

ELECTROCHEMISTRY OF TRANSITION METAL COMPLEXES

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Complexo I

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Abbreviations

bpy = 2,2'-bipyridine. BPC = 1-butylpyridinium chloride.
COT = cyclooctatetraene. dmdepe = 1-(dimethylphosphino)-2-(diethylphosphino)ethane.
dmpe = 1,2-bis(dimethylphenylphosphino)ethane.
LpnH = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olate. dppe = 1,2-bis(diphenylphosphino)ethane. Fc = ferrocenyl group.
FcH = ferrocene. Mc = metallocenyl group. McH = metallocene. NHE = normal hydrogen electrode.
OEP = octaethylporphyrin. S.c.e. = saturated calomel electrode.
TM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.
TPP = tetraphenylporphyrin. tryp = 2,2',2'' - terpyridine.

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1 - INTRODUCTION

Following the exploratory works undertaken by Wilkinson,⁽¹⁻⁵⁾ Fischer^(6,7) and Viček,⁽⁸⁻¹⁰⁾ a pioneering and systematic study on a wide range of organometallic complexes was undertaken since 1966 by Dessy.⁽¹¹⁾

The success of this work opened-up a growing interest on the application of electrochemical techniques to the study of organometallic compounds, and a few reviews have appeared, dealing either with the general electrochemical behaviour of the transition⁽¹²⁻¹⁶⁾ and main group^(14,15) metal compounds or, more specifically, with their electrochemical synthesis.⁽¹⁷⁻²⁰⁾

It is the purpose of this account (which is not a comprehensive review) to present and discuss relevant studies within recent trends on the electrochemistry of transition metal complexes with metal-carbon bond (organometallic species) or with ligands related to (e.g., isoelectronic with) ligating organic moieties, such as dinitrogen which is isoelectronic with carbonyl or isocyanide.

The first reactions deal with electrochemical oxidation and reduction, and particular attention is given to the electrooxidation studies of transition metal complexes in low oxidation states since the well documented electrochemical reduction of complexes in higher oxidation states has previously been covered in detail by other authors⁽¹²⁻¹⁶⁾.

The other selected topics include the electrochemical quantification of redox and electronic properties of 16-electron metal sites (in octahedral transition metal complexes) and of the net electron donor/acceptor character of their ligands; correlations of redox properties ($E_{1/2}$) with reactivity, electronic character of the ligands, charge transfer band energies, n.m.r. parameters, etc.; electrochemistry of redox series of transition metal complexes with redox active ligands; electrosyntheses and catalysis; electroactivation of ligands; application in the mechanistic studies of chemical reactions.

These subjects are outlined from the standpoint of the organometallic/inorganic chemist, the analytical applications and the evaluation of stability constants being excluded. Moreover, these applications have been the object of a recent review,⁽²¹⁾ as well as the following topics which will not be covered by the present work unless occasionally: complexes of macrocyclic ligands and complexes with bio-inorganic significance. However, within the latter subject, a few studies in the Nitrogen Fixation field will be pointed out

since they were not previously presented.

Most of the studies of the present lesson were undertaken in non-aqueous solvents (for stability or solubility reasons) and emphasis will be focused on the application of inert solid electrodes, namely in platinum or vitreous carbon, which are commonly more suitable for the study of electrooxidations than the dropping mercury electrode.

II - ELECTROCHEMICAL OXIDATION

The development of the study of the electrochemical oxidation of organometallic complexes followed the chemical preparation of these species with transition metals in low oxidation state. Hence, apart from the electrooxidation study of metallocene-type complexes, it is not yet so well documented as the electroreduction behaviour which has been the subject of a wider study.

Most of the known electrochemical oxidation reactions of organometallic complexes can be classified according to the way depicted in figure 1 where RMQ denotes a neutral or ionic organometallic complex, R a carbon-bonded ligand (or ligands), and Q the other co-ligands (with organic and/or inorganic character).

The complex can usually undergo one or two one-electron oxidations (reactions i and ii) which may be reversible (this feature is displayed more commonly by the first electrooxidation than by the second one). The dioxidized (e.g., dicationic) complex is usually electronically unsaturated, unstable and reacts with other species present in the medium such as the solvent (reaction iii) or the electrolyte.

The monooxidized (e.g., monocationic) species may also be unstable and undergo a disproportionation reaction or a dimerization (ix), or further chemical reactions involving the ligands which are labilized or activated upon the electrochemical oxidation (reactions iv-viii).

If the oxidation occurs at a non-inert mercury electrode, polynuclear mercurated species may be formed (reactions x). Metal-metal bond rupture of dimeric species may also result from the electrochemical oxidation (reactions xi).

A - One-electron (reversible) oxidations

A change of structure does not occur in one-electron reversible oxidation reactions which lead to stable oxidized species by an electronic

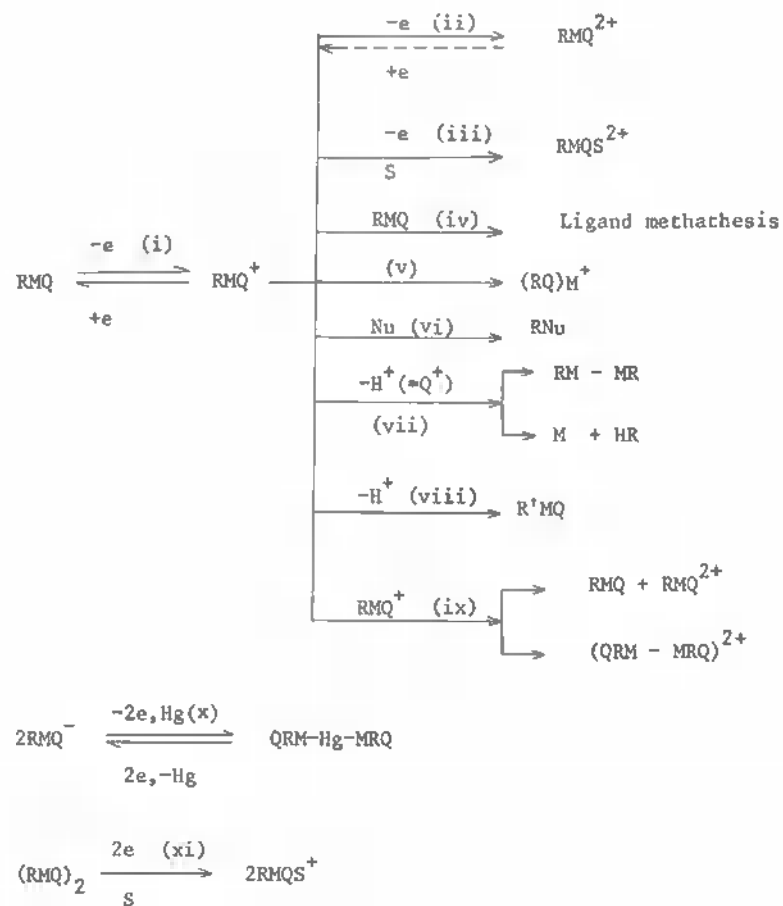
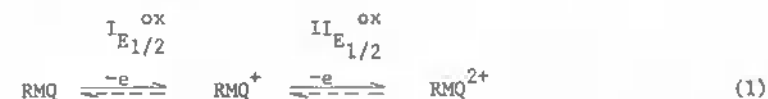


Figure 1 - Types of reactions in the electrochemical oxidation of organotransition metal complexes

process which is not complicated by coupled chemical reactions. Hence, the value of $E_{1/2}^{\text{ox}}$ is meaningful on the attempt to get correlations between the redox properties of the complexes and other parameters which are dependent on their electronic and stereochemical structure; however, this subject will be treated in another section.

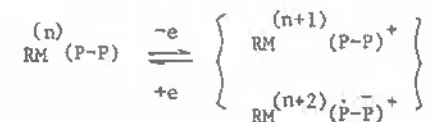
The derived monooxidized species may also undergo a further oxidation reaction which may be reversible (equations 1)



Well documented examples of one-electron reversible electrooxidations involve eighteen-electron transition-metal compounds with bidentate phosphorus ligands and metallocene complexes. Other examples (e.g., bis- π -arene complexes and compounds with ferrocenyl ligands) will be cited throughout this work.

(a) Eighteen-electron complexes with bidentate phosphines

Eighteen-electron transition-metal organometallic complexes with bidentate phosphorus ligands, regardless of geometry or metal oxidation state, can usually undergo electrochemical oxidation to the corresponding 17-electron species which may exhibit a considerable stability in spite of the unusual oxidation state the metal may present. The ability of the bidentate phosphorus ligand to facilitate the oxidation and to stabilize the 17-electron species has been rationalised⁽²²⁾ by considering an "internal disproportionation" of the molecule as the result of a delocalization of the metal d unpaired electron into the phosphorus orbitals leaving the metal in a more common and stable oxidation state (reaction 2).

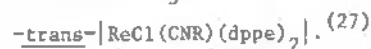
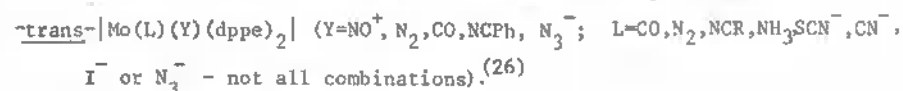
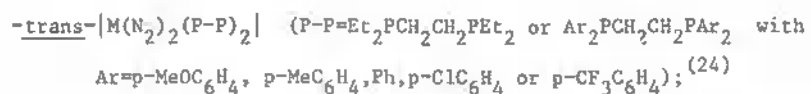
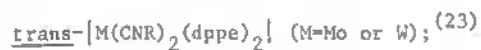


This rationale is corroborated by the observed ^{181}Ta and ^{31}P hyperfine interactions of the e.s.r. spectrum of $[\text{Ta}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{dmpe})][\text{BF}_4]^{(22)}$

Examples of these oxidation reactions of 18-electron complexes with bidentate phosphines are known for a wide variety of metals, oxidation states

and geometries, namely the 7-coordinated group V metal(I) complexes of the type $[MX(CO)_2(P-P)_2]$ ($M=Ta, Nb$; $X=halide, H, CH_3$; $P-P=dmpe$ or $dmdepe$), (22) the bis(cyclopentadienyl)tantalum(III) complex $[Ta(\eta^5-C_5H_5)_2(dmpe)]^+$, (22) and the 8-coordinated complexes of the group VI metal(0) or group VII metal(I) site $[M(P-P)_2]$ ($M=Mo$ or W ; $P-P=dppe$ or related bidentate phosphine) of the type $[MLL'(P-P)_2]$.

Examples of the latter may be cited:



All these complexes exhibit reversible one-electron oxidations at a Pt electrode and some of them undergo also a second one-electron reversible oxidation step.

The high electron richness of the group VI Mo(0) and W(0) complexes induces a facile oxidation at very negative half-wave potential values relative to s.c.e. (e.g., $E_{1/2}^{ox}$ lies in the -0.6 to -0.4 V range for



(b) Metallocene-type complexes

The electrochemical behaviour of metallocene-type complexes has been widely investigated in both aqueous and nonaqueous organic solvents, as well as, recently, in aprotic Lewis acid molten salts (e.g., $AlCl_3$ -1-butylpyridium chloride).

Examples are given in figure 2 for metallocenes $[M(\eta^5-C_5H_5)_2]$ ($M=Fe, Ru, Os, Co, Ni$) which, by oxidation, lead to the corresponding metallocinium ions $[M(\eta^5-C_5H_5)_2]^n$ ($M=Fe, (1,29,30)Co, (31); n=1. M=Ru, (1,29,32), Os, (29,33)Ni (34-37); n=1 \text{ or } 2$).

The anionic 20-electron complex $[Co(\eta^5-C_5H_5)_2]^-$ is also known to undergo two one-electron reversible oxidation reactions to cobaltocene

and cobalticinium cation. (31)

20 - e	19 - e	18 - e	17 - e	16 - e
$CoCp_2^-$	$CoCp_2$	$FeCp_2$ $RuCp_2$ $OsCp_2$	$FeCp_2^+$ $RuCp_2^+$ $OsCp_2^+$	$RuCp_2^{2+}$ $OsCp_2^{2+}$
$NiCp_2$	$NiCp_2^+$	$CoCp_2^+$ $NiCp_2^{2+}$		
		$Fe(\eta^5-C_5Me_5)_2$	$Fe(\eta^5-C_5Me_5)_2^+$	$Fe(\eta^5-C_5Me_5)_2^{2+}$

Figure 2 - Metallocene- and metallocinium-type complexes

Sixteen-electron dications of the type $[M(\eta^5-C_5H_5)_2]^{2+}$ were quoted for Ru(IV) and Os(IV) but not for Fe(IV), in agreement with a suggested (33) decrease of the half-filled d^5 configuration stability of the monocation with increasing atomic number, which accounts for the formation of those metal d^4 species.

However, strong Lewis acid $AlCl_3$ -based molten solvents are known (38-40) to stabilize radical cations and a decamethylferricinium dication, $[Fe(\eta^5-C_5Me_5)_2]^{2+}$ was electrochemically generated by constant potential coulometry of $[(\eta^5-C_5Me_5)_2Fe]$ in $AlCl_3$ /1-butylpyridinium chloride(BPC)(1.5/1) melt, at a vitreous carbon electrode. (41)

Cyclic voltammetry shows that the neutral decamethylferrocene in this melt undergoes two one-electron reversible oxidations to the mono- and the dication, respectively, with a large potential separation ($\Delta E_{1/2} \approx 1.68$ V), the first half-wave oxidation potential being ca. 530 mV lower than that of the ferrocene complex in agreement with the electron donating effect of the methyl ring substituents. (41)

The unsubstituted ferricinium cation $[Fe(\eta^5-C_5H_5)_2]^+$ is also oxidized in $AlCl_3$ /BPC melt, but only a multielectron irreversible wave was observed just prior to the oxidation wave of the solvent. (41)

The stability of the ferrocene (FcH) and ferricenium (FcH^+) ion, the reversibility and solvent-independent character of the redox (FcH^+/FcH) couple led to its application⁽⁴²⁾ as an internal standard for electrochemical measurements in non-aqueous solvents. The standard reduction potential $E^\circ(\text{FcH}^+/\text{FcH})$ is assumed to be the same (0.400 V vs. the normal hydrogen electrode)⁽⁴³⁾ in any solvent as measured in water, and the potentials of other redox processes vs. the FcH^+/FcH couple are reproducible* and directly comparable among different solvents.⁽⁴²⁾

The use of this redox couple as an internal reference also helps to judge the reversibility and the number of electrons involved in the redox process under study.

In case there is overlap of the redox waves of the FcH^+/FcH couple and of the system under study, the cobalticenium/cobaltocene redox couple ($E^\circ = -0.918$ V vs. NHE)⁽⁴³⁾ may be used as the internal standard.

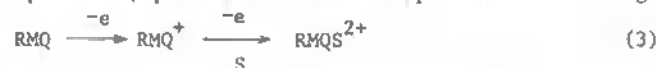
Formal potentials of ferrocene⁽⁴³⁻⁴⁶⁾ and their derivatives^(44,45,47,48) have been measured in aqueous or acidic medium (acetic acid-perchloric acid mixtures where the ferrocenes display a higher solubility) by potentiometric titration with an oxidizing titrant such as potassium dichromate. Values in some organic solvents (such as MeOH and NCMe) have also been quoted for ferrocene^(43,49-51) and for cobaltocene.⁽⁴³⁾

B - Electrochemical oxidations with coupled chemical reactions

The electronic deficiency of a metal site as a result of its electrochemical oxidation may often promote its reactivity namely towards nucleophiles and examples will be considered. Disproportionation of the unstable monooxidized species to compounds with more common oxidation states may also occur.

(a) Reaction with solvent

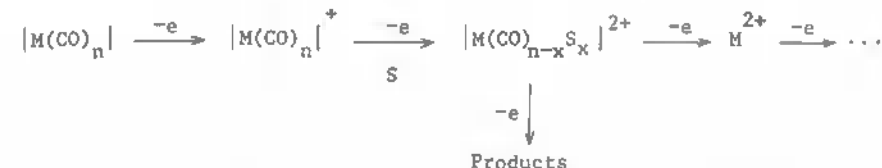
Nucleophilic attack by the solvent at the electrochemically oxidized complex has been considered a possible step following the electrochemical process (equation 3 which corresponds to iii in figure 1).



Hence, e.g., cyclic voltammetric studies of the binary metal carbonyls $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Mo}$ or W) and $[\text{Fe}(\text{CO})_5]$, at a Pt electrode in

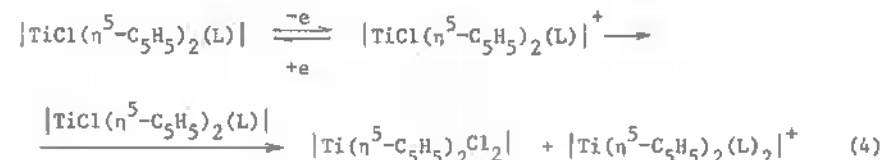
* The effects of variables such as type and degradation of reference electrode, and liquid junction potentials are thus cancelled.

$\text{NCMe} = [\text{Bu}_4\text{N}][\text{BF}_4]$, evidence the oxidative formation of an unstable monocationic species which is less stable than the chromium analogue (see later) and probably undergoes a nucleophilic attack by the solvent. The current function $|i_p/(\partial^{1/2} C_0)|$ for the redox process suggests that the electrode process is diffusion controlled and a two-electron reaction is involved on a short time scale whereas multielectron reactions occur on a longer time, the following mechanism being suggested:⁽⁵²⁾

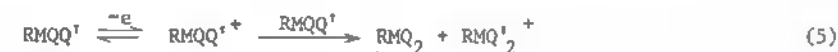


(b) Ligand metathesis

The electrochemical oxidation of the titanocene monochloride $[\text{TiCl}(\eta^5\text{-C}_5\text{H}_5)_2(\text{L})]$ ($\text{L} = \text{thf}$ or PMe_2Ph) - studied by voltammetry on a disc electrode, by linear potential sweep voltammetry and by controlled potential electrolysis - affords the cationic species $[\text{TiCl}(\eta^5\text{-C}_5\text{H}_5)_2(\text{L})]^+$ which undergoes ligand exchange with the parent neutral species to give $[\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ and $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{L})_2]^+$ (reaction 4).⁽⁵³⁾



This study evidences the possibility of ligand metathesis between two molecules of a complex when a change in the oxidation state occurs, and may be considered an example of the following general scheme:

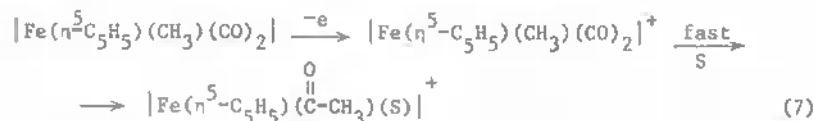


(c) Insertion into a metal-carbon bond

Insertion reactions into a metal-carbon bond may be promoted by oxidation (equation 6).



Hence, carbonyl ligand may be activated towards insertion into a M-C bond by electrochemical oxidation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_3)(\text{CO})_2]$ in acetonitrile at a Pt electrode (equation 7). (54)



This migratory insertion on oxidation of the Fe(II) complex is a fast reaction even at low temperature and is probably assisted by coordination of solvent. (54)

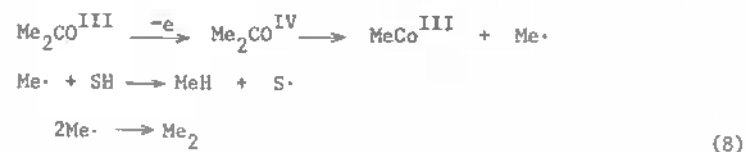
Other examples of activation of ligands upon metal electro-oxidation are given in section VIII. B.C.

(d) Metal-carbon bond cleavage

The electrooxidation of an organometallic complex may result in the labilization of the metal-carbon bond.

Hence, the electrochemical oxidation of monoalkyl(chelate)cobalt(III) complexes - monoalkylcobaloximes and related Schiff's base compounds - which has been widely studied in the last few years, involves a reversible one-electron process to give alkylcobalt(IV) species in which the alkyl ligand (R) can undergo a nucleophilic displacement (e.g., by species such as halide ions, water, pyridine or the macrocyclic ligand L to give RX, ROH, RPy⁺ or LR, respectively). (55-58)

Electrochemical studies have also been reported⁽⁵⁹⁾ for the dialkylcobalt(III) macrocycles trans- $[\text{Co}(\text{CH}_3)_2(\text{DpnH})]$ and trans- $[\text{Co}(\text{CH}_3)_2(\text{TIM})]^+$ in acetonitrile at a Pt electrode. They undergo a one-electron irreversible oxidation to a transient dialkylcobalt(IV) cation which suffers a spontaneous homolytic cleavage of one Co-C bond to give a free methyl radical which forms ethane by radical-radical coupling. The proposed mechanism of the reaction is shown by equations 8 where the macrocyclic ligand has been omitted for clarity and SH denotes the solvent. (59)



(e) Proton elimination

As a result of oxidation of a transition metal complex, proton loss may occur from the metal (in a transition metal hydride complex) with possible metal-metal bond formation or reductive elimination, or from a ligand according to the following general equations 9 and 10, which correspond to reactions vii and viii of figure 1, respectively).



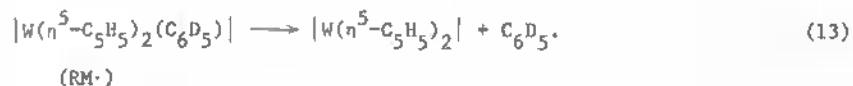
Examples of the latter process are given in section VIII. A.C.2 whereas the former reaction type is exemplified now.

Oxidation of a neutral diamagnetic hydride complex gives a cationic paramagnetic species from which proton elimination occurs readily (equation 11), the resulting metal-centered radical undergoing dimerization (equation 12) or reductive elimination. (60)



Examples are given by the oxidation of the hydridic complexes $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{H}]$ in $\text{CH}_3\text{CN}-[\text{NBu}_4][\text{BF}_4]$ at a Pt electrode with formation of the dimeric species $[\text{W}_2(\eta^5\text{-C}_5\text{H}_5)_4\text{H}_2]$ and $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6]$. (60)

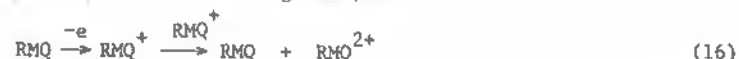
The cationic radical complex formed in the oxidation of the hydridic compound may alternatively undergo a reductive elimination namely in the formation of benzene from $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_6\text{H}_5)\text{H}]$. On the basis of deuterium-labeling studies, this reaction is proposed to proceed either via the generation of an organic radical followed by hydrogen atom abstraction from the solvent (equations 13,14) or via a direct intramolecular elimination of benzene by removal of a hydrogen atom from the cyclopentadienyl ligand (equation 15).



The formation of C_6D_5H instead of C_6D_6 , from the labeled complex $|W(\eta^5-C_5H_5)_2(C_6D_5)D|$, rules out a direct elimination process. (60)

(f) Disproportionation

An unstable oxidized complex may undergo disproportionation to species with more common metal oxidation states (equation 16 which corresponds to reaction ix.a of figure 1).



Hence, anodic oxidation of $|Cr(CO)_6|$ at a Pt electrode in $NMe_4-Bu_4N|BF_4|$ produced the 17-electron cationic $|Cr(CO)_6|^+$ species whose e.s.r. spectrum was followed during constant current electrolysis (of the parent complex) and after switching off the current; the e.s.r. signal then decayed by a second-order process which corresponds conceivably to the disproportionation of the unstable monocation. The overall electrode reaction during a preparative electrolysis was shown to be, by coulometry, a two-electron process and no $\nu(CO)$ bands were observed in the infrared spectrum of the anolyte at the end of the electrolysis. (52) The following mechanism (equations 17) is then proposed (52) for the overall reaction.



(g) Dimerization

Metal-metal bond formation may follow the oxidation of a transition metal complex according to the general reaction 18 (which is process ix.b of

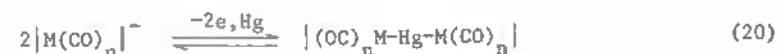
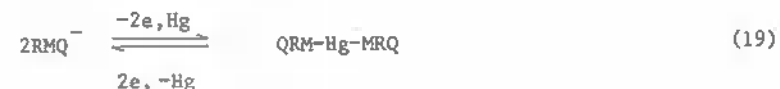
figure 1) and an example is provided by the oxidation of the Vaska's complex $|IrX(CO)(PR_3)_2|$ at a platinum electrode. The reaction occurs irreversibly to $Ir(II)$ and, on the basis of the absence of a



paramagnetic e.p.r. signal, a dinuclear metal-metal product is suggested (61) to be formed.

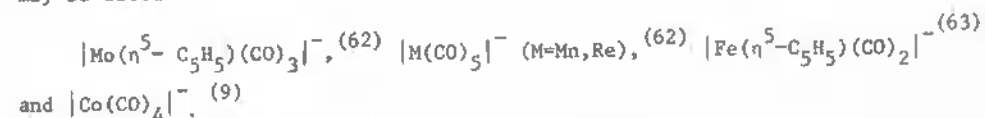
(h) Formation of polynuclear mercurated species

Electrochemical oxidation at a mercury electrode of anionic metal carbonyls results in the formation of trimetallic linear species with mercury bridging two transition metals (equations 19 or 20, corresponding to reactions x of figure 1).



The parent anionic complexes are regenerated upon electrochemical reduction of the polynuclear product with liberation of mercury.

Examples of anionic carbonyl species which undergo these reactions may be cited:



Other (cationic) polynuclear mercurated species, $[(IrX(CO)(PR_3)_2)_nHg]^{2+}$ ($n=3,4$) are reported to be formed in the electrochemical oxidation of the neutral Vaska's complex $|IrX(CO)(PR_3)_2|$ ($X=Cl, Br, I$) at the anodically polarized mercury electrode in $CH_2Cl_2-Bu_4N|ClO_4|$. (64) It is believed (64,65) that the electrode process consists on the oxidation of the mercury electrode followed by coordination of the Vaska's complex to the mercury ions. As proved by chemical studies, (65) the $|IrX(CO)(PR_3)_2|$ complex behaves as a Lewis base towards oxidizing ions such as Hg^{2+} , Cu^{2+} or Fe^{3+} to afford addition compounds.

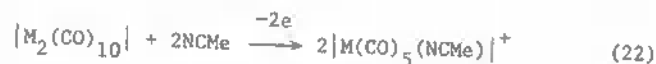
(i) Metal-metal bond rupture of a dinuclear complex

Metal-metal bond rupture of a dinuclear complex may result from its electrochemical oxidation followed by attack by a nucleophile, e.g., the solvent (equation 21 - xi in figure 1).



Hence, electrochemical oxidation of the neutral dinuclear carbonyl complexes $[\text{M}_2(\text{CO})_{10}]$ ($\text{M}=\text{Mn}, \text{Re}$)⁵² (at a Pt electrode in acetonitrile or dichloromethane) or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ ⁽⁶⁶⁾ (at a Pt or carbon electrode in acetonitrile, dichloromethane or acetone) results in the M-M bond rupture with involvement of solvent (S) leading to the irreversible formation of the cationic monomeric solvated species $[\text{M}(\text{CO})_5(\text{S})]^+$ (unstable) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{S})]^+$. In the latter complex the solvent molecule may be further replaced by neutral (phosphine) or anionic ligands to yield derived iron complexes which may be isolated.⁽⁶⁶⁾

The group VII cationic solvated species may undergo a two-electron reduction with liberation of solvent to generate the anionic $[\text{M}(\text{CO})_5]^-$ complexes which may be prepared by controlled potential reduction. The observed behaviour may be exemplified by reactions 22 and 23 carried out in acetonitrile ($\text{M}=\text{Mn}$ or Re).⁽⁵²⁾



Although metal-metal bond rupture may result from the oxidation of a dinuclear complex (as shown by the abovementioned examples), the presence of a bridging ligand may allow the retention of such a bond and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]_2(\mu\text{-dppe})$ undergoes a one-electron reversible oxidation to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]_2(\mu\text{-dppe})^+$ which disproportionates in solution forming the corresponding dicationic species.⁽⁶⁷⁾

III - ELECTROCHEMICAL REDUCTION

The electrochemical reductions of transition metal complexes have been, in general, the subject of a more widespread study than the electrochemical oxidations, the latter following the preparation of complexes with metals in lower oxidation states. However, exceptions are known and, e.g., the electrochemical oxidation study of ferrocenes preceded the investigation of their electrochemical reduction.

A - One-electron reversible reduction

Although chemical reductions of metallocene-type complexes often lead to decomposition, metallocene anions may be prepared in some cases by electrochemical reduction.

Hence, e.g., substituted ferrocenes with electron-acceptor substituents (such as nitro-, p-nitrophenyl-, p-cyanophenyl- and benzoyl-) are known^(68,69) to undergo a one-electron reversible reduction (e.g., in acetonitrile or dimethylformamide at a Hg-pool cathode) to afford stable radical anions.

More recently, a reversible electrochemical reduction of ferrocene and some derivatives with an electron-donor substituent [methyl- or $-\text{CH}_2\text{C}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_5)$] has been reported⁽⁷⁰⁾ in dimethylformamide- $[\text{Bu}_4\text{N}][\text{I}]$ at low temperature (e.g., ca. -30°C); further one-electron reduction to the dianions has been quoted by other authors.^(71,72) At higher temperatures a two-electron reduction occurs following an ECE type mechanism (section III.B.b.6).

Unsubstituted or mono- or di-substituted cobalticinium ions (18-electron species) may undergo two successive one-electron reversible reductions (at a Hg electrode) to give^(31,73) cobaltocene (19-electrons) and the cobaltocene anion (20-electrons), respectively, and synthetic applications of these electrochemically generated species will be referred to later.

Although metal-halogen bond cleavage has been reported⁽⁷⁴⁻⁷⁷⁾ to occur in the one-electron reduction of dihalides of bis(cyclopentadienyl)titanium, $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]$; recent studies undertaken by other authors^(78,79) indicate that in thf (or dimethylformamide) the first electron transfer is both an electrochemically and a chemically reversible process affording the stable anionic complexes $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]^-$; however, halide dissociation is observed upon the second electron transfer process.

B - Electrochemical reduction with coupled chemical reactions

The mechanisms of the chemical reactions coupled to the electrochemical reduction of an organometallic species were systematically investigated by Dessy⁽¹¹⁾ since 1966 and continued by Lehmkuhl.^(17,18)

Examples which were recognized by these authors are cited in figure 3 which also includes other reaction types which have been identified more recently. Some electrochemical reductions with synthetic value will be mentioned in another section.

As general comments, one may refer that the reduction (i) of a mononuclear complex may be followed by any of the following processes:

- Dimerization with bridging ligand (ii);
- Elimination of anionic ligand(s) Q^- (e.g., halide) (iii) with formation of the MR organometallic radical which undergoes further reactions:
 - Reduction (iii.1), hydrogen abstraction from the solvent or the electrolyte (e.g., tetraalkylammonium salt) to give an hydride complex (iii.2), addition of another ligand (iii.3), dimerization with metal-metal bond formation (iii.4), disproportionation (iii.5), reaction with the cathode metal mercury to form mercurated species (iii.6) and transfer of an organic group (R) to the cathode mercury (iii.7).
- Elimination of a carbanion (R^-) to give the MQ radical (iv) which may undergo further reduction to give Q^- and metal M (iv.1) or to give a new LMQ^- complex by addition of a new ligand (L) (iv.2); LMQ^- may then undergo further reduction or electrophilic attack.
- Electrophilic attack (v), (vi.1.1)
- Further reduction (vi) followed by elimination of an anionic Q^- (vi.1) or R^- (vi.2) ligand; the anionic organometallic species RM^- derived from (vi.1) may then react with the solvent or undergo attack by an electrophile.

