Photochemistry and Electrochemistry of Triosmium Clusters, The Non-Carbonyl Co-Ligand Makes the Difference

Bakker, M.J.

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Influence of Metal Core Composition on Redox- and Photochemical Properties of the Clusters

$[H_{4-x}Ru_{4-x}Rh_x(CO)_{12}]$ $(x = 0, 2, 3, 4)$

Abstract

The electrochemical and photochemical properties of the clusters $[H_2Ru_2Rh_2(CO)_{12}]$, $[HRuRh_3(CO)_{12}]$ and $[Rh_4(CO)_{12}]$ were studied in order to evaluate the influence of the metal core composition in the series $[H_{4-x}Ru_{4-x}Rh_x(CO)_{12}]$ $(x = 0, 2, 3, 4)$.

Just as for $[H_4Ru_4(CO)_{12}]$, electrochemical reduction of the hydride-containing clusters $[H_2Ru_2Rh_2(CO)_{12}]$ and $[HRuRh_3(CO)_{12}]$ results in (sequential) loss of hydrogen producing the anions $[HRuRh_2(CO)_{12}]^-$, $[Ru_2Rh_2(CO)_{12}]^{2-}$ and $[RuRh_3(CO)_{12}]^-$, respectively. These anions can also be prepared from the parent clusters via chemical routes. Electrochemical reduction of $[Rh_4(CO)_{12}]$ does not result in the formation of a stable tetranuclear anion. Instead, $[Rh_4(CO)_{13}]^-$ and $[Rh_5(CO)_{13}]^{2-}$, detected in the course of IR spectro-electrochemical experiments, are the major reduction products, most likely formed from the CO-loss product $[Rh_4(CO)_{12}]^{2-}$ by fast redox condensation reactions. Re-oxidation of the two reduction products neatly generates the starting cluster together with $[Rh_4(CO)_{12}]$.

Unlike $[H_4Ru_4(CO)_{12}]$ that undergoes photochemical CO-dissociation, $[H_2Ru_2Rh_2(CO)_{12}]$ and $[Rh_4(CO)_{12}]$ appeared to be completely photostable in neat hexane and dichloromethane as well as in the presence of 1-octene.
Introduction

The chemical properties of transition metal carbonyl clusters can be strongly influenced by the introduction of non-carbonyl co-ligands. This is particularly well demonstrated by the different photochemical behaviour of the triangular clusters \([\text{Os}_3(\text{CO})_{12}]\) (refs 1,2), \([\text{O}_3(\text{CO})_{10}(1,3\text{-diene})]\) (Chapter 5) and \([\text{Os}_3(\text{CO})_{10}(\text{diimine})]\) (Chapters 2 and 3, and references therein). For all three clusters the primary photochemical event is Os-Os bond cleavage. Similar CO-bridged photoproducts are formed for \([\text{Os}_3(\text{CO})_{12}]\) and \([\text{Os}_3(\text{CO})_{10}(1,3\text{-diene})]\), although in the case of the 1,3-diene ligand the open-core structure is considerably more stable. By contrast, biradical and zwitterionic open-core photoproducts are formed in the case of \([\text{Os}_3(\text{CO})_{10}(\text{diimine})]\).

An alternative approach to changing the cluster is the systematic variation of the composition of the metal core, for instance by replacement of the osmium atoms in \([\text{Os}_3(\text{CO})_{12}]\) by one or two other metal atoms, thereby creating mixed-metal clusters. In the last decades the number of reported mixed-metal clusters has strongly increased. One of the most complete series consists of the close-packed tetrahedral clusters \([\text{H}_x\text{M}_4(\text{CO})_{12}]\) with \(\text{M} = \text{Fe}, \text{Ru}, \text{Co} \text{ and } \text{Rh}\) (\(x = 0-4\), depending on the metal core composition).\(^3\) Whereas for the iron-containing clusters only the Fe-Ru series is reasonably well presented, all combinations have been reported for the other three metals (with the exception of the unstable cluster \([\text{CoRh}_3(\text{CO})_{12}]\)). The structures and reactivity trends in these series have been reviewed by Pakkanen \textit{et al.}\(^3\)

![Figure 1](image)

**Figure 1.** Schematic molecular structures of the clusters \([\text{H}_x\text{Ru}_4-\text{Rh}_x(\text{CO})_{12}]\) (\(x = 0, 2, 4\)).

Figure 1 presents the molecular structures of three clusters of the series \([\text{H}_x\text{Ru}_x\text{Rh}_x(\text{CO})_{12}]\) (\(x = 0 - 4\)). The number of bridging hydrides equals that of the ruthenium atoms, thereby obeying the electron counting rules.\(^4\) According to their crystal structures \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\) and \([\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]\) possess only terminal carbonyls.\(^5,6\) In the remaining clusters with two or more rhodium atoms three carbonyls bridge the edges of the
Influence of Metal Core Composition in \([H_{4-x}Ru_{x}Rh_{4}(CO)_{12}]\)

triangular cluster face with the largest number of Rh atoms.\textsuperscript{7-9} The hydride ligands preferentially bridge a Ru–Ru edge.

