

# INFLUENCE OF METAL CORE COMPOSITION ON REDOX PROPERTIES AND PHOTOREACTIVITY OF THE CLUSTERS $[H_{4-x}Ru_{4-x}Rh_x(CO)_{12}]$ ( $x = 0, 2, 3, 4$ )

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Electrochemical properties of tetrahedral clusters  $[H_2Ru_2Rh_2(CO)_{12}]$ ,  $[HRuRh_3(CO)_{12}]$  and  $[Rh_4(CO)_{12}]$  were investigated in order to evaluate the influence of metal core composition in the series  $[H_{4-x}Ru_{4-x}Rh_x(CO)_{12}]$  ( $x = 0-4$ ). The cluster  $[H_3Ru_3Rh(CO)_{12}]$  was not available in sufficient quantities. As reported for  $[H_4Ru_4(CO)_{12}]$ , electrochemical reduction of the hydride-containing clusters  $[H_2Ru_2Rh_2(CO)_{12}]$  and  $[HRuRh_3(CO)_{12}]$  also results in (stepwise) loss of hydrogen, producing the anions  $[HRu_2Rh_2(CO)_{12}]^-$ ,  $[Ru_2Rh_2(CO)_{12}]^{2-}$  and  $[RuRh_3(CO)_{12}]^-$ . These anions can also be prepared from the neutral parent clusters *via* chemical routes. Electrochemical reduction of  $[Rh_4(CO)_{12}]$  does not result in the formation of any stable tetranuclear anion. Instead,  $[Rh_5(CO)_{15}]^-$  and  $[Rh_6(CO)_{15}]^{2-}$  are the major reduction products detected in the course of IR spectroelectrochemical experiments. Most likely, these cluster species are formed from the secondary CO-loss product  $[Rh_4(CO)_{11}]^{2-}$  by fast redox condensation reactions. Their reoxidation regenerates parent  $[Rh_4(CO)_{12}]$ , together with some  $[Rh_6(CO)_{16}]$ . Unlike  $[H_4Ru_4(CO)_{12}]$  that undergoes photochemical CO-dissociation,  $[H_2Ru_2Rh_2(CO)_{12}]$  and  $[Rh_4(CO)_{12}]$  are completely photostable in neat hexane and dichloromethane as well as in the presence of oct-1-ene.

**Keywords:** Ruthenium; Rhodium; Mixed-metal clusters; Redox properties; Hydrides; Carbonyl complexes; IR spectroscopy; Spectroelectrochemistry; Electrochemistry; Photochemistry.

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  $[Os_3(CO)_{12}]$  (refs<sup>1,2</sup>),  $[Os_3(CO)_{10}(1,3\text{-diene})]$  (ref.<sup>3</sup>) and  $[Os_3(CO)_{10}(\alpha\text{-diimine})]$  (ref.<sup>4</sup>). For all three clusters, primary photochemical event is the Os–Os bond cleavage. Similar CO-bridged photoproducts are formed for  $[Os_3(CO)_{12}]$  and  $[Os_3(CO)_{10}(1,3\text{-diene})]$ , although in the case of the 1,3-diene ligand<sup>3</sup>, the open-core cluster photoproduct is considerably

more stable. By contrast, biradical and zwitterionic open-core photo-products are formed in the case of  $[\text{Os}_3(\text{CO})_{10}(\alpha\text{-diimine})]$ .

An alternative approach to changing the cluster properties and reactivity 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  $\text{M} = \text{Fe}, \text{Ru}, \text{Co}$  and  $\text{Rh}$ ;  $x = 0\text{--}4$ , depending on the metal core composition<sup>5</sup>. Whereas for the iron-containing clusters only the Fe–Ru series is fairly well represented, all combinations have been reported for the other three metals (with the exception of the unstable cluster  $[\text{CoRh}_3(\text{CO})_{12}]$ ). The structure and reactivity trends in these series have been reviewed by Pakkanen *et al.*<sup>5</sup>

Figure 1 presents the molecular structures of three clusters in the series  $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$  ( $x = 0, 2, 4$ ). The number of bridging hydrides equals that of the ruthenium atoms, thereby obeying the electron counting rules<sup>6</sup>. According to their crystal structures,  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  and  $[\text{H}_3\text{Ru}_3\text{Rh}(\text{CO})_{12}]$  possess only terminal carbonyls<sup>7,8</sup>. In the remaining clusters with two or more rhodium atoms, three carbonyls bridge the edges of the triangular cluster face with the largest number of Rh atoms<sup>9–11</sup>. 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<sup>12</sup> and substitution of CO by  $\text{PPh}_3$  are fast at room temperature<sup>13</sup>.  $[\text{Rh}_4(\text{CO})_{12}]$  is rapidly converted into  $[\text{Rh}_6(\text{CO})_{16}]$  (with a lower CO/Rh ratio) already in refluxing hexane<sup>14,15</sup>. 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  $\text{PPh}_3$  at room temperature<sup>16</sup>, whereas in the case of  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  this reaction requires thermal activation<sup>17,18</sup>. However,

