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PROGRESS IN CLUSTER ELECTROCHEMISTRY

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A. INTRODUCTION

The redox reactions of transition metal complexes are reviewed in several reports [1–4], but transition metal cluster electrochemistry has been the object of only one review, published in 1982 [5]. Since that time, much progress has been made in this area. The aim of the present report is to summarize recent results in cluster electrochemistry and to point out several new trends.

A promising field is the synthesis of low-dimensional solids containing zero-valent or low-valent metals for the development of solid state materials containing organometallic molecules. For example, the reaction of the cationic cluster $[Nb_3Cl_6(C_6Me_6)_3]^+$ with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and LiTCNQ gives a solid-state structure in which the cation $[Nb_3Cl_6(C_6Me_6)_3]^{2+}$ alternates with $(TCNQ)_2^{2-}$ dimers in a bent chain configuration [6]. This example is reminiscent of organic charge transfer

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complexes. There are different reasons for which clusters may participate in cooperative transport phenomena. As they behave as electron reservoirs [7], many reversible one-electron transfer reactions may occur, and hence clusters are able to adopt a range of formal valence states. In addition, unsaturated coordination sites on the cluster may enhance the reactivity of these rather stable species. Thus, at least two advantages are offered at the same time, i.e. multiple oxidation levels and coordination sites readily accessible on these synthetic molecular compounds intermediate between molecules and crystals.

In metal cluster complexes, the frontier orbital concerned with electrochemical oxidation and reduction has been qualitatively assigned. The highest occupied molecular orbital (HOMO) is usually a σ-bonding MO of metal–metal bond character, and the lowest unoccupied molecular orbital (LUMO) is an antibonding MO of metal–metal bond character [7–14]. As a result, clusters are subject to fragmentation by electrochemical oxidation or reduction, i.e. rupture of the metal–metal interactions, which leads to metal carbonyl cluster fragments of lower nuclearity [15,16]. It has been shown that the metal core cohesion may be reinforced towards fragmentation by chelation, capping by donor ligands or by heteroatoms (C, N, P, S, etc.) bonded to the metallic framework. These examples have provided information on the effect of ligands on the electrochemistry of clusters.

Whereas most clusters undergo multiple one-electron redox steps, several examples of multi-electron reactions, involving structural changes, have been reported. These irreversible electron-transfer reactions usually take place most often according an ECE mechanism. In the case of a two-electron reduction step, the mechanism has been interpreted by stepwise one-electron transfers in which the product of the first electron transfer is unstable, may rearrange and in turn is reduced. When a multi-electron reaction occurs, the cluster structure is also often broken leading to fragments of lower nuclearity than the starting compound.

Activations of clusters induced by electron-transfer processes are powerful routes for finding new processes or improving old ones [17,18]. The electron induced nucleophilic substitution in carbonyl clusters is an efficient and rapid method for the synthesis of cluster derivatives. Several results on this subject have appeared in recent years, since there is considerable interest in elucidating the mechanism of electron-transfer catalysed reactions that involve paramagnetic intermediates. These studies are connected with those using redox reagents, photochemistry or sonochemistry in homogeneous redox catalysis.

The relation between structure and electrochemical reactivity in clusters is examined herein. Redox reactions in clusters may be divided into two principal classes corresponding to the two parts of this report.

First, a majority of clusters undergo reversible one-electron transfer reactions (oxidation or reduction). These compounds have "close-packed" structures or contain ligands or heteroatoms able to stabilize the radical anion/cation electrochemically generated. These clusters include the carbide capped clusters with Co_3C core and derivatives, the tetrahedral clusters of the type $[Co_4(CO)_{12}]$ and the cubane-like clusters. Other complexes of lower and higher nuclearity are also subject to stepwise one-electron processes and may be considered as sinks and sources of electrons, according to their delocalized cluster bonding mode. The radical anions are more reactive towards nucleophilic substitution than the starting species, which are rather unreactive. Thus, electron-induced nucleophilic substitution is now a new, efficient and rapid method for ligand exchange reactions and for the synthesis of new compounds.

Several examples of one-step multi-electron transfer reactions have been reported in the literature. A common feature of these clusters is an "open" structure which may be responsible for cluster breakdown. The particular reaction of a single two-electron transfer including structural changes has been intensively studied. Clusters with a heterometallic core are also subject to multi-electron processes which can be related to the electrochemistry of metal–metal bonded carbonyl complexes.

B. ONE-ELECTRON TRANSFER PROCESSES IN CLUSTER ELECTROCHEMISTRY

(i) Redox chemistry of monocapped trimetal carbonyl clusters

A series of about twenty publications [19–35], under the general title "Paramagnetic Organometallic Molecules" dealt with the redox chemistry of the capped cluster with the following frameworks: CCo_3 [19,20,23]. SCo_3 [29], SCo_2Fe [29], C_2Co_2 [27]. The capping heteroatom, C or S, reinforces the metallic core cohesion in such a way that the radical anions electrogenerated in reduction are stable enough to be studied. Indeed, all these clusters characteristically undergo a one-electron reduction leading to radical anions, shown to exist by ESR spectroscopy. These species are active in nucleophilic substitution and electron-induced reactions [31]. It has been shown that the additional electron of the radical anion occupies an antibonding orbital centered on the metallic core [20,23,29,31]. The important question of the stability of this radical anion was correlated to the metal–metal bond strength, the ligand configuration around the cluster, temperature, ion-pairing or anion–cation associations [32]. The heteronuclear cluster radical anion $[SCo_2Fe(CO)_9]^{\dot{-}}$ shows a long half-life, although the unpaired electron density is unequally distributed over the metallic core [29].

A series of clusters with the following frameworks: $RECo_3$ (R = Me, Ph; E = Ge, P), $RECo_2M$ (R = Me, Ph; E = C, Ge; M = Cr, Mo, W: R = Me, Ph; E = P; M = Fe) and RPCoMM′ (R = Me, Ph; M = Fe; M′ = Mo, Ni), has been investigated by electrochemical and spectral measurements [34]. Incorporation of another metal, M or M′, into the Co_3 framework induces kinetic instability of their radical anions and the behaviour of these clusters has been correlated with steric and electronic effects of the metal and capping atoms [34].

A second related series of publications by the same group [36–47] entitled "Electron-transfer in Organometallic Clusters", detailed electrochemical studies of numerous clusters derived from the compound $[RCCo_3(CO)_9]$. The studies involved electron-transfer catalyzed substitutions and redox behaviour of mixed-valence cluster compounds. In the latter, the transition-metal cluster is linked to another redox center, ferrocene. The complex $[FcCCo_3(CO)_9]$ (Fc = ferrocene) exhibits the redox series $(+1, 0) \rightleftarrows (0, 0) \rightleftarrows (0, -1)$ [46]. The reduction center is the cluster which forms a radical anion as detected by ESR, whereas the oxidation center is the Fc moiety as shown by IR, Mössbauer and electronic spectra. There is a weak interaction between both redox sites: the cyclopentadienyl ring of Fc is a π donor to the cluster which is shown to be an electron withdrawing substituent to the ring. The $(+1, +1)$ oxidation state becomes accessible by coordination of an additional Lewis base ligand on the cluster. To explain the overall trends in electrochemical and spectral data, both inductive and mesomeric parameters were considered by the authors [46].

The clusters $[FcCCo_3(CO)_{9-n}L_n]$ ($n = 1$, PPh_3, $P(C_6H_{11})_3$, $P(OPh)_3$; $n = 2$, $P(OPh)_3$, $P(OMe)_3$; $n = 3$, $P(OMe)_3$, $P(OPh)_3$) undergo a sequence of several discrete one-electron reactions [37] (CO ligands omitted for clarity)

$$^{+}FcCCo_3L \overset{+e}{\rightleftarrows} FcCCo_3L \overset{+e}{\rightarrow} FcCCo_3L^{-} \overset{\text{fast}}{\rightarrow} \left\{ \begin{array}{c} [FcCCo_3(CO)_9]^{-} \\ + \\ \text{decomposition} \end{array} \right.$$

$$^{+}FcC^{+}Co_3L_2 \overset{+e}{\leftarrow} FcC^{+}Co_3L_2 \overset{+e}{\rightleftarrows} FcCCo_3L_2 \rightarrow FcCCo_3L_2^{-}$$

$$\rightarrow \left\{ \begin{array}{c} [FcCCo_3(CO)_9]^{-} \\ + \\ \text{decomposition} \end{array} \right.$$

$$Fc^{+}C^{+}Co_3L_3 \overset{+e}{\rightarrow} Fc^{+}CCo_3L_3 \overset{+e}{\rightarrow} FcCCo_3L_3 \rightarrow [FcCCo_3L_3]^{-}$$

The authors conclude that there are localized valence sites in these clusters, for which the Hush model holds [37].