For metal-metal bonded di- or trinuclear complexes, reduction commonly results in metal-metal bond cleavage.

A few examples of these reaction types may be mentioned.

(a) Dimerization with a bridging ligand

A dinuclear complex with a bridging ligand may be formed in the

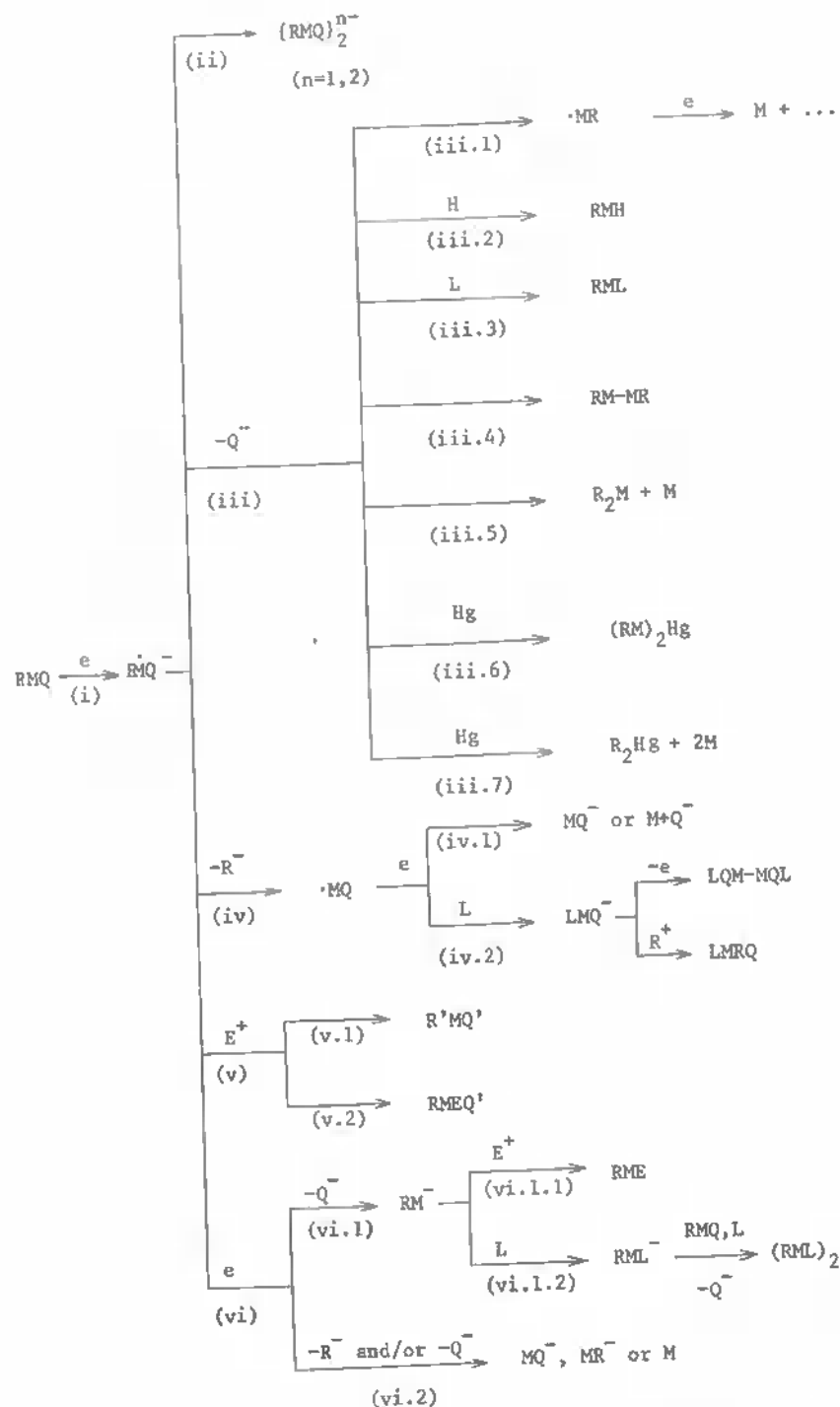
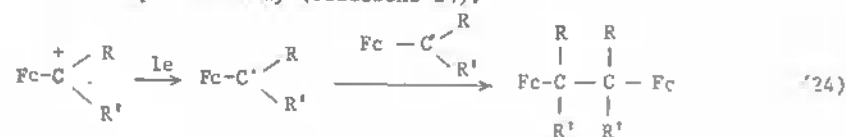


Figure 3 - Types of reactions in the electrochemical reduction of organometallic complexes.

electrochemical reduction of RMQ as a result, e.g., of simple dimerization of the reduced ("anionic") species RMQ^- to give $(\text{RMQ})_2^{2-}$ or from the reaction of RMQ^{2-} (formed by a two-electron reduction) with the parent RMQ species to afford $(\text{RMQ})_2^-$ (reactions i,ii of figure 3).

Hence, e.g., ferrocenylcarbocations may undergo one-electron transfer electrochemical reduction at a dropping-mercury electrode (in H_2O /dioxan or dimethylformamide - HClO_4) to afford the corresponding ferrocenylalkyl radicals which dimerise spontaneously (reactions 24).⁽⁸⁰⁾



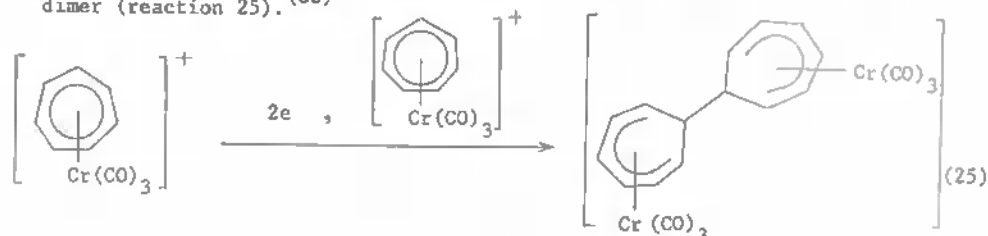
(R, R' = H, Me, Ph, Fc, etc)

One-electron steps may also be involved in other cases, namely in the formation of $[\{\text{WF}(\text{dppe})_2\}(\text{NNCR}_2\text{CR}_2\text{NN})\{\text{WF}(\text{dppe})_2\}]$ from the reduction of the diazoalkane complexes $\text{trans-}[\text{WF}(\text{NN}=\text{CR}_2)(\text{dppe})_2]^+$ (R=H or Me) at a Hg pool.⁽⁸¹⁾

The reaction is believed to occur via a one-electron transfer to give the metallo-radical $[\text{WF}(\text{NN}=\text{CR}_2)(\text{dppe})_2]$. The carbon-carbon coupling of the diazomethane ligands may then occur via radical-radical coupling or by electrophilic attack of the parent cationic diazoalkane complex upon the neutral metallo-radical species followed by further one-electron reduction (the nucleophilic character of the carbon atom in the neutral radical complex was proved by protonic attack and by alkylation).⁽⁸¹⁾

An example involving a two-electron reduction may be cited.

The cationic cycloheptatrienyl complex $[\text{Cr}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_3]^+$ in acetonitrile undergoes a two-electron reduction at Pt to give the corresponding anion which reacts with the parent species to afford a carbon-carbon bonded dimer (reaction 25).⁽⁸²⁾

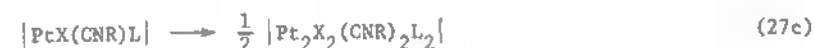


This reaction follows the general process depicted in equation (26).



The formation of the dimeric complex may be assisted by ligand dissociation as shown by the following example.

The cationic isocyanide complexes of Pt(II) $\text{trans-}[\text{PtX}(\text{CNR})\text{L}_2]^+$ (R=aryl, L=tertiary phosphine) in acetonitrile - $[\text{Bu}_4\text{N}][\text{ClO}_4]$ are reduced at a Pt or Hg electrode to a dimeric platinum(I) species (equations 27) with bridging isocyanide ligands which undergoes a subsequent reduction to platinum(0) compounds not yet fully characterized.⁽⁸³⁾ the dissociation of a



phosphine ligand allows the formation of the vacant coordination site which is favourable to the terminal to bridging rearrangement of the isocyanide ligands.

The general scheme of this reaction may be given by equation 28.

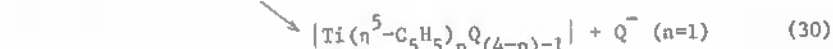
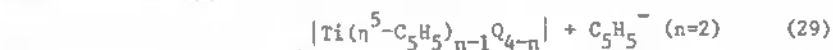


(b) Elimination of an anionic ligand followed by further reactions of the organometallic radical

Dissociation of an anionic ligand following an electrochemical reduction is a process with an opposing effect to the electronic charge build-up at the complex as a result of the reduction, and is observed commonly. The derived organometallic radical may react further in a number of ways.

A few examples are cited.

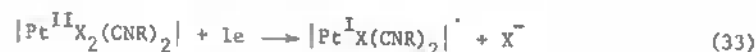
Electrochemical reduction of the cyclopentadienyl Ti(IV) complexes $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_n\text{Q}_{4-n}]$ (Q=R, OAr or OSiR_2 , where R is an alkyl and Ar is an aryl group; n=1 or 2) in thf at a Pt or glassy carbon electrode affords the radical anions $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_n\text{Q}_{4-n}]^\cdot$ which rearrange to the corresponding neutral monocyclopentadienyl Ti(III) complexes according to the following ways (reactions 29 and 30):⁽⁸⁴⁾



These reactions follow the general equations 31 and 32, which correspond to equations (iii.1) and (iv) (the latter involving metal-carbon bond rupture) of figure 3.



The *cis* and *trans* dihalogenobis(isocyanide)platinum(II) complexes $[\text{PtX}_2(\text{CNR})_2]$ (R = cyclohexyl, *tert*-butyl), in propylene carbonate or acetonitrile solutions, undergo, at a Pt or Au electrode, a first irreversible one-electron reduction to Pt(I) with liberation of halide ion, whereas the second monoelectronic reduction step affords Pt(0) (which deposits on the electrode) with decomposition of the complex (equations 33 and 34).⁽⁸⁵⁾

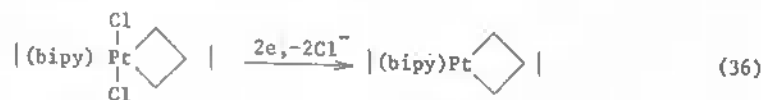


These reactions follow the general pattern of equation 35 corresponding to process (iii.1) of figure 3



However, the isoelectronic triphenylphosphine complexes $[\text{PtCl}_2(\text{PPh}_3)_2]$ are electrochemically reduced directly to Pt(0). The stabilization of the Pt(I) radical in the isocyanide complexes is explained in terms of the stronger electron back-donation of the isocyanide ligand compared to ligating phosphine.⁽⁸⁵⁾

Other two-electron reductions with two halide ligand dissociations are known to occur, *e.g.*, in reaction 36 of synthetic value in the preparation of the Pt(II) complex $[(\text{bipy})\text{Pt}-\text{CH}_2\text{CH}_2\text{CH}_2]$.⁽⁸⁶⁾

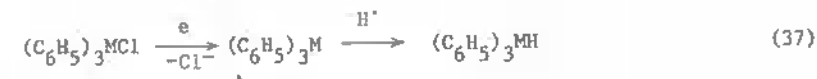


The $[(\text{bipy})\text{Pt}-\text{CH}_2\text{CH}_2\text{CH}_2]$ complex may undergo a further one-electron reversible reduction to the corresponding paramagnetic anion.⁽⁸⁶⁾

The bipyridyl ligand in this 16-electron species is labile to substitution and a series of platinacyclobutane complexes of bisphosphine, *t*-butyl isocyanide, carbon monoxide and phenylacetylene can be prepared by this way.⁽⁸⁶⁾

(b.1) Hydrogen abstraction

Hydrogen abstraction from the solvent (or the supporting electrolyte, *e.g.*, tetraalkylammonium salt) by the organometallic radical derived from one-electron reduction has been postulated in the formation of silicon and germanium hydride compounds, *e.g.*, according to equations 37 (where M=Si or Ge)⁽⁸⁷⁾ which correspond to reaction (iii.2) of figure 3.



The formation of the hydride probably occurs via reaction of the solvent (glyme) with an intermediate M(III) radical which, however, was not detected by cyclic voltammetry due to its high unstability.

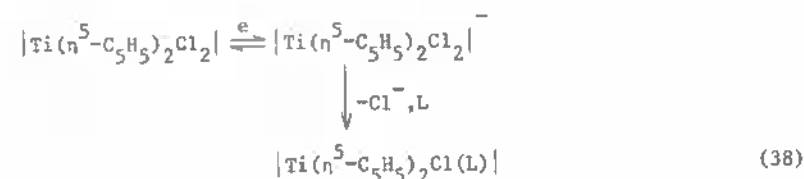
The present author, however, is not aware of any organotransition metal complex where this type of reaction was demonstrated.

Protonic attack at the reduced transition metal site is nevertheless a possible proposal in some cases, *e.g.*, to account for the unstability of the electrochemically generated cobaltocene anion from electroreduction of cobaltocene in acetonitrile.⁽³¹⁾

(b.2) Ligand exchange

Ligand exchange may result from the dissociation of an anionic ligand promoted by electrochemical reduction.

Hence, the metal-halogen bond cleavage in the following examples (equations 38) allows the replacement of the halide ligand by a neutral ligand in the anionic reduced species.⁽⁷⁷⁾ They exemplify reaction (iii.3) of figure 3.



(where L=thf or dimethylformamide)

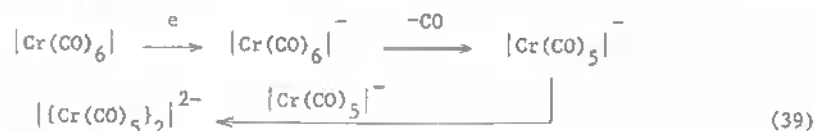
(b.3) Dimerization

Metal-metal bonded dinuclear complexes may be formed by dimerization of the reduced complex with ligand (anionic or neutral) dissociation.

Dinuclear Rh(0) complexes formulated as $[\{\text{RhL}_4\}_2]$ (L=tertiary phosphine)

have been prepared by electrochemical reduction of the mononuclear Rh(I) species $[\text{RhClL}_2]$ with chloride ligand dissociation. This reaction exemplifies the process (iii.4) of figure 3. (88)

Dimeric carbonyl complexes, e.g., $[\{\text{Cr}(\text{CO})_5\}_2]^{2-}$ may be formed in a similar way, although involving dissociation of a neutral ligand rather than an ionic one; metal-carbon bond cleavage also occurs as a result of the reduction (reactions 39). (89)



(b.4) Disproportionation

Cathodic deposition of a metal may occur from disproportionation of an organometallic radical generated by electrochemical reduction.

An example is given by the deposition of highly pure aluminium from the electrolytic reduction of adducts of trialkylaluminium (R_3Al) with Lewis bases (MX), e.g., $2\text{Et}_3\text{Al} \cdot \text{XM}$ which may be formulated as the ionic species $\text{M}^+[\text{Et}_3\text{Al} \cdot \text{X} \cdot \text{AlEt}_3]^-$ (where $\text{X}=\text{H}$ or halide; $\text{M}=\text{Na}$, K or NR_4).

The mechanism has not yet been ascertained but a known proposal involves the dissociation into an organometallic cation $[\text{AlEt}_2]^+$ which, upon reduction, generates the $\cdot\text{AlEt}_2$ radical which undergoes disproportionation (reaction 40). (17,18,90-92)



The technique can be applied to other main-group metals such as Ga, In, Tl and also to Zn and Cd.

(b.5) Reactions with mercury cathode

Electrochemical reduction, at a mercury cathode, of some transition metal complexes may result in the formation of mercurated di- or trimetallated complexes following the general reaction (iii.6) of figure 3. Transfer to cathodic mercury of an organic group (R) from the organometallic radical (RM.) such as an organolead compound is also a known reaction which corresponds to process (iii.7) of figure 3.

Examples of these reactions will be given in another section (VIII.A.e.1.11).

(b.6) Elimination of a carbanion. Metal-carbon bond cleavage

The above sections exemplify reactions which proceed by the dissociation of an anionic ligand (Q^-), generally an halide, as a result of the electrochemical reduction, followed by further reactions of the derived organometallic radical (RM.); an example involving a neutral carbon ligand (Q) carbonyl, was also cited (section b.3), the dissociation resulting in M-C bond cleavage.

However, a carbanion (R^-) may also dissociate from the metal site as a result of the reduction and the derived species (formed through M-C bond rupture) may also be involved in further reactions.

Examples of carbanion dissociation induced by a one-electron electrochemical reduction were previously given (equations 29 and 31), and reactions involving two-electron reductions are now cited.

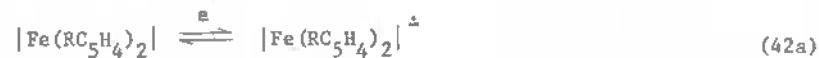
Neutral alkyl or aryl carbonyl complexes of groups VI-VIII can undergo such a type of reaction to give anionic complexes and the carbanions which may be stabilized by protonation due to traces of water present in the solvent medium (equations 41 which correspond to the overall process iv.1 of figure 3). $[\text{MR}(\text{CO})_5]$ ($\text{M}=\text{Mn}, \text{Re}$)⁽⁹³⁾ and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{R}(\text{CO})_2]$ ⁽⁹⁴⁾ react in this



way.

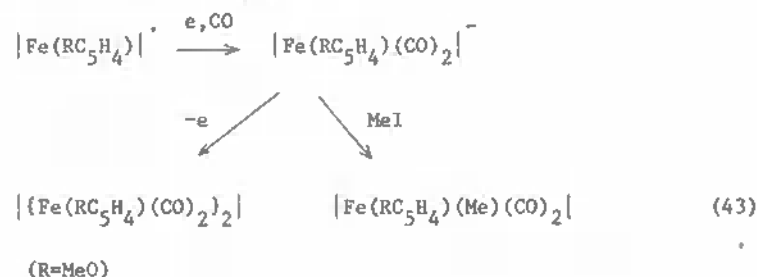
Although, at low temperature, ferrocene and derivatives with an electron donor substituent can undergo reversible one-electron electrochemical reductions, as it was previously mentioned (section III.A), at higher temperatures a two-electron reduction with metal-carbon bond cleavage occurs following an ECE mechanism. (70)

The complex product of the chemical step is suggested⁽⁷²⁾ to be the half-sandwich monocyclopentadienyl-iron radical $[\text{Fe}(\text{RC}_5\text{H}_4)]^\cdot$ (reactions 42).



These reactions follow the general scheme (iv.1) of figure 3.

The neutral radical $[\text{Fe}(\text{RC}_5\text{H}_4)]^\cdot$, or solvated derived species such as $[\text{Fe}(\text{RC}_5\text{H}_4)\text{S}_2]^\cdot$ (S=solvent), is highly reactive (it was not isolated) reacting with CO to afford (for R=MeO), after further reduction, the acetyl-cyclopentadienyldicarbonyliron anion which can be oxidized at a Pt electrode to a dinuclear neutral complex and reacts with MeI to give a neutral σ -methyliron complex (reactions 43).⁽⁷¹⁾



These reactions are represented by the general process (iv.2) of figure 3.

(c) Electrophilic attack

Electrochemical reduction of a transition metal complex may activate a ligand or the metal itself towards attack by an electrophile (e.g., reaction types v.1 and v.2 of figure 3) and this behaviour may have important synthetical applications.

The reduction process may involve one or two electrons and one or two protons, and halide dissociation may also occur (reaction types v and vi.1.1 of figure 3). The electrophile is often a proton but may also be an organic species such as an organohalide or carbon dioxide.

Examples of these reactions will be found in other sections and now only a brief list is mentioned:

- Reduction of carbene ligand to σ -alkyl, e.g., in complexes $[\text{Fe}(\text{TPP})(\text{CX})]$ [TPP= *meso*-tetraphenyl-porphyrin; $\text{X}=\text{C}(\text{C}_6\text{H}_4\text{Cl-4})_2, \text{CPh}_2$ or S] by a $2e+1H^+$ (and also a $1e+1H^+$) process (section VIII. A.c.1).
- Reduction of ketone and acid functional groups at cyclopentadienyl ligand in substituted ferrocene-type complexes ($2e+2H^+$ and $1e+1H^+$ processes (section VIII.A.d).
- Reduction of organo hydrazido(2-) ligands (NNR_2) to amines (HNR_2) ($2e+2H^+$ process) and to hydrazines (H_2NNR_2) ($2e+2e+2H^+$ process) in complexes $[\text{MoBr}(\text{NNR}_2)(\text{dppe})_2]^+$ formed by alkylation of dinitrogen

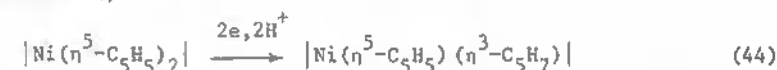
in $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ (section VIII.C.a).

- Electrophilic attack at a cyclopentadienyl ligand in metallocene-type complexes.

Examples:

Reactions of alkyl halide or CO_2 with cobaltocene or cobaltocene anion derived from cobalticinium through a one-electron or an overall two-electron electrochemical reduction, respectively (section VIII.A.C.1).

Proposed protonation of nickelocene to yield an allyl-type ligand (reaction 44).⁽³⁵⁾



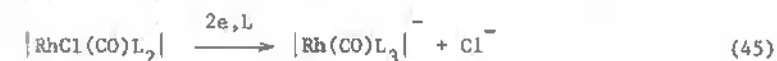
- Electrophilic attack of organohalide at the reduced metal (oxidative addition reaction), occurring, e.g., in the catalytic electrochemical reduction of alkyl halides by square planar macrocyclic nickel complexes (section VIII.B.a - e.g., figure 14).

(d) Further reduction with elimination of an anionic ligand followed by other reactions

In the previous section (b), dissociation of an anionic ligand occurs as a result of a one-electron reduction.

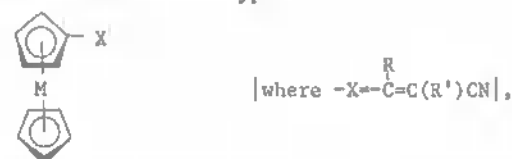
However, examples are also known which involve loss of an anionic ligand only after an overall two-electron reduction process. The ligand which undergoes dissociation may be inorganic (Q^- , such as halide) or a carbanion (R^-) (or both), and the derived organometallic species may be involved in further reactions such as electrophilic attack at a ligand [see the previous section (c)], reaction with solvent or formation of a dinuclear species.

Hence, e.g., a two-electron reduction of the Rh(I) complex $[\text{RhCl}(\text{CO})\text{L}_2]$, in the presence of L (triphenylphosphine), yields the Rh(-I) species $[\text{Rh}(\text{CO})\text{L}_3]^-$ and Cl^- (reaction 45); a dinuclear Rh(o) complex is formed, at ambient temperature, according to reaction (46).⁽⁹⁵⁾

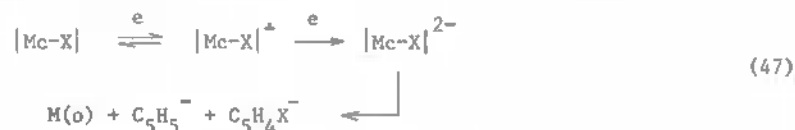


These reactions correspond to the sequence (vi.1.2) of figure 3.

Electrochemical reduction of β -metallocenyisubstituted α,β -unsaturated nitriles of the type



in aprotic solvent (thf or acetonitrile) at a dropping mercury electrode, occurs through a reversible one-electron transfer to afford an anion radical, followed by an irreversible one-electron process with cleavage of the metal-cyclopentadienyl bond to give substituted and unsubstituted cyclopentadienyl anions and the metal (reactions 47) which exemplify process (vi.2) of figure 3; disproportionation of the anion radical may also occur, giving the unstable dianion in an overall apparent single-electron wave. (96)



(where Mc is a metallocenyl group: ferrocenyl, ruthenocenyl or osmocenyl group).

(e) Electrochemical reduction of polynuclear complexes

Although the metal-metal bonds may be retained on the reduction of cluster species — e.g., the double cubane type $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{3-}$ with three thiolate bridges between the two Mo nuclei (97) and complexes with metal-metal multiple bonds — e.g., $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Mo}_2(\text{C}_3\text{H}_7\text{COO})_4]^{+}$ (98,99) with possible formation of mixed-valence complexes, the reduction of di- or tri-metallic complexes usually results in the metal-metal bond rupture.

(e.1) Dinuclear complexes

The reduction of a dinuclear complex may involve a two-electron (to afford two metallate species) or a one-electron process to give an anionic complex and a paramagnetic species which may dimerize or react with the electrode mercury (see figure 4 where M denotes a mononuclear metal site, often a metallic polycarbonyl).

Examples of types (i) and (ii.1) are given by the reactions 48 (100,101) and 49 (62) whereas type (ii.3) is known for the electrochemical reduction of

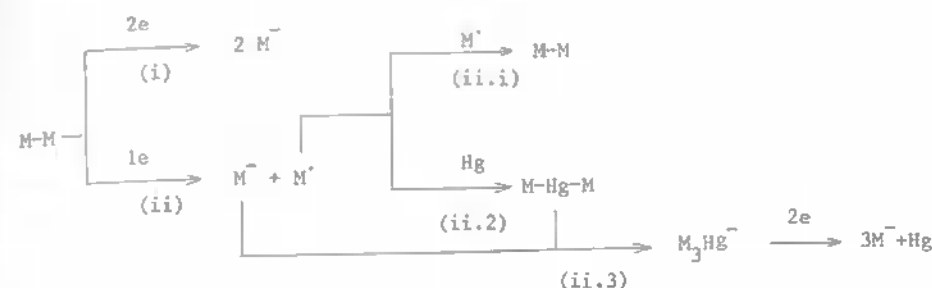
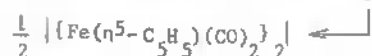


Figure 4 - Possible types of reactions in the electrochemical reduction of organotransition dinuclear complexes

the dimeric complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ in thf/ $[\text{NBu}_4][\text{BF}_4]$ at a dropping mercury electrode. (102)

The $\text{M}^{\cdot-}$ radical, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^{\cdot-}$, reacts with mercury electrode to give a neutral trinuclear complex with bridging mercury which upon reaction with the anion $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ affords a tetrametallic species $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_3\text{Hg}$; this complex may undergo further reduction to three monomeric anions M^- with Fe-Hg bond cleavage. The anionic complex M^- may also be formed by one-electron electrochemical reduction of the monomeric species $[\text{FeX}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ ($\text{X}=\text{H}$, halide, CN, GeCl₃, GePh₃, SnCl₃, SnPh₃, SiPh₃), with X^- ligand dissociation (102) (a well known sequence type was mentioned in previous sections — i,iii in figure 3).

(e.2) Trinuclear complexes

Cathodic reduction of linear trimetallic complexes results in metal-metal bond cleavage usually according to reaction (50) for Hg(II) as the central metal.



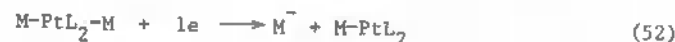
where, e.g., $\text{M}=[\text{Co}(\text{CO})_4]_2$, (9) $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$, (62,63,74) $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ and $[\text{Mn}(\text{CO})_5]$, (93,103) or $[\text{Fe}(\text{CO})_3(\text{NO})]$. (104)

Similar reduction products although formed by a one-electron process, are observed in the cathodic reduction of the Am(I) compounds $(\text{M-Au-M})^-$

(reaction 51). (105,106)



However, different paramagnetic heterobimetallic Pt(I) complexes are formed in the cathodic reduction, on a Pt or Au electrode, of Pt(II) isocyanide compounds of the type $M-PtL_2-M$, according to the proposed (105) reaction

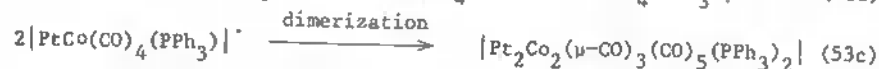
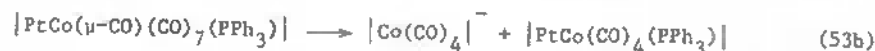


where $M = [Cr(\eta^5-C_5H_5)(CO)_3]$, $[Mo(\eta^5-C_5H_5)(CO)_3]$, $[W(\eta^5-C_5H_5)(CO)_3]$, $[Mn(CO)_5]$, $[Fe(CO)_3(NO)]$, $[Co(CO)_4]$; $L = Bn^tNC$ or $cyclo-C_6H_{11}NC$.

The stabilization of the isocyanide Pt(I) radical is suggested to result from the π -acceptor character of the isocyanide ligand. This radical, detected by e.s.r., was not fully characterized and is involved in further reaction, probably undergoing dimerization or reaction with the solvent. (105,106)

The related triangular platinum-dicobalt clusters $[PtCo_2(\mu-CO)(CO)_7(PPh_3)]$ and $[PtCo_2(\mu-CO)(CO)_6(dppe)]$ are also electrochemically reduced at a solid or mercury electrode, in aprotic medium, through a one-electron irreversible process with liberation of $[Co(CO)_4]^{\cdot-}$ and generation of radicals. (107)

The heterotetranuclear cluster $[Pt_2Co_2(\mu-CO)_3(CO)_5(PPh_3)_2]$ was isolated in good yield from the electrochemical reduction of $[PtCo_2(\mu-CO)(CO)_7(PPh_3)]$, and its formation occurs probably by dimerization of the radical $[PtCo(CO)_4(PPh_3)]^{\cdot-}$ (which however was not detected by e.s.r. possibly due to its short lifetime), according to equations 53. (107)



Each of the clusters $[PtCo_2(\mu-CO)(CO)_7(PPh_3)]$ and $[PtCo_2(\mu-CO)(CO)_6(dppe)]$ undergoes two one-electron oxidation steps, the first being reversible.

IV - ELECTROCHEMICAL QUANTIFICATION AND PREDICTION OF REDOX AND ELECTRONIC PROPERTIES OF METAL SITES AND LIGANDS

Although correlations between the redox potential and other properties of complexes, their ligands or metal sites (energy of charge transfer bands, ionization energy, Hammett's σ parameter, etc.) are already well documented (they will be mentioned in chapters V and VI), only recently a systematic proposal was attempted to quantify the relationships between the redox potential and the structure and constitution of a complex.

This work was initiated by Pickett (26) through the electrochemical study of 18-electron octahedral complexes $[M_6L]$ with 16-electron square pyramidal metal sites $\{M_5\}$ (figure 5).

