



High-yield syntheses of $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ and $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ working in ethylene glycol solution under 1 atm of CO

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ARTICLE INFO

Article history:

Received 15 June 2009

Received in revised form 26 July 2009

Accepted 27 July 2009

Available online 6 August 2009

Keywords:

Rhodium

Carbonyl clusters

Ethylene glycol

Silica surface

Organometallic synthesis

ABSTRACT

The anionic rhodium carbonyl clusters $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ and $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ can be easily prepared by a new simple and high yield one-pot synthesis starting from $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ dissolved in ethylene glycol and involving two steps: (i) treatment of $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ under 1 atm of CO at 50 °C to give $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$; (ii) addition of a base ($\text{CH}_3\text{CO}_2\text{Na}$ or Na_2CO_3) followed by reductive carbonylation under 1 atm of CO at an adequate temperature (50 °C for $[\text{Rh}_7(\text{CO})_{16}]^{3-}$; 150 °C for $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$). These new syntheses are more convenient than those previously reported, especially since such clusters are not accessible via silica surface-mediated reactions. This different behavior is due to the particular stabilization on the silica surface and under 1 atm of CO of an anionic carbonyl cluster, called A, which does not allow the formation of a higher nuclearity carbonyl cluster, called B, which was shown to be the key-intermediate in the synthesis of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ working in ethylene glycol solution. Although it was not possible to isolate crystals of A and B suitable for X-ray structural determination, a combination of cyclovoltammetry, one of the few examples so far available of the use of this technique for anionic rhodium carbonyl clusters, infrared spectroscopy and elemental analyses suggest that A and B are probably the never reported $[\text{Rh}_7(\text{CO})_{14}]^-$ and $[\text{Rh}_{15}(\text{CO})_{28}]^{3-}$ clusters, respectively. In particular the tentative formulation of the two clusters was carried out by a non-conventional method based on the existence of a linear correlation between carbonyl frequencies of the main band and the [(charge/Rh atoms)/CO number] ratio.

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1. Introduction

Since the discovery of the synthesis of $[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{Rh}_6(\text{CO})_{16}]$ by reaction of anhydrous rhodium trichloride and copper or zinc powder, under 200 atm of carbon monoxide and at moderate (25–80 °C for $[\text{Rh}_4(\text{CO})_{12}]$) or high (higher than 80 °C for $[\text{Rh}_6(\text{CO})_{16}]$) temperature [1], a lot of work has been dedicated to the preparation of various neutral and anionic rhodium carbonyl clusters by reductive carbonylation in solution working under mild conditions (1 atm CO, room temperature) of RhCl_3 or $[\text{Rh}(\text{CO})_2\text{Cl}_2]$ [2–7].

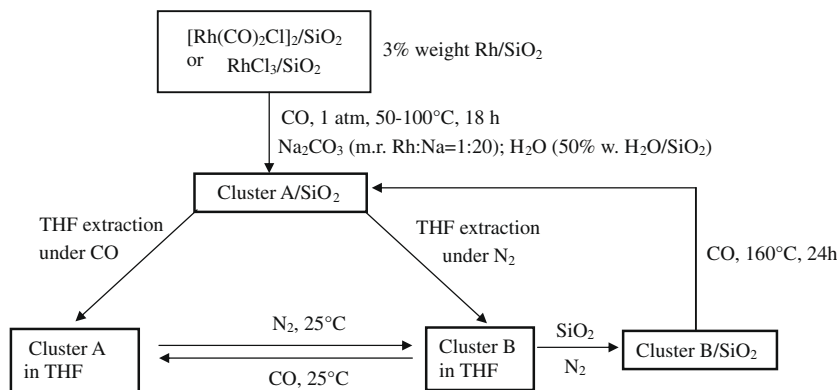
More recently neutral ($[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{Rh}_6(\text{CO})_{16}]$) and anionic ($[\text{Rh}_5(\text{CO})_{15}]^-$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$) rhodium carbonyl clusters have been prepared by some of us by mild reductive carbonylation (1 atm CO) of $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ or $[\text{Rh}(\text{CO})_2\text{Cl}_2]$ supported on the silica surface working at room temperature in the presence of an

adequate surface basicity [8]. As preliminary results (see Scheme 1) it was also reported that reductive carbonylation at relatively high temperatures (50–100 °C) of $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ or $[\text{Rh}(\text{CO})_2\text{Cl}_2]$ supported on silica in the presence of Na_2CO_3 (molar ratio $\text{Na}_2\text{CO}_3:\text{Rh} = 10:1$) and water affords a new unidentified high nuclearity carbonyl cluster called A that can be extracted, under a CO stream, from the surface by treatment with tetrahydrofuran. This latter one, stable under CO atmosphere, easily converts into another still unidentified cluster, called B by bubbling N_2 into its tetrahydrofuran solution. The reaction is reversible: further bubbling of 1 atm of CO regenerates A [8].

Due to the above evidence that an increase of the temperature, easily achieved when working on the silica surface as reaction medium, may produce the synthesis of unknown new rhodium carbonyl clusters, and because, to our knowledge, the effect of a significant increase of the temperature on this kind of reductive carbonylations at atmospheric pressure has never been investigated when working in basic solution, we started a detailed investigation working in ethylene glycol, a high boiling solvent with non-acidic OH groups that could mimic the role and polarity of the OH groups of the silica surface [9,10]. In this paper, we report

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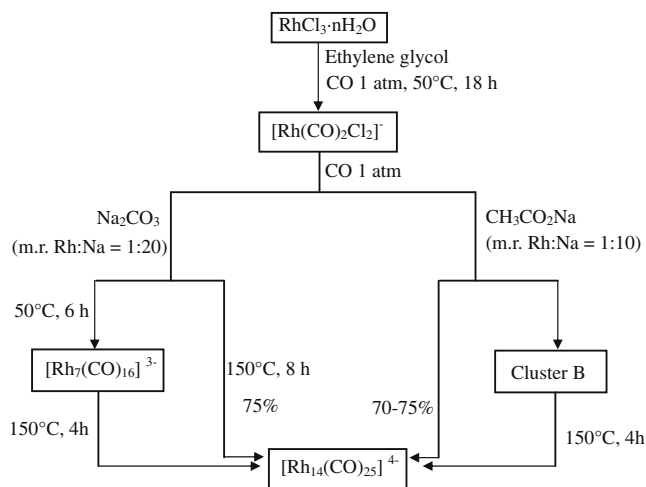
Scheme 1. Formation and reactivity of cluster A and cluster B on the silica surface [8].