Independently, the electrochemical reduction of similar capped clusters $[PhMCo_3(CO)_n]$ (M = Si, $n = 11$ and M = Sn, $n = 12$) has been studied [48].

In both cases, the radical anions $[PhMCo_3(CO)_n]^{\cdot-}$ are formed, which easily decompose into $[Co(CO)_4]^-$ anion and other products. Only the silicon radical anion is sufficiently stable to be reoxidized: a half-life of 2.3 s at 25 ° C has been calculated.

The 48-electron triangular bicapped clusters derived from $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu^3\text{-}CO)(\mu^3\text{-}NSiMe_3)]$ have been studied by cyclic voltammetry. Whereas some of them show simultaneous two-electron oxidation and reduction, other compounds display only one-electron processes. This redox chemistry has been rationalized in terms of ligation effects [49]. The 48-electron cluster $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ displays a reversible reduction couple tentatively assigned to a one-electron process [50], but the chemical reduction in order to obtain the corresponding 49-electron species was unsuccessful. The two-electron oxidation of the cluster $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]$ generates the corresponding dication which undergoes deprotonation with NEt_3 to form the monocation $[Co_3(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)(\mu_3\text{-}N)]^+$. A reexamination of the 49-electron cluster $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2]$ and its C_5H_4Me-containing derivative showed one-electron oxidations to give the 48-electron monocation [49]. Also reported are the electrochemical measurements of the cluster $[Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)]$ [51]. Electrochemical effects of variation in the nature of the terminal and capping ligands in the cluster series $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}X)(\mu_3 - Y)]$ ($x = 0, 1, 5$, $X = CO$, $Y = NR$, NH) were found to be intriguingly varied and highly unusual [51].

In conclusion, the 48-electron homonuclear monocapped cobalt clusters were generally found to undergo one-electron reversible reduction leading to the respective 49-electron monoanion. In contrast reversible oxidizability was not a general characteristic of any of these systems, except for several Lewis base derivatives which exhibit one-electron reversible oxidation at fast scan rates and/or at low temperature. In the corresponding heteronuclear metal clusters, the electrochemical behaviour of most mixed metal systems was more complex which made the cyclic voltammetric data difficult to interpret. The principal applications of these studies are electron-induced nucleophilic substitutions and the study of mixed-valence cluster compounds.

(ii) Electron-induced nucleophilic substitutions in clusters

Single electron-transfer processes are regarded as important pathways in organic chemistry and biochemistry [52], and the reactivity of radical species electrochemically generated is of great interest [53]. For metal carbonyl clusters, severe reaction conditions are often required to bring about substitution with simple donor molecules. Thermal reactions proceed at elevated temperatures and the resulting increase in reactivity often results in polysubstitution or further transformation of the ligand after complexation to the metal cluster [54]. Photochemistry, redox reagents and sonochemistry are also used in order to increase cluster reactivity in substitution reactions [55]. Photo-induced electron-transfer reactions have been successfully developed parallel to electron-induced substitution reactions. The latter reactions correspond to an overall $\bar{E}C\bar{E}$ electrochemical mechanism which was first discovered for the aqueous $[Cr(CN)_6]^{3-}$ anion reduction [56]. The aromatic nucleophilic substitutions SRN_1 investigated by Bunnett and others [57–59] are also analogous to this reaction.

The first example of an electron-induced nucleophilic substitution reaction in clusters appeared in 1981 [60]. The first reduction wave of the complex $[YCCo_3(CO)_9]$ (Y = Ph, Cl) drops nearly to zero in the presence of nucleophiles L (L = phosphines or phosphites), whereas a new wave appears at the more cathodic potential expected for the substitution product $[YCCo_3(CO)_8L]$. Whereas the thermal reaction of ligand substitution may produce a random mixture of polysubstituted products in low yields, the electron-induced reaction offers a convenient route for the synthesis of a single substituted product at a controlled electrode potential, provided potential conditions are fulfilled. Furthermore, the carbonyl group around the cluster may be replaced stepwise by more basic ligands. As an example, the electron-induced replacement of CO ligands by $[P(OMe)_3]$ ligands in the cluster $[Fe_3S_2(CO)_8(C_3H_2S_2)]$ proceeds stepwise and leads to the new derivatives $\{Fe_3S_2(CO)_{8-n}(C_3H_2S_2)\text{-}[P(OMe)_3]_n\}$ ($n = 1, 2, 3$), in good yield, according to the described square reaction scheme [61,62].

The number of exchangeable CO ligands in the clusters depends on the basicity and steric hindrance (cone angle) of the nucleophilic reagent used. Only two substitutions occur with $(P(OPh)_3$ and one with PPh_3 in the preceding example.

A chemical reagent, for example sodium diphenylketyl in THF (ca. 0.025 M) which generates radicals, may replace the electrode in the electron-induced reaction. While the thermal reaction of $[H_4Ru_4(CO)_{12}]$ with Lewis bases L gives all possible derivatives $[H_4Ru_4(CO)_{12-n}L_n]$ ($n = 0$–4), stoichiometric products are obtained [55] by addition of catalytic amounts of $Ph_2CO^{\cdot-}$. The range of Lewis bases studied included isocyanides, tertiary phosphines and phosphites, tertiary arsines and stibines. The substitutions were found to be highly specific and up to four ligands L were introduced into the cluster.

High yielding syntheses of Lewis base derivatives of carbonyl clusters by electron-induced reactions have been reported in the literature [30,31,47,55, 60,61]. Electron-induced substitution occurs on the cluster $[Ru_3(CO)_9(\mu_3\text{-}NAr)_2]$ with CNR at the axial site and with PR_3 at the equatorial site [63].

Metal carbonyl anions or other electron-rich species may act as nucleophiles. The formation of metal–metal bonds in the synthesis of the clusters $[RCCo_2M(\eta^5\text{-}C_5H_5)(CO)_8]$ (R = Me, Ph, H; M = Cr, Mo, W) and $[RCCo_2Fe(\eta^5\text{-}C_5H_5)(CO)_7]$ have been reported [39]. Long-lived cluster radical anions are required in such reactions. Their stability and the chain process efficiency is strongly dependent on the metal–metal interactions since the frontier orbital LUMO is usually antibonding metallic in character.

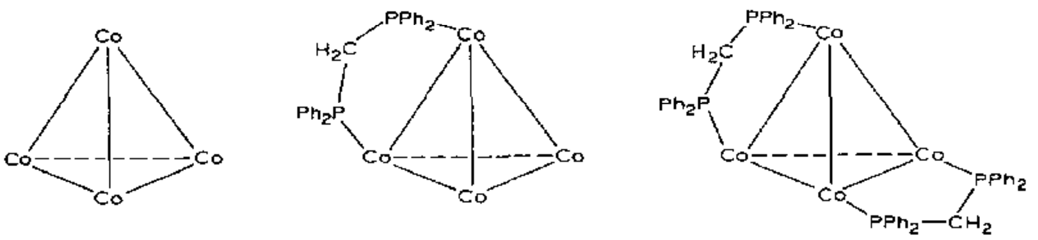
The net charge on the metallic core is dependent on the properties of the ligand (e.g. basicity, steric hindrance, cone angle, chelating effects). The ligands may contribute to the stabilization of the cluster radical anions. Temperature and bulk conditions (solvent, supporting electrolyte, residual water, oxygen, ion-pairing effects) may also influence the chain process [32]. The reaction also needs rapid electron transfer from one radical anion to another and good leaving groups on the cluster, such as CO or $[(Co(CO)_4]^-$, contribute to the efficiency of the reaction. Potential E^0 conditions are required. The end of the chain reaction is less known: decay of the radical anions, reoxidation of the product. All the conditions for an efficient chain process have been discussed in several publications [30–32, 47].

The radical anions of the bicapped tetracobalt clusters $[Co_4(CO)_{10}(\mu^4\text{-}PPh)_2]$ and derivatives $[Co_4(CO)_{10-x}(\mu_4\text{-}PPh)_2L_x]$, examined by Richmond and Kochi [64], undergo facile CO substitution via a prior dissociation of carbon monoxide. This slow elimination step is of high importance for the overall process. Further replacement of carbonyl ligands to afford more highly substituted derivatives has been shown to be less efficient. The mechanism of substitution proposed is in agreement with that found for other tetracobalt clusters of the type $[Co_4(CO)_9\ HC(PPh_2)_3]$ [65]. The bicapped triiron cluster radical anion $[Fe_3(\mu_3\text{-}PPh)_2(CO)_9]^{-}$ also suffers rapid ligand substitution by CO replacement with various phosphines [66,67]. Two isomeric forms of the radical anion have been described [67]. The opening of the μ_3-PPh capping ligand to μ_2-coordination plays a role in the mechanism of ligand substitution and in the reaction of the dianion.