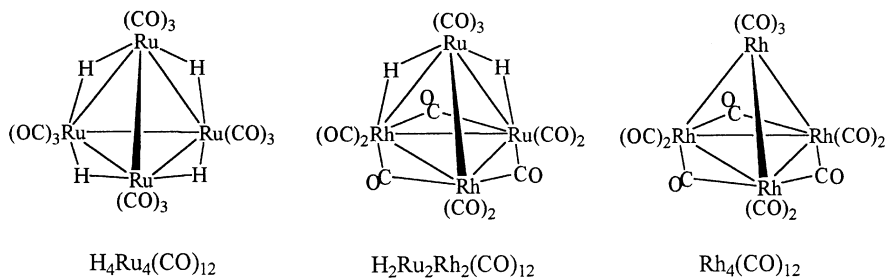


FIG. 1  
Schematic molecular structures of the clusters  $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$  ( $x = 0, 2, 4$ )

the latter cluster undergoes photochemical dissociation of CO, which in the presence of  $\text{PR}_3$  ( $\text{R} = \text{Ph}, \text{OMe}$ ) results in photosubstitution to give  $[\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{PR}_3)]$  (refs<sup>18,19</sup>). In the presence of alkenes, photocatalytic isomerisation and stoichiometric hydrogenation occur *via* the intermediate  $[\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{alkene})]$ , the latter reaction becoming photocatalytic in the presence of  $\text{H}_2$  (refs<sup>18,20</sup>). 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.*<sup>21</sup> According to this study, reduction leads to sequential loss of hydrogen and formation of the anions  $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$  and  $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$ . In the presence of  $\text{PPh}_3$ , formation of the radical anion  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]^{\bullet-}$  initiates electron-transfer-chain (ETC) substitution of CO, producing the mono- and disubstituted derivatives<sup>21</sup>. On the contrary, reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  has been proposed to induce fragmentation of the cluster<sup>22</sup>.

From the literature survey it becomes clear that the tetrahedral clusters  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  and  $[\text{Rh}_4(\text{CO})_{12}]$  differ appreciably in their thermal, photochemical and electrochemical reactivity. In this work the investigated series has been extended with  $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$  ( $x = 2, 3$ ) and  $[\text{Rh}_4(\text{CO})_{12}]$  has been reinvestigated.  $[\text{H}_3\text{Ru}_3\text{Rh}(\text{CO})_{12}]$  is not included, as it proved impossible to prepare the cluster pure in a sufficient amount<sup>8</sup>. The principal goal of this study has been to learn whether the redox and photochemical properties of the mixed-metal clusters are intermediate or rather different compared to those of the homonuclear tetraruthenium and tetrarhodium clusters. This target is in line with our general interest in activation of low-nuclearity transition metal clusters by photochemical and electrochemical means.

## RESULTS AND DISCUSSION

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

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

$[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$ 

Cyclic voltammetry has indicated that the cluster  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  is irreversibly reduced at the cathodic peak  $R_1$  in dichloromethane at room temperature and  $\nu = 100 \text{ mV s}^{-1}$  (Fig. 2a). The more negative cathodic process  $R_2$  is attributed to reduction of a secondary product generated at  $R_1$ . In order to identify the latter species, the reduction at  $E_{p,c}(R_1)$  was performed *in situ* using an IR spectroelectrochemical cell. The  $\nu(\text{CO})$  bands of the parent cluster are replaced with new bands that lie  $30\text{--}50 \text{ cm}^{-1}$  lower in frequency compared to those of the parent cluster (Table II). The close correspondence between the IR  $\nu(\text{CO})$  patterns indicates that the structure of the metal-carbonyl framework has been preserved. Indeed, comparison with literature data (Table II) has revealed that the detectable reduction product is the cluster anion  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  formed by hydrogen loss<sup>23</sup>. Upon further reduction of  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  at  $E_{p,c}(R_2)$ , the  $\nu(\text{CO})$  bands are replaced by a new set corresponding to the dianion  $[\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]^{2-}$  (ref.<sup>23</sup>). Both reduction products of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$ , the anion  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  and

TABLE I  
Redox potentials for the clusters  $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$  ( $x = 0, 2, 3, 4$ ) and some reduction products<sup>a</sup>

Cluster	Solvent	$E_{p,c}(R_1)$	$E_{p,c}(R_2)$	$E_{p,a}^b$
$[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$	$\text{CH}_2\text{Cl}_2$	-1.85		+0.77
$[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$	$\text{CH}_2\text{Cl}_2$	-1.43	-2.33 <sup>c</sup>	+0.82
$[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$ <sup>d</sup>	DME		-2.10	+0.23
$[\text{HRuRh}_3(\text{CO})_{12}]$	$\text{CH}_2\text{Cl}_2$	-1.36	-2.15 <sup>e</sup>	+0.96
$[\text{Rh}_4(\text{CO})_{12}]$	$\text{CH}_2\text{Cl}_2$	-1.26		+1.15
$[\text{Rh}_6(\text{CO})_{15}]^{2-}$				-0.92(O <sub>1</sub> ) <sup>f</sup>
$[\text{Rh}(\text{CO})_4]^-$				-0.55(O <sub>2</sub> ) <sup>f</sup>
$[\text{Rh}_5(\text{CO})_{15}]^{2-}$				-0.28(O <sub>3</sub> ) <sup>f</sup>

<sup>a</sup> Conditions:  $5 \cdot 10^{-4} \text{ M}$  cluster and  $10^{-1} \text{ M}$   $\text{Bu}_4\text{NPF}_6$ ,  $T = 298 \text{ K}$ , Pt disk electrode ( $r = 0.4 \text{ mm}$ ),  $\nu = 100 \text{ mV s}^{-1}$ ; potentials are given in V vs  $E_{1/2}(\text{Fc}/\text{Fc}^+)$ . <sup>b</sup> Oxidation potentials for the parent clusters and some reduction products; the oxidations were not studied in detail.

<sup>c</sup> Reduction potential for the anion  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$ . <sup>d</sup> Prepared by chemical reduction of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  with  $[\text{Fe}^I(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{Me}_6)]$  in DME. <sup>e</sup> Reduction potential for the anion  $[\text{RuRh}_3(\text{CO})_{12}]^-$ . <sup>f</sup> See Fig. 5.

the dianion  $[\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]^{2-}$ , were previously prepared by redox condensation reactions between  $[\text{Ru}_3(\text{CO})_{12}]$  and  $[\text{Rh}(\text{CO})_4]^-$ . Their structure has been solved by X-ray diffraction<sup>23</sup>. Similarly to the parent cluster, three carbonyls bridge the edges of the  $\text{RuRh}_2$  plane in  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  and the single hydride ligand bridges a Ru–Ru bond. The additional electron in  $[\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]^{2-}$  requires two more carbonyls to bridge the remaining Ru–Rh bonds.