the results of this investigation which led to convenient one-pot high yields syntheses of $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ and $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ together with the isolation, also in ethylene glycol solution, of B. In addition we showed the key role of both $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ and B as intermediates in the production of the clusters of higher nuclearity up to $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$. Without suitable crystals for X-ray crystallography, the characterization of A and B was attempted by a cyclic voltammetric investigation and by a linear correlation of some features of the infrared spectra of A, B, $[\text{Rh}_7(\text{CO})_{16}]^{3-}$, $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$, which we are able to define.

2. Results and discussion

2.1. New convenient syntheses of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ and $[\text{Rh}_7(\text{CO})_{16}]^{3-}$

It was reported that bubbling 1 atm of CO at 50 °C into a solution of $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ in ethylene glycol slowly (ca. 18 h) leads to the formation of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ [11]. We have now found that an increase of the temperature at 150 °C under a flow of 1 atm of CO for about 8 h in the presence of a base like $\text{CH}_3\text{CO}_2\text{Na}$ (molar ratio Rh:Na = 1:10) affords in 70–75% yields $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ ($\nu_{\text{CO}} = 1972 \text{ cm}^{-1}$ (s) and 1819 cm^{-1} (m), see Scheme 2) isolated by addition of an aqueous solution of $[\text{NMe}_3\text{Benzyl}]^+\text{Cl}^-$ (ν_{CO} in CH_3CN as $[\text{NMe}_3\text{Benzyl}]^+$ salt = 1967 (s), 1832 (m) and 1813 (m) cm^{-1}) to the reaction mixture. Similar yields are obtained by working under the same conditions, but using a higher basicity (Na_2CO_3 instead of $\text{CH}_3\text{CO}_2\text{Na}$; molar ratio Rh:Na = 1:20; see Scheme 2).



Scheme 2. Anionic rhodium carbonyl clusters syntheses in ethylene glycol solution.

Such an easy and high yield synthesis of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ by reductive carbonylation under 1 atm CO of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ is a significant improvement. In fact, the previously reported synthesis involves a tedious multi-step procedure (pyrolysis of $\text{Na}_2[\text{Rh}_{12}(\text{CO})_{30}]$ or a mixture of $[\text{Rh}_4(\text{CO})_{12}]$ and NaOH in 2-propanol under N_2 at 80 °C for 10–12 h, followed by fractional precipitation from an aqueous solution to give $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ which reacts with the bromide anion in CH_3CN to generate $[\text{Rh}(\text{CO})_2\text{Br}]^-$ and $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ with final low global yields (less than 20%) [12]. Higher yields of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ (60%) were reported but working under high pressure (CO:H₂ = 1:1; ca. 14 atm) for 6 h, at 150–160 °C, starting from $[\text{Rh}(\text{CO})_2(\text{acac})]$ dissolved in tetraethylene glycol dimethyl ether in the presence of cesium benzoate and *N*-methylmorpholine [13].

The reductive carbonylation of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ in ethylene glycol solution and at lower temperature (about 50 °C) by bubbling 1 atm of CO for either 6 or 24 h, affords in the presence of a relatively strong basicity (Na_2CO_3 , molar ratio Rh:Na = 1:20) $[\text{Rh}_7(\text{CO})_{16}]^{3-}$, isolated by addition of an aqueous solution of $[(\text{PPh}_3)_2\text{N}]\text{Cl}$ or $[\text{NMe}_4]\text{Cl}$, in 80% yield (ν_{CO} in CH_3CN as $[(\text{PPh}_3)_2\text{N}]^+$ salt = 1956 (vs), 1818 (s) and 1772 (s) cm^{-1}). This is a one-pot and high yield convenient method to obtain this latter cluster, starting from RhCl_3 via the easy intermediate synthesis of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$, since the anion $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ was previously obtained in high yield (88%) as morpholinium salt working at room temperature in aqueous methanol solution in the presence of alkali hydroxides (or alkali metals in THF) but starting from a cluster such as $[\text{Rh}_4(\text{CO})_{12}]$ [7]. By keeping the reaction mixture containing $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ at higher temperature (150 °C) under a flow of 1 atm of CO, after about 4 h, $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ (see Scheme 2) is formed, suggesting that $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ is an intermediate in the formation of the higher nuclearity cluster $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$.

Besides, when $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ is treated under the same conditions (flow of 1 atm of CO at 50 °C for 6 h) but working with a lower basicity, obtained by addition of $\text{CH}_3\text{CO}_2\text{Na}$ (molar ratio Rh:Na = 1:10) instead of Na_2CO_3 , the previously reported [8] but still unidentified cluster B (ν_{CO} as Na^+ salt in THF = 2037 (w), 2000 (s) and 1863 (m, br) cm^{-1}) is formed (see Scheme 2). An increase of the temperature till 150 °C under a flow of 1 atm of CO leads again, after about 4 h, to the formation of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ (see Scheme 2), suggesting that B is another intermediate in the step by step synthesis of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ from $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$. Interestingly the reductive carbonylation under rather similar conditions produces different carbonyl clusters when carried out on the silica surface as reaction medium [8]. In this latter case, the products obtained working under different conditions are $[\text{Rh}_4(\text{CO})_{12}]$, $[\text{Rh}_6(\text{CO})_{16}]$, $[\text{Rh}_5(\text{CO})_{15}]^-$, $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and finally A, while in ethylene glycol solution the products, also obtained working under different conditions are $[\text{Rh}_7(\text{CO})_{16}]^{3-}$,

