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Review

Electronic interactions in organometallic dimers. An electrochemical approach ☆

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Abstract

A simple electrochemical criterion is employed for an approximate evaluation of the electronic interaction between redox centres in π-conjugated organometallic dimers. This approach allows one to predict the results of the use of such organometallic complexes (and related polymers) as precursors of mixed-valence compounds (in solution) and low-dimensional conducting or non-linear optical materials (in the solid state). Chemical complications following the redox processes often alter the electrochemical response. In such cases, this approach is only useful if the experimental conditions (measurements at high scan rates or sub-ambient temperatures) are chosen carefully.

Keywords: Cobalt; Ruthenium; Bridged species; Electronic interaction; Electrochemistry

1. Introduction

Organic compounds having conjugated π-systems can act as electronic bridges between transition metal atoms. There is much current research on such organometallic polymers, because they may be useful precursors for mixed-valence (MV), low-dimensional conductive (LDC) and non-linear optical (NLO) materials [1].

Organometallic compounds are suitable for producing such precursors because of their ability to adopt a wide range of valence states, to undergo electrochemically and chemically reversible electron-transfer reactions at electrode potentials modulated by the electronic characteristics of the ancillary ligand and because they may be easily linked by polydentate ligands to form polymers [2].

Whatever molecular hyperpolarizability or intramolecular conductivity is desired, the necessary (but not sufficient) requirement is high electronic delocalization through the organic chain. In principle, electrochemical techniques in solution are able to reveal moderate-to-strong electronic interactions between redox centres, provided they undergo fully reversible processes. This approach has been extensively developed with tricobalt clusters [3] and with arenechromium derivatives [4].

For a dinuclear compound (A)—L—L—(A′) consisting of two similar (apart from the oxidation state) redox centres (A, A′) linked by a polydentate ligand (L—L) two extreme cases can be considered:

(i) There is no electronic interaction between the two redox cores (L—L is an insulator). The E^0 values for the redox processes differ by a small statistical factor, ca. 36 mV at 298 K, and in polarography/CV a single wave/peak (having the slope of a one-electron transfer, but the height of a two-electron process) is observed (valence-trapped systems).

(ii) There is complete charge delocalization over the two centres (L—L is a conductor). The $E^{0\prime}$ values for the two redox processes differ by about 600–700 mV and in polarography/CV two well-resolved waves/peaks (each corresponding to one electron) are observed (valence-delocalized systems).

Between these extremes, a large number of organometallic compounds exist having weakly interacting redox centres. The quantitative relationship be-

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☆ Dedicated to Professor F. Calderazzo on the occasion of his 65th birthday.

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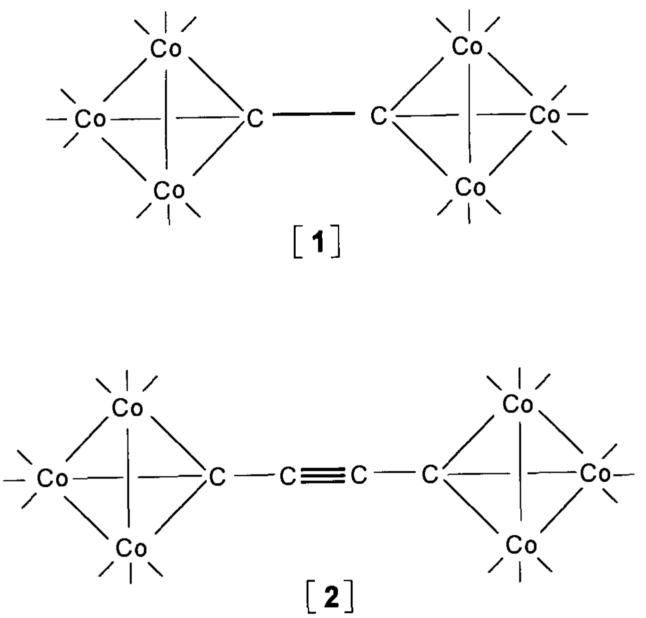


Fig. 1. Sketch of the structure of $[Co_3(CO)_9C—CCo_3(CO)_9]$ (**1**) and $[Co_3(CO)_9C—(C≡C)—CCo_3(CO)_9]$ (**2**).

tween $\Delta E^{0'}$ and electron delocalization is not simple, since structural reorganization, solvation and ion pairing effects play a role [4].

2. Results and discussion

We have synthesized and then tested by means of electrochemical techniques a number of dinuclear compounds having unsaturated chains linking two redox active cores. Some routes to these dimers were serendipitous while some employed the coordination of metal units to a preformed bidentate proligand.