The bicapped rhodium–triiron unsaturated cluster $[(\eta^5\text{-}C_5Me_5)RhFe_3(CO)_8(PPh)_2]$ reversibly binds CO to form a saturated cluster [68]. Both species undergo facile one-electron redox changes with minimal structural changes as shown by the ESR spectra. The quenching of the unsaturated anion radical can also be effected by other ligands such as trimethyl phosphite.

An interesting result [43] of these ligand-induced substitutions is the generation of dicluster bridged species by phosphine ligands, e.g., $\{[RCCo_3(CO)_8]_2\ (\mu\text{-dppe})\}$ (dppe = bis (diphenyl phosphino)ethane). Polymeric clusters are not produced.

For highly symmetrical tetrahedral clusters where the excess negative



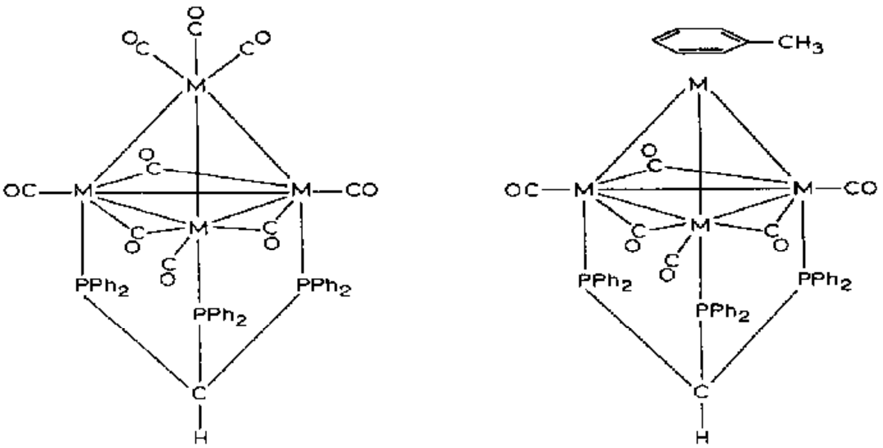
I II III

Fig. 1. Schematic representation of cluster **I**, $[Co_4(CO)_{12}]$; cluster **II**, $Co_4(CO)_{10}$dppm; cluster **III**, $[Co_4(CO)_8(dppm)_2]$ (CO ligands omitted for clarity).

charge may be delocalized from the metal core on the CO ligands, it is important to determine ligand effects on the electron density at the metallic core. A qualitative molecular orbital diagram [7] of $[M_4(CO)_{12}]$ (M = Co, Rh) is used to rationalize the electrochemical results of these derivatives. The highest occupied molecular orbitals (HOMO) are metal–metal bonding orbitals $(a_1 + e + t_2)$ whereas the lowest unoccupied molecular orbitals (LUMO) involved in electrochemical reduction are metal–metal antibonding $(t_1 + t_2)$ orbitals. Thus, both reduction and oxidation will tend to weaken the metal–metal interactions in such clusters, leading to fragile cluster anions and cations or cluster breakdown. In order to maintain the metal core intact, the role of the ligands is examined in this section. If cluster integrity is to be preserved, for instance during homogeneous catalysis, chelating ligands may avoid fragmentation. Examples of prevented fragmentations of reduced and oxidized cluster anion and cation radicals are provided below.

An electrochemical comparative study has been made [69] of the tetranuclear clusters $[Co_4(CO)_{12-2n}\ (Ph_2PCH_2PPh_2)_n]$ ($n = 0$, 1, 2) in order to determine the ligand effects (Fig. 1, clusters **I**, **II**, **III**).

Whereas cluster **III** shows the $(+1/0)$, $(0/-1)$, $(-1/-2)$ redox couples to be reversible, only the $(0/-1)$ redox couple is reversible for clusters **I** and **II**. Successive substitution of the CO ligands by the chelating ligands $(Ph_2PCH_2PPh_2)$, reinforce the cluster cohesion as shown by the changes in the redox properties followed in situ by cyclic voltammetry. The cluster anions were characterized by their ESR signals. A relationship is observed between the number of phosphorus ligands and the $E_{1/2}$ of the $(0/-1)$ redox couples, and also with the electronic frequencies corresponding to a metal–metal transition. The frontier orbital LUMO energy ΔG is increased by about 10.5 kcal per $(Ph_2PCH_2PPh_2)$ ligand bonded to the cluster (calculated for the first reduction step). The electrochemical standard rate



IV V

Fig. 2. Schematic representation of clusters **IV**, [$Co_4(CO)_9$ tripod] and **V**, [$Co_4(CO)_6(\pi$-toluene)tripod].

constant for this transfer was found to be of the same order of magnitude for all the clusters studied, $k_s = 4.4 \times 10^{-3}$ cm s^{-1}.

These results are in agreement with those previously obtained [5] on the series $Fe_3(CO)_{12-n}$ L_n ($n = 0, 2$; L = PPh_3). Each CO replaced by a PPh_3 ligand caused a cathodic shift of ca. 200 mV of the first reduction potential.

Another electrochemical study [70] of the effect of the tripod ligand ($HC(PPh_2)_3$) capping one face of the tetrahedron (Fig. 2) confirmed these conclusions. The electrochemical behaviour of cluster **IV** is quite similar to that of cluster **III**. Substitution of three CO by the tripod ligand would be expected to shift the $E_{1/2}$ of the $(0/-1)$ redox couple by 600 mV cathodically, in close agreement with the value of 590 mV experimentally obtained. Comparable values of k_s and ΔG were obtained for clusters **IV** and **V**. A cathodic shift of ca. 450 mV was obtained for the $E_{1/2}$ corresponding to first reduction of cluster **V** compared with **IV** which is similar to that found in the electrochemical first oxidation step of these compounds. As expected, the tripod stabilized clusters are easier to oxidize than the parent [$Co_4(CO)_{12}$], but this oxidation process is only reversible for complexes **IV** and **V**. In the radical anion $[\mathbf{IV}]^{\dot{-}}$, a CO ligand apically bonded to the cobalt atom was found to be substitution labile. Indeed, no electron-induced ligand substitution was obtained with $[\mathbf{V}]^{\dot{-}}$, whereas $[\mathbf{IV}]^{\dot{-}}$ was easily substituted.

The nature of the metal influences the electrochemistry of the tetrahedral carbonyl clusters $M_4(CO)_{12}$ ($M_4 = Co_4$, Co_2Rh_2, Rh_4). The redox behaviour of cluster **IV** was examined when the Co_4 unit was replaced by a Co_2Rh_2 (cluster **VI**) and a Rh_4 (cluster **VII**) metallic core in the [$M_4(CO)_9$

tripod] cluster series. Only a small difference between the half-wave potentials of compounds **IV** and **VI** was obtained. In contrast, complex **VII** exhibits one-electron reduction and oxidation steps at more negative potentials. Thus, in the complex **VI**, the LUMO energy level is not greatly displaced compared with that for complex **IV**, in agreement with a small Rh component. Under CO gas, the reversibility of the first reduction step of **VII** is enhanced. The decomposition of the radical anion $[\mathbf{VII}]^{\dot{-}}$ involves the reversible loss of CO. The effect of cation size of the supporting electrolyte on the redox behaviour of **VII** has also been examined [70]. Thus, the reduction potentials in all these complexes are cathodically shifted as the basicity of metals increases. Furthermore, the stability of the anion radicals formed decreases as the metal basicity increases from Co to Rh. Similar conclusions were reached [70] from the electrochemical study of the isostructural series $M_4(CO)_{12}$ ($M_4 = Co_4, Co_2Rh_2, Rh_4$).

Another series of clusters studied in this laboratory [71] involved replacement of one Co atom by an Fe or Ru atom. These $[MCo_3(CO)_{12}]^-$($M = Fe$, Ru) clusters are anionic compounds which exhibit two close one-electron reductions at potentials more cathodic than the analogous $[Co_4(CO)_{12}]$ complex. They are more difficult to reduce as the basicity of the metal increases from Fe to Ru. In a poor donor solvent, like 1,2-$C_2H_4Cl_2$, the two waves overlap, whereas in donor solvents (DMF, DMSO, CH_3CN) the two waves are separated by about 200 mV. A radical is generated at the first reduction step, as shown by ESR (22 lines hyperfine structure). In a poor donor solvent, this radical is immediately reduced to a dianionic species, whereas in a donor solvent, an electrochemical transfer catalyzed reaction, in which a CO ligand is exchanged with a solvent molecule, occurs. The stability of the reduced species is low; among the fragmentation products $[Co(CO)_4]^-$ could be characterized. An irreversible four-electron oxidation leads also to cluster fragmentation, as obtained with the cluster parent $[Co_4(CO)_{12}]$.