$[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ and strangely enough B. By comparing the products obtained by reductive carbonylation of Rh(I) carbonyl species either working on the silica surface or in ethylene glycol solution but in the presence of the same amount of Na_2CO_3 (molar ratio Rh:Na = 1:20; Schemes 1 and 2), it is not surprising that A is formed on the silica surface [8] instead of $[\text{Rh}_7(\text{CO})_{16}]^{3-}$. In fact, in the presence of the same amount of base a lower basicity is usually achieved on the silica surface when compared to solution [14]. However, unexpectedly, by working in ethylene glycol solution with a relatively low basicity (molar ratio Rh: $\text{CH}_3\text{CO}_2\text{Na}$ = 1:10) under 1 atm of CO at 50 °C, B is obtained instead of A, although it is known that A is the species stable under CO in THF solution [8]. We have found that cluster A, prepared on the silica surface as previously reported [8], is readily converted at 50 °C into cluster B even under 1 atm of CO when dissolved in ethylene glycol solution in the presence of $\text{CH}_3\text{CO}_2\text{Na}$, whereas by working in the absence of a base or at room temperature it does not convert. Following this latter observation, since an increase of temperature leads to the conversion of B into $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ when working in ethylene glycol, we investigated the possible conversion of A into B and then into $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ working on the silica surface, as reaction medium. However, when $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ supported on the silica surface in the presence of Na_2CO_3 (molar ratio Rh:Na = 1:20) is heated at 100 °C for 18 h under CO and in the presence of water (50% wt. $\text{H}_2\text{O}/\text{SiO}_2$) to give A, no further reaction is observed even raising the temperature till 160 °C for 24 h. Therefore A is so much stabilized by the silica surface that, not being converted into B, it cannot give $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$. In agreement with this statement, B, obtained for instance in ethylene glycol solution and supported on the silica surface in the presence or in the absence of $\text{CH}_3\text{CO}_2\text{Na}$, under 1 atm of CO at 160 °C, is readily converted to A only (see Scheme 1), thus confirming the high stability of this latter on the silica surface. This is another example of a role of the silica surface as reaction medium in controlling the selectivity of the reductive carbonylation process and in defining the stability of carbonyl clusters when supported. So, we may have, as in the present case, different reaction pathways when working on the silica surface or in a solvent like ethylene glycol, although, in other cases [9,10,14] this solvent may reproduce quite well reductive carbonylation reactions which occur on the silica surface.

2.2. Attempts to characterize cluster A and cluster B

All attempts to obtain crystals suitable for X-ray structural characterization of A or B by using a lot of techniques and various bulky cations failed. The only crystals good for X-ray characterization, obtained from a CH_2Cl_2 -pentane solution of the trimethylbenzylammonium salt of the anionic cluster B (after several months) turned out to be the trimethylbenzylammonium salt of the known cluster anion $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ (characterized by an infrared spectrum: ν_{CO} in THF = 2067 (m), 2049 (s), 2040 (s), 2003 (w), 1778 (m, br) cm^{-1} [5], completely different from that of B). It appears thus that B is only relatively stable under N_2 and slowly transforms into $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, more stable under N_2 . It is known that this latter cluster, dissolved in tetrahydrofuran, is readily converted to $[\text{Rh}_5(\text{CO})_{15}]^-$ under 1 atm of CO [5,6]. In the same manner, by bubbling 1 atm of CO into a tetrahydrofuran solution of B, A is obtained [8]. Such a reversible behavior suggests that B could be an anionic high nuclearity carbonyl cluster which reacts with CO to give A with a higher CO vs. Rh ratio, but probably of slightly lower nuclearity. The high nuclearity of B is supported by its infrared spectrum very similar to that of the well characterized cluster $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ (ν_{CO} in CH_3CN = 2040 (vw), 1998 (s, br), 1850 (m, br), 1825 (m, br), 1805 (m, br) cm^{-1} [12], as NMe_4^+ salt), but B shows a different reactivity since it is not converted into $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ by adding $[\text{NEt}_4]\text{Br}$, contrarily to $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ [12]. The infrared spectrum

(ν_{CO} in THF = 2043 (w), 2020 (s) and 1840 (w, br) cm^{-1}) of A, as Na^+ salt, is similar to that of the known cluster of slightly lower nuclearity $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_3]^{2-}$ (ν_{CO} in THF = 2020 and 1840 cm^{-1} [13], as $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt), but A does not show any hydride signal in the ^1H NMR spectrum.

In order to get some significant information from the infrared spectra of A and B, we investigated carefully the infrared carbonyl frequencies of the main band of anionic rhodium clusters of increasing nuclearity. It turned out that if one divides carbonyl clusters in medium and high nuclearity clusters a good linear correlation appears by plotting the carbonyl frequency of the main band vs. [(charge/Rh atoms)/CO number]. In Fig. 1 is shown the linear correlation found for the case of medium nuclearity clusters with a CO number/Rh atoms ratio (R) bigger than 2: $[\text{Rh}_5(\text{CO})_{15}]^-$, ν_{CO} main band: 2010 cm^{-1} [6]; $[\text{Rh}_6(\text{CO})_{15}]^{2-}$, ν_{CO} main band: 1975 cm^{-1} , in this case there are two equally strong main bands: 1990 and 1960 cm^{-1} , so we took the medium value [7]; $[\text{Rh}_7(\text{CO})_{16}]^{3-}$, ν_{CO} main band: 1955 cm^{-1} [7]; $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, ν_{CO} main band: 2045 cm^{-1} , in this case there are two equally strong main bands: 2049 and 2040 cm^{-1} , so we took the medium value [5] whereas Fig. 2 reports the linear correlation found for relatively high nuclearity clusters with a R ratio lower than 2: $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$, ν_{CO} main band: 1960 cm^{-1} [12]; $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$, ν_{CO} main band: 1998 cm^{-1} [12]; $[\text{Rh}_{15}(\text{CO})_{30}]^{3-}$, ν_{CO} main band: 2000 cm^{-1} [15]; $[\text{Rh}_{17}(\text{CO})_{30}]^{3-}$, ν_{CO} main band: 2009 cm^{-1} , in this case there are two equally strong main bands: 2018 and