Two dinuclear complexes $[Co_3(CO)_9C—CCo_3(CO)_9]$ (**1**) and $[Co_3(CO)_9C—(C≡C)—CCo_3(CO)_9]$ (**2**) (Fig. 1), can be obtained as by-products from the reaction of $[Co_2(CO)_8]$ with CCl_4, a reaction which affords mainly $[Co_3(CO)_9CCl]$. Some electronic interaction through the carbon chains is expected for both compounds since structural investigations have shown C—C bond distances consistent with π-delocalization. The overall electrochemical responses of **1** and **2** indicate strong electronic interaction between the two Co_3 redox centres via the carbon chain [5]. The electrochemical response of **1** is interesting. The first two reductions (peaks A and B) show the directly-associated re-oxidation peaks (A′ and B′) (Fig. 2). The i_p^a/i_p^c ratio is 0.70 for the first peak system (A/A′) and 0.73 for the second peak system (B/B′) at a scan rate of 50 mV s^{-1}. Two other re-oxidation peaks (C and D) are observed at potentials more positive than those of B′ and A′, respectively. They arise from chemical complications, since they disappear as the scan rate is increased or the temperature is lowered in these experimental conditions both of the above i_p^a/i_p^c ratios become unity.

It has been shown [3] by means of spectroelectrochemistry that the electrogenerated anions quickly isomerize to species with bridging CO groups, which are presumably able to reduce electron density at the metals (Fig. 3). The re-oxidation of such isomeric anions is therefore expected to occur at more anodic potentials than those of their unbridged counterparts, and we assign peaks C and D to such processes. The imposition of a holding period (5 s) at the inversion potential ($E_\lambda = -1.30$ V) increases the height of peaks C and D with respect to those of peaks B′ and A′. However, a holding period after peak A has been traversed ($E_\lambda = -0.70$ V) is less effective in increasing the height of peak D with respect to that of peak A′. Hence the isomerization takes place mainly when the dianion $[\mathbf{1}]^{2-}$ is generated. A similar change from a terminal to a bridging structure has been observed crystallographically in $[MeCCo_3(CO)_{9-x}(PR_3)_x]$ ($x = 1$ or 3), where the increase in electron density on the Co_3 moiety induced by phosphine ligands is dissipated by the bridging CO groups [6].

It should be noted that, pressed discs of microcrystals of **1** and **2** clusters show no electrical conductivity, probably because of interparticle contact resistance,

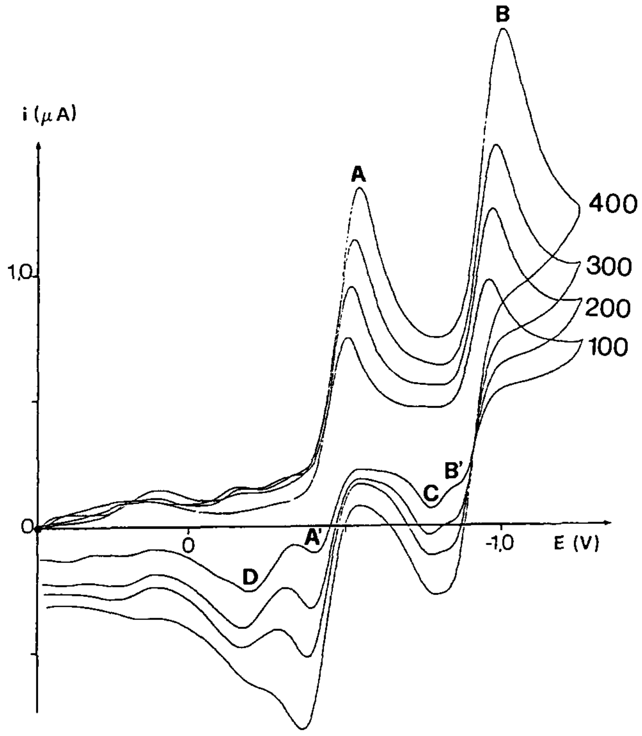


Fig. 2. Cyclic voltammetric (CV) responses of a tetrahydrofuran (THF) solution of **1** within the potential range 0.00 to −1.30 V vs. SCE. The working electrode was a hanging mercury drop electrode (HMDE); the scan rate varied from 100 to 400 mV s^{-1}.

