[Rh_6(CO)_{15}I]^-$ | −70 to 30 | 183.3(ds); 232.9, 239.2(qs) | 23d |
| $[Rh_7(CO)_{16}]^{3-}$ | −70 | 198.2, 205.7, 206.4(d); 218.0, 229.5(t); 254.3(q) | 23f |
| | 30 | 198.2, 206.4(d); 217.5(b); 229.5(t); 254.3(q) | |
| $[Rh_7(CO)_{16}I]^{2-}$ | −30 | 218.5(oct) | 23a |
| $[Rh_{12}(CO)_{30}]^{2-}$ | −70 to 50 | 183.4, 186.1, 186.3(d); 211.5(t); 237.4(m) | 23g |
| $[Rh_{13}(CO)_{24}H_3]^{2-}$ | 20 | 209.9(b); 229.6(5) | 23h |
| $[Rh_{13}(CO)_{24}H_2]^{3-}$ | −80 to 20 | 209.8(b); 235.4(t) | 23h |
| $[Rh_{14}(CO)_{25}]^{4-}$ | −40 | 184.3, 191.1(d); 208.0(m); 231.0(q); 249.5(t) | 9a |
| | 40 | 192.9(d); 213.1(b) | |
| | 140 | 221.1(m) | |
| $[Rh_{15}(CO)_{27}]^{3-}$ | −90 | 180.1, 182.8, 187.5(d); 213.1, 219.7, 226.2(nrm); 238.1(m) | 4 |
| | 40 | 182.5(d), 210.0(m), 215.7(m) | |

[a] Downfield from $(CH_3)_4Si$; d = doublets; t = triplet; q = quartet; qs = quartets; sep = septet; oct = octet; m = multiplet; nrm = non-resolved multiplet; b = broad unresolved multiplet.

change under 1 atm of 45% $^{13}CO$ at ambient temperature in acetone solution, or at 40°C in sulfolane. The NMR spectra were collected at 40, 80, 120, 140 and 160°C by sequentially monitoring the solutions for at least 1–2 hours at each temperature and obtaining one spectrum at 40°C after each spectrum recorded at higher temperature. For protons, usually 16 K data points were collected over a 5000 Hz sweep width to give a resolution of 0.31 Hz/channel. Accumulation of 288 transients using a 20 μsec pulse width and 1.6 sec acquisition time was made. Carbon-13 NMR data were obtained at 25.2 MHz by accumulation of 500–20,000 transients using a 15 μsec pulse width ( ~ 30° flip angle) and 0.8192 acquisition time. A 7500 Hz sweep width was used with 12,320 data points to give a 0.61 Hz/channel resolution. The slight differences between the chemical shifts reported in this work and in the literature (Table 1) for some compounds may be due to solvent or temperature-induced shifts, among other factors. In fact, we have detected a thermally induced (40–180°C) shift in the range of 0.3 to 1.0 ppm in some instances, in sulfolane solutions.

## Results and discussion

The well known identification of rhodium carbonyl complexes, in particularly polynuclear species, by $^{13}C$ NMR spectroscopy (Table 1) suggested this technique for the study of the thermal reactivity of rhodium carbonyl clusters and related complexes. We examined, in the first place, the thermal reactions of several $[Rh(CO)_4]^-$ salts because this anion participates in the chemistry of the clusters under high pressure of synthesis gas [1,5]. It was also expected that the factors involved in the aggregation reactions required for the formation of the clusters would be more evident when the starting material was a highly reduced (metal atom/negative charge, 1/1), mononuclear carbonyl anion. It was found that the reactivity of $[Rh(CO)_4]^-$ is a function of the counterion (Table 2 and Fig. 1) and that the degradation of the ammonium cation in these reactions paralleled the appearance of cluster products. Similar results were found when rhodium carbonyl anionic clusters were converted into species of higher nuclearity under pyrolytic conditions, as discussed below. In any case, we did not obtain any evidence to indicate that the decomposition of the ammonium cations occurs via a Hoffman

TABLE 2

THERMAL REACTIVITY OF THE SALTS OF $[Rh(CO)_4]^-$

| Cation | Temperature (°C)/ time (h) | Observations [a] |
|---|---|---|
| $[Cs(18\text{-crown-}6]_2]$ | 40–120/2 | No changes detected |
| | 160/2 | p.c. to insoluble rhodium-containing products [b] |
| | 180/2 | c.c. to insoluble rhodium-containing products |
| $[(C_2H_5)_4N]^+$ | 120/2 | No changes detected |
| | 160/2 | c.c. to $[Rh_7(CO)]_6]^{3-}$ and $[Rh_9(CO)_{-18}]^{3-}$ |
| $[PhCH_2N(C_2H_5)_3]^+$ | 80–100/2 | p.c. to $[Rh_7(CO)_{16}]^{3-}$ |
| | 120/2 | c.c. to $[Rh_7(CO)_{16}]^{3-}$ and $[Rh_9(CO)_{-18}]^{3-}$ |

[a] p.c. and c.c. mean partial and complete conversion, respectively, of the starting anion; the suggested identification of the products has been on the spectra obtained by cooling the system to 40°C after reaction at high temperature, or/and on the pattern noted while at this temperature. [b] Metallic rhodium is one of the main components in this material.

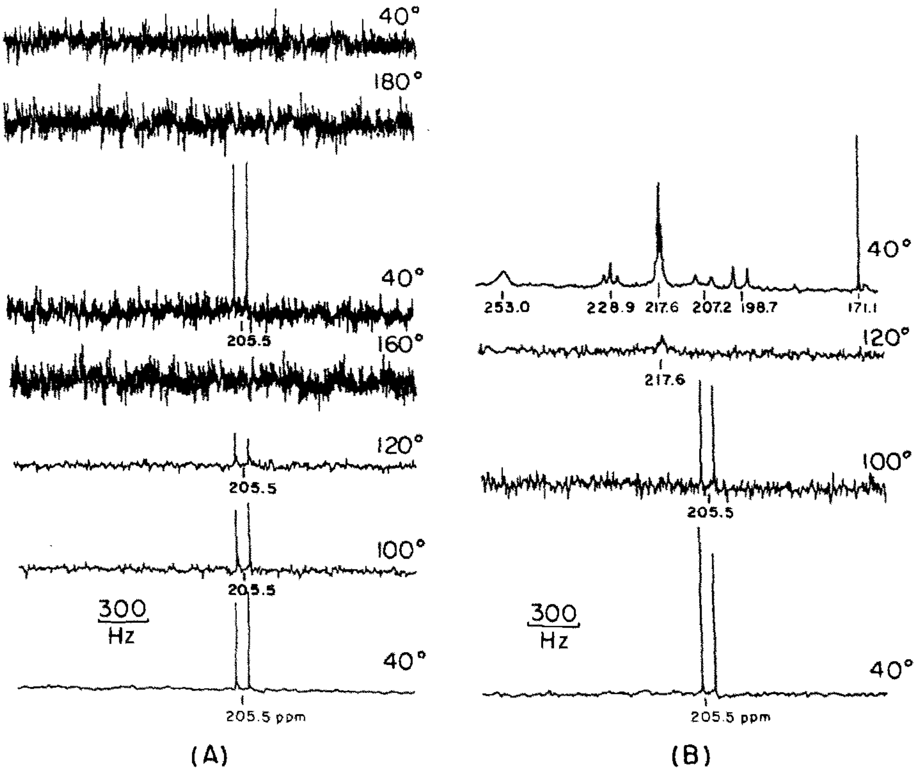


Fig. 1. $^{13}$C variable temperature NMR study of $[Rh(CO)_4]^-$ salts: (a) $[Cs(18\text{-crown-}6)_2]^+$ and (b) $[PhCH_2N(C_2H_5)_3]^+$.