The clusters \([\text{Rh}_4(\text{CO})_{12}]\) and \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\) are quite different in reactivity. For the former cluster CO exchange\textsuperscript{10} and substitution of CO by PPh\textsubscript{3} are fast at room temperature.\textsuperscript{11} \([\text{Rh}_4(\text{CO})_{12}]\) is rapidly converted into \([\text{Rh}_6(\text{CO})_{16}]\) (with a lower CO/Rh ratio) already in refluxing hexane.\textsuperscript{12,13} Also \([\text{HRuRh}_3(\text{CO})_{12}]\) and \([\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]\) undergo fast substitution of CO by PPh\textsubscript{3} at room temperature,\textsuperscript{14} whereas this reaction requires thermal activation in the case of \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\).\textsuperscript{15,16} However, the latter cluster undergoes photochemical dissociation of CO, which in the presence of PR\textsubscript{3} (R = Ph, OMe) results in photosubstitution to give \([\text{H}_4\text{Ru}_4(\text{CO})_{11}(PR_3)]\).\textsuperscript{16,17} In the presence of alkenes photocatalytic isomerization and stoichiometric hydrogenation occurs via the intermediate \([\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{alkene})]\), the latter reaction becoming photocatalytic in the presence of H\textsubscript{2}.\textsuperscript{16,18} On the other hand, no photoreactions have been reported for \([\text{Rh}_4(\text{CO})_{12}]\). The redox behaviour of \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\) in THF has been thoroughly investigated by Osella et al.\textsuperscript{19} According to this study, reduction leads to sequential loss of hydrogen and formation of the anions \([\text{H}_2\text{Ru}_4(\text{CO})_{12}]^-\) and \([\text{H}_2\text{Ru}_4(\text{CO})_{12}]^-\), respectively. In the presence of PPh\textsubscript{3} formation of the radical anion \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]^-\) initiates electron-transfer-chain (ETC) substitution of CO, producing the mono- and disubstituted derivatives.\textsuperscript{19} On the contrary, reduction of \([\text{Rh}_4(\text{CO})_{12}]\) has been proposed to lead to fragmentation of the cluster.\textsuperscript{20}

From the literature survey it becomes clear that \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\) and \([\text{Rh}_4(\text{CO})_{12}]\) differ appreciably in their thermal, photochemical and electrochemical reactivity. This chapter deals with an investigation of the influence of the composition of the tetrahedral metal core on the redox- and photochemical properties within the extended series of clusters \([\text{H}_{4-x}\text{Ru}_x\text{Rh}_4(\text{CO})_{12}]\) (\(x = 0, 2, 3, 4\)). \([\text{H}_2\text{Ru}_3\text{Rh}(\text{CO})_{12}]\) is not included, as it was not possible to prepare a sufficient amount of the pure complex.\textsuperscript{6} The aim of this study is to learn whether the properties of the mixed-metal clusters are intermediate or clearly different to those of the homonuclear tetraruthenium and tetrarhodium clusters. This goal is in line with our general interest in activation of small metal clusters by photochemical and electrochemical means.

**Results and Discussion**

**Redox Behaviour of \([\text{H}_{4-x}\text{Ru}_x\text{Rh}_x(\text{CO})_{12}]\) (\(x = 2, 3, 4\))**

The redox properties of the clusters \([\text{H}_{4-x}\text{Ru}_x\text{Rh}_x(\text{CO})_{12}]\) (\(x = 2, 3, 4\)) and their reduction paths were investigated by cyclic voltammetry and IR spectroelectrochemistry. The redox potentials of the clusters are presented in Table 1. The IR \(\nu(\text{CO})\) wavenumbers of the parent clusters and their reduction products are given in Table 2, together with the relevant literature data.
Table 1. Redox potentials for the clusters \([H_{x}Ru_{x}Rh_{d}(CO)_{12}] (x = 0, 2, 3, 4)\) and some reduction products\(^a\)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Solvent</th>
<th>(E_{pc}(R_1))</th>
<th>(E_{pc}(R_2))</th>
<th>(E_{pa})(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([H_{2}Ru_{2}(CO)_{12}])</td>
<td>CH(_2)Cl(_2)</td>
<td>-1.85</td>
<td>-2.33(^c)</td>
<td>0.82</td>
</tr>
<tr>
<td>([H_{3}Ru_{2}Rh_{2}(CO)_{12}])</td>
<td>CH(_2)Cl(_2)</td>
<td>-1.43</td>
<td>-2.10</td>
<td>0.23</td>
</tr>
<tr>
<td>([HRu_{2}Rh_{2}(CO)_{12}]^{-})(^d)</td>
<td>DME</td>
<td>-1.36</td>
<td>-2.15(^e)</td>
<td>0.96</td>
</tr>
<tr>
<td>([HRuRh_{3}(CO)_{12}])</td>
<td>CH(_2)Cl(_2)</td>
<td>-1.26</td>
<td>+1.15</td>
<td></td>
</tr>
<tr>
<td>([Rh_{4}(CO)_{12}]^{-})</td>
<td>CH(_2)Cl(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([Rh_{6}(CO)_{15}]^{2-})</td>
<td>DME</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([Rh(CO)_{4}]^{-})</td>
<td></td>
<td></td>
<td></td>
<td>0.55 (O(_2)) (^f)</td>
</tr>
<tr>
<td>([Rh_{5}(CO)_{15}]^{2-})</td>
<td></td>
<td></td>
<td></td>
<td>-0.28 (O(_2)) (^f)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: 5 \times 10^{-4} \text{ M cluster and 0.1 M NBu}_{4}\text{PF}_{6}, T = 298 K, Pt disc electrode, \(v = 100 \text{ mV s}^{-1}\); potentials are given in \(V \text{ vs } E_{1/2}(\text{Fc/Fc}^+)\). \(^b\) Oxidation potentials for the parent clusters and some reduction products; the oxidations were not studied in detail. \(^c\) Reduction potential for the anion \([HRu_{2}Rh_{2}(CO)_{12}]^{-}\). \(^d\) Prepared by chemical reduction of \([H_{2}Ru_{2}Rh_{2}(CO)_{12}]\) with \([\text{Fe}^{+}(\text{Cp})(\text{C}_{6}\text{Me}_{6})]\) in DME. \(^e\) Reduction potential for the anion \([RuRh_{3}(CO)_{12}]^{-}\). \(^f\) See Figure 5.

