



# Aqueous-organic biphasic redox-chemistry of high-hydride content rhodium clusters: Towards immobilisation of redox-switchable H<sub>2</sub> binding materials on a surface

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## ABSTRACT

Water-insoluble phosphine-surface-stabilised rhodium clusters [Rh<sub>6</sub>(PR<sub>3</sub>)<sub>6</sub>H<sub>12</sub>][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub> (R = cyclohexyl, Ar<sup>F</sup> = (3,5-CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) can be immobilised onto suitable glassy carbon, graphite, or tin-doped indium oxide (ITO) electrode surfaces. When immersed into alcohol/aqueous electrolyte media, they display stable voltammetric responses consistent with the formation of organic microdroplet | aqueous electrolyte two-phase conditions which are similar to those observed in corresponding anhydrous (CH<sub>2</sub>Cl<sub>2</sub>) solution phase. This results in an electrode surface that is straightforwardly modified with cluster materials that can uptake or release dihydrogen depending on their redox-state. The results presented herein lead to a slight re-evaluation of the originally reported hydrogen store and release cycle for this system.

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## 1. Introduction

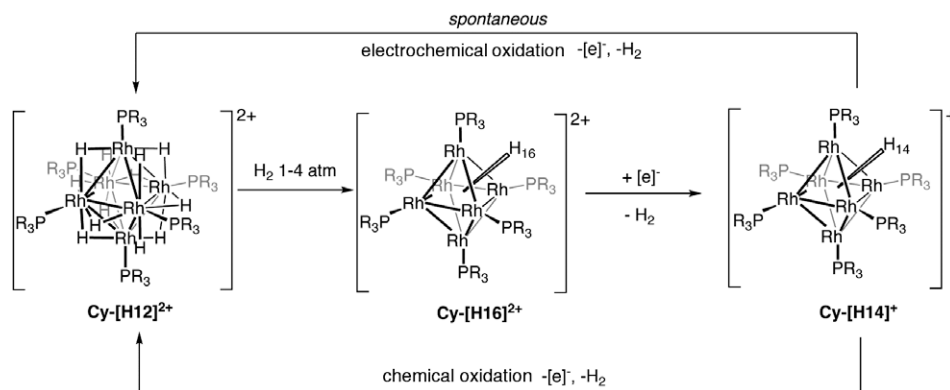
We have recently reported on the cluster materials [Rh<sub>6</sub>(PR<sub>3</sub>)<sub>6</sub>-H<sub>12</sub>][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub> [R = Cy, <sup>i</sup>Pr; Ar<sup>F</sup> = (3,5-CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], **R-[H12][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>** (Scheme 1) [1,2]. These octahedral rhodium clusters are shrouded in alkyl phosphine ligands and support 12 hydrido ligands that span every Rh–Rh edge. Molecular-orbital calculations show that these molecules are unsaturated in the sense that there is a low-lying, effectively double-degenerate, LUMO-set of orbitals available for the uptake of up to four electrons (Scheme 2). Cyclic voltammetry and chemical redox experiments (performed under strict exclusion of water and oxygen) underscore this and show the reversible, sequential, uptake to two electrons to ultimately give neutral **R-[H12]<sup>0</sup>** [3,4]. Alternatively, four electrons from the bonding pairs in two H<sub>2</sub> molecules can satisfy the empty orbitals' requirements, leading to **R-[H16][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>**, for which calculations and experimental evidence point towards H<sub>2</sub>-like ligands on the metal cluster-surface [3–5]. The addition of H<sub>2</sub> is reversible by subjecting **R-[H16][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>** to a vacuum, and others have also reported on reversible multiple dihydrogen addition to unsaturated clusters [6]. We have recently demonstrated that these facets of redox behaviour and reversible binding of H<sub>2</sub> can be combined in the

solution phase (CH<sub>2</sub>Cl<sub>2</sub>) to give redox-switched hydrogen release for a well-defined cluster material for the triscyclohexylphosphine congener [3,7]. The events that occur are initial chemical reduction of **Cy-[H16][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>** to produce a putative unstable intermediate **Cy-[H16][BAR<sub>4</sub><sup>F</sup>]** that loses H<sub>2</sub> to afford **Cy-[H14][BAR<sub>4</sub><sup>F</sup>]** (Scheme 1). Re-oxidation in solution by addition of [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] ultimately results in **Cy-[H12][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>** which is available for H<sub>2</sub> uptake again. These events can also be promoted electrochemically, and in this case we suggested that two molecules of H<sub>2</sub> are lost quickly on initial reduction (*t*<sub>1/2</sub> ~ 170 ms), to form **Cy-[H12][BAR<sub>4</sub><sup>F</sup>]**, a slightly different order to that observed on chemical reduction. Although these materials show impracticably low hydrogen uptake/release capacity (*ca.* 0.1 w/w%), their ability to work under ambient conditions of room temperature and pressure while also showing fast release kinetics by application of an external electronic stimulus makes them, we believe, unique. Of more general interest is that the change in population of the frontier cluster orbitals results in different properties, **Cy-[H16]<sup>2+</sup>** and **Cy-[H14]<sup>+</sup>** will not uptake H<sub>2</sub> while **Cy-[H12]<sup>+</sup>** and **Cy-[H12]<sup>2+</sup>** do (Scheme 2) [3], which is potentially useful behaviour with regard to the study and exploitation of redox-switchable properties in functional molecules.