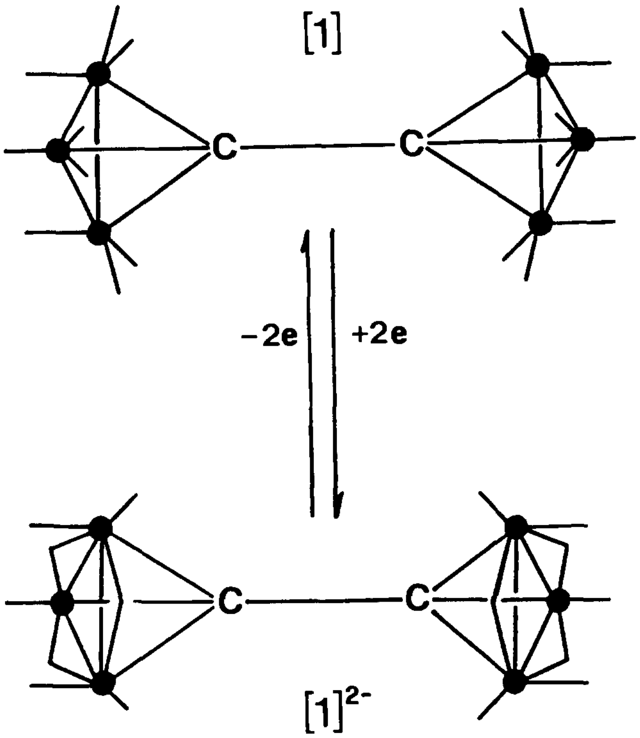
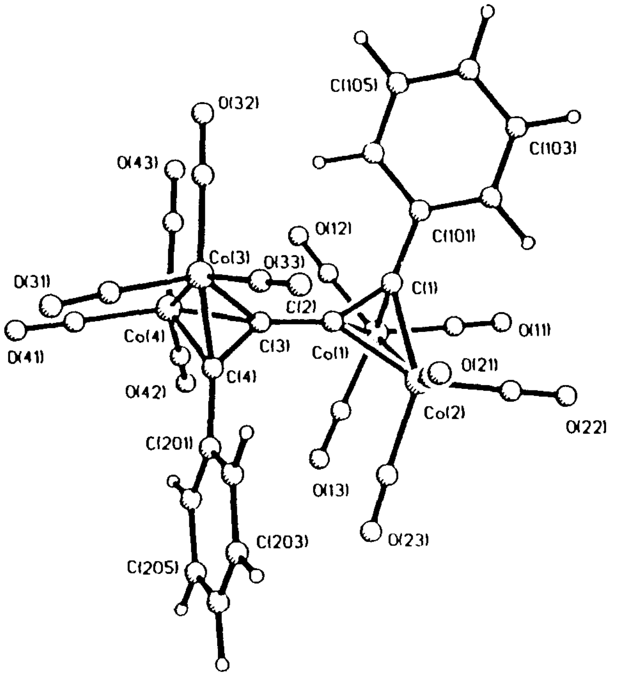


Fig. 3. Proposed interconversion between terminal and bridged forms of **1** upon reduction.



[3]

Fig. 4. Molecular structure of [{$Co_2(CO)_6$}$_2$(PhC≡C—C≡CPh)] (**3**) taken from Ref. 9.

but their controlled thermal decomposition gives electrically conductive materials [7].

We have synthesized several symmetrical dinuclear complexes, where the organic chain acts as a bridge between two $Co_2(CO)_6$ or Ni_2Cp_2 fragments using 1,4-butadiynes RC≡C—$(C_6H_4)_n$—C≡CR (R = Ph, n = 0, 1, or 2; R = H, n = 1) and studied their electrochemical behaviour. This was to determine whether if the well-known σ/π coordination [8] of bimetallic moieties to the acetylenic 'arms' of the bridging ligand is able to bring about some degree of electronic interaction between the two redox centres. Similar Co_2 derivatives have previously been obtained serendipitously, i.e. [{$Co_2(CO)_6$}$_2$(PhC≡C—C≡CPh)] (**3**) by the reaction of [$Co_2(CO)_8$] with PhC≡CMPPh$_3$ (M = Ag or Au) [9], and [{$Co_2(CO)_6$}$_2$(Me_3SiC≡C—C≡CSiMe_3)] by deprotonation of [$Co_2(CO)_6$(Me_3SiC≡CH)] with LiN^{i}Pr$_2$, followed by quenching with H_2O [10]. The X-ray structure of **3** [9] shows that the two 'Co_2C_2' cores adopt the usual pseudotetrahedral geometry with the alkyne bond lying essentially perpendicular to the Co—Co vector. The original linearity of the diyne is lost (Fig. 4).

The electrochemical behaviour of monomeric [$Co_2(CO)_6$(alkyne)] derivatives is well known. At room temperature a one-electron diffusion-controlled reduction process is followed by fast chemical complications. A further ill-defined reduction step occurs near the solvent discharge, but this process was not analyzed in the present study. The chemical reversibility of the first process can be enhanced by electron-withdrawing substituents (e.g. CF_3) or, to a lesser extent, by sterically demanding alkyne substituents [11].