A linear correlation was experimentally observed between $E_{1/2}^{OX}$ of a series of complexes $[M_6L]$ with a common $\{M_5\}$ site and $E_{1/2}^{OX}$ of their homologues in a isoelectronic and isostructural reference series with pentacarbonylchromium, $[Cr(CO)_5]$, as the metal centre. (26)

This linear relationship may be expressed by the following equation

$$E_{1/2}^{OX} [M_6L] - E_{1/2}^{OX} [M_6(CO)] = \beta \{ E_{1/2}^{OX} [Cr(CO)_5L] - E_{1/2}^{OX} [Cr(CO)_6] \} \quad (54)$$

where carbonyl was taken as a reference ligand, or by the simplified form

$$E_{1/2}^{OX} [M_6L] = E_s + \beta \cdot P_L \quad (55)$$

where

$$E_s = E_{1/2}^{OX} [M_6(CO)] \quad (56)$$

and

$$P_L = E_{1/2}^{OX} [Cr(CO)_5L] - E_{1/2}^{OX} [Cr(CO)_6] \quad (57)$$

Three electrochemical parameters are then defined: (26)

E_s - A measure of the electron-richness of the metal site;

β - A measure of the electronic sensitivity (polarisability) of the metal site to a change of ligand L;

P_L - A measure of the net electron donor/acceptor character of the ligand.

P_L values have already been quoted for a considerable number of ligands (see Table 1). (26,27)

Carbonyl, the reference ligand, has $P_L=0$, by definition.



Figure 5 - Eighteen-electron octahedral complex $[M_8L]$ with 16-electron square pyramid metal site $\{M_8\}$.

NO^+ , a weak electron donor, exhibits a very high P_L value (+1.40 V), whereas in the opposite extreme is hydroxide ($P_L = -1.55$ V), and other anionic strong net electron donor/acceptor ligands.

Isocyanides, when binding in a linear geometry, behave generally as considerable stronger net electron donors (P_L in the -0.44 to -0.33 V range) than their isoelectronic CO ($P_L=0$) and N_2 ($P_L=-0.07$ V) ligands. However, when

TABLE 1. Ligand parameter P_L for various ligands

L	P_L (Volt)	L	P_L (volt)
NO^+	1.40	NH_3	-0.77
CO	0.00	CF_3COO^-	-0.78
N_2	-0.07	NCS ⁻	-0.88
$P(OPh)_3$	-0.18	CN ⁻	-1.00
$CNC_6H_3Cl_2-2,6$	-0.33*	NCO ⁻	-1.16
PPh_3	-0.35	I^-	-1.15
CNC_6H_4Cl-4	-0.37*	Br^-	-1.17
CNPh	-0.38	Cl^-	-1.19
$CNC_6H_4CH_3-2$	-0.38*	H^-	-1.22
$CNC_6H_4CH_3-4$	-0.39*	N_3^-	-1.26
$CNC_6H_4OCH_3-4$	-0.40*	OH^-	-1.55
NCPPh	-0.40		
CNMe	-0.43		
CNBu	-0.44*		
NCMe	-0.58		
Py	-0.59		

All values are taken from reference (26) except those denoted by * which are given by reference (27).

they ligate the electron-rich $\{ReCl(dppe)_2\}$ site, they are stronger net electron acceptors (their geometry is probably bent), and they present higher P_L values (equation 58 where P_L values are in volts),⁽²⁷⁾ in the gross range 0.0 to -0.14 V, thus approaching N_2 and CO in their net electron acceptor character.

$$P_L(\text{CNR bent}) = P_L(\text{CNR linear}) + 0.3 \quad (58)$$

The abovementioned linear relationish (equation 55) between $E_{1/2}^{OX}$ and P_L was observed for a variety of 16-electron metal sites and their E_s and β parameters were estimated (Table 2).

The higher electron-rich Mo(o) metal sites display lower E_s values than the Fe(II) and the Re(I) sites and, within each series with a common metal, anionic species are more electron rich (lower E_s values) than the neutral ones and the latter are more electron-rich than the cationic ones, as expected.

Once the electrochemical E_s , β and P_L parameters are known for a metal site and a ligand, it is possible to predict the half-wave oxidation potential of a new element of a series as well as to identify a complex which $E_{1/2}^{OX}$ value is known (see equation 55). An example of the latter type of application is given by the detection and identification in solution of the unstable complex trans- $[Mo(N_2)(NH_3)(dppe)_2]$ $E_{1/2}^{OX}$ experimentally observed at -0.72 V in agreement with the estimated value of -0.75 V versus s.c.e.) formed in situ by the reaction of trans- $[Mo(N_2)_2(dppe)_2]$ with ammonia in thf.⁽²⁵⁾

Table 2. E_s and β parameters for various 16-electron metal sites

$\{M_s\}$	E_s (Volt) (vs s.c.e)	β
$\{Mo(NO)(dppe)_2\}^+$	+0.91	0.51
$\{Mo(CO)(dppe)_2\}$	-0.11	0.72
$\{Mo(N_2)(dppe)_2\}$	-0.13	0.84
$\{Mo(NCPh)(dppe)_2\}$	-0.40	0.82
$\{Mo(N_3)(dppe)_2\}^-$	-1.00	1.0
$\{FeH(dppe)_2\}^+$	+1.04	1.0
$\{Re(N_2)(dppe)_2\}^+$	+1.20	0.74
$\{ReCl(dppe)_2\}$	+0.68*	3.4*

All values are taken from reference (26) except those denoted by * which are given by reference (27).

Based on these electrochemical parameters, it is also possible to propose some criteria for the coordination of ligands to a metal site and for the chemical reactivity of the derived complexes.⁽²⁶⁾ Examples of the former are mentioned as follows, whereas the latter will be considered separately in the next section.

Metal sites with a low electron-richness (highly positive E_s values) bind preferably ligands which are strong electron donors (with negative and low P_L values).

Dinitrogen, with a high P_L value (near zero) binds preferably a metal site with low E_s although dinitrogen complexes are known with metal sites presenting E_s values within a wide range (from +1.3 to -1.3 V). However, when N_2 binds a site with a high E_s value, the ligand in trans position presents a low P_L value, i.e., it is a strong electron donor; the metal site then has a high polarisability (β). Hence, as a general comment, one may refer that dinitrogen binding to a metal site is favoured by low E_s (high electron-richness) and high β (high polarisability) of the metal centre.⁽²⁶⁾

V - HALF-WAVE POTENTIAL AND CHEMICAL REACTIVITY

A comparison of the half-wave potentials of related complexes (or of the electron-richness, E_s , of their metal sites, or of the P_L values of their ligands) within a series or in comparable series may allow the prediction of some features of the relative chemical reactivity.

Recent applications are found in the field of chemical nitrogen fixation, and examples are also quoted by studies of reversible oxygen uptake.

A - Dinitrogen versus isocyanide reactivity

A study of that type was undertaken⁽²⁸⁾ for the two isoelectronic series of dinitrogen, isocyanide, and carbonyl complexes trans-[ReCl(L)(dppe)₂], (A), and trans-[MoL₂(dppe)₂], (B).

Both types of complexes undergo in $\text{thf}/[\text{Bu}_4\text{N}][\text{BF}_4]$ a one-electron reversible oxidation and a plot of $E_{1/2}^{\text{OX}}$ of the Re(I) complexes versus their Mo(o) homologues is shown in figure 6.

From this plot it is clearly seen that the point that corresponds to dinitrogen lies substantially off the straight line followed by the other species, the dinitrogen complex of Re(I) presenting a $E_{1/2}^{\text{OX}}$ value which is much lower than the value expected on the basis of the trend followed by the other complexes. This may be interpreted as the result of a much weaker electron

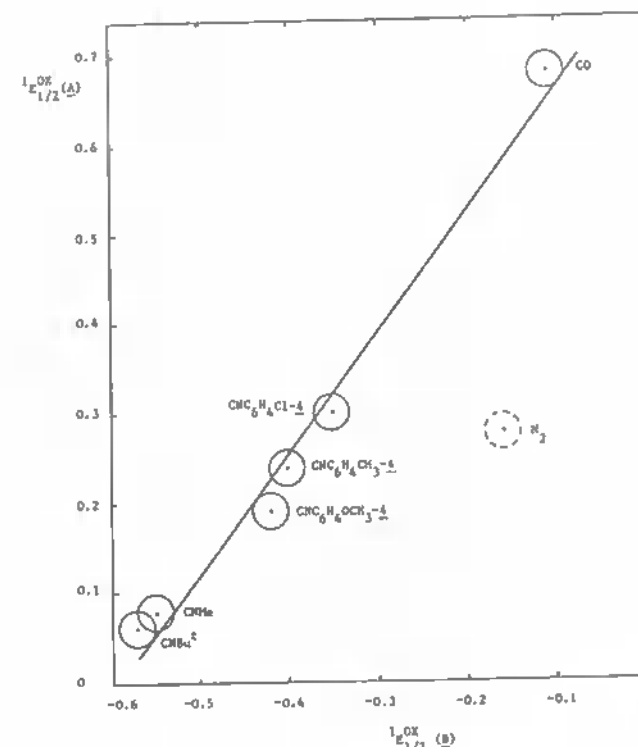
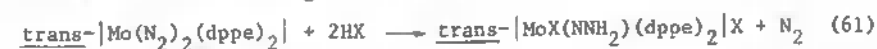
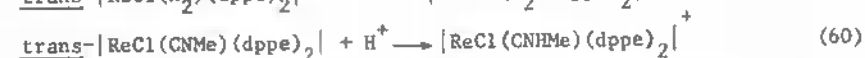


Figure 6 Plot of $E_{1/2}^{\text{OX}}$ for [ReCl(L)(dppe)₂], (A), versus $E_{1/2}^{\text{OX}}$ for [MoL₂(dppe)₂], (B), [L=N₂, CO, CNR].

acceptor character of N_2 when binding the Re(I) site than what would be expected on the basis of the behaviour of the isoelectronic CO and CNR ligands.

Hence, this study evidences that dinitrogen presents, relative to isocyanides, a weaker versatility of accommodation to a decrease in the electron richness of the metal site [when changing from the Mo(o) centre to the less electron-rich Re(I) site]. This rationale agrees with the lack of protonation of N_2 when binds the Re(I) site, although ligating isocyanides can undergo such reaction,^(108,109) and both (N_2 and CNR) are susceptible to attack by acid when binding the more electron rich Mo(o) site⁽¹¹⁰⁻¹¹²⁾ - see, e.g., reactions 59-62.



B - Electrophilic versus nucleophilic attack at dinitrogen

The variation of the reactivity with redox potential of other

dinitrogen complexes with different metal sites was also studied (26,113) and a few observations may be mentioned (figure 7):

- Electron-poor complexes with $E_{1/2}^{OX} > \text{ca. } +0.8 \text{ V}$ react with a nucleophile (LiMe in thf at 25°C) which may attack N_2 (in $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{N}_2)]$, $E_{1/2}^{OX} = 1.2 \text{ V}$), (114) CO (in $\text{trans-}[\text{Re}(\text{CO})_2\text{Cl}(\text{N}_2)(\text{PPh}_3)_2]$, $E_{1/2}^{OX} = +1.37 \text{ V}$) (115) or the metal (in $\text{trans-}[\text{Re}(\text{CO})_3\text{Cl}(\text{PPh}_3)_2]$, $E_{1/2}^{OX} = +1.37 \text{ V}$ to give the metathesis product $\text{trans-}[\text{FeMe}(\text{CO})_3(\text{PPh}_3)_2]$; (115) the site of attack cannot yet be predicted.
- Electron-rich dinitrogen complexes with a metal site with sufficiently low E_s value ($< \text{ca. } 0$) may be protonated, the proton attack occurring at the N_2 ligand or at the metal centre, depending on the value of P_L in the series $\text{trans-}[\text{Mo}(\text{N}_2)\text{L}(\text{dppe})_2]$ as it was shown above.
- Linitrogen complexes with metal sites of intermediate E_s values - e.g., $[\text{FeCl}(\text{dppe})_2]$ ($E_s = +0.64 \text{ V}$) or $[\text{Fe}(\text{NCMe})(\text{dppe})_2]^+$ - are unreactive towards protonation or LiMe (in thf at 25°C).

C - Influence of a co-ligand on the reactivity of dinitrogen

The influence of a co-ligand L upon the chemical reactivity of a dinitrogen complex, $\text{trans-}[\text{Mo}(\text{N}_2)\text{L}(\text{dppe})_2]$, was related to electrochemical parameters (P_L, E_s) and the conclusions, which are summarized in figure 8, may be mentioned as follows: (25)

- As the net electron-donor character of the ligand L increases (i.e., P_L becomes more negative), the stability of the mono- and di-oxidized species increases (i.e., the stability of the M-N_2 bond increases).
- Ligating N_2 is susceptible to undergo protonation when P_L is in the range ca. 0.0 to -0.6 V , whereas for $P_L < -0.8 \text{ V}$ the more reducing metal site appears to reduce the solvated protons to dihydrogen to give an unstable oxidized species which loses N_2 .
- In reactions with alkyl halides, complexes with sufficiently negative oxidation potentials and high reducing power (P_L sufficiently negative) can undergo an outer-sphere electron transfer reaction (e.g., reactions 63). (24,25,116)

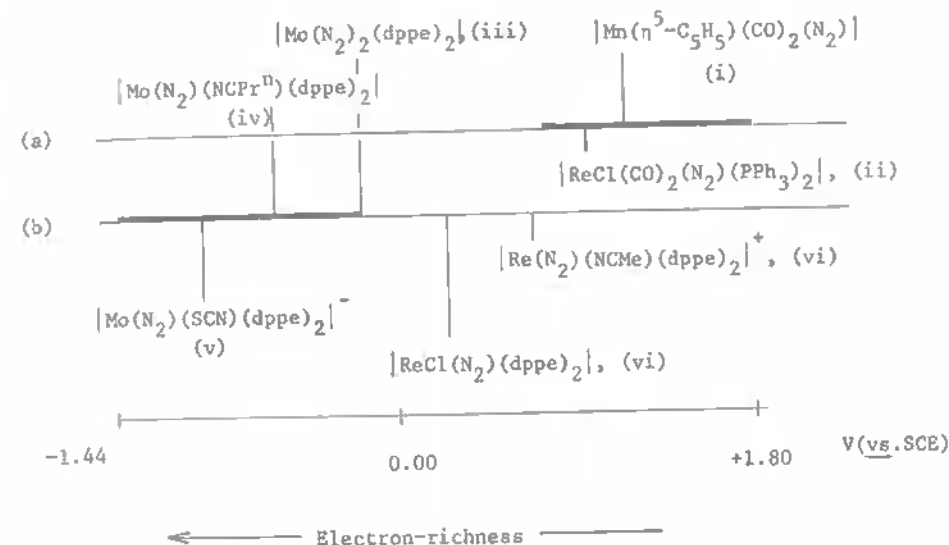
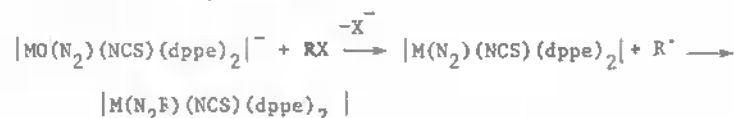
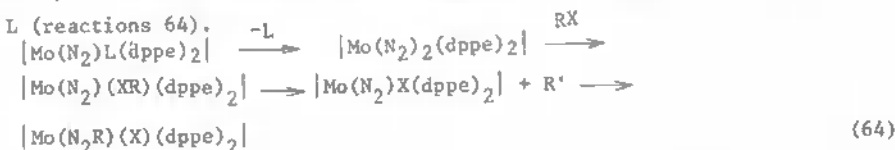


Figure 7 - Variation of reactivity of dinitrogen complexes with redox potential.

(a) Reaction with LiMe(thf, 25°C). (b) Reaction with H_2SO_4 (thf, 25°C)

(i) Attack at N_2 by LiMe. (ii) Attack at CO by LiMe. (iii) Protonation at N_2 or Mo . (iv) Protonation at N_2 . (v) Oxidation by H^+ . (vi) Unreactive towards attack by H^+ or LiMe.

However, other complexes with a weaker reducing power and with a labile L ligand (such as, N_2 or NCPri^i), react with alkyl halides via an inner-sphere redox process, the rate-determining step being the initial loss of L (reactions 64).



Moreover, complexes which present a high reducing power and have a labile ligand may react via both pathways - e.g., the reaction of $[\text{Mo}(\text{N}_2)(\text{N}_3)(\text{dppe})_2]^-$ with Bu^nI .

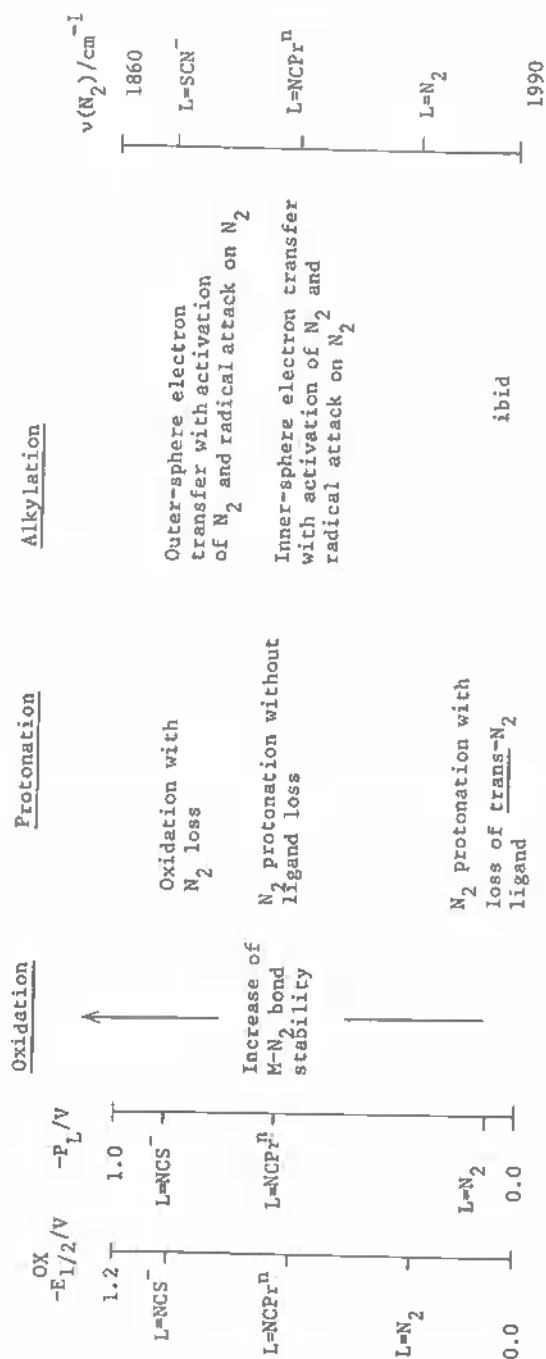
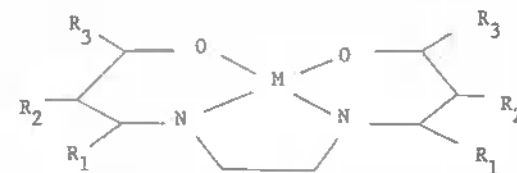


Figure 8 - Dependence of reactivity of complexes $trans-[Mo(N_2)L(dppe)_2]$ on the redox potential and P_L ligand parameter. (25)

D - Reversible oxygen uptake reactions

The reversible oxygen uptake reactions of cobalt complexes are of important biochemical significance, e.g., in the attempt to understand the chemical role of heme in hemoglobin and myoglobin.

The ability of some neutral cobalt(II)⁽¹¹⁷⁾ and nickel(II)⁽¹¹⁸⁾ quadridentate Schiff base complexes of the type



to react reversibly with oxygen was shown to be closely related to the half-wave oxidation potential, a linear correlation being found⁽¹¹⁷⁾ between this electrochemical parameter and the equilibrium constant ($\log K_{O_2}$) for oxygen adduct formation (equation 65) in series of Co(II) complexes $[CoL_4B]$ (B is a unidentate ligand in the axial position; various equatorial L_4 or axial B ligands were considered).



In the O_2 adduct complexes, the O_2 may be viewed as a superoxide (O_2^-) ligating Co(III), as revealed by e.s.r. studies. Hence, the formation of the adduct (equation 65) corresponds to an electron transfer from Co(II) to the O_2 ligand and thus relates to the redox behaviour of the complexes.⁽¹¹⁷⁾

O_2 uptake (or the stability of the adduct) is thus favoured by an increase in electron density at the metal atom which is measured by $E_{1/2}^{OX}$.⁽¹¹⁷⁾ However, if the electron density at the metal exceeds a limit, the complex is irreversibly oxidized.⁽¹¹⁸⁾

VI - HALF-WAVE POTENTIAL AND PHYSICAL PARAMETERS

The oxidation (or reduction) potential of a complex reflects the energy of its HOMO (or LUMO, respectively) orbital and the electron-richness of the metal centre. Hence, it is not surprising that it may be related to other properties of the complex which may also depend on those parameters, such as the chemical reactivity (mentioned in the previous section), the energy of a metal $\rightarrow$ ligand charge transfer band, the ionization potential of the central metal ion, etc.

Examples of redox potential-physical parameters relationships are now cited.

A - Half-Wave Oxidation potential and HOMO energy

The oxidation potential measures the energy difference between the oxidized and the reduced species, including various effects such as differences in solvation energies and in the heats of formation of the complexes. However, since the electron removed is expected to leave the HOMO orbital, a correlation between the energy of this orbital and the oxidation potential for a series of related complexes would be predictable.

In agreement with this prediction, a linear correlation between $E_{1/2}^{OX}$ of the $[Mn(CNMe)_n(CO)_{6-n}]^+$ complexes and the calculated HOMO energy (figure 9) was observed by Fenske: (119)* the greater stability of the HOMO corresponds

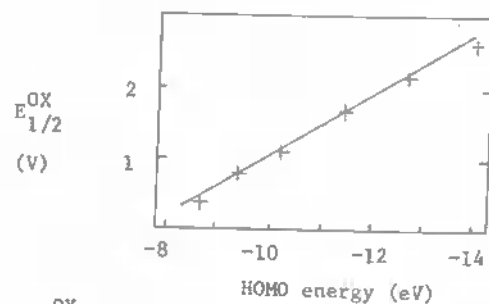


Figure 9. $E_{1/2}^{OX}$ versus HOMO energy for $[Mn(CNMe)_n(CO)_{6-n}]^+$ complexes. (119)

* However, the slope of the line is quite different from the expected unit value (A.A. Vičák, personal communication)

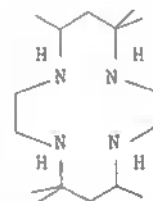
to an increased difficulty of electron removal (higher $E_{1/2}^{OX}$ value).

B - Half-wave potential and gas-phase ionization potential

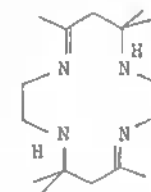
A change in the lowest ionization potential and in the half-wave oxidation potential may both reflect a variation in the electron density at the central atom. A linear correlation may then be observed between $E_{1/2}$ and the ionization potential, namely in chromium sandwich compounds of the chromocene- or bis(η^6 -arene)-type and their substituted derivatives. Hence, e.g., the effect of an electron-donating substituent (such as methyl) causes an increase of electron density on the metal site with resulting decrease in the half-wave oxidation potential and in the ionization potential, as it is observed in the series $[M(\eta^6-C_6H_6)_2]$, $[M(\eta^6-C_6H_5CH_3)_2]$ and $[M(\eta^6-C_6H_3(CH_3)_3)_2]$ ($M=Cr, Mo$ or Nb). (120)

Similar relationships between $E_{1/2}^{OX}$ and the ionization potential (I_p) for a given valence change of the corresponding gaseous metal ions $[E_{1/2}^{OX} \text{ versus } I_p(M^I \rightarrow M^{II}); I_{1/2}^{OX} \text{ versus } I_p(M^{II} \rightarrow M^{III})]$ were reported (121) for complexes of Co, Ni and Cu with macrocyclic tetraaza (nitrogen donor) ligands of the trans-tetramine (cyclam) type shown below, whereas the same trend is observed (122) for $E_{1/2}^{red} (M^{II} \rightarrow M^I)$ versus $I_p(M^I \rightarrow M^{II})$ in Fe, Co, Ni and Cu complexes of the trans-diene type macrocyclic ligand.

These observed linear relationships also evidence that the electron is removed from the metal and not from a ligand-based orbital.



trans-tetramine
type ligand



trans-diene
type ligand

C - Half-wave potential and ligand field stabilization energy

A linear relationship was also observed (122) in low-spin d^6 Co(III) octahedral-type complexes $[CoLX_2]^+$ (where L is a macrocyclic nitrogen donor ligand of the trans-tetramine or trans-diene type - see above) between the

half-wave reduction potential $E_{1/2}^{\text{red}}$ ($\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$) and the ligand field stabilization energy of the axial X ligand ($X = \text{Br}, \text{Cl}, \text{H}_2\text{O}, \text{N}_3, \text{NCS}, \text{NH}_3, \text{CN}$).

All the t_{2g} orbitals are filled in these low-spin $\text{Co}(\text{III})$ complexes and on reduction the incoming electron occupies an e_g LUMO orbital. The higher the ligand field stabilization energy of X, the more destabilized are the e_g orbitals and the more difficult is the reduction; hence, higher ligand field strengths correspond to lower $E_{1/2}^{\text{red}}$.

Similar relationships are followed by other octahedral-type $\text{Co}(\text{III})$ complexes, such as $[\text{CoL}_6]^{n+}$ ($L' = \text{H}_2\text{O}, \text{NH}_3$; $n = +3$. $L' = \text{CN}$; $n = -3$). (123, 124)

D - Half-wave potential and electron donor/acceptor character of the ligands

A general linear expression (valid for 18-electron octahedral-type complexes with a 16-electron square pyramid metal site, $[\text{M}_s\text{L}]$) of $E_{1/2}^{\text{OX}}$ versus the net electron donor/acceptor character of the ligand L (equation 55) was proposed and discussed previously (chapter IV). It was then defined (equation 57) a new electrochemical ligand parameter (P_L) which constitutes a measure of its net electron donor/acceptor character.

However, other parameters (e.g., σ Hammett substituent constants and i.r. stretching frequencies of unsaturated ligands) are known which reflect the electron donor or withdrawal behaviour of a ligand and correlations with half-wave potentials have been reported. Examples are now cited.

(a) $E_{1/2}$ versus σ Hammett constant

(a.1) Substituted cyclopentadienyl complexes

Anodic half-wave potentials have been quoted for a variety of substituted metallocenes and they correlate with substituent constants and shifts of bands in the electronic spectra of the complexes.

Hence, e.g., a linear correlation was found between $E_{1/2}^{\text{OX}}$ and Hammett σ_p of the substituent in the monosubstituted ferrocene $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{X})]$ species. (125, 126)

Related substituent effects were found in substituted cobaltocene species: substituents with electron donor character (such as alkyls and NH_2) favour the oxidation whereas those with electron acceptor character (carboxylic acids and carboxylates) have an opposite effect. (73, 127)

Correlations between $E_{1/2}^{\text{OX}}$ and σ_p constants were also quoted for other substituted metallocenes, e.g., ruthenocenes. (128)

Chronopotentiometric quarter-wave potentials, $E_{1/4}$, measured at a Pt electrode, of mono- and di-substituted ferrocenes (with 1,1' orientation of the substituents) also correlate linearly with the summation of the Hammett σ_p substituent constants. (129) The absence of a direct interaction between the rings is evidenced by the additivity of the substituent effects in disubstituted ferrocenes with one substituent in each ring. (130)

Other less satisfactory linear relationships were observed for Hammett σ_m or Taft σ^* substituent parameters, thus substantiating a considerable effect of the resonance interactions between substituents and the ferrocene centre. Steric effects of bulky substituents do not appear to be present probably due to the cyclopentadienyl ring rotation around the iron atom, thus allowing the approach of this atom to the electrode. (129) It is, however, known (131) that oxidation is favoured by the distortion of the rings when they are bridged by a short-chain bridge.

The mono cyclopentadienyl complexes of the type $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ (where M is a group VII transition metal, Mn or Re) can generally also undergo a one-electron reversible oxidation at a platinum electrode in acetonitrile with $[\text{Et}_4\text{N}][\text{BF}_4]$ and the effect on the oxidation potential of the substituent is analogous to that observed with substituted metallocenes; the replacement of a carbonyl ligand by a better electron donor species such as phosphine results, as expected, in an increase of that potential. Moreover, the Re complexes are harder to oxidize than their Mn analogues. (132)

(a.2) Substituted η^6 -arene complexes

As mentioned above, the conjugation between the aromatic ring and the substituent plays a considerable part in the transfer of the substituent electronic effects to the metal of a metallocene series.

However, in substituted dibenzenechromium $[\text{Cr}(\eta^6\text{-arene})_2]$ complexes - which are isoelectronic and isostructural with ferrocene - the conjugation of the substituents with the ligating ring is weaker and the inductive mechanism plays the major role in such transfer as evidenced from the linear correlation between the half-wave potentials, $E_{1/2}$, and the meta-substituent constants (σ_m^+) (an acceptable fit was not observed for para-substituent constants). (133) A linear correlation was also quoted for $E_{1/2}$ vs. E_{σ_m} (the sum of the Hammett meta-parameter). (120) The electrochemical studies were undertaken by rotating disc electrode (Pt or Au) techniques (133) or at a Pt "flag" working electrode (120) in dimethylsulfoxide with a Bu_4N^+ salt: in the oxidation of the neutral $\text{Cr}(\text{o})$ complexes and in the reduction of the

cationic Cr(I) species one electron reversible redox waves were observed.

The different correlations observed for the dibenzene complexes and the metallocene species conceivably are related to the different type of π -MO's involved in bonding to the metal. Hence, although in metallocenes predominates the interaction of the ring π orbitals with the metal d_{xz} and d_{yz} orbitals (with resulting electronic ligand to metal transfer and decrease of the C-C bond order), (134) in the benzene complexes the ring C-C bond order decrease results mainly from the interaction between the metal $d_{x^2-y^2}$ and d_{xy} orbitals and the ligand π^* orbitals with a resulting electronic transfer from the metal to these ring orbitals. Hence, the resonance transfer of the substituent electronic effects to the metal atom is not favoured in the dibenzene species.

(a.3) Isocyanide and other complexes

Aryl isocyanide complexes are invariably harder to oxidize than their alkyl homologues in agreement with the higher electron withdrawing ability of the aryl substituent.

Moreover, within an aryl isocyanide series, with a variable substituent, such as $[\text{Cr}(\text{CNC}_6\text{H}_4\text{X})_6]$, (135) $[\text{Mn}(\text{CNC}_6\text{H}_4\text{X})_6]\text{PF}_6$, (136) $[\text{FeBr}(\eta^5\text{-C}_5\text{H}_5)(\text{CNC}_6\text{H}_4\text{X})_2]$ (137) and $\text{trans-}[\text{M}(\text{CNC}_6\text{H}_4\text{X})_2(\text{dppe})_2]$ (M=Mo or W), (23) linear correlations (see, e.g., figure 10) have been observed between $E_{1/2}^{\text{OX}}$ data and σ_p or σ_m Hammett substituent group(X) parameters.