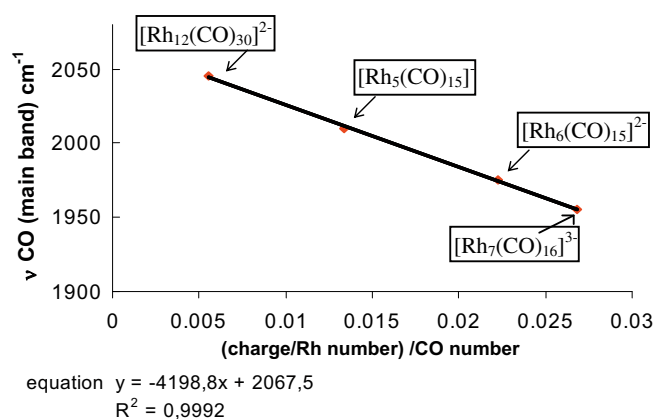


Fig. 1. Linear correlation for medium nuclearity Rh anionic carbonyl clusters with a R ratio ($R = \text{CO number}/\text{Rh atoms}$) bigger than 2 ($R^2 = \text{linear correlation coefficient}$).

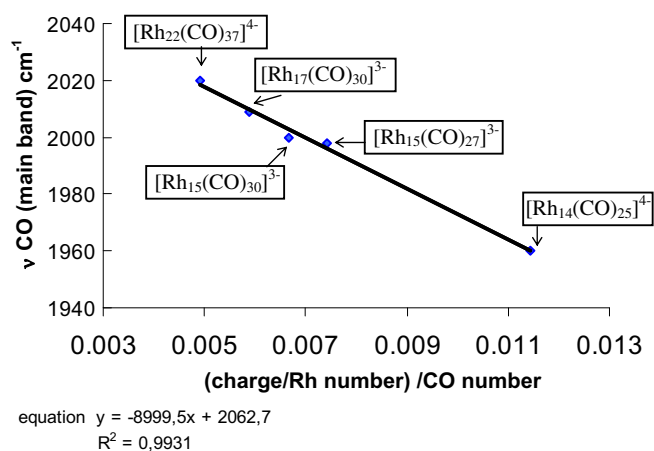


Fig. 2. Linear correlation for relatively high nuclearity Rh anionic carbonyl clusters with a R ratio ($R = \text{CO number}/\text{Rh atoms}$) lower than 2 ($R^2 = \text{linear correlation coefficient}$).

2000 cm^{-1} , so we took the medium value [16]; $[\text{Rh}_{22}(\text{CO})_{37}]^{4-}$, ν_{CO} main band: 2020 cm^{-1} [17]).

However, since for cluster A and cluster B neither the ratio charge/Rh atoms nor the number of CO ligands are known, we carried out a cyclic voltammetric (CV) investigation to get other indirect information. To our knowledge, only a few data were available in the literature about the electrochemistry of anionic rhodium carbonyl clusters, namely, those provided by the recent study by Longoni and coworkers [18]; therefore we had to complement our CV study on A and B (this latter generated in situ by bubbling nitrogen in a acetonitrile solution of A), with the CV investigation on four reference clusters of decreasing CO vs. Rh ratio, *i.e.* $[\text{Rh}_{12}(\text{CO})_{30}][\text{NET}_4]_2$ (CO:Rh = 2.50), $[\text{Rh}_7(\text{CO})_{16}][\text{NET}_4]_3$ and

$[\text{Rh}_7(\text{CO})_{16}][(\text{PPh}_3)_2\text{N}]_3$ (CO:Rh = 2.28), together with $[(\text{PPh}_3)_2\text{N}]\text{Cl}$ as a reference for the $[(\text{PPh}_3)_2\text{N}]^+$ cation CV pattern, and $[\text{Rh}_{14}(\text{CO})_{25}][\text{NET}_4]_4$ (CO:Rh = 1.78). Selected CV patterns at 0.2 V s^{-1} are provided in Fig. 3 for $[\text{Rh}_{12}(\text{CO})_{30}][\text{NET}_4]_2$, $[\text{Rh}_7(\text{CO})_{16}][\text{NET}_4]_3$, $[\text{Rh}_{14}(\text{CO})_{25}][\text{NET}_4]_4$, and A before and after nitrogen bubbling to generate B. The CV pattern of ferrocene (Fc), equimolar with the reference clusters, is also included as a standard for a reversible mono-electronic charge transfer. However it must be pointed out that peak currents, at constant electron number and electron transfer mechanism, are expected to decrease significantly with increasing size of the cluster, *i.e.* decreasing diffusion coefficient of the reacting molecule, in accordance with Stokes' law. Therefore, with respect to our very large carbonyl clus-