Figure 2. Cyclic voltammograms of (A) \([H_{2}Ru_{2}Rh_{2}(CO)_{12}]\) and (B) \([HRuRh_{3}(CO)_{12}]\) in dichloromethane (\(v = 100 \text{ mV/s}; T = 293 K\)).

\([H_{2}Ru_{2}Rh_{2}(CO)_{12}]\)

Cyclic voltammetry shows that the cluster \([H_{2}Ru_{2}Rh_{2}(CO)_{12}]\) is irreversibly reduced at the cathodic peak \(R_1\) in dichloromethane at room temperature and \(v = 100 \text{ mV/s}\) (Figure 2). A second cathodic process \(R_2\) due to reduction of a secondary product generated at \(R_1\) is observed at more negative potential.

In order to identify the reduction product(s) formed, the cathodic step \(R_1\) was studied \textit{in situ} with IR spectroelectrochemistry. On reduction the \(\nu(\text{CO})\) bands of the parent cluster were
Influence of Metal Core Composition in \([H_{4-x}Ru_{4-x}Rh_x(CO)_{12}]\)

replaced by new bands of a reduction product that lie 30 - 50 cm\(^{-1}\) lower in frequency compared those of the parent cluster (Table 2). The close correspondence between the IR \(\nu(CO)\) patterns indicates that the structure of the metal-carbonyl framework has been preserved. Indeed, comparison with literature data (Table 2) has revealed that this product is the cluster anion \([HRu_2Rh_2(CO)_{12}]^-\) formed by hydrogen loss.\(^{21}\) Upon further reduction of \([HRu_2Rh_2(CO)_{12}]^-\) at \(E(R_2)\) the \(\nu(CO)\) bands are replaced by a new set corresponding to the dianion \([Ru_2Rh_2(CO)_{12}]^{2-}\).\(^{21}\) Both reduction products of \([H_2Ru_2Rh_2(CO)_{12}]\), the anion \([HRu_2Rh_2(CO)_{12}]^-\) and the dianion \([Ru_2Rh_2(CO)_{12}]^{2-}\), were previously prepared by redox condensation reactions between \([Ru_3(CO)_{12}]\) and \([Rh(CO)_4]^+\), and structurally characterized by X-ray diffraction.\(^{21}\) Similarly to the parent cluster, three carbonyls bridge the edges of the RuRh\(_2\) plane in \([HRu_2Rh_2(CO)_{12}]^-\) and the only hydride bridges a Ru–Ru bond. The extra electron in \([Ru_2Rh_2(CO)_{12}]^{2-}\) requires two additional carbonyls to bridge the remaining Ru–Rh bonds.

**Scheme 1. Reduction pathways for the cluster \([H_2Ru_2Rh_2(CO)_{12}]\)**

\[
[H_2Ru_2Rh_2(CO)_{12}] \rightarrow \ \text{+ e}^- \ \rightarrow \ [HRu_2Rh_2(CO)_{12}]^- \rightarrow \ [Ru_2Rh_2(CO)_{12}]^{2-}.
\]

**Figure 3. IR spectra of \([H_2Ru_2Rh_2(CO)_{12}]\) (----) and its reduction product \([HRu_2Rh_2(CO)_{12}]^-\) (-----) in DME prepared by chemical reduction with 1 equivalent of \([Fe'(Cp)(C_6Me_6)]\).**

Alternatively, the reduction products of \([H_2Ru_2Rh_2(CO)_{12}]\) could be prepared in quantitative yield by chemical reduction in dimethoxyethane (DME). Addition of one equivalent of the reducing agent \([Fe'(Cp)(C_6Me_6)]\) to a solution of \([H_2Ru_2Rh_2(CO)_{12}]\) neatly
produced [HRu2Rh2(CO)12]−, as was confirmed by IR spectroscopy (see Figure 3 and Table 2). Addition of a second equivalent mainly led to precipitation. The IR spectrum proved the presence of a small amount of the dissolved dianion [Ru2Rh2(CO)12]2−. Importantly, upon addition of one equivalent of the parent cluster [H2Ru2Rh2(CO)12] the precipitate disappeared and the anion [HRu2Rh2(CO)12]− was present as the only species in solution. Apparently, a similar conproportionation reaction takes place, as has been observed between [H4Ru4(CO)12]9− and [H2Ru4(CO)12]2−.19