The two reduction waves could be separated by about 600 mV with the butterfly cluster $[MCo_3(CO)_{10}C_2Ph_2]^-$ in which the C_2Ph_2 ligand increases the stability of the reduced species.

These few examples taken in the Co_4 series show that these basically tetrahedral clusters have very homogeneous electrochemical behaviour which may be strongly dependent on the ligand environment.

The effect of different ligand environments on the electronic structure of tetrahedral clusters like $[Co_4(CO)_{12}]$, $[(\eta\text{-}C_6H_6)Co_4(CO)_9]$, $[Co_4(CO)_9$ tripod], $[(\eta\text{-}C_6H_6)Co_4(CO)_6$ tripod] has been examined recently [72] by SCF-X_α-DV calculations. These theoretical results were compared with spectroscopic and electrochemical measurements and the following conclusions reached:

(i) There is a strong correlation between the calculated charge on the tetracobalt core and the ease of cluster reduction and oxidation ($E_{1/2}$).

(ii) Redox potentials do not correlate well with the HOMO and the LUMO energies.

(iii) Ligand effects are additive, which allows the prediction of redox potentials and supports the notion of delocalized cluster bonding.

(iv) Tetrahedral metal clusters behave as delocalized sources and sinks of electrons.

The unsaturated clusters $[Os_4(CO)_{12}(AuPR_3)_2]$ ($R_3 = Et_3$, Ph_3, $MePh_2$) undergo two reversible one-electron reductions, to the $[Os_4(CO)_{12}(AuPR_3)_2]^-$ and $[Os_4(CO)_{12}(AuPR_3)_2]^{2-}$ anions [73]. The existence of mono-anionic species was confirmed by ESR spectroscopy. The reduction can also be achieved chemically (4% Na–Hg amalgam): the unstable dianion was characterized by IR ν_{CO} absorption bands.

The enhanced reactivity of carbonyl cluster anions has recently been utilized in the catalytic reduction of terminally unactivated olefins. The reaction sequence in which the first step is the loss of a carbonyl ligand [74]

$$[Ru_3(NCO)(CO)_{10}]^- \rightleftarrows CO + [Ru_3(NCO)(CO)_9]^-$$

$$[Ru_3(NCO)(CO)_9]^- + H_2 \rightarrow [H_2Ru_3(NCO)(CO)_9]^-$$

$$[H_2Ru_3(NCO)(CO)_9^- + \text{olefin} + CO \rightarrow \text{alkane} + [Ru_3(NCO)(CO)_{10}]^-$$

is the first example of a catalytic reaction that proceeds under mild enough conditions that the cluster may remain intact during the cycle. The first step is reminiscent of the CO loss in the electron-induced substitution reaction.

Thus, the reactivity of anionic radical clusters with various nucleophiles will be adaptable to homogeneous reaction conditions, leading to new interesting syntheses. An important question that remains unsolved as yet is the reaction of radical cation clusters with nucleophilic and electrophilic reagents, currently under investigation in this laboratory [65].

(iii) Cubane-like cluster electrochemistry

Clusters with four metal atoms containing four triply bridging ligands are model systems in bacterial ferrodoxins and in iron sulphur proteins [75]. As they undergo several reversible one-electron transfer reactions, they are considered as electron "sponges". The structural distortions occurring upon redox reactions have been reviewed recently [76]. Examples of such well known compounds are the following clusters: $[(\eta^5\text{-}C_5H_5)_4Fe_4L_4]$ (L = S or CO), $[Fe_4S_4(SR_4)]^{2-/3-}$ ($R = p\text{-}C_6H_4Me$, CH_2Ph and the Se analogue $[Fe_4Se_4(S\text{–}p\text{-}C_6H_4Me)_4]^{2-/3-}$, $[Fe_4S_4(S\text{–}cys)_4]$ (cys = cysteine, in ferredoxin), $[Fe_4(NO)_4(\mu_3\text{-}S)_4]$ [77].

It has been shown that $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_8]^{3-}$ catalyze the reduction of C_2H_2, both in MeOH/THF and in H_2O [78], and of C_2D_2 in H_2O [79] under controlled-potential electrolysis, giving C_2H_4 and $C_2D_2H_2$. Furthermore, CH_3NC and CH_3CN undergo catalytic successive two-electron reductions at the triple bonds by the reduced species of those clusters [80]. Also the $[Fe_4S_4(SR)_4]^{2-}$ anionic cluster has been shown to catalyze the electroreduction of carbon dioxide to formate in DMF solution, and CO [81] at a more anodic potential of (~ 0.7 V) than that of CO_2.

Synthetic analogues for the Fe_4S_4 centers in non-heme iron proteins are well known. These complexes have been extensively studied mainly by Holm and Ibers [82]. In clusters of this type, the iron atoms in the Fe_4S_4 cores are tetrahedrally coordinated by three of the triply bridging sulfide ions and a terminal RS^- or Cl^- ligand. Mixed terminal ligand clusters have also been characterized, and studied electrochemically, e.g., $[Fe_4S_4(SR)_{4-n}X_n]^{2-}$ ($n = 1$–4, $X = Cl^-, OAc^-$) [83], $[Fe_4S_4(SPh)_2Cl_2]^{2-}$ [84], $[Fe_4S_4(SPh)_2(Et_2dtc)_2]^{2-}$ [85] (dtc = dithiocarbamate), $[Fe_4S_4(Et_2dtc)_4]^-$ and $[Fe_4S_4(Et_2dtc)_4]$ [86]. A simple hydrocarbon electrolyte $(n\text{-}Bu_4N)BF$, (3 toluene) allows the observation of all members of the $[Fe_4S_4(SPh)_4]^{n-}$ electron-transfer series, with $n = 1$–4 [87]. The structural and redox chemistry of the clusters $[Fe_4S_4(SR)_4]^{2-}$ (R = t-alkyl) have been investigated [88] in order to determine the same cluster in different environments and the stability of the oxidized species $[Fe_4S_4(SR)_4]^-$.

A novel cubane-type cluster with the Mo_4S_4 core, $[Mo_4S_4(edta)_2]^{3-}$ (edta = ethylenediaminetetraacetate^{4-}) has been synthesized. The cluster undergoes two quasi-reversible one-electron waves, leading to the dianion and tetraanion without drastic change in structure [89]. Electrochemical studies of $[Fe_4S_4(S\text{–}2,\ 4,\ 6\text{-}(i\text{-}Pr)_3\ C_6H_2)_4]^{2-}$ and $[Fe_4S_4(S\text{–}2,3,5,6\text{-}Me_4C_6H)_4]^{2-}$ show the $-1/-2$ redox couple to be reversible [90]. In the series $[Fe_4S_4(SR)_4]^{1-,2-,3-}$, the Fe–SR distances clearly increase as the mean oxidation state decreases [91]. The recently synthesized cluster $[V\ Fe_3S_4Cl_3(DMF)_3]^-$ has a mean Fe oxidation state $\leq +2.5$ [92].

An extensive series of synthetic Mo–Fe–S clusters with the $MoFe_3S_4$ cubane core is known [93]. About ten Mo–Fe–S double-cubane and two single-cubane clusters have been determined by X-ray diffraction methods. Several features of these clusters are similar to those of the Mo sites in MoFe protein·and the MoFe cofactor of the enzyme nitrogenase [94]. Electron-transfer series of the $MoFe_3S_4$ double cubane clusters: $[Mo_2Fe_6S_8(SR)_8]^{n-}$ ($n = 2$–5), $[Mo_2Fe_6S_8(\mu_2\text{-}OMe)_3\ (S\text{–}t\text{-}Bu)_6]^{n-}$ ($n = 1$–5) have been investigated [95], together with those of several related clusters [96,97]. Single cubane-type clusters with the MFe_3S_4 core (M = Mo, W) have been synthesized and the properties of their oxidized and reduced forms examined [98]. The structural properties of the reduced cluster $[(Fe_4S_4(SR)_4]^{3-}$

substantiate that the $-2/-3$ redox couple is isoelectronic with the prevalent electron-transfer process of ferrodoxins containing [4 Fe–4 S] sites [99].

Parallel to these studies, both bacterial and plant proteins can be reduced when Mg^{2+} promotes electron transfer by forming a bridge between the highly negatively charged ferrodoxin molecule and carboxylate groups on the graphite electrode surface [100]. In addition, the existence of a facile cluster oxidation process for clostridium pasteurianum ferrodoxin was established according to the reaction [101a].

$$[4\ \text{Fe–4 S}]^{2+} \rightleftarrows \underset{\substack{\downarrow \\ \text{degradation products}}}{[4\ \text{Fe–4 S}]^{3+}} + e$$

Reactions of electron-transfer proteins at electrodes have been reviewed recently [101b]. Recent reports [79,80,102,103] indicate that the $[Mo_2Fe_6S_8(SR)_8]^{5-}$ double-cubane cluster may have catalytic properties similar to those of nitrogenase where the enzyme is an electron-transfer mediator in the biological reduction of nitrogen to ammonia [104].