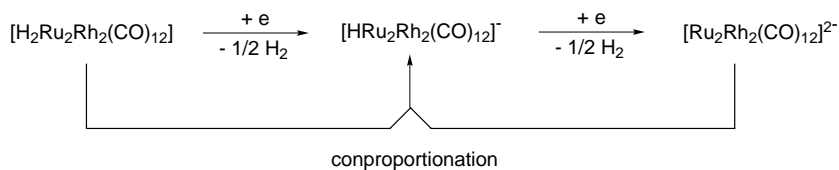
TABLE II

IR  $\nu(\text{CO})$  wavenumbers of the clusters  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$ ,  $[\text{HRuRh}_3(\text{CO})_{12}]$ ,  $[\text{Rh}_4(\text{CO})_{12}]$  and their reduction products

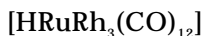
Cluster	Solvent	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$	$\text{CH}_2\text{Cl}_2$	2 108 vw, 2 084 s, 2 063 s, 2 057 sh, 2 030 m, 2 018 sh
	DME	2 111 w, 2 086 s, 2 036 s, 2 053 s, 2 033 m, 2 010 sh
$[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$	$\text{CH}_2\text{Cl}_2^a$	2 065 w, 2 030 s, 2 010 s, 1 975 m, 1 953 sh
	DME <sup>b</sup>	2 065 w,br, 2 028 s, 2 006 s, 1 979 m, 1 953 w, 1 849 w
	THF <sup>c</sup>	2 070 w, 2 064 w, 2 027 s, 2 007 s, 1 979 ms, 1 972 sh
$[\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]^{2-}$	$\text{CH}_2\text{Cl}_2^a$	1 965 s, 1 954 sh, 1 931 s, 1 885 w, 1 817 w
	DME <sup>b</sup>	2 035 w, 2 016 w, 1 999 w, 1 965 s, 1 956 sh, 1 934 s
	THF <sup>c</sup>	2 029 mw, 2 015 w, 1 963 s, 1 952 s, 1 931 ms, 1 885 mw
$[\text{HRuRh}_3(\text{CO})_{12}]$	$\text{CH}_2\text{Cl}_2$	2 108 w, 2 077 s, 2 067 vs, 2 033 m, 2 010 m, 1 930 w
$[\text{HRuRh}_3(\text{CO})_{12}]^{-a,d}$	$\text{CH}_2\text{Cl}_2$	2 075 w, 2 032 s, 2 012 s, 1 989 sh, 1 948 sh, 1 844 m
$[\text{HRuRh}_3(\text{CO})_{12}]^{-e}$	THF	2 071 m–w, 2 024 s, 2 015 ms, 2 006 s, 1 987 m–s, 1 949 w
$[\text{Rh}_4(\text{CO})_{12}]$	THF	2 108 vw, 2 073 vs, 2 040 m, 1 876 m
$[\text{Rh}_6(\text{CO})_{16}]$	THF	2 075 vs, 2 061 sh, 2 043 w, 1 809 m
$[\text{Rh}_5(\text{CO})_{15}]^{-f}$	THF	2 045 s, 2 010 vs, 1 868 m, 1 838 m, 1 785 m
$[\text{Rh}_6(\text{CO})_{15}]^{2-g}$	THF	2 050 vw, 1 990 sh, 1 984 s, 1 960 m, 1 767 m–s
$[\text{Rh}_4(\text{CO})_{11}]^{2-g}$	THF	1 930 vs, 1 810 s
$[\text{Rh}(\text{CO})_4]^{-h}$	THF	2 000 vw, 1 895 vs

<sup>a</sup> Prepared by *in situ* reduction within the IR OTTLE cell. <sup>b</sup> Prepared by chemical reduction of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  with  $[\text{Fe}^I(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{Me}_6)]$  in DME. <sup>c</sup> Taken from ref.<sup>23</sup> <sup>d</sup> Prepared by deprotonation with  $\text{Et}_4\text{NOH}$ . <sup>e</sup> Taken from ref.<sup>24</sup> <sup>f</sup> Taken from ref.<sup>26</sup> <sup>g</sup> Taken from ref.<sup>29</sup> <sup>h</sup> Taken from ref.<sup>28</sup>

Alternatively, the reduction products of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  could be prepared in quantitative yield by chemical reduction in dimethoxyethane (DME). Addition of one equivalent of the reducing agent  $[\text{Fe}^{\text{I}}(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{Me}_6)]$  to a solution of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  produced smoothly  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$ , as was confirmed by IR spectroscopy (Fig. 3 and Table II). Addition of a second equivalent of the 19e complex mainly led to precipitation. The IR spectrum proved the presence of a small amount of the dissolved dianion  $[\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]^{2-}$  (ref.<sup>23</sup>). Importantly, upon addition of one equivalent of the parent cluster  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$ , the precipitate redissolved and the anion  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  was present as the only species in the solution. Apparently, a similar comproportionation reaction takes place, as was observed between  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  and  $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$  (ref.<sup>21</sup>). Reduction pathways for the cluster  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  are shown in Scheme 1.