Table 2. IR ν(CO) wavenumbers of the clusters [H2Ru2Rh2(CO)12], [HRuRh3(CO)12], and [Rh4(CO)12]− and their reduction products

<table>
<thead>
<tr>
<th>cluster</th>
<th>solvent</th>
<th>ν(CO) (cm−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H2Ru2Rh2(CO)12]</td>
<td>CH2Cl2</td>
<td>2108(vw), 2084(s), 2063(s), 2057(sh), 2030(m), 2018(sh), 1905(w), 1852(w)</td>
</tr>
<tr>
<td></td>
<td>DME</td>
<td>2111(w), 2086(s), 2036(s), 2053(s), 2033(m), 2010(sh), 1907(w), 1854(w)</td>
</tr>
<tr>
<td>[HRu2Rh2(CO)12]−</td>
<td>CH2Cl2</td>
<td>2065 (w), 2030(s), 2010(s), 1975(m), 1953(sh), 1834(w), 1813(w)</td>
</tr>
<tr>
<td></td>
<td>DMEb</td>
<td>2065(w,br), 2028(s), 2006(s), 1979(m), 1953(w), 1849(w), 1821(w)</td>
</tr>
<tr>
<td></td>
<td>THFc</td>
<td>2070(w), 2064(w), 2027(s), 2007(s), 1979(ms), 1972(sh), 1954(mw), 1850(m), 1823(m)</td>
</tr>
<tr>
<td>[Ru2Rh2(CO)12]3−</td>
<td>CH2Cl2</td>
<td>1965(s), 1954(sh), 1931(s), 1885(w), 1817(w), 1787(w), 1765(w)</td>
</tr>
<tr>
<td></td>
<td>DMEb</td>
<td>2035(w), 2016(w), 1999(w), 1965(s), 1956(sh), 1934(s), 1888(w), 1785(w), 1767(w)</td>
</tr>
<tr>
<td></td>
<td>THFc</td>
<td>2029(mw), 2015(w), 1963(s), 1952(s), 1931(ms), 1885(mw), 1815(w), 1786(w), 1764(m)</td>
</tr>
<tr>
<td>[HRuRh3(CO)12]</td>
<td>CH2Cl2</td>
<td>2108(w), 2077(s), 2067(vs), 2033(m), 2010(m), 1930(w), 1904(w), 1874(m)</td>
</tr>
<tr>
<td>[HRuRh3(CO)12]−</td>
<td>CH2Cl2</td>
<td>2075(w), 2032(s), 2012(s), 1989(sh), 1948(sh), 1844(m), 1829(m), 1800(sh)</td>
</tr>
<tr>
<td>[HRuRh3(CO)12]−</td>
<td>THF</td>
<td>2071(mw), 2024(s), 2015(ms), 2006(s), 1987(ms), 1949(w), 1848(m), 1836(ms), 1814(mw)</td>
</tr>
<tr>
<td>[Rh4(CO)12]</td>
<td>THF</td>
<td>2108(vw), 2073(vs), 2040(m), 1876(m)</td>
</tr>
<tr>
<td>[Rh4(CO)12]−</td>
<td>THF</td>
<td>2075(vs), 2061(sh), 2043(w), 1809(m)</td>
</tr>
<tr>
<td>[Rh5(CO)13]−</td>
<td>THF</td>
<td>2045(s), 2010(vs), 1868(m), 1838(m), 1785(m)</td>
</tr>
<tr>
<td>[Rh4(CO)13]−</td>
<td>THF</td>
<td>2050(vw), 1990(sh), 1984(s), 1960(m), 1767(ms)</td>
</tr>
<tr>
<td>[Rh4(CO)11]−</td>
<td>THF</td>
<td>1930(vs), 1810(s)</td>
</tr>
<tr>
<td>[Rh(CO)3]−</td>
<td>THF</td>
<td>2000(vw), 1895(vs)</td>
</tr>
</tbody>
</table>

a Prepared by in situ reduction in the IR OTTLE cell. b Prepared by chemical reduction of [H2Ru2Rh2(CO)12] with [Fe(Cp)(C6Me6)] in DME. c Taken from ref. 21. d Prepared by deprotonation with NEt4OH. e Taken from ref. 22. f Taken from ref. 23. g Taken from ref. 24. h Taken from ref. 25.