The effect of the substituent on the electrochemical process is a combined inductive and resonance interaction as evidenced by the better linear

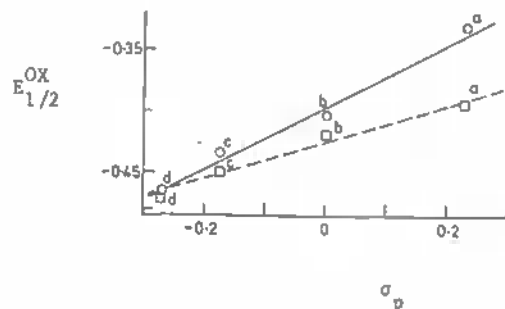


Figure 10 - Plot of $E_{1/2}^{\text{OX}}$ against σ_p for $\text{trans-}[\text{M}(\text{CNC}_6\text{H}_4\text{X})_2(\text{dppe})_2]$, M=Mo or W (open circles correspond to W). X=Cl(a), H(b), Me(c) or OMe(d). (23)

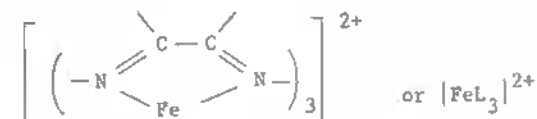
correlation of $E_{1/2}^{\text{OX}}$ with σ_p or σ_m than e.g., with the σ_I Taft inductive parameter or the σ_R pure resonance parameter. (23,135)

Moreover, a substantially better correlation of $E_{1/2}^{\text{OX}}$ with Hammett's σ_p^+ constant than with σ_p appears to be valid in $\text{trans-}[\text{ReCl}(\text{CNC}_6\text{H}_4\text{X})(\text{dppe})_2]$ complexes, suggesting that the HOMO is conjugated to the aryl substituent. (27)

In all the cases, $E_{1/2}^{\text{OX}}$ increases with the Hammett constant, in agreement with the stabilization of the HOMO as a result of an increase in the electron acceptor character of a ligand.

The same trend is observed in complexes with other substituted organic ligands, namely the organodiazenido complexes $[\text{Mo}(\text{NNC}_6\text{H}_4\text{X})(\text{S}_2\text{CNMe}_2)_3]$. (138) E.s.r. data indicate that the HOMO is essentially metal in character and the better correlation for $E_{1/2}^{\text{OX}}$ versus σ (rather than σ^+ or σ^-) evidences that the HOMO is not conjugated to the aryl substituent.

The effect of substituents of the CN unsaturated diazadiene(diimine) ligands on the half-wave oxidation potential of the Fe(II) chromophore complexes



was studied, and a linear correlation (of the type of equation 66)

was observed between $E_{1/2}^{\text{OX}}$ and the summation of the σ^* Taft polar (excludes mesomeric effects) and E_s steric parameters of the substituents. (139-141)

$$E_{1/2} = E_{1/2}^0 + \rho \sum \sigma^* + \delta \sum E_s \quad (66)$$

(b) $E_{1/2}$ versus the energy of a charge transfer band

Linear inverse correlations between $E_{1/2}^{\text{OX}}$ and the energy ($1/\lambda$) of metal to ligand charge transfer bands in series of complexes with isocyanide ligands have been observed for a number of species namely the series $\text{trans-}[\text{M}(\text{CNC}_6\text{H}_4\text{X})_2(\text{dppe})_2]$ (M=Mo or W) (figure 11) (142) and $[\text{M}(\text{CNR})_x(\text{CO})_{6-x}]$ (x=1, M=Cr; (143) x=2 or 3, M=Cr or Mo; (143) x=6, M=Cr, Mo or W (144)).

Since in these complexes $E_{1/2}^{\text{OX}}$ increases linearly with the electron withdrawing ability (Hammett σ constant) of the ligand, a few conclusions may be mentioned:

- Both the HOMO and the LUMO are stabilized by the electron acceptor character of the ligand.

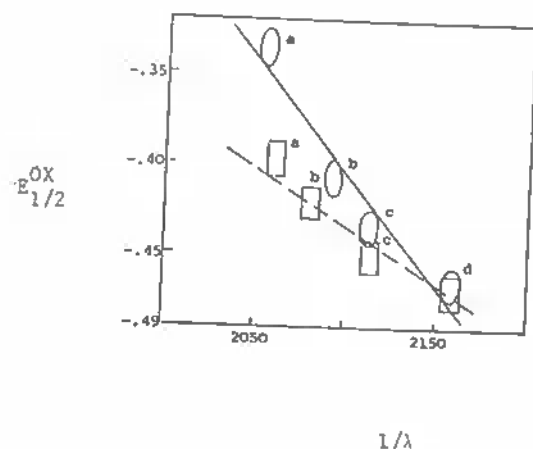


Figure 11. Plot of $E_{1/2}^{OX}$ (volt) versus $1/\lambda$ ($\text{cm}^{-1} \times 10^{-1}$) for $\text{trans-[M(CN}_6\text{H}_4\text{X)}_2(\text{dppe})_2]$ ($\text{M}=\text{Mo}$ or W ; Circles correspond to W). $\text{X}=\text{Cl(a), H(b), Me(c), OMe(d)}$. (142)

- The LUMO shows a greater dependence than the HOMO on this factor.

The same observations were reported (28) for the $\text{trans-[ReCl(CNR)(dppe)}_2]$ complexes, and they have been rationalized (142) on the basis of simplified π -MO schemes with a HOMO resulting from contributions of both the metal and the isocyanide orbitals, whereas the LUMO is mainly based on π CN-antibonding ligand orbitals.

A related inverse (although not linear) dependence of $E_{1/2}^{OX}$ on the energy of a charge transfer band was observed in substituted ferrocenes their $E_{1/2}^{OX}$ values appearing to follow a direct linear relationship with the wavelength shifts of the bands (at ca. 440 nm and 324 nm) of their electronic spectra. (126) The substituents considered have -I inductive effect and, except for those with mesomeric effects, the increase of $E_{1/2}^{OX}$ (which follows the -I effect) parallels a bathochromic shift (to higher wavelengths) of both electronic bands.

Those bands correspond to the $e_{2g} - a_{1g}^*$ (440 nm) and $e_{2g} - a_{2u}^*$ (324 nm) transitions, the e_{2g} being the HOMO whereas the a_{1g}^* and a_{2u}^* are the LUMO orbitals.

Both e_{2g} and a_{1g}^* have a high metal participation whereas a_{2u}^* has a predominant ring character; hence the 440 nm transition has a high metal d-d character whereas the 324 nm transition has a metal-cyclopentadienyl ligand charge transfer character. (126)

An increase in the electron withdrawing ability of the substituent results in the stabilization of the HOMO orbital (thus the increase of $E_{1/2}^{OX}$) and both the LUMO orbitals, the energy of the latter being more affected than the former, as it was observed for the abovementioned $\text{Cr(o)}, \text{Mo(o)}, \text{W(o)}$ or Re(I) isocyanide complexes.

However, a direct linear correlation between $E_{1/2}^{OX}$ and the energy of the metal to ligand charge-transfer band was reported (145) for $[\text{Fe(1,10-phenanthroline)}_2(\text{CNBX}_3)_2]$ ($\text{X}=\text{Me, H, F, Cl}$ or Br) as X varies: the LUMO is probably, essentially phenanthroline- π^* in character and is not unaffected by a change of X , whereas the HOMO energy depends directly on X ; hence, both $E_{1/2}^{OX}$ and the energy of the charge transfer band depend essentially only on the energy of the HOMO, i.e., on the effect of X and the direct linear correlation is observed.

Nevertheless a departure from a linear relationship between $E_{1/2}^{OX}$ and the energy of a metal ligand charge transfer band has been recognized often and may be due, e.g., to differences in the enthalpy of solvation between the oxidized and the reduced species, as it was proposed (140,141) for some tris(diimide)iron(II) complexes with bulky substituents in the diimide ligand.

(c) $E_{1/2}^{OX}$ versus infra-red stretching frequencies

Since intra-red stretching frequencies of unsaturated ligands ($\text{X}=\text{Y}$) such as N_2 , CO and NO reflect the electron-acceptance of their π^* orbitals (from metal filled d orbitals) which is dependent on the electron richness of the metal site, it is not surprising that correlations between $E_{1/2}^{OX}$ and $\nu(\text{X}=\text{Y})$ have been reported: a lowering in the $\nu(\text{X}=\text{Y})$ value corresponds to an inverse in the electron rich character of the metal centre and thus to a decrease in $E_{1/2}^{OX}$.

Linear plots of $E_{1/2}^{OX}$ versus $\nu(\text{X}=\text{Y})$ have been quoted, e.g., for the nitrosyl $[\nu(\text{N}=\text{O})]$ complexes $\text{trans-[Mo(NO)L(dppe)}_2]^n$ ($\text{L}=\text{NCR}, n=+1, \text{L}=\text{NCS}^-, \text{NCO}^-, \text{N}_3^-, \text{I}^-, \text{H}^-, \text{OH}^-; n=0$) (26) and $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{LL}']^+$ ($\text{L, L}'=\text{Lewis base ligand such as tertiary phosphine or phosphite, CO or bipyridine}$), (146) as well as for the dinitrogen $[\nu(\text{N}=\text{N})]$ and carbonyl $[\nu(\text{C}=\text{O})]$ species $\text{trans-[Mo(N}_2\text{ or CO)L(dppe)}_2]^n$ ($\text{L}=\text{NCR, CO, N}_2, \text{NH}_3; n=0, \text{L}=\text{CN}^-, \text{SCN}^-, \text{N}_3^-; n=1$). (25)

The same general trend, although not expressed by a linear plot, was observed grossly in other complexes such as the isocyanide $[\nu(\text{C}\equiv\text{N})]$ $\text{trans-}[\text{W}(\text{CNR})_2(\text{dppe})_2]$ ⁽²³⁾ and $\text{trans-}[\text{ReCl}(\text{CNR})(\text{dppe})_2]$ ⁽²⁷⁾ complexes, and the carbonyl $[\nu(\text{C}=\text{O})]$ trinuclear $[\text{HgCo}_2(\text{CO})_{8-x}(\text{P}(\text{OMe})_3)_x]$ ($x=0,2,4$ or 6). ⁽¹⁴⁷⁾ species.

(d) $E_{1/2}$ versus X-ray photoelectron spectroscopy binding energy

For the series of tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP) complexes of iron $[\text{Fe}(\text{TPP})\text{X}]$ and $[\text{Fe}(\text{OEP})\text{X}]$ ($\text{X}^-=\text{Cl}^-, \text{Br}^-, \text{ClO}_4^-$ or N_3^-) the half-wave potentials for reduction of Fe(III) (measured in CH_2Cl_2 at a Pt electrode) correlate linearly with the $\text{Fe}2p_{3/2}$ binding energies measured by X-ray photoelectron spectroscopy. ⁽¹⁴⁸⁾

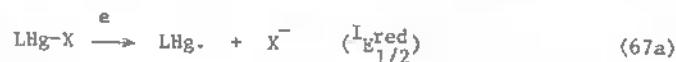
This has been explained in terms of a common dependence of those parameters on the charge density about the Fe(III) site (which is dependent on the electron donor ability of the halide or pseudo-halide X ligand): an increase in the charge density leads to a decrease in the half-wave potential and in the binding energy of the Fe core electrons. ⁽¹⁴⁸⁾

(e) Other cases

The effects of the electronic properties of ligands on $E_{1/2}$ are often discussed, although usually in a qualitative way without the attempt to get well defined correlations with physical parameters.

This type of approach is convenient in the qualitative interpretation of the relative redox behaviour of related complexes and a few examples are mentioned, involving organomercurials and complexes with sulphur bonded ligands.

Organomercury halides of the type $[\text{HgXL}]$ (L=organic ligand) undergo electrochemical reduction in two one-electron steps (reactions 67), with rupture of the Hg-X bond (to give the LHg radical) in the first step which is followed by formation of the carbanion L^- in the second step. ⁽¹⁴⁹⁾



Although the first half-wave reduction wave ($I_{E_{1/2}}^{\text{red}}$) is mainly

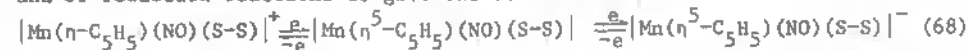
dependent on X (and not on L), a linear relationship was reported between $II_{E_{1/2}}^{\text{red}}$ and the electronic affinity of the radical $\text{L} \cdot$ or the basicity of the carbanion L^- (expressed by pK_a of the acid LH). ⁽¹⁴⁹⁾

Moreover, when interaction of the C-Hg σ -bond with the π -system of L (σ, π -conjugation) is possible (e.g., when an aldehyde, a ketone or an allyl group is present in L), $II_{E_{1/2}}^{\text{red}}$ is less negative (the second step reduction is then favoured) than in the other cases where such a σ, π -conjugation effect is absent. ⁽¹⁵⁰⁾

Within the electrochemical studies which evidence the dependence of $E_{1/2}$ on the electronic electron donor/acceptor character of the ligands, the following examples may be cited for complexes with sulphur bonded ligands.

The thio-bridged binuclear complexes $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{L})(\mu\text{-SR})_2]$ ($\text{M}=\text{Mo}$, $\text{L}=\text{NO}$; $\text{M}=\text{Fe}$, $\text{L}=\text{CO}$; $\text{R}=\text{alkyl}$ or aryl) or $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\mu\text{-SR})_2]$ ($\text{M}=\text{Co}$, Ni) undergo a one-electron reversible oxidation (dicationic Fe and Ni species are also formed irreversibly at a Pt electrode, and the half-wave potential is dependent on R, the aryl groups corresponding to higher values than those observed for the alkyl species, in agreement with the stronger π acceptance of the former. ⁽¹⁵¹⁾

Although in $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{I})(\text{S-S})]^-$ only an ill-defined one-electron oxidation step was observed, the related 1,2- and 1,1-dithiolate manganese complexes $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{S-S})]^z$ ($z=0$ or -1 ; S-S = ligand derived from *cis*-1,2-disubstituted ethylene dithiolates, benzene-1,2-dithiols, $\text{S}_2\text{C}=\text{X}$ where $\text{X}=\text{C}(\text{CN})_2$, $\text{C}(\text{CN})(\text{CO}_2\text{Et})$, $\text{N}(\text{CN})$, NMe_2 or NEt_2) undergo reversible oxidation and/or reduction reactions to give the redox series ^(152,153)



Within these complexes the half-wave potentials for the various couples become increasingly negative as the electron-acceptor ability of the sulphur ligand substituents decreases.

The related thioxanthate complexes $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})(\text{S}_2\text{CSK})]$ undergo a reversible one-electron oxidation reaction to the corresponding cationic species and although the half-wave potentials for this process are not appreciably sensitive to R, they occur at values which are about 100 mV higher than those observed for the corresponding dithiocarbamates in agreement with the greater electron-withdrawing ability of the thioxanthate ligand relative to the dithiocarbamate. ⁽¹⁵⁴⁾

E - Half-wave potential and n.m.r. parameters

N.m.r. parameters (chemical shifts and coupling constants) have

been also correlated with the half-wave potential as shown by the following examples.

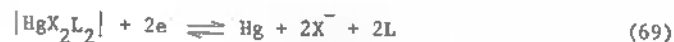
A correlation was observed between $E_{1/2}^{\text{red}}$ of the $[\text{Co(en)}_3]^{3+/2+}$ (en=ethylenediamine) redox couple and $\delta(^{59}\text{Co})$ n.m.r. chemical shift in various solvents (from nitromethane to hexamethylphosphoric acid triamide, corresponding to a wide range of Gutmann donor numbers from 2.7 to 38.8): with decreasing $E_{1/2}^{\text{red}}$, the $\delta(^{59}\text{Co})$ values are shifted to higher field corresponding to an increase in electron density at the metal with increasing the Gutmann donor number of the solvents (an inverse linear relationship is observed between this parameter and $E_{1/2}^{\text{red}}$ - see section G).

These features are explained⁽¹⁵⁵⁾ by considering the outer-sphere solvation of the complexes through a donor-acceptor interaction between the ethylenediamine ligand and a donor solvent molecule (S), $\text{Co} \cdots \text{N} \cdots \text{H} \cdots \text{S}$. This interaction is favoured by the increase in polarity of the N-H bond on coordination of the en ligand, and is more pronounced for Co(III) than for Co(II) due to the stronger electron acceptance of the former.

The electrochemical studies of this Co(III)/Co(II) system were performed at a dropping mercury electrode using a Ag/AgCl electrode in aqueous KCl solution as the reference electrode. The values of $E_{1/2}^{\text{red}}$ were referred to $E_{1/2}^{\text{red}}$ of the bisphenylchromium (I/O) couple in the respective solvents in order to eliminate the influence of variable diffusion potentials at the aqueous/non-aqueous interface.⁽¹⁵⁵⁾

In cyclopentadienyl complexes, $E_{1/2}$ may correlate with the n.m.r. chemical shift of the $\eta^5\text{-C}_5\text{H}_5$ protons, as it was observed in the oxidation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CNC}_6\text{H}_4\text{X})_2\text{Br}]$: $E_{1/2}^{\text{OX}}$ increases linearly with both the electron acceptance of the substituent (X) (as measured by its Hammett σ parameter) and the chemical shift $\delta(\text{C}_5\text{H}_5)$. Hence, a decrease in the electron richness of the metal hampers its oxidation and is accompanied by a C_5H_5 proton chemical shift to lower field.⁽¹³⁷⁾

Mercury(II) dihalide diphosphine complexes $[\text{HgX}_2\text{L}_2]$ (X=Cl, Br, I; L=tertiary phosphine) undergo, at a Hg electrode, reversible two-electron reductions with formation of elemental mercury, free halide and free phosphine (reaction 69).



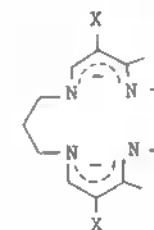
The half-wave reduction potential in this series of complexes is shown to follow direct linear correlations with $\delta(^{31}\text{P})$, $\delta(^{199}\text{Hg})$ and $J_{\text{P-Hg}}$ n.m.r. data.⁽¹⁵⁶⁾

F - Half-wave potential and ligand structural parameters in macrocyclic complexes

The redox potential of the central metal in complexes with macrocyclic ligands is sensitive to the effects which determine the structure (and thus the electronic properties) of these ligands. Hence, e.g., it is dependent on the size of the macrocyclic cavity, the coordination number, the degree of unsaturation of the chelate ring, the nature and position of the ring substituents and the change of the macrocyclic ligand.⁽¹⁵⁷⁻¹⁶¹⁾

The Ni(II)/Ni(III) redox couple with tetraaza cyclic macrocyclic ligands has been widely studied and $E_{1/2}$ may span over a wide range (ca. 2V) by changes in the structure of the macrocycle. The redox behaviour of these complexes has been interpreted on the basis of two interesting properties of this type of ligands:⁽¹⁵⁷⁾ strong in-plane metal-nitrogen interactions which raise the energy of the orbital (essentially metal localized) from which the electron is removed in the oxidation of Ni(II) to Ni(III) (thermodynamic effect); steric protection of the oxidized metal cation in a closed framework against other reagents (solvent, etc.) (kinetic effect). These effects favour the formation of stable complexes with the metal in an unusually high oxidation state and this effect has been recognized since the pioneering work of Olson and Vasilevskis.⁽¹⁶²⁾

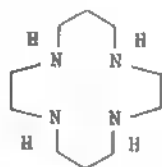
Direct linear relationships between $E_{1/2}^{\text{OX}}$ and d-d transition energies and also between $E_{1/2}^{\text{OX}}$ and Hammett σ values of substituents in macrocyclic ligands have been reported, e.g., for the Ni(II) complexes with the macrocyclic dianionic ligand⁽¹⁶³⁾



However, these types of correlations are not distinctive of macrocyclic complexes, have already been mentioned, and the present section focuses on other types of relationships which are typical of complexes with tetraaza macrocyclic rings.

(a) Ring size and other stereochemical parameters

In a comparative electrochemical study of polyaza n-dentate ($n=4,5$ or 6) amine macrocyclic complexes of Ni(II), $[\text{Ni}(\text{macrocycle})]^{2+}$, in acetonitrile at a Pt electrode, it was observed⁽¹⁵⁷⁾ that the value of $E_{1/2}^{\text{OX}}$ of the Ni(II)/Ni(III) redox couple was minimum (less positive) [i.e., the oxidation of Ni(II) to Ni(III) was most favoured] for the symmetric 14-membered tetraaza ligand (1,4,8,11-tetraazacyclotetradecane, denoted by $|14|\text{aneN}_4$)



This ligand appears to have the best size to surround Ni(II) cation and to establish strong in-plane coordinative bonds. For a contraction or an expansion of the ligand cavity (atomicity lower or higher than 14), a decrease of the electron donating ability occurs as a result of the in-plane distortion of the nitrogen atoms, and $E_{1/2}^{\text{OX}}$ may increase drastically.⁽¹⁵⁷⁾

However, an increase in ring size favours the reduction of Ni(II) to Ni(I) ($E_{1/2}^{\text{red}}$ becomes less negative) although the Ni(II) $\rightarrow$ Ni(III) oxidation becomes less facile. This may be accounted for by considering an increase in the ideal metal-donor atom distance (ideal "hole size") with the increase of electron density at the metal upon reduction: Ni(III) $\rightarrow$ Ni(II) $\rightarrow$ Ni(I).⁽¹⁶⁰⁾

Other stereochemical effects may be invoked to explain the effect of axially oriented methyl substituents on the macrocyclic ring.

Although the Ni(II) complexes are four-coordinate, the Ni(III) derivatives are hexa-coordinate with two axially coordinated solvent molecules and non-bonding interactions [which are more pronounced in the complexes of Ni(III) than of the larger Ni(II) ion] occur between these ligands and the axially oriented methyl groups on the ring. As a result of this extra strain energy to overcome, electrochemical oxidation is hampered.

The redox potential $E_{1/2}^{\text{red}}$ $[\text{Co(III)} \rightarrow \text{Co(II)}]$ of the hexacoordinated $\text{trans-}[\text{Co}(|13-16|\text{aneN}_4)\text{Cl}_2]^+$ complexes is also sensitive to the ring size and correlates (roughly linearly) with the conformation strain energy calculated as the enthalpy arising from bond length deformations, non-bonded interactions, bond angle deformations and torsional angle deformations. The sequence

correspond to $|16| > |15| > |13| > |14|$ and agrees with the opposite order of stability.⁽¹⁶⁴⁾

According to the observed correlation between $E_{1/2}^{\text{red}}$ and the strain energy, Co(III) is favoured over Co(II) (reduction only occurs at more negative potential values) as the strain energy of the Co(III) complex decreases which suggests that the corresponding property of the Co(II) product complex plays an insignificant role, i.e., the strain energy is largely relieved upon reduction of the central metal ion $[\text{Co(III)} \rightarrow \text{Co(II)}]$ (a less strained ligand chelation occurs in the ion with a larger radius).⁽¹⁶⁴⁾

In these $\text{trans-}[\text{Co}(|13-16|\text{aneN}_4)\text{Cl}_2]^+$ complexes the ligand field strength due to macrocyclic ligand strength (Dq^{xy}) does not correlate with the strain energy (and, hence, with $E_{1/2}^{\text{red}}$) but the observed order of Dq^{xy} , $|13| > |14| > |15| > |16|$, may be rationalized in the following way by considering the macrocyclic ligand as a stiff elastic band which encircles the metal ion: the ligand $|14|\text{aneN}_4$ presents the best size to fit Co(III) (Dq^{xy} is normal for saturated amines) and a constrictive effect of the smaller ring $|13|\text{aneN}_4$ on the metal ion increases the metal-nitrogen interaction and hence results in an enhancement in Dq^{xy} , whereas a decrease of Dq^{xy} results from the dilative (stretching) effect on the Co(III)-N bonds due to the larger $|15|\text{aneN}_2$ and $|16|\text{aneN}_2$ rings.⁽¹⁶⁴⁾

(b) Ligand unsaturation

Ligand unsaturation also influences the half-wave potential which undergoes an anodic shift with increasing unsaturation; hence, an increased stability of the lower valent state [e.g., Co(I)⁽¹⁶⁵⁾ or Ni(II)⁽¹⁶⁰⁾] with respect to the higher valent one results from increasing the degree of ligand unsaturation.

The magnitude of the $E_{1/2}$ shift is further enhanced by the presence of a conjugated α -diimine in the macrocyclic ring and, e.g., the extent of electron density delocalization is such that in the reduction of $[\text{Ni}(|14|1,3\text{-dieneN}_4)]^+$, the electron is added to a ligand antibonding π^* orbital (as evidenced by e.p.r. data) and not to a metal localized ($d_{x^2-y^2}$) orbital as observed in the reduction of the unsaturated complex $[\text{Ni}(|14|1,4,8,11\text{-tetraeneN}_4)]^{2+}$ with isolated imines.⁽¹⁶⁰⁾

(c) Additivity of ligand structural parameters

The effects (ΔE) of various factors on the reversible half-wave potential of macrocyclic tetraaza complexes were shown to be additive and, e.g., the following contributions were proposed for the Ni(II)/Ni(III) redox

couple⁽¹⁶⁰⁾.

	ΔE (mV)		ΔE (mV)
Ring size		Two axial methyl groups	+183
14 → 15	+225	Isolated imine	+43
14 → 16	+375	α -Diimine	+170
		Delocalized charge	-430

Analogous additivity relationships were found in the Fe(II)/Fe(III) ^(160,166) and Co(I)/Co(II) ^(165,166) couples : e.g., in the former, the two axial methyl group effect is +110 mV, the isolated imine effect is +49 mV and the α -diimine contribution is +304 mV.

6 - Solvent and supporting electrolyte effects on the half-wave potential

The half-wave potential of a transition metal complex depends not only on the intrinsic properties of the metal site and ligands but also on factors which are controlled by the solvent and the supporting electrolyte.

These "extrinsic" effects on $E_{1/2}$, which result from the interaction of components of the medium (solvent or ions of the supporting electrolyte) with the complex under study or its electron transfer derived product, have not yet been widely studied but a few examples may be cited.

An inverse linear relationship was reported⁽¹⁵⁵⁾ between $E_{1/2}^{\text{red}}[\text{Co(en)}_3]^{3+/2+}$ referred to the bisphenylchromium(I/O) couple to avoid the interference of the contributions due to ligand junction potentials and the Gutmann donor numbers of a wide range of donor solvents (see section E), the half-wave reduction potential being shifted to more negative values with increasing the donor number of the solvent. $E_{1/2}^{\text{red}}$ also relates to the ^{59}Co resonance value (a decrease in the former corresponds to an upfield shift of the later) and all these results are rationalised by considering the outer-sphere solvation of $[\text{Co(en)}_3]^{3+}$ and, to a lesser extent of the Co(II) complex through a donor-acceptor interaction between the solvent molecules and the H atoms of the en ligands (see section E).⁽¹¹⁵⁾

At a Pt electrode the dimeric tetra- μ -carboxylato-dirhodium(II) $[\text{Rh}_2(\text{O}_2\text{CR})_4]$ complexes are reversible oxidized by a single electron to the mixed Rh(III)-Rh(II) species, and for R=Et the dependence of $E_{1/2}^{\text{OX}}$ on the solvent was studied:⁽¹⁶⁷⁾ a linear inverse plot of $E_{1/2}^{\text{OX}}$ (referred to

$E_{1/2}^{\text{OX}}$ of the ferrocene/ferrocinium couple, in order to eliminate the influence of liquid junction potentials) versus Gutmann donor numbers was observed as in the abovementioned $[\text{Co(en)}_3]^{3+/2+}$ system. However, in the rhodium complexes, the relationship is interpreted by considering the bonding ability of the solvent at a free axial position of the rhodium metal in the dinuclear complex. The decrease of $E_{1/2}^{\text{OX}}$ with an increase of the solvent donicity is a result of the expected destabilization of the HOMO.⁽¹⁶⁷⁾

An analogous relationship between $E_{1/2}^{\text{red}}$ and the Gutmann donor number of the solvent was reported for a series of iron(III) complexes with hexadentate ligands derived from triethylenetetramine and various substituted salicylaldehydes.⁽¹⁶⁸⁾

In both the dirhodium(II) $[\text{Rh}_2(\text{O}_2\text{CR})_4]$ and the iron(III) series, the half-wave (oxidation and reduction, respectively) potential is also dependent on the substituent (of the carboxylato or of the salicylaldehyde derived ligand, respectively), a linear relationship being observed with the summation of the inductive and polar Taft substituent constants.

The half-wave potential may also vary with the nature of the electrolyte and interesting linear correlations (of the type of equation 70) between the half-wave reduction potential of tris(acetylacetonato)iron(III) at a mercury electrode and the reciprocal of the cationic unsolvated radius ($1/r_M^+$) of the supporting electrolyte M^+ClO_4^- ($\text{M}^+=\text{Li}^+, \text{Na}^+, \text{K}^+, \text{NEt}_4^+$) were reported for a variety of solvents.⁽¹⁶⁹⁾

$$E_{1/2} = E_{1/2}^0 + \mu(1/r_M^+) \quad (70)$$

In this expression, $E_{1/2}^0$ and μ are the intercept and the slope observed for each solvent. The dependence of μ on the nature of the solvent was also investigated and a linear inverse plot of μ versus the Gutmann donor number of the solvent was experimentally observed. Hence, for a common electrolyte, the dependence of $E_{1/2}$ on the donicity of the solvent follows the trend already mentioned for the dirhodium(II) and the iron(III) species. No correlation was found between μ and the dipole moment or the dielectric properties of the solvent, thus ruling out a pure electrostatic interaction.

The effect of the electrolyte (a decrease in the cationic radius results in an increase of $E_{1/2}^{\text{red}}$, favouring the reduction) was interpreted by considering the coordinative relaxation of the reduced product, $[\text{Fe(acac)}_3]^-$, to allow the transfer of an acetylacetonato ligand to the M^+ electrolyte cation (equations 71, where the subscript solv. denotes a solvated species). The Lewis acidic character of the alkali metal cation M^+ (and hence its





interaction with an electron donating species) increases with the reciprocal of the radius, $1/r_{\text{M}^+}$, and is believed to be much stronger than any of the other species which are involved in equations 71; these facts are suggested to present a high influence on the electrochemical process

The dependence of the redox properties on both the nature of the solvent and the supporting electrolyte has also been observed in acetylacetonato complexes of Mn(III)⁽¹⁷⁰⁾ and Cu(II).⁽¹⁷¹⁾

VII - ELECTROCHEMISTRY OF REDOX SERIES

A redox series of complexes is defined as a set of complexes which present identical composition but differ in the overall number (n) of electrons. Hence, the following sequence (72) (with more than two redox steps) represents such a series:



where m is the number of ligands and z is the charge of the complex.

A systematic study of the redox properties of these series was undertaken⁽¹⁷²⁾ for the cases L is a redox active ligand (a ligand which, in the uncomplexed form, can undergo a reduction or an oxidation) with a bidentate character and belonging to a conjugated system (e.g., a dipyridyl or a β -diketone).⁽¹⁷²⁾

These complexes present a strong ligand-ligand interaction and their electrochemical properties have then been interpreted by considering them, in a limiting case, as being formed by a central metal atom and a "cluster" of inter-acting ligands (L_m).