SCHEME 1



The cyclic voltammogram of  $[\text{HRuRh}_3(\text{CO})_{12}]$  in  $\text{CH}_2\text{Cl}_2$  is presented in Fig. 2b. At  $\nu = 100 \text{ mV s}^{-1}$  and room temperature, the cluster undergoes irreversible reduction (cathodic peak  $R_1$ ). Reduction within the IR OTTLE cell has re-

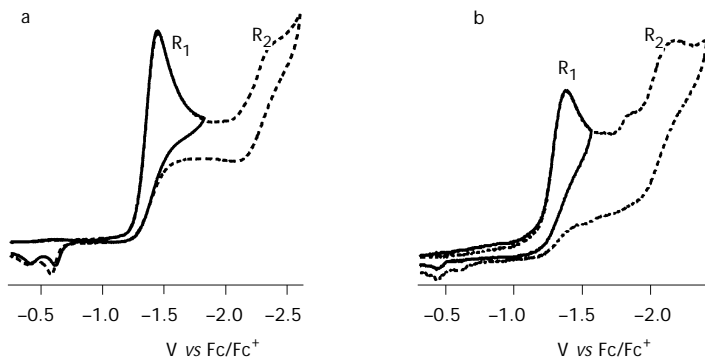


FIG. 2  
Cyclic voltammograms of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  (a) and  $[\text{HRuRh}_3(\text{CO})_{12}]$  (b) in dichloromethane ( $\nu = 100 \text{ mV s}^{-1}$ ;  $T = 293 \text{ K}$ )

vealed formation of the anion  $[\text{RuRh}_3(\text{CO})_{12}]^-$ , previously reported by Fumagalli *et al.*<sup>24</sup>, together with a small amount of unidentified side-products with  $\nu(\text{CO})$  absorptions at 2 084, 1 939 and 1 770  $\text{cm}^{-1}$ . Alternatively, the anion  $[\text{RuRh}_3(\text{CO})_{12}]^-$  could be obtained by deprotonation of  $[\text{HRuRh}_3(\text{CO})_{12}]$  in dichloromethane with one equivalent of  $\text{Et}_4\text{NOH}$  (Fig. 4),

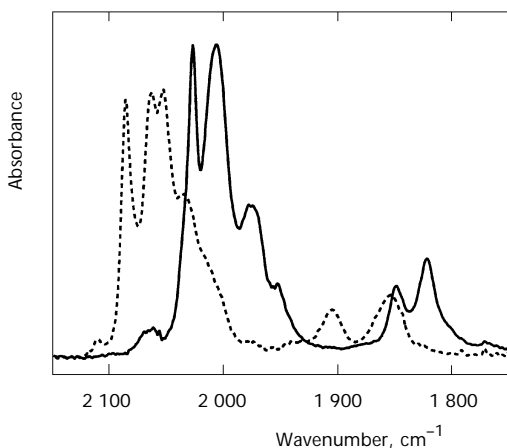


FIG. 3

IR spectra of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  (---) and its reduction product  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  (—) prepared in DME by chemical reduction with 1 molar equivalent of  $[\text{Fe}^1(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{Me}_6)]$

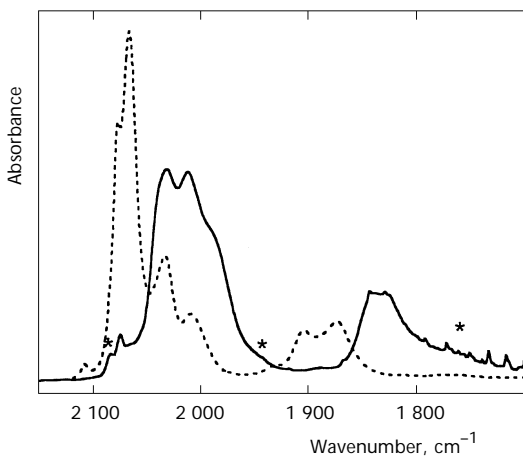
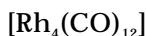


FIG. 4

IR spectra of  $[\text{HRuRh}_3(\text{CO})_{12}]$  (---) and its product  $[\text{RuRh}_3(\text{CO})_{12}]^-$  (—) prepared by deprotonation with  $\text{Et}_4\text{NOH}$  in dichloromethane (asterisks denote the  $\nu(\text{CO})$  bands due to some minor side products)

which proved to be a suitable deprotonation agent for the related clusters  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  and  $[\text{H}_4\text{Ru}_4(\text{CO})_{10}(2,2'\text{-bipyridine})]$  (ref.<sup>25</sup>). According to its reported crystal structure, the anion  $[\text{RuRh}_3(\text{CO})_{12}]^-$  contains five bridging carbonyls, leaving only one Ru–Rh edge unbridged<sup>24</sup>.



The cyclic voltammogram in Fig. 5 confirms that reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  at  $E_{p,c}(\text{R}_1)$  is irreversible at room temperature in dichloromethane at  $\nu = 100 \text{ mV s}^{-1}$ . Upon scan reversal beyond  $\text{R}_1$ , small anodic peaks are observed at  $E_{p,a}(\text{O}_1) = -0.92 \text{ V}$ ,  $E_{p,a}(\text{O}_2) = -0.55 \text{ V}$  and  $E_{p,a}(\text{O}_3) = -0.28 \text{ V vs Fc/Fc}^+$ , which will be assigned below. The reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  remains fully irreversible also at low temperatures ( $T = 203 \text{ K}$ ;  $\nu = 100 \text{ mV s}^{-1}$ ).