[HRuRh3(CO)12]

The cyclic voltammogram of [HRuRh3(CO)12] in CH2Cl2 is presented in Figure 2. At v = 100 mV/s and room temperature the cluster undergoes an irreversible reduction (cathodic peak
Influence of Metal Core Composition in \([H_{4},Ru_{4},Rh_{3}(CO)_{12}]\)

Reduction in the IR OTTLE cell has revealed that the anion \([RuRh_3(CO)_{12}]^-\), previously reported by Fumagalli et al.,\(^{22}\) is produced, together with a small amount of unidentified side-products with \(\nu(CO)\) absorptions at 2084, 1939, 1770 cm\(^{-1}\). Alternatively, the anion \([RuRh_3(CO)_{12}]^-\) could be obtained by deprotonation of \([HRuRh_3(CO)_{12}]\) in dichloromethane with one equivalent of the \(\text{NEt}_4\text{OH}\) (see Figure 4), which had been proven to be a suitable deprotonation agent for the related clusters \([H_4Ru_4(CO)_{12}]\) and \([H_4Ru_4(CO)_{10}(2,2'-bipyridine)]\).\(^{26}\) According to its reported crystal structure, the anion \([RuRh_3(CO)_{12}]^-\) contains five bridging carbonyls, leaving only one Ru–Rh edge unbridged.\(^{22}\)

![Figure 4. IR spectra of \([HRuRh_3(CO)_{12}]\) (- - -) and its product \([RuRh_3(CO)_{12}]^-\) (-----) prepared by deprotonation with \(\text{NEt}_4\text{OH}\) in dichloromethane (the asterisks denote the \(\nu(CO)\) bands of some minor side products).](image)

![Figure 5. Cyclic voltammogram of the cluster \([Rh_4(CO)_{12}]\) in dichloromethane(\(\nu = 100 \text{ mV/s}; T = 293 \text{ K}\)).](image)
[Rh₄(CO)₁₂]

The cyclic voltammogram in Figure 5 shows that at room temperature [Rh₄(CO)₁₂] undergoes irreversible reduction in dichloromethane at the cathodic peak $R₁ (\nu = 100 \text{ mV/s})$. Upon scan reversal beyond $R₁$ small anodic peaks are observed at $E_{p,a}(O₁) = -0.92 \text{ V}$, $E_{p,a}(O₂) = -0.55 \text{ V}$ and $E_{p,a}(O₃) = -0.28 \text{ V}$ vs Fc/Fc⁺, which will be assigned below. The reduction of [Rh₄(CO)₁₂] remains fully irreversible at low temperatures ($T = 203 \text{ K}$; $\nu = 100 \text{ mV/s}$).

![Absorbance vs Wavenumbers (cm⁻¹) for [Rh₄(CO)₁₂] and [Rh₆(CO)₁₂] clusters]

**Figure 6.** IR spectra of the anionic clusters formed upon reduction of [Rh₄(CO)₁₂] (top) and products of their re-oxidation (bottom). The starting IR spectrum of [Rh₄(CO)₁₂] (---) is also depicted for comparison.
The reduction path of [Rh₄(CO)₁₂] was further studied by IR spectroelectrochemistry. Independently of the solvent used, either dichloromethane or THF, the same mixture of reduction products was formed (see Figure 6A). The IR data presented below and in Table 2 concern THF solutions, as the literature data on related reduction products are only available in this solvent. The main product was identified as the pentanuclear anion [Rh₅(CO)₁₅]⁻ (ν(CO) bands at 2045, 2009, 1869, 1840 and 1785 cm⁻¹). Also some [Rh₆(CO)₁₅]²⁻ was formed, as evidenced by the ν(CO) bands at 1985 (sh), 1960 and 1772 cm⁻¹. Weak bands at 2078, 2062 and 1750 cm⁻¹ due to minor side-products could not be assigned. No detectable amounts of the fragmentation product [Rh(CO)₄]⁻ and/or the CO-loss product [Rh₄(CO)₁₁]²⁻ were observed, not even when the experiment was repeated in butyronitrile at 203 K.

Electrochemical re-oxidation of the mixture of reduction products occurred in two steps according to the thin-layer cyclic voltammogram (at ca. -0.8 and 0.0 V vs Fe/Fe⁺ in dichloromethane). It is likely that these two re-oxidation steps correspond to the anodic processes O₁ and O₂ in the conventional cyclic voltammogram shown in Figure 5. In the first re-oxidation step [Rh₆(CO)₁₅]²⁻ was oxidized to give the neutral cluster [Rh₆(CO)₁₆]. The main reduction product [Rh₅(CO)₁₅]⁻ was oxidized in the second step producing the starting material [Rh₄(CO)₁₂] (ca. 50% recovery) and additional [Rh₆(CO)₁₆]. Thus, reduction of [Rh₄(CO)₁₂] and subsequent re-oxidation of the formed products lead to formation of a neat mixture of the starting material [Rh₄(CO)₁₂] and [Rh₆(CO)₁₆] (see Figure 6B).