At ambient temperatures **3** undergoes an apparent single two-electron reduction (peak A′ in Fig. 5). One might be tempted to conclude that there is no electrochemically detectable electronic communication between the Co_2 cores. However, it is clear that a fast chemical decomposition following the reduction prevents proper electrochemical analyses. It is found that the two-electron peak (A′) gradually splits into two

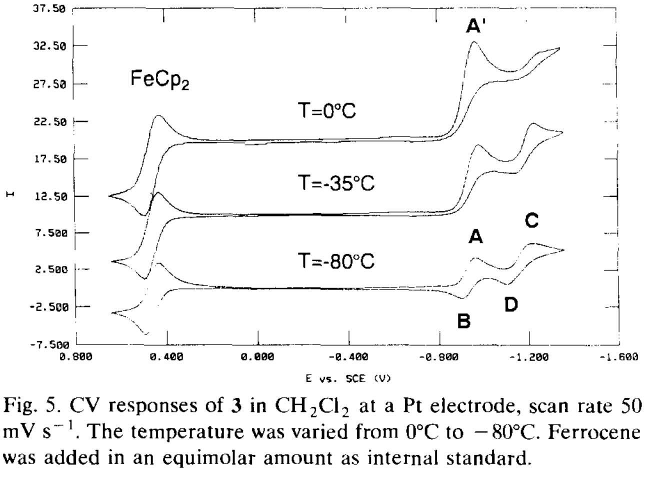


Fig. 5. CV responses of **3** in CH_2Cl_2 at a Pt electrode, scan rate 50 mV s^{-1}. The temperature was varied from 0°C to −80°C. Ferrocene was added in an equimolar amount as internal standard.

one-electron peaks (A and C, respectively in Fig. 5) as the temperature is lowered. At −80°C chemical complications are completely quenched, so that full chemical reversibility is achieved, as shown by the directly associated re-oxidation peaks. The thermodynamic $E^{0\prime}$ values can be evaluated as $(E_p{}^c + E_p{}^a)/2$: $E^{0\prime}(0,0/0,1) = -0.94$ V, $E^{0\prime}(0,1\text{-}/1\text{-},1\text{-}) = -1.16$ V. The value of $\Delta E^{0\prime}$(220 mV) indicates moderate electronic communication [12].

Taking account of the fact that the monomeric (dangling) derivative [{$Co_2(CO)_6$}(PhC≡C—C≡CPh)] (**4**) is reduced at a formal electrode potential ($E^{0\prime}(0/1\text{-}) = -0.96$ V, very close to the $E^{0\prime}(0,0/0,1\text{-})$ value of **3**, a reasonable mechanism can be proposed to simulate the electrochemical behaviour of **3**. The key step involves the formation of the monomeric derivative **4** and $[Co(CO)_4]^-$ from the decomposition of the electrogenerated monoanion $[\mathbf{3}]^-$. The anion $[Co(CO)_4]^-$ has been identified by means of IR spectroscopy (peak at 1893 cm^{-1}) during controlled-potential exhaustive electrolysis in an optically transparent thin-layer electrode (OTTLE) cell. The monomeric derivative undergoes a further one-electron reduction in turn at the same $E^{0\prime}(0,0/0,1\text{-})$ potential as **3** (Fig. 6). The fit between the experimental CV responses at different temperatures (Fig. 5) and digital simulations employing different values of the homogeneous rate constant, k, lends support to the proposed mechanism, and, by means of an Arrhenius plot, allows an approximate evaluation of the activation energy, E_a, of the decomposition of $[\mathbf{3}]^-$ as ca. 10 kcal mol^{-1}.