The reduction path of  $[\text{Rh}_4(\text{CO})_{12}]$  was further studied by IR spectroelectrochemistry. Independently of the solvent used, dichloromethane or THF, the same mixture of reduction products was formed at room temperature (Fig. 6a). The IR  $\nu(\text{CO})$  wavenumbers presented below and in Table II, concern THF solutions, as the relevant literature data have only been available for this solvent. The main product has been identified as the pentanuclear anion  $[\text{Rh}_5(\text{CO})_{15}]^-$  ( $\nu(\text{CO})$  bands at 2 045, 2 009, 1 869, 1 840 and 1 785  $\text{cm}^{-1}$ )<sup>26</sup>. Also some  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  was formed, as evidenced by the  $\nu(\text{CO})$  bands at 1 985 sh, 1 960 and 1 772  $\text{cm}^{-1}$  (ref.<sup>27</sup>). Weak bands at 2 078, 2 062 and 1 750  $\text{cm}^{-1}$  due to minor side-products could not be assigned. No detectable amounts of the fragmentation product  $[\text{Rh}(\text{CO})_4]^-$  and/or the CO-loss product  $[\text{Rh}_4(\text{CO})_{11}]^{2-}$  were observed<sup>26,28</sup>. The same result was ob-

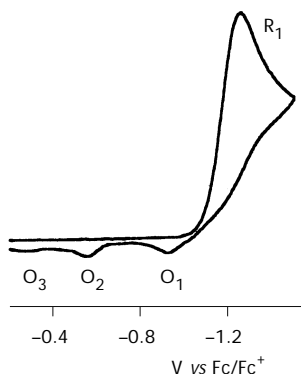


FIG. 5

Cyclic voltammogram of the cluster  $[\text{Rh}_4(\text{CO})_{12}]$  in dichloromethane ( $\nu = 100 \text{ mV s}^{-1}$ ;  $T = 293 \text{ K}$ )



tained when the IR spectroelectrochemical experiment was repeated in butyronitrile at 203 K.

Electrochemical reoxidation of the mixture of reduction products in  $\text{CH}_2\text{Cl}_2$  occurred in two steps localised in the corresponding thin-layer cyclic voltammogram at *ca*  $-0.8$  and  $0$  V vs  $\text{Fc}/\text{Fc}^+$ . These two reoxidation steps can be attributed to the anodic processes  $\text{O}_1$  and  $\text{O}_3$  in the conventional cyclic voltammogram shown in Fig. 5. In the first anodic step,  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  was oxidised to give the neutral cluster  $[\text{Rh}_6(\text{CO})_{16}]$  (ref.<sup>15</sup>). The main reduction product  $[\text{Rh}_5(\text{CO})_{15}]^-$  was oxidised in the second an-

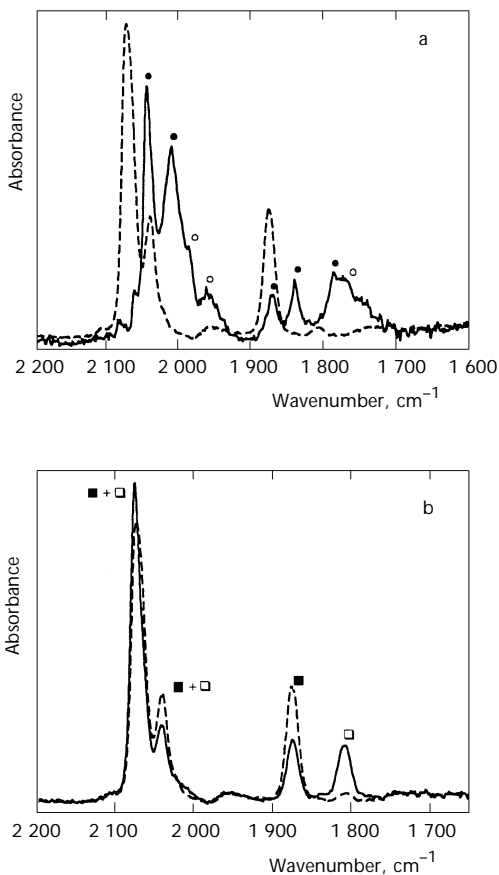
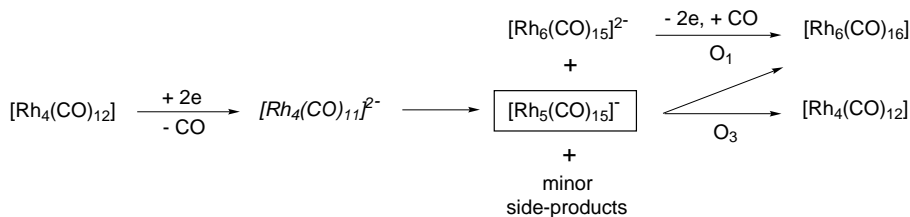


FIG. 6

IR spectra of the anionic clusters ( $\bullet$   $[\text{Rh}_5(\text{CO})_{15}]^-$ ,  $\circ$   $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ ) formed upon reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  (a) and products of their re-oxidation ( $\blacksquare$   $[\text{Rh}_4(\text{CO})_{12}]$ ,  $\square$   $[\text{Rh}_6(\text{CO})_{16}]$ ) (b). The starting IR spectrum of  $[\text{Rh}_4(\text{CO})_{12}]$  (---) is also depicted for comparison

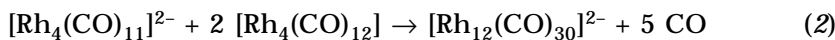
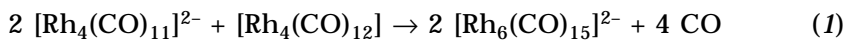
odic step, producing the starting material  $[\text{Rh}_4(\text{CO})_{12}]$  (ca 50% recovery) and additional  $[\text{Rh}_6(\text{CO})_{16}]$ . The resulting IR spectrum of the mixture of the starting material  $[\text{Rh}_4(\text{CO})_{12}]$  and  $[\text{Rh}_6(\text{CO})_{16}]$  after both anodic steps passed is depicted in Fig. 6b.