Scheme 2 summarizes the reduction and re-oxidation pathways of [Rh₄(CO)₁₂] and its reduction products, respectively. Clearly, reduction of [Rh₄(CO)₁₂] leads to formation of anionic clusters of higher nuclearity. This result is not unexpected, as it is known from the work of Chini and co-workers that rhodium cluster anions such as [Rh₄(CO)₁₁]²⁻, the likely reduction intermediate, are highly reactive and easily undergo redox condensation reactions with neutral rhodium clusters. As examples may serve the formation of [Rh₆(CO)₁₅]²⁻ and [Rh₁₂(CO)₃₀]²⁻ according to eqs 1 and 2. In the presence of liberated CO the anion [Rh₅(CO)₁₅]⁻ can be formed from [Rh₄(CO)₁₁]²⁻, [Rh₆(CO)₁₅]²⁻ or [Rh₁₂(CO)₃₀]²⁻. It can also be formed according to eq 3, provided mononuclear [Rh(CO)₄]⁻ is present.

\[
\begin{align*}
2[Rh_4(CO)_{11}]^{2-} + [Rh_4(CO)_{12}] & \rightarrow 2[Rh_6(CO)_{15}]^{2-} + 4CO \\
[Rh_4(CO)_{11}]^{2-} + 2[Rh_4(CO)_{12}] & \rightarrow [Rh_{12}(CO)_{30}]^{2-} + 5CO \\
[Rh_4(CO)_{12}] + [Rh(CO)_4]^− & \rightarrow [Rh_5(CO)_{15}]^−
\end{align*}
\]

On the basis of eqs 1 and 2, it is tentatively proposed that the CO-loss product [Rh₄(CO)₁₁]²⁻ is initially formed upon reduction of [Rh₄(CO)₁₂]. This dianion is rapidly consumed by redox condensation reactions with the parent cluster and secondary reduction products, preventing its observation even at low temperatures (see Scheme 2). Dissociation of CO was also proposed to occur on reduction of the related cluster [Rh₄(CO)₆(tripod)], which...
nearly became reversible under 1 atmosphere of CO. They suggested that \([\text{Rh}_4(\text{CO})_{12}]^+\) undergoes an one-electron reduction step to give the radical anion \([\text{Rh}_4(\text{CO})_{12}]^-\), which then undergoes fragmentation, \(\text{[Rh(CO)}_4\text{]}^-\) being one of the products. Support for the formation of the radical anion \([\text{Rh}_4(\text{CO})_{12}]^-\) was given by the observation of a paramagnetic species by EPR spectroscopy, generated by exhaustive electrolysis of a solution of \([\text{Rh}_4(\text{CO})_{12}]\) in 1,2-dichloroethane at 233 K. However, according to our observation the reduction of \([\text{Rh}_4(\text{CO})_{12}]\) remains completely irreversible at 203 K in the ms cyclovoltammetric time domain. The paramagnetic species therefore cannot be assigned to the intact tetrahedral radical anion \([\text{Rh}_4(\text{CO})_{12}]^-\). The suggestion by Rimmelin et al. that reduction of \([\text{Rh}_4(\text{CO})_{12}]\) leads to fragmentation, was based on the observation that the anodic peak \(O_2\) in the cyclic voltammogram (see Figure 5) occurs at the same potential as the oxidation of the mononuclear anion \([\text{Rh(CO)}_4]^-\) (as determined in an independent experiment). However, \([\text{Rh(CO)}_4]^-\) can also be formed as a reactive side-product of a redox-condensation reaction. It was not observed with IR spectroelectrochemistry (vide supra), probably due to its fast consumption according to eq 3.

**Scheme 2. Redox reactions of the cluster \([\text{Rh}_4(\text{CO})_{12}]\)**

\[
[\text{Rh}_4(\text{CO})_{12}] + 2e^- + \text{CO} \rightarrow [\text{Rh}_5(\text{CO})_{13}]^{2-} \quad \text{and} \quad [\text{Rh}_6(\text{CO})_{16}]^{2-} + 2e^- \rightarrow [\text{Rh}_4(\text{CO})_{12}]
\]

**Photoreactivity of \([\text{H}_4\text{Ru}_4\text{Rh}_x(\text{CO})_{12}] (x = 0, 2, 4)\)**

The photochemistry of \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\) has been studied in detail by Graff and Wrighton. This cluster undergoes photodissociation of CO, providing pathways to phosphine-substituted products and to (photocatalytic) isomerization and hydrogenation of alkenes. In the next section a study of the photochemical properties of \([\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]\) and \([\text{Rh}_4(\text{CO})_{12}]\) is presented.

**[H\textsubscript{2}Ru\textsubscript{2}Rh\textsubscript{2}(CO)\textsubscript{12}]**

The cluster \([H_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]\) strongly absorbs at 350 nm, i.e. at higher energy than \([H_4\text{Ru}_4(\text{CO})_{12}] (\lambda_{\text{max}} = 364 \text{ nm})\). At room temperature \([H_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]\) is thermally stable in neat hexane and dichloromethane, and in the presence of 0.1 M 1-octene. Thermal reactions occur with PPh\(_3\) and with alkynes (4-octyne, diphenylacetylene), thereby excluding their use.
for the study of the photochemical reactivity of this cluster. \([\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]\) appeared to be completely photostable on broad-band irradiation with a mercury lamp \((\lambda > 250 \text{ nm})\) in hexane, dichloromethane and also in hexane with 0.1 M 1-octene. In order to find out if any short-lived photoproduc t is reversibly produced on a subsecond time scale, the cluster was also studied in hexane with nanosecond time-resolved UV-vis absorption spectroscopy (time resolution of 7 ns). The absence of any observable transient upon 355 nm excitation suggests that either no photoreaction takes place, or that the photoproduc t reverts to the parent cluster on a sub-nanosecond time scale. It must be noted that under the same conditions no CO-loss photoproduc t was observed for \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]\), apparently due to a low photoreaction quantum yield.