elimination reaction [10]. Instead, the parallel between the reduction potential of the cations [11] and their ability to inhibit the increase in the nuclearity of the rhodium anions: $Cs^+ > [(C_2H_5)_4N^+ > [PhCH_2N(C_2H_5)_3]^+ > [HN(CH_3)(CH_2CH_2)_2O]^+ > [H_2N(CH_2CH_2)_2O]^+$ suggested the participation of electron transfer processes between these two types of species in the aggregation reactions of the anions. Accordingly, we have noted the formation of bibenzyl, $[PhCH_2CH_2Ph]$, and triethylamine (Fig. 2) during the pyrolysis of the $[PhCH_2N(C_2H_5)_3]^+$ salts of $[Rh(CO)_4]^-$ and of the polynuclear rhodium anions, as previously reported for the one-electron polarographic reduction of this cation [11] (eq. 5). On the other hand, the high reduction potential of the cesium cation may be responsible for the different behavior of these salts. These observations apply to the systems based on $[Rh(CO)_4]^-$ and on polynuclear anions, as well. For instance, the oxidation of $[Rh(CO)_4]^-$ into $[Rh_7(CO)_{16}]^{3-}$ may occur with the participation of $Rh_2(CO)_8$ (eq. 6 and 7) although we could not detect $Rh_2(CO)_8$ in this system. In spite of that, our proposal is based on the preliminary structural study of the $Rh_9$ cluster shown below, the formation of $Rh_6(CO)_{16}$ during the oxidation of $[Rh(CO)_4]^-$ with protonic acids [12], the reaction of this anion with $Rh_4(CO)_{12}$ to give $[Rh_7(CO)_{16}]^{3-}$ [9c–e], and the aggregation-fragmentation reactions between $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$ and $Rh_2(CO)_8$ [1,2]. On the other hand, the reactions of $[Rh(CO)_4]^-$ with the morpholinium cations above resulted in a similar oxidation of this anion into $[Rh_7(CO)_{16}]^{3-}$, even upon attempting the preparation of these salts at temperatures below 0°C. These results precluded us from examining the thermal reactivity of these salts by $^{13}C$ NMR spectroscopy, but it indicated the lability of these species and the decomposition of the $[H(R)N(CH_2CH_2)_2O]^+$ (R = H, $CH_3$) salts. We attempted the identification of the decomposition products of these cations during the thermolysis of their $[Rh_7(CO)_{16}]^{3-}$ salts (Table 3). It was noted that ca. 30% of the initial cation were degraded after 0.3 h at 160°C as indicated, for instance, by the decrease of the $^{13}C$ NMR signals of $[H_2N(CH_2CH_2)_2O]^+$ (46.1 and 72.9 ppm). Unfortunately, we have not been able yet to unequivocally assign the resonances of the resulting decomposi-

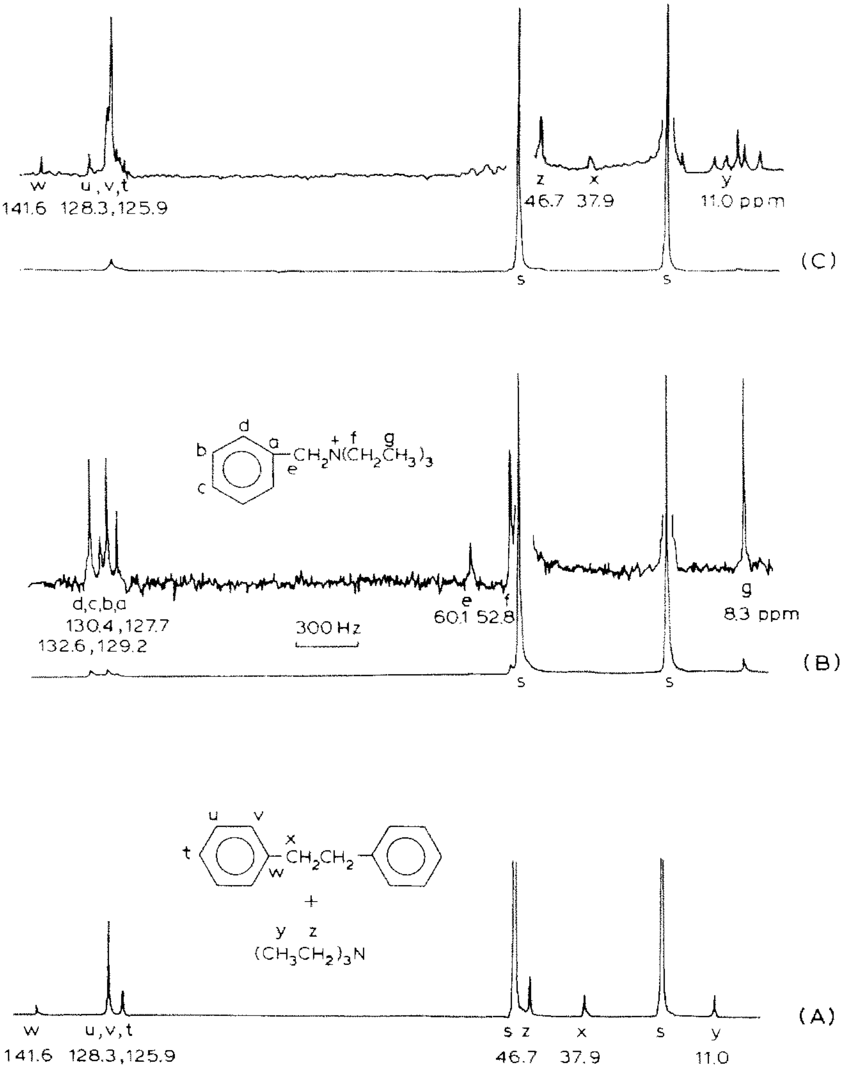


Fig. 2. $^{13}C$ NMR spectra of: (A) bibenzyl, $PhCH_2CH_2Ph$ and $(C_2H_5)_3N$; (B) $[PhCH_2N(C_2H_5)_3]^+$ salt of $[Rh(CO)_4]^-$ at 40°C before pyrolysis and (C) the same solution as in B but after pyrolysis.

TABLE 3. THERMAL REACTIVITY OF THE SALTS OF SOME RHODIUM CARBONYL CLUSTERS CONTAINING LESS THAN TEN METAL ATOMS

| Clusters | Cation | Temperature (°C) time (h) | Observations[a] |
|---|---|---|---|
| $[Rh_6(CO)_{15}]^{2-}$ | $(Cs(18\text{-}Crown\text{-}6)_2]^+$ | 40/1 | p.c. to $[Rh_9(CO)_{\sim 18}]^{3-}$ and uncharacterized products |
| | | 120/2 | c.c. to $[Rh_9(CO)_{\sim 18}]^{3-}$ and uncharacterized products |
| | | 160/2 | c.c. to $[Rh_{14}(CO)_{25}]^{4-}$, $[Rh_9(CO)_{\sim 18}]^{3-}$ and $[Rh(CO)_4]^-$(after cooling at 40°C) |
| | $[(C_2H_5)_4N]^+$ | 40–160 | As above |
| | $[PhCH_2N(C_2H_5)_3]^+$ | 40–160 | As above |
| $[Rh_6(CO)_{15}Br]^-$ | $[(C_2H_5)_4N]^+$ | 40/2 | No changes detected |
| | | 80/2 | p.c. to uncharacterized products |
| | | 120/2 | c.c. to the products above |
| | | 140/2 | c.c. to $[Rh_{15}(CO)_{27}]^{3-}$, $[Rh(CO)_2Br_2]^-$ and another mononuclear species (after cooling at 40°C) |
| $[Rh_7(CO)_{16}]^{3-}$ | $[Cs(18\text{-}Crown\text{-}6)_2]^+$ | 40/2 | No changes detected |
| | | 160/3 | Traces of $[Rh_9(CO)_{\sim 18}]^{3-}$ and $[Rh(CO)_4]^-$ (after cooling at 40°C) |
| | | 180/2 | $[Rh(CO)_4]^-$,<br>$[Rh_{14}(CO)_{25}]^{4-}$<br>and metallic rhodium |
| | $[(CH_3)_4N]^+$ | 40–180 | As above |
| | $[(C_2H_5)_4N]^+$ | 40–180 | As above |
| | $[PhCH_2N(C_2H_5)_3]^+$ | 80/4 | No changes detected |
| | | 140/2 | c.c. to $[Rh_9(CO)_{\sim 18}]^{3-}$ |
| | | 160.10[a] | c.c. to $[Rh_{15}(CO)_{27}]^{3-}$ |
| | | 180/4 | As above |
| | $[HN(CH_3)(CH_2CH_2)_2O]^+$ | 80/2 | No changes detected |
| | | 100/2 | c.c. to $[Rh_9(CO)_{\sim 18}]^{3-}$ and metallic rhodium |
| | $[(H)_2N(CH_2CH_2)_2O]^+$ | 80/2–100/1 | As above |
| $[Rh_7(CO)_{16}Br]^{2-}$ | $[(C_2H_5)_4N]^+$ | 40/2–60/2 | No changes detected |
| | | 100/2 | c.c. to $[Rh_{14}(CO)_{25}]^{4-}$,<br>$[Rh_{15}(CO)_{27}]^{3-}$,<br>$[Rh(CO)_2Br_2]^-$<br>and $Rh_6(CO)_{16}$ (after cooling to 40°C) |
| $[Rh_7(CO)_{16}I]^{2-}$ | $[(C_2H_5)_4N]^+$ | 40/2–60/2 | No changes detected |
| | | 120/2 | c.c. to $[Rh_{15}(CO)_{27}]^{3-}$, $[Rh_2(CO)_4I_2$, $Rh_6(CO)_{16}$ (after cooling to 40°C) |
| $[Rh_9(CO)_{\sim 18}]^{3-}$ | $[PhCH_2N(C_2H_5)_3]^+$ | 40/2–160/2 | No changes detected |
| | | 180/2 | c.c. to $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{27}]^{3-}$ (after cooling to 40°C) |

[a] p.c. and c.c. means partial and complete conversion, respectively, of the starting anion. The suggested identification of the products is usually based on the spectral features observed by cooling the system at 40°C after reaction at a specified temperature or/and on the pattern noted while at this temperature. The presence of unidentified intermediates at the higher temperatures is indicated in some instances by the resonances observed under these conditions.