Cyclic voltammetry shows that the clusters $[Mo_2Fe_6S_8(SR)_9]^{3-}$ ($R = p\text{-}C_6H_4Cl$, C_6H_5, $p\text{-}C_6H_4CH_3$, C_2H_5) undergo two successive one-electron reductions, the standard heterogeneous electrochemical rate constants of which have been estimated to be $\sim 2 \times 10^{-2}$ cm s^{-1} [105]. The multielectron reductions of alkyl azides with $[Mo_2Fe_6S_8(SPh)_8]^{3-}$ and $[Mo_2Fe_6S_8(\mu\text{-}SEt)_3(SCH_2CH_2OH)_6]^{3-}$ in homogeneous systems and with a $\{(n\text{-}Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]\}$ modified glassy-carbon electrode lead to ammonia and hydrazine as eight and six-electron products, respectively, accompanied by other identified products, with large turnover numbers [106].

(iv) Halide clusters of molybdenum and tungsten

The discovery of intense luminescence from $[Mo_6Cl_{14}]^{2-}$ [107] and the analogous $[Mo_6Br_{14}]^{2-}$ and $[W_6Cl_{14}]^{2-}$ [108] clusters has led Gray and coworkers to investigate chemical and electrochemical properties of Mo and W halide clusters. Five $[M_6X_{14}]^{2-}$ (M = Mo, X = Cl, Br; M = W, X = Cl, Br) cluster ions exhibit reduction waves. A quasi-reversible reduction wave for $(MoCl_{14})^{2-}$ was attributed to the $[Mo_6Cl_{14}]^{2-/3-}$ couple [109].

The $\{[(n\text{-}C_4H_9)_4N]_2\ Mo_5Cl_3\}$ and $\{[(n\text{-}C_4H_8)_4N]_2Mo_5Br_{13}\}$ clusters show two quasi-Nernstian redox couples in CH_2Cl_2 solutions [110]. Both their electrochemically stable oxidation and reduction products, $[Mo_5X_{13}]^-$ and $[Mo_6X_{13}]^{3-}$ respectively, have been isolated as their tetrabutylammonium salts and studied by their electronic and EPR spectra as well as magnetic susceptibility measurements at variable temperature.

(v) One-electron irreversible transfer reactions

Electrochemically generated radicals may have short lifetimes, leading to irreversible one-electron transfers on the mean cyclic voltammetry time scale. For instance, clusters of the series $[(M\{\mu_2\text{-}M'(NR_2)_2\}(CO))_3]$ ($M =$ Pd, Pt; $M' =$ Ge, Sn) undergo reversible one-electron reductions followed by two irreversible reduction steps at more negative potentials [111]. In contrast, each related complex $\{M[M'(NR_2)_2]_3\}$ undergoes two irreversible reduction steps. ESR used to characterize first reduction products indicates that the Pd-containing radical anions are less stable than the corresponding Pt-containing species $[(Pt\{\mu\text{-}M'(NR_2)_2\}(CO))_3]$.

Also the redox properties of the cluster $[Ru_3(CO)_{12}]$ have been reexamined [112] in detail. The reduction includes a two-electron exchange and ring opening to give $[Ru_3(CO)_{12}]^{2-}$ which then undergoes CO loss followed by ring closure to give the $[Ru_3(CO)_{11}]^{2-}$ anion. The intermediates in the scheme are the linear anion $[Ru_3(CO)_{12}]^{\dot{-}}$ and the triangulo anions $[Ru_3(CO)_{12}]^{\dot{-}}$ and $[Ru_3(CO)_{11}]^{\dot{-}}$.

The triangular anion cluster $[HRu_3(CO)_{10}(SiEt_3)_2]^-$ has been studied by X-ray crystallography, NMR spectroscopy and electrochemical methods [113]. The reaction

$$[H\,Ru_3(CO)_{11}]^- + 2\,Et_3SiH \rightleftarrows [H\,Ru_3(CO)_{10}(SiEt_3)_2]^- + CO + H_2$$

could be monitored in situ by cyclic voltammetry. The one-electron oxidation of the anion leads to the neutral cluster which has a short lifetime.

Five cluster ions $[M_6X_{14}]^{2-}$($M =$ Mo, $X =$ Cl, Br; $M =$ W, $X =$ Cl, Br, I) show irreversible oxidation waves at potentials more positive than their respective one-electron oxidation couples [109].

The unsaturated clusters $[Os_4(CO)_{12}(AuPR_3)_2]$ ($R_3 = Et_3$, Ph_3, $MePh_2$) undergo two irreversible one-electron oxidation steps at −40 °C [73].

Thus, clusters with metals of lower basicity (for instance Pd compared to Pt), with weak donor ligands and with unsaturated valence-electron count (58 e^- instead of 60 e^- for a tetranuclear carbonyl cluster), may undergo irreversible one-electron transfer reactions.

C. MULTIELECTRON TRANSFER PROCESSES IN CLUSTERS

(i) Mechanism of the electrochemical metal–metal bond rupture

Whereas most clusters undergo multiple one-electron redox steps, a number of other clusters exhibit two-electron waves that involve structural changes which it is often not possible to characterize. A single, two-electron reduction requires that the reduction potential for the introduction of the second electron to be more anodic than that of the first. As the first electron enters into a σ-antibonding molecular orbital of metal–metal bond character, the metal bond order is weakened, the energy of the LUMO is lowered and hence the second reduction is thermodynamically more favorable than the first. Several such examples involving bielectronic processes have been reported.

The binuclear complex $[Fe_2(PPh_2)_2(CO)_6]$, in which the $Fe_2(PPh_2)_2$ core is non-planar (the crystallographic Fe–Fe distance is 2.623 Å) exhibits a single two-electron reduction to the corresponding dianion [114]. The crystal structure of the latter shows the Fe_2P_2 core to be planar and the absence of an iron–iron bond is apparent from the Fe–Fe separation of 3.630 Å. Thus, the two-electron reduction causes metal–metal bond breaking. Bridging ligands like PPh_2 avoid fragmentation, but a different geometry of the reduced complex is obtained. The mechanism of the electrochemical metal–metal bond rupture in dimetallic carbonyl complexes without bridging ligands has been investigated recently [115,116].

The overall two-electron irreversible reduction of $[Mn_2(CO)_{10}]$ and $[M(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (M = Mo, W) leads to anions according to

$$M{-}M + 2e \rightarrow 2M^-$$

where $M = Mn(CO)_5$, $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ and $W(CO)_3(\eta^5\text{-}C_5H_5)$.

The electrochemical and ESR results are consistent with an ECE mechanism

$$\text{E} \qquad M{-}M + e \rightarrow [M{-}M]^-$$

$$\text{C} \qquad [M{-}M]^- \xrightarrow{\text{fast}} M^- + M^\cdot \text{ (heterolytic cleavage of the metal–metal bond)}$$

$$\text{E} \qquad M^\cdot + e \rightleftarrows M^-$$

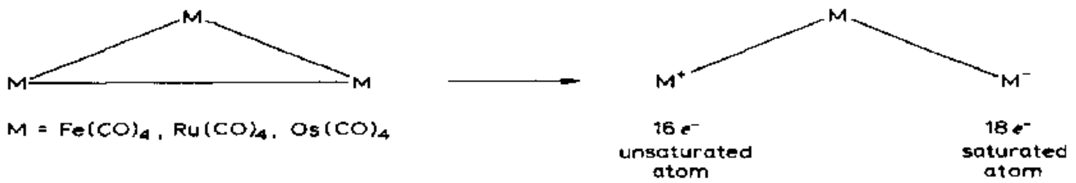
The mechanism of the electrooxidation has also been published

$$M{-}M \rightleftarrows [M{-}M]^+ + e$$

$$[M{-}M]^+ \xrightarrow{\text{fast}} M^+ + M^\cdot$$

$$M^\cdot \rightleftarrows M^+ + e$$

Thus, both oxidation and reduction result in metal bond cleavage. This is not surprising as the LUMO orbital involved in reduction is antibonding metallic in character whereas the HOMO involved in oxidation is a bonding orbital [114].



Scheme 1

In the series of carbonyl clusters $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) an alternative mechanism for chemical substitution of the CO ligands by more basic ligands has been presented [117]. The key step is the heterolytic rupture of a metal–metal bond in the trimetal unit, according to Scheme 1.

This mechanism may also apply to clusters of higher nuclearity and lower symmetry such as $[Os_6(CO)_{18}]$ [117].