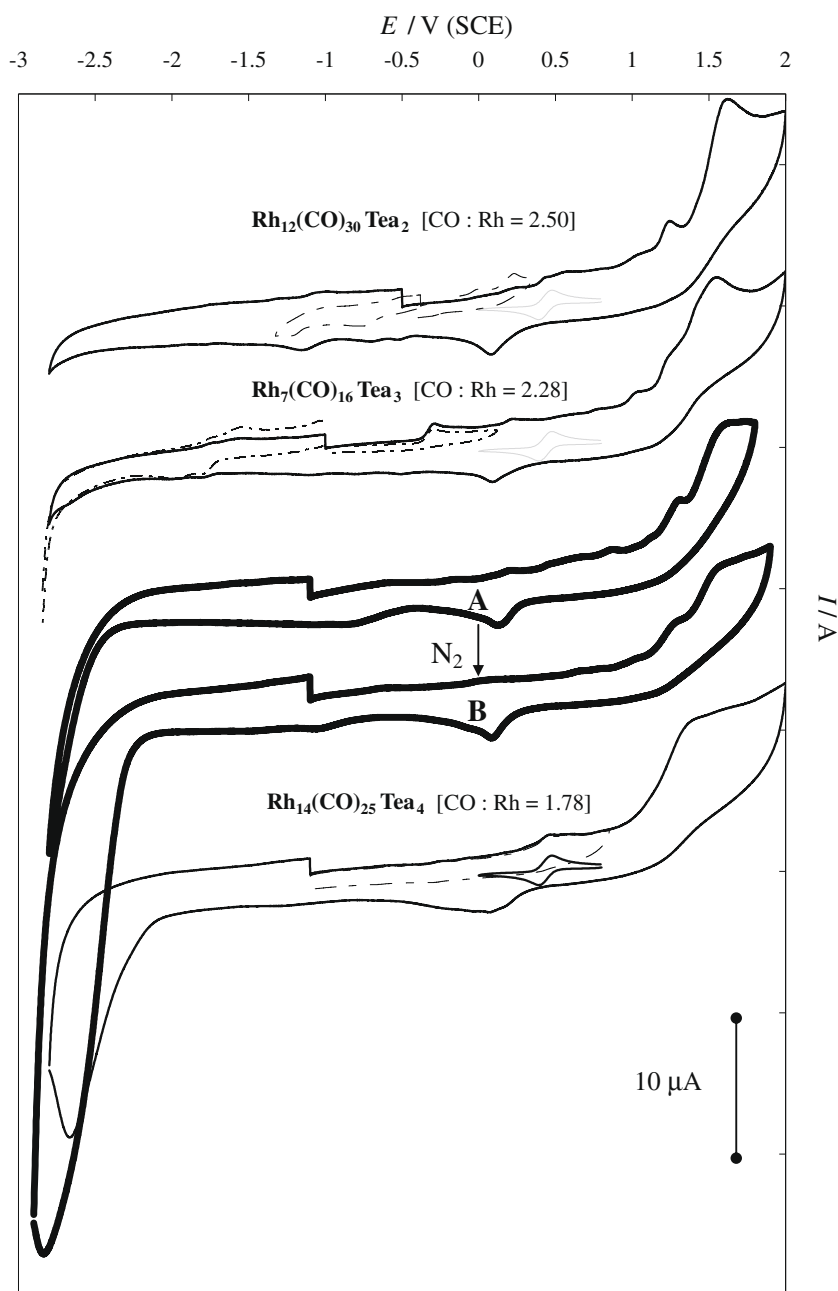


Fig. 3. CV patterns on GC electrode, in acetonitrile +0.1 M TBAP medium, of the three reference clusters $[\text{Rh}_{12}(\text{CO})_{30}][\text{NET}_4]_2$, $[\text{Rh}_7(\text{CO})_{16}][\text{NET}_4]_3$ and $[\text{Rh}_{14}(\text{CO})_{25}][\text{NET}_4]_4$ (all of them 0.00025 M); of cluster A (20 mg in 25 cm^3 solution) and of the same after 2 h nitrogen bubbling to promote its conversion into cluster B. $T = 298 \text{ K}$, scan rate = 0.2 V s^{-1} . CV patterns of 0.00025 M ferrocene are superimposed to the CV patterns of the reference clusters, for comparison's sake. In the three reference compound cases, voltammograms on narrower potential ranges have been added in dashed lines, affording better evaluation of the first anodic and cathodic peaks, unaffected by previous processes.

ters, the Fc peak should be regarded only as an “upper threshold” standard for a mono-electronic electron transfer current. For the same reason, the peak currents corresponding to a single electron transfer should decrease following the increasing size: $\text{Fc} \gg [\text{Rh}_7(\text{CO})_{16}]^{3-} > [\text{Rh}_{12}(\text{CO})_{30}]^{2-} > [\text{Rh}_{14}(\text{CO})_{25}]^{4-}$.

The oxidative region of the CV patterns of all the clusters taken as reference features a series of small oxidation peaks, associated to subsequent oxidations of the different metal sites of the cluster cage, followed by a huge, complex multielectronic signal starting at about -1.2 V(SCE), which should be associated to the final oxidative collapse of the whole cluster (to which corresponds the complex reduction peak at $-0.3/-0.4$ V(SCE)). For $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ the reproducibility and significance of the whole, complex peak system in the $-0.3/-1.2$ V region (with a first neat, chemically irreversible oxidation peak at -0.30 V(SCE), having $E_p - E_{p/2} = 43$ mV half-peak width at 0.2 V s^{-1}) was confirmed working with a different counter anion (i.e. $[\text{Rh}_7(\text{CO})_{16}][(\text{PPh}_3)_2\text{N}]_3$). Moreover, the CV patterns obtained for $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ appear to be in good agreement with those obtained in the detailed electrochemical study of the same complex reported in the above paper by Longoni and coworkers [18], which was in the same medium and on the same surface, although with a different supporting electrolyte and at much higher concentration. The clusters of higher nuclearity $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ feature even more complex (and less distinguishable due to the very small peaks, on account of the lower diffusion coefficients) oxidation patterns before the final oxidative breakdowns, including both reversible and irreversible peaks.

Similar considerations apply to the reductive region of the CV patterns, featuring a complex and hardly distinguishable series of reversible and irreversible reduction peaks. In the $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ case a huge signal at about -2.7 V appears, possibly associated to the reductive collapse of the whole cluster. On the contrary such reductive collapse peak is not so perceivable for $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ in the available potential window.

Since the low diffusion coefficients of these very bulky molecules result in too low peak currents for a detailed mechanistic analysis in the central region of their CV patterns at our working concentrations, the most useful feature concerns the positions of the large peaks accounting for their final oxidative and reductive breakdowns. In particular, it clearly appears that the decrease of the CO vs. Rh ratio results in a regular decrease of the cluster stability in both the reduction and oxidation regions, in the sequence $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ (CO:Rh = 2.50) $>$ $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ (CO:Rh = 2.28) $>$ $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ (CO:Rh = 1.78). In this context looking at the CV patterns of cluster A and cluster B, it appears that (i) the general features of both CV patterns are consistent with those of the reference clusters; (ii) the prolonged nitrogen bubbling in a solution of A produces B, resulting in a shrinking of the cluster stability window, its CV pattern gradually becoming more similar to that of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ cluster; this trend is fully consistent with the expected lower CO vs. Rh ratio in the structure of B with respect to A; (iii) the ratio R ($R = \text{CO number/Rh atoms number}$) could be 2.1 for A and 1.9 for B (see Fig. 3). Therefore, inserting the carbonyl frequency of the main band and the possible ratio R , suggested by the cyclic voltammetric investigations, in the linear equations reported in Figs. 1 and 2, some hypotheses about the nature of A and B can be made.