TABLE 4

THERMAL REACTIVITY OF THE SALTS OF LARGE RHODIUM CARBONYL CLUSTERS

| Clusters | Cation | Temperature (°C)/ time (h) | Observations [a] |
|---|---|---|---|
| $[Rh_{12}(CO)_{30}]^{2-}$ | $[Cs(18\text{-Crown-}6)_2]^+$ | 80/2 | p.c. to $[Rh_{15}(CO)_{27}]^{3-}$ |
| | | 120/2 | c.c. to $[Rh_{15}(CO)_{27}]^{3-}$ and an unknown product |
| | $[(C_2H_5)_4N]^+$ | 80/2–120/2 | As above |
| | $[PhCH_2N(C_2H_5)_3]^+$ | 80/2–120/2 | As above |
| $[Rh_{13}(CO)_{24}H_3]^{2-}$ | $[Cs(18\text{-Crown-}6)_2]^+$ | 80/3 | No changes detected |
| | | 120/2 | p.c. to $[Rh_{15}(CO)_{27}]^{3-}$ and an unidentified product |
| | | 140/2 | c.c. to the products above |
| | $[(C_2H_5)_4N]^+$ | 80/3 | No changes detected |
| | | 120/2 | c.c. to $[Rh_{15}(CO)_{27}]^{3-}$ and an unidentified product |
| | $[PhCH_2N(C_2H_5)_3]^+$ | 80/3 | No changes detected |
| | | 100/2 | c.c. to $[Rh_{15}(CO)_{27}]^{3-}$ and an unidentified product |
| $[Rh_{13}(CO)_{24}H_2]^{3-}$ | $[Cs(18\text{-Crown-}6)_2]^+$ | 80/3 | No changes detected |
| | | 120/2 | p.c. to $[Rh_{15}(CO)_{27}]^{3-}$ and an unidentified product |
| | | 140/2 | c.c. to the products above |
| | $[(Ph_3P)_2N]^+$ | 80/2 | p.c. to $[Rh_{15}(CO)_{27}]^{3-}$ and an unidentified product |
| | | 120/1 | c.c. to the products above |
| $[Rh_{15}(CO)_{27}]^{3-}$ | $[Cs(18\text{-Crown-}6)_2]^+$ | 40/2–160/3 | No changes detected |
| | $[(CH_3)_4N]^+$ | 40/2–160/3 | As above |
| | $[(C_2H_5)_4N]^+$ | 40/2–160/3 | As above |
| | $[(Ph_3P)_2N]^+$ | 40/2–140/2 | No changes detected |
| | | 160/3 | p.c. to $[Rh_{14}(CO)_{25}]^{4-}$ and an uncharacterized product |
| | | 180/2 | p.c. to the products above |
| $[Rh_{14}(CO)_{25}]^{4-}$ | $[Cs(18\text{-Crown-}6)_2]^+$ | 80/2–160/4 | No changes detected |
| | | 180/0.5 | p.c. to insoluble materials and rhodium mirror |
| | | 180/2 | c.c. to the products above |
| | $[(C_2H_5]_4N]^+$ | 80/2–180/3 | As above |
| | $[PhCH_2N(C_2H_5)_3]^+$ | 80/2–160/4 | No changes detected |
| | | 180/2 | c.c. to $[RH_{15}(CO)_{27}]^{3-}$, insoluble materials and rhodium mirror |

[a] See Footnotes on Table 2.

tion products; by contrast, the formation of $[Rh_9(CO)_{\sim 18}]^{3-}$ was clearly noted in these experiments in agreement with the results below:

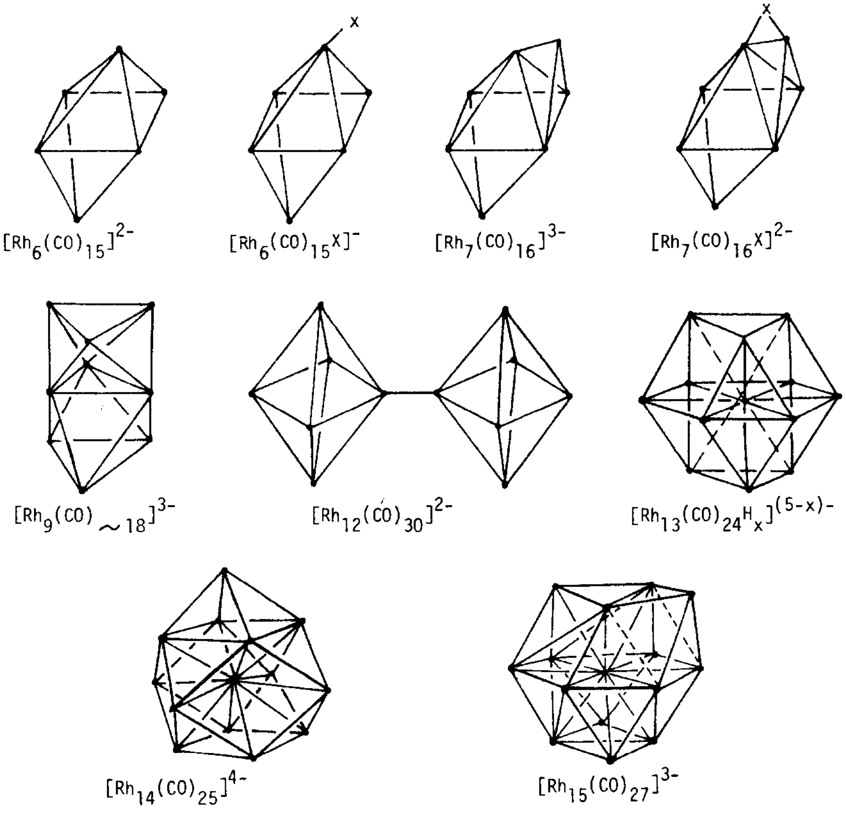
$$2[PhCH_2N(C_2H_5)_3]^+ + 2e^- \rightarrow 2[PhCH_2N(C_2H_5)_3] \rightarrow PhCH_2CH_2Ph + N(C_2H_5)_3 \tag{5}$$

$$2[Rh(CO)_4]^- \rightarrow Rh_2(CO)_8 + 2e^- \tag{6}$$

$$3[Rh(CO)_4]^- + 2Rh_2(CO)_8 \rightleftarrows [Rh_7(CO)_{16}]^{3-} + 12CO \tag{7}$$

The systematic pyrolytic study of anionic rhodium carbonyl clusters illustrates the influence on the thermal reactivity of these species by the type of polyhedra (Scheme 1), the presence of ligands other than carbon monoxide, and the nature of the counterions. For instance, we have noted the following trends in the increase of the thermal reactivity of clusters based on an octahedral cage (Table 3) and more complicated polyhedra (Table 4): $[Rh_7(CO)_{16}]^{3-} > [Rh_7(CO)_{16}X]^{2-}$, $[Rh_6(CO)_{15}X]^- > [Rh_6(CO)_{15}]^{2-}$, and $[Rh_{14}(CO)_{25}]^{4-}$, $[Rh_{15}(CO)_{27}]^{3-} > [Rh_{13}(CO)_{24}H_x]^{(5-x)-} > [Rh_{12}(CO)_{30}]^{2-}$. We initially expected that the increase in the degree of reduction of the clusters would facilitate [13] the redox reaction between the anion and the counterions. Instead, the stability found for the bigger and more reduced clusters (Tables 3 and 4) indicated that other factors should be considered. It is conceivable that the adoption of specific polyhedra would influence the thermal reactivity of the clusters as a result of the electronic distribution involved in each instance [14], or because of the thermodynamic preference at high temperatures for cages with an increased number of rhodium–rhodium bonds [15]. The formation of $[Rh_{14}(CO)_{25}]^{4-}$ as the end-product in our pyrolytic studies and the thermal stability of this anion are both in agreement with that possibility.

SCHEME 1. Metal frameworks of some rhodium carbonyl clusters relevant to this work.