A - Number of elements of a redox series

In a redox series, the maximum number (N_{max}) of redox steps is given by

$$N_{\text{max}} = N_M + m N_L \quad (73)$$

where N_M is the number of metal based redox steps and N_L is the number of electrons the free ligand (L) can exchange (e.g., if the most oxidized form is taken as reference, N_L corresponds to the number of electrons the ligand can be reduced).

N_{max} is, however, also governed by other factors such as the overall charge of the complex and, e.g., if N_M is large, the charge of the most reduced

complexes may be highly negative and too unstable.

Moreover, for the high overall negatively charged species, the E^0 values for ligand based redox steps move towards more negative potentials and may eventually become inaccessible. Hence, e.g., for $[\text{Cr}(\text{dipy})_3]^z$ redox series, $N_M=3$, $N_L=2$ and then $N_{\text{max}}=3+3 \times 2=9$; however, only six steps are observed: further steps would correspond to negative charges (z) lower than -3 and are out of experimental reach.

Hence, it is common to find that the number of experimentally accessible redox steps is lower than N_{max} .

From the analysis of various experimental data⁽¹⁷³⁻¹⁷⁶⁾ it was proposed⁽¹⁷²⁾ the following generalization:

The N_{max} redox steps are divided into N_M separated steps and N_L sets of one electron steps each containing m individual steps (see the Ir series in figure 12).

This can be interpreted on the basis of MO-calculations for the complexes considered as being formed by the metal atom and a cluster of interacting L_m ligands.

In a simplified way the redox behaviour of the series $[\text{M}(\text{dipy})_3]^z$ (figure 13) may be interpreted as follows. They belong to the ML_3^z type, and each ligand (with a vacant π -antibonding orbital and $N_L=2$) contributes with one redox orbital. Due to ligand-ligand interactions, the set of these three degenerate orbitals is split and a "triplet" of redox steps results from their stepwise half-filling whereas another "triplet" arises from the stepwise filling-up of the same orbitals; the energy between each level is small, corresponding to the third case of the ΔE^0 criterion (see below).

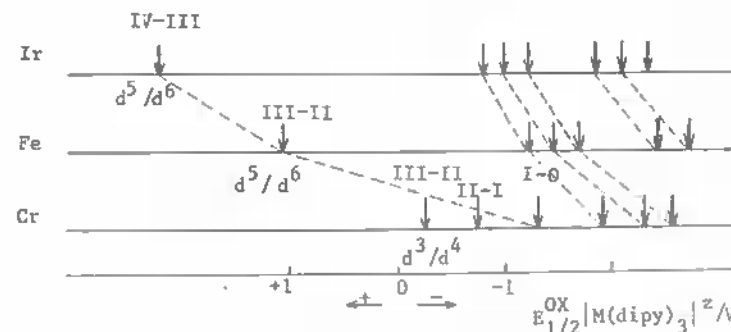


Figure 12 - Redox steps in the redox series $[\text{M}(\text{dipy})_3]^z$.⁽¹⁷²⁾

Clearly distinguished redox steps occur in so-called "well-behaved" series (e.g., Ir and Fe series in figure 12) which correspond to high energy separation between metal and ligand based orbitals with resulting weak mixing of metal d and ligand π -antibonding orbitals. However, the series may deviate from this behaviour and in the opposite limit one cannot distinguish between metal- and ligand-based redox steps. The Cr series of figure 12 corresponds to an intermediate case where a considerable metal and ligand orbitals mixing occurs.

The various redox states of a redox series are not equally stable and, e.g., on the basis of simplified MO considerations, an extra stabilization energy is expected for L_{π} ligand "clusters" with half-filled or fully occupied redox orbitals, in analogy with the known behaviour of free metal ions, e.g., with d^5 or d^{10} electronic configurations.

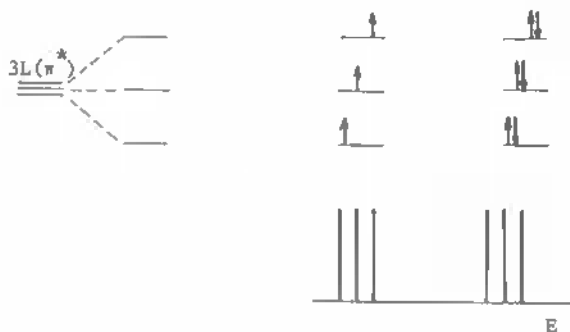


Figure 13 - Ligand based redox steps in the redox series $|M(dipy)_3|^{2+}$

B - Estimation of metal-based redox steps

Although the prediction of the value of this parameter is not yet fully established, some empirical rules have been proposed. (172)

Hence, e.g., the most common oxidation states of the metal in

complexes with redox inactive ligands are considered and the reduction (or oxidation) potentials (E^0) of the redox processes involved are compared according, e.g., to the following limit criteria proposed⁽¹⁷⁷⁾ on the basis of experimental evidence and MO-calculations:

Redox step 1	Redox step 2	$\Delta E^0 = E_1^0 - E_2^0$
$a \xrightarrow{E_1^0} a^1$	$a^1 \xrightarrow{E_2^0} a^2$	0,3-0,9 V
$a^1 \xrightarrow{E_1^0} a^2$	$a^2 \xrightarrow{E_2^0} a^2 b^1$	1,5-3V
Redox steps which correspond to ionization from closely spaced orbitals or from a nearly degenerate set of orbitals in the course of which changes in orbital and spin pairing are comparable		0,2-0,5 V

where a and b denote redox orbitals in the complex.

If E^0 for a redox step is known (experimentally measured or with an expected value on the basis of experimental values known for other complexes), the ranges for the E^0 values of other redox steps (and, hence, the possibility of their detection) may be predicted grossly.

Hence, e.g., chromium, with a most frequent d^3 configuration, a common d^3-d^6 range and $E^0(d^3-d^4)$ away from the limits of the experimentally available potential range, is expected to exhibit three redox steps ($N_M=3$) (see figure 12); a fourth redox step (d^3-d^2) may, however, be observed in the presence of ligands which can stabilize a high positive charge at the metal.

However, iron has d^5 and d^6 configurations as the most frequent ones, d^5-d^6 step is observed but d^6-d^7 is expected to occur at a much lower potential (second case in the abovementioned ΔE^0 criterion) and is not observed; moreover, d^4-d^5 would be at a considerable higher E^0 value than $E^0(d^5-d^6)$ (the latter being higher than the corresponding value for $Cr d^3-d^4$) and is also not detected. Thus, $N_M=1$ for iron (figure 12).

VIII - ELECTROSYNTHESIS AND CATALYSIS

Electrochemistry may constitute a powerful preparative tool of organometallic complexes. They may also behave as intermediate species, generated in situ, in the synthesis of organic compounds. Examples are also known with the involvement of catalytic organometallic intermediates.

The electrochemical activation of a ligand may play a fundamental role in these reactions as this topic will be considered further in the fields of nitrogen fixation and carbon dioxide activation.

A - Electrosynthesis of organometallic complexes

(a) Introduction

Electrochemical oxidation or reduction of a transition metal complex constitutes a potential versatile route for the preparation of a wide variety of new species which, however, may be difficult to isolate due to their unstability or to the non-selectivity of the redox process with possible formation of mixtures of products.

Simple oxidized or reduced complexes, sometimes with the transition metal in an unusual oxidation state, may be prepared, generally by controlled potential electrolysis.

Hence, e.g., paramagnetic isocyanide complexes of $Mo(I)$ or $W(I)$, trans- $[M(CNR)_2(dppe)_2]^+$ ($R=alkyl$ or $aryl$) may be prepared by electrochemical

oxidation of the neutral parent species;⁽²³⁾ the same cationic species are obtained by chemical oxidation.⁽¹⁴²⁾

Electrochemical oxidation, or reduction, of $Ni(II)$ complexes of certain tetraaza macrocyclic ligands of the trans-tetramine and trans-diene types mentioned in section VI.B, leads to the corresponding complexes with unusual tripositive, or unipositive, respectively, nickel oxidation states.⁽¹⁶²⁾

Similar complexes of copper in the uncommon +3 oxidation state may also be prepared by constant potential electrolysis of parent $Cu(II)$ species in the -15 to -20°C range (at higher temperatures, the former converts into the latter).⁽¹⁷⁸⁾

However, the occurrence of chemical reactions coupled to the electrochemical process may lead to other complexes with different ligands and/or structures, following a variety of possible sequences as shown in chapters II and III.

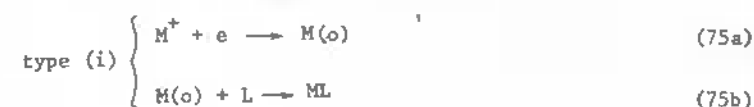
, Activation of a ligand may also result from oxidation or reduction of a complex and new derived organometallic species may be obtained upon chemical reaction.

Moreover, organometallic compounds may be electrochemically synthesised in cathodic or anodic processes with the direct involvement of the metal electrode (sacrificial electrode) to which the organic ligand binds, and examples of these systems will also be mentioned briefly.

(b) Electrochemical reaction in the presence of a suitable ligand

By electrochemical reduction of a system composed of a metal centre in the presence of a suitable ligand (or ligand precursor) an organometallic complex may be synthesized.

Cycloolefinic complexes have been electrosynthesized in this way (general equation 74) according to two possible pathways, one involving a primary metal reduction followed by ligand coordination (equation 75) and the other one proceeding through a reduction of the ligand prior to coordination to a metal (equations 76).^(17,18)



where M^+ and $M(o)$ correspond typically to a hard and a soft acid, and L^- and L to a hard and a soft base.

The metal centre M^+ may be electrochemically generated at the anode, by anodic dissolution of this electrode.

Type (i)

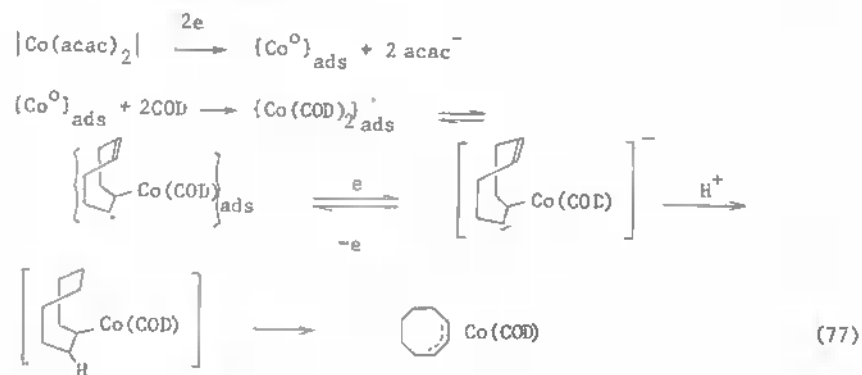
Within this scheme, a variety of cycloolefinic complexes of first row group IV to VIII transition metals have been synthesized by electrochemical reduction of the corresponding acetylacetonato species in the presence of the appropriate olefin. (17,18,179-182)

Examples include the electrolytic reduction of $[Ni(acac)_2]$ (in pyridine using tetrabutylammonium bromide as supporting electrolyte and aluminium as the anode) in the presence of 1,5-cyclooctadiene () cyclooctatetraene () or 1,5,9-cyclododecatriene () to give bis(1,5-cyclooctadiene)nickel(o), cyclooctatetraenenickel(o) and 1,5,9-cyclododecatrienenickel(o) respectively. (182)

The $(\eta^3\text{-cyclooctenyl})\text{-}1,5\text{-cyclooctadienecobalt(I)}$ complex



was synthesized (180) in a similar way by electrolysis of $[Co(acac)_2]$ in the presence of 1,5-cyclooctadiene(COD). The reaction was postulated to proceed through the following sequence

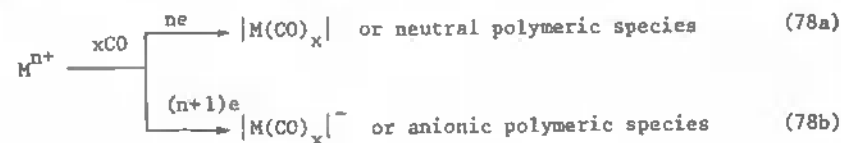


where the index "ads" refers to species adsorbed at the electrode.

The chemical synthesis corresponding to these electrochemical preparations of cycloolefinic complexes were not yet known when the latter were performed.

Other low valent transition metal complexes may be prepared by related routes, namely mono- or polymeric-polycarbonyls, which are

synthesized by electrochemical reduction of the parent acetylacetonato species, $[M(acac)_n]$ ($M = V, Cr, Mn, Fe, Co, Ni$) at an inert electrode (graphite or stainless steel) in dimethylformamide- $Bu_4N^+ Br^-$ under CO (50-200 atm). The anode is in aluminum and the overall processes, at the cathode, may be given by equations 78, whereas at the anode occurs

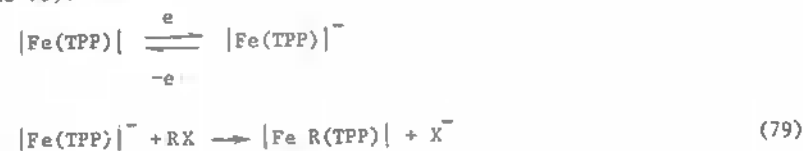


the oxidation of Al to Al^{3+} . (183-186)

These reactions may present a considerable yield (over 60%) but difficulties, from the synthetic point of view, result from the low selectivity. (183-186)

Metal-carbon bond formation may also result from the reaction of an electrochemically generated reduced species with an alkyl halide. Examples which refer nickel complexes involved as intermediates in the catalytic reduction of alkyl halides are given in section B.a.

Another example is given by the synthesis of the σ -alkyliron(II) porphyrin complexes $[FeR(TPP)]$ (where TPP=tetraphenylporphyrin) by electrophilic attack of alkyl halide (RX) at the iron(I) complex $[Fe(TPP)]^-$ electrochemically generated from the reduction of the parent iron(II) compound $[Fe(TPP)]$ (reactions 79). (187)

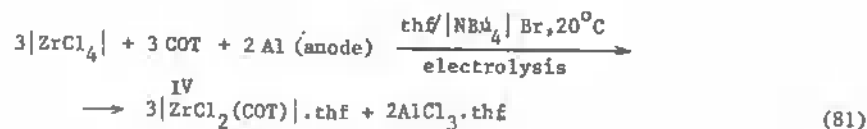
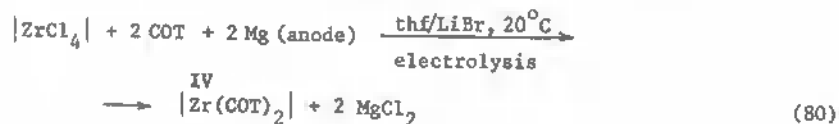


The reactivity of the iron(I) intermediate complex towards the alkyl halide follows the electron-donating character of the ring, and the reaction mechanism is suggested to be of the S_N2 type involving substitution of the halogen ion by the iron(I) compound.

Type(ii)

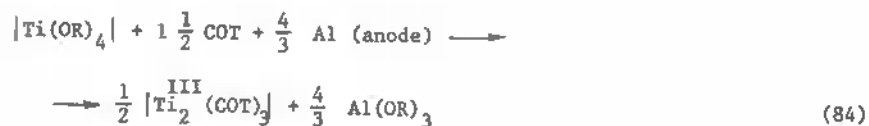
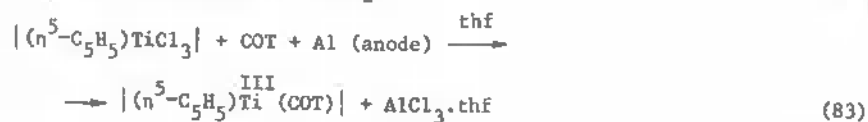
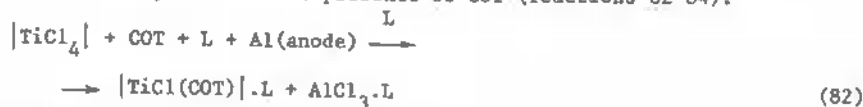
The examples cited above correspond to the electrosynthesis of low valent transition metal complexes through reduction of a metal site in the presence of a suitable ligand. However, the synthesis may result from the electrochemical reduction of a ligand precursor with retention of the metal oxidation state.

An example is given by the electrolytic reduction of cyclooctatetraene (COT) to the dianion (COT^{2-}) in the presence of $[\text{ZrCl}_4]$ in thf, using a Mg or an Al anode (reactions 80 and 81).^(179,188)



The central metal ion may be formed by dissolution of a sacrificial anode and, e.g., the cyclooctatetraenenickel complex was synthesized⁽¹⁸⁸⁾ by the anodic dissolution of a soluble Ni anode in the presence of COT, by using a cell without diaphragm.

Examples are known where both the metal and the ligand may undergo electrochemical reduction, as in the electrosynthesis of $[\text{Ti}^{\text{III}}\text{Cl}(\text{COT})] \cdot \text{L}$ (where L=thf or pyridine), $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}^{\text{III}}(\text{COT})]$ or $[\text{Ti}_2^{\text{III}}(\text{COT})_3]$ by electrolysis of parent Ti(IV) species in the presence of COT (reactions 82-84).⁽¹⁸¹⁾



(c) Electrochemical generation of an intermediate complex with a reactive ligand

Electrochemical oxidation or reduction of an organometallic complex may result in its activation namely towards a nucleophilic or electrophilic agent, or a radical species, thus allowing the synthesis of derived complexes

which often may be conveniently prepared by electrochemical generation of the activated intermediate complex in the presence of a suitable reagent, the chemical reaction occurring in situ.

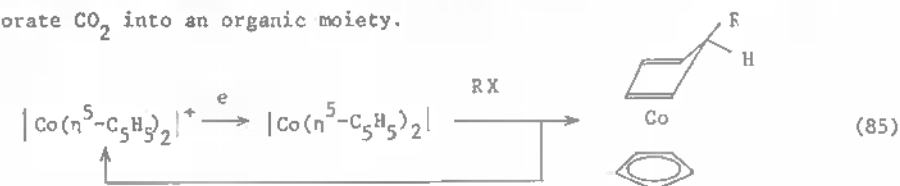
(c.1) Electroreduction followed by reaction with electrophile

Substituted cyclopentadiene cobalt cyclopentadienyls have been easily prepared by this route in high yields,⁽¹⁸⁹⁾ although their chemical preparations present considerable difficulties and were even unknown, e.g., as in the case of trisubstituted species.

Cobalticenium salts are stable species, easy to prepare,⁽¹⁹⁰⁾ which can undergo two one-electron reversible reduction reactions to give neutral and anionic cobaltocene species.^(73,191)

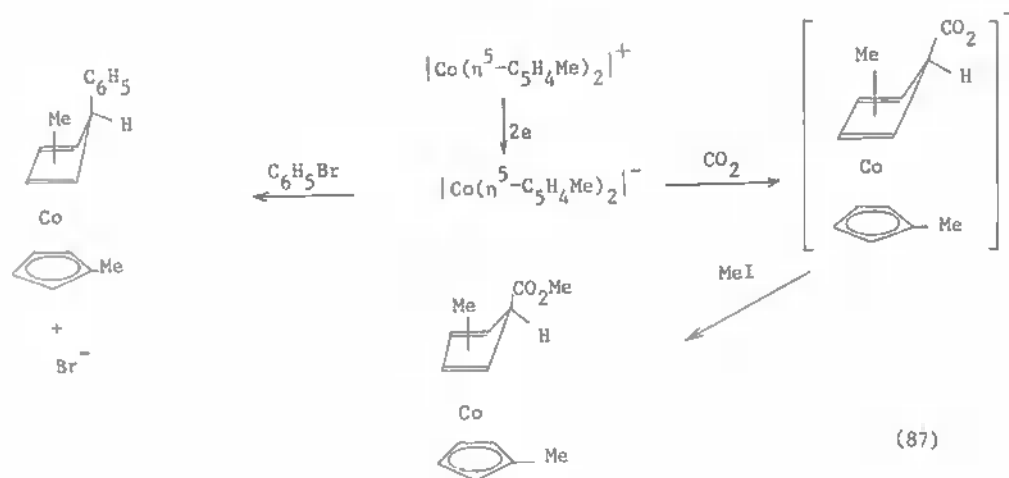
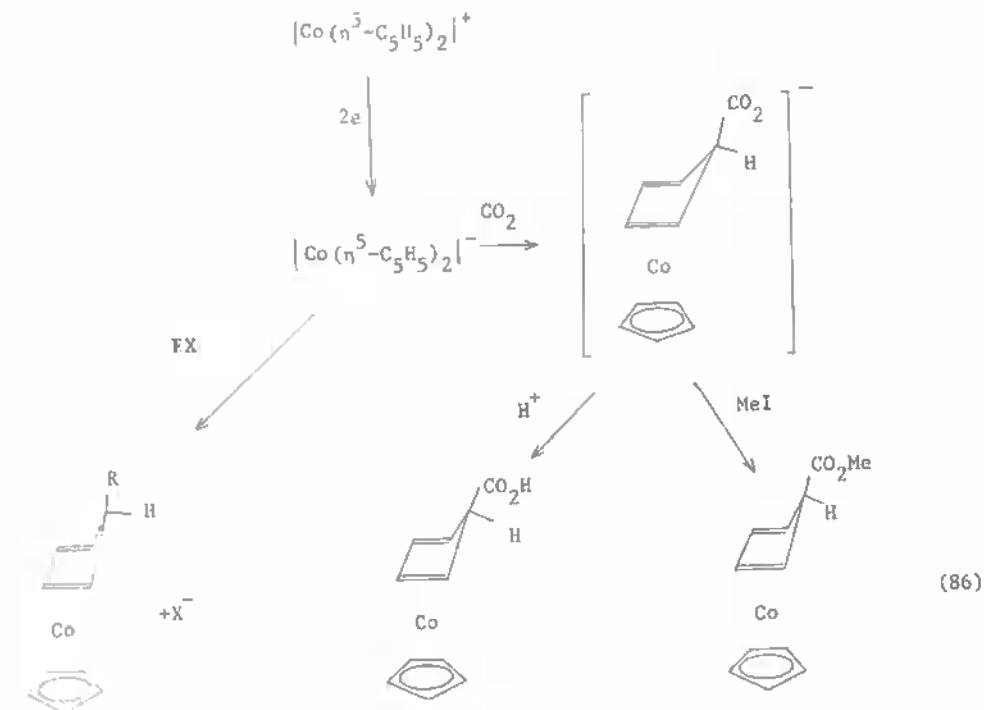
Both cobaltocene and the anion are unstable complexes, hard to prepare chemically, but easily obtained electrochemically from the corresponding cobalticenium salts. They can then react in situ with a suitable electrophile, such as an alkyl halide or carbon dioxide, to give substituted cyclopentadiene species.

These reactions are summarized by sequences 85-87 and they may constitute a convenient route to trisubstituted cyclopentadiene species (when starting from disubstituted cobalticenium salts) (reactions 87) and a way to incorporate CO_2 into an organic moiety.



In reactions (85) the formation of the monosubstituted cyclopentadiene species is accompanied by the partial regeneration of the cobalticenium ion (in an equal molar amount) which can undergo a new reduction, the electrochemical process allowing a quantitative yield based on cobaltocene although the chemical preparation alone would correspond to a 50% yield limit.⁽¹⁸⁹⁾

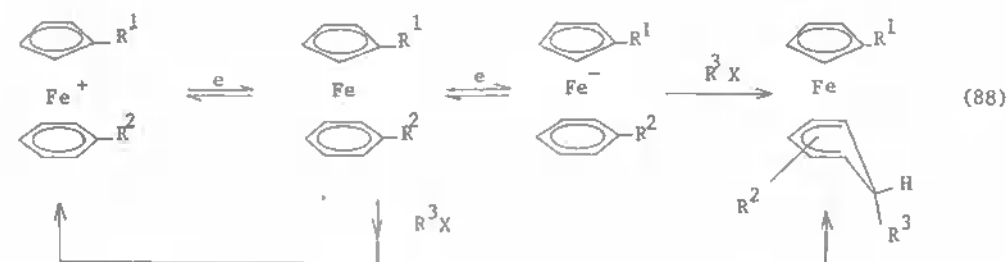
The carboxycyclopentadiene species, derived from attack of CO_2 at the cobaltocene anion (reactions 86 and 87)⁽¹⁸⁹⁾, can undergo further reaction with an electrophile (H^+ or alkyl halide) to give the carboxylic acid or corresponding ester.



The trisubstituted species appear as mixtures of the isomers with 1-2 and 1-3 disubstituted cyclopentadiene ligand. (189)

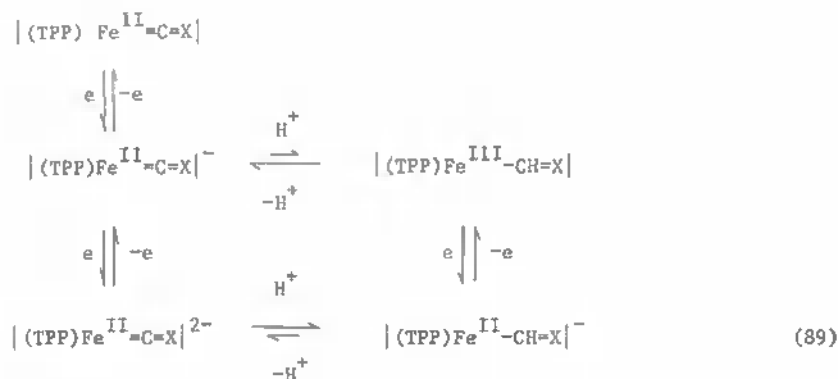
$(\eta^5\text{-Cyclopentadienyl})(\eta^6\text{-arene})\text{iron}$ cations may undergo electrochemical/chemical reactions analogous to those reported for cobalticenium-type species.

Hence, they may be reduced electrochemically in two successive single-electron steps to the corresponding radicals and anions which react with electrophilic reagents (such as alkyl halides R^3X) to yield substituted cyclohexadienyl derivatives in a regio- and stereo-specific way (R^3 in the exo position) (reactions 88). (192)



The reaction of the neutral 19-electron radical complex with R^3X is believed to proceed by a radical mechanism involving an electron transfer between the metal species and the organohalide to give a cationic complex and the organic R radical; attack of this radical at the neutral complex affords the final substituted cyclohexadienyl derivative. (192) The same radical mechanism has been established for the reaction of cobaltocene, $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$, with R^3X to give $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{R}^3)]$.

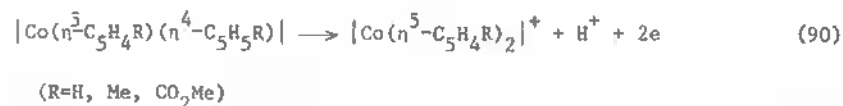
Electrochemical reduction of a complex may activate a ligand towards protonation and, e.g., the σ -alkyliron(II) porphyrins $[\text{Fe}(\text{TPP})(\text{CH}=\text{X})]$ [TPP = meso-tetraphenylporphyrin; $\text{X} = \text{C}(\text{C}_6\text{H}_4\text{Cl-4})_2$, $\text{C}(\text{C}_6\text{H}_5)_2$ or S] have been reported to be formed upon a (2-electron + H^+)-reduction of the corresponding carbeneiron(II) compounds, according to the proposed reactions (89). (193)



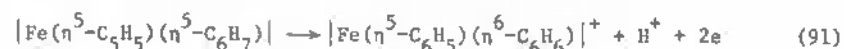
Other examples will be cited (section C) in the field of nitrogen fixation.

(c.2) Electrooxidation followed by proton elimination or other reactions

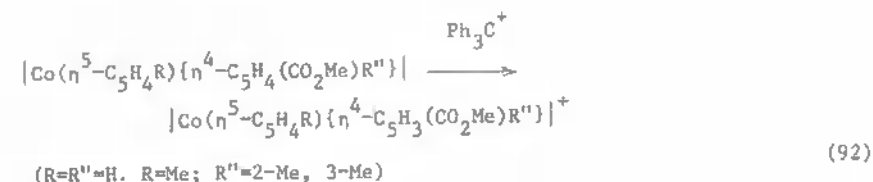
Electrochemical oxidation of a hydride transition metal complex may result in loss of proton from the metal as it was illustrated in section II.B.e. However, proton elimination from an organic ligand may also be promoted by oxidation of the complex and, e.g., the substituted Co complexes prepared as described above, which may be denoted as $[\text{Co}(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^4\text{-C}_5\text{H}_4\text{R}'\text{R}'')]^+$, may undergo electrochemical or chemical oxidation and when presenting an exo hydrogen atom, they lead to the corresponding substituted cobalticenium salts (equation 90). (194)



An analogous reaction (91) occurs with the isoelectronic iron(II) complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_6\text{H}_7)]$. (192)

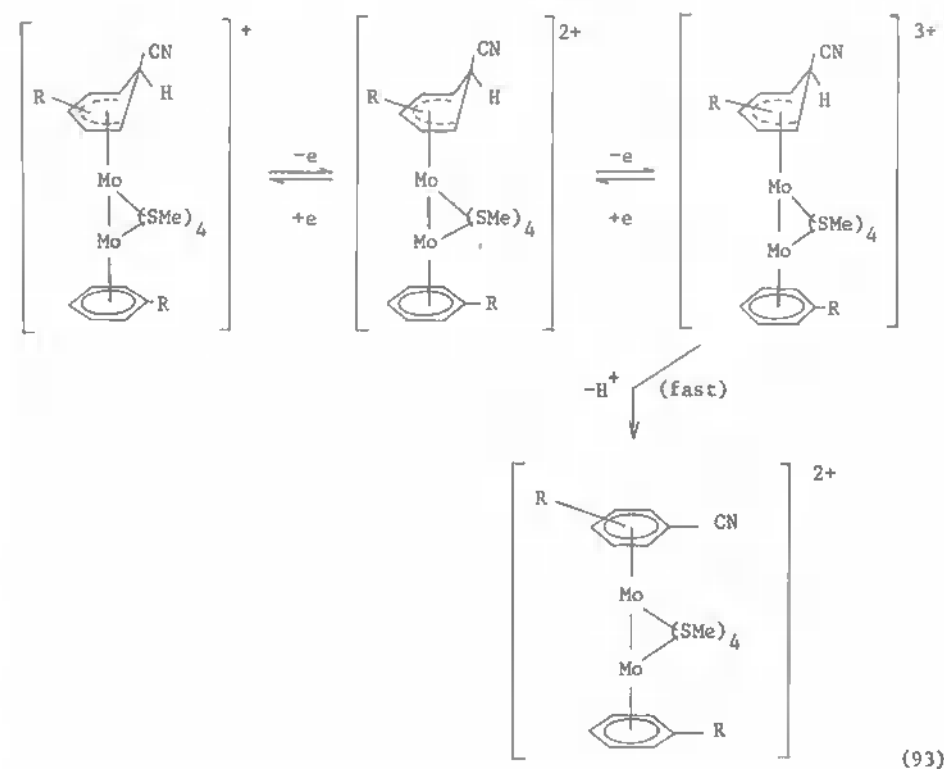


When the exo substituent is Me or Ph, degradation of the cobalt species occurs, but if CO₂Me is the exo substituent, oxidation by $[\text{Ph}_3\text{C}]^+[\text{BF}_4]^-$ (triphenylmethyl tetrafluoroborate) results in the endo hydrogen elimination to give the substituted cobalticenium salt in quantitative yield (equation 92). (194)



This novel route to the synthesis of cobalticenium salts (involving electrochemically generated intermediate complexes) allowed the preparation of the first trisubstituted cobalticenium salts.