Similar conclusions can be extended to clusters which possess several metal–metal bonds as has been noted by Lauher [7].

(ii) Structural changes induced by electron transfer

Structural changes accompanying electrode reactions in clusters have been reviewed recently by Geiger [118]. About twenty systems are discussed, comprising triangular, cubane-like, octahedral and larger clusters like metallocarboranes. The molecular changes that occur with organometallic compounds during charge-transfer reactions have been reviewed [119].

For a two-electron transfer, a concerted process or a stepwise process with a detectable intermediate may occur. Another difficulty is that most of the electrochemical reactions are not chemically reversible. Cluster breakdown occurs by oxidation, reduction, or the addition of a donor ligand. The resulting fragments, which are very reactive, often rearrange into molecules of lower nuclearity which must be isolated and identified by analytical methods.

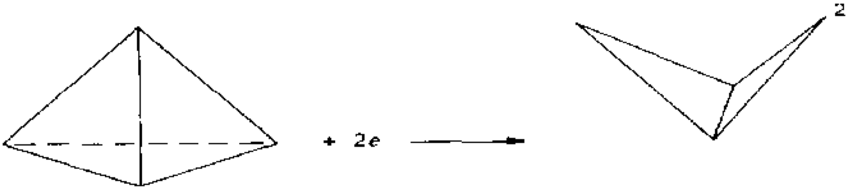
The cluster $[Os_6(CO)_{18}]$ undergoes a chemically reversible two-electron reduction near 0.0 V, leading to the corresponding dianion. Whereas the starting neutral complex has a bicapped tetrahedral structure, the dianion has an octahedral metallic core. The authors [120] showed that stepwise one-electron transfers occur ($E_0^2 > E_0^1$). The first electron-transfer step is followed by a structural change from the bicapped tetrahedron to an octahedron. On the contrary, the ruthenium analog $[Ru_6(CO)_{18}]^{2-}$ which is oxidized at +0.17 V gives a highly unstable product. The electrochemical synthesis of the neutral cluster from the dianion was unsuccessful.

Another example of reorientation in clusters induced by electron transfer is obtained with the 46-electron *closo*-$Fe_3(CO)_9(RC_2R)$ series and the related *nido*-$H_2M_3(CO)_9(EtC_2Et)$ (M = Ru, Os), $[Os_3(CO)_{10}(EtC_2Et)]$ and $[FeCo_2(CO)_9(EtC_2Et)]$ complexes [121]. In the *nido* series, two irreversible one-electron reduction steps have been observed, leading to the mono- and di-anions associated with cluster breakdown. In contrast, the *closo* clusters undergo two near reversible one-electron reduction steps. Spectroscopic data on the electrochemically generated dianions strongly suggest that the orientation of the alkyne moiety relative to the metallic triangle is changed from perpendicular to parallel. The changes in the acetylene ligand orientation in clusters has recently been reviewed [122].

(iii) Heteronuclear metal clusters

The most studied tetranuclear carbonyl clusters are $[M_4(CO)_{12}]$ (M = Co, Rh, Ir) with a C_{3v} solid state structure for Co and Rh clusters only, and full T_d symmetry, for the Ir cluster, all having 60 valence electrons.

As predicted by the calculations (LCAO-MO semiempirical) of Lauher [7], if two electrons are added to the antibonding orbital LUMO corresponding to the two-electron bond along the edge of the metallic M_4 tetrahedron, a butterfly structure with 62 electrons should result:



The anion $[Re_4(CO)_{12}]^{2-}$ is an example of such a 62-electron ion with the D_{2h} butterfly geometry [7].

Clusters having many close metal–metal interactions with "close-packed" compact structures (like $M_4(CO)_{12}$) resemble the bulk metal more closely than do clusters with "open" structures (like $[Re_4(CO)_{12}]^{2-}$).

Thus from our experimental studies on clusters we distinguish two families of compounds: (i) those with "close-packed" structures (for which the electron-reservoir concept holds) which undergo multiple reversible one-electron reduction/oxidation steps in which the metallic core remains intact [123], (ii) those with "open" structures which behave rather like metal–metal bonded compounds [124,125]: the electrochemical reduction/oxidation reactions result in an irreversible opening of a metal–metal bond (overall two-electron irreversible transfer which may be interpreted in terms of the mechanisms proposed by Kadish et al. [115,116]). These properties may be illustrated by the following examples.

In the $[M_4(CO)_{12}]$ (M = Co, Rh) series, the related $(M_4(CO)_{12-n}P_n]$ (P = phosphine ligands) clusters undergo two successive one-electron reduction steps and a single one-electron oxidation step [70] when chelating phosphine ligands are able to stabilize the radical anion/cation obtained. These radicals can be characterized by their ESR spectra. Also, the "close-packed" structure carbide cluster $[Co_8(CO)_{18}C]^{2-}$ undergoes several one-electron steps [123]. The heteroatom carbon reinforces the stability of the radicals electrochemically generated.

In contrast, in the "open-structure" planar clusters of the series $[M_2M'_2(CO)_6(\eta^5\text{-}C_5H_5)_2(PR_3)_2]$ (M = Pt, Pd; M′ = Cr, Mo, W) (Fig. 3) the

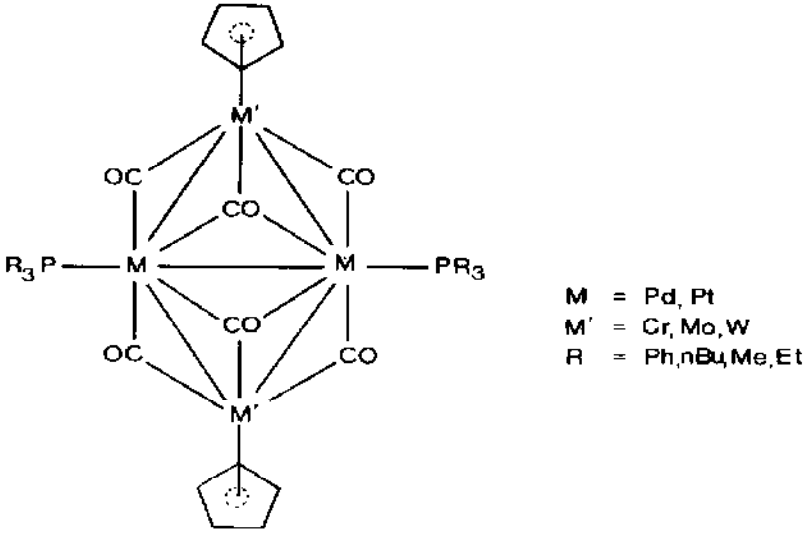


Fig. 3. The planar clusters $[M_2M'_2(CO)_6(\eta^5\text{-}C_5H_5)_2(PR_3)_2]$.

compounds undergo an overall irreversible two-electron reduction step leading to their fragmentation into products of lower nuclearity [124]. Thus after exhaustive reduction (2 F mol^{-1}), two types of cluster fragments could be identified: $[M'(CO)_3(\eta^5\text{-}C_5H_5)]^-$ anion and zero-valent M-containing species. From the experimental results, it was assumed that the LUMO is antibonding and mainly centered on the Pt–Pt or Pd–Pd bond in the compounds. The clusters behave during reduction like binuclear metal–metal bonded carbonyl complexes rather than delocalized sinks of electrons. These compounds also undergo two one-electron oxidation steps. The monocations generated at the first oxidation are stable as seen by their ESR signals which are consistent with a hole delocalized on the four metals, weakly interacting with the metallic centers (no hyperfine structure). The dications obtained are only stable for $M = Pt$ and $M' = Mo$, W, on the time-scale of cyclic voltammetry. Thus, in contrast to reduction [125] these compounds behave in oxidation as delocalized sources of electrons.

The role of solvent donicity is also of importance for the stabilization of reduced and oxidized cluster species. For instance, in donor solvent [126] like DMF or DMSO, the cluster anion $[RuCo_3(CO)_{12}]^-$ undergoes two one-electron reduction steps, whereas only a single two-electron wave is obtained in the poor donor solvent 1,2-$C_2H_4Cl_2$ [127]. Thus it is possible in this example to separate a single two-electron wave into two one-electron waves.