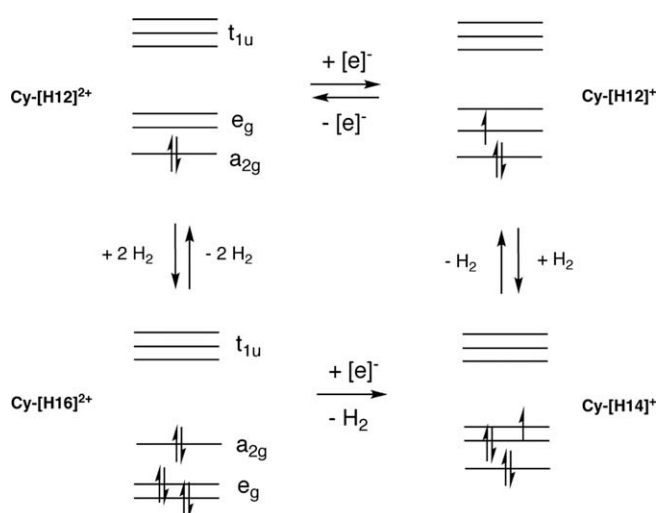
In this paper, we explore the deposition of these cluster materials onto electrode surfaces in an attempt to take the well-defined solution-phase redox behaviour and H<sub>2</sub> gain/loss characteristics into an aqueous surface regime. Although the total amount of

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**Scheme 1.** Previously reported redox-switched hydrogen store/release in the clusters  $[Rh_6(PR_3)_6H_{12}][BAR_4^F]_2$  ( $R = Cy$ ),  $[BAR_4^F]^-$  anions not shown.



**Scheme 2.** Relationship between frontier molecular orbital population and  $H_2$ -uptake ability for  $[Rh_6(PCy_3)_6H_{12}][BAR_4^F]_2$ , **Cy-[H12]** $[BAR_4^F]_2$ , (idealised  $O_h$  symmetry) [4].

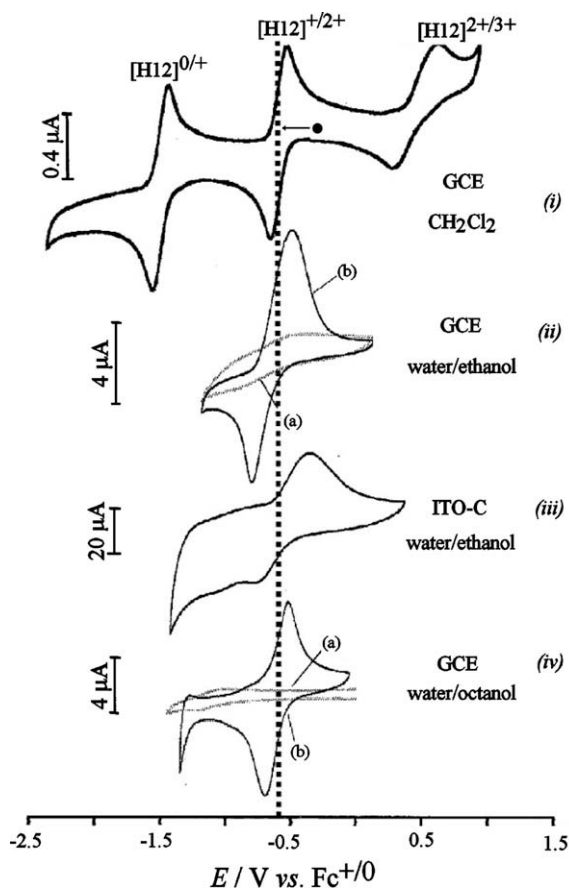
hydrogen stored and released is always going to be small (*vide supra*) the opportunity to move from solution-phase chemistry to that of materials immobilised on electrode surfaces is clearly of significant interest towards the development of possible future strategies for the storage of hydrogen. Immobilisation of cluster materials on electrode surfaces by establishing covalent chemical bonds between the surface and redox-active molecule have been reported previously, e.g. polyoxometallates [8], metal halide clusters,  $\{M_6X_{12}\}^{n+}$  ( $X = Cl, Br, I$ ) [9] and tri-ruthenium [10] or tri-nickel complexes [11]. In some cases ligand-loss (e.g. CO) from these immobilised clusters can also be effected by oxidation, demonstrating redox-promoted changes in the surface-bound structure [12]. Alternatively, redox-active microparticles of organometallic and coordination complexes can be mechanically attached to carbon electrodes and studied in aqueous solvent/electrolyte systems in which the complex under investigation is not soluble in all accessible oxidation states [13,14]. More recently, the method of microdroplet immobilisation has been developed [15]. This method allows highly water-insoluble materials to be dissolved in non-polar water-immiscible solvents and then immobilised at an electrode in the form of microdroplets. In contact with the aqueous electrolyte phase the resulting liquid | liquid biphasic system exhibits interesting and versatile reactivity consistent with simultaneous electron and ion transfer [16]. These attractive alternative methodologies to chemical modification avoid the need to covalently

attach molecules to the electrode surface – which can often involve multi-step modification of both the redox-active materials and the surface. As far as we are aware these methods have not been used to study the redox-behaviour of cluster species on a surface.

In this contribution, we report that the  $Rh_6$  cluster **Cy-[H12]** $[BAR_4^F]_2$  can be coated onto suitable electrodes under aqueous and aqueous/alcohol electrolyte media and reveal redox-behaviour consistent with microdroplet immobilisation at the electrode surface. Moreover, the redox processes under these biphasic conditions are very similar to those previously observed for strictly anhydrous  $CH_2Cl_2$  solution-phase. The nature of these processes is further investigated with voltammetry, microscopy, and electro-spray mass ionisation spectroscopy (ESI-MS). It is also shown that the hydrogen adsorption and release chemistry for the cluster family **Cy-[Hn] $^{m+}$**  is robust under biphasic conditions and not affected by the presence of water – potentially opening the way for the development of these and related cluster materials as surface immobilised redox-switchable functional or catalytic materials.