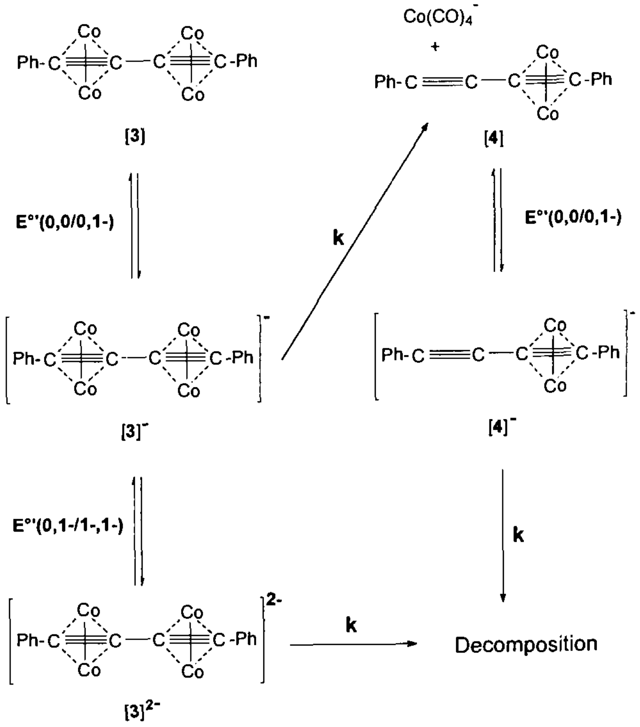


Fig. 6. Proposed mechanism for the electrochemical reduction of butadiyne derivatives, $RC{\equiv}C{-}(C_6H_4)_n{-}C{\equiv}CR$ (R = Ph, $n = 0$, 1, or 2; R = H, $n = 1$).

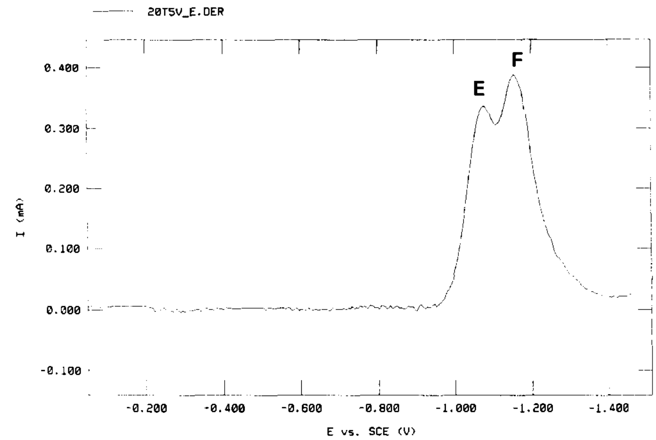


Fig. 7. Derivative neopolarogram elaborated from the CV response of a CH_2Cl_2 solution of **5** at −20°C employing an HMDE, scan rate 1 V s^{-1}.

The CV response of [{$Co_2(CO)_6$}$_2$(Ph—C≡C—(C_6H_4)—C≡C—Ph)], (**5**), having a *p*-phenylene moiety interposed between the two acetylene units, is similar to that of **3**. Chemical decomposition can be quenched at −20°C with a scan rate of 5 V s^{-1}. However, the presence of the phenylene spacer decreases the electronic communication between the two Co_2 moieties [12]. Indeed, the $\Delta E^{0\prime}$ value cannot be immediately evaluated from the CV response, since the two peaks (E and F) overlap strongly. However, a pulse technique such as square-wave voltammetry (SWV) [13] can be employed to resolve these peaks ($E^{0\prime}(0,0/0,1\text{-}) \approx E_{su}(E) = -1.06$ V, $E^{0\prime}(0,1\text{-}/1\text{-},1\text{-}) \approx E_{su}(F) = -1.14$ V vs. SCE, $\Delta E^{0\prime} = 80$ mV). An alternative technique for peak resolution enhancement is the so-called *derivative neopolarography* [14], where the CV data are first semi-integrated (producing *neopolarograms*) and then differentiated with respect to time (producing *derivative neopolarograms*). The result of such a data analysis for the CV response of **5** at 5 V s^{-1} is shown in Fig. 7. Two reduction maxima are observed (E and F), each affording, in the perfectly reversible case, the $E^{0\prime}$ value of the corresponding process, viz. $E^{0\prime}(0,0/0,1\text{-}) = -1.08$ V, $E^{0\prime}(0,1\text{-}/1\text{-},1\text{-}) = -1.16$ V, $\Delta E^{0\prime} = 80$ mV, in accord with the SWV data [12].

Similar electrochemical behaviour is also observed for [{$Co_2(CO)_6$}$_2$(HC≡C—(C_6H_4)—C≡CH)] (**6**). The structures of similar dinuclear species have been determined [15]. Due to the C—H groups, the chemical decomposition of the electrogenerated monoanion is very fast. Chemical reversibility at −20°C can only be achieved at scan rates (CV) and frequencies (SWV) at least an order of magnitude greater than those previously employed [12].