Scheme 2 summarises the reduction and reoxidation pathways of  $[\text{Rh}_4(\text{CO})_{12}]$  and its reduction products, respectively. Clearly, reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  leads to the formation of anionic clusters of higher nuclearity. This result is not unexpected, as it is known from the work of Chini *et al.*



SCHEME 2

that rhodium cluster anions such as  $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ , the likely reduction intermediate in this case, are highly reactive and easily undergo redox condensation reactions with neutral rhodium clusters. As examples may serve the formation of  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  and  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  according to Eqs (1) and (2) (ref.<sup>29</sup>). In the presence of liberated CO, the anion  $[\text{Rh}_5(\text{CO})_{15}]^-$  can be formed from  $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ ,  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  or  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  (refs<sup>26,29</sup>). It can also be formed according to Eq. (3), provided mononuclear  $[\text{Rh}(\text{CO})_4]^-$  also occurs in the reduction path<sup>26</sup>.



On the basis of Eqs (1) and (2) we propose tentatively that the dianion  $[\text{Rh}_4(\text{CO})_{11}]^{2-}$  is initially produced by a CO-loss reaction from reduced  $[\text{Rh}_4(\text{CO})_{12}]$ . This compound 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  $[\text{Rh}_4(\text{CO})_9(\text{tripod})]$ , which became nearly reversible under 1 atm of CO (ref.<sup>22</sup>). The reduction pathway of  $[\text{Rh}_4(\text{CO})_{12}]$  given in Scheme 2 is different from that proposed by Rimmelin *et al.*<sup>22</sup>. In their interpretation, the primary one-electron reduction step produces detectable radical anion  $[\text{Rh}_4(\text{CO})_{12}]^{\bullet-}$ , which undergoes concomitant fragmentation to  $[\text{Rh}(\text{CO})_4]^-$  as one of the products. Support for the formation of the radical anion  $[\text{Rh}_4(\text{CO})_{12}]^{\bullet-}$  was given by the recorded EPR spectrum of a paramagnetic species 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 experimental data, the reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  remains completely irreversible at 203 K on the millisecond time scale of cyclic voltammetry. The paramagnetic species can therefore hardly be assigned to the intact tetrahedral radical anion  $[\text{Rh}_4(\text{CO})_{12}]^{\bullet-}$ . The suggestion by Rimmelin *et al.* that reduction of  $[\text{Rh}_4(\text{CO})_{12}]$  leads to fragmentation, was based on the independent assignment of the secondary anodic peak  $\text{O}_2$  in the cyclic voltammogram of  $[\text{Rh}_4(\text{CO})_{12}]$  (see Fig. 5) to the oxidation of the mononuclear anion  $[\text{Rh}(\text{CO})_4]^-$ . However,  $[\text{Rh}(\text{CO})_4]^-$  can also be formed as a reactive side-product of a redox-condensation reaction<sup>29</sup>. It was not observed using IR spectroscopy and thin-layer cyclic voltammetry (*vide supra*), probably due to its fast consumption according to Eq. (3).

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

The photochemistry of  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  has been studied in detail by Wrighton *et al.*<sup>18,19</sup>. This cluster undergoes CO photodissociation, providing pathways to phosphine-substituted products and to (photocatalytic) isomerisation and hydrogenation of alkenes. In the next section, the attempted photoactivation of  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  and  $[\text{Rh}_4(\text{CO})_{12}]$  is presented.

#### $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$

The cluster  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  strongly absorbs at 350 nm, *i.e.* at higher energy than  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  ( $\lambda_{\text{max}} = 364$  nm). At room temperature,  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  is thermally stable in neat hexane and dichloromethane as well as in the presence of  $10^{-1}$  M oct-1-ene. Thermal reactions occur with  $\text{PPh}_3$  and with alkynes (oct-4-yne, diphenylacetylene), thereby excluding their utility 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 ( $\lambda > 250$  nm) in hexane, dichloromethane and also in hexane with  $10^{-1}$  M oct-1-ene. In order to find out if any short-lived photoproduct 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 photo-reaction takes place, or that the photoproduct reverts to the parent cluster on a sub-nanosecond time scale. In this regard it must be noted that under the same experimental conditions, no CO-loss photoproduct 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. Even though in the reduced cluster metal-metal and metal-hydride bonds are expected to be weaker, this anion proved photostable under broad-band irradiation both in neat THF and in THF containing  $10^{-1}$  M oct-1-ene.

### $[\text{Rh}_4(\text{CO})_{12}]$

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 band tailing into the visible region. The cluster undergoes rapid thermal reaction with  $\text{PPh}_3$  already at room temperature<sup>13</sup>. By contrast, it is thermally stable in neat hexane and in hexane with  $10^{-1}$  M oct-1-ene at room temperature. We have found that the cluster is also photostable upon broad-band irradiation ( $\lambda_{\text{irr}} > 250$  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 $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$ ( $x = 0, 2, 3, 4$ )*

The clusters  $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$  ( $x = 0, 2, 3, 4$ ) have in common that their reduction is totally chemically irreversible at room temperature already on the millisecond time scale of cyclic voltammetry. The reduction potentials of the mixed-metal clusters  $[\text{H}_{4-x}\text{Ru}_{4-x}\text{Rh}_x(\text{CO})_{12}]$  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 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 heterometallic ruthenium–rhodium clusters and that of  $[\text{Rh}_4(\text{CO})_{12}]$  on the other hand. 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  $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$  (ref.<sup>21</sup>). Even 4e-reduced  $[\text{Ru}_4(\text{CO})_{12}]^{4-}$  can be prepared, although not *via* a direct electrochemical way<sup>30</sup>. The mixed-metal clusters  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  and  $[\text{HRuRh}_3(\text{CO})_{12}]$  also undergo (stepwise) loss of hydrogen upon reduction. Apparently, if the tetrahedral clusters bind one or more hydride ligands, they are lost upon reduction of the cluster, thereby preserving the electron-precise  $\text{M}_4(\text{CO})_{12}$  core. The anions thus formed are also quite stable. It remains to confirm whether the hydrogen-loss reaction is a general property of hydride-containing clusters of the whole tetrahedral  $[\text{H}_x\text{M}_4(\text{CO})_{12}]$  family, with  $\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{Co}, \text{Rh}$  and  $\text{Ir}$  and  $x = 1-4$ . In contrast to this,  $[\text{Rh}_4(\text{CO})_{12}]$ , which does not contain any hydride ligands, responds to the reduction by release of CO, yielding yet unobserved but highly probable  $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ . The cluster core of this dianion is highly labile and higher-nuclearity clusters, in particular  $[\text{Rh}_5(\text{CO})_{15}]^-$  and  $[\text{Rh}_6(\text{CO})_{15}]^-$ , are rapidly 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 occur for instance between the CO-loss dianions  $[\text{M}_3(\text{CO})_{11}]^{2-}$  and the neutral parent cluster  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M} = \text{Ru}, \text{Os}$ )<sup>31-33</sup>.