The pyrolysis of ionic salts of rhodium carbonyl clusters indicated the important roles of $[Rh(CO)_4]^-$ and the cationic counterions in the thermal growth of these clusters. For instance, the presence of a counterion not readily amenable to reduction, such as cesium, slowed down but did not completely inhibit the thermal growth of the clusters. The occurrence of a redox reaction involving this cation and the cluster anions was not easily accepted by us because of the relatively high redox potential of cesium [11]. Instead, the formation of a larger cluster is associated in these cases to the release of the highly reduced anion $[Rh(CO)_4]^-$, as illustrated by the behavior of the $[Rh_7(CO)_{16}]^{3-}$ salts (Fig. 3 and Table 3). The cesium salt of this anion remained mostly unchanged after 3 h at 160°C, but $[Rh(CO)_4]^-$ (205.5 ppm) was detected along with traces of the $Rh_9$ anionic cluster (217.6 ppm) under these conditions or with $[Rh_{14}(CO)_{25}]^{4-}$ (192.9, 213.1 ppm) and insoluble-rhodium containing residues after 2 h at 180°C [16] (eq. 8). The same behavior has been observed with salts of symmetric ammonium cations such as $[(CH_3)_4N]^+$ and $[(C_2H_5)_4N]^+$, probably because of their high reduction potential [11]. It appears the disproportionation of the initial anion into less reduced clusters and the more reduced $[Rh(CO)_4]^-$ is the preferred pathway for the release of negative charge by the starting anion in the presence of these counterions. In contrast, this interpretation is not extended to the salts of $[HN(R)(CH_2CH_2)_2O]^+$ or $[PhCH_2N(C_2H_5)_3]^+$ due to the undetectability of $[Rh(CO)_4]^-$ and the formation, instead, of $[Rh_9(CO)_{\sim 18}]^{3-}$ and other cluster products (Table 3). The reduction of these counterions by electron

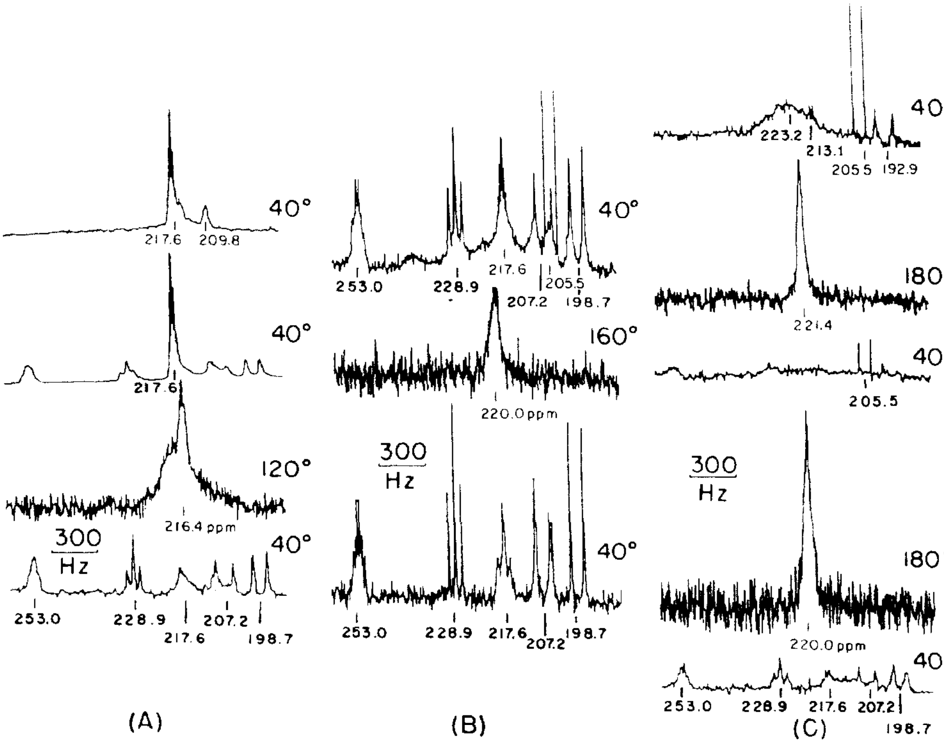


Fig. 3. $^{13}C$ variable temperature NMR study of: (A) $[PhCH_2N(C_2H_5)_3]_3[Rh_7(CO)_{16}]$ and (B) $[Cs(18\text{-crown-}6)_n]_3[Rh_7(CO)_{16}]$ at 160°C and (C) at 180°C.

transfer from the rhodium anions may occur with (eq. 5) or without the intermediacy of $[Rh(CO)_4]^-$. The only two instances where the thermal reactivity of the clusters was cation-independent involved $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$.

$$3\,Cs_3[Rh_7(CO)_{16}] \xrightarrow{180^\circ C} 5\,Cs[Rh(CO)_4] + Cs_4[Rh_{14}(CO)_{25}] + 2\,Rh^0 + 3\,CO \qquad (8)$$

The potential formation of unknown intermediates at high temperature initially emerged from the previous experiments. For instance, the detection of $[Rh(CO)_4]^-$ and $[Rh_{14}(CO)_{25}]^{4-}$ in the experiments above was only possible after cooling the system to 40°C, while the resonance detected at 180°C has the chemical shift expected for the coalescence band of $[Rh_7(CO)_{16}]^{3-}$ (220.3 ppm). We do not have a simple explanation for these observations at this time. It is possible that unsaturated species would be formed at the higher temperatures ($D$(Rh–CO) = 39 kcal/mol) [16] and this would lead to fragmentation into smaller species upon cooling ($D$(Rh–Rh) = 27 kcal/mol) [15]. In fact, the presence of unassigned resonances at high temperatures which are converted into patterns assigned to known species after cooling was also observed with the salts of $[Rh_6(CO)_{15}]^{2-}$, $[Rh_6(CO)_{15}X]^-$, $[Rh_7(CO)_{16}X]^{2-}$, $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ ($x = 2$, 3) (Fig. 4–10). The discussion below illustrates this aspect of our study. For instance, the thermal degradation of the cesium salt of $[Rh_6(CO)_{15}]^{2-}$ occurred under mild conditions, 1.0 h at 40°C, with the appearance of an unassigned band (214.2 ppm), together with the characteristic multiplet of the cluster (208.8 ppm) (Fig. 4); the irreversible formation of $[Rh_9(CO)_{\sim 18}]^{3-}$ (217.6 ppm) occurred at 80°C together with the appearance of another product associated with the band at 219.9 ppm. The formation of $[Rh_{14}(CO)_{25}]^{4-}$, in this case (192.9 and 213.1 (br/ppm) appears to be associated with the transformation of the products formed at 120–160°C upon cooling to 40°C as indicated by the absence at these temperatures of the coaslescence band of $[Rh_{14}(CO)_{25}]^{4-}$ (221.1 ppm), and the disappearance at 40°C of the unassigned resonances together with the persistance of the band associated with $[Rh_9(CO)_{\sim 18}]^{3-}$. In fact, the occurrence of fragmentation-aggregation reactions of the species present at the higher temperatures is also indicated by the appearance after cooling to 40°C of the doublet assigned to $[Rh(CO)_4]^-$ at 205.5 ppm. In any case, the thermal inertness of $[Rh_9(CO)_{\sim 18}]^{3-}$ in the presence of the cesium counterion is in contrast with the reactivity of some of its ammonium salts. For instance, this cluster was unchanged in its $[PhCH_2N(C_2H_5)_3]^+$ salt after 2 h at 160°C as shown by the reversible appearance of the coaslescence band, 217.6 ppm, of the anion after cooling to 40°C (Fig. 7), but it was transformed into $[Rh_{14}(CO)_{25}]^{4-}$ (192.9 and 213.1 (br) ppm) and $[Rh_{15}(CO)_{27}]^{3-}$ (182.5, 210.0 and 215.7 ppm) by further warming at 180°C followed by cooling to 40°C. We attempted to study the solution structure of the $Rh_9$ cluster looking for information concerning the carbonyl distribution of this cluster but the carbonyl fluxionality of some of these ligands even at −80°C precluded such effort.

The reactivity of the larger clusters follows the behavior already described above for the species of lower nuclearity. For instance, $[Rh_{12}(CO)_{30}]^{2-}$ was irreversibly converted into unknown materials at 80–120°C (213.9 and 204.9, 212.0 ppm) respectively, with the transformation of the product associated with the latter resonance into $[Rh_{15}(CO)_{27}]^{3-}$ occurring upon cooling to 40°C (Fig. 8). A similar reactivity was exhibited by the salts of the $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ ($x = 2$, 3) anions.