Since A, on the basis of its CV pattern, may have a value of R ratio bigger than 2, it is reasonable to insert it in the linear correlation reported in Fig. 1 whereas B, with a R ratio lower than 2, may be inserted in the linear correlation reported in Fig. 2. It follows that if the charge of A is -1 , it could be $[\text{Rh}_7(\text{CO})_{14}]^-$; if the charge is -2 , it could be $[\text{Rh}_9(\text{CO})_{19}]^{2-}$; if the charge is -3 , it could be $[\text{Rh}_{11}(\text{CO})_{24}]^{3-}$; finally if the charge is -4 , it could be $[\text{Rh}_{13}(\text{CO})_{28}]^{4-}$. According to elemental analysis of its sodium salt (see Section 4) A could be $[\text{Rh}_7(\text{CO})_{14}]^-$ [19].

Besides, if the charge of B is -1 , it could be $[\text{Rh}_9(\text{CO})_{17}]^-$; if the charge is -2 , it could be $[\text{Rh}_{12}(\text{CO})_{23}]^{2-}$; if the charge is -3 , it could be $[\text{Rh}_{15}(\text{CO})_{28}]^{3-}$; finally if the charge is -4 , it could be $[\text{Rh}_{17}(\text{CO})_{33}]^{4-}$. In the elemental analysis, the sodium salt of cluster B (see Section 4) analyzes to the composition $\text{Na}_3\text{Rh}_{15}\text{C}_{28}\text{O}_{28}$, suggesting that B is the anionic cluster $[\text{Rh}_{15}(\text{CO})_{28}]^{3-}$ [19].

3. Conclusion

In this work we report the new high yield and one-pot syntheses of $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ and $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ starting from $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ dissolved in ethylene glycol and involving two steps: (i) treatment of $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ under 1 atm of CO at 50°C to give $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$; (ii) addition of the base ($\text{CH}_3\text{CO}_2\text{Na}$ or Na_2CO_3) followed by reductive carbonylation under 1 atm CO at an adequate temperature (50°C , $[\text{Rh}_7(\text{CO})_{16}]^{3-}$; 150°C , $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$). These syntheses (see Scheme 1) are more convenient than those previously reported in the literature [7,12,20,21]. Interestingly, this reaction pattern is totally different from that reported using the silica surface as reaction medium [8]. In this latter case the clusters $[\text{Rh}_5(\text{CO})_{15}]^-$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ are formed together with cluster A, not isolated working in ethylene glycol solution (see Scheme 1). We have clarified that the cluster $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ cannot be obtained working on the silica surface in the presence of bases due to the lack of formation of an anionic cluster B obtained only in solution from A by bubbling nitrogen [8]. Cluster B is one of the key-intermediates, which can be isolated and which subsequently affords $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ (under CO at and 150°C) when working in ethylene glycol solution in the presence of bases. Such high stability of B in ethylene glycol solution even in the presence of CO is not observed on the silica surface where B is quickly converted under CO to A, which does not react further, being very stable on the silica surface under 1 atm of CO even at 160°C . Therefore, we have another evidence that the particular stabilization of some cluster species by the silica surface may lead to a different selectivity when using the silica surface instead of a solvent as reaction medium.

Finally, in this work we have evidenced a linear correlation between the main carbonyl band vs. [(charge/Rh atoms)/CO number] for a series of both medium and high nuclearity anionic rhodium clusters. By combining such linear correlations with a cyclic voltammetry investigation and elemental analyses, we suggested that A could be proposed as $[\text{Rh}_7(\text{CO})_{14}]^-$ and B as $[\text{Rh}_{15}(\text{CO})_{28}]^{3-}$. Interestingly, these two clusters interconvert easily in tetrahydrofuran solution by bubbling nitrogen (A into B) or CO (B into A), as other anionic clusters of similar nuclearity (e.g. $[\text{Rh}_5(\text{CO})_{15}]^-$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$), and work is in progress in order to understand if this interconversion involves other species. Although it was not possible, due to the lack of suitable crystals, for a structural X-ray investigation of A and B, it is worth to remark that working at relatively high temperatures, thanks to the initial use of silica as reaction medium, it was possible to obtain new anionic rhodium clusters of medium and high nuclearity despite the very large amount of work done on the synthesis of this class of anionic clusters in the last thirty years.

4. Experimental

4.1. General comments

$\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ (40.93% wt. Rh) was purchased from Engelhard, while $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was prepared according to the literature [22]. All the salts and solvents used were purchased from Sigma-Aldrich. THF was freshly distilled prior to use. SiO_2 (Aerosil® 200 Degussa, with a nominal surface area of $200\text{ m}^2/\text{g}$) was used after treatment in vacuum (10^{-2} Torr) at 25°C for 3 h. The surface

reactions were monitored by infrared spectroscopy, the samples being studied as nujol mull. All reaction products were initially identified by infrared spectroscopy, their spectra being compared to those of pure samples. Elemental analyses were carried out in the Dipartimento di Chimica Inorganica, Metallorganica e Analitica “Lamberto Malatesta” of the Università degli Studi di Milano.