Interestingly, the thermal and redox reactivity sharply contrasts with the photochemistry. In the studied cluster series, only  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  is photo-reactive, undergoing CO dissociation as the primary photochemical event, whereas the clusters  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  and  $[\text{Rh}_4(\text{CO})_{12}]$  are photostable. Apparently, no specific bonds are sufficiently weakened and cleaved upon their optical excitation.

Concluding, the mixed-metal clusters  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  and  $[\text{HRuRh}_3(\text{CO})_{12}]$  do not possess any novel electrochemical or photochemical properties or reactivity compared to the homonuclear clusters  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  and  $[\text{Rh}_4(\text{CO})_{12}]$ . This study has proved that the reduction pathway is basically not determined by the metal–metal bonds in the tetrahedral cluster core, but by the presence or absence of hydride ligands. In the ruthenium-containing clusters  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ ,  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  and  $[\text{HRuRh}_3(\text{CO})_{12}]$ , the hydride ligands are lost upon reduction in order to preserve the stable electron-precise  $\text{M}_4(\text{CO})_{12}$  core. Importantly, the reduction of the hydride-lacking tetrarhodium cluster  $[\text{Rh}_4(\text{CO})_{12}]$  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 cluster anions. The mixed-metal cluster  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  and its anion  $[\text{HRu}_2\text{Rh}_2(\text{CO})_{12}]^-$  are photostable like  $[\text{Rh}_4(\text{CO})_{12}]$ .

## EXPERIMENTAL

### Materials and Preparations

The clusters  $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$  (refs<sup>14,15</sup>),  $[\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}]$  (ref.<sup>9</sup>),  $[\text{HRuRh}_3(\text{CO})_{12}]$  (ref.<sup>10</sup>) and  $[\text{Rh}_6(\text{CO})_{16}]$  (refs<sup>14,15</sup>) were prepared according to published procedures.  $[\text{Rh}_4(\text{CO})_{12}]$  (Alfa) was used as purchased. The supporting electrolyte  $\text{Bu}_4\text{NPF}_6$  (Aldrich) was recrystallised twice from ethanol and dried *in vacuo* at 80 °C overnight. The base  $\text{Et}_4\text{NOH}$  was purchased from Fluka as a 25% solution in MeOH. Ferrocene was used as received from BDH. Solvents of analytical grade quality (hexane, dichloromethane, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME)), all purchased from ACROS, were dried over sodium wire (hexane, THF, DME) or  $\text{CaH}_2$  (dichloromethane) and freshly distilled under nitrogen prior to use. The 19e reducing agent  $[\text{Fe}^I(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{Me}_6)]$  was prepared by reduction of precursor  $[\text{Fe}^{II}(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{Me}_6)]\text{PF}_6$  with 1% Na/Hg in DME according to the procedure described in ref.<sup>34</sup>

### Spectroscopic Measurements

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

### Spectroelectrochemical Measurements

Cyclic voltammetry was performed in a gas-tight cell under dry argon. The cell was equipped with a Pt disc working (apparent surface area of 0.42  $\text{mm}^2$ ), Pt wire auxiliary and Ag wire pseudoreference electrodes. The working electrode was carefully polished with a 0.25  $\mu\text{m}$  grain diamond paste. All redox potentials are reported against the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple used as an internal standard<sup>35</sup>. The solutions for cyclic voltammetric experiments were typically 5 · 10<sup>-4</sup> M in the cluster compounds and 10<sup>-1</sup> M in  $\text{Bu}_4\text{NPF}_6$ . 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 optically transparent thin-layer electrochemical (OTTLE) cells, equipped with a Pt minigrad working electrode (32 wires per cm) and  $\text{CaF}_2$  optical windows<sup>36,37</sup>. The spectroelectrochemical samples were typically 5 · 10<sup>-3</sup> 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 nitrogen using standard Schlenk techniques. The cluster concentration was typically 10<sup>-3</sup>–10<sup>-4</sup> mol dm<sup>-3</sup>. A Philips HPK 125 W

high-pressure mercury lamp, equipped with the appropriate cut-off filters, served as a light source for continuous-wave irradiation. The experimental set-up for the nanosecond time-resolved UV-VIS absorption measurements has been described in detail elsewhere<sup>4a</sup>.