## 2. Results and discussion

A typical solution cyclic voltammogram for **Cy-[H12]** $[BAR_4^F]_2$  dissolved in anhydrous  $CH_2Cl_2$  is shown in Fig. 1(i) for a potential region which encompasses the **Cy-[H12] $^{2+/+}$**  reversible couple [ $E_{mid} = -0.59$  V vs.  $Fc^{0/+}$  with  $E_{mid} = 1/2(E_p^{ox} + E_p^{red})$ ] the reversible **Cy-[H12] $^{+/0}$**  couple [ $E_{mid} = -1.55$  V vs.  $Fc^{0/+}$ ], and the quasi-reversible **Cy-[H12] $^{3+/2+}$**  oxidation [ $E_{mid} = +0.52$  V vs.  $Fc^{0/+}$ ] [3]. To investigate cluster immobilisation at the electrode surface we initially attempted to deposit solid **Cy-[H12]** $[BAR_4^F]_2$  by simple mechanical transfer of crystalline material, as developed by Bond et al. [13]. This resulted only in a very weak electrochemical response using a variety of electrolyte combinations. In contrast, deposition onto glassy carbon or graphite by evaporation of a  $CH_2Cl_2$  solution did produce an electrochemical response. The aqueous phase for voltammetric measurements was chosen as 0.01 M  $Na[BAR_4^F]$  in 3:2 EtOH:H<sub>2</sub>O, the ethanol being required to dissolve  $Na[BAR_4^F]$  and also promote microdroplet formation (*vide infra*). Fig. 1(ii) shows that under these conditions a reduction–oxidation process occurred in a potential range consistent with the expected **Cy-[H12] $^{2+/+}$**  process, although the response was only weak. Surprisingly, there was a dramatic improvement when 15 equiv. of  $[NBu_4][BAR_4^F]$  were co-deposited with **Cy-[H12]** $[BAR_4^F]_2$ . Fig. 1(ii)b shows that a well-defined and reversible reduction response is obtained, now more consistent with the process observed in anhydrous  $CH_2Cl_2$ . This voltammetric process remained stable over more than 20 potential cycles. When the potential was scanned over a wider range evidence for the **Cy-[H12] $^{+/0}$**  process and for the **Cy-[H12] $^{3+/2+}$**  process



**Fig. 1.** Cyclic voltammograms (scan rate  $100 \text{ mV s}^{-1}$ ) for the reduction and oxidation of (i)  $\text{Cy-[H12][BAR}_4\text{]}_2$  in solution at a 3 mm diameter glassy carbon disc electrode in anhydrous  $\text{CH}_2\text{Cl}_2$  solution (ca.  $0.1 \text{ mM Cy-[H12][BAR}_4\text{]}_2$ ,  $0.01 \text{ M [NBu}_4\text{][BAR}_4\text{]}_2$ ), (ii)  $\text{Cy-[H12][BAR}_4\text{]}_2$  deposited onto a 3 mm diameter glassy carbon electrode and immersed in 3:2 EtOH:H<sub>2</sub>O ( $0.01 \text{ M Na[BAR}_4\text{]}_2$ ) (a) without and (b) with co-deposition of  $[\text{NBu}_4][\text{BAR}_4\text{]}_2$ , (iii)  $\text{Cy-[H12][BAR}_4\text{]}_2$  deposited onto a  $10 \text{ mm} \times 10 \text{ mm}$  ITO electrode modified with a monolayer of carbon nanoparticles and immersed in 3:2 H<sub>2</sub>O:EtOH ( $0.01 \text{ M Na[BAR}_4\text{]}_2$ ) with co-deposition of  $[\text{NBu}_4][\text{BAR}_4\text{]}_2$ , and (iv)  $\text{Cy-[H12][BAR}_4\text{]}_2$  co-deposited with  $[\text{NBu}_4][\text{BAR}_4\text{]}_2$  onto a 3 mm diameter glassy carbon electrode immersed in aqueous  $0.01 \text{ M K[PF}_6\text{]}$  (a) without and (b) with  $50 \mu\text{L}$  1-octanol added into the electrolyte solution. Mark and arrow indicates starting potential and direction of scan.

were also obtained (not shown). Therefore, the redox system  $\text{Cy-[H12]}^{n+}$  appears to be chemically highly robust in the presence of an aqueous environment. The ratio of 3:2 EtOH/H<sub>2</sub>O as the supporting electrolyte solvent was found to be optimal. Higher proportions of EtOH resulted in solubilisation of the electroactive material at the electrode (*i.e.* the first scan showed a strong response, subsequent scans showed essentially no response), while less afforded no electrochemical response. Presumably the ethanol-rich organic droplets required for redox-behaviour are not formed at lower ethanol concentrations, while the ethanol also allows for solubilisation (and thus movement) of the  $\text{Na[BAR}_4\text{]}_2$  between the aqueous electrolyte and microdroplet. Optimisation experiments to determine the maximum coverage obtainable on the surface by measuring the current on reduction by sequential deposition of small portions ( $2 \mu\text{L}$ ) of a  $2.5 \times 10^{-4} \text{ M}$  solution of  $\text{Cy-[H12][BAR}_4\text{]}_2$  revealed that the current drawn plateaued after  $10 \mu\text{L}$  of this solution had been added, which gave a maximum charge of  $9.3 \times 10^{-6} \text{ C}$ . This represents an efficiency of observed electrochemical reduction of only 3.9%.