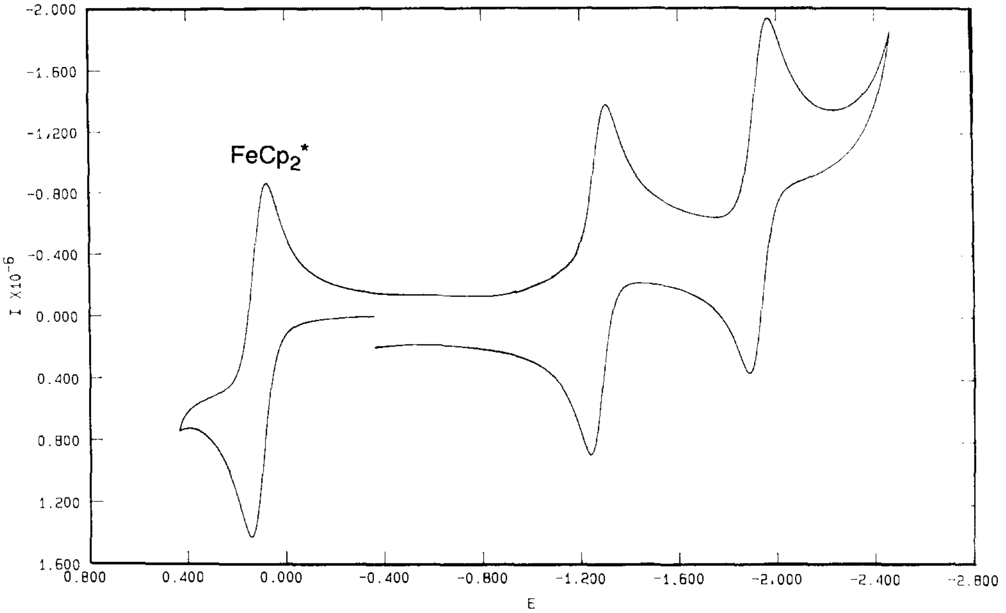


Fig. 8. CV response of a THF solution of [$\{Ni_2Cp_2\}_2$(Ph—C≡C—C≡C—Ph)] (7) at a Pt electrode, scan rate 200 mV s^{-1}. Decamethylferrocene was added in an equimolar amount as internal standard.

In contrast, the isoelectronic and isostructural [$\{Ni_2Cp_2\}_2$(Ph—C≡C—C≡C—Ph)] (**7**) shows two chemically reversible one-electron reductions at room temperature (Fig. 8) in the potential range in which reduction of the monomeric [Ni_2Cp_2(alkyne)] derivatives occurs, thus indicating strong electronic interaction between the Ni_2 cores [16] ($\Delta E^{0\prime} = 670$ mV).

Unfortunately, 1,4-diphenylbuta-1,3-diyne cannot act as a bridge for larger trimetal clusters because of the steric demands of the phenyl groups. Deeming et al. showed that the activated cluster [$Os_3(CO)_{10}(NCMe)_2$] reacts with PhC≡C—C≡CPh to produce a monomeric derivative [$\{Os_3(CO)_9(\mu$-CO)$\}$(PhC≡C—C≡CPh)], in which only one of the alkyne groups is coordinated. More forcing reaction conditions resulted in C—C bond breakage [17]. We have therefore chosen to study the reaction of 4,4′-diethynylbenzene with trimetallic clusters. Two [$\{Ru_3(CO)_9(\mu$-CO)$\}_2$(HC≡C—C_6H_4—C≡CH)] (**8**) and [$\{Ru_3(CO)_9(\mu$-H)$\}_2$(C≡C—C_6H_4—C≡C)] (**9**), can be obtained from the reaction of HC≡C—C_6H_4—C≡CH with the activated cluster [$Ru_3(CO)_{10}(NCMe)_2$] (Fig. 9). Both clusters show a chemically irreversible single peak/wave corresponding to two electrons in cyclic voltammetry and d.c. polarography [18]. Unfortunately, neither for **8** nor **9** can the chemical decomposition following the reduction be quenched, even on lowering the temperature to −80°C, or on increasing the scan rate to 50 V s^{-1}. Thus no electronic communication can be revealed by this approach.

We have also investigated possible electronic delocalization through bis(diphenylphosphino)acetylene, $Ph_2PC{\equiv}CPPh_2$, dppa. Several reports have described diphosphaacetylenes as bridging between clusters [19]. The presence of π-unsaturation in the dppa chain could permit some degree of delocalization, provided that the M—P σ-bonding allows this delocalization through the unoccupied d-orbitals of the phosphorus atoms [20]. We have therefore synthesized [$\{Ru_3(CO)_{11}\}_2(\mu$-dppa)] (**10**) [21] and [$\{PhCCo_3(CO)_8\}_2(\mu$-dppa)] (**11**) [22].