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## REFERENCES AND NOTES

1. Ford P. C.: *J. Organomet. Chem.* **1990**, *383*, 339.
2. Leadbeater N. E.: *J. Chem. Soc., Dalton Trans.* **1995**, 2923.
3. Bakker M. J., Vergeer F. W., Hartl F., Jina O. S., Sun X. Z., George M. W.: *Inorg. Chim. Acta* **2000**, *300–302*, 597.
4. a) Bakker M. J., Hartl F., Stufkens D. J., Jina O. S., Sun X. Z., George M. W.: *Organometallics* **2000**, *19*, 4310; b) Nijhoff J., Bakker M. J., Hartl F., Stufkens D. J., Fu W.-F., van Eldik R.: *Inorg. Chem.* **1998**, *37*, 661.
5. Pakkanen T. A., Pursiainen J., Venalainen T., Pakkanen T. T.: *J. Organomet. Chem.* **1989**, *372*, 129.
6. Farrar D. H., Goudsmit R. J. in: *Metal Clusters* (M. Moskovits, Ed.), p. 29. Wiley, New York 1986.
7. Wilson R. D., Wu S. M., Love R. A., Bau R.: *Inorg. Chem.* **1978**, *17*, 1271.
8. Pursiainen J., Pakkanen T. A.: *J. Chem. Soc., Dalton Trans.* **1989**, 2449.
9. Pursiainen J., Pakkanen T. A., Heaton B. T., Seregini C., Goodfellow R. G.: *J. Chem. Soc., Dalton Trans.* **1986**, 681.
10. Pursiainen J., Pakkanen T. A., Jaaskelainen J.: *J. Organomet. Chem.* **1985**, *290*, 85.
11. Wei C. H.: *Inorg. Chem.* **1969**, *8*, 2394.
12. Heaton B., Longhetti L., Mingos D. M. P., Briant C. E., Minshall P. C., Theobald B. R. C., Garlaschetti L., Sartorelli U.: *J. Organomet. Chem.* **1981**, *213*, 333.
13. Kennedy J. R., Basolo F., Trogler W. C.: *Inorg. Chim. Acta* **1988**, *146*, 75.
14. Knox S. A. R., Koepke J. W., Andrews M. A., Kaesz H. D.: *J. Am. Chem. Soc.* **1975**, *97*, 3942.
15. Martinengo S., Giordano G., Chini P.: *Inorg. Synth.* **1990**, *28*, 242.
16. Pursiainen J., Pakkanen T. A.: *Acta Chem. Scand.* **1989**, *43*, 463.
17. Piacenti F., Bianchi M., Frediani P., Benedetti E.: *Inorg. Chem.* **1971**, *10*, 2759.
18. Graff J. L., Wrighton M. S.: *Inorg. Chim. Acta* **1982**, *63*, 63.
19. Bentsen J. G., Wrighton M. S.: *J. Am. Chem. Soc.* **1984**, *106*, 4041.
20. Doi N., Tamaru S., Koshizuka K.: *J. Mol. Cat.* **1983**, *19*, 213.
21. Osella D., Nervi C., Ravera M., Fiedler J., Strelets V. V.: *Organometallics* **1995**, *14*, 2501.
22. Rimmelin J., Lemoine P., Gross M., Bahsoun A. A., Osborn J. A.: *Nouv. J. Chim.* **1984**, *9*, 181.
23. Fumagalli A., Italia D., Malatesta M. C., Ciani G., Moret M., Sironi A.: *Inorg. Chem.* **1996**, *35*, 1765.
24. Fumagalli A., Bianchi M., Malatesta M. C., Ciani G., Moret M., Sironi A.: *Inorg. Chem.* **1998**, *37*, 1324.

25. Nijhoff J., Bakker M. J., Hartl F., Freeman G., Ingham S. L., Johnson B. F. G.: *J. Chem. Soc., Dalton Trans.* **1998**, 2625.
26. Fumagalli A., Koetzle T. F., Takusagawa F., Chini P., Martinengo S., Heaton B. T.: *J. Am. Chem. Soc.* **1980**, 102, 1740.
27. The cluster  $[\text{Rh}_6(\text{CO})_{16}]$  undergoes irreversible reduction at  $E_{\text{p,c}} = -1.18 \text{ V vs Fc/Fc}^+$ . Conditions: cyclic voltammetry in dichloromethane at room temperature and  $\nu = 100 \text{ mV s}^{-1}$ . IR spectroelectrochemistry showed that this reduction step produces the dianion  $[\text{Rh}_6(\text{CO})_{15}]^{2-}$  ( $\nu(\text{CO})$  at 2 000 sh, 1 990 s, 1 964 m, 1 789 sh, 1 750  $\text{cm}^{-1}$ ), and some minor side-product(s) ( $\nu(\text{CO})$  at 2 045, 2 031  $\text{cm}^{-1}$ ). On reoxidation, the parent cluster was recovered for about 75%.
28. Garlaschelli L., Della Pergola R., Martinengo S.: *Inorg. Synth.* **1990**, 28, 211.
29. Martinengo S., Fumagalli A., Chini P., Albano V. G., Ciani G.: *J. Organomet. Chem.* **1976**, 116, 333.
30. Inkrott K. E., Shore S. G.: *Inorg. Chem.* **1979**, 18, 2817.
31. Bhattacharyya A. A., Nagel C. C., Shore S. G.: *Organometallics* **1983**, 2, 1187.
32. Downard A. J., Robinson B. H., Simpson J., Bond A. M.: *J. Organomet. Chem.* **1987**, 320, 363.
33. Krause J. A., Siriwardane U., Salupo T. A., Wermer J. R., Knoeppel D. W., Shore S. G.: *J. Organomet. Chem.* **1993**, 454, 263.
34. Astruc D., Hamon M., Lacoste M., Desbois M.-H., Roman E. in: *Organometallic Synthesis* (R. B. King, Ed.), Vol. IV, p. 172. Elsevier, Amsterdam 1988.
35. Gritzner G., Kůta J.: *Pure Appl. Chem.* **1984**, 56, 461.
36. Krejčík M., Daněk M., Hartl F.: *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, 317, 179.
37. Hartl F., Luyten H., Nieuwenhuis H. A., Schoemaker G. C.: *Appl. Spectrosc.* **1994**, 48, 1522.



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