The cluster  $\text{Cy-[H12][BAR}_4\text{]}_2$  appears to be relatively inert towards water and ethanol as well as to air on the open bench. Samples kept in open vessels for a day on the bench show less than 1%

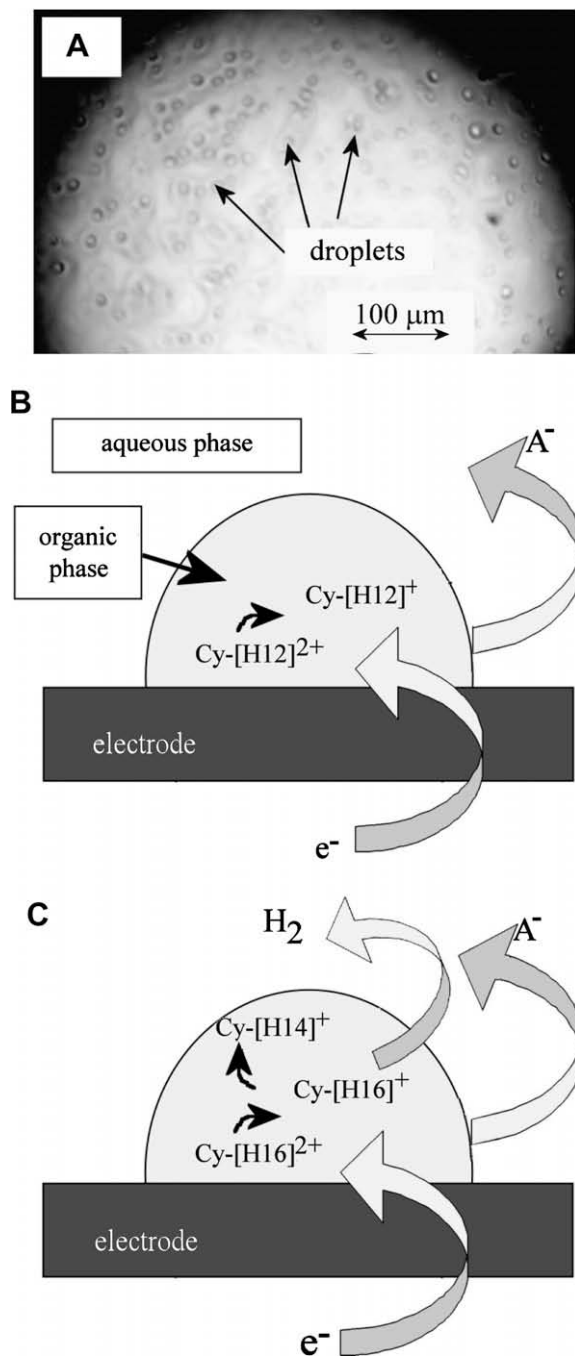
decomposition by NMR and ESI-MS. The stability of this material towards air and moisture under bench top conditions is still a surprise given that the cluster material is formally unsaturated, but is exploited here by the use of an aqueous electrolyte without special precautions apart from bubbling Ar gas through the solution. We have recently reported that reactivity of the cluster species  $^i\text{Pr-[H16][BAR}_4\text{]}_2$  with water requires the presence of a hydrogen acceptor (*tert*-butylethene) but there was no equivalent reaction with the sterically more shrouded  $\text{Cy-[H12][BAR}_4\text{]}_2$  [17] – a further indication of the complex's stability to water and the influence upon reactivity that the alkyl phosphines can impart.

In order to further explore the electrochemical process responsible for the well-defined  $\text{Cy-[H12]}^{2+/+}$  redox process in the immobilised cluster, the type of electrode was changed. When deposited onto ITO (with a monolayer of carbon nanoparticles and poly-dialyldimethylammonium chloride – PDDAC – applied to allow facile electron transfer [18]) the co-deposition of  $[\text{NBu}_4][\text{BAR}_4\text{]}_2$  again allowed reversible voltammetric responses to be obtained for  $\text{Cy-[H12][BAR}_4\text{]}_2$  (see Fig. 1(iii)). Glassy carbon or basal-plane pyrolytic graphite (bppg) electrodes worked equally well and could be used interchangeably.

Optical microscopy images for the ITO electrode (with a monolayer of carbon nanoparticles and PDDAC) with  $\text{Cy-[H12][BAR}_4\text{]}_2$  and 15 equiv. of  $[\text{NBu}_4][\text{BAR}_4\text{]}_2$  co-immobilised immersed in 3:2 ethanol:H<sub>2</sub>O with  $0.01 \text{ M Na[BAR}_4\text{]}_2$  provided clear evidence for the formation of microdroplets of a separate phase. Fig. 2 shows microdroplets of ca.  $10 \mu\text{m}$  average size, which presumably contain  $\text{Cy-[H12][BAR}_4\text{]}_2$  and  $[\text{NBu}_4][\text{BAR}_4\text{]}_2$ . We suggest that the latter salt is required to enable the formation of an ethanol-rich organic phase that contains the redox-active cluster, separate from the aqueous electrolyte phase in the microdroplet. During the reduction of  $\text{Cy-[H12][BAR}_4\text{]}_2$  in the organic phase, anion transfer to the aqueous phase must occur to balance the overall charges (see Fig. 2B). The overall mechanism for the reduction and re-oxidation of  $\text{Cy-[H12][BAR}_4\text{]}_2$  at the electrode surface is depicted in Fig. 2B. The transfer of the electron to the rhodium cluster is accompanied by the expulsion of an anion (to maintain charge neutrality) and during re-oxidation the anion has to transfer back into the organic phase. Under such a regime, changing the anion in the aqueous phase would be expected to show a characteristic move of the voltammetric response, depending on the transfer potential of the anion [19]. Experiments conducted in the aqueous/ethanol mix using  $\text{K[PF}_6\text{]}$  rather than  $\text{Na[BAR}_4\text{]}_2$  resulted in a shift of  $E_{\text{mid}}$  to more positive potential by  $50 \text{ mV}$  – consistent with this. Further evidence for microdroplet formation comes from the observation that when aqueous  $0.01 \text{ M K[PF}_6\text{]}$  is employed as the electrolyte there is essentially no voltammetric response, but on addition of a small (1% v/v) amount of 1-octanol very well-defined peaks are observed that are very similar in current height to those observed with the 3:2 ethanol:H<sub>2</sub>O mix (see Fig. 1(iv)).