Clusters built around the Pd–Pd, Pd–Pt or Pt–Pt bond (all metals being in the formal +1 oxidation state) constitute a new class of heterometallic

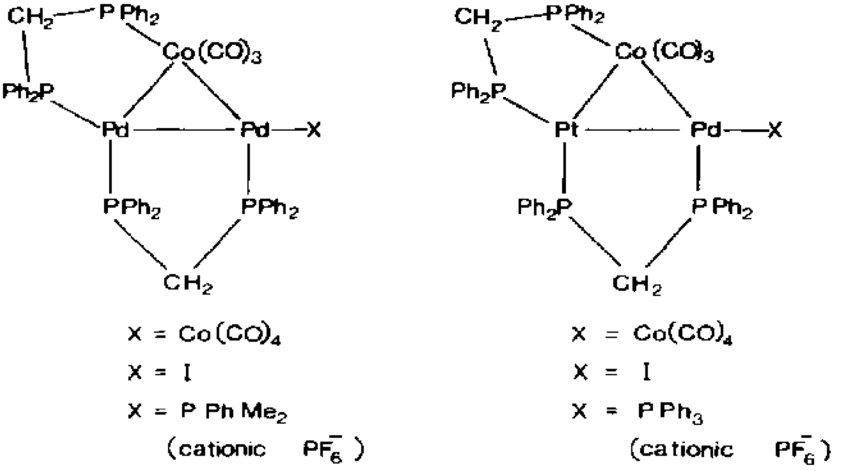


Fig. 4. The triangular clusters with the Pd_2Co and PtPdCo metal core.

compounds. As an example, the triangular cluster $[CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3]$ in which the Pt–Pt bond is bridged by a PPh_2 group and by the $[Co(CO)_3PPh_3]$ group, exhibits an electrochemically reversible one-electron reduction. The reduced species is unstable and the $[Co(CO)_3PPh_3]^-$ anion has been identified as one of the decomposition products [128]. An irreversible one-electron oxidation also occurs at 0 V vs. S.C.E. The cluster is easier to oxidize and more difficult to reduce than two other triangulo-clusters with a $PtCo_2$ core: $[Co_2Pt(\mu\text{-}CO)(CO)_7PPh_3]$ and $[Co_2Pt(\mu\text{-}CO)(CO)_6(Ph_2PCH_2CH_2PPh_2)]$ [129]. This result is in agreement with a strengthening effect of the bridging group $\mu\text{-}PPh_2$.

Furthermore, the nature of the metal atoms, Pd or Pt, in the metal–metal bond may influence the electrochemical reduction. Thus, in DMSO, the triangular $[Pd_2CoI(CO)_3(\mu\text{-dppm})_2]$ and $[\{Pd_2Co(CO)_3(\mu\text{-dppm})_2PR_3\}(PF_6)]$ clusters, both of which contain a Pd–Pd bond, undergo two quasi-reversible one-electron reductions, whereas the related compounds with Pt–Pd bonds, $[PtPdCoI(CO)_3(\mu\text{-dppm})_2]$ and $[\{PtPdCo(CO)_3(\mu\text{-dppm})_2PR_3\}PF_6]$ (Fig. 4) undergo a single quasi-reversible two-electron reduction (dppm = $Ph_2PCH_2PPh_2$). Similar results were obtained on the cluster $[Pd_2Co(CO)_3(CO)(\mu\text{-dppm})_2]PF_6$ and the corresponding compound with a Pd–Pt bond [130].

Similar conclusions are also found [131] for the tetranuclear complexes $[Pd_2Co_2(CO)_7(\mu\text{-dppm})_2]$ (two one-electron reductions) and $[PtPdCo_2(CO)_7(\mu\text{-dppm})_2]$ (a single two-electron reduction step). In the latter compounds, the metallic core consists of a Pd_2Co or a PdPtCo triangle to which a $[Co(CO)_4]$ group is coordinated through a Pd–Co or Pt–Co exocyclic bond.This bond is easy to cleave, which offers an enhanced reactivity for anion exchange.

The triangular clusters, $[M_2Co(CO)_2(dppm)_3]^+$ ($M_2 = Pd_2$, PdPt), in which the M_2Co core is maintained on each edge by a dppm ligand undergo reversible two-electron oxidations in DMSO, in a single step. The role of the chelating ligands appears to be important in maintaining the clusters' cohesion [133].

A single irreversible four-electron oxidation step is common with clusters of the type $[M_4(CO)_{12}]$ (M = Co, Rh) [69,70], leading to cluster breakdown.

(iv) Electrochemistry of carbide clusters

The "close-packed" structure of carbide clusters and other compounds for which an heteroatom (C,N,S,P) maintains the metal core, may be responsible for original redox behaviour in this type of complex. For example, in $[M_5(CO)_{15}C]$ clusters (M = Fe, Ru, Os), the carbide inside the metal core may be considered to hold the cluster together. It donates four electrons to the cluster without occupying coordination sites on the periphery.

The cluster $[Fe_5(CO)_{15}C]$ was shown to be reduced to the dianion $[Fe_5(CO)_{14}C]^{2-}$ in a single two-electron transfer followed by the loss of one CO ligand [133].

The electrochemical (and chemical) reduction of $[M_5(CO)_{15}C]$ clusters (M = Ru or Os) produces [134] the corresponding dianion $[M_5(CO)_{14}C]^{2-}$. X-ray analysis of the $[N(PPh_3)_2]^+$ salt of the osmium cluster $[Os_5(CO)_{14}C]^{2-}$ shows that the square pyramidal Os_5C core geometry is retained. The dianion $[Os_5(CO)_{15}C]^{2-}$ reacts with two equivalents of $[Au(PPh_3)Cl]$ to give the neutral complex $[Os_5(CO)_{14}C\{Au(PPh_3)\}_2]$.

The cluster $\{[Co_8(CO)_{18}C](NMe_3CH_2C_6H_5)_2\}$ undergoes three one-electron reversible steps, whereas the clusters $\{[Co_6(CO)_{15}C](NMe_3CH_2C_6H_5)_2\}$ and $\{[Rh_6(CO)_{15}C](Et_4N)_2\}$, show irreversible reduction and oxidation steps [123]. This difference may be ascribed to structural differences between the compounds (Fig. 5). For $[Co_8(CO)_{18}C]^{2-}$, the Co–Co distances are all of the same order of magnitude ("close-packed" cluster) whereas in $[Co_6(CO)_{15}C]^{2-}$ there are fewer close metal–metal interactions ("open" geometry). Also, the charge distribution for $[Co_6(CO)_{15}C]^{2-}$ may be responsible for the lower stability of its oxidized and reduced forms compared with that of the $[Co_8(CO)_{18}C]^{2-}$ cluster anion. In the isostructural clusters, $[Co_6(CO)_{15}C]^{2-}$ and $[Rh_6(CO)_{15}C]^{2-}$ (trigonal prismatic, 90 valence electrons), the Co complex is easier to reduce than the Rh complex as expected from the increase of the metal–metal interaction and of the metal basicity from Co to Rh, which shifts the antibonding LUMO level to higher energy.

These redox properties may be compared to that obtained by Zanello et al. [135] on the metal–sulfur cluster $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$ having octahedral

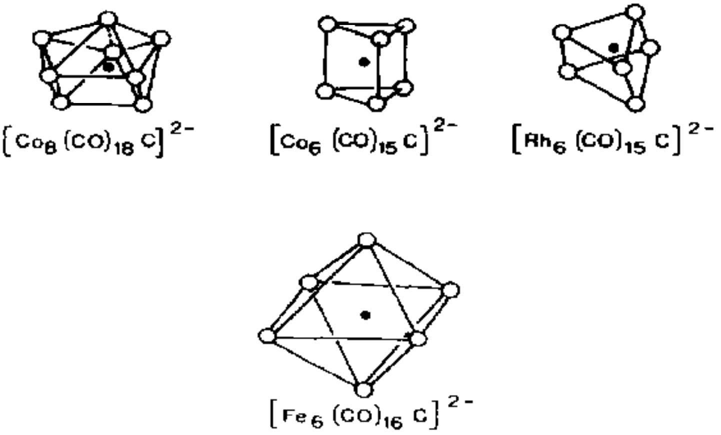


Fig. 5. The metallic core of the carbide clusters.

close-packed structure. Three quasi-reversible oxidation–reduction steps are accessible by cyclic voltammetry: a cathodic one-electron reduction and two anodic one-electron oxidations. Thus, four oxidation states 0/+1/+2/+3 of the cluster may be reached in which the 0/+1 and +2 cluster form have been characterized [135,137], according to

$$[Co_6S_8(PEt_3)_6] \underset{+e}{\overset{-0.5\text{ V}}{\rightleftarrows}} [Co_6S_8(PEt_3)_6]^+ \overset{+0.25\text{ V}}{\underset{}{\overset{-e}{\rightleftarrows}}} [Co_6S_8(PEt_3)_6]^{2+}$$

$$\overset{+0.95\text{ V}}{\overset{-e}{\rightleftarrows}} [Co_6S_8(PEt_3)_6]^{3+}$$

The cluster of higher nuclearity with the Co_8 framework shows only three oxidation states [135], according to

$$[Co_8S_6(SPh)_8]^{5-} \underset{+e}{\overset{-1.12\text{ V}}{\rightleftarrows}} [Co_8S_6(SPh)_8]^{4-} \underset{+e}{\overset{-0.52\text{ V}}{\rightleftarrows}} [Co_8S_6(SPh)_8]^{3-}$$

(v) Electrochemical synthesis of clusters

Several examples of this promising field are now available in the literature, including cluster modifications by ligand exchange.