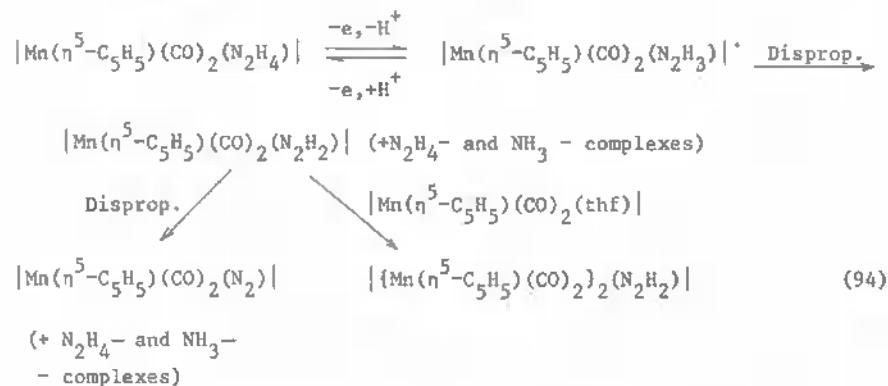
The dicationic complexes $[(\eta^6\text{-RC}_6\text{H}_4\text{CN})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^{2+}$ with a π -cyanobenzene ligand are formed by controlled potential electrolysis - in propylene carbonate- $[\text{Et}_4\text{N}][\text{PF}_6]$ at a Pt electrode - of the cationic species $[(\eta^5\text{-RC}_6\text{H}_5\text{CN})\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^6\text{-RC}_6\text{H}_5)]^+$ with a cyanocyclohexadienyl ligand. (195) This reaction proceeds by a two-electron oxidation-proton elimination mechanism (equation 93) which is also suggested to be involved in the known (196) synthesis of free, substituted arenes by oxidation of cyclohexadienyl complexes



(93)

of various transition metals which are formed upon addition of a nucleophile (e.g., CN)⁻ to a π -complexed arene ligand - the overall reaction corresponds to a formal replacement of hydride by the nucleophile at a π -arene ligand.

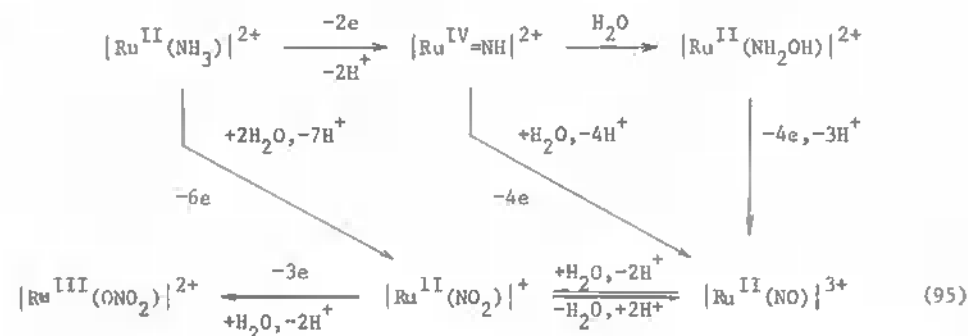
An inorganic ligand may also undergo deprotonation upon electrochemical oxidation of the complex, as observed, e.g., in the oxidation of the amino complex $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NH}_3)]$ (in thf at a Pt electrode) to the hydrazino and dinitrogen species $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{L})]$ ($\text{L}=\text{N}_2\text{H}_4$ or N_2).⁽¹⁹⁷⁾ The hydrazine complex is oxidized in thf at a Pt electrode to the dinitrogen complex and to the binuclear diazene species $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2(\text{N}_2\text{H}_2)]$ via an intermediate mononuclear diazene compound derived by disproportionation of an hydrazido(l-) radical species formed by proton elimination promoted by the oxidation of the parent hydrazine complex according to the proposed scheme of reactions 94.⁽¹⁹⁷⁾



Facile oxidation of a ligand (such as ammonia primary amine or azide) bound to bipyridine complexes of Ru(II) has been reported to result from an initial oxidation of Ru(II) to Ru(III) and provides interesting examples of electrochemical activation of a ligand to oxidation.

Coordinated ammonia can undergo oxidation to nitrate at a single metal site by electrolysis of an aqueous solution of $[\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})(\text{NH}_3)]$ ($\text{trpy}=2,2',2''\text{-terpyridine}$; $\text{bpy}=2,2'\text{-bipyridine}$).⁽¹⁹⁸⁾

The reaction is believed⁽¹⁹⁸⁾ to be initiated by the oxidation of Ru(II) to Ru(III) followed by disproportionation of $[\text{Ru}^{\text{III}}(\text{trpy})(\text{bpy})(\text{NH}_3)]^+$ to give an imidoruthenium(IV) complex and the parent $[\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})(\text{NH}_3)]$ species. Ligating nitrite is an intermediate in the conversion of nitrate and the proposed reaction pathway is shown by reactions 95.



The final oxidation of the nitrito ligand in $[\text{Ru}^{\text{II}}(\text{trpy})(\text{bpy})(\text{NO}_2)]^+$ was also studied in detail and it is believed to involve the initial electrochemical oxidation of Ru(II) to Ru(III) followed by conversion of the ligating nitrite into nitrosyl and nitrato ligands.⁽¹⁹⁹⁾

Facile oxidative dehydrogenation of an amine ligand may also follow the (electro)chemical oxidation of the metal and, e.g., the nitrile complexes $[\text{Ru}(\text{bpy})_2(\text{N}\equiv\text{CR})_2]^{2+}$ are formed upon electrochemical (or chemical) oxidation of the primary amine complexes $[\text{Ru}(\text{bpy})_2(\text{NH}_2\text{CH}_2\text{R})_2]^{2+}$ ($\text{NH}_2\text{CH}_2\text{R} =$ allylamine, benzylamine and *n*-butylamine).⁽²⁰⁰⁾

The overall reaction is given by equation 96 and it is believed to be initiated by the oxidation of Ru(II) to Ru(III) followed by a sequence of net two-electron steps involving imine intermediates.



In the previous examples involving electrochemical activation of a ligand bound at a $\{\text{Ru}^{\text{II}}(\text{bpy})_2\}$ site, deprotonation of the ligand occurs on oxidation. However, a non-hydrogenated ligand may also undergo oxidation as in the conversion of azide to dinitrogen (equation 97) which is also believed

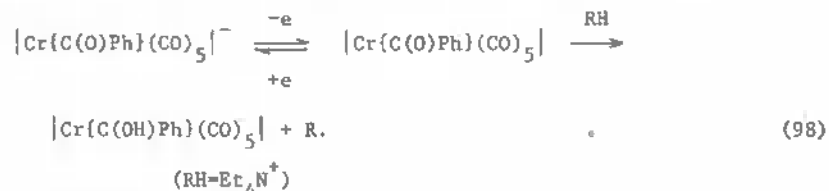


to be initiated by oxidation of Ru(II) to Ru(III). Kinetic studies of this reaction suggested either a rate-determining intramolecular electron transfer from the azide to the $\text{Ru}(\text{III})$ site or a metal-nitrene formation.⁽²⁰¹⁾

An electrochemically generated oxidized intermediate organometallic complex may also undergo a reaction typical for an organic radical as in the preparation of the hydroxycarbene compound $[\text{Cr}(\text{C}(\text{OH})\text{Ph})(\text{CO})_5]$ by electrolytic

oxidation of the acylchromium(o) species $[\text{Cr}(\text{COPh})(\text{CO})_5]^-$ in $\text{CH}_3\text{CN}-[\text{NEt}_4][\text{ClO}_4]$ at a Pt electrode. (202)

The neutral paramagnetic acylchromium(I) intermediate $[\text{Cr}(\text{COPh})(\text{CO})_5]$, as detected by e.s.r., presents the unpaired electron density highly ligand centered and abstracts an hydrogen atom from the electrolyte(RH) in a similar way to known oxygen-centered organic radicals. The reaction sequence is depicted by equations 98 and the overall process formally corresponds to the electrochemical oxidation of a hydrogen donor substrate (RH) (equation 99).

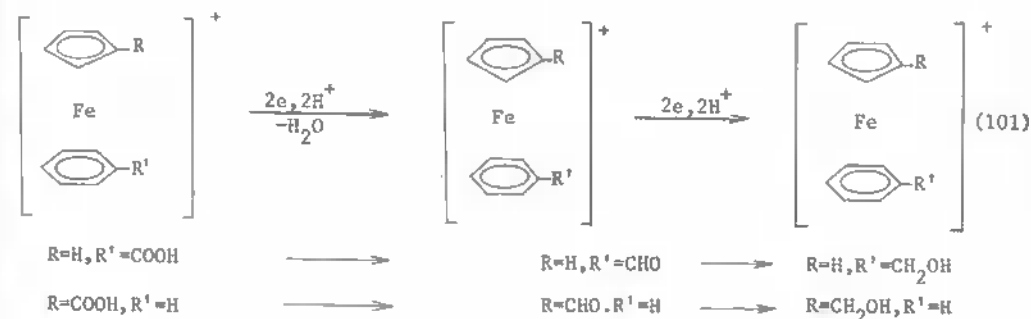
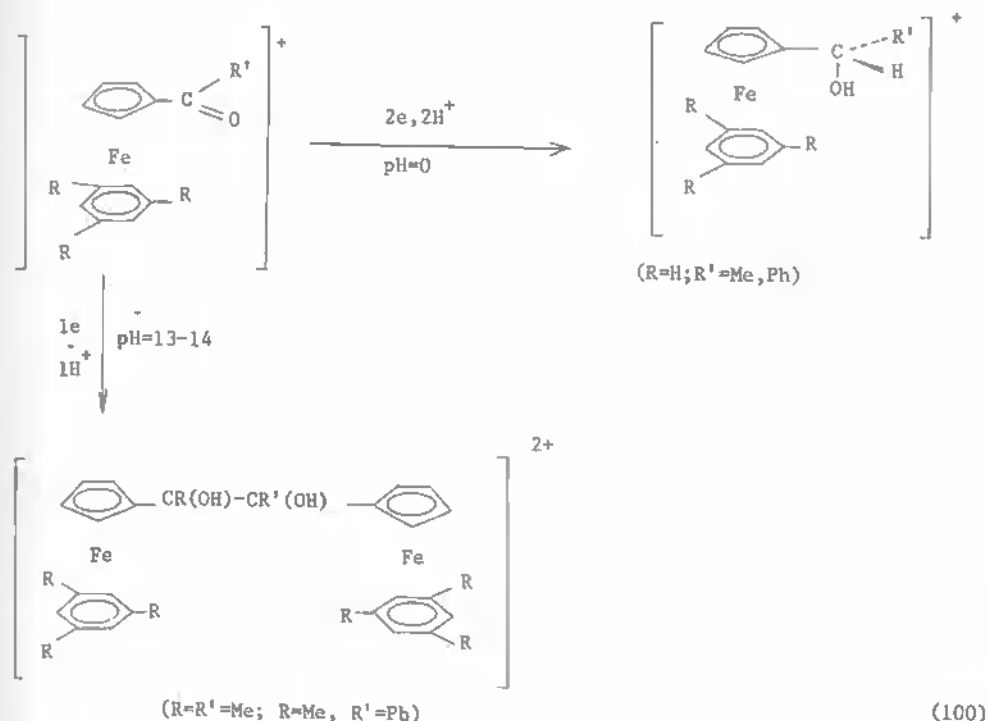


(d) Electrochemical reduction of ligand functional groups

Functional groups, such as $>\text{C}=\text{O}$, $-\text{COOH}$, $>\text{C}=\text{N}-\text{OH}$, $-\text{CH}=\text{CH}-$ in metallocene type complexes, may undergo electrochemical reduction and new organometallic complexes with derived functional moieties may be synthesized by preparative electrolysis. (203-205) These electrochemical reductive synthesis may differ from the chemical reduction reactions which the same species may undergo, e.g., the former being regiospecific on the functional group such as in the following examples.

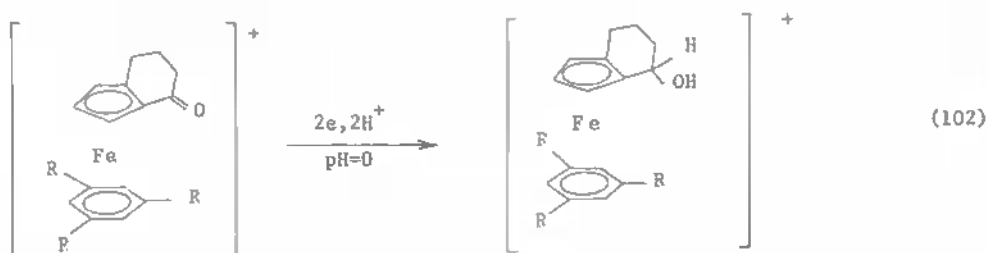
Ketone functional groups in cyclopentadienyl(arene)iron(II) cationic species may be regioselectively reduced at a mercury electrode to secondary alcohols (at low pH) or pinacols (at high pH) (reactions 100), whereas acids undergo similar reactions to primary alcohols (reactions 101).

These electrochemical reactions are regiospecific on the functional group rather than on the ligand ring, in contrast to the chemical reduction (by BH_4^-) which occurs also at the benzene in the ketone species to give η^5 -cyclohexadienyl ligand. It is also known (205,206) that the chemical reduction by BH_4^- of acids or esters, in these Fe(II) complexes, is regiospecific on the arene ligand (not at the functional group) which yields η^5 -cyclohexadienyl; an inversion of the regiospecific nature of the reduction is then observed when considering the electrochemical reduction instead of the chemical one.



The carboxylic acid functional group is activated towards reduction by the cationic metal centre since, under identical experimental conditions, reduction of uncoordinated benzoic acid does not occur. (205)

Reduction of α -oxotetramethylenecyclopentadienyl(arene)iron(II) was also studied, and both the electrochemical and the chemical reaction occur stereospecifically in trans position relative to the metal (exo side of the ring) to give only the endo alcohol product (reaction 102). (205)



(e) Electrosynthesis at sacrificial electrodes

In the cases mentioned above, the synthesised organometallic complexes present central metals derived from added metal site systems such as a parent organometallic compound.

However, examples of cathodic or anodic processes are known where the electrode metal itself behaves not only as the source of, or sink for, electron, but also as the source of the ligating metal centre of the organometallic product. Then reactions are said to involve sacrificial electrodes and occur mostly with representative elements or group IIB transition metals, although various examples have also been quoted for other transition metal group elements; they have already been reviewed, (19,20) and now only representative or more recent cases will be mentioned.

These direct electrochemical syntheses may offer some advantages over corresponding preparative chemical methods such as the following ones:

- A metal (which may often be obtained in a high purity state and is easy to store) may be used as a starting material from which the final compound may be directly synthesised, a situation which is not common in preparative chemistry (although vapour phase synthesis

and the preparation of Grignard reagents may involve the direct application of metals).

- The yields are often high on the basis of metal consumption, and other reagents (such as, e.g., organic halides) which are present in excess can be used again for further synthesis.
- Certain compounds with corresponding difficult chemical access may be conveniently prepared by simpler electrochemical synthesis.
- The electrochemical experimental conditions involve often ambient temperatures and do not require efficient high-vacuum systems.

The last two advantages present a wider significance, corresponding to the favourable application, in some cases, of general electrosynthesis over preparative chemical methods.

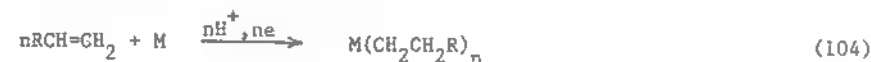
(e.1) Cathodic processes

I - Electrosynthesis from non-organometallic compounds

Electrolysis of carbonyl compounds (ketones (207-212) or aldehydes (213) in aqueous acidic medium), other unsaturated species (e.g., olefins, acrylonitrile) (214,215) or organic halides (e.g., alkyl halides) (216-218) at a suitable cathode (such as Hg, Cd, Pb, Sn or Tl) may result in the formation of organometallic compounds presenting the cathode metal (M) as the central element (equations 103-105).



(M=Hg, n=2. M=Pb, n=4)



(M=Hg, n=2. M=Sn, n=4)



(M=Hg, n=2. M=Pb, Sn; n=4)

The mechanism of these reactions appears to depend e.g., on the nature of the solvent, electrolyte and cathode material, conflicting data have been presented in some cases, and it has not yet been ascertained.

Possible hypotheses have been put forward which will not be dealt

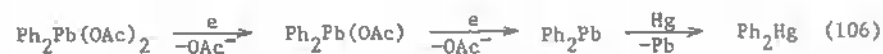
with in detail: formation of the organometallic compound by interaction of a carbanion (primarily formed by electrochemical reduction of the organic substrate) with the electrode metal cation of the crystal lattice of the cathode (ionic mechanism);⁽²²²⁾ formation of the organometallic compound by interaction of radicals (generated at the cathode) with the cathode metal (radical mechanism);⁽²²³⁾ involvement of an intermediate chemisorbed compound of the organic substrate and the metal with resulting formation of a metal-carbon covalent bond.⁽²²⁴⁾

The organometallic compounds formed in the cathodic reduction of organic compounds may be intermediate species to final organic products (see section B).

II - Electrosynthesis involving a parent organometallic compound

Diphenylmercury, Ph_2Hg , may be obtained by electrochemical reduction of organometallic derivatives of lead at a mercury cathode.

Hence, controlled potential electrolysis of diphenyllead diacetate (at the second reduction step) or triphenyllead monoacetate (at the first reduction step) yield diphenylmercury quantitatively (reactions 106 and 107).⁽⁸⁷⁾



These reactions provide examples for the following possible route observed in the electroreduction of an organometallic compound RMQ (which corresponds to process iii.7 of figure 3):



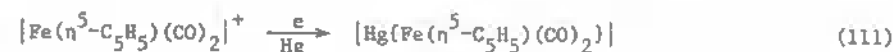
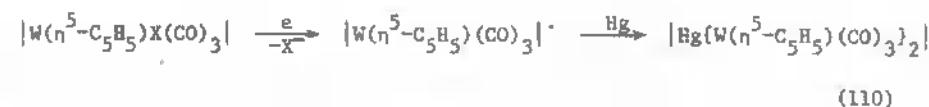
Formal insertion of mercury into a metal-metal bond of a dinuclear carbonyl complex may also occur upon electrochemical reduction of the latter at a mercury cathode, to afford trimetallic species, as observed in the formation of $[\text{Hg}\{\text{M}(\text{CO})_5\}_2]$ ($\text{M}=\text{Mn}$ or Re) from $[\text{M}_2(\text{CO})_{10}]$ (reaction 109).⁽⁶³⁾



A mononuclear ionic species, $[\text{M}(\text{CO})_5]^-$, is suggested to be formed, which, upon reoxidation, gives $\text{M}(\text{CO})_5^+$, the latter attacking the electrode

to afford the final trinuclear complexes.⁽⁶³⁾

Other mercurated di- or tri-metallated complexes (the latter with bridging mercury) may be formed in similar way from mononuclear transition metal complexes [see, e.g., equations 110⁽¹⁰³⁾ and 111⁽⁶³⁾] and the reaction may proceed through metal-halide bond cleavage as a result of the electroreduction (equation 110).



These reactions illustrate process (iii.6) of figure 3.

(e.2) Anodic processes

Anodic processes applied to the synthesis of organometallic compounds may involve the electrolysis of solutions (or melts) of other previously prepared parent organometallic species (such as Grignard reagents, organoaluminum or organoboron complexes). The reaction formally corresponds to a transmetalation, proceeding by the exchange between the metal ion of the latter compound and the metal ion formed by dissolution of the anodic electrode.

However, various methods have already been developed for anodic direct (one-step) electrosynthesis of organometallic species by electrochemical oxidation of the anode metal (sacrificial electrode) in the presence of a suitable (organic) ligand precursor, i.e., without requiring the previous preparation of a parent organometallic compound. The formation of complexes with the metal in a relatively low oxidation state appears to constitute an interesting feature associated to these electrochemical oxidation methods.

I - Electrosynthesis from non-organometallic compounds

(i) Reactions with organohalides

Electrochemical oxidation of a metal anode (M , either a main group or a transition metal) in the presence of an organohalide (RX) in an organic solvent may lead to the formation of an organometal halide which corresponds formally to the overall oxidative insertion reaction (equation 112).



(M = Cd, (225,226) Zn, (227) Ni, (228,229) Pd; (229) n=1.
M=Ti, Zr-Hf, (233) Sn; (228) n=2. R=alkyl, aryl,
fluoroalkyl or fluoroaryl. X=halide).

The neutral organometallic R_nMX_n species may be stabilized as adducts with neutral ligands (such as 2,2'-bipyridine, dimethyl sulphoxide, 1,10-phenanthroline, 1,4-dioxane, dppe, acetonitrile).

A similar electrochemical method has been used to prepare the anions $[RMX_2]^-$ (M=Zn (230) or Cd (231)) as their tetra-n-propylammonium salts, by adding an excess of $[R_4N]X$ to the electrolysis solution.

Products with different stoichiometries may also be obtained: R_3MX (for M=Ti, Zr, Hf) (233) or RMX_2 (for M=In). (234)

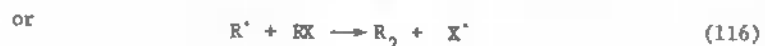
These electrochemical methods may present considerable synthetic advantages over the chemical preparative methods, namely avoiding the use of high temperatures and the difficulties encountered in the separation of mixtures of different products formed in the chemical reactions, e.g., in the known chemical methods of synthesis of organotin halides (direct reaction of metallic tin with the organohalide in the presence of a catalyst at temperatures of 100-180°C, or reaction of R_4Sn with SnX_4 , also at high temperatures, which gives mixtures of mono-, di- and tri-halide species). (228)

Mainly on the basis of the current efficiency (or electrical yield) at constant current (expressed as mol metal dissolved per Faraday of electricity) and detection of products at the anode and cathode, the general mechanism of equations 113 and 114 (with involvement of radical species) was suggested. (225-234)



The cathodic reduction yields X^- and $R^\cdot$ and migration of X^- to the anode is followed by reactions (114).

A cathodic generation of hydrocarbon R_2 was detected and it might be explained by either



but the latter reaction was ruled once since no appreciable amounts of X_2 were detected at the cathode.

Reactions (114c) and (114d) constitute a chain process (with $X^\cdot$ as the chain carrier) and explain the high current efficiencies (with values generally higher than 2 mol MF^{-1}) observed for Cd (226) and Sn. (228) However, in the Zn system the values of the current efficiency (lower than 1) are remarkably lower than those observed for Cd and Sn, and then reaction (114d) appears to have a small importance ($X^\cdot$ formed in reaction 114c gives X_2 which was detected near the anode). (230)

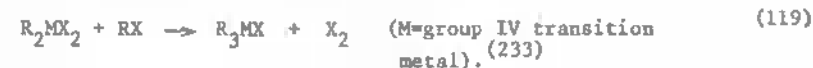
The formation of the abovementioned products ($RInX_2$ and R_3MX where M is a group IV transition metal) with stoichiometries which are different from those shown in equation (112) may also be explained by similar mechanisms although involving the following distinct steps:



which would replace steps (114c) and (114d);



or



Organoaluminum halides may also be electrochemically synthesized by anodic dissolution of aluminum in an organic solvent in the presence of an organohalide, (235,236) and the formation of bis(dichloroaluminum)methane, $Cl_2AlCH_2AlCl_2$, by using dichloromethane as the organohalide is believed to occur (236) by a mechanism which is similar to that mentioned above.

(ii) Other reactions

The presence of ligands or ligand precursors other than organohalides in the anodic dissolution of a metal electrode may also allow the electrosynthesis of a variety of both inorganic and organometallic complexes. Generally the ligand (organic or inorganic) presents a formal anionic charge, but examples are also known which involve neutral ligands to afford cationic complexes.

(ii.1) Formation of cationic complexes by reactions with neutral ligands

Cationic complexes of the type $[ML_n][BF_4]_n$ (n=2 or 3, depending on

M; L=NCMe or dimethylsulphoxide) have been recently synthesised in one-step by electrochemical oxidation of both transition and main-group metals (M=V, Cr, Mn, Fe, Co, Ni, Zn, Cd or In), usually in a low oxidation state (II or III), in the presence of the neutral ligand L and HBF_4 .⁽²³⁷⁾ The tetrafluoroboric acid was used as a source of a suitable counter ion for salt formation, and the overall anode reaction may be represented by equation (120).



Although the method appears to have been applied only to a strict number of ligands, certainly it is susceptible of a much wider application to other neutral ligands namely for the preparation of organometallic complexes.

(ii.2) Reactions with olefins

An example of electrosynthesis of an olefinic complex by anodic dissolution of a soluble metal anode was already mentioned (section A.b - type ii reactions): formation of cyclooctatetraenenickel in the electrolysis of cyclooctatetraene with a nickel anode in a cell without a diaphragm.⁽¹⁸⁸⁾

Similar methods may be used in the preparation of cyclopentadienyl (or derivatives) manganese complexes by electrolysis of cyclopentadiene (or its derivatives) with a soluble manganese anode (or, alternatively, in the presence of a manganese salt).⁽²³⁸⁾

(ii.3) Reactions with halides

Neutral and anionic anhydrous halides, MX_n (or their adducts, e.g., with the acetonitrile or methanol solvent) and MX_n^m , with the metal often in a relatively low oxidation state [e.g., V(II), Cr(III), Mn(II), Fe(II)], may be conveniently synthesised by electrochemical halogenation of a metal anode at ambient conditions, without requiring the high temperatures associated with the chemical preparative methods; the latter also differ from the former in that they afford usually the halides of the high oxidation state of the metal.

Examples of neutral halides which may be electrosynthesised by this way are found in all the transition-element groups as well as in the IIIA group (overall reaction 121); the anionic metal halides may be prepared



(M=Ti, Zr or Hf; n=4. M=V, n=2. M=Cr, n=3. M=Mn, Fe, Co, Ni; n=2. M=Cu; n=1 or 2. M=Zn, n=2. M=In; n=1 or 3).

(overall reaction 122) by carrying out the electrolysis in the presence of an excess of a tetraalkylammonium salt.⁽²³⁹⁻²⁴¹⁾



(M=Ti, Zr or Hf; n=6 (m=2); n=4 (m=1). M=Fe, n=4, m=1. M=Co or Ni, n=4, m=2. M=Au, n=4, m=1. M=Cd, n=3, m=1. M=In, n=5, m=2; n=2, m=1. M=Sn, n=6, m=2).

The suggested⁽²⁴¹⁾ mechanism for these reactions presents some similarities with the proposed one (see above) for the formation of organometallic species from reactions of organohalides.

At the cathode reduction of X_2 occurs and the X_2^- product migrates to the anode where it reacts with the metal electrode. A chain process is also involved as suggested by the high current efficiencies (typically in the 1-20 range and non-integral) (equations 123 and 124).

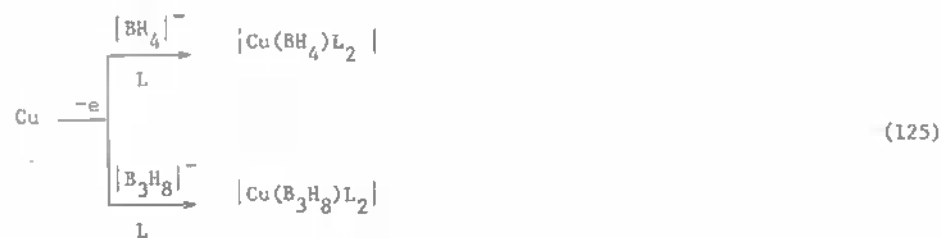


These metal halogenation reactions do not yield organometallic compounds but they deserve to be mentioned in this context since the metal halides formed are of synthetic value for the chemical preparation of other complexes particularly of organometallic character.

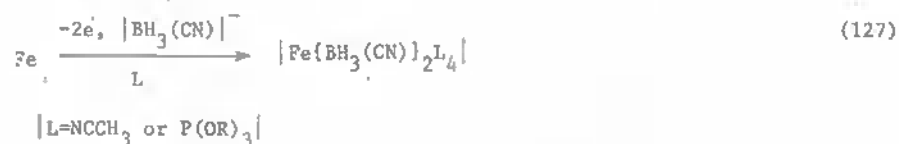
(ii.4) Reactions with hydroborates

Electrochemical oxidation of metals in non-aqueous solvents is a convenient method for the synthesis of metalloborane complexes.

Electrolysis of non-aqueous (e.g., ethanol or acetonitrile) solutions of octahydrotriborate(1-), $[\text{B}_3\text{H}_8]^-$ or tetrahydroborate at a Cu or Ag anode in the presence of a phosphine ligand leads to metal dissolution and formation of metalloboranes (equations 125 and 126).⁽²⁴²⁾



Similarly, electrolysis of an acetonitrile solution of cyanotrihydroborate [BH₃(CN)]⁻ at an iron anode yields [Fe{BH₃(CN)}₂(NCCH₃)₄],⁽²⁴³⁾ whereas the phosphite complexes [Fe{BH₃(CN)}₂{P(OR)₃}₄] are formed in the presence of the appropriate phosphite,⁽²⁴⁴⁾ in an overall two-electron transfer process (equation 127).



However, at molybdenum or vanadium anodes, the principal borane-containing product is [BH₃(CN)BH₂(CN)]⁻, formed by oxidation of [BH₃(CN)]⁻.⁽²⁴³⁾

(ii.5) Reactions with weak protic acids

A weak protic acid is generally an unsuitable starting material for the direct chemical synthesis of a complex from the metal element. However, when the metal is used as the anode of an electrochemical cell, weak acids such as acetylacetone may constitute convenient sources of their conjugate bases as ligands for the one-step electrosynthesis of complexes. The over-all reaction is given by equation 128; the anionic basic ligand is generated

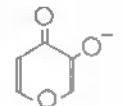


(with H₂) by the cathodic process (overall equation 129) whereas the complex is formed in the anodic process (equation 130).



Examples of compounds prepared by this method may be cited:^(245,246)

- Acetylacetonate complexes, [ML_n] (M = Zr, Hf; n=4. M=Ti, V, Cr, Fe, In; n=3. M=Mn, Co, Ni, Cu, Zn; n=2. L⁻ = CH₃COCHCOCH₃⁻)

- 3-Hydroxy-4H-pyran-4-onate complexes, [ML_n] (M=Fe, In; n=3. M=Co, Ni, Cu; n=2. L⁻ is the ligand ).

II - Electrosynthesis involving a parent organometallic compound

This method has already been reviewed⁽¹⁹⁾ and only some representative examples will now be briefly cited.

Organometallic species of the type MR_n (M=Zn, n=2.⁽²⁴⁷⁾ M=Al,⁽²⁴⁸⁾ B⁽²⁴⁹⁾; n=3. M=Pb,⁽²⁵⁰⁾ Si;⁽²⁵¹⁾ n=4) have been electrosynthesised by electrolysis of ethereal solutions of the corresponding Grignard reagents (RMgX) using the appropriate anode metal (M) which undergoes anodic dissolution (equation 131).