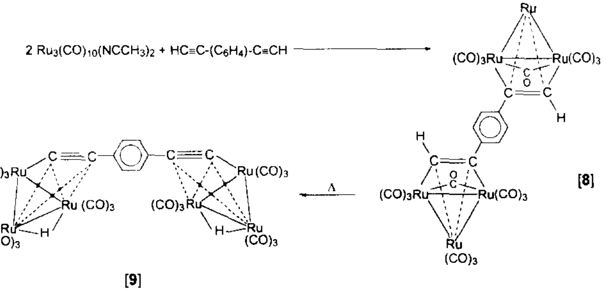
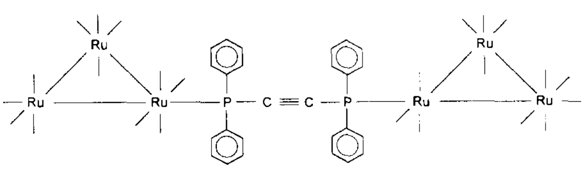
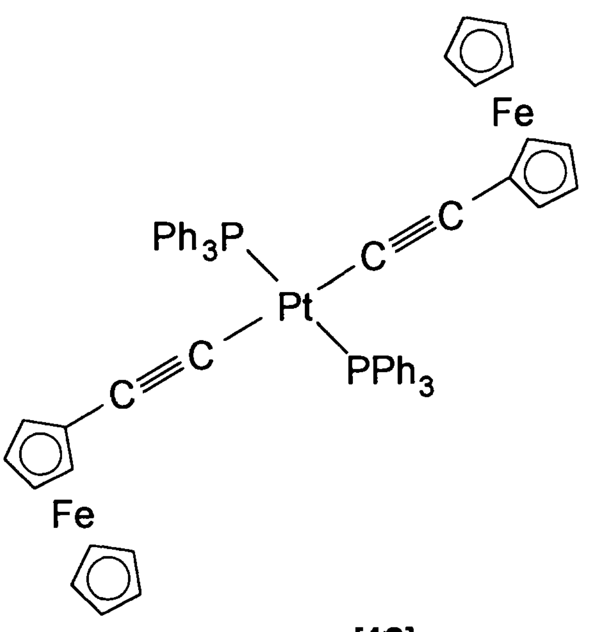


Fig. 9. Scheme for the synthesis and structures of [$\{Ru_3(CO)_9(\mu$-CO)$\}_2$(HC≡C—C_6H_4—C≡CH)] (**8**) and [$\{Ru_3(CO)_9(\mu$-H)$\}_2$(C≡C—C_6H_4—C≡C)] (**9**).



[10]

Fig. 10. Sketch of the structure of [$\{Ru_3(CO)_{11}\}_2(\mu$-dppa)] (**10**).



[12]

Fig. 11. Sketch of the structure of *trans*-[Pt(PPh$_3$)$_2$(—C≡C—Fc)$_2$] (12).

The structure of **10**, originally proposed by Bruce et al. [23] on the basis of spectroscopic data, is shown in Fig. 10. The two ruthenium triangles are symmetrical linked by the diphosphinoacetylene via the two phosphorus atoms which occupy two equivalent equatorial sites on each Ru$_3$ moiety. Bruce's hypothesis has been corroborated by a subsequent X-ray structural determination of the isoelectronic [{Os$_3$(CO)$_{11}$}$_2$(μ-dppa)] [24].

Unfortunately, the *i–E* responses of **10** and **11** are complicated by subsequent fast chemical reactions, leading to M—P bond breaking. For example, the electrochemical data on **10** suggest a mechanism as shown below

$$[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})] + 2e \rightarrow [\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]^{2-}$$

$$[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]^{2-} \rightarrow [Ru_3(CO)_{11}(\eta^1\text{-dppa})] + [Ru_3(CO)_{11}]^{2-}$$

$$[Ru_3(CO)_{11}(\eta^1\text{-dppa})] + e \rightarrow [Ru_3(CO)_{11}(\eta^1\text{-dppa})]^{-}$$

The first step represents the two-electron reduction of **10**, followed by dissociation of the dianion into [Ru$_3$(CO)$_{11}$]$^{2-}$ and the 'dangling' complex [Ru$_3$(CO)$_{11}$ (η^1-dppa)], which in turn is reduced at somewhat more negative potential in a one-electron step. The CV response of an authentic sample of [Ru$_3$(CO)$_{11}$(η^1-dppa)] and controlled potential exhaustive electrolysis in an OTTLE cell confirms this view. The overall mechanism of reduction of **10** and **11** is similar to that discussed for [{RCCo$_3$(CO)$_8$}$_2$(μ-dppe)][(dppe = bis(diphenylphosphino)ethane; R = Ph or Me) where the electrochemically-induced formation of [RCCo$_3$(CO)$_7$(dppe)] has been proposed [25]. For **10** and **11**, the rigidity of the linear —C≡C— chain in the dppa skeleton prevents chelation to a single metal atom or across a metal–metal bond.