4.2. Synthesis of $[Rh_{14}(CO)_{25}]^{4-}$ in the presence of CH_3CO_2Na

About 0.200 g of $RhCl_3 \cdot 3H_2O$, (0.795 mmol) was dissolved in 30 ml of ethylene glycol in a 100 ml three-necked flask, with a refrigerator and an equipment to bubble CO. The reaction mixture was stirred for 18 h at 50 °C, bubbling 1 atm of CO. The resulting yellow solution showed two carbonyl bands at 2000 and 2075 cm^{-1} typical of $[Rh(CO)_2Cl_2]^-$. 1.081 g of $CH_3CO_2Na \cdot 3H_2O$ (7.95 mmol, molar ratio Rh:Na = 1:10) were thus added to the $[Rh(CO)_2Cl_2]^-$ solution which was kept at 150 °C under 1 atm of CO with a vigorous stirring. The solution became dark. After 8 h only one species was present, characterized by ν_{CO} at 1972 (s) and 1819 (m) cm^{-1} , typical of $[Rh_{14}(CO)_{25}]^{4-}$. By addition of an aqueous solution of $[NMe_3Benzyl]Cl$ (0.300 g in 100 ml of degassed water) to the reaction mixture $[NMe_3Benzyl]_4[Rh_{14}(CO)_{25}]$ precipitated. The precipitate was washed with isopropanol and treated for few hours under vacuum (10^{-2} Torr). $[NMe_3Benzyl]_4[Rh_{14}(CO)_{25}]$ was obtained with a 70–75% yield (ν_{CO} in CH_3CN = 1967 (s), 1832 (m) and 1813 (m) cm^{-1}). Anal. Calc. for: C, 28.46; H, 2.33; N, 2.04. Found: C, 28.90; H, 2.50; N, 2.15%.

4.3. Synthesis of $[Rh_{14}(CO)_{25}]^{4-}$ in the presence of Na_2CO_3

About 0.200 g of $RhCl_3 \cdot 3H_2O$, (0.795 mmol) was dissolved in 30 ml of ethylene glycol in a 100 ml three-necked flask, with a refrigerator and an equipment to bubble CO. The reaction mixture was stirred for 18 h at 50 °C, bubbling CO. The resulting yellow solution showed two carbonyl bands at 2000 and 2075 cm^{-1} typical of $[Rh(CO)_2Cl_2]^-$. About 0.843 g of Na_2CO_3 (7.95 mmol of Na_2CO_3 , molar ratio Rh:Na = 1:20) was thus added to the $[Rh(CO)_2Cl_2]^-$ solution which was kept at 150 °C under 1 atm of CO with a vigorous stirring. The solution became dark. After 8 h only one species was present, characterized by ν_{CO} at 1972 (s) and 1819 (m) cm^{-1} , typical of $[Rh_{14}(CO)_{25}]^{4-}$. By addition of an aqueous solution of $[(PPh_3)_2N]Cl$ (0.300 g in 100 ml of degassed water) to the reaction mixture $[(PPh_3)_2N]_4[Rh_{14}(CO)_{25}]$ precipitated. The precipitate was washed with isopropanol and treated for few hours under vacuum (10^{-2} Torr). $[(PPh_3)_2N]_4[Rh_{14}(CO)_{25}]$ was obtained with a 75% yield (ν_{CO} in CH_3CN = 1967 (s), 1832 (m) and 1813 (m) cm^{-1}). Anal. Calc. for: C, 47.25; H, 2.79; N, 1.43. Found: C, 47.10; H, 2.82; N, 1.43%.

4.4. Synthesis of $[Rh_7(CO)_{16}]^{3-}$ in the presence of Na_2CO_3

About 0.200 g of $RhCl_3 \cdot 3H_2O$, (0.795 mmol) was dissolved in 30 ml of ethylene glycol in a 100 ml three-necked flask, with a refrigerator and an equipment to bubble CO. The reaction mixture was stirred for 18 h at 50 °C, bubbling CO. The resulting yellow solution showed two carbonyl bands at 2000 and 2075 cm^{-1} typical of $[Rh(CO)_2Cl_2]^-$. About 0.843 g of Na_2CO_3 (7.95 mmol of Na_2CO_3 , molar ratio Rh:Na = 1:20) was thus added to the $[Rh(CO)_2Cl_2]^-$ solution which was kept at 50 °C under 1 atm of CO with a vigorous stirring. The solution became dark green. After 6 h only one species was present, characterized by ν_{CO} at 1963 cm^{-1} (s), typical of $[Rh_7(CO)_{16}]^{3-}$. By addition of an aqueous solution of $[(PPh_3)_2N]Cl$ (0.300 g in 100 ml of degassed water) to the reaction mixture $[(PPh_3)_2N]_3[Rh_7(CO)_{16}]$ precipitated. The precipitate was washed with isopropanol and treated for few hours under vacuum (10^{-2} Torr). $[(PPh_3)_2N]_3[Rh_7(CO)_{16}]$ was obtained

with a 80% yield (ν_{CO} in CH_3CN = 1956 (vs), 1818 (s) and 1772 cm^{-1} (s)). Anal. Calc. for: C, 53.48; H, 3.23; N, 1.51. Found: C, 53.80; H, 3.40; N, 1.67%.

4.5. Formation of cluster B in ethylene glycol solution

About 0.200 g of $RhCl_3 \cdot 3H_2O$, (0.795 mmol) was dissolved in 30 ml of ethylene glycol in a 100 ml three-necked flask, with a refrigerator and an equipment to bubble CO. The reaction mixture was stirred for 18 h at 50 °C, bubbling CO. The resulting yellow solution showed two carbonyl bands at 2000 and 2075 cm^{-1} typical of $[Rh(CO)_2Cl_2]^-$. About 1.081 g of $CH_3CO_2Na \cdot 3H_2O$ (7.95 mmol, molar ratio Rh:Na = 1:10) was added to the $[Rh(CO)_2Cl_2]^-$ solution which was kept at 50 °C under 1 atm CO with a vigorous stirring. The solution became dark. After 6 h, only one species was present, characterized by ν_{CO} at 2001 cm^{-1} . By addition of an aqueous solution of $[NMe_3Benzyl]Cl$ (0.300 g in 100 ml of degassed water) to the reaction mixture $[NMe_3Benzyl]_x [B]$ precipitated. The precipitate was washed with isopropanol and treated for few hours under vacuum (10^{-2} Torr) (ν_{CO} in THF = 2037 (w), 2000 (s), 1863 (m, br) cm^{-1}).