M=Zn, n=2

M=Al, B; n=3

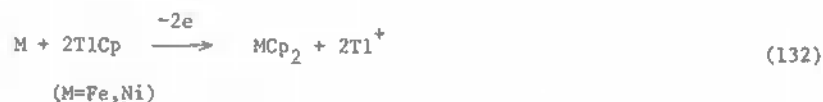
M=Pb, Si; n=4

Organoaluminum and organoboron compounds have also been used as starting materials for other organometallic species, MR_n of Mg (n=2), Zn, Cd or Hg (n=2), Al or In (n=3), Sn (n=4), Sb or Br (n=3),⁽²⁵²⁾ but their too low electrical conductivity (or of their solutions) does not allow the direct application in electrolysis; they have to be mixed with other compounds such as salts of alkaline metals, alkyl halides, metal hydrides or other organometallic species, in order to give conducting solutions suitable to undergo electrolysis. The electrical conductivity of these mixtures appears

to be explained by the formation of dissociating complexes, e.g., $[\text{NaZn}(\text{C}_2\text{H}_5)_3]$ in the mixture of $\text{Zn}(\text{C}_2\text{H}_5)_2$ with $\text{Na}(\text{C}_2\text{H}_5)$, which undergoes partial dissociation to the Na^+ and $[\text{Zn}(\text{C}_2\text{H}_5)_3]^-$ ions. (253)

Organic radicals appear to present generally a fundamental role in the mechanism of these reactions, the metal-carbon bond (of the organometallic product) being formed by the reaction of a radical (produced during the electrolysis) with the anode metal.

These preparative methods have been applied almost exclusively to representative elements or to the group IIB transition metals ($\text{Zn}, \text{Cd}, \text{Hg}$), but examples are also known to involve a transition metal of a different group as observed in the formation of ferrocene or nickelocene by electrolysis of cyclopentadienylthallium(I) in dimethylformamide by using an iron or a nickel anode (equation 132). (254)

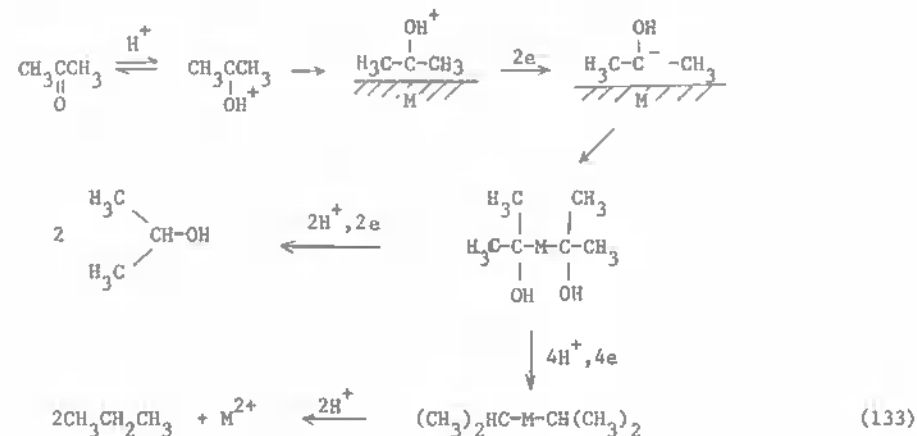


Trinuclear carbonyl complexes of the type $\text{M}(\text{M}'(\text{CO})_n)_2$ (M=metal electrode such as Zn or Cd ; $\text{M}'=\text{Mn}$, $n=5$; $\text{M}'=\text{Co}$, $n=4$) may also be prepared at sacrificial anodes (M) from parent dinuclear species $[\text{M}'_2(\text{CO})_{2n}]$: the cathodic process generates the mononuclear anions $[\text{M}'(\text{CO})_n]^-$ which migrate to the anode and react with this electrode to afford the trinuclear products. (20)

B - Organometallic Intermediates in Organoelectrosynthesis

Although it is well recognized the importance of organometallic species on the synthesis of various organic compounds, the electrochemical generation *in situ* of organometallic intermediates did not yet received the deserved attention. However, examples involving catalytic organometallic species are already known and will be mentioned below.

This section deals only with well established examples with inert electrodes, although in other cases the metal electrode (e.g., Hg) may be present in the intermediate organometallic species as suggested (255) for the electroreduction of acetone to isopropyl alcohol or propane which is believed to proceed by the ionic mechanism of sequence (133).



According to this proposal, organometallic intermediates are derived from an adsorbed carbanion which is formed by a two-electron reduction step of the pre-adsorbed protonated form of the acetone in acidic medium.

The involvement of the metal electrode in the chemical process, through interaction with radical or ion intermediates, may result in the occurrence of competitive pathways and in the formation of a variety of species which may constitute a drawback to a clear synthesis. Hence, the electrochemical reduction of 1-iododecane and 1-bromodecane at a mercury cathode in dimethylformamide is shown to yield decane, 1-decene and 1-decanol; the alcohol is suggested to be formed by a heterogeneous, electrode-assisted ionization of the carbon-halogen bond which enhances the halide displacement by hydroxide ion produced by electrolysis of traces of water in the solvent. Didecylmercury, which is electroinactive, may also be formed by a radical mechanism involving adsorbed decyl radicals. (256)

The type of reactions with chemical participation of the metal electrode will not be considered again, and the following examples deal only with inert electrode processes.

(a) Catalytic electrochemical reduction of organic halides

Electrochemical reduction of organic halides (e.g., alkyl bromides) may occur at a quite negative potential requiring a large overpotential. However, catalytic carbon-carbon bond formation through electroreduction at less negative potentials of various types of organic halides (alkyl-, (257-263) aryl-, (257, 263-265) benzyl- (257, 263) and allyl- (266) halides) in the presence of a metal centre has been achieved by various authors.

The coupled products, formed according to the general reaction (134) may arise from a free-radical pathway which is believed to involve low-valent



transition metal complexes which are reactive towards the alkyl halide to afford carbon σ -bonded organometallic intermediates.

Organometallic species with, e.g., the $\{RNi^{III}X\}$ (258-262) or the $\{RNi^{II}X\}$ (263,265) groups have been postulated as important intermediates in systems which incorporate macrocyclic complexes of nickel or the phosphinic compounds $[NiX_2(PPh_3)_2]$, respectively, whereas alkyl cobalt complexes with the $\{(n-C_4H_9)Co\}$ moiety were unambiguously evidenced⁽²⁶⁷⁾ in the reduction of butyl bromide by cobalamine or tetraphenylporphin complexes of Co(II).

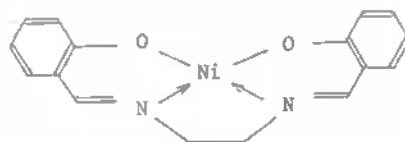
Besides the coupled R-R products, other organic species may be formed in these electrocatalytic reductions, such as olefins and alkanes (disproportionation products), hydrocarbons derived from radical attack at the solvent, and various organic compounds formed via the involvement of other substrates (olefins) in the catalytic process.

The catalytic electrochemical reduction of alkyl halides by cyclic tetraamine or tetradentate Schiff base type complexes of Ni(II) (258-262) will now be mentioned in more detail since it exemplifies the abovementioned points and constitutes one of the most well studied processes which affords a variety of products.

(a.1) In the absence of other substrates

In the presence of square planar macrocyclic nickel(II) complexes of the types shown below, alkyl halides may be catalytically reduced to organic radicals or carbanions at potentials which are much more favourable (e.g., about 1V higher) than those required in the absence of the nickel(II) catalyst. (258-262)

The macrocyclic complexes are of the cyclic trans-tetramine type mentioned in section VI.B, $[NiL^1]^{2+}$, or present a tetradentate Schiff base type ligand (salen), $[NiL_2]$, as exemplified by



In the absence of the alkyl halide, these square planar Ni(II) species, $[NiL]^{2+}$, undergo a one-electron reversible reduction at a Pt electrode (in acetonitrile) to give the nickel(I) $[NiL]^{n-1}$ complexes which are stabilized by the tetradentate macrocyclic ligands. In the presence of an alkyl halide, it is believed that these Ni(I) species undergo oxidative addition reactions and octahedral organonickel(III) complexes are proposed to be formed upon nucleophilic attack by the Ni^I species on the alkyl halide. Alkyl radicals or carbanions may be formed with possible regeneration of the parent electroactive nickel(II) complexes according to the scheme of figure 14. (262)

The path for the reaction depends, e.g., on the stability of the Ni-C bond: route (i) which generates a free radical intermediate is favoured by the lability of this bond with resulting rapid cleavage, whereas a higher stability of such a bond allows further reduction to occur with retention of the Ni-C bond [route (ii)]. Route (iii) corresponds to an electrophilic attack of the alkyl halide at the Ni-C bond.

The final products of the reduction are R-R, RH, olefins or RCH_2CN whose formation involves a radical or a carbanion route.

Hence, e.g., in the $[NiL^1]^{2+}$ - alkyl halide system ($L^1=5,5,7,12,12,14$ -hexamethyl-1,4,8,11-tetra-azacyclotetradecane), R-R may occur from dimerisation of a free-radical intermediate (R·) (which may be the major route for a primary radical), whereas RH and an olefin are formed from a radical disproportionation (which may predominate for tertiary radicals); reaction of a radical with the solvent may also lead to an hydrocarbon (see equations 135-137). (258)



A carbanion intermediate may account for the observed products in some cases, namely in the electrolytic reduction of n-octyl bromide in the presence of $[NiL^1]^{2+}$ (reactions 138 and 139). (258)



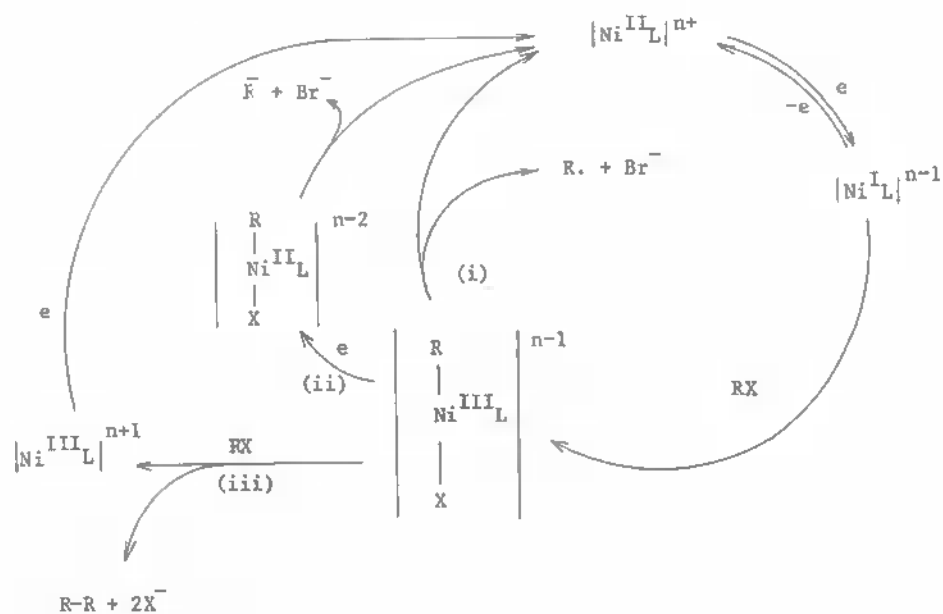


Figure 14 - Catalytic routes for the electrochemical reduction of alkyl halides by square planar macrocyclic nickel complexes

Both the cyclic tetraamine and the tetradentate Schiff base complexes appear to react by similar mechanisms, but the Ni-C bond in the latter seems to be weaker and, in contrast to the former, the structure of the Schiff base ligand has only a little effect on the reactivity of such a bond.

Controlled-potential reductions of the Ni(II) complexes have been carried out in the presence of a 10-fold excess of alkyl halide, and in various cases the overall reaction appears to have the stoichiometry of equation (140), the major products being formed by dimerisation of the

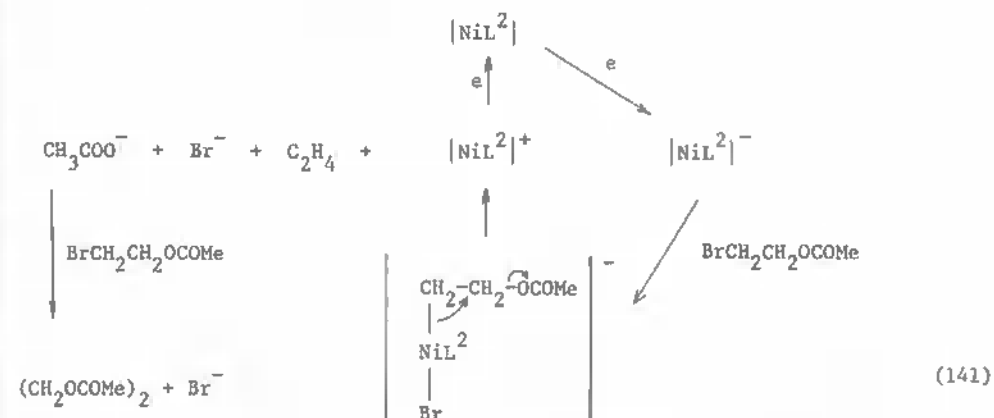


radical intermediate.



Examples of the products from these reactions are shown in Table 3.

Although the expected products from the electrolysis are also formed, in minor amounts, in the presence of bromoethyl acetate, the major product, 1,2-ethanedioldiacetate is probably derived through a competitive route involving attack of $\text{BrCH}_2\text{CH}_2\text{OCOMe}$ by an acetate leaving group (from the organometallic intermediate) according to the proposed⁽²⁶⁰⁾ two-electron scheme (141).



The electrochemical reduction of alkyl halides in the systems is not always catalytic and electroinactive compounds may be formed, e.g., through various side reactions of the electroactive Ni(II) species with X^- or R^- . Hence, an octahedral dibromide inactive species may precipitate out of the solution, thus removing the electroactive complex (reaction 142).⁽²⁶²⁾



Moreover, an inactive species was suggested to be formed upon deprotonation at one nitrogen atom of a cyclic tetraamine ligand by reaction of the Ni(II) complex with R^- (RH is the other product of this reaction).⁽²⁶²⁾

It is also worthwhile to mention that the alkyl halide activation in these systems occurs in homogeneous solution using a Pt electrode, thus avoiding the difficulties derived from the formation of bonds between the radical or carbanion intermediates and the metal of the electrode which would lead to sideways reaction paths as may be observed in direct electrochemical reduction at a mercury cathode.⁽²⁵⁶⁾

Table 3. Products from the controlled-potential reduction of Ni(II) complexes in the presence of a 10-fold excess of alkyl halide, in MeCN-[NBu₄][BF₄] at a Pt cathode.

Complex (a)	Substrate	n (b)	R-R	RH	Products (%) (c)		Ref
					Olefin (C ₈ H ₁₆)	RCH ₂ CN	
[NiL ¹] ²⁺	n-C ₈ H ₁₇ I	5	61	29	C ₆ H ₁₃ CH=CH ₂ (5)	6	258
	n-C ₈ H ₁₇ Br	2	8	66		6	258
	C ₆ H ₁₃ CH(Br)Me	11	46	33	C ₆ H ₁₃ CH=CH ₂ (11)		258
	t-C ₈ H ₁₇ Br	11	9	31	{ C ₅ H ₁₁ CM=CH ₂ (32) C ₄ H ₉ CH=CM ₂ (9)		258
	n-C ₈ H ₁₇ I	11	72	5	C ₆ H ₁₃ CH=CH ₂ (2)		258
[NiL ²]	n-C ₈ H ₁₇ Br	11.3	77	6	C ₆ H ₁₃ CH=CH ₂ (4)		260, 261
	C ₆ H ₁₃ CH(Br)Me	11	27	32	C ₆ H ₁₃ CH=CH ₂ (7)		258
	t-C ₈ H ₁₇ Br	11	9	28	{ C ₅ H ₁₁ CM=CH ₂ (20) C ₄ H ₉ CH=CM ₂ (6)		258
	EtOOCCH ₂ CH ₂ Br	11.1	63	28	EtOOCCH=CH ₂ (9)		260
	NCCH ₂ CH ₂ Br	11.4	30	10	NCCH=CH ₂ (6)		260
	PhCH ₂ CH ₂ Br	11.3	57	16	PhCH=CH ₂ (22)		260
	MeOCOCH ₂ CH ₂ Br (d)	17.5	4	10	MeOCOCH=CH ₂ (10)		260

(a) [NiL¹]²⁺ = (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)nickel(II).

[NiL²] = [N,N'-ethylenebis(salicylideneiminato)]nickel(II)

(b) Mol e/mol Ni. (c) Based on alkyl halide consumed. (d) Main product 1,2-ethanedithiolacetate (21%).

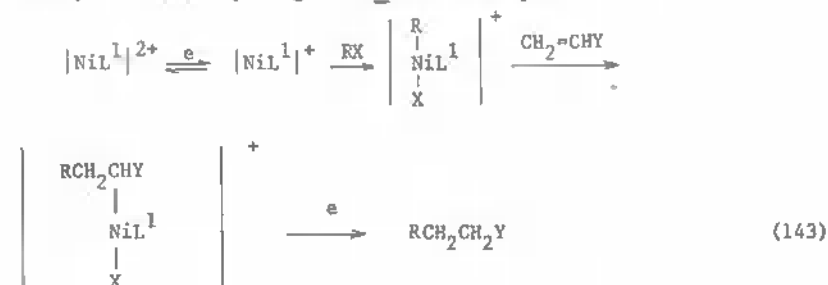
(a.2) In the presence of olefins

The electrochemical reduction of alkyl halides by the abovementioned macrocyclic complexes of nickel is believed to proceed via organometallic intermediates which may generate free radicals. The possibility to use these reactive species in further organic synthesis by generating them in the presence of suitable organic molecules has also been explored.

Hence, if the reductive electrolysis is carried out in the presence of an olefin, two possible modes of reaction have been observed: insertion of an activated olefin into a Ni-C bond and radical addition to the olefinic double bond.

The former type of reaction occurs with the cyclic tetraamine species, such as [NiL¹]²⁺, whereas the latter is observed for the tetradentate Schiff base type complexes since they exhibit much weaker Ni-C bonds which cleave rapidly without presenting a sufficient lifetime to allow the insertion reaction to occur.

The insertion reaction of the activated olefin CH₂=CHY in the [NiL¹]²⁺ - alkyl halide system is believed to occur as shown in reactions (143) and the new metal-carbon bond formed is cleaved by further reduction to yield RCH₂CH₂Y with generation of an unidentified electroinactive metal species. (259) The reaction is not catalytic, terminating after the reduction of one mol of RX/mol of complex and the passage of 2F/mol of complex,

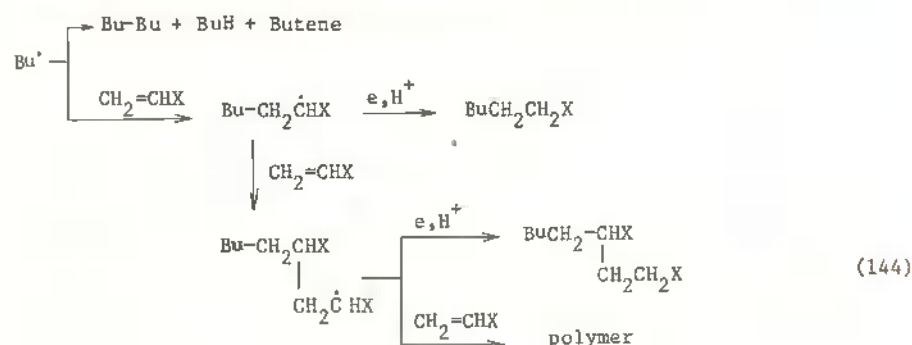


1-Bromobutane, 2-bromobutane and t-butyl bromide are examples of the alkyl halides tested, (259) whereas the following olefins were studied: CH₂=CHCN, CH₂=CHCOOEt, CH₂=CHCOEt, CH₃CH=CHCOCH₃, C₃H₇CH=CHCHO, C₆H₅CH=CHCHO and EtOOCCH=CHCOOEt. The yields (non-catalytic) of products were very high for acrylonitrile, ethyl vinyl ketone and ethyl acrylate. Some of the tested olefins could be reduced directly at the Pt electrode, but only at a more negative potential than the observed in the presence of the nickel complex/alkyl halide system. (259)

The rate of the insertion reaction is dependent on the type of olefin, being fastest for terminal olefins with an electron withdrawing group.

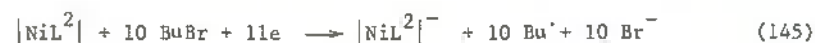
However, as mentioned above, if the reduction of an activated olefin occurs in the presence of a system of the type tetradentate Schiff base complex/alkyl halide, the product distribution is believed to result from the free radical addition to the double bond. (260)

The $[\text{NiL}^2]/\text{BuBr}/\text{CH}_2=\text{CHCN}$ (or $\text{CH}_2=\text{CHCOOEt}$) systems were studied - Table 4 - and their cyclic voltammograms shown to be very similar to those observed in the absence of the olefin, thus suggesting that the basic reaction between $[\text{NiL}^2]^-$ and BuBr remains unchanged upon addition of the olefin. The reactions are catalytic and a conceivable mechanism (for primary and secondary butyl radical) has been proposed (260) according to reactions (144).



The t-butyl radical addition occurs, however, at the α carbon atom of the olefin.

The butyl radical was generated by Ni-C bond cleavage as shown in route (i) of figure 14, through the overall stoichiometry shown in the reaction (145).



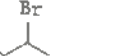
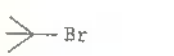
(b) Polymerization and oligomerization of olefins

Active species in the polymerization or oligomerization of olefins may be conveniently prepared (with the metal in the appropriate oxidation state) by electrochemical generation in situ in the presence of a suitable ligand.

Hence, electrochemical reduction of Ni(II) species* - e.g.,

* Electrochemical reduction of other metal salts, such as $[\text{Co}(\text{acac})_2]$, is also known (268) to induce the oligomerization of butadiene

Table 4 - Main products from the catalytic reduction of butyl bromides by $[\text{NiL}^2]$ in the presence of an olefin^(a) (260)

BuBr	Olefin	
	$\text{CH}_2=\text{CHCN}$ n ^(b) Product (%) ^(c)	$\text{CH}_2=\text{CHCOOEt}$ n ^(b) Product (%) ^(c)
	15  (28)	16  (41)
	18  (41)	20  (56)
	17  (47)	19  (64)

(a) $[\text{NiL}^2]$: BuBr: olefin = 1:10:50

(b) F/mol $[\text{NiL}^2]$.

(c) Based on BuBr.

$[\text{NiCl}_2]$, (269,270) $[\text{NiCl}_2(\text{PR}_3)_2]$, (269) $[\text{Ni}(\text{Py})_4](\text{ClO}_4)_2$ (270,271) or $[\text{Ni}(\text{acac})_2]$ (182) generally in the presence of an electron-donor ligand (such as PPh_3) forms a zerovalent nickel compound - e.g., $[\text{Ni}(\text{PPh}_3)_4]$ (270) - which converts butadiene mainly, e.g., to 4-vinylcyclohexene, (269) 1,5-cyclooctadiene, (269) or to the linear oligomers n-octadiene, (270) n-dodecatriene, (270) or n-hexadecatetraene. (270) The nickel(o) species may display catalytic activity (such as in the formation of the cyclic oligomers)* and the product distribution depends on the initial nickel compound, the added ligand, the solvent, electrolyte and the applied reduction potential.

The suggested (270) mechanism (involving π -allyl intermediates) for the butadiene conversion to linear or branched oligomers by electrolysis of alcoholic solutions of $[\text{NiCl}_2]$ in the presence of an electron donor species (L) is illustrated in figure 15.

* Various zerovalent nickel complexes are known (272) to catalyze the chemical cyclooligomerization of butadiene.

A zerovalent Ni compound is formed by electrochemical reduction of the Ni(II) species. Butadiene is believed to replace ligand L to give complexes (A) and (B) (if L is a non-labile chelating ligand such as dppe, a decreasing in the activity results). (269)

Hydrogenation (the source of hydrogen may be the solvent) or alkoxylation of species (A) and (B) lead to final organic products. Insertion of butadiene into a Ni-C bond is also suggested to be involved in the formation of 5-VDD, 5-VTDT and NHDT: hydrogenation of the allylic 1-carbon of complex (A) or the 3-carbon of complex (B) results in the destruction of the rare gas configuration of the central metal and in the activation of the other π -allylic groups; insertion of butadiene into the Ni-C(6) bond of complex (A) or into the Ni-C(10) or C(12) bond of complex (B) forms species (C) or (D), respectively, which, upon further hydrogenation, lead to the final products.

The reactions depicted in figure 15 are generally non catalytic but for $L=PPh_3$, n -octatriene (NOT) and alkoxyoctadiene (MOD) are formed catalytically. (270)

(c) Other reactions

Electrochemical activation of acyl ligands in organometallic complexes may result in the formation of organic species such as ketones and organic esters.

Hence, electrochemical oxidation of acyliron(II) complexes labilizes the acyl ligand and, e.g., the neutral complex $[Fe(\eta^5-C_5H_5)(CCH_3)(CO)_2]$ is irreversibly oxidized in acetonitrile at a Pt electrode to the unstable acyliron(III) cation radical which, in the presence of EtOH, affords ethylacetate in high yield probably via a nucleophilic attack of the alcohol. (273)

However, electrochemical oxidation of the anionic complex $[Fe(\eta^5-C_5H_5)(CN)(CCH_3)(CO)]^-$ at a Pt electrode in acetonitrile gives, in a reversible way, a more stable paramagnetic neutral acyliron(III) compound which upon thermal decomposition affords acetone in high yield and aldehyde (CH_3CHO) in minor amount; the formation of acetone is proposed to occur by a reversible decarbonylation of the acetyl ligand followed by a cross coupling of the derived 17-electron methyliron(III) species with the acetyliron(III) radical.

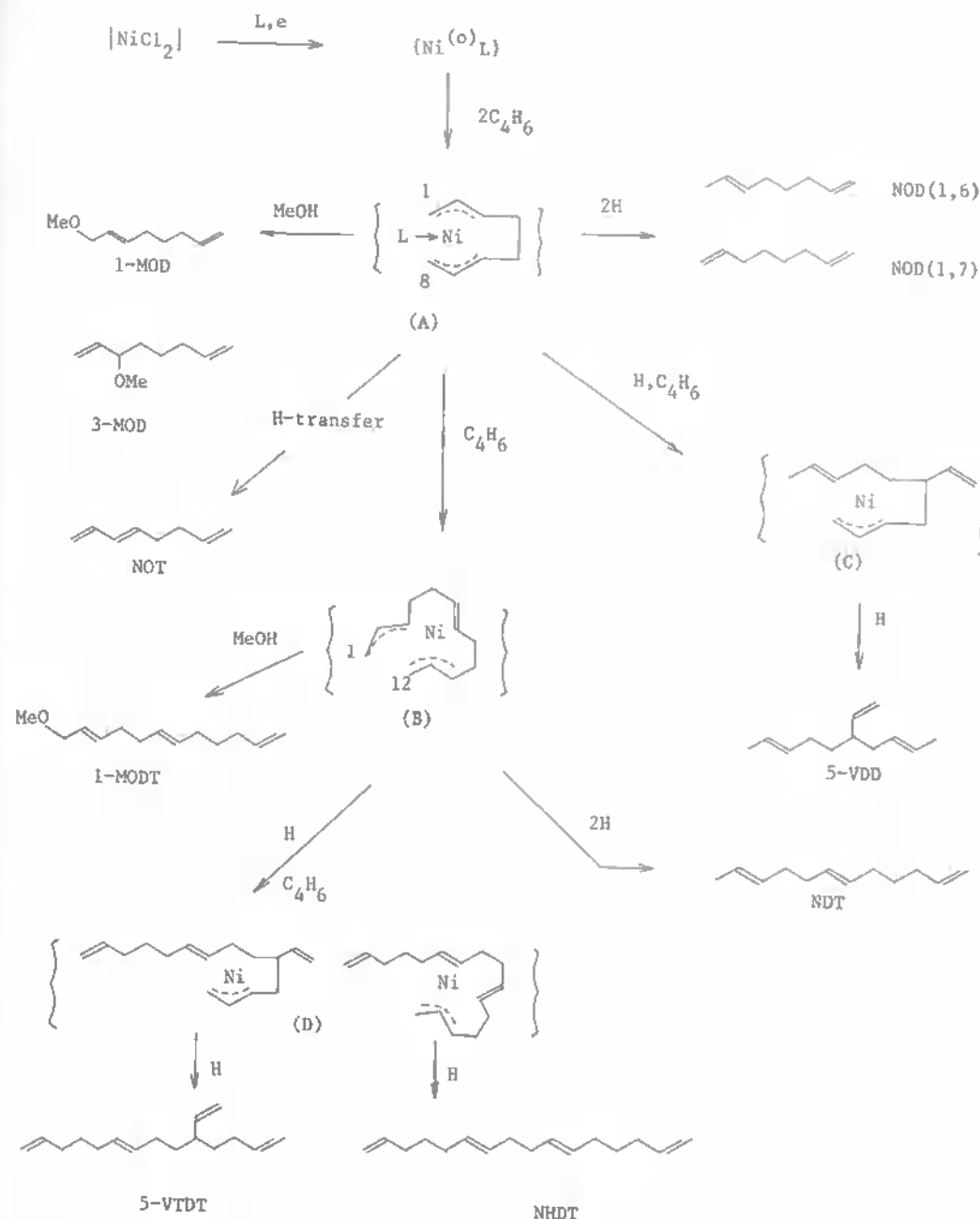


Figure 15 - Suggested (270) mechanism for the butadiene acyclic oligomerization in the presence of Ni(0) species.
 NOD=Octadiene. 1-MOD=1-methoxyocta-2,7-diene. 3-MOD=3-methoxyocta-1,7-diene. NOT=octa-1,3,7-triene. 1-MODT=1-methoxydodeca-2,6,11-triene. 5-VDD=5-vinyldeca-2,8-diene. NDT=dodeca-1,6,10-triene. 5-VTDT=5-vinyltetradeca-1,8,13-triene. NHDT=hexadeca-1,6,10,15-tetraene.

(d) Final remarks. Indirect electrosynthesis via
non-organometallic carriers

As it was previously mentioned, this section deals with organometallic complexes. Hence, the study of electrochemical systems with other types of species and in which there is no evidence for the involvement of an organometallic species has not been mentioned.

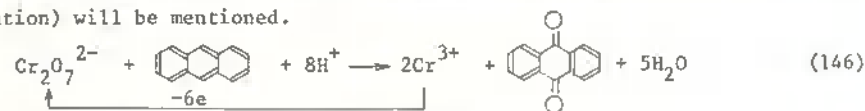
However, in order to exemplify the importance of such systems in catalytic reactions, and since they involve conceptual analogies with the abovementioned organometallic catalytic processes, examples will be given for the electrochemical generation of oxidation catalysts (for alcohols, aldehydes and unsaturated hydrocarbons) and for a reduction catalyst (for reductive coupling of organohalides) in electrocatalytic redox processes.

These systems illustrate the application of indirect electrolytic synthesis of organic species without involving (or without evidence for the involvement of) an organometallic intermediate.