Once again, the fast decomposition of the electrogenerated anion hampers any simple test. The instability of Co$_3$—P bonds upon reduction has been clearly demonstrated [26]. Studies on the electrochemical behaviour of [{PhCCo$_3$(CO)$_6$(dppe)}$_2$(μ-dppa)], where the electronic density on the cluster cores is enough to

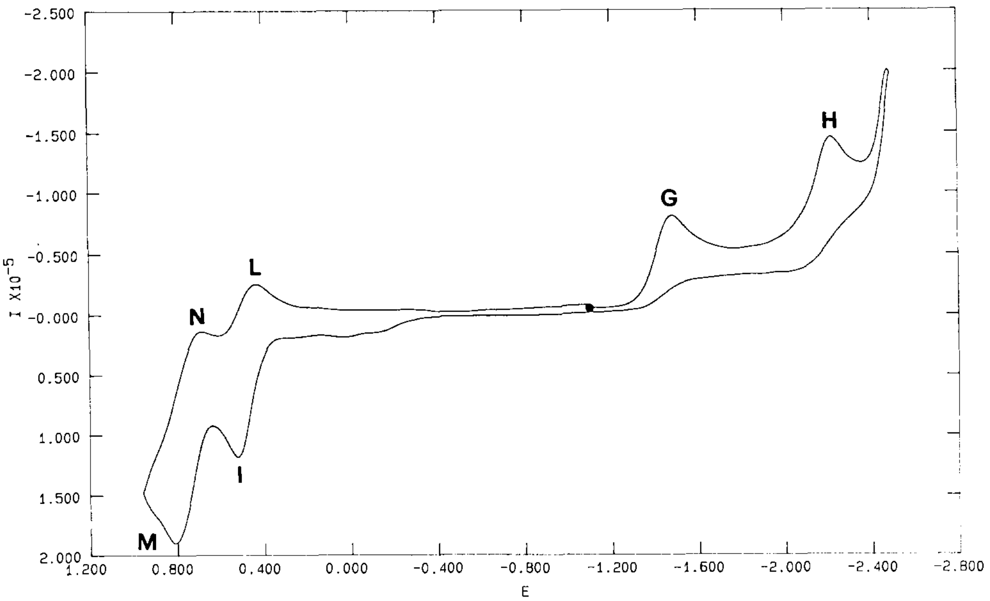


Fig. 12. CV response of a THF solution of **12** at an HMDE, scan rate 200 V s^{-1}, ambient temperature.

make the oxidation process accessible and reversible, are in progress [22].

Finally, we studied a 'rod-like' organometallic complex, *trans*-[$Pt(PPh_3)_2(—C{\equiv}C—Fc)_2$] (Fc = ferrocenyl) (**12**). This is ideally suited for electrochemical study. It contains two reversible redox centres (the Fc moieties) bonded by the π-conjugate '$—C{\equiv}C—Pt—C{\equiv}C—$' chain (which may be considered a model of the repeat unit in an organometallic polymer). Moreover, the Pt^{II} centre is itself electroactive. The structure of **12** (Fig. 11) can reasonably be inferred from the pseudo-polymeric structure of *trans*-[$Pt(PPh_3)_2(H)(—C{\equiv}C—Fc)$], determined by X-ray diffraction [27].

The electrochemical response of **12** (Fig. 12) shows two reversible one-electron oxidations centred on the Fc moieties (couples of peaks I/L and M/N), indicating moderate electronic communication between the redox units through the organic chain and the Pt hinge, ($\Delta E^{0\prime} = 260$ mV) [28]. The electron interaction found in **12** is stronger than that evaluated under similar experimental conditions for $Fc—C{\equiv}C—C{\equiv}C—Fc$ ($\Delta E^{0\prime} = 100$ mV) [29]. The insertion of the square-coordinated Pt^{II} into the diyne chain, although it increases the distance between the two Fc redox centres, guarantees a higher rigidity of the structure and a better overlap of the π-orbitals. Two irreversible one-electron reductions are also detected (peaks G and H) in the CV response of **12** (Fig. 12) and assigned to the stepwise $Pt^{II} \rightarrow Pt^{0}$ process. It seems that the transient Pt^{I} intermediate is somewhat stabilized by electron delocalization over the external ferrocenyl units. These assignments have been made by comparison with the electrochemical behaviour of several model complexes, ethynylferrocene, [$HC{\equiv}CFc$] *trans*-[$Pt(PPh_3)_2(—C{\equiv}C—Ph)_2$] and *trans*-[$Pt(PPh_3)_2(—C{\equiv}C—Ph)(—C{\equiv}C—Fc)$]. Each represents a building block of the overall molecule and thus provides information on the specific electron-transfer processes undergone by a given redox centre.

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