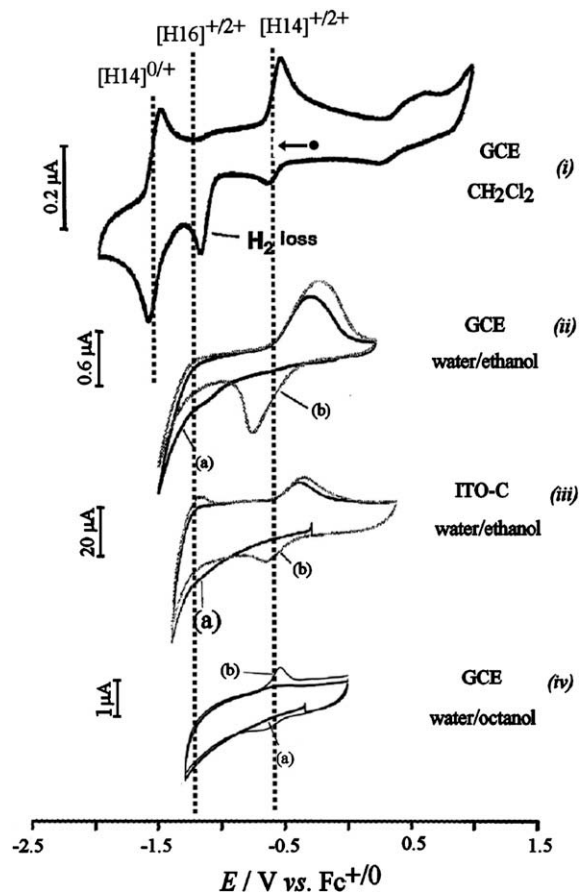
Whatever the exact nature of the surface immobilised species a number of experiments indicate successful deposition on the surface: removing the electrode and depositing in fresh electrolyte results in the same voltammograms, rinsing the electrode with  $\text{CH}_2\text{Cl}_2$  results in washing off of the cluster material and effectively no electrochemical response is observed (*i.e.* only background response) when placed back in the *same* electrolyte solution, and an ESI-MS spectrum of material washed off the electrode ( $\text{CH}_2\text{Cl}_2$ ) after a number of cycles shows the only cluster material to be present as  $\text{Cy-[H12]}^{2+}$ .

With the immobilisation of the cluster  $\text{Cy-[H12][BAR}_4\text{]}_2$  on the electrode surface established, charging the electrode with H<sub>2</sub> (1 atm, 5 min) or depositing preformed  $\text{Cy-[H16][BAR}_4\text{]}_2$  [2] on the electrode surface, resulted in a new electrochemical response (see Fig. 3(ii)). The reduction occurs at a negative potential of  $-1.15 \text{ V vs. Fc}^{+/0}$  and appears highly irreversible. Upon cycling



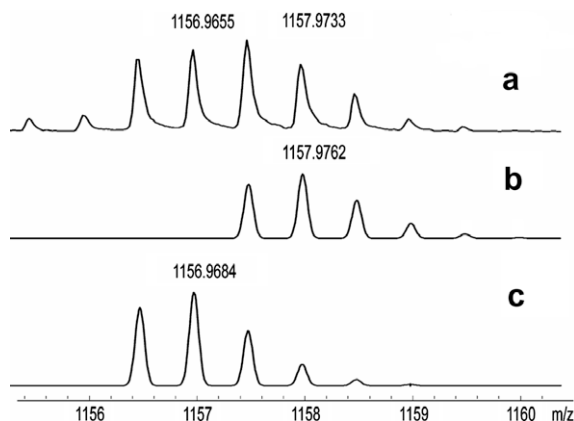
**Fig. 2.** (A) Optical micrograph showing microdroplet formation for the ITO electrode (with a monolayer of carbon nanoparticles and PDDAC) with **Cy-[H12][BAR<sub>4</sub>F<sub>4</sub>]** immobilised and 15 equiv. of [NBu<sub>4</sub>][BAR<sub>4</sub>F<sub>4</sub>] co-immobilised immersed in 3:2 ethanol:H<sub>2</sub>O with 0.01 M Na[BAR<sub>4</sub>F<sub>4</sub>]. (B) Schematic description of the biphasic redox process during **Cy-[H12]<sup>2+/+</sup>** reduction. (C) Schematic description of the biphasic redox process during **Cy-[H16]<sup>2+/+</sup>** reduction. A<sup>-</sup> = anion, [BAR<sub>4</sub>F<sub>4</sub>]<sup>-</sup>.

the potential back to positive potential and into a second reduction cycle the familiar response for the **Cy-[H12]<sup>2+</sup>** is observed. This indicates that H<sub>2</sub> loss had occurred on reduction, as previously observed in anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution (*cf.* Fig. 3(i)). Thus on the first scan, Fig. 3(ii)a, an irreversible redox event at ( $E_{\text{red}} = -1.15$  V) is observed, **Cy-[H16]<sup>2+/+</sup>**, which is followed by an oxidation peak centred at  $E_{\text{ox}} = -0.31$  V. On the second scan, Fig. 3(ii)b, this peak is accompanied by a reversible reduction peak at  $E_{\text{red}} = -0.79$  V ( $E_{1/2} = -0.51$  V,  $\Delta E_p = 0.56$  V), attributed to a species that has lost H<sub>2</sub>. Purging the solution with H<sub>2</sub> re-establishes the original cyclic