The reactivity of these clusters in the presence of the most inert counterions is illustrated by the behavior of the cesium salt of the dianion. This cluster is only partially degraded after treatment at 80–120°C (Fig. 9) as suggested by the presence of its spectral pattern (209.0 and 229.0 ppm), after cooling to 40°C together with the resonances assigned above to $[Rh_{15}(CO)_{27}]^{3-}$; the quantitative conversion into this cluster, and an unidentified product (204.9 ppm) was detected after warming to 140°C and cooling to 40°C. Unfortunately, we could not assign any of the remaining bands present in the high temperature spectra of this cluster. On the other hand, practically the same behavior has been observed for the $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ clusters in the presence of more reactive counterions, such as the ammonium or bis(triphenylphosphine)iminium cations, as illustrated by the behavior of the latter

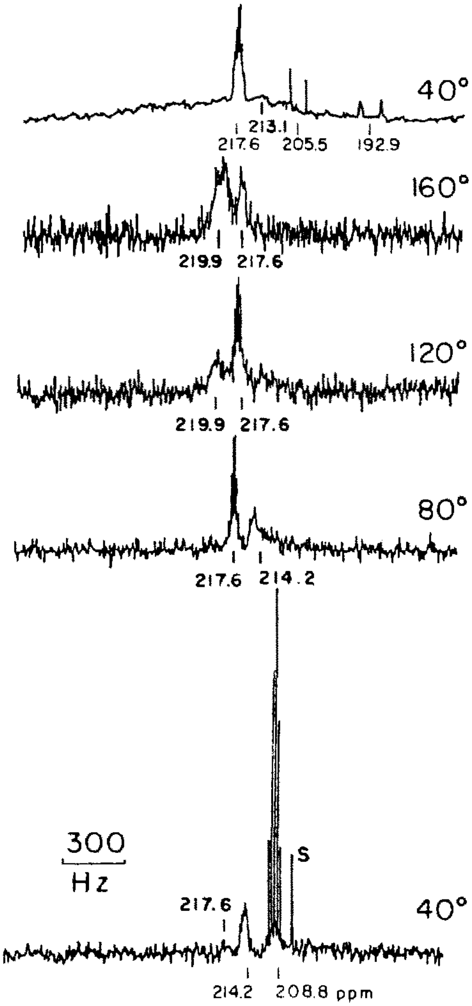


Fig. 4. $^{13}C$ NMR spectra of $[Cs(18\text{-crown-}6)_2]_2[Rh_6(CO)_{15}]$ in acetone-$d_6$ at 40°C and sulfolane from 80 to 160°C.

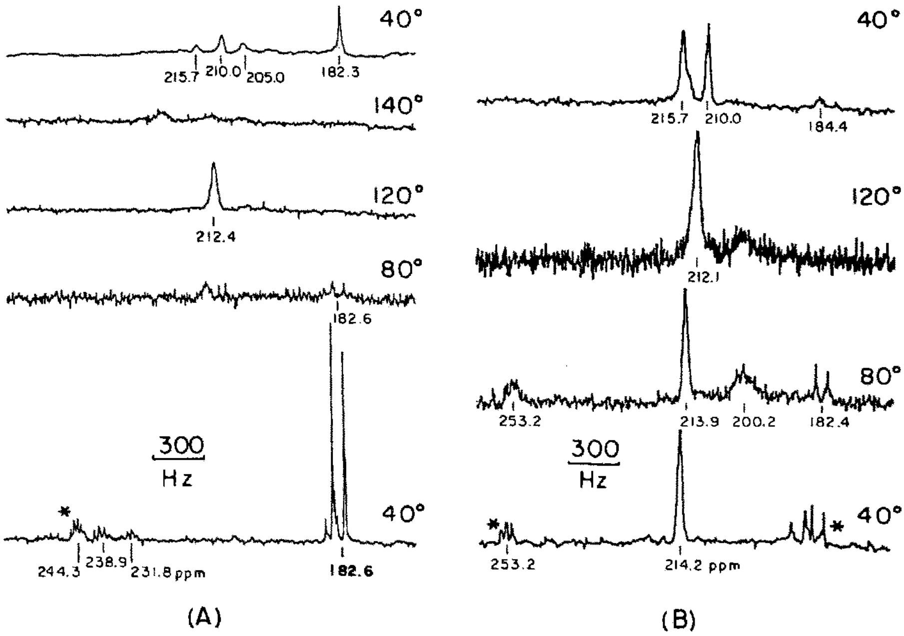


Fig. 5. $^{13}C$ variable temperature NMR study of: (A) $[(C_2H_5)_4N][Rh_6(CO)_{15}Br]$ and (B) $[(C_2H_5)_4N]_2[Rh_7(CO)_{16}I]$. * These resonances are not observed in the literature spectra of these clusters under different conditions, e.g., solvent, temperature, and counterions.

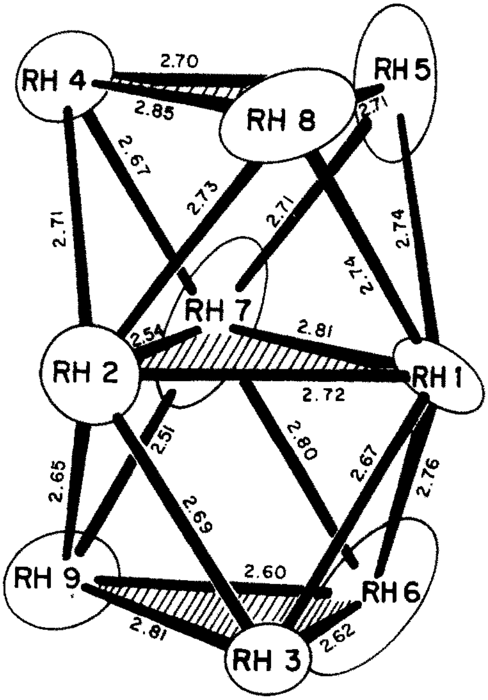


Fig. 6. ORTEP of the metal core of the nonarhodium carbonyl anion, showing the intermetallic contacts in Å.

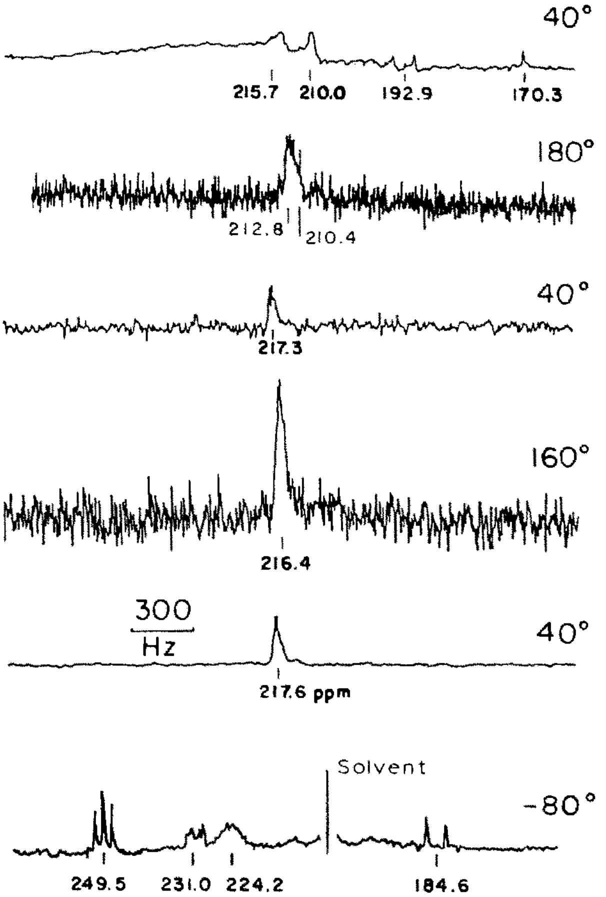


Fig. 7. $^{13}$C variable temperature NMR study of the pyrolysis of $[PhCH_2N(C_2H_5)_3]^+$ salt of the nonarhodium cluster anion.

salt of the trianion (Fig. 9). The $[Rh_{13}(CO)_{24}H_2]^{3-}$ cluster was partially degraded by warming to 80°C as shown by the detection, after cooling to 40°C, of the resonances assigned to this cluster (209.0, 235.0 ppm), together with an unassigned resonance at 215.4 ppm and the bands characteristic of $[Rh_{15}(CO)_{27}]^{3-}$. The complete degradation of $[Rh_{13}(CO)_{24}H_2]^{3-}$ into the two latter products occurred under more forcing conditions, 120°C, as indicated by the spectral features obtained at 40°C. The different intensity ratio of the resonances at 210.0 and 215.7 ppm in that spectrum and in the one associated with $[Rh_{15}(CO)_{27}]^{3-}$ is probably a consequence of the ability of the product associated with the band at 215.4 ppm to withstand these conditions. The remaining bands could be associated with the coalescence of the carbonyls present in the clusters detected at the lower temperatures or with products present at high temperatures. One of the resonances, 200.2 ppm, is only detectable at 80 to 120°C; and it has a chemical shift different than those generally associated with mono- or poly-nuclear complexes, but similar to those reported for some binuclear rhodium carbonyl complexes (Table 1). Finally, the thermal interconver-