The photoreactivity of the anionic cluster \([\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-\), prepared by chemical reduction of \([\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]\), was also studied. Although in the reduced cluster metal-metal and metal-hydride bonds are expected to be weaker, this anion was photostable under broad-band irradiation both in neat THF and in THF containing 0.1 M 1-octene.

\([\text{Rh}_4(\text{CO})_{12}]^-\)

The UV-vis spectrum of \([\text{Rh}_4(\text{CO})_{12}]^-\) exhibits an absorption maximum at 305 nm with a shoulder at 330 nm and a broad absorption tailing into the visible region. The cluster undergoes rapid thermal reaction with PPh\(_3\) already at room temperature.\(^{11}\) By contrast, it is thermally stable in neat hexane and in hexane with 0.1 M 1-octene at room temperature. We have found that the cluster is also photostable upon broad-band irradiation \((\lambda > 250 \text{ nm})\) under these conditions, in agreement with the absence of literature data on photochemical reactions of \([\text{Rh}_4(\text{CO})_{12}]^-\). At the same time no transient species could be observed for \([\text{Rh}_4(\text{CO})_{12}]^-\) in hexane with nanosecond time-resolved UV-vis absorption spectroscopy.

**Comparison of the Clusters \([\text{H}_{4-x}\text{Ru}_x\text{Rh}_x(\text{CO})_{12}] (x = 0, 2, 3, 4)\)**

The clusters \([\text{H}_{4-x}\text{Ru}_x\text{Rh}_x(\text{CO})_{12}] (x = 0, 2, 3, 4)\) have in common that their reduction is irreversible at room temperature already on the ms time scale of cyclic voltammetry. The reduction potentials of the mixed-metal clusters \([\text{H}_{4-x}\text{Ru}_x\text{Rh}_x(\text{CO})_{12}]\) with \(x = 2, 3\) are intermediate to those of \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]^-\) and \([\text{Rh}_4(\text{CO})_{12}]^-\), and decrease with an increasing number of rhodium atoms. The reduction potentials of the clusters with \(x = 2, 3\) are rather close to that of \([\text{Rh}_4(\text{CO})_{12}]^-\), these three clusters being isostructural with respect to their metal-carbonyl geometry.

There is a remarkable difference in the stability of the tetrahedral cluster core of the reduction products of \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]^-\) and the ruthenium-rhodium clusters on one hand, and that of \([\text{Rh}_4(\text{CO})_{12}]^-\) on the other. Reduction of homonuclear \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]^-\) leads to sequential loss of hydrogen and formation of the **stable** anions \([\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-\) and \([\text{H}_2\text{Ru}_4(\text{CO})_{12}]^-\).\(^{19}\) Even the tetraanion \([\text{Ru}_4(\text{CO})_{12}]^-\) can be prepared, though not via a direct electrochemical way.\(^{28}\) The mixed-metal clusters \([\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]^-\) and \([\text{HRuRh}_3(\text{CO})_{12}]^-\) undergo (sequential) loss of hydrogen upon reduction, just as the homonuclear cluster \([\text{H}_4\text{Ru}_4(\text{CO})_{12}]^-\). In fact, if the cluster possesses one or more \(\mu_3\)--CO bridges they are lost upon reduction of the
cluster, thereby preserving the electron-precise $M_4(CO)_{12}$ core. The anions thus formed are also quite stable. It is interesting to learn whether the hydrogen loss reaction is a general property of hydride-containing clusters of the tetrahedral $[H_xM_4(CO)_{12}]$ family with $M =$ Fe, Ru, Os, Co, Rh and Ir and $x = 1 - 4$. In contrast to this, $[Rh_4(CO)_{12}]$, which does not contain any hydride ligands, responds to reduction by release of CO yielding unobserved but highly probable $[Rh_4(CO)_{11}]^{2-}$: The cluster core of this dianion is very labile and higher nuclearity clusters, in particular $[Rh_5(CO)_{15}]^-$ and $[Rh_6(CO)_{13}]^-$, are formed via a complex sequence of redox condensation reactions with the parent cluster and secondary reduction products. Redox condensation reactions have also been reported to take place for instance between the CO-loss dianions $[M_3(CO)_{11}]^{2-}$ and the neutral parent cluster $[M_3(CO)_{12}]$ ($M =$ Ru, Os).\textsuperscript{29-31}

Interestingly, the thermal and redox reactivity sharply contrasts with the photochemistry. Here only $[H_4Ru_4(CO)_{12}]$ is photoreactive, undergoing CO dissociation as the primary photochemical event, whereas the clusters $[H_2Ru_2Rh_2(CO)_{12}]$ and $[Rh_4(CO)_{12}]$ are both photostable. Apparently, no specific bonds are sufficiently weakened and subsequently broken upon optical excitation.