**Fig. 3.** Cyclic voltammograms (scan rate  $100 \text{ mV s}^{-1}$ ) for the reduction and oxidation of (i) **Cy-[H16][BAR<sub>4</sub>F<sub>4</sub>]<sub>2</sub>** in solution at a 3 mm diameter glassy carbon disc electrode in anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution (ca. 0.1 mM **Cy-[H16][BAR<sub>4</sub>F<sub>4</sub>]<sub>2</sub>**, 0.01 M [NBu<sub>4</sub>][BAR<sub>4</sub>F<sub>4</sub>]), (ii) **Cy-[H16][BAR<sub>4</sub>F<sub>4</sub>]<sub>2</sub>** deposited onto a 3 mm diameter glassy carbon electrode and immersed in 3:2 EtOH:H<sub>2</sub>O (0.01 M Na[BAR<sub>4</sub>F<sub>4</sub>]) with co-deposition of [NBu<sub>4</sub>][BAR<sub>4</sub>F<sub>4</sub>] (a) first cycle and (b) second cycle, (iii) **Cy-[H16][BAR<sub>4</sub>F<sub>4</sub>]<sub>2</sub>** deposited onto a 10 mm × 10 mm ITO electrode modified with a monolayer of carbon nanoparticles and immersed in 3:2 H<sub>2</sub>O:EtOH (0.01 M Na[BAR<sub>4</sub>F<sub>4</sub>]) with co-deposition of [NBu<sub>4</sub>][BAR<sub>4</sub>F<sub>4</sub>] (a) first cycle and (b) second cycle, and (iv) **Cy-[H16][BAR<sub>4</sub>F<sub>4</sub>]<sub>2</sub>** deposited onto a 3 mm diameter glassy carbon electrode immersed in aqueous 0.01 M K[PF<sub>6</sub>] with 50 μL 1-octanol added into the electrolyte solution and co-deposition of [NBu<sub>4</sub>][BAR<sub>4</sub>F<sub>4</sub>] (a) first cycle and (b) eighth cycle. Mark and arrow indicates starting potential and direction of scan.

voltammogram (e.g. Fig. 3(ii)a) demonstrating that the H<sub>2</sub> loss and gain at the surface immobilised cluster can be cycled. Essentially the same electrochemical behaviour is observed on ITO dip-coated with C-nanoparticles (Fig. 3(iii)) and with octanol rather than ethanol (Fig. 3(iv)). ESI-MS experiments of material washed from the electrode after a number of cycles on a basal plane pyrolytic graphite (bppy) electrode have been completed (bppy was used to maximise the surface area of the electrode in contact with deposited material) and show that **Cy-[H14]<sup>2+</sup>** ( $m/z$  calc.: 1156.4, obs.: 1156.5) has been formed on reduction, indicating that 1 equiv. of H<sub>2</sub> is lost per cluster molecule on the first reduction sweep. Monocationic **Cy-[H14]<sup>+</sup>** is not observed by ESI-MS. We have previously noted [3] that this species can be observed by ESI-MS under strictly anaerobic conditions and is likely that the sampling method used here means that fast oxidation to form **Cy-[H14]<sup>2+</sup>** occurs once the sample is removed from the Ar-purged electrolyte. Notwithstanding this, it is clear that a cluster with 14 hydrido ligands has been formed on reduction. However, the major component of the material on the surface of the electrode still is unreacted **Cy-[H16]<sup>2+</sup>** ( $m/z$  calc.: 1157.5, obs.: 1157.5), while there is also a small amount of **Cy-[H12]<sup>2+</sup>** ( $m/z$  calc.: 1155.5, obs.:



**Fig. 4.** ESI-MS ( $\text{CH}_2\text{Cl}_2$ ) solution of the initial  $\text{Cy-[H16]}^{2+}$  deposit on a bppg electrode after being held at  $-1.2\text{ V}$  after 3 h. (a) Experimental spectrum. (b) Simulated spectrum for  $\text{Cy-[H16]}^{2+}$ . (c) Simulated spectrum for  $\text{Cy-[H14]}^{2+}$ . Lower mass, low intensity, peaks are due to  $\text{Cy-[H12]}^{2+}$  and do not change in relative intensity over time.

1155.5). Holding the potential at  $-1.2\text{ V}$  results in a steady increase in the amount of  $\text{Cy-[H14]}^{2+}$  observed by ESI-MS, although complete consumption was not achieved, even after 3 h (Fig. 4).  $\text{Cy-[H12]}^{2+}$  does not increase in relative concentration (as measured by ESI-MS). While this lack of complete conversion no doubt depends on droplet size, mobility of  $[\text{NBu}_4][\text{BAr}_4^{\text{F}}]$  and other factors, these results never-the-less unequivocally show that  $\text{H}_2$  loss occurs in the organic microdroplet on reduction, mirroring that observed in  $\text{CH}_2\text{Cl}_2$  solution. The slow conversion to  $\text{Cy-[H14]}^{2+}$  also mirrors the low efficiency of the electrochemical processes calculated for  $\text{Cy-[H12]}^{2+/+}$ .

### 3. Implications for redox-promoted $\text{H}_2$ loss

We have previously reported that electrochemical reduction of  $\text{Cy-[H16][BAr}_4^{\text{F}}]_2$  resulted in the ejection of two molecules of  $\text{H}_2$  to form  $\text{Cy-[H12][BAr}_4^{\text{F}}]$  which can then be oxidised to form  $\text{Cy-[H12][BAr}_4^{\text{F}}]_2$ , a cluster material available for the uptake of two molecules of  $\text{H}_2$  – thus completing the  $\text{H}_2$  store and release cycle. These conclusions were based on the observation that the cyclic voltammogram after reduction of  $\text{Cy-[H16][BAr}_4^{\text{F}}]_2$  was identical to that of  $\text{Cy-[H12][BAr}_4^{\text{F}}]_2$  [3,7]. However, we also reported that chemical reduction using  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$  first formed  $\text{Cy-[H14][BAr}_4^{\text{F}}]$ , which on chemical oxidation, using added  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ , reformed  $\text{Cy-[H12][BAr}_4^{\text{F}}]_2$ . We reconciled these apparent differences between electrochemical and chemical observations by ready loss of  $\text{H}_2$  at the electrode surface during voltammetry from the  $\text{Cy-[H14]}^{n+}$  cluster material. The surface electrochemistry coupled with the ESI-MS results reported herein suggest that, in fact, electrochemical reduction forms  $\text{Cy-[H14][BAr}_4^{\text{F}}]$  as is observed in solution, i.e. only one  $\text{H}_2$  is lost on reduction. This apparent discrepancy can be further reconciled by consideration of the solution-phase cyclic voltammogram of independently synthesised  $\text{Cy-[H14][BAr}_4^{\text{F}}]$  [3] which, remarkably, is essentially identical to that of  $\text{Cy-[H12][BAr}_4^{\text{F}}]_2$ , and does not show any features that might be associated with  $\text{H}_2$  loss. Underscoring these observations, calculations on model systems ( $\text{PH}_3$  for  $\text{PCy}_3$ ) [4] indicate that  $\text{H-[H14][BAr}_4^{\text{F}}]$  is slightly more stable than  $\text{H-[H12][BAr}_4^{\text{F}}] + \text{H}_{2(g)}$  (Gibbs free energy difference =  $12\text{ kJ mol}^{-1}$ ). Thus the combination of ESI-MS analysis of the products of electrochemical reduction of surface immobilised or chemical solution-phase reduction of  $\text{Cy-[H16][BAr}_4^{\text{F}}]_2$  coupled with the close similarity of the electrochemical response of  $\text{Cy-[Hn][BAr}_4^{\text{F}}]$  ( $n = 12$  and  $14$ ), support the revised view that reduction of  $\text{Cy-[H16][BAr}_4^{\text{F}}]_2$  results in the ejection