4.6. Preparation of supported $RhCl_3 \cdot nH_2O/SiO_2$ (3% wt. Rh/SiO₂) added with Na_2CO_3

A slurry of silica (10.14 g), $RhCl_3 \cdot nH_2O$ (0.743 g, 3% wt. Rh/SiO₂), 3.14 g di Na_2CO_3 (molar ratio Rh:Na = 1:20) and degassed H_2O (ca. 300 ml) was stirred overnight in a 500 ml two-necked flask under N_2 at 25 °C. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final light yellow powder was stored under N_2 .

4.7. Preparation of supported $[Rh(CO)_2Cl_2]/SiO_2$ (3% wt. Rh/SiO₂) added with Na_2CO_3

A slurry of silica (10.17 g), $[Rh(CO)_2Cl_2]$ (0.576 g, 1.482 mmol, 3% wt. Rh/SiO₂), Na_2CO_3 (3.142 g; 29.64 mmol; molar ratio Rh:Na = 1:20) and degassed CH_2Cl_2 (ca. 300 ml) was stirred overnight in a 500 ml two-necked flask under N_2 at 25 °C. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final beige powder was stored under N_2 .

4.8. Formation of cluster A and cluster B starting from $RhCl_3 \cdot nH_2O/SiO_2$

The light yellow powder, obtained supporting $RhCl_3 \cdot nH_2O$ (0.743 g, 3% wt. Rh/SiO₂) and Na_2CO_3 (3.14 g, molar ratio Rh:Na = 1:20) on silica, as above described, was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N_2 flow [22]. The powder was treated under vacuum (10^{-2} Torr), then, after addition of degassed water (5 ml, 50% wt. H_2O/SiO_2), exposed to CO (1 atm) for 48 h at 50 °C. The colour became light brown. The nujol spectrum under CO showed one band with ν_{CO} 2020 cm^{-1} . Extraction of the resulting powder under CO onto a porous septum with THF (ca. 200 ml), afforded a brown solution of A (ν_{CO} in THF: 2043 (w), 2020 (s), 1840 (m) cm^{-1} , Anal. found: C, 14.71) which was evaporated to dryness under vacuum (10^{-2} Torr) and stored under CO.

When the extraction was carried out in THF solution under N_2 , B was obtained (ν_{CO} in THF: 2037 (w), 2000 (s), 1863 (m, br) cm^{-1} ; ν_{CO} in nujol 2000 cm^{-1} , anal. found C 13.0) and stored under N_2 .

4.9. Formation of cluster A and cluster B starting from $[Rh(CO)_2Cl_2]/SiO_2$

The light yellow powder, obtained supporting $[Rh(CO)_2Cl_2]$ (0.576 g, 3% wt. Rh/SiO₂), Na_2CO_3 (3.142 g; molar ratio

Rh:Na = 1:20) on the silica surface, as above described, was transferred into a cylindrical Pyrex vessel (diameter 40 mm, length 350 mm) under a N₂ flow [22]. The powder was treated under vacuum (10⁻² Torr), then, after addition of degassed water (5 ml, 50% wt. H₂O/SiO₂), exposed to CO (1 atm) for 18 h at 100 °C. The colour became light brown. The nujol spectrum under CO showed one band with ν_{CO} 2020 cm⁻¹. Extraction of the resulting powder under CO onto a porous septum with THF (ca. 200 ml), afforded a brown solution of A (ν_{CO} in THF: 2043 (w), 2020 (s), 1840 (m) cm⁻¹, Anal. found: C, 14.51) which was evaporated under vacuum to dryness (10⁻² Torr) and stored under CO. When the extraction was carried out under N₂ with THF, the final solution of B was obtained, which was evaporated to dryness under vacuum (ν_{CO} in THF: 2037 (w), 2000 (s), 1863 (m, br) cm⁻¹, ν_{CO} in nujol 2000 cm⁻¹, Anal. found: C, 13.58) and stored under N₂.

4.10. Interconversion of cluster A and cluster B

By bubbling N₂ for 5 h in a THF or ethylene glycol solution of a salt of A obtained as above described, B was formed quantitatively. This latter was readily (5 min) converted in A, by bubbling CO in its THF or ethylene glycol solution.

4.11. Electrochemical investigation

The cyclic voltammetric (CV) investigation was performed at scan rates ranging from 0.05 to 10 V s⁻¹ using an Autolab PGSTAT 12 potentiostat/galvanostat (EcoChemie, The Netherlands), run by a PC with GPES software, compensating the ohmic drop by the positive feedback technique [23], with a glassy carbon GC (AMEL, radius 1.5 mm) as the working electrode, a platinum counter-electrode, and an aqueous saturated calomel electrode (SCE) as the operating reference electrode (the half-wave potential of the ferricinium/ferrocene redox couple, recommended by IUPAC for inter-solvent comparison of potential scales [24] being 0.395 V when measured in acetonitrile with 0.1 M tetrabutylammonium perchlorate supporting electrolyte against our saturated SCE. The cell was thermostated at 298 K. The working solutions (at concentrations ranging from 0.00025 to 0.0005 M for the reference rhodium clusters, or 20 to 40 mg in 25–30 cm³ with a small insoluble residue in the case of A) were made up in acetonitrile (Merck, HPLC grade), added with 0.1 M tetrabutylammonium perchlorate (FLUKA) as the supporting electrolyte, and were carefully

deaerated by nitrogen bubbling. The polishing procedure for the working GC electrode consisted of surface treatment with diamond powder (Aldrich, diameter 1 μm) on a wet cloth (DP-Nap, Struers).

Acknowledgments

We deeply thank Prof. Ugo for fruitful discussions, Dr. Femoni and Dr. Tiozzo for a sample gift of [NEt₄][Rh₁₅(CO)₂₅(CH₃CN)] and Dr. Rizzato for X-ray diffraction studies. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (PRIN 2003, Research Title: Proprietà di singole molecole ed architetture molecolari funzionali supportate: caratterizzazione chimico-fisica, sviluppo di sintesi chimiche e di sistemi per l'indagine) and by the Centro Nazionale delle Ricerche (CNR).

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