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## Electronic interactions in bridged bis(cluster) assemblies – a comparison of *para*-CB<sub>10</sub>H<sub>10</sub>C, *para*-C<sub>6</sub>H<sub>4</sub> and C<sub>4</sub> bridges

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### Abstract

The electrochemical response of *bis*-Co<sub>2</sub>C<sub>2</sub>(CO)<sub>4</sub>(μ-dppm) complexes featuring bridging *para*-CB<sub>10</sub>H<sub>10</sub>C (**5**) and *para*-C<sub>6</sub>H<sub>4</sub> (**6**) moieties are similar, each exhibiting two oxidations separated by ca. 100 mV, and two reductions separated by 80 mV, evidencing a degree of “electronic communication”. A computational study of these systems and of the butadiyndiyl-bridged species (**7**) reveals an increasing contribution from the bridge π-orbitals in the frontier MO’s of the monocations **5**<sup>+</sup> < **6**<sup>+</sup> < **7**<sup>+</sup>. Thus, while similar conclusions about electronic interactions between the cluster-based redox probes through the cluster or organic bridges may be drawn from electrochemical studies, the mechanism by which these effects transmitted is subtly different in each case. **To cite this article:** B. Le Guennic et al., C. R. Chimie 8 (2005).

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### Résumé

Les études menées sur les complexes *bis*-Co<sub>2</sub>C<sub>2</sub>(CO)<sub>4</sub>(μ-dppm) à pont *para*-CB<sub>10</sub>H<sub>10</sub>C (**5**) et *para*-C<sub>6</sub>H<sub>4</sub> (**6**) montrent un comportement électrochimique similaire. Chacun d’entre eux présente deux oxydations et deux réductions, respectivement séparées d’environ 100 et 80 mV, qui traduisent quelque « communication électronique ». Une étude théorique de ces systèmes et du composé apparenté à pont butadiényle (**7**) indique une augmentation de la participation des orbitales π de l’espace organique dans les orbitales moléculaires frontières des monocations, dans l’ordre **5**<sup>+</sup> < **6**<sup>+</sup> < **7**<sup>+</sup>. Si des conclusions similaires sur la communication entre les deux sondes rédox via les ponts cluster et/ou organique peuvent être tirées à partir des études électrochimiques, il semble cependant que le mécanisme par lequel ces effets sont transmis diffère sensiblement dans chacun des cas. **Pour citer cet article :** B. Le Guennic et al. C. R., Chimie 8 (2005).

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## 1. Introduction

Of all neutral parent carboranes known, the cage of icosahedral *para*-carborane 1,12- $C_2B_{10}H_{12}$  **1** is the most robust after 1,10- $C_2B_8H_{10}$  in terms of high thermal and chemical stabilities, and only degrading under extreme basic conditions [1]. The robustness of the cage is largely attributed to its much discussed ‘three-dimensional aromaticity’ [2]. However the terminal hydrogens of the *para*-carborane cage can easily be replaced by a variety of organic and inorganic substituents resulting in a diverse derivative chemistry [3,4]. As the cage in *para*-carborane has a five-fold symmetry through the axis of the cage carbons and the hydrogens at the cage carbons are easily substituted, there has been much interest in this carborane as a linker/building block for liquid crystalline materials [4–6], rigid rods [7] and materials with large hyperpolarisabilities [6,8–10].

Many experimental and theoretical studies on *para*-carborane derivatives have shown little or no  $\pi$ -conjugation between the cage and an unsaturated organic group, such as aromatic rings [10,11], ethynyls [6,12,13] and nitriles [12], or an anionic borane cage,  $B_{12}H_{11}^{2-}$  [9]. However recent carbon-13 NMR and UV–vis studies of various 1,12-diaryl-*para*-carboranes with organic electron donor and acceptor substituents show evidence of electronic transmission via the *para*-carborane cage [14]. The rate of hydrolysis of *C-para*-carboranylbenzyl toluene-*para*-sulphonates, where organic electron acceptors and donors are present at the second cage carbon, has been shown to depend on the acceptor/donor substituent giving further support for the transmission of electronic effects via the carborane cage [15]. The cyclic voltammetry response of the *para*-carborane complex with a  $CpFe(CO)_2$  group at each cage carbon is characterised by two discrete one-electron oxidations, clearly indicating transmission of electronic effects via the carborane cage, and similar conclusions could be drawn by comparison of the spectroscopic properties of this complex with those of closely related complexes [16].

Cobalt octacarbonyl,  $Co_2(CO)_8$ , and phosphine-substituted derivatives such as  $Co_2(CO)_6(\mu-dppm)$ , readily coordinate to alkynes  $RC\equiv CR'$  through the displacement of two carbonyl ligands to give tetrahedral  $Co_2C_2$  clusters of general form  $Co_2(\mu-RC_2R')(CO)_4(L_2)$  ( $L = CO$ , phosphine). The electrochemical response of the hexacarbonyl derivatives is characterised by a one-electron, diffusion-controlled reduction, which is often complicated by subsequent fast chemical reactions arising from cleavage of the Co–Co bond [17]. The chemical reversibility of the reduction process is improved through the presence of electron-withdrawing or bulky groups on the alkyne [18]. The introduction of phosphine [19] or phosphite ligands [20] results in the observation of a one-electron oxidation process within the electrochemical window of solvents such as  $CH_2Cl_2$  and THF. The oxidation becomes more chemically reversible with increasing number of phosphite ligands, or through the use of *bis*-(diphenylphosphino)methane (dppm).

As we were interested in the mechanism by which electronic effects are transmitted through the *para*-carborane cage, here we synthesised a *para*-carborane cobalt cluster system with a  $Co_2(\mu-RC_2R')(CO)_4(\mu-dppm)$  substituent at both carbons of the *para*-carborane cluster. This compound was investigated by a combination of voltammetry and DFT-based computational work, and the electronic structures of redox-active cobalt clusters spanned by a 1,12- $C_2B_{10}H_{10}$  bridging moiety were examined. These results are compared with the properties of systems featuring more conventional 1,4- $C_6H_4$  and  $C\equiv CC\equiv C$  ( $C_4$ ) bridging moieties. Part of this work has been communicated elsewhere [21].

## 2. Results and discussion

### 2.1. Synthesis and characterisation

The reaction of the mono-ethynyl carborane **2** [22] with  $Co_2(CO)_6(\mu-dppm)$  in refluxing benzene afforded dark red **4** (40%), which was isolated from the reaction mixture by preparative TLC (Scheme 1). The IR  $\nu(CO)$

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