of only one equivalent of  $\text{H}_2$  and not two – as previously thought. Pleasingly, this revision now intuitively fits the schematic molecular orbital scheme shown in Scheme 2 in terms orbital populations in as much that spontaneous  $\text{H}_2$  loss from  $\text{Cy-[H14][BAr}_4^{\text{F}}]$  would seem less likely given that no high-lying orbitals are occupied, and also reconciles subtle differences between experiment and computation [4]. It does not, however, alter significantly our previous observations that these clusters undergo redox-promoted  $\text{H}_2$ -loss and gain, and as far as we are aware they are still unique in this regard. That chemical oxidation of  $\text{Cy-[H14]}^{2+}$  using  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{PF}_6]$  results in the generation of  $\text{Cy-[H12]}^{2+}$  and not  $\text{Cy-[H14]}^{2+}$  [3], as is observed electrochemically, still remains to be resolved.

### 4. Conclusions

That  $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{12}][\text{BAr}_4^{\text{F}}]_2$ ,  $\text{Cy-[H12][BAr}_4^{\text{F}}]_2$ , unexpectedly shows a lack of reactivity towards  $\text{H}_2\text{O}$  allows conditions to be developed which allow  $\text{Cy-[H12][BAr}_4^{\text{F}}]_2$  to be immobilised at an electrode surface and reduced or oxidised in aqueous electrolyte. In the presence of dihydrogen the  $\text{Cy-[H16][BAr}_4^{\text{F}}]_2$  cluster is formed *in situ* and during one-electron reduction 1 equiv. of  $\text{H}_2$  is lost to give  $\text{Cy-[H14][BAr}_4^{\text{F}}]_2$  at the electrode surface. This process is greatly facilitated by the addition of alcohol to the electrolyte and excess  $[\text{NBu}_4][\text{BAr}_4^{\text{F}}]$  to the surface immobilised, aqueous insoluble, cluster material. These have the dual role of encouraging organic-phase microdroplet formation and also allowing for anion transfer to and from the microdroplet on reduction and oxidation of the cluster. This relatively straightforward methodology removes the need for elaborate chemical functionalisation of the cluster-periphery to allow surface binding and suggests that many other cluster materials that show interesting redox-promoted characteristics can be straightforwardly screened for surface redox behaviour. Given that many cluster materials act as electron sinks or reservoirs this has potential implications for the development of electrochemically switched functional materials based on cluster molecules. However, the low storage capacity of the cluster (0.1% w/w) coupled with the low electrochemical efficiency ( $\sim 4\%$ ) means that these materials are impracticable for the storage and release of  $\text{H}_2$ .

### 5. Experimental

#### 5.1. Chemicals and reagents

Potassium hexafluorophosphate, ferrocene, ethanol, dichloromethane, octanol, poly(diallyldimethylammonium chloride) (PDDA) (very low molecular weight) 35 wt.% in water and carbon nanoparticles (ca. 9–18 nm diameter, Emperor 2000, Cabot Corporation) were obtained commercially and used without further purification.  $[\text{Na}][\text{BAr}_4^{\text{F}}]$  [20],  $[\text{Bu}_4\text{N}][\text{BAr}_4^{\text{F}}]$  [21],  $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{12}][\text{BAr}_4^{\text{F}}]_2$  [2],  $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{16}][\text{BAr}_4^{\text{F}}]_2$  [2]  $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{12}][\text{BAr}_4^{\text{F}}]$  [3] and  $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{14}][\text{BAr}_4^{\text{F}}]$  [3] were prepared according to literature methods. Demineralized and filtered ( $0.22\ \mu\text{m}$ ) water was taken from a Millipore Milli-Q purification system.

#### 5.2. Instrumentation

Voltammetric experiments were carried out using an Autolab PGSTAT302N potentiostat system (EcoChemie, NL) with a platinum wire counter electrode and a silver wire pseudo-reference electrode (calibrated vs. internal ferrocene). Working electrodes employed were a 3 mm diameter glassy carbon electrode, a 5 mm basal plane graphite electrode and tin-doped indium dioxide (ITO) coated glass ( $1\text{ cm} \times 4\text{ cm}$ ,  $30\ \Omega$  per square, Image Optics,

Basildon, UK). ITO electrodes were cleaned prior to use by sonication in ethanol, rinsing with water and overnight drying at 120 °C. ITO electrodes were modified with carbon nanoparticles following the procedure detailed by Marken and co-workers [18]. Mass spectra were recorded on a Bruker Daltonics Micro-TOF in positive ionisation mode.