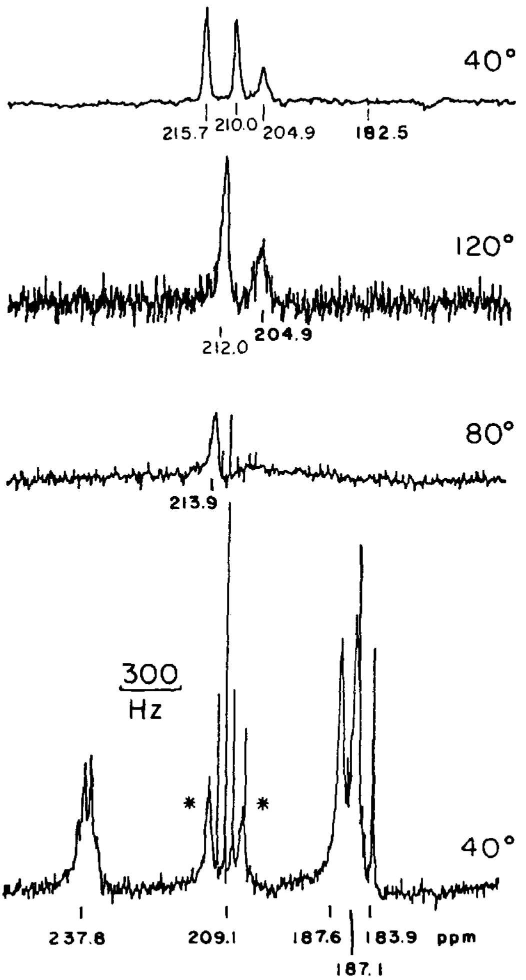


Fig. 8. $^{13}$C variable temperature NMR study of $[PhCH_2N(C_2H_5)_3]_2[Rh_{12}(CO)_{30}]$. * These resonances are not observed in the literature spectra of these clusters under different conditions, e.g., solvent, temperature, and counterions.

sion of $[Rh_{15}(CO)_{27}]^{3-}$ and $[Rh_{14}(CO)_{25}]^{4-}$ are apparent from the comparison of the spectral patterns previously assigned to these clusters (182.5, 210.0, 215.7 and 192.9, 213.4 ppm, respectively) following periods at temperatures between 80 and 180°C (Fig. 10). Unfortunately, we are unable to assign the remaining resonances present in these spectra at the higher temperatures. The formation of $[Rh_{15}(CO)_{27}]^{3-}$ occurred together with the appearance of insoluble rhodium containing materials such as metallic rhodium upon warming $[Rh_{14}(CO)_{25}]^{4-}$ salts at 180°C.

The influence of ligands other than carbon monoxide in the fragmentation of the cluster anions at high temperatures is reflected on the reactivity of the halo-substituted species relative to the parent compounds (Table 3). The salts of $[Rh_6(CO)_{15}Br]^-$ irreversibly reacted at 80°C (Fig. 5a) forming an uncharacterized product (212.4 ppm) that was irreversibly converted at 100°C into $[Rh_{14}(CO)_{25}]^{4-}$

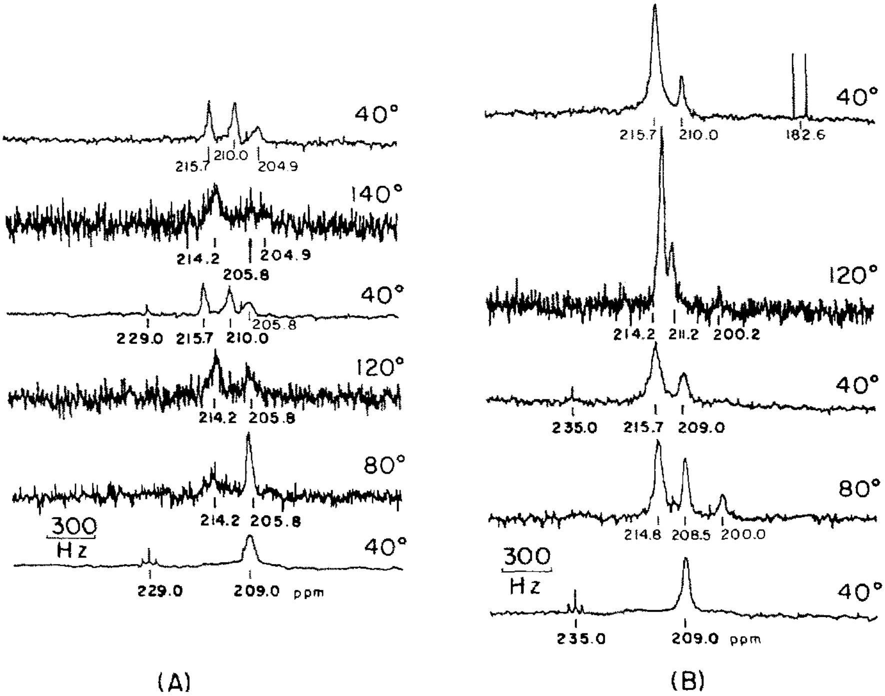


Fig. 9. $^{13}C$ variable temperature NMR study of (A) $[Cs(18\text{-crown-}6)_2]_2[Rh_{13}(CO)_{24}H_3]$ and (B) $[(Ph_3P)_2N]_3[Rh_{13}(CO)_{24}H_2]$.

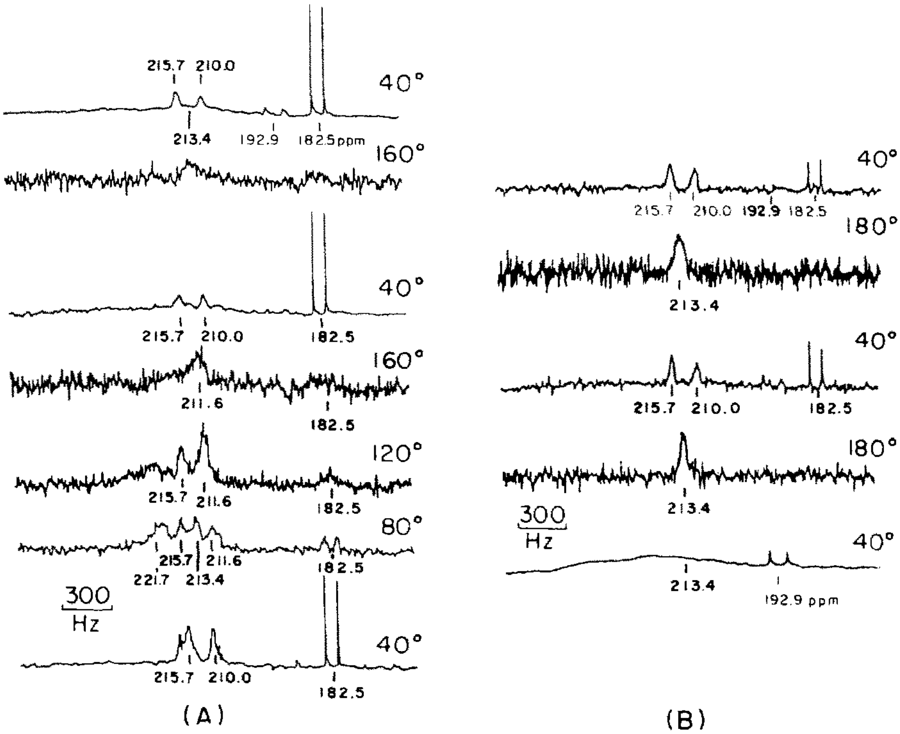


Fig. 10. $^{13}C$ variable temperature NMR spectra of (A) $[(Ph_3P)_2N]_3[Rh_{15}(CO)_{27}]$ and (B) $[(PhCH_2N(C_2H_5)_4[Rh_{14}(CO)_{25}]$.

(192.5, 213.1 (br), $[Rh_{15}(CO)_{27}]^{3-}$ (182.5, 210.0, and 215.7 ppm), $[Rh(CO)_2Br_2]^-$, (182.3 ppm), and another mononuclear complex (205.0 ppm). By contrast, the salts of $[Rh_7(CO)_{16}X]^{2-}$ (X = Br, I) reacted at lower temperature than the corresponding $[Rh_7(CO)_{16}]^{3-}$ salts, giving different products. The halo-substituted $Rh_7$ dianions (Fig. 5b) reacted with the irreversible generation of uncharacterized products at 80°C (200.2 ppm) and at 120°C (212.1 ppm), and the formation as end-products of the barely soluble $Rh_6(CO)_{16}$ and $[Rh_{15}(CO)_{27}]^{3-}$ (eq. 9) but $Rh_2(CO)_4I_2$ was also detected in the case of the iodide derivative while $[Rh(CO)_2Br_2]^-$ and $[Rh_{14}(CO)_{25}]^{4-}$ were also noted with the bromo-containing cluster. The presence of the latter products may be due to the reaction of $[Rh_{15}(CO)_{27}]^{3-}$ with bromide ion, previously reported by Chini et al. [17] (eq. 10). The absence of $[Rh_{14}(CO)_{25}]^{4-}$ among the products from the iodo-containing cluster is suggested to be caused by the formation of $Rh_2(CO)_4I_2$. The variations in the degree of reduction of the halo-substituted species with respect to the unsubstituted clusters could not be causing the changes in reactivity because of the different trends. Instead, the variations in the thermal reactivity of these clusters may be correlated with the differences in the stereochemistry of the halide-containing anions, since the halogen atom is bonded to a rhodium atom on an octahedral cage [18] in $[Rh_6(CO)_{15}X]^-$, and to a rhodium atom capping one of the faces of the same type of cage in $[Rh_7(CO)_{16}X]^{2-}$ [9f]. The structural comparison of this cluster with $[Rh_{15}(CO)_{27}]^{3-}$ and the facile detachment of the capping rhodium atom of this anion with halides and amines (Eq. 10) provide the basis for the previous proposal.