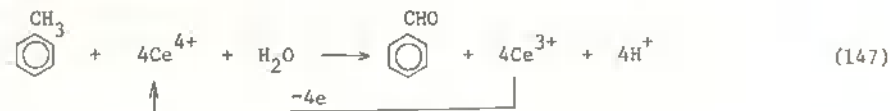
In an indirect electrochemical synthesis, an oxidizing (or reducing) agent (a "carrier", which is usually inorganic) is generated at the working electrode and then reacts chemically with the substrate, e.g., in a separate vessel; the carrier is then returned to the working electrode for regeneration in a catalytic process. Examples of inorganic oxidizing carriers are given by S_2O_8 , $Ce(IV)$, Tl^{3+} , MnO_4^- , MnO_2 , $Cr_2O_7^{2-}$, whereas Sn^{2+} , $Ti(III)$, $Ti(II)$ and $Cr(II)$ are examples of reducing carriers.

Although much less studied than direct electrosynthetic electrochemical processes, indirect electrolytic synthesis has also industrial applications since as long as the beginning of the century.

As an example of an industrial electroorganic indirect process the anodic oxidation of anthracene [to anthraquinone by using $Cr(VI)$ as the oxidizing carrier - equation 146] may be cited. This system was reviewed⁽²⁷⁴⁾ and now only a few more recent examples of indirect electrosynthesis (yet without industrial application) will be mentioned.



Indirect electrolytic oxidation of toluene (and chlorotoluene) to the corresponding aldehyde (equation 147) was studied by using $Ce(IV)$ as oxidant which is (re)generated at a platinized titanium anode. According to a cost estimate, an industrial process based on this electrosynthesis would appear economically attractive.⁽²⁷⁵⁾

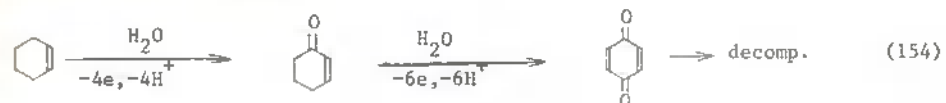
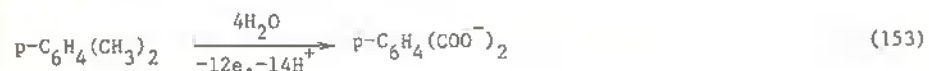


Electrolytic two-electron oxidation of the $Ru(II)$ complex $[(trpy)(bpy)Ru(H_2O)]^{2+}$ ($trpy=2,2',2''$ -terpyridine; $bpy=2,2'$ -bipyridine) in aqueous buffer solution at a Pt anode results in the reversible formation of the monooxo $Ru(IV)$ species $[(trpy)(bpy)Ru=O]^{2+}$ which is an oxidant of a variety of organic substrates under mild conditions; the oxo $Ru(IV)$ compound is regenerated by oxidation at the electrode.⁽²⁷⁶⁾

The overall electrocatalytic process is shown by reactions (148) [where $Ru=Ru(trpy)(bpy)$]; the balancing reaction at the cathode is the reduction of H^+ to dihydrogen. 2-Propanol and ethanol are oxidized to acetone (reaction 149) and acetate (reactions 150 and 151), respectively, acetaldehyde is

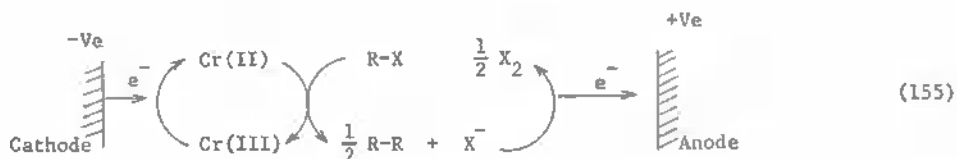


oxidized to acetate (reaction 151), whereas toluene is oxidized to benzoate (equation 152) p-xylene to terephthalate dianion (equation 153) and cyclohexene first to 2-cyclohexen-1-one and then to p-benzoquinone (equation 154).⁽²⁷⁶⁾



The catalytic activity of the oxoRu(IV)/Ru(II) system was also transferred to the electrode surface by deposition, at this surface, of thin polymeric films with the $\{(bpy)(H_2O)Ru^{II}\}$ group bound to poly-4-vinylpyridine.⁽²⁷⁷⁾

An example of an indirect electrocatalytic reduction process is given by the reductive C-C coupling of organic halides (RX) to hydrocarbons (R-R) by catalytic amounts of electrochemically generated Cr(II) as the reducing agent as shown by reactions (155) ($X=Cl, Br$, $R=-CH_2-C_6H_5$, $-CH_2-CH=CH_2$).⁽²⁷⁸⁾



The chromium(II) is formed by electrochemical reduction of chromium(III) in dimethylformamide at a glassy carbon cathode at a higher potential than the required for the cathodic reduction of the halides. The Cr(II) species was not isolated, being continuously regenerated electrochemically during the reaction.

The yields obtained for the reduction of benzylic and allylic halides are comparable to those known for the chemical $CrCl_3/LiAlH_4$ system and the electrochemical method offers considerable advantages over the latter: allows the use of catalytic amounts of the chromium reagent, the reaction can be run in a continuous process and the product is easily isolated by extraction with cyclohexane.

Moreover, electrochemical generation in situ, and in a controlled way, of expensive redox reagents may constitute a convenient and advantageous alternative to a chemical preparative process.

C - Electroactivation of Ligands

It is well documented the activation a species can undergo upon coordination to a transition metal site. Moreover, a variation in the electron richness of the binding centre may be often easily accomplished by electrochemical oxidation or reduction and hence the reactivity of a ligand may be, in some cases, conveniently controlled by electroactivation.

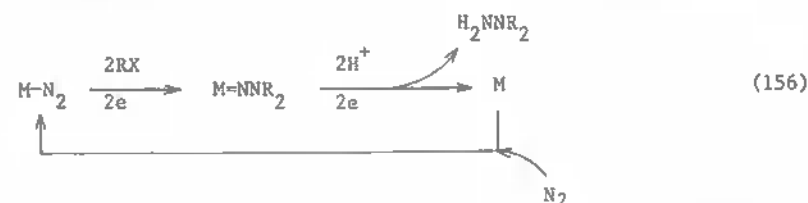
Examples have already been given, e.g., in sections II.B.c, II.B.e, VIII.A.c, VIII.A.d and VIII.B.c, and they may lead to new complexes and/or organic compounds.

Instances in illustration of the synthetic importance of the electrochemical activation of ligands are also known in the fields of nitrogen fixation and carbon dioxide activation and they are cited in this section.

(a) Electrochemical activation of ligating organohydrazido(2-): reduction to free organohydrazines.

Dialkylhydrazido(2-) ligands, NNR_2 , may be formed upon dialkylation of coordinated N_2 in $trans-[Mo(N_2)_2(dppe)_2]$. They may undergo further chemical reduction to give organonitrogenous compounds by destructive methods without regeneration of a metal site with N_2 co-ordinating ability.⁽²⁷⁹⁾

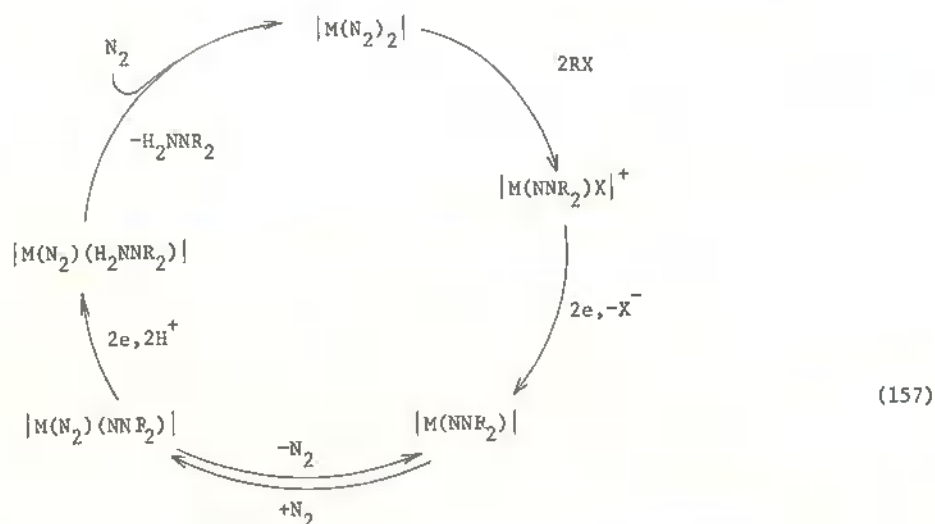
However, upon electrochemical activation, dialkylhydrazido(2-) ligands may be converted to free organohydrazines, H_2NNR_2 , in such reducing conditions that the metal product species can ligate again N_2 , thus a reduction cycle being completed^(280, 281) according to the overall process (156) where M denotes a metal site.



Hence, e.g., free organohydrazine $H_2NNCH_2(CH_2)_3CH_3$ is formed in the electrochemical reduction (controlled potential electrolysis) of $trans-[MoBr\{NNCH_2(CH_2)_3CH_3\}(dppe)_2]^+$ at a Pt electrode in $thf/[NBu_4][BF_4]$ under N_2 with regeneration of the parent $trans-[Mo(N_2)_2(dppe)_2]$ complex (in yields up to 45%).⁽²⁸⁰⁾

The reaction is believed to proceed via the proposed⁽²⁸⁰⁾ chemical/electrochemical cycle (157) when the electroreduction plays a fundamental role in the activation of the organodiazenido(2-) ligand and the regeneration of a metal site with an electron-richness sufficient to bind and activate incoming N_2 .

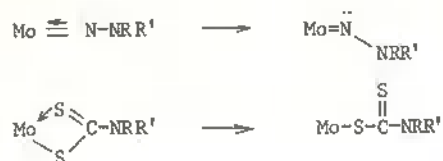
The organohydrazine was determined by g.l.c. and by in situ cyclic voltammetry on the catholyte after the controlled potential electrolysis.



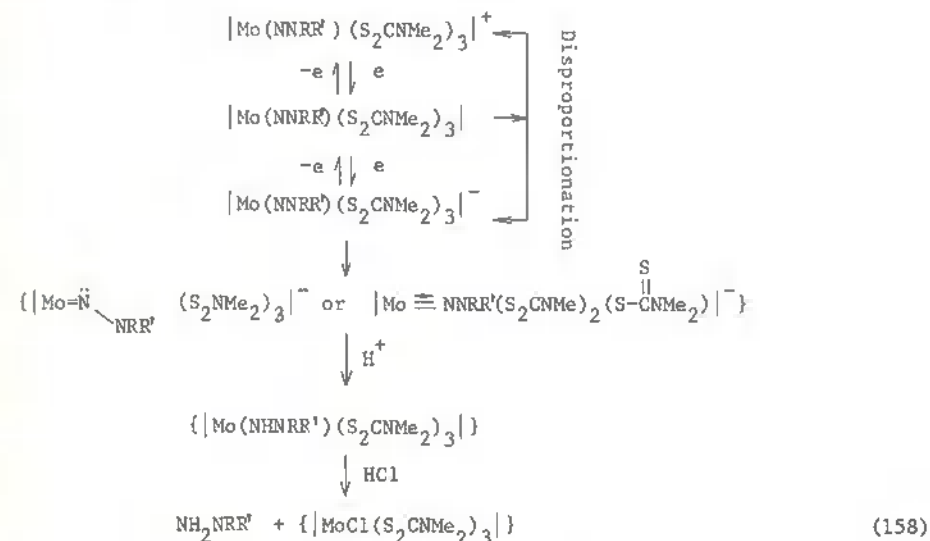
Electrochemical activation of hydrazido(2-) ligands towards electrophiles, at other metal sites, is also known to result in the formation of free organohydrazine upon attack by acid which does not occur without the previous electroreduction.

Hence, 2-electron reduction of the 18-electron dithiocarbamate-hydrazido(2-) complexes $[\text{Mo}(\text{NNRR})(\text{S}_2\text{CNMe}_2)_3]^+$ (R=alkyl or aryl) results in the activation of the NNR_2 moiety towards attack by electrophiles, and free hydrazine $\text{NH}_2\text{NMe}(\text{Ph})$ in ca. 57% yield is formed upon reduction/protonation of the parent complex. ⁽²⁸²⁾

The hydrazido(2-) ligand in the parent 18-electron complexes behaves as a 4-electron ligand, and in the 20-electron species formed by the 2-electron reduction probably one of the following possible rearrangements occurs to give an 18-electron reduced complex:



The reduction of the organohydrazido(2-) ligand may then proceed via the proposed⁽²⁸²⁾ scheme (158) (where species in braces have not been isolated).



The study of hydrazido(2-) ligands deserve an important role in the field of nitrogen fixation since an hydrazido(2-) species, $\text{Mo}=\text{NNH}_2$, is believed⁽²⁸³⁾ to be a step in the catalytic reduction of N_2 by nitrogenase.

Although the hydrazido(2-) ligands in the abovementioned 18-electron dithiocarbamate complexes were prepared from hydrazine, in the diphosphine complexes $[\text{Mo}(\text{NHR}_2)\text{X}(\text{dppe})_2]^+$ cited previously, they result from alkylation of N_2 ligand and constitute an intermediate stage in the reduction to hydrazines.

(b) Electrochemical reduction of dinitrogen to ammonia

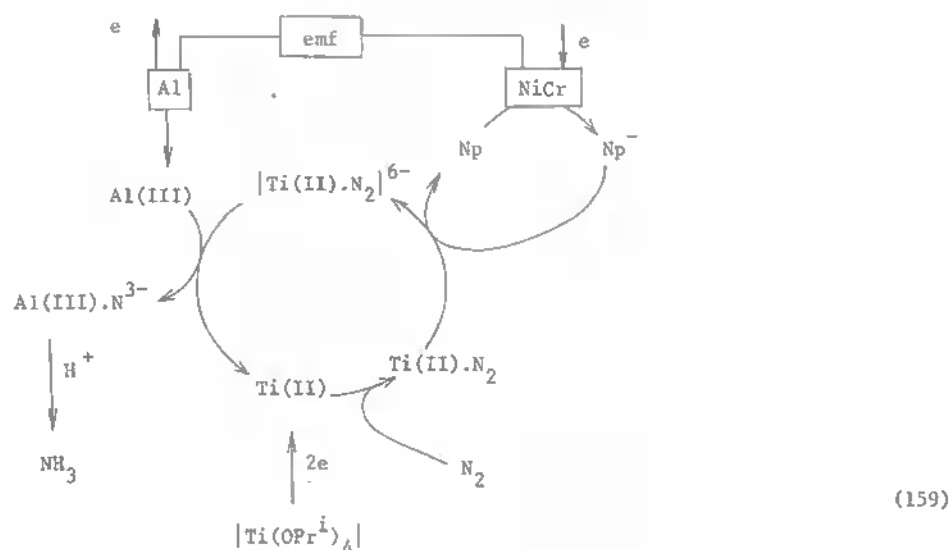
Dinitrogen can be reduced electrochemically to ammonia in the presence of a transition metal site which is believed to activate N_2 and constitute an electron mediator to this ligand.

Electrochemical catalytic systems are known which operate at ambient temperature and pressure. (284-286)

Hence, when a solution (60 ml) of $[\text{Ti}(\text{OPr}^i)_4] \cdot (1.68 \text{ mmol})$, $\text{Al}(\text{OPr}^i)_3$ (42 mmol) and naphthalene (7.6 mmol) in 1,2-dimethoxyethane with tetrabutylammonium chloride (8.6 mmol) was electrolyzed at 40V during 11 days (at 20°C and under a slow stream of N_2), and then hydrolyzed by treatment with aqueous sodium hydroxide, a 610% yield of NH_3 (based on Ti) was obtained. (284) The reaction was carried out in an electrolytic cell with an aluminum anode and a nickel / chromium cathode. During the essay (11 days), 0.155 faradays

passed through the cell and 15.1 mmol of aluminum were lost from the anode to the solution.

By analogy with the Vol'pin catalytic dinitrogen reduction chemical systems, (287) it is suggested (284) that the catalytic species involves Ti(II) which can bind N_2 , and that $Al(OPr)_3$ behaves as a Lewis acid being able to break the titanium-nitride bond with regeneration of the Ti(II) catalytic species (scheme 159). Naphthalene is believed to play the role of an electron carrier, being reduced, by the Ni/Cr cathode, to naphthalide which reduces the dinitrogen-Ti(II) species. (284)



The analogous chemical system (with sodium, instead of the electric current, as the reducing agent) was also shown to be catalytic but presents a lower reduction yield.

Dinitrogen may also be electrochemically reduced to hydrazine by electrolysis of buffered methanolic solutions of Mo(V). (288)

(c) Electrochemical reduction of CO_2

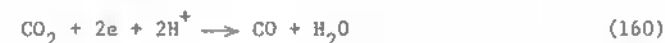
Carbon dioxide, a potential carbon source of paramount importance in the attempt to develop alternative energy routes, has already been the subject of electrochemical study.

Hence, it may undergo a direct electrochemical reduction to formic acid (or the formate ion) in aqueous medium, (289,290) whereas in aprotic media reduction to oxalate (in N,N-dimethylformamide), (291-293) and to carbon monoxide (carbonate is also formed) (in dimethylsulphoxide) (294) have been reported. Other organic products such as mono and dicarboxylated species are formed by electrolytic reduction of mixtures of carbon dioxide with an olefin (291,295) or an organohalide. (291)

Since some of the products of the CO_2 reduction (formic acid and carbon monoxide) may be further reduced to methanol, the prospects of the production of methanol by electrochemical reduction of carbon dioxide were evaluated. (296) An overall low energy efficiency results from the large overpotential which is observed for the direct electrochemical CO_2 reduction in either aqueous or non-aqueous medium (the reduction only occurs at potentials below ca. -2V vs.s.c.e.).

However, it has been reported (297) that certain transition metal complexes, such as tetraazamacrocyclic compounds of Ni(II) or Co(II) of the type $[ML]^{2+}$ (where L is a tetradentate trans-diene ligand-see section VI.B) can behave as redox-activated catalysts, their reduced forms of metal(I) promoting the electrochemical reduction of CO_2 , in an indirect and catalytic way, to occur at more favourable electrode potentials.

Hence, CO_2 is catalytically reduced to CO (equation 160) (with evolution of H_2) by controlled potential coulometry of aqueous or aqueous acetonitrile solution of the abovementioned macrocyclic complexes using a mercury working electrode, at potentials between -1.3 and -1.6 V vs. SCE which are cathodic for the M(II)/M(I) couple.



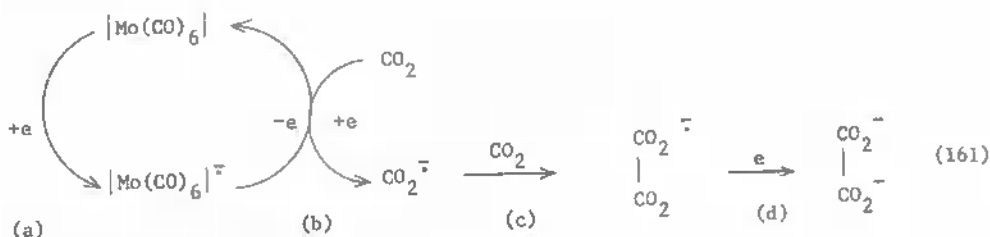
The systems exhibit catalytic activity, e.g., of ca. 9 turnovers per hour per mol of metal complex at ambient room temperature (a turnover being defined as 1 equivalent of electrons passed through the cell per mol of catalyst) and for catalyst concentrations of 1.2 mM.

The formation of CO and H_2 requires the presence of a protic source and the reduction of CO_2 and H^+ is suggested to occur through a common metal hydride intermediate.

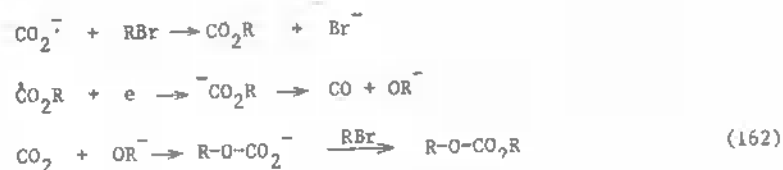
Electrocatalytic reductions at a Pt electrode of CO_2 to oxalate mediated by a metal carbonyl, $[Mo(CO)_6]$, has also been reported in acetonitrile although at a less favourable potential than the required for the abovementioned Ni(II) or Co(II) macrocycles.

In the $[\text{Mo}(\text{CO})_6]$ system, the CO_2 irreversible reduction potential is observed at a value ($-2.6 \text{ V vs. s.c.e.}$) which is ca. 0.4 V anodic relative to the value (-3.0 V) observed for the direct CO_2 reduction in identical experimental conditions but in the absence of the metal carbonyl.⁽⁸⁹⁾

The proposed⁽⁸⁹⁾ mechanism involves attack of the electrogenerated $\text{CO}_2^{\cdot -}$ radical anion at CO_2 according to scheme (161).



If the electrolytic reduction of molybdenum hexacarbonyl is carried out in the presence of both CO_2 and an alkyl halide ($n\text{-BuBr}$), the major product is di- n -butyl carbonate formed by a preferential (faster) attack of the $\text{CO}_2^{\cdot -}$ radical anion on the alkyl halide rather than on carbon dioxide, according to the postulated⁽⁸⁹⁾ sequence (162) which follows steps (a) and (b) of scheme (161).



IX - ELECTROCHEMICAL STUDIES ON THE MECHANISMS OF CHEMICAL REACTIONS

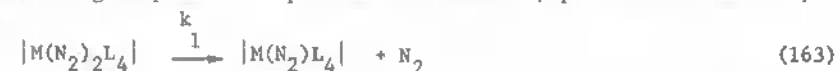
Electrochemistry has also been applied to the study of chemical reactions of transition metal complexes, namely by monitoring (by cyclic voltammetry) a reactant, a product, or an intermediate, and by detecting types of mechanism and evaluating rate constants and thermodynamic $\Delta H^\ddagger$ and $\Delta S^\ddagger$ parameters.

A few recent examples of application involving dinitrogen complexes are now cited.

A - Substitution reactions of dinitrogen

The replacement of dinitrogen in the bis(dinitrogen) complexes

$[\text{M}(\text{N}_2)_2\text{L}_4]$ ($\text{M}=\text{Mo}, \text{W}$; $\text{L}=\text{monophosphine}$ or $\frac{1}{2}$ diphosphine) by a variety of ligands L' (namely isocyanides and nitriles) was monitored by cyclic voltammetry and shown to follow a dissociative (I_d) mechanism. Under pseudo first-order conditions the rate controlling step is first order in the N_2 complex and zero order in L' concentration, the value of the rate constant being independent of the L' ligand, in agreement with N_2 loss being the common rate-controlling step of the replacement reactions (equations 163 and 164).^(116,298)



The mono-substituted complexes may be isolated, e.g., when $\text{L}'=\text{NCR}$, but further dinitrogen replacement occurs with isocyanide, the strong electron-acceptor character of the latter presenting a N_2 labilizing effect. The formation of the mixed dinitrogen-isocyanide intermediate complex was not observed in the reactions of $\text{trans-}[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ with isocyanides, but the $\text{cis-}[\text{Mo}(\text{N}_2)(\text{CNMe})(\text{PMe}_2\text{Ph})_4]$ species was detected by cyclic voltammetry (and ^{31}P n.m.r.) in the formation of $\text{cis-}[\text{Mo}(\text{CNMe})_2(\text{PMe}_2\text{Ph})_4]$ from the reaction of isocyanide with $\text{cis-}[\text{Mo}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$.⁽²⁹⁸⁾

The intermediate mixed dinitrogen-isocyanide complex $\text{cis-}[\text{Mo}(\text{N}_2)(\text{CNMe})(\text{PMe}_2\text{Ph})_4]$ exhibits an irreversible oxidation wave at an intermediate potential ($E_p^{\text{ox}} = -0.45 \text{ V vs. SCE}$ at a Pt electrode in $\text{thf}/[\text{NBu}_4][\text{BF}_4]$) between those of the parent bisdinitrogen complex (-0.23 V) and the bisisocyanide product (-0.62 V). The displacement of N_2 from this mixed intermediate complex was also monitored by cyclic voltammetry and the data support a second N_2 loss as the rate-determining step (equations 165-168, where $k_1=0.020 \text{ s}^{-1}$ and $k_2/k_1=5$, at 273 K).⁽²⁹⁸⁾



B - Alkylation reactions of dinitrogen

The mechanism of the alkylation, acetylation and aroylation reactions of $\text{trans-[M(N}_2)_2(\text{dppe})_2]$ ($\text{M}=\text{Mo}$ or W) by organic halides (RX) was studied by cyclic voltammetry and e.s.r. and shown to proceed, usually, as the above-mentioned replacement reactions, by the initial rate-limiting dissociation of one N_2 ligand followed by addition of the organic halide (coordinated through the halogen to the metal atom).⁽¹¹⁶⁾ In the unstable intermediate, $[\text{M(N}_2)(\text{XR})(\text{dppe})_2]$, the carbon-halogen bond undergoes homolysis and the organic free radical attacks the remaining N_2 ligand to give a diazenido species, $[\text{Mo(N}_2\text{R)X(dppe)}_2]$, as the primary alkylation product (reactions 64).⁽¹¹⁶⁾

In this study the concentrations in thf of the $[\text{M(N}_2)_2(\text{dppe})_2]$ complex and, in some cases, of products, were monitored by cyclic voltammetry and the free radicals were detected by e.s.r. studies which were also consistent with the formation of a non-symmetrical Mo(I) species $\text{cis-[MoX(N}_2)(\text{dppe})_2]$ (see reactions 64).

The secondary alkylation of ligating N_2 , i.e., the alkylation of the diazenido complex $[\text{M(N}_2\text{R)(X)(dppe)}_2]$ into the hydrazido(2-) species $[\text{M(N}_2\text{R}_2)(\text{X)(dppe)}_2]$, is first order in complex and in alkyl halide and follows a bimolecular nucleophilic substitution mechanism ($\text{S}_{\text{N}}2$) (reaction 169).⁽²⁴⁾



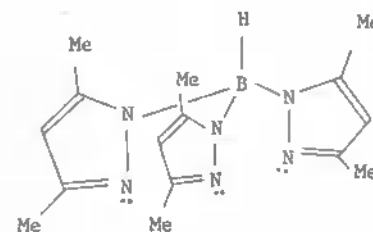
The rates of these reactions are sensitive to both the metal and the co-ligands, the primary alkylation being accelerated by factors which encourage N_2 loss (when inner-sphere electron transfer to RX occurs), whereas the same factors inhibit the secondary alkylation which occurs by an associative mechanism. Hence, e.g., an increase in the electron-rich character of the metal site stabilizes ligating N_2 (with slowing down of the first alkylation) whereas favours the second alkylation due to the increasing nucleophilic character of the diazenido N_2R ligand.

In reactions (64), the primary alkylation was shown to proceed through loss of N_2 and via an inner-sphere electron transfer to the organohalide. However, when the metal site presents a very high electron-richness, such as in the anionic thiocyanato complex $[\text{M(N}_2)(\text{SCN)(dppe)}_2]^-$ (which is oxidized at a very low $\text{E}_{1/2}^{\text{OX}}$ value), the alkylation is first order in complex and in the organohalide, and is believed to occur via an outer-sphere electron transfer from the metal to RX (reactions 63).^(24,25) In this case, the primary and the secondary alkylations are favoured by the same factors.

C - Other reactions

Electrochemistry may also be a useful tool in the investigation of the mechanisms of a variety of other reactions, namely the following ones which have been studied recently by electrochemical techniques.

The unsaturated complex $[\text{Mo(L)(NO)I}_2]^-$ with the bulky tris-3,5-dimethylpyrazolylborato ligand $[\text{L}=\text{HB}(\text{Me}_2\text{C}_3\text{HNN})_3]^-$

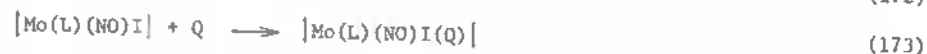
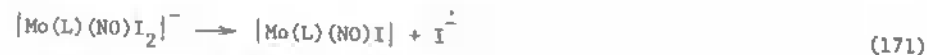


reacts with alcohols, primary amines, hydrazines and thiols (QH) to give complexes $[\text{Mo(L)(NO)I(Q)}]$,⁽²⁹⁹⁻³⁰¹⁾ formally derived from replacement of I^- ligand by Q^- , and the mechanism of these reactions was electrochemically studied.⁽³⁰²⁾

It was then observed (by cyclic voltammetry) the remarkably easy one-electron reversible reduction of the unsaturated complex $[\text{Mo(L)(NO)I}_2]^-$ which may be reduced by a basic solvent such as alcohol, amine, thiol or even water.

Moreover, the reduced paramagnetic anionic species, $[\text{Mo(L)(NO)I}_2]^-$, which may be prepared by controlled-potential electrolysis and detected by e.s.r., can undergo a dissociative loss of I^- (whose oxidation peaks may be identified by cyclic voltammetry) with formation of a new paramagnetic species $[\text{Mo(L)(NO)I}]$, detected by e.s.r.

On the basis of these observations, a mechanism was proposed⁽³⁰²⁾ according to the reactions (170-174).



Hence, although nitrosyl complexes can often undergo ligand replacement reactions via an associative route,⁽³⁰³⁾ the displacement of I^- at the easily reducible complex $[Mo(L)(NO)I_2]$ with a bulky ligand proceeds through a dissociative process at an anionic reduced intermediate species $[Mo(L)(NO)I_2]^-$.

X - FINAL REMARKS

This work covered only a few topics within the broad field of complex electrochemistry and others, also in current development, could be selected namely the electrochemical study of mixed-valence complexes (e.g., of Fe, (304-308) Ru, (309-317) Fe and Ru, (318) Fe and Co, (319) Pt⁽³²⁰⁾ or Cu^(321,322)), the electrochemical behaviour of complexes with biological significance [such as molybdenum-iron-sulphur clusters,⁽³²³⁻³²⁵⁾ iron-sulphur and iron-porphyrin centres,^(187,326-331) and inorganic models of cobalamines⁽³³²⁻³³⁴⁾] or metal complex modified electrodes.^(277,335)

However, the examples presented in the selected areas of this work clearly illustrate the wide application of electrochemistry on the study of organotransition metal complexes (namely of organometallic type), in the rationalization and prediction of their electronic properties and chemical reactivity as well as in the ability to induce them according to a convenient profile.

It is already documented the application of electrochemical parameters on the quantification of the electronic properties of metal sites and ligands, and the recognition of correlations between those parameters and others derived from the application of techniques such as n.m.r., e.p.r. and electronic spectroscopy.

Important advances in structural and mechanistic studies may result from the association of these technique to Electrochemistry and from the extension of the work to wide ranges of different types of complexes.

From the activation of ligands by coordination to a metal centre, the possibility of convenient synthesis of derived species may result, and Electrochemistry may give rise to the favourable activating electronic conditions (in metal sites and/or ligands) for the preparation of new compounds.

Redox processes are often followed by chemical reactions and from the electrochemical/chemical coupling a synthetic versatility (namely of catalytic nature) may result.

The development of the control of selectivity is, however, an important requirement to be fulfilled on the aim to get a better benefit from the application of the great potentialities of the chemical electrosyntheses.

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