**Conclusions**

The mixed-metal clusters $[H_2Ru_2Rh_2(CO)_{12}]$ and $[HRuRh_3(CO)_{12}]$ do not possess any novel electrochemical or photochemical properties compared to the homonuclear clusters $[H_4Ru_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$. From this study, it becomes clear that the reduction pathways are not determined by the metals in the metal core, but by the presence or absence of hydride ligands. If one or more hydride ligands are present, as is the case for $[H_4Ru_4(CO)_{12}]$, $[H_2Ru_2Rh_2(CO)_{12}]$ and $[HRuRh_3(CO)_{12}]$, these ligands are lost upon reduction in order to preserve the stable electron-precise $M_4(CO)_{12}$ core. Importantly, the reduction of the hydride-lacking tetrarhodium cluster $[Rh_4(CO)_{12}]$ does not lead to complete fragmentation, as was previously reported, but to dissociation of CO and subsequent redox condensation reactions with the parent cluster and secondary reduction products, yielding higher nuclearity clusters. The mixed-metal cluster $[H_2Ru_2Rh_2(CO)_{12}]$ and its anion $[HRu_2Rh_2(CO)_{12}]$ is photostable just as $[Rh_4(CO)_{12}]$.

**Experimental Section**

**Materials and Preparations**

The clusters $[H_4Ru_4(CO)_{12}]$ (refs 12,13), $[H_2Ru_2Rh_2(CO)_{12}]$ (ref. 7), $[HRuRh_3(CO)_{12}]$ (ref. 8) and $[Rh_4(CO)_{12}]$ (ref. 12,13) were prepared according to published procedures. $[Rh_4(CO)_{12}]$ (Alfa) was used as purchased. The supporting electrolyte NBu$_4$PF$_6$ (Aldrich) was recrystallized twice from ethanol and dried in vacuo at 80°C overnight. The salt NEt$_4$OH was purchased from Fluka as a 25% solution in MeOH. Ferrocene was used as received from BDH. Solvents of analytical grade quality (n-
Influence of Metal Core Composition in \([\text{H}_4\text{Ru}_4\text{Rh}_2(\text{CO})_{12}]\)

hexane, dichloromethane, THF, dimethoxyethane (DME)), all purchased from ACROS, were dried over sodium wire (n-hexane, THF, DME) or CaH\(_2\) (dichloromethane) and freshly distilled under nitrogen prior to use. The reducing agent \([\text{Fe}^1\text{(Cp)}(\text{C}_6\text{Me}_6)]\) was prepared by reduction of \([\text{Fe}^3\text{(Cp)}(\text{C}_6\text{Me}_6)]^+(\text{PF}_6)^-\) with 1% Na/Hg in DME according to the procedure described in ref. 32.

**Spectroscopic Measurements**

FTIR spectra were recorded on Bio-Rad FTS-7 or Bio-Rad FTS-60A spectrometers (16 scans at 2 cm\(^{-1}\) resolution). The UV-vis absorption spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer.

**(Spectro)electrochemical measurements**

Cyclic voltammetry was performed in a gastight cell under an atmosphere of dry argon. The cell was equipped with a Pt disc working (apparent surface area of 0.42 mm\(^2\)), Pt wire auxiliary and Ag wire pseudo-reference electrodes. The working electrode was carefully polished with a 0.25 \(\mu\)m grain diamond paste. All redox potentials are reported against the ferrocene-ferrocenium (Fc/Fc\(^+\)) redox couple used as an internal standard.\(^33\) The solutions for cyclic voltammetric experiments were typically 5 \(\times\) 10\(^{-4}\) M in the cluster compounds and 0.1 M in NBu\(_4\)PF\(_6\). The potential control was achieved with a PAR Model 283 potentiostat equipped with positive feedback for ohmic-drop compensation. Infrared spectroelectrochemical experiments were performed with an optically transparent thin-layer electrochemical (OTTLE) cell, equipped with a Pt minigrid working electrode (32 wires per cm) and CaF\(_2\) optical windows.\(^34,35\) The spectroelectrochemical samples were typically 5 \(\times\) 10\(^{-3}\) M in the cluster compounds. A PA4 potentiostat (EKOM, Czech Republic) was used to carry out the controlled-potential electrolyses.

**Photochemistry**

All photochemical samples were prepared under a nitrogen atmosphere using standard inert gas techniques. The cluster concentration was typically 10\(^{-3}\)-10\(^{-4}\) mol dm\(^{-3}\). A Philips HPK 125 W high pressure mercury lamp, equipped with the appropriate cut-off filters, served as a light source, for continuous-wave photochemistry. The experimental set-up for the nanosecond time-resolved UV-vis absorption measurements has been described in detail in Chapter 2.

**References**

The cluster $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ undergoes irreversible reduction at $E_{p,c} = -1.18 \, \text{V vs Fe/Fe}^+$ according to cyclic voltammetry in dichloromethane at room temperature and $\nu = 100 \, \text{mV/s}$. IR spectro-electrochemistry showed that this reduction step leads to formation of the dianion $[\text{Rh}_6(\text{CO})_{13}]^{2-}$ ($\nu(\text{CO})$ (CH$_2$Cl$_2$): 2000(sh), 1990(s), 1964(m), 1789(sh), 1750(m)) and some minor side-products ($\nu(\text{CO})$ (CH$_2$Cl$_2$): 2045, 2031 cm$^{-1}$). On re-oxidation the parent cluster was recovered for about 75%.
Influence of Metal Core Composition in [H₆Ru₆Rh₃(CO)₁₅]