### 5.3. Procedures

Electrolyte solutions were degassed by purging with argon for 40 min prior to carrying out the electrochemical experiments, which were conducted under a low flow of argon. However, due to the robust nature of **Cy-[H12][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>**, drop-coating was carried out under atmospheric conditions without special precautions. Typically, 30 µL of a solution of 1 mg **Cy-[H12][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>** in 1 mL dichloromethane (0.25 mM) was drop-coated onto the electrode using a Hamilton syringe (100 µL). For the experiments involving co-deposition of [Bu<sub>4</sub>N][BAR<sub>4</sub><sup>F</sup>], 15 equiv. were added to a 0.25 mM dichloromethane solution of **Cy-[H12][BAR<sub>4</sub><sup>F</sup>]<sub>2</sub>** and the resulting solution was drop-coated onto the electrode.

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### References

- [1] M.J. Ingleson, M.F. Mahon, P.R. Raithby, A.S. Weller, *J. Am. Chem. Soc.* 126 (2004) 4784–4785.
- [2] S.K. Brayshaw, M.J. Ingleson, J.C. Green, J.S. McIndoe, P.R. Raithby, G. Kociok-Kohn, A.S. Weller, *J. Am. Chem. Soc.* 128 (2006) 6247–6263.
- [3] S.K. Brayshaw, A. Harrison, J.S. McIndoe, F. Marken, P.R. Raithby, J.E. Warren, A.S. Weller, *J. Am. Chem. Soc.* 129 (2007) 1793–1804.
- [4] S.K. Brayshaw, J.C. Green, N. Hazari, A.S. Weller, *Dalton Trans.* (2007) 1781–1792.
- [5] S.K. Brayshaw, M.J. Ingleson, J.C. Green, P.R. Raithby, G. Kociok-Kohn, J.S. McIndoe, A.S. Weller, *Angew. Chem., Int. Ed.* 44 (2005) 6875–6878.
- [6] (a) R.D. Adams, B. Captain, C. Beddie, M.B. Hall, *J. Am. Chem. Soc.* 129 (2007) 986–1000;  
(b) R.D. Adams, B. Captain, L. Zhu, *J. Organomet. Chem.* 693 (2008) 819–833;  
(c) A.S. Weller, J.S. McIndoe, *Eur. J. Inorg. Chem.* (2007) 4411–4423.
- [7] S.K. Brayshaw, J.C. Green, N. Hazari, J.S. McIndoe, F. Marken, P.R. Raithby, A.S. Weller, *Angew. Chem., Int. Ed.* 45 (2006) 6005–6008.
- [8] (a) A. Kuhn, F.C. Anson, *Langmuir* 12 (1996) 5481–5488;  
(b) D.L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* 36 (2007) 105–121.
- [9] (a) N. Prokopuk, D.F. Shriver, *Chem. Mater.* 10 (1998) 10–12;  
(b) N. Prokopuk, D.F. Shriver, *Chem. Mater.* 11 (1999) 1230–1236.
- [10] (a) T. Michi, M. Abe, S. Takakusagi, M. Kato, K. Uosaki, Y. Sasaki, *Chem. Lett.* 37 (2008) 576–577;  
(b) M. Abe, A. Sato, T. Inomata, T. Kondo, K. Uosaki, Y. Sasaki, *J. Chem. Soc., Dalton Trans.* (2000) 2693–2702;  
(c) M. Abe, T. Michi, A. Sato, T. Kondo, W. Zhou, S. Ye, K. Uosaki, Y. Sasaki, *Angew. Chem., Int. Ed.* 42 (2003) 2912–2915.
- [11] G.M. Ferrence, J.I. Henderson, D.G. Kurth, D.A. Morgenstern, T. Bein, C.P. Kubiak, *Langmuir* 12 (1996) 3075–3081.
- [12] (a) S. Ye, W. Zhou, M. Abe, T. Nishida, L.F. Cui, K. Uosaki, M. Osawa, Y. Sasaki, *J. Am. Chem. Soc.* 126 (2004) 7434–7435;  
(b) W. Zhou, S. Ye, M. Abe, T. Nishida, K. Uosaki, M. Osawa, Y. Sasaki, *Chem. Eur. J.* 11 (2005) 5040–5054.
- [13] A.M. Bond, R. Colton, F. Daniels, D.R. Fernando, F. Marken, Y. Nagaosa, R.F.M. Vansteveninck, J.N. Walter, *J. Am. Chem. Soc.* 115 (1993) 9556–9562.
- [14] S.J. Vickers, M.D. Ward, *Electrochem. Commun.* 7 (2005) 389–393.
- [15] C.E. Banks, T.J. Davies, R.G. Evans, G. Hignett, A.J. Wain, N.S. Lawrence, J.D. Wadhawan, F. Marken, R.G. Compton, *Phys. Chem. Chem. Phys.* 5 (2003) 4053–4069.
- [16] M.J. Bonne, C. Reynolds, S. Yates, G. Shul, J. Niedziolka, M. Opallo, F. Marken, *New J. Chem.* 30 (2006) 327–334.
- [17] T.M. Douglas, S.K. Brayshaw, P.R. Raithby, A.S. Weller, *Inorg. Chem.* 47 (2008) 778–780.
- [18] M. Amiri, S. Shahrokhian, F. Marken, *Electroanalysis* 19 (2007) 1032–1038.
- [19] S.M. MacDonald, M. Opallo, A. Klamt, F. Eckert, F. Marken, *Phys. Chem. Chem. Phys.* 10 (2008) 3925–3933.
- [20] W.E. Buschmann, J.S. Miller, *Inorg. Synth.* 33 (2002) 85–87.
- [21] (a) R.J. LeSuer, C. Buttolph, W.E. Geiger, *Anal. Chem.* 76 (2004) 6395–6401;  
(b) R.J. LeSuer, W.E. Geiger, *Angew. Chem., Int. Ed.* 39 (2000) 248–250.