A detailed electrochemical study of the overall two-electron reduction of the $[Au_9(PPh_3)_8]^{3+}$ cluster ion has been published [138]. Two consecutive one-electron transfers (ECE mechanism), separated only by 40 mV in their half-wave potentials occur, followed by a fast conproportionation equilibrium with a constant of 4.7 at 298 K according to:

$$[Au_9(PPh_3)_8]^{3+} + [Au_9(PPh_3)_8]^{+} \rightleftarrows 2[Au_9(PPh_3)_8]^{2+}$$

ESR experiments on the paramagnetic radical dication suggest that the energy differences between the +1, +2 and +3 oxidation states are small. The entropy differences between the +3 and +1 cluster ions is attributed to solvent reorganization and not to the accompanying structural changes. The $[Au_9(PPh_3)_8]^+$ cluster cation could be isolated during the cathodic reduction ($2\ F\ mol^{-1}$) of the corresponding trication [139], recrystallized (yield 40–50%) and characterized by X-ray crystallography. Differences in the crystallographic structure of the (+1) and (+3) cluster cations are apparent, but in solution the situation is not necessarily the same, as shown by the solution NMR spectra of both species. Stereospecific selective electrochemical synthesis of isomers of $\{(CF_3)_6C_6Co_2(CO)_2[P(OMe)_3]_2\}$ have been achieved via radical anions [47].

Electron-transfer catalyzed reactions (see Section A) offer a rapid and efficient route for the synthesis of new compounds or modified clusters. For example, the synthesis of mixed cluster $[RCCo_2M(\eta^5\text{-}C_5H_5)(CO)_8]$ (R = Me, Ph, H; M = Cr, Mo, W) with the Co_2M (M = Cr, Mo) framework may be achieved by direct nucleophilic attack of $[M(CO)_3(\eta^5\text{-}C_5H_5)]^-$ on the electrochemically generated $[RCCo_3(CO)_9]^-$ cluster radical anion [34].

Exchange of a $Co(CO)_3$ unit in a radical anion, electrochemically generated $\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6\}^{\dot{-}}$ by the isoelectronic fragment $[Mo(CO)_2(\eta^5\text{-}C_5H_5)]$, occurs in the presence of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$, leading to the new complex [39] $[(CO)_3Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2(\eta^5\text{-}C_5H_5)]$.

The thermal reaction between $\{[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6\}$ and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^-$ leads to the same product, which undergoes chemically reversible one-electron reductions at two separate redox centers. The electrochemical synthesis is not a catalyzed reaction, but an electron assisted synthesis (thermal or photochemical reaction between $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ does not give the new Co–Mo complex). This example illustrates the reactivity of metal carbonyl anions as nucleophiles.

Transformation of a linear structure to an A-frame structure may be achieved electrochemically. For example the electrochemical reduction of the $[Pt(2,6\text{-}Me_2C_6H_3NC)_4]\ (PF_6)_2$ complex on a Hg pool in described conditions [140] gave a mixture of two characterized products: $[Pt_2(2,6\text{-}Me_2C_6H_3NC)_6](PF_6)_2 \cdot CH_2Cl_2$ (14%) and $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_8](PF_6)_2$ (47%). The latter linear trinuclear Pt cluster reacts with phosphines (PPh_3 and dppm) to give, respectively, $[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6(PPh_3)_2](PF_6)_2 \cdot CH_2Cl_2$ and $[Pt_3(dppm)_2(2,6\text{-}Me_2C_6H_3NC)_4](PF_6)_2 \cdot CH_2Cl_2$.

The formation of the latter compound can be regarded as resulting from insertion of a 14-*e* fragment $[Pt(2,6\text{-}Me_2C_6H_3NC)_2]$ into the Pt–Pt bond of the dinuclear species.

According to Yamamoto et al. [140], the linear structure is transformed into an A-frame structure as shown by X-ray crystallography.

The electrochemical synthesis of $[\eta^5\text{-}C_5H_4R)_2TiSe_5$ by ultrasound-induced electrochemical reduction of grey Se powder followed by addition of $\{(\eta^5\text{-}C_5H_4R)_2TiCl_2\}$ (R = H, i-Pr), has been reported [141] and the properties of the new complex studied.

The one-pot electrochemical synthesis of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_4S_4(H_2O)_9]^{5+}$ cluster ions has recently been reported [142], by reduction at a Hg pool of the complex $Na_2[Mo_2S_2O_2\ (\text{cysteine})_2]\cdot 3H_2O$. The above procedure has been extended to the preparation of selenido and tellurido analogues [143].

The cluster $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CO)][P(C_6H_5)_4]$ undergoes a one-electron reduction leading to the paramagnetic unstable complex $[Fe_3(CO)_{10}CCH_3]^{2-}$ which regenerates the starting complex on contact with air. Treatment of the electrochemically generated $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^{2-}$ with methanol gives the cluster anion $[Fe_3(CO)_9(\mu_3\text{-}C\equiv CCH_3)]^-$ [144].

D. CONCLUSION

Many investigations have described systematic electrochemical behaviour of different types of clusters. In particular an extensive series of papers is devoted to monocapped triangular metal carbonyl clusters containing homonuclear and heteronuclear metal species and the possibilities of electron-induced substitutions on these types of clusters has been explored. Also, mixed-valence cluster compounds were synthesized and electrochemically studied for the first time. Cubane-like clusters, which serve as models for ferrodoxin and nitrogenase are now under active investigation, in particular with regard to their catalytic activity which has been found successful for an increasing number of reactions. Clusters of higher nuclearity may also undergo several one-electron oxidation/reduction reactions, the mechanism of which has been studied.

Thus, a wide range of clusters may undergo reversible one-electron reactions. From this point of view, they are considered as sources and sinks of electrons, i.e. electron "reservoirs". However, electrochemically-generated radicals are often not stable. Conditions for the increase of their stability are now available: chelating ligands, presence of a heteroatom which reinforces the metallic core, basicity of the metals, ion-pairing effects and bulk conditions. Generally, heteronuclear metal cluster ions are less stable than are the corresponding homonuclear species. The radical clusters obtained are reactive species whereas the starting clusters are often unreactive. Only the reaction of radical anion clusters with nucleophilic reagents has been investigated. No information is available about the reactivity of radical cation clusters, in particular with electrophilic reagents.

A promising field is therefore offered by cluster electrochemistry, in particular with the electrosynthesis of new compounds or modified species. The possibility offered by bridging two clusters together seems to be of great utility in the elaboration of cluster polymers or clusters alternating with other types of compounds (TCNQ, TTF or ferrocene).

As the frontier orbital LUMO involved in reduction is mostly antibonding metallic in character, whereas the HOMO orbital involved in oxidation is bonding, both electrochemical reductions and oxidations in clusters will tend to weaken the metal–metal interactions. Thus, many one-electron oxidation and reduction reactions are irreversible in clusters. Several examples of multielectron transfer processes are also available in the literature. The particular case of a single two-electron reduction has been studied by three authors. A stepwise process with a detectable intermediate may occur. An electrochemical–chemical–electrochemical reaction, in which the chemical step corresponds to an established structural change in the cluster, has been described. The reorientations in clusters induced by electron transfer are now under active investigation, despite the difficulties associated with such studies. The electrochemical behaviour of heteronuclear metal clusters is more intricate: certain compounds may behave like binuclear metal–metal bonded carbonyl complexes, rather than delocalized sources and sinks of electrons in spite of their delocalized bonds.

In general, a lot of data is available for the reduction process in cluster electrochemistry, while oxidation has been less studied and is not well understood. Irreversibility of the oxidation processes is one of the reasons for the limited information in this area.

Cluster breakdown has been described, but cluster fragments of lower nuclearity are rarely characterized. The reactivity of these fragments is unknown. In conclusion, cluster electrochemistry is now a field of growing interest with many possible applications in electrosynthesis and in electrocatalysis as well as in the mimicking of biological processes.

It is now established that molecular nitrogen can be catalytically reduced to NH_3 and N_2H_4 at a mercury cathode in methanol in the presence of Mo(III) + lecithin catalysts [145] at ambient temperature and pressure. Pospisil et al. suggest that the active species may be a cluster containing a Mo_4–OMgO–Mo_4 framework [146]. Thus, processes based on the electrochemical reduction of both N_2 and CO_2 and involving clusters, show a very large research potential.

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