$$3[Rh_7(CO)_{16}Br]^{2-} \rightarrow [Rh_{15}(CO)_{27}]^{3-} + Rh_6(CO)_{16} + 3\,Br^- + 5CO \tag{9}$$

$$[Rh_{15}(CO)_{27}]^{3-} + 2\,Br^- \rightleftarrows [Rh_{14}(CO)_{25}]^{4-} + [Rh(CO)_2Br_2]^- \tag{10}$$

The effects of halide ligands on the fragmentation of the clusters suggested a similar behavior for other ligands such as amines. This observation, together with the known fragmentation of $[Rh_{15}(CO)_{27}]^{3-}$ by amines [4] and the formation of amines during the thermal degradation of ammonium cations previously mentioned suggested testing the effects of adding amines to these systems. We added *N*-methylmorpholine to a solution of the cesium salt of $[Rh_7(CO)_{16}]^{3-}$ (N/Rh, atom ratio, 4/1) and it was found that $[Rh(CO)_4]^-$ and $[Rh_{14}(CO)_{25}]^{4-}$ are formed in this case as also observed in the absence of the amine (Table 3), but the formation of insoluble rhodium materials was inhibited by the amine. The addition of *N*-methylmorpholine to the cesium salt of $[Rh_{14}(CO)_{25}]^{4-}$ retarded the formation of insoluble products (Table 4) allowing more extended warming periods at 180°C without precipitation, while the addition of amine to a solution of the $Rh_9$ cluster caused the conversion of this cluster into $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{27}]^{3-}$ to occur at milder conditions (2 h at 140°C) than in the absence of amines (Table 3). This observation and the inherent stability of the $Rh_9$ cluster (Table 3) indicates that the transformation of this anion into other products, noted during the pyrolysis of the ammonium salts of other cluster anions may be due to the formation of amine during the degradation of these cations. In contrast, the addition of cesium as the benzoate salt to a solution of $[PhCH_2N(C_2H_5)_3]_3[Rh_7(CO)_{16}]$ (Cs/Rh, 0.25) resulted in the partial degradation of the anion after 2 h at 160°C while a quantitative reaction occurred in the absence of the cesium salt (Table 3). The presence of both the alkali cation and the amine in a system resulted in the partial inhibition of the aggregation reactions of clusters and of the formation of insoluble-rhodium containing materials such as metallic rhodium. This pseudo-synergistic behavior is ascribed to the high reduction potential of the cesium cation and to the ability of the amines to promote the formation of $[Rh_{14}(CO)_{25}]^{4-}$. The interaction of the amine with fragments detachable from the cluster offers a suitable pathway for fragmentation, as already reported with $[Rh_{15}(CO)_{27}]^{3-}$ [4]. In fact, the coordination of the amine to the capping rhodium atoms of clusters has been already mentioned [19], and it may be the first step in the removal of these atoms from a cluster.

The formation of the $Rh_9$ cluster during the pyrolysis of the salts of $[Rh_7(CO)_{16}]^{3-}$ (Table 3) suggests that the fragmentation of this cluster generates mono- or bi-nuclear complexes that could aggregate to the unconverted cluster increasing its size. Unfortunately, speculation concerning this topic is hindered by our inability to determine accurately the number of carbonyls and the degree of reduction of the cluster [20a]. For instance, a paramagnetic cluster should be formed in the case of a $Rh_9$ tetra-anionic species but a more conventional diamagnetic cluster would result in the case of a tri-negative anion; in fact, paramagnetic high nuclearity rhodium carbonyl clusters have not been reported [13]. These observations, the limitations of our structural study and other additional chemical considerations [20b] leave open the possibility that the $Rh_9$ species would have resulted from the aggregation of binuclear species such as $Rh_2(CO)_8$ to $[Rh_7(CO)_{16}]^{3-}$ (eq. 11 and 12). In fact, the determination of the metal cage of the $Rh_9$ species allows the comparison between the metal skeleton of this cluster and $[Rh_7(CO)_{16}]^{3-}$. The structure of the $Rh_9$ species shows a metal frame consisting of three staggered metal triangles (Fig. 6) never found before in a rhodium cluster [20c] but well established for polynuclear platinum species [21]. Such arrangement of metal atoms could result from the addition of two rhodium atoms around the capping rhodium atom of $[Rh_7(CO)_{16}]^{3-}$. The increased number of metal–metal interactions in the $Rh_9$ cluster may be responsible, at least in part, for the increased inertness of this species relative to $[Rh_7(CO)_{16}]^{3-}$.

$$3[Rh_7(CO)_{16}]^{3-} \rightarrow 3[Rh(CO)_4]^{-} + 2[Rh_9(CO)_{\sim 18}]^{3-} \qquad (11)$$

$$[Rh_7(CO)_{16}]^{3-} + Rh_2(CO)_8 \rightarrow [Rh_9(CO)_{\sim 18}]^{3-} \qquad (12)$$

## Other observations and conclusions

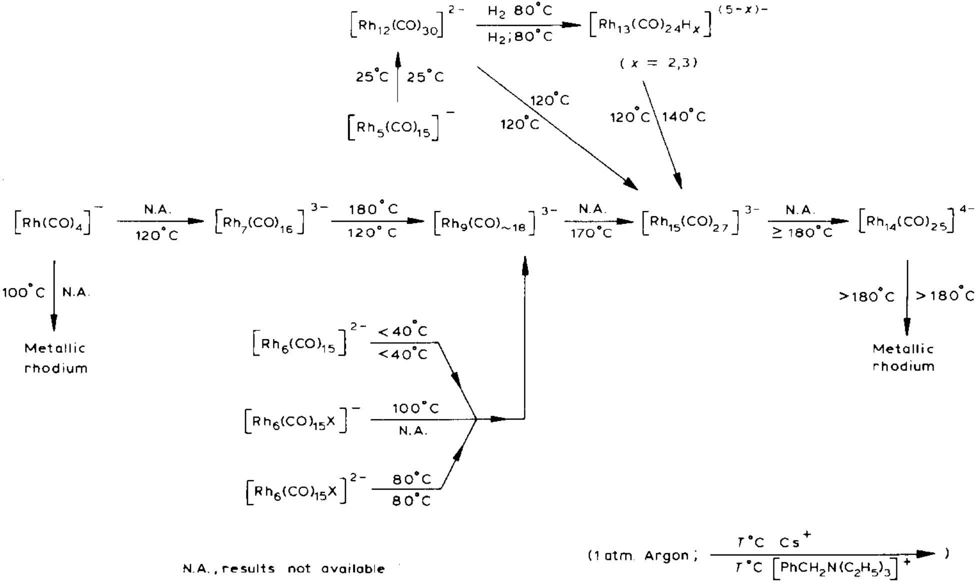
Our study has been limited to the evaluation of a few salts of representative rhodium carbonyl anions with characteristic counterions over a specific temperature range but we have not evaluated all the possible combinations of these cations and anions at each temperature. In spite of that, we consider that our results illustrate the effect that the nature of the cations has on the thermal growth of rhodium carbonyl clusters with the exception of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_{12}(CO)_{30}]^{2-}$ (Tables 3, 4). The causes for the insensitivity of these anions to the nature of the cations are not obvious, but may be related to the readily formation of an intermediate proposed to be associated with both clusters [22]. We have described that cations with a high reduction potential slow down the thermal growth of these clusters and the formation of $[Rh(CO)_4]^-$ as a pathway for the decrease in the degree of reduction of the clusters. The stability observed for these salts in the case of

$[Rh(CO)_4]^-$ (Table 1) indicates that the increase in the size of the clusters could occur without the intermediacy of redox reaction between the cluster anions and their counterions. The release of $[Rh(CO)_4]^-$ by a cluster should be accompanied, under our conditions, by the formation of a coordinatively unsaturated polynuclear moiety. This moiety could undergo further fragmentation or participate in aggregation reactions with other mono-, bi- or poly-nuclear fragments yielding larger clusters. A similar reactivity may be indeed expected with the salts of these clusters and cations more amenable to reduction, but the detection of $[Rh(CO)_4]^-$ would be precluded in this case by a redox reaction involving this anion and the cation (eq. 5–7; Table 2).

We have suggested the formation of $[Rh_{15}(CO)_{27}]^{3-}$ as one of the end-products in some of our systems on the basis of resonances usually assigned to this cluster: 182.5(d), 210.0(m), and 215.7(m). However, we have noted in some instances the variable intensity ratios of these resonances. This may be due to the presence of additional clusters exhibiting resonances with similar shifts. For instance, one of such species may be $[Rh_{22}(CO)_{37}]^{4-}$, which has been recently reported [6b] to be formed during the pyrolysis of the sodium salt of $[Rh_{13}(CO)_{24}H_3]^{2-}$. Unfortunately, the $^{13}C$ NMR spectrum of the product was not reported.

These studies have also shown that the reactions of rhodium carbonyl clusters under extreme thermal conditions lead to the transformation of species of lower nuclearity into larger clusters (Scheme 2), with $[Rh_{14}(CO)_{25}]^{4-}$ formed as the end-product of some of these reactions. Moreover, it seems, from the appearance of a rhodium mirror upon subjecting the cesium salts of $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh(CO)_4]^-$ to extreme temperatures (Tables 2 and 4), that these two species provide suitable paths for the formation of metallic rhodium at high enough temperatures. In contrast, the precipitation of rhodium-containing materials in these systems occurs at higher temperatures in the presence of amines. The same relative effect is noted working with these systems under high pressure of carbon monoxide and hydrogen

SCHEME 2.



[24]. The inhibition of the precipitation of such materials is ascribed to the ability of amines to enhance the transformation of rhodium carbonyl clusters, under inert gases, into a species of relatively higher thermal stability such as $[Rh_{14}(CO)_{25}]^{4-}$, and to facilitate clusters fragmentation into $[Rh(CO)_4]^-$ under high pressure of carbon monoxide. In addition, we ruled out the possibility that our observations would be due solely to kinetically controlled processes on tbe basis of the inertness of the $Cs^+$ and $[(CH_3)_4N]^+$ salts of $[Rh_7(CO)_{16}]^{3-}$, $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{25}]^{3-}$ even after 24–48 h at 160–170°C and because of the ready changes induced in these clusters upon changing the nature of the cations or the temperature (Tables 3 and 4). Finally, it should be noted that our observations are probably related to the effects that the presence of amines and alkali-cations have on the solubility of rhodium complexes when present as co-additives in catalyst systems used for the conversion of carbon monoxide and hydrogen into polyols [24]. The interaction of the amines with the apical rhodium atoms of some clusters, as previously reported [4] in the case of $[Rh_{15}(CO)_{27}]^{3-}$ (eq. 10), is suggested to be responsible for the relative inhibition in the formation of rhodium-containing insoluble materials in those systems. The predominant presence in these systems of clusters with this structural feature, such as $[Rh_5(CO)_{15}]^-$, $[Rh_7(CO)_{16}]^{3-}$, $[Rh_{15}(CO)_{27}]^{3-}$, $[Rh_{14}(CO)_{25}]^{4-}$ or $[Rh_{22}(CO)_{35}H_x]^{(5-x)-}$ provide also circumstantial evidence concerning our hypothesis. The important role of the apical rhodium atom in the reactivity of the clusters is also indicated by the facilitation of cluster fragmentation resulting from the coordination of ligands to the capping metal atom as described above for $[Rh_7(CO)_{16}X]^{2-}$ [25]. The relevance of these observations in relation to the role(s) of polynuclear complexes in catalytic systems active for the conversion of carbon monoxide and hydrogen into polyols [26] is under study, and it will be discussed in a forthcoming report [27].

*Supplementary material available*

A complete listing of the data and calculations used in the structural study of the cesium-18-crown-6 salt of the nonarhodium anion is available) *.

## Acknowledgement

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* See NAPS document no. 04024 for 37 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only $12.85 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada add postage of $4.50 for the first 20 pages and $1.00 for each 10 pages of material thereafter, or $1.50 for microfiche postage.

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11 The redox potential of these cations are reported in different solvents for cesium and for the quaternary ammonium cations. In spite of that it is possible to establish the following trend: $Cs^+/Cs^0$ (2.933 to 3.44 volts depending upon the solvents); $[(C_2H_5)_4N]^+/[(C_2H_5)_4N]$ (2.80 volts); $[(CH_3)_4N]^+/[(CH_3)_4N]$ (2.60 volts); $[PhCH_2N(C_2H_5)_3]^+/[PhCH_2N(C_2H_5)_3]$ (2.20 volts) all as obtained from (a) G. Milazzo and S. Caroli, Tables of Standard Electrode Potentials, John Wiley and Sons, New York, 1978, p. 18; (b) H.O. House, E. Feng, and P. Preet Norton, J. Org. Chem., 36 (1971) 2371; (c) B.C. Southworth, R. Osteryoung, K.D. Fleischer, and F.C. Naschod, Anal. Chem., 33 (1961) 208; (d) J.D. Littlehailes and B.J. Woodhall, Discuss. Faraday Soc., (1968) 167; and (e) M.M. Baizer (Ed.), Organic Electrochemistry, Marcel Dekker, New York, 1973, p. 229. The degradation of $[PhCH_2NR_3]^+$ by a one-electron reduction has been found (ref. 11c) to yield $R_3N$ and bibenzyl. It has been proposed that this reaction occurs with the formation of the radical species $[PhCH_2\dot{N}R_3]$ as an intermediate.

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15 The dissociation bond energies reported in ref. 13 for (Rh–Rh) = 27 and (Rh–CO) = 39 kcal $mol^{-1}$ indicate that the formation of rhodium–rhodium bonds is an endothermic process.

16 The formation of a rhodium mirror on the walls of the NMR tube was noted during the pyrolysis of $[Cs(18\text{-crown-}6)_2][Rh(CO)_4]$. It seems probably that the appearance of metallic rhodium in systems for which this compound is present could be caused by the same behavior.

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20 (a) A black crystal of $[Cs(18\text{-crown-}6)_{1-25}][Rh_9(CO)_{\sim 18}]^{n-}$ ($n = 3$ or 4) having approximate dimensions of 0.05 × 0.30 × 0.30 mm was used for the study. The space group was determined to be *Pccn*, and the orthorhombic unit cell parameters and other calculated parameters are: $a = 24.413(11)$, $b = 50.866(11)$, $c = 19.945(16)$ Å, $V$-24767.8 $A^3$, $Z = 8$ and $F_W = 3704.38$ with a density of 1.99 $g/cm^3$. A total of 12802 reflections were collected and the structure was solved by direct methods. A total of 13 atoms were initially located from an *E*-map prepared using 450 reflections. The poor crystal quality only allowed the location of 97 of the 2165 reflections employed to solve the structure and resulted in agreement factors of 19.6 and 24.0. This was due to the severe disorder found for the 18-crown-6-molecules and for the carbonyl ligands. In spite of that, we feel confident about the solution of the metal core. Structural study by Dr. Jan M. Troup, Molecular Structure Corporation, College Station, Texas.

(b) The diamagnetism of the salts of the $Rh_9$ cluster is consistent with our ability to run the NMR spectra of these materials. The infrared spectrum of this cluster in solution shows bands at 1990(m), 1965(s), 1810(m) and 1793(m) $cm^{-1}$.

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25 The study of these halogen-substituted species was undertaken because of the difficulties found in attempts to isolate analogous species such as $[Rh_7(CO)_{16}H]^{2-}$ or $[Rh_7(CO)_{16}(CH_2O)]^{3-}$. The importance of these species to the potential role(s) of clusters in the catalytic hydrogenation of carbon monoxide impelled us to attempt the preparation of $[Rh_7(CO)_{16}H]^{2-}$ by protonation of $[Rh_7(CO)_{16}]^{3-}$ with $CF_3SO_3H$ in acetone solution at −70°C. Although it appeared from $^1H$ NMR studies that hydride species were formed we could not isolate them. Instead, we noticed the formation of $[Rh_9(CO)_{-18}]^{3-}$ upon raising the temperature of the system to ca −10°C. Nevertheless, $^{13}C$ NMR studies of this reaction conducted at −70°C suggest that the protonation of $[Rh_7(CO)_{16}]^{3-}$ may be initially occurring in the triangular face opposite to the capping rhodium atom.

26 The existence of cluster complexes containing the coordinated formyl moiety under controlled laboratory conditions has been previously described by us to occur by reaction of the clusters with hydride donors, see R.L. Pruett, R.C. Schoening, J.L. Vidal, and R.A. Fiato, J. Organometal. Chem., 182 (1979) C57; and R.C. Schoening, J.L. Vidal and R.A. Fiato ibid., 206 (1981) C43.

27 J.L. Vidal and W.E. Walker, in preparation.

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*Note added in proof.* A recent report by S. Martinengo, A. Fumagalli, R. Bonfiche, G. Ciani, and A. Sironi synthetic path and the solid state structure of $[Rh_9(CO)_{19}]^{3-}$. We believe that this anion is the same as the nonarhodium trianionic cluster studied